Computational Modelling of Energy Absorption Characteristics of Epoxy/CNT Nanocomposites

by

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Thesis submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy at the Faculty of Science and Engineering, University of Limerick, Ireland

Submitted to the University of Limerick, September 2014
Abstract

Epoxy-based composite laminates frequently behave as brittle materials under various types of loading, from quasi-static to impact, as they cannot absorb/dissipate enough energy. Matrix cracks develop due to the brittle nature of epoxy, which after further crack growth can cause delaminations and catastrophic failure. Carbon nanotubes (CNTs) offer promising means for enhancing energy absorption characteristics of epoxy matrices, through CNT crack-bridging, and enhanced nonlinear deformation of the epoxy. However, better understanding of the relationship between process-induced nanocomposite morphologies (e.g. CNT distribution, CNT functionalisation and CNT curvature) and nanocomposite properties is crucial for a successful exploitation of these materials for energy absorbing applications. This work addressed this issue from a computational perspective by focussing on two cases, (1) crack resistance characteristics of epoxy/CNT nanocomposites in tension, and its (2) rate-dependent nonlinear compressive behaviour across different strain rates.

It was found in case (1) that CNTs significantly reduce the crack driving force in epoxy and increase strains to failure as a result of the damage propagation at the epoxy-CNT interface. Particularly, enhancements of shear stiffness, shear strength and mode II fracture energy of epoxy-CNT interfaces via CNT functionalisation and minor increases of low sp³-bond densities in the interwall phase of DWCNTs were shown to increase the crack resistance of the nanocomposite.

However, major focus was on case (2), and related development of a holistic multiscale modelling approach that links various nanocomposite length scales in a sequential manner. In particular, CNT and interface properties were
predicted from molecular mechanics/dynamics and used in a mesoscale model that was formulated within the representative volume element (RVE) concept, nonlinear finite element (FE) framework and employed first-order nonlinear homogenisation. It was found that the nanocomposite nonlinear compressive stress-strain response cannot be accurately captured by 2D RVEs (assuming the plane strain condition), when compared to 3D RVEs, primarily because of the stress transfer effect and the particle interaction accurately captured only in 3D.

In general, the multiscale models predicted that the increasing CNT aspect ratio, CNT volume fraction and CNT alignment enhance the nonlinear finite strain compressive response by increasing the yield peak true stress and changing the post-yield deformation behaviour from softening to hardening. Also, the CNT alignment was identified as the major factor for enhancing the nonlinear stress-strain response at both quasi-static and impact rates of strain. However, weak van der Waals (vdWs) bonding at the epoxy/CNT interface as well as CNT curvature significantly limit their reinforcement capabilities as predicted in terms of the nanocomposite Young’s modulus and yield peak stress.

The model validation involved the preparation of epoxy/CNT nanocomposites composed of randomly distributed and oriented CNTs of low mass fraction, mechanical testing under quasi-static compressive loading and the study of fracture surfaces and obtained CNT morphologies using scanning electron microscopy (SEM). 3D models agreed relatively well with the results of experimental programme, when CNT waviness and imperfect bonding at the epoxy-CNT interface were taken into account.
Declaration

The substance of this thesis is the original work of the author. It has not been submitted to any other university, higher education institution or for any other academic award. Where use of the work of others has been made, it has been acknowledged and fully referenced.

David Weidt

Date 24/09/14
Acknowledgements

First and foremost, I would like to express my gratitude to my supervisor Dr. Łukasz Figiel for his constant support during the past four years. I appreciate his professional guidance, feedback as well as patience, which kept me on the right track towards the completion of my study.

I would like to thank Prof. Martin Buggy for supervising me during the first two years and for his valuable advices around my work. I am very thankful to Prof. Michael McCarthy for his support and feedback in the closing stages of this thesis.

I gratefully acknowledge the PhD scholarship from the Irish Research Council (IRC) and the Irish Centre for High-End Computing (ICHEC) for the computing resources and technical support. I would also like to express my thanks to the department of Mechanical, Aeronautical and Biomedical Engineering (MABE) and the Material and Surface Science Institute (MSSI) at the University of Limerick for providing excellent facilities.

Thanks to Micheal O’Regan, Michael Bezuidenhout, Robert Telford and Edmond Tobin for proof-reading my work and for the help in the laboratory. I also owe gratitude to Dr. Ulrich Timm who convinced me to pursue a PhD in Ireland.

Finally, I would like to thank my parents and my sister for giving me nice breaks from my study in Germany.
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Notations and conventions

Throughout the thesis, symbols of equations are explained immediately after their first appearance. General notation rules and conventions are given below.

General conventions

Equations, figures and tables are numbered relative to chapters. Within the text, figures and tables are referenced using their caption names together with their numbers. Equations are referenced using their numbers. References are listed at the end of the thesis in alphabetic order with respect to the first author’s surname.

General notation

- Regular typeface: scalar constants
- Bold typeface: vector and tensor constants
- Regular italic typeface: scalar variables
- Bold italic typeface: vector and tensor variables

\( A \) Area of the crack surface
\( A_c \) Edward-Vilgis strain-energy function
\( A_{\text{CNT}} \) Amplitude of the carbon nanotube
\( A_{\text{continuum}} \) Cross-sectional area of effective fibre
\( A_{\text{tubular}} \) Cross-sectional area of tubular carbon nanotube representation
\( \bar{B} \) Isochoric left Cauchy-Green tensor
\( C \) Vogel equation constant
\( C \) In-plane stiffness
$C_x$ Modified force constant

$C_\rho$ Bond angle variation constant

$C_r$ Bond-stretching force constant

$C_\tau$ Torsional resistance force constant

$D$ Flexural rigidity

$\bar{D}$ Isochoric rate of deformation

$\bar{D}^e$ Elastic part of isochoric rate of deformation

$D_e$ Damage evolution displacement

$D_f$ Failure displacement

$D_i$ Damage initiation displacement

$\bar{D}^v$ Viscous part of isochoric rate of deformation

$E$ Young’s modulus

$\Delta E$ Energy change

$\Delta E_1$ Mode I energy contribution for crack closure

$\Delta E_{II}$ Mode II energy contribution for crack closure

$\Delta E_{III}$ Mode III energy contribution for crack closure

$EA$ Tensile resistance

$E_{cell}$ Young’s modulus of the unit-cell

$E_{CNT}$ Young’s modulus of the carbon nanotube based on a solid cross-section

$E^{\text{compression}}_{33}$ Longitudinal compressive Young’s modulus of the multi-walled carbon nanotube

$E_{eff}^{\text{CNT}}$ Young’s modulus of the carbon nanotube based on a tubular cross-section

$E_{ERM}$ Effective reinforcing modulus of carbon nanotubes

$EI$ Flexural rigidity
$E_m$ Young’s modulus of the matrix

$E_{pe}$ Plane-strain Young’s modulus

$E_{\text{pull-out}}$ Carbon nanotube pull-out energy

$E_{33}^S$ Surface longitudinal Young’s modulus of the carbon nanotube

$E_t$ Longitudinal Young’s modulus of transversely isotropic material

$E_{33}^{\text{tension}}$ Longitudinal tensile Young’s modulus of the multi-walled carbon nanotube

$E_{33}^{\text{zig-zag}}$ Longitudinal Young’s modulus of the zig-zag carbon nanotube

$E_{33}^{\text{armchair}}$ Longitudinal Young’s modulus of the armchair carbon nanotube

$F$ Interatomic force

$\mathbf{F}$ Deformation gradient tensor

$\mathbf{\bar{F}}$ Isochoric (deviatoric) part of the deformation gradient tensor

$\mathbf{F}_f$ Force vector of relevant corner node

$F_{2j}$ Reaction force at node j in $x_2$ direction

$\mathbf{F}_{\text{macro}}$ Macroscopic deformation gradient tensor

$F_{\text{pull}}$ Pull-out force

$\mathbf{F}_{\text{RVE}}$ Deformation gradient tensor field within the representative volume element

$\mathbf{F}_{\text{vol}}$ Volumetric part of the deformation gradient tensor

$f$ Sp$^3$-bond density

$f_{x(2)}$ Component in the $x$-direction of the force vector at node 2

$G$ Shear modulus

$G_{12}$ In-plane shear modulus of the multi-walled carbon nanotube

$G_{\text{IIc}}$ Mode II critical energy release rate

$G_{12}^{\text{armchair}}$ In-plane shear modulus of the armchair carbon nanotube

$G_{31}^{\text{armchair}}$ Longitudinal shear modulus of the armchair carbon nanotube
$G_c$  Critical fracture energy

$G_{IJ}$  Torsional stiffness

$G_m$  Matrix shear modulus

$G_p$  In-plane shear modulus of transversely isotropic material

$G_l$  Longitudinal shear modulus of transversely isotropic material

$G_{12}^{\text{zig-zag}}$  In-plane shear modulus of the zig-zag carbon nanotube

$G_{31}^S$  Surface longitudinal shear modulus of the carbon nanotube

$G_{31}^{\text{zig-zag}}$  Longitudinal shear modulus of the zig-zag carbon nanotube

$G_{31}$  Longitudinal shear modulus of the multi-walled carbon nanotube

$H$  Hardening modulus

$\Delta H_0$  Activation enthalpy associated with structural change

$I$  Second-order identity tensor

$J$  Volume ratio

$K$  Interfacial shear stiffness

$K_{12}$  In-plane bulk modulus of the multi-walled carbon nanotube

$K_{12}^{\text{armchair}}$  In-plane bulk modulus of the armchair carbon nanotube

$K_b$  Bulk modulus

$K_p$  In-plane bulk modulus of transversely isotropic material

$K_{12}^{\text{zig-zag}}$  In-plane bulk modulus of the zig-zag carbon nanotube

$L$  Length of the beam

$\bar{L}$  Isochoric velocity gradient

$L_{\text{eff}}$  Effective length of carbon nanotube

$M$  Number of carbon nanotube walls

$N$  Number of carbon nanotubes

$N$  Exterior unit normal

$R$  Universal gas constant
\( R \) Distance away from the nanotube where the matrix is not deformed due to the pull-out

\( R \) Carbon nanotube chiral vector

\( S \) Cohesive zone parameter for interfacial shear strength

\( \bar{S}^b \) Isochoric bond-stretching stress

\( \dot{\bar{S}}^b \) Objective rate of isochoric bond-stretch stress/Jaumann rate

\( \dot{S}^b \) Rate of deviatoric bond-stretch stress

\( \bar{S}^c \) Isochoric conformational stress

\( \bar{S}^c_i \) Principle stresses of the isochoric conformational stress

\( S^{\text{eff}} \) Effective compliance tensor

\( S^{\text{eff}}_{ij} \) Components of the effective compliance tensor

\( T \) Temperature

\( T^* \) Reference temperature

\( \dot{T} \) Rate of adiabatic heating

\( T_\infty \) Vogel temperature

\( T_{f\sigma} \) Fictive temperature

\( T_{f\sigma\infty} \) Final fictive temperature

\( T'_{f\sigma} \) Reference structure/fictive temperature

\( T_{\text{min}} \) Minimum tangent modulus

\( U \) Total steric potential energy

\( U_r \) Bond stretching energy

\( U_{\text{vdWs}} \) Van der Waals interaction energy

\( U_\phi \) Dihedral angle torsion energy

\( U_\theta \) Bond angle bending energy

\( U_{\omega} \) Out-of-plane torsion energy

\( V \) Volume of the deformed representative volume element
$V_0$ Volume of the undeformed representative volume element

$VF$ Carbon nanotube volume fraction in axisymmetric model

$V_p$ Pressure activation volume

$V_s$ Shear activation volume

$W$ Continuum spin

$X$ Position vector of a point on the undeformed boundary of the representative volume element

$\bar{X}_1$ Mean of ensemble 1

$\bar{X}_2$ Mean of ensemble 2

$X_j$ Position vector of a node on a relevant corner of the undeformed boundary

$a$ Crack length

$a_\sigma$ Time-stress shift factor

$b$ Length of the long edge of the representative volume element

$c$ Specific heat

$d_{\text{CNT}}$ Diameter of the carbon nanotube

$d$ RVE side length

$e_3$ Unit vector associated with 3-axis

$e_x$ Unit vector associated with x-axis

$e_y$ Unit vector associated with y-axis

$e_z$ Unit vector associated with z-axis

$g_{2k}^k$ Displacement of node $k$ in $x_2$ direction

$h$ Distance between outermost and innermost shell surface of carbon nanotube

$k_{3x}$ Direction cosine of unit vectors associated with 3-axis and x-axis

$k_{3y}$ Direction cosine of unit vectors associated with 3-axis and y-axis
\( k_{3z} \)  Direction cosine of unit vectors associated with 3-axis and z-axis
\( l_{0CNT} \)  Initial carbon nanotube length
\( l_{1CNT} \)  Final carbon nanotube length
\( l_c \)  Critical length of embedded carbon nanotube
\( l_{CNT} \)  Carbon nanotube length
\( l_{emb} \)  Embedded length of carbon nanotube
\( l_{Model} \)  Length of axisymmetric model
\( m \)  Scalar of the carbon nanotube unit vector 2
\( n \)  Scalar of the carbon nanotube unit vector 1
\( n_1 \)  Size of ensemble 1
\( n_2 \)  Size of ensemble 2
\( n' \)  Ensemble size
\( p \)  Unknown pressure
\( q_i \)  Eigenvectors of the isochoric left Cauchy-Green tensor
\( r_{Model} \)  Radius of axisymmetric model
\( r \)  Atomic distance
\( r_0 \)  Carbon-carbon bond length
\( r_1 \)  Carbon nanotube unit vector 1
\( r_2 \)  Carbon nanotube unit vector 2
\( r_{CNT} \)  Carbon nanotube radius
\( r_i \)  Inner carbon nanotube radius
\( r_{is} \)  Radius of inner shell of carbon nanotube
\( r_o \)  Outer carbon nanotube radius
\( r_{os} \)  Radius of outer shell of carbon nanotube
\( s \)  Ensemble standard deviation
\( s_1 \)  Standard deviation of ensemble 1
\( s_2 \)  Standard deviation of ensemble 2
Interface traction

Traction vector

$\bar{t}^*$  Welch’s test statistic

$t'$  t-value based on Student’s distribution

$t_{\text{CNT}}$  Carbon nanotube wall thickness

$t_{\text{IF}}$  Interface thickness

$u$  Interatomic sliding separation

$u_{pc}$  Fluctuation displacement arising from the nanocomposite morphology

$u_{\text{RVE}}$  Displacement applied to representative volume element

$v$  Local CNT axis unit vector

$\bar{v}$  Average CNT axis vector

$w$  Width of the carbon ring

$x$  Position vector of a point on the deformed boundary of the representative volume element

$x_E$  Position vector of a node on the edges of the deformed boundary

$x_F$  Position vector of a node on the faces of the deformed boundary of the representative volume element

$x_i$  Position vector of a node on a relevant corner of the deformed boundary

$x_J$  Position vector of a node on the corners of the deformed boundary

$x_{(2)}$  Component in the x-direction of the position vector at node 2

$\alpha$  Significance level

$\beta$  Shear lag constant

$\beta$  Angle between loading direction $x$ and average vector $\bar{v}$ of carbon nanotube phase

xx
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_i^{3x}$</td>
<td>Angle between axis 3 and $x$ at the i-th integration point within a given carbon nanotube</td>
</tr>
<tr>
<td>$\beta_{\text{ar}}$</td>
<td>Arithmetic mean of $\beta$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Separation</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Depth of the potential well</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Second order strain tensor</td>
</tr>
<tr>
<td>$\varepsilon_{ij}$</td>
<td>Components of the second order strain tensor</td>
</tr>
<tr>
<td>$\dot{\varepsilon}_M$</td>
<td>True strain rate</td>
</tr>
<tr>
<td>$\varepsilon_{\text{macro}}$</td>
<td>Macroscopic strain tensor</td>
</tr>
<tr>
<td>$\varepsilon_{M\text{(app)}}$</td>
<td>Applied nominal strain</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>Softening strain limit</td>
</tr>
<tr>
<td>$\bar{\varepsilon}^{\varepsilon}$</td>
<td>Sum of the invariants of the viscous strain increments</td>
</tr>
<tr>
<td>$\varepsilon_0^{\varepsilon}$</td>
<td>Strain range over which rejuvenation occurs</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Bond twisting angle</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Deformed boundary of the representative volume element</td>
</tr>
<tr>
<td>$\Gamma_0$</td>
<td>Undeformed boundary of the representative volume element</td>
</tr>
<tr>
<td>$\phi\Delta c$</td>
<td>Effective specific heat difference</td>
</tr>
<tr>
<td>$\gamma_S$</td>
<td>Crack surface energy per unit area</td>
</tr>
<tr>
<td>$\lambda_b$</td>
<td>Buckling wavelength</td>
</tr>
<tr>
<td>$\lambda_{\text{CNT}}$</td>
<td>Carbon nanotube wavelength</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Elastic network principle stretches</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$\nu_{31}$</td>
<td>Major Poisson’s ratio of the multi-walled carbon nanotube in tension</td>
</tr>
<tr>
<td>$\nu_{31\text{armchair}}$</td>
<td>Major Poisson’s ratio of the armchair carbon nanotube</td>
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<tr>
<td>$\nu_{31\text{compression}}$</td>
<td>Major Poisson’s ratio of the multi-walled carbon nanotube in compression</td>
</tr>
<tr>
<td>$\nu_{31\text{tension}}$</td>
<td>Major Poisson’s ratio of the multi-walled carbon nanotube in tension</td>
</tr>
</tbody>
</table>
\( \nu \) \_\text{lp}  \quad \text{Major Poisson’s ratio of transversely isotropic material}

\( \nu \text{\_31}\_\text{zig-zag} \)  \quad \text{Major Poisson’s ratio of the zig-zag carbon nanotube}

\( \theta \)  \quad \text{Bond angle}

\( \rho \)  \quad \text{Density}

\( \sigma \)  \quad \text{Distance at which the potential is zero}

\( \sigma \)  \quad \text{Second order Cauchy stress tensor}

\( \bar{\sigma} \)  \quad \text{Isochoric Cauchy stress}

\( \bar{\sigma}^b \)  \quad \text{Bond-stretching part of the isochoric Cauchy stress}

\( \sigma_c \)  \quad \text{Critical fracture stress}

\( \sigma_{\text{CNT}} \)  \quad \text{Carbon nanotube tensile strength}

\( \sigma_{ij} \)  \quad \text{Components of the second order stress tensor}

\( \sigma_m \)  \quad \text{Mean (hydrostatic) stress}

\( \sigma_{\text{macro}} \)  \quad \text{Macroscopic Cauchy stress}

\( \sigma_{\text{pl}} \)  \quad \text{Yield strength with an offset of 1\% of plastic strain}

\( \bar{\sigma}_{\text{RVE}} \)  \quad \text{Volume average of Cauchy stress tensor field of representative volume element}

\( \sigma_{\text{RVE}} \)  \quad \text{Cauchy stress tensor field of representative volume element}

\( \sigma_{xx} \)  \quad \text{Component (xx) of the Cauchy stress tensor}

\( \sigma_Y \)  \quad \text{Yield peak stress}

\( \tau \)  \quad \text{Relaxation time}

\( \tau_0^* \)  \quad \text{Viscoelastic relaxation time at reference temperature}

\( \tau_0 \)  \quad \text{Relaxation time in the linear viscoelastic limit}

\( \tau_{\text{oct}}^b \)  \quad \text{Octahedral shear component of the bond-stretch stress}

\( \tau_{\text{IF}} \)  \quad \text{Carbon nanotube-polymer interfacial shear strength based on Kelly-Tyson force balance approach}

\( \bar{\tau}_{\text{IF}} \)  \quad \text{Average interfacial shear strength}

\( \mathring{\tau}_{\text{IF}} \)  \quad \text{Maximum interfacial shear strength based on Cox shear lag theory}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$</td>
<td>Degrees of freedom</td>
</tr>
<tr>
<td>AFEM</td>
<td>Atomistic finite element modelling</td>
</tr>
<tr>
<td>$AR$</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>CFRP</td>
<td>Carbon fibre-reinforced polymer</td>
</tr>
<tr>
<td>$CIW$</td>
<td>Confidence interval width</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CRR</td>
<td>Cooperatively rearranging region</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DWCNT</td>
<td>Double-walled carbon nanotube</td>
</tr>
<tr>
<td>EF</td>
<td>Effective fibre</td>
</tr>
<tr>
<td>FE</td>
<td>Finite element</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite element modelling</td>
</tr>
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<td>HDPE</td>
<td>High-density polyethylene</td>
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<tr>
<td>LEFM</td>
<td>Linear elastic fracture mechanics</td>
</tr>
<tr>
<td>MCFEM</td>
<td>Monte Carlo finite element modelling</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>$MF$</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
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<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
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<tr>
<td>PBC</td>
<td>Periodic boundary condition</td>
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<td>RVE</td>
<td>Representative volume element</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SSA</td>
<td>Specific surface area</td>
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<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
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<tr>
<td>$TERR$</td>
<td>Total energy release rate</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>VCCT</td>
<td>Virtual crack closure technique</td>
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<tr>
<td>vdWs</td>
<td>Van der Waals</td>
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Chapter 1

Introduction

1.1. Background

Since a quarter of a century, attention in composite research has been shifted to the relatively new class of composite materials called nanocomposites, where at least one material component has to exhibit a dimension at the nanoscale (1-100 nm). The main reason for that shift is the emergence of nanoparticles (e.g. carbon nanotubes, graphene, nanoclays, cellulose nanowhiskers, nanosilica, nanoalumina), which promise property enhancements to a wide variety of matrices such as polymers or metals. In general, those property enhancements are expected due to: (1) an outstanding ratio of surface area to volume, i.e. specific surface area (SSA), which is available to interact with a matrix material, and (2) outstanding multifunctional properties (e.g. high stiffness, electrical and thermal conductivities). For example, large SSA particles, which are relatively well dispersed in a nanocomposite system at small concentrations (<10 mass%) result in small interparticle distances and an enormous interfacial area. When compared to traditional filler materials such as aluminium oxides or carbon fibres, the length scale transition from micro to nano shows substantial enhancements in interfacial interaction area of three orders of magnitude (see Fig. 1.1).
Figure 1.1: Distribution of conventional microscale and nanoscale fillers; (a) Al$_2$O$_3$, (b) carbon fibre and (c) CNTs of the same 0.1 volume% in a reference volume of 1 mm$^3$ (Adapted from Ma, Siddiqui et al. 2010); particle number (a) 2, (b) 255 and (c) $4.42 \times 10^8$; interfacial area (a) $6 \times 10^{-8}$ m$^2$, (b) $8 \times 10^{-7}$ m$^2$ and (c) $3 \times 10^{-4}$ m$^2$ (calculated using particle dimensions provided in Table 2 of Ma, Siddiqui et al. 2010).

This highlights the importance of successful interfacial engineering (e.g. surface functionalisation of nanofillers) in nanoscale systems since many physical and mechanical properties are governed by surface and interface behaviour. As a result, extraordinary properties of nanoscaled fillers in, for example, stiffness, resilience, electrical and thermal conductivity promise substantial effects on the macroscopic properties of the nanocomposite.

Nanofillers in polymeric matrices have been prepared and suggested for a range of applications. Those applications exploit for example the exceptional electrical conductivity of carbon nanotubes (CNTs) for lightning strike protection (Gou et al. 2010), antistatic coatings (Sandler et al. 2003), or electromagnetic interference shielding (Zhang, Ni et al. 2007). The number of nanoparticles with their specific geometrical characteristics and properties (mechanical, electrical, thermal, optical, chemical) is reflected in the vast field of potential applications ranging from flame retardants (Laoutid et al. 2009), scratch resistant coatings (Musil 2000), food packaging films with improved barrier properties (Arora and Padua 2010), up to polymers with increased rate of biodegradability (Ray and Bousmina 2005) for biomedical devices.

One of the main reasons for the popularity of polymeric nanocomposites is that industrial fabrication methods for traditional thermoplastic polymers (e.g. extrusion or injection molding) or thermoset-based composite materials such as
the vacuum assisted resin transfer molding for carbon fibre-reinforced polymer (CFRP) laminates are directly applicable to polymeric nanocomposites, thus, facilitating their preparation using conventional manufacturing routes.

In the aerospace and wind-turbine industries, epoxy resin-based CFRP laminates promise to meet current environmental demands for the reduction of fuel consumption, efficient energy generation and the long-term structural and environmental durability. When compared to metals, they are very attractive due to their good specific stiffness/strength, improved fatigue life and corrosion resistance.

However, one of the remaining issues, which still compromise the use of epoxy-based laminates in high-performance applications, is their relatively brittle behaviour when exposed to in-service impact events such as those caused by foreign objects. Therefore, improvement of the energy absorption characteristics of those materials is an important research goal for material scientists and engineers working with composite materials.

Applying a surface coating composed of CNTs and epoxy or incorporating CNTs into the epoxy matrix of CFRP laminates offers means to improve the energy absorption at low CNT concentrations. Enhancement in energy absorption characteristics are expected to be brought by two main deformation mechanisms: (1) improved nonlinear finite deformation of epoxy in compression due to the presence of CNTs and (2) CNT crack bridging mechanisms accompanied by CNT pull-out and interface debonding in tension.

Nevertheless material composition (e.g. CNT volume fraction, CNT aspect ratio) and the manufacturing method-induced nanocomposite morphology (e.g. CNT distribution, CNT orientation, CNT functionalisation) have a main impact on macroscopic properties and, thus, on the energy absorption of epoxy/CNT nanocomposites. Theoretically, CNTs aligned and optimally distributed within
the epoxy matrix promise to provide the maximum enhancement in stiffness in the direction of CNT alignment. However, obtaining homogenous CNT dispersion and a controlled degree of CNT alignment within polymeric matrices still remains a significant research challenge.

Hence, understanding the relationship between process-induced morphology and resulting macroscopic behaviour is an important engineering task. Advanced material modelling can complement experimental work and assist experimentalists in exploring this relationship systematically.

**1.2. Motivation**

A systematic investigation of morphological parameters such as CNT aspect ratio or CNT distribution/orientation solely by experiments is time consuming and imposes significant challenges on nanocomposite preparation. For example, an increase in CNT volume fraction is often observed to lead to changes in the agglomeration behaviour and, thus, to a different final CNT distribution when applied dispersion/functionalisation methods did not work to satisfaction (e.g. Tseng et al. 2007). Hence, the effect of CNT volume fraction on the macroscopic behaviour can be a combined effect composed of CNT volume fraction and CNT distribution. Experimental studies are prone to interaction of two or more factors and, thus, they are frequently unable to apportion the effect of a single parameter on the mechanical response. On the other hand, advanced computational material modelling allows for the study of morphology aspects in a more systematic manner, for example by changing one factor at a time. Hence, the advanced computational material modelling is, therefore, a complementary approach to experimental work in exploring the morphology-property relationships for nanocomposites. In addition, it carries an economic advantage over costly and time consuming experimental work.
However, development of a robust and reliable nanocomposite computational modelling approach poses other challenges. The mechanical response of epoxy/CNT nanocomposites is complex due to its hierarchical structure, which results from several length and time scales involved, spanning the nanometre scale and the macroscale. Further elucidation below provides a short excursion into different length scales of the hierarchical structure of the nanocomposite.

At the atomistic scale, CNTs consist of a small number of carbon atoms, arranged in hexagons, with a given chirality and possible defects. Variations in those structural characteristics can alter mechanical properties of isolated CNTs. The same applies to the interface, where interaction between CNT and polymer is affected by intra- and inter-atomic interactions like inter-atomic bonding, discrete distribution of bonding as well as bond breaking and rebonding mechanisms. The corresponding time scale for atoms and molecules in motion is the femtosecond scale (Zewail 2000).

In comparison, the microscale of the nanocomposite can be characterized by CNT agglomerations, i.e. local differences between CNT concentrations that may result in zones of different stiffness compared to the surrounding nanocomposite. Concerning the time scales, structural relaxation or motion in polymer chains may take several seconds.

Hence, robust macroscopic predictions need to account for those aspects at different scales. Holistic multiscale computational modelling techniques must be developed and applied to cope with that range of time and length scales, to predict the macroscopic response of nanocomposites.

Clearly, for the model to complement and then replace experimental tests with simulations requires the model prediction to be an accurate representation of the real material behaviour. Thus, robust multiscale modelling demands experimental validation to confirm its degree of accuracy. The comparison
between experimental outcome and model predictions allows drawing conclusions about the robustness of the applied multiscale modelling approach and answer the question whether sufficient detail was included within the multiscale framework. Validation can be conducted under specific conditions, i.e. for example for certain nanocomposite morphologies or in a smaller range of the strain rates, in order to save costs of the experiments, and then used to evaluate the material behaviour in the full range of the operating regime. However, predictions outside the validated regime have to be handled with care since the accuracy might decrease when approaching extremes of the operating regime.

Therefore, this work follows a combined experimental-computational approach to develop a reliable multiscale model for the prediction of the energy absorption characteristics for epoxy/CNT nanocomposites. The focus herein is put on the non-linear and strain rate dependent compressive behaviour of those materials. Despite its practical importance only few experimental studies focussed the nonlinear compressive response of CNT/epoxy nanocomposites (e.g. Dassios et al. 2012) and even less research considered the behaviour under high strain rates. To this date the author is only aware of one study investigating the nonlinear compressive behaviour of CNT/epoxy nanocomposites under impact rates of strain (see Gómez-del Río et al. 2014). Likewise, using numerical methods, the compressive response of CNT/polymer nanocomposites has only been sparsely researched. Nanocomposite behaviour under compressive loading (e.g. CNT instability and damping behaviour) was predicted using molecular dynamics (MD) and multiscale finite element modelling (FEM) (Namilae and Chandra 2006, Rafiee and Moghadam 2012, Li and Chou 2006). The proposed models did not, however, consider sufficiently large deformations (important as an energy absorbing mechanism), strain rate dependence (occurring during impact), and nanocomposite morphological
effects (e.g. CNT orientation, nanoparticle interactions) for the prediction of the nanocomposite mechanical response.

1.3. Objective of the thesis

The main goal of this work is to develop a multiscale computational model for the prediction of the mechanical response of epoxy/CNT nanocomposites under compressive loads. The model will then be used to give better insight into morphology-property relations and, thus, draw conclusions in terms of applicability of epoxy/CNT systems as impact-resistant nanocomposite. In order to study the energy absorption characteristics under tensile loading, the fracture resistance of epoxy/CNT nanocomposite will be investigated in presence of interfacial damage propagation within the epoxy-CNT interface and interwall interface. The following elements will be combined in order to develop the multiscale computational model for the nanocomposite under compression:

1) Representative volume element (RVE) concept-based generator capable of reproducing three-dimensional process-induced nanocomposite morphologies defined in terms of CNT distribution, CNT orientation and CNT waviness
2) Physically-based constitutive ‘glass-rubber’ model (Buckley et al. 2004) able to capture the nonlinear strain rate dependent behaviour of the epoxy matrix
3) Traction-separation laws representing imperfect bonding based on weak van der Waals (vdWs) interactions between CNTs and epoxy matrix
4) Effective fibre (EF) concept based on molecular mechanics calculations of CNTs (Shen and Li 2004, Shen and Li 2005) to represent the continuum mechanical response of single- and multi-walled CNTs
5) Nonlinear numerical homogenisation to bridge the RVE and macroscopic scales, and predict the overall response of the nanocomposite

The robustness of the multiscale modelling approach will be evaluated by comparing the predictions with experimental results. The validation will focus on randomly oriented and distributed CNT/epoxy nanocomposites subjected to uniaxial compression under quasi-static strain rates and will involve the following steps:

1) Preparation of pure epoxy and CNT/epoxy nanocomposite samples using common processing methods
2) Quasi-static compression testing of pure epoxy and CNT/epoxy nanocomposites
3) Evaluation of obtained nanocomposite morphologies and fracture surfaces (i.e. CNT dispersion) using scanning electron microscopy (SEM)

Once this main goal is achieved, important aspects of process-induced nanocomposite morphology such as CNT waviness, and imperfect epoxy/CNT interaction will be studied. This will enable the identification of key factors that are believed to control energy absorption characteristics and hence, it will point out the potential of CNT/epoxy systems towards impact-resistant applications.

1.4. Outline of the thesis

In Chapter 2, a literature review is presented. Epoxy/CNT nanocomposites are reviewed in detail with respect to their advanced preparation methods and their final mechanical performances. Commonly applied multiscale modelling methodologies are discussed, and an additional focus is put on nanocomposite morphology effects (e.g. CNT alignment or CNT waviness) on the nanocomposite mechanical response.
The potential of aligned epoxy/CNT nanocomposites towards energy absorption applications is demonstrated for two simple case studies using finite element modelling in Chapter 3:

1) Crack resistance characteristics of epoxy reinforced with aligned double-walled CNTs (DWCNTs) in the vicinity of a matrix crack under tensile loads

2) Rate dependent compressive response of epoxy/CNT nanocomposites with aligned single-walled CNTs (SWCNTs)

In Chapter 4, the 3D multiscale modelling approach is proposed, where the scales and phenomena of interest are captured. The constitutive behaviour of CNT and epoxy/CNT interface is described there. Moreover, the reconstruction of nanocomposite morphology through the developed 3D RVE-based tool integrated with Finite Element software ABAQUS and nonlinear numerical homogenisation procedure are presented.

Chapter 5 reports the comparison between predictions of the compressive behaviour of CNT/epoxy systems by 3D and 2D computational models. Results show that despite their computational efficiency 2D models compromise the accuracy of their predictions. 3D models are shown to be the natural choice to capture CNT morphologies and predict the nonlinear compressive behaviour of the nanocomposites.

In Chapter 6, the validation of the 3D multiscale modelling approach is discussed. Thus, the experimental part of the work consisting of nanocomposite preparation, quasi-static compression tests and SEM of obtained fracture surfaces are presented and the experimental data is compared against their computational predictions. Furthermore, the effects of CNT waviness and filler-matrix vdWs interaction on the compressive response of epoxy/CNT nanocomposites are studied.
The main findings and conclusions are summarised in the final Chapter 7, and recommendations for future work are made.
Chapter 2

Literature review

2.1. Fundamentals of CNTs

Carbon nanotubes are tubular cylinders of covalently bonded carbon atoms, whose ends may be capped by hemi-fullerenes. Since the discovery of CNTs by Iijima (1991) numerous researchers have been reporting unique properties of this new form of carbonaceous structure. Today, CNTs are well-known as the stiffest fibres with a longitudinal Young’s modulus around 1 TPa (Lu 1997), highly unusual electrical and excellent thermal conductivity up to $2 \times 10^7$ S/m (Ebbesen et al. 1996) and 2000 W/mK (Fujii et al. 2005) respectively. Further they possess an exceptional high aspect ratio with lengths up to 550 mm (Zhang et al. 2013), low mass density in the bulk phase around 1.3 g/cm$^3$ (Gao et al. 1998) and high flexibility and resilience (Falvo et al. 1997). All these unique properties give rise to a wide range of possible applications interesting for industry and science, such as nanoprobes (Dai et al. 1996), in antistatic coatings (Sandler et al. 2003), field emitters (Rinzler et al. 1995, Semet et al. 2002) or as mechanical reinforcements (Lourie and Wagner 1999).

CNTs are produced by three main techniques: arc discharge, laser ablation and chemical vapour deposition (CVD). Depending on the synthesis procedure carbon nanotubes can vary in tube length, tube diameter, chirality, waviness, type and amount of impurities, defect density and number of sidewalls. The latter is used to categorize CNTs into two main classes: single-walled carbon
nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (see Fig. 2.1).

The molecular structure of a SWCNT is described by a single sheet of graphene that has been rolled up into a tubular shape. The sp\(^2\) orbital hybridisation is responsible for its characteristic honeycomb crystal lattice as well as strong \(\sigma\)-bonds between the carbon atoms within the sheet plane. A pair of indices \((n, m)\) is used to describe the orientation of the graphite network relative to the tube axis. The indices are scalars of the chiral vector \(\mathbf{R}\) that is a linear combination of the unit vectors \(\mathbf{r}_1\) and \(\mathbf{r}_2\) according to \(\mathbf{R} = nr_1 + mr_2\) (see Fig. 2.2).

Figure 2.1: Structure of (a) single-walled carbon nanotube and (b) multi-walled carbon nanotube (from Wernik and Meguid 2010).

Figure 2.2: Illustration of CNT chirality on unrolled graphene; armchair: \(n=m\); zig-zag: \(n=0 \land m \neq 0\) or \(n \neq 0 \land m=0\); all other configurations are named chiral. Dashed and dotted lines refer to the boundaries of the unrolled graphene sheets. Influences of CNT chirality on electrical conductivity according to Moniruzzaman and Winey (2010)(see legend).
The MWCNTs are more complex and can be considered as a coaxial composition of 2 to 50 SWCNTs held together through secondary (weak) vdWs bonding with constant radial distance close to the interlayer spacing of graphene sheets (0.34 nm). The aforementioned weak interwall interaction indicates low friction and easy sliding between the walls.

However, structural defects in CNTs may affect the sliding ability, affect the axial tensile strength, the modulus of the CNTs (Cheng et al. 2009, Peng, Locascio et al. 2008), and alter the geometrical appearance of the tube to a kinked, bulging or even more distorted form. In general, those defects are side-effects of the production process, but can also be generated purposely via mechanical manipulation, electron or ion beam irradiation to tailor the mechanical and electronic properties of the CNT (Sammalkorpi 2004).

First measurements of the Young’s modulus of CNTs were performed by Treacy et al. (1996). They thermally induced vibrations on cantilevered MWCNTs within a transmission electron microscope (TEM) and calculated an average Young’s modulus of 1.8 TPa. Many papers investigating the mechanical performance of CNTs, both experimentally and theoretically, then followed. However, a large scatter exists among available experimental data, which can be attributed to the large variety of CNTs (number of sidewalls, chiralities, dimensions, defect densities etc.), different modelling assumptions especially for the cross-sectional area and the difficulty in achieving a proper testing facility at the nanoscale with controlled loading and an appropriate measuring/acquisition method. As a consequence of the latter, the mechanics of CNTs became a favoured topic in theoretical and computational studies. Today researchers commonly agree that under the assumption of a tubular cross-section with wall thickness equal to the interlayer spacing around 0.34 nm,

Yakobson and co-workers (Yakobson et al. 1996, Yakobson et al. 1997) showed with MD simulations that under various loading conditions (tension, compression, bending and torsion) and for small strain deformations the CNT strain energy increases quadratically with elongation, bending angle and torsion angle, which is in accordance to Hooke’s law. Furthermore, they found abrupt changes in morphology of the CNTs due to buckling instabilities (Yakobson et al. 1996, Yakobson et al. 1997) as soon as their linear elastic limit is exceeded. Global buckling and local buckling are supported by various experimental studies of SWCNTs and MWCNTs (Ruoff and Lorents 1995, Iijima et al. 1996, Falvo et al. 1997, Lourie et al. 1998). Noteworthy is the remarkable resilience of the CNTs with reversibility of the buckling. The tubes could be bent through large angles without causing damage or structural defects. Furthermore, the distances between the walls of a thick MWCNT were observed not to alter and the wavelength of the characteristic wrinkling or rippling (see Fig. 2.3) permeates through the inner walls (Poncharal et al. 1999). This indicates a strong repulsive force acting between the C-atoms of the walls of MWCNTs.
2.2. Processing of CNT/epoxy nanocomposites

An enormous interest in CNTs as nanofiller material was brought about by their excellent properties (see Section 2.1). However, even after several years of research the full potential of CNTs remains still unused due to two main manufacturing challenges, which need to be resolved in order to transfer the superb properties of CNTs to the nanocomposite (Gojny and Schulte 2004): (1) the proper dispersion and (2) accurate surface modification to create the desired interfacial bonding.

First, CNTs are nano-scaled particles and exhibit a large specific surface area (SSA, surface area per unit mass). As a result, intrinsic vdW’s forces, usually considered to take part in relatively weak secondary bonding, have a relatively strong effect at this scale. In detail, they are responsible for the CNT’s tendency to stick to each other and to form agglomerated bundles (Ma, Siddiqui et al. 2010, Gojny et al. 2005). The large aspect ratio and waviness of CNTs bring further intensification of that agglomeration phenomenon through the possibility of entanglements (see Fig. 2.4). Hence, a homogeneous dispersion in an epoxy resin and good wetting are not easy to achieve. Moreover, once a
relatively good dispersion is obtained, maintaining a stable dispersion and minimising the process of reagglomeration are also of concern (Ma, Mo et al. 2010, Li et al. 2007).

Figure 2.4: SEM micrograph of entangled MWCNT agglomerates (from Ma, Siddiqui et al. 2010).

Secondly, CNT-walls are inert and can only interact with the polymer via weak vDWs forces. This may lead to insufficient stress transfer. Modifying the surface properties of CNTs through functionalisation promises a better interfacial bonding and, thus, enhanced stress transfer (Gojny et al. 2005).

Conclusively, an efficient manufacturing method for CNT nanocomposites aims at separating individual CNTs from the agglomerates via mechanical dispersion and their stabilisation in the matrix. Various advanced methods were applied to mechanically disperse the CNTs uniformly, like for example high speed shear mixing (Ganguli et al. 2005), ball milling (Li et al. 2007), calendering (three roll mill) (Gojny et al. 2005) and probe ultrasonication (Zhu et al. 2004) (see Fig. 2.5).
Figure 2.5: (a) Shear mixer with schematic illustration (Ma, Siddiqui et al. 2010), (b) Schematics of ball milling (Generalic 2011), (c) calendering (EXAKT 2011), (d) probe/horn sonication (from Ma, Siddiqui et al. 2010).

Applying ultrasound energy is the most commonly used technique. Ultrasound shock waves are sent through the solvent to the agglomerates, where they provoke a detachment of the outer nanotubes from the bundle. In probe sonicators the energy is focused in the small sized tip, which may result in CNT damage (Lu et al. 1996). In contrast, the calendering process/three roll milling is often used to homogenise more viscous polymer/CNT mixtures that are not diluted by solvents (Gojny et al. 2005). The machine consists of a feeding, a centre and an apron roller, which rotate at different velocities, where the centre one rotates in the opposite direction. The material in the hopper is drawn between the feeding and centre roller. High shear forces are applied to material between the two gaps.

Functionalisation methods can be divided into covalent and non-covalent functionalisation methods. Covalent bonds are created on the sidewalls and/or the CNT ends between carbon atoms and functional entities. According to Ma, Siddiqui et al. (2010) two possible strategies exist. The first strategy is based on the direct covalent sidewall functionalisation (see Fig. 2.6B), which is characterised by a change of the orbital hybridisation from \( \text{sp}^2 \) to \( \text{sp}^3 \) through
the attachment of highly reactive reagents like fluorine (C–F) (Mickelson et al. 1998).

The second strategy revolves around the defect functionalisation (see Fig. 2.6A) that uses existing or generated defects (e.g. using acids or plasma) such as vacancies, heptagons and pentagons or open CNT ends, which become stabilised by carboxylic groups (C–COOH) for example (Liu et al. 1998). In both cases, additional chemical reactions are possible in order to obtain the functional groups favoured (Ma, Siddiqui et al. 2010).

Polymer wrapping (see Fig. 2.6D) (e.g. Curran et al 1998) and surfactant treatment (see Fig. 2.6C) (e.g. Geng et al. 2008) are typical non-covalent functionalisation methods. Polymer wrapping is believed to originate from vdwS and π–π stacking interaction between CNT and polymer chains, which participate in the formation of supramolecular complexes of CNTs (Ma, Siddiqui et al. 2010). Non-ionic surfactants are adsorbed onto the surface due to strong hydrophobic attraction between CNT and the tail group of surfactant.
This is followed by self-assembling of surfactant molecules into micelles above a critical micelle concentration (Geng et al. 2008).

Polar functional groups and surfactants change the hydrophobic nature of CNTs into hydrophilic one, what makes CNTs soluble in many organic solvents. Solvents are, therefore, preferably used for the dispersion of functionalised nanotubes. Furthermore the dispersion state is effectively stabilised through electrostatic/steric repulsive forces (Li et al. 2007, Ma, Siddiqui et al. 2010).

2.3. Mechanics of CNT/epoxy nanocomposites

Effective load transfer from the matrix to embedded fillers and filler load bearing ability are essential for efficient mechanical reinforcements. The same applies to CNTs used as nanoscale filler material. Schadler et al. (1998) found a good load transfer of MWCNT/epoxy nanocomposites using Raman spectroscopy. Carbon nanotubes in matrix systems provide load transfer similar to conventional short fibre composites. For example, Lourie and Wagner (1999) observed the formation of damage doublets in two parallel and adjacent straight carbon nanotubes embedded in a polymer matrix. Such damage clusters usually occur in traditional non-continuous fibre reinforced composites due to a redistribution of stress from a failed fibre to its intact neighbour. The authors suggested that the fundamentals of continuum mechanics of fibre composites hold to some degree in carbon nanotubes embedded in polymer matrices. Li and Chou (2003b) coupled atomistic FEM (AFEM) with FEM to study the load transfer computationally. Their interfacial shear stress distributions and CNT tensile stress distribution are in a qualitative agreement with classical respectively modified shear lag models (cf. Cox 1952, Clyne 1989). Likewise, other traditional models for short fibre composites like the Kelly-Tyson model (Kelly and Tyson 1965) were considered to be convenient tools to
get insights into reinforcement effect, interfacial stress transfer and load bearing ability of CNTs. In this context, the Kelly-Tyson force balance approach was adopted for hollow tubes by Wagner et al. (1998), leading to the following relation between tube geometry (outer and inner tube radii $r_o$ and $r_i$), mechanical properties (tensile strength $\sigma_{\text{CNT}}$, interface shear strength $\tau_{\text{IF}}$) and embedded critical CNT length $l_c$:

$$\tau_{\text{IF}} = \frac{r_o}{l_c} \left(1 - \frac{r_i^2}{r_o^2}\right) \sigma_{\text{CNT}}.$$  \hspace{1cm} (2.1)

The critical length $l_c$ is the minimum embedded CNT length at which CNT fracture occurs, provided the maximum tensile stress in the CNT is equal to the tensile strength of the CNT. From an engineering point of view, the critical CNT length is an important threshold value (lower bound) because the maximum axial CNT stress will be achieved locally in the middle of the CNT. Larger CNT lengths increase the portion of the CNT that is loaded with the maximum axial CNT stress. Hence, CNT lengths above this critical value are often referred to as ‘effective’ CNT lengths which enable the composite to transfer a bigger load fraction onto the CNT. Due to the wide range of CNT diameters and/or experimentally observed CNT strengths, Wagner (2002) concluded using Eq. (2.1) that a wide range of interfacial shear strengths or critical CNT lengths are in principle attainable. Assuming the interface shear strengths $\tau_{\text{IF}}$ to be a material constant (50, 100, 300 MPa), obtained for example via functionalisation, Fig. 2.7 shows the variability in critical lengths with variations in SWCNT tensile strength.
Micro-mechanical interlocking, chemical bonding and vdWs interaction are relevant types of polymer/CNT interactions affecting the interfacial shear strength $\tau_{IF}$ (Strus et al. 2009). It is well known that weak vdWs forces make up the smallest portion contributing to the interfacial shear strength and chemical bonding the highest portion. Interlocking is expected to be caused by imperfect CNT structures or differences in thermal expansion coefficients.

The modified force-balance approach (see above) was used by Wagner et al. (1998) to calculate interface shear strength values for a MWCNT/polymer (urethane/diacrylate oligomer) from a single nanotube fragmentation test. Values of the order of 500 MPa were obtained, which is one order of magnitude larger than in conventional fibre composites. However, the authors speculate that the reason for that were strong covalent bonds occurring between CNT and that kind of polymer matrix.

The interface shear strength of the epoxy/CNT interface was determined experimentally by Cooper et al. (2002). Non-functionalised CNTs bridging the
holes in microtomed epoxy thin films were manipulated using a scanning probe microscope tip. They calculated an average interface shear strength $\tau_{IF}$ by dividing the pull-out force by the interfacial area of the embedded nanotube. Values for MWCNTs between 318 and 376 MPa for short embedded lengths and values between 35 and 91 MPa for tubes with longer embedded lengths were obtained.

It must be mentioned that the dependence of the average interfacial shear strength $\tau_{IF}$ on embedded CNT length $l_{emb}$ is in agreement with Cox’s shear lag theory. The relation between $\tau_{IF}^{max}$ and $\tau_{IF}$ is (Barber et al. 2006)

$$\tau_{IF} = \tau_{IF}^{max} \frac{\tanh(\beta l_{emb})}{\beta l_{emb}},$$

(2.2)

with a shear lag constant $\beta$:

$$\beta = \sqrt{\frac{2G_m}{E_{CNT}r_{CNT}^2 \ln(R/r_{CNT})}},$$

(2.3)

where $G_m$ is the shear modulus of the matrix, $E_{CNT}$ is the Young’s modulus of the CNT, $r_{CNT}$ is the radius of the CNT and $R$ is the distance away from the nanotube where the matrix is not deformed due to the pull-out (Barber et al. 2006). It can be shown from Eq. (2.2) that $\tau_{IF}$ approaches the maximum interface shear strength $\tau_{IF}^{max}$ as the embedded length is decreasing. One must also point out that the interfacial shear strength $\tau_{IF}$ obtained from the Kelly-Tyson model assumes a homogenous shear stress along the shear stress transfer length (Kelly and Tyson 1965). Hence, care must be exercised when comparing results employing different shear strengths assumptions/definitions.

In contrast, Barber et al. (2006) obtained maximum interface shear strength $\tau_{IF}^{max}$ values of 30 MPa for pristine MWCNTs and 151 MPa for modified (carboxyl groups) MWCNTs from nanotube pull-out tests from an epoxy matrix.
Nanotube pull-out tests from a polyether ether ketone (PEEK) matrix by Tsuda et al. (2011) revealed even smaller values between 3.5–14 MPa for an average interface shear strength $\tau_{IF}$.

### 2.3.1. Stiffness and strength

It is well recognised that a significant interface shear strength between CNTs and epoxy is essential for an effective load transfer and, thus, stiffness improvements (see Section 2.3). Also a uniform distribution of CNTs within the epoxy matrix due to a good state of dispersion (see Section 2.2) is advantageous because it maximizes stress transfer to the CNT.

CNT agglomerates (or bundles) are believed to be significantly responsible for nanocomposite strength reductions (e.g. Tseng et al. 2007, Liu and Wagner 2005, Lachman and Wagner 2010, Zhu et al. 2003, Zhu et al. 2004, Valentini et al. 2008) and the saturation of the nanocomposite Young’s or flexural modulus with increasing CNT mass fraction (e.g. Bai and Allaoui 2003, Tseng et al. 2007, Ma et al. 2007, Geng et al. 2008). CNT agglomerations may behave as imperfections/voids inducing stress-concentrations and, thus, early failure to the nanocomposite, similarly to micro-filled particulate polymer composites. This is especially the case when CNTs are in direct contact due to easy CNT-to-CNT sliding, similarly to the interwall sliding (Cumings and Zettle 2000), and incomplete impregnation (wetting) by epoxy (Ajayan et al. 2000). Localised regions of higher CNT concentrations fully impregnated with epoxy, also sometimes referred to as agglomerates, are expected to be less detrimental to the nanocomposite strength (e.g. Gojny et al. 2005).

Both, interface shear strength and dispersion can be improved via functionalisation (see Fig. 2.8), as explained in Section 2.2. As a matter of fact, successful experimental studies on CNT/epoxy nanocomposites without using
functionalisation or advanced dispersion methods are rare (exceptions: e.g. Allaoui et al. 2002, Bai and Allaoui 2003, Bai 2003).

Direct comparison of the final nanocomposite properties obtained from functionalised and non-functionalised CNTs was undertaken by multiple research groups. Zhu et al. (2003) employed a combination of defect-functionalisation with fluorine groups and sidewall-functionalisation with carboxylic groups. They obtained an increase in Young’s modulus of 24% and an increase in tensile strength of 19% by using functionalised over non-functionalised SWCNTs (1 mass%). Those enhancements were attributed to the covalent CNT-epoxy bonding and to the significantly better dispersion state of functionalised CNTs within the epoxy matrix.

The same group obtained further improvements in mechanical behaviour by using 1 mass% of SWCNTs functionalised with amino-terminated moieties (Zhu et al. 2004), showing an increase in Young’s modulus of 25% and tensile strength of 30% when compared to nanocomposites composed of non-functionalised SWCNTs.

Qualitatively similar effects of amino-functionalisation were obtained by Gojny and co-workers (Gojny et al. 2004, Gojny et al. 2005). However, the effect of
amino-functionalisation of 0.5 mass% of double-walled CNTs (DWCNTs) on nanocomposite properties was significantly smaller with an increase of 7% in Young’s modulus and 2% in tensile strength (Gojny et al. 2005).

Liu and Wagner (2005) compared two different epoxy systems, a glassy epoxy and a rubbery epoxy system. Their experiments showed that moieties with terminal amino groups (glycolitic polypropyleneoxide triamine) have a significantly larger effect on nanocomposite Young’s modulus with an increase of 22%, and tensile strength with an increase of 46%, when a rubbery epoxy system with 1 mass% of MWCNTs was used instead of a glassy epoxy system. In contrast, CNT functionalisation in conjunction with a glassy epoxy system resulted in an increase in Young’s modulus of around 4% and a negligible effect on tensile strength. However, a poor dispersion of functionalised CNTs was obtained in the latter case.

Ma et al. (2007) studied the effect of silane functionalisation and obtained an increase in flexural modulus of around 13% and an increase in flexural strength of around 14% for the case of 0.25 mass% of MWCNTs.

Tseng et al. (2007) focused on the grafting of maleic anhydride via plasma modification and achieved due to functionalisation an enhancement of the Young’s modulus around 43% and tensile strength around 88% for MWCNT mass fractions of 1%.

Additional successful work on functionalisation accompanied by strength and stiffness improvements may be found in Valentini et al. (2007) and Geng et al. (2008). In the study of Valentini et al. (2007) functionalisation resulted in an increase in Young’s modulus around 2% and in tensile strength around 140%. Geng et al. (2008) obtained an increase of 14% in both, flexural modulus and strength.
When considering all the stated work on functionalisation effects, one can conclude that:

(1) The use of non-functionalised nanotubes leads, on average, to a reduction in tensile strength and elongation at break when compared to pure epoxy—this effect can be especially attributed to the poor dispersion state of non-functionalised CNTs as mentioned earlier.

(2) Functionalised CNTs lead to an enhancement of tensile strength when compared to pure epoxy (e.g. Zhu et al. 2003, Zhu et al. 2004, Tseng et al. 2007, Valentini et al. 2007)

However, quite a number of studies investigated the stiffness and strength of epoxy/CNT nanocomposites with quantitatively and qualitatively very different results. When compared to pure epoxy, a CNT mass fraction of 1% resulted for example in a stiffness decrease of 19% (Hernández-Pérez et al. 2008) or in an increase of 105% (Tseng et al. 2007). The variety of CNT types, epoxy systems, dispersion methods, and functionalisation strategies, as well as the difficulty of quantification of the dispersion quality (Kim et al. 2012) are reflected in the large scatter of resulting nanocomposite properties. To date, CNT’s reinforcement effect has been far behind theoretical expectations obtainable with classical micromechanics rules. The tendency of CNTs to exist in entangled bundles and to agglomerate was tackled by applying advanced dispersion methods and CNT functionalisation methods. However, it seems that in nanocomposites CNT agglomeration cannot be completely avoided and agglomerates and well-dispersed CNTs coexist in the nanocomposite (cf. Gojny et al. 2005).

Likewise, it is believed that a random CNT orientation, as it is usually obtained by compounding with CNT powder, substantially limits the potential of CNTs as reinforcement. Hence, different experimental approaches have been used to
generate epoxy nanocomposites that exhibit aligned CNT morphologies. There are two main strategies in their production route: (1) CNT alignment prior to compounding or (2) alignment after compounding. Template synthesis methods (e.g. Li et al. 1996, Che et al. 1998, Li et al. 1999, Zhang et al. 2000, Sohn et al. 2001) or plasma enhanced chemical vapour deposition (e.g. Ren et al 1998, Bower et al. 2000) have been applied to synthesise arrays and forests of aligned CNTs. Aligned buckypaper was produced by filtration of CNT suspensions under a magnetic field (e.g. Walters et al. 2001) and the ‘Domino pushing’ technique (Wang et al. 2008). Obtained CNT papers, mats or forests are then further processed through impregnation with epoxy and subsequent in-situ polymerisation (e.g. Wardle et al. 2008, Dassios et al. 2012). Alignment of CNTs in epoxy have been achieved through ultra-microtome cutting (e.g. Ajayan et al. 1994), applying an electric (e.g. Martin et al. 2005) or magnetic field (e.g. Garmestani et al. 2003) to the compound.

The effect of CNT alignment on quasi-static mechanical performance of CNT/epoxy nanocomposites was investigated in several studies. For example, Abdalla et al. (2010) found, using dynamic mechanical analysis (DMA), an increase of 32% in glassy shear storage modulus due to partial CNT alignment in MWCNT/epoxy samples that were cured in a magnetic field. Al-Haik et al. (2004) performed nanoindentation experiments and obtained an increase of 30–38% in elastic modulus when comparing magnetically aligned and randomly orientated CNT/epoxy composites. CNT forests/epoxy nanocomposites were tested via nanoindentation in the work of Cebeci et al. (2009). Aligned CNT/epoxy samples show negligible deviations when compared to samples of similar volume fractions of random CNT orientation. However, significant larger volume fractions of aligned CNT/epoxy nanocomposites were successfully manufactured, finally leading to a larger stiffness increase when compared to the maximum stiffness improvement obtained from randomly
oriented CNTs with a smaller volume fraction. The quasi-static compressive response of epoxy impregnated mats of vertically aligned MWCNTs of 27% CNT volume fraction were studied by Dassios et al. (2012). The Young’s modulus was increased by 25% through incorporation of CNTs into epoxy.

Another critical factor is the ability of the CNTs to change the bulk mechanical properties of the epoxy phase in their vicinity. Apparent evidence of an interphase between CNT and polymer can be found in SEM micrographs of Ding et al. (2003), showing CNT sheathing on fracture surfaces of MWCNT/polycarbonate (PC) nanocomposites (see Fig. 2.9). Since CNTs exhibit a large SSA, such interphases can make up a large volume fraction of the matrix.

![SEM micrograph of polymer coated CNT protruding from the MWCNT/PC fracture surface (from Ding et al. 2003).](image)

The following two proposed mechanisms may be involved in a formation of an interphase with properties different from the bulk epoxy. First, a disruption of the epoxy network due to phase segregation near the CNTs leading to changes of monomer/hardener ratio and, therefore, local changes of crosslink densities (see Putz et al. 2008). The result will be a weaker/tougher interphase with less crosslinks. Secondly, the CNT may alter the mobility of the polymer chains. However, predictions of the nanofiller effect are difficult (Grady et al. 2012). For
example, enhanced chain mobility may occur in two distinct cases: (1) unfavourable energetic interaction (weak vdWs interaction) due to easy sliding, and (2) favourable energetic interactions (π–π-stacking interaction, covalent bonding) due to a decrease in chain entanglements near the CNT. The latter type of interaction may also favour immobilisation of polymer chains as discussed by Putz et al. (2008) or Gojny and Schulte (2004). However, Putz et al. (2008) obtained an increase in glass transition $T_g$ of the nanocomposite, as compared to pure epoxy, which indicates a strengthened interphase, only in the case of a lightly crosslinked system, but not for highly crosslinked systems. The authors used the concept of cooperatively rearranging regions (CRRs) from the Adam-Gibbs model of the glass transition to explain this effect. The CRR volume decreased significantly with crosslink density resulting in a loss of cooperativity (communication between CRRs) and, therefore, in a loss of interphase behaviour. As a consequence, the authors concluded for highly crosslinked thermosets a reduced capability of interphase forming.

### 2.3.2. Interface aspects: Fracture and damping behaviour

Energy absorption enhancements due to CNT incorporation in polymers arise from two main dissipative processes: fracture and damping. Both processes are strongly connected through the polymer/CNT interface, where interfacial damage and frictional sliding govern the macroscopic response.

Several studies have indicated the potential of well dispersed CNTs in enhancing fracture and/or impact toughness of epoxy matrices (Zhu et al. 2003, Park et al. 2004, Fidelus et al. 2005, Ganguli et al. 2005, Gojny et al. 2005, Liu and Wagner 2005, Ganguli et al. 2006, Ma et al. 2007, Hernández-Pérez et al. 2008, Yu et al. 2008, Lachman and Wagner 2010). However, to date the mechanisms of the toughness improvements in nanocomposites remain not fully understood and identified. Energy dissipation mechanisms seem to be more significant in
polymer/CNT composites than in short-fibre composites (Wichmann et al. 2008).

Fiedler et al. (2006) argued that the significant increase in interfacial area in nanotube composites may contribute to an enhancement in energy dissipation due to interfacial fracture.

However, in contrast, Chen et al. (2007) pointed out that energy dissipation due to interfacial debonding are more difficult for nanoscaled particles. Similar, Sun et al. (2009) used traditional fracture mechanics equations to explain the underlying size effect. They considered the effect of nanofiller size on the critical stress using the analogy to Griffith-type fracture mechanics for a crack of size $a$ located in the centre of an infinite plate, the critical fracture stress $\sigma_c$ can be expressed as

$$\sigma_c = \sqrt{\frac{2E\gamma_s}{\pi a}}, \quad (2.4)$$

with Young’s modulus $E$ and crack surface energy per unit area $\gamma_s$. They associated the crack length with an imperfection represented by an isometric particle, and then assumed that for a maximum crack length $a$, equal to the particle size, the critical fracture stress increases significantly when the particle size decreases to the nanometre scale.

However, CNTs are not isometric and exhibit lengths up to several mm, and indeed, unstable crack extension was found for embedded non-functionalised MWCNTs by Ganesan et al. (2011). The authors computed the critical interface fracture energy $G_c$ to be in the range of 0.05–0.25 J/m$^2$ from nanoindenter assisted CNT pull-out within an SEM.

Interface fracture in form of nanotube pull-out was identified as one of the most dominant mechanisms contributing to the fracture toughness of CNT-based
nanocomposites (Wernik and Meguid 2010). Pull-out is closely associated with the crack bridging phenomenon since it occurs near the propagating crack tip, where the crack surfaces are interconnected through intact CNTs (see Fig. 2.10). Fiedler et al. (2006) obtained evidence of DWCNTs and MWCNTs bridging cracks in epoxy matrices via TEM and SEM. Watts and Hsu (2003) identified CNT bridging in polymer films via TEM micrographs. Further evidence can also be found in Prashantha et al. (2009).

Consider a crack propagating in a matrix, which has just passed the CNT, and CNT and polymer/CNT interface are still intact and begin to deform through the opening of the crack tip. A number of processes are possible (see Fig. 2.11): (1) CNT pull-out without fracture when the CNT/polymer interface is weak and/or the CNT length is below the critical length (see Fig. 2.11b), (2) fracture of the CNT, when the interface is strong and the length of the CNTs is exceeded beyond its critical value, thus, promoting an enhanced shear stress transfer through the interface (see Fig. 2.11c) (see Blanco et al. 2009), (3) a sword-in-sheath pull-out can occur in case of MWCNTs (see Xia and Curtin 2004), if only the outer wall of a MWCNT has failed, and the inner walls are still available for being pulled out within the fraction of the outer layer (see Fig. 2.11d), (4) bridging accompanied by partial debonding (see Fig. 2.11e), as well as combinations of (1)–(4) may also occur.
However, Lachman and Wagner (2010) explained that the critical lengths of CNTs are often much larger than their typical physical lengths, because of their high strength. Hence, the dominant failure process during crack bridging is the failure of the interface and pull-out of the entire CNT (see Fig. 2.11b). As a consequence, the pull-out is not suppressed like it is the case in traditional short fibre composites.

**Figure 2.11:** Possible mechanism at fracture surfaces: (a) initial state of the CNT, (b) CNT pull-out, (c) CNT rupture, (d) sword-in-sheath pull-out, (e) bridging and partial interface debonding (from Gojny et al. 2005).

Further, the authors used a classical pull-out energy model to explain the commonly observed fracture toughness improvements in CNT nanocomposites with increasing interface shear strength (as a result of functionalisation) (e.g. Park et al. 2004, Gojny et al. 2005, Ganguli et al. 2006, Geng et al. 2008, Lachman and Wagner 2010) that contradicts traditional composites exhibiting fibre lengths above their critical values. They considered that the energy dissipated by the fibre pull-out $E_{\text{pull-out}}$ for a fibre volume fraction $V_F$, with pull-out length of half the CNT length $l_{\text{CNT}}$, CNT radius $r_{\text{CNT}}$ and interfacial shear strength $\tau_{\text{IF}}$ can be expressed as (cf. Hull and Clyne 1996)

$$E_{\text{pull-out}} = V_F l_{\text{CNT}}^2 \tau_{\text{IF}} / 12 r_{\text{CNT}}.$$  \hspace{1cm} (2.5)
Regarding traditional short fibre composites, fibre fracture reduces the pull-out length to half the critical CNT length $l_c$. Substituting $l_{\text{CNT}}$ by the Kelly-Tyson expression $l_c = r_{\text{CNT}} \sigma_{\text{CNT}} / \tau_{\text{IF}}$ leads to

$$E_{\text{pull-out}} = VFr \sigma^2 / 12 \tau_{\text{IF}},$$

(2.6)

where $\sigma_{\text{CNT}}$ is the axial strength of the CNT. The linear proportionality between interface shear strength and the pull-out energy from Eq. (2.5) has turned into an inverse proportionality. Hence, Eq. (2.5) explains qualitatively the fracture toughness enhancement due to CNT surface functionalisation in CNT nanocomposites, while for traditional short fibre composites, Eq. (2.6) complies with fracture toughness reduction due to an increase in interfacial shear strength.

Besides CNT bridging, CNT deformation, CNT pull-out and CNT fracture, other energy dissipation mechanisms have been identified to coexist in CNT composites. For example, Gojny et al. (2005) observed shear-bands in the epoxy matrix around the agglomerates of amino functionalised DWCNTs, which was attributed to void nucleation caused by plastic deformation of the matrix. Hence, Fiedler et al. (2006) argued that partial agglomeration can promote toughening through micromechanical mechanisms such as crack deflection at agglomerates, void nucleation and inelastic matrix deformation. However, experimental data for the same type of CNT (functionalised and non-functionalised) indicates significant fracture toughness enhancements with improved state of dispersion (e.g. Lachman and Wagner 2010). This suggests that nanoscale pull-out mechanisms can be more significant than micromechanical mechanisms in contributing to the toughness of CNT/epoxy composites.

Energy dissipation at small strains is believed to arise from interfacial slippage of carbon nanotubes within the polymer matrices (e.g. Koratkar et al. 2005),
wall-to-wall sliding within MWCNTs (e.g. Suhr et al. 2005) and nanotube to nanotube sliding (e.g. Auad et al. 2009). Buldum and Lu (1999) studied interfacial sliding via molecular mechanics and observed frictional „stick-slip“ motion. Zhou et al. (2004) developed a micromechanical model based on „stick-slip“ frictional motion and validated by experiments. The authors concluded that the enormous SSA of CNTs is one of the dominant factors providing significant damping enhancements when compared to other filler types, such as carbon black or carbon whiskers.

Interfacial friction converts kinetic energy into thermal energy and influences the viscoelastic performance of the nanocomposite. Properties obtained using DMA such as loss modulus and loss factor/tangent η are measures of energy dissipation/damping. Experimental studies employing DMA have shown the significant effects of CNTs on the viscoelastic damping capacity (Suhr et al. 2005, Auad et al. 2009, Montazeri 2013). It is noteworthy to mention that in general, the functionalisation is believed to have a detrimental effect on loss modulus due to the inhibition of interfacial sliding (cf. Suhr et al. 2005, Suhr and Koratkar 2008, Montazeri 2013) (see Fig. 2.12).

![Figure 2.12: Loss tangent curves for epoxy and nanocomposite samples with different mass fractions (from Montazeri 2013).](image-url)
2.3.3. Compressive finite strain and strain rate dependent behaviour

Plastic deformation of CNT/epoxy nanocomposites as an energy absorbing mechanism has been relatively sparsely studied. In contrast to the brittle behaviour of epoxy in tension, a prominent feature of epoxy undergoing compressive loading is its plastic deformation up to 100% of true strain (Buckley et al. 2001) across various strain rates (from static to impact). In the case of a pure shear, plastic deformations up to 50% of shear strains are possible (Fiedler et al. 2001). Under tensile loading epoxy exhibits brittle behaviour with deformations in general limited to around 5% of strain (Buckley et al. 2001, Fiedler et al. 2001). This strain range in compression gives substantial room for energy absorption mechanisms such as improved plastic deformation. From an engineering perspective, plasticity plays a major role in absorbing impact energy during crashes or foreign body collision.

Small concentrations of CNTs promise substantial effects on the nonlinear response. CNTs exhibit an enormous resilience and flexibility (Falvo et al. 1997) and are, therefore, favoured as filler material able to operate over such a wide range of strains. Furthermore due to their large aspect ratio, networks of CNTs are expected to constrain the epoxy matrix geometrically and, thus, this is believed to enforce an enhanced stress state within the matrix material that leads to an accelerated plastic deformation.

However, little research focussed on the compressive response of CNT/epoxy nanocomposites. Schadler et al. (1998) investigated the load transfer in epoxy nanocomposites of random MWCNT morphologies in compression and tension by measuring the second-order Raman peak at 2700 cm$^{-1}$. A significant difference between compression and tension, as obtained by Raman spectroscopy and standard mechanical tests, was attributed to the better load
transfer to the inner CNT walls under compressive loading. The compression tests of MWCNT/epoxy samples by Srivastava (2012) showed improvements in Young’s modulus and strength over pure epoxy samples.

The finite strain and quasi-static compressive response of epoxy impregnated mats of vertically aligned MWCNTs (MWCNT forests) was studied by Dassios et al. (2012). An increase in compression strength—here considered as stress at the onset of compaction—of about 275% was obtained when comparing the response of the impregnated nanocomposite mat with the non-impregnated CNT forest. Fracture of embedded CNTs occurred at 60% of applied strain for the nanocomposite mat. Furthermore the composite mat was found to retain its structural integrity up to 95% of applied strain.

Even less research has dealt with the strain rate dependent compressive response of CNT/polymer nanocomposites. Jindal et al. (2013) studied PC nanocomposites containing randomly oriented MWCNTs using Split-Hopkinson pressure bar at strain rates around 2200 s\(^{-1}\). The authors found that low concentrations of non-functionalised MWCNTs (0.5 mass%) significantly enhance impact absorption capacity of pure PC by 10–20%. After-impact SEM images demonstrated that CNTs maintain their structure at high strain rates.

Split-Hopkinson pressure bar experiments for randomly oriented MWCNTs/high-density polyethylene (HDPE) nanocomposites were performed by Al-Lafi et al. (2010). The impact energy increased (both for the pristine polymer and the nanocomposite), while yield strength decreased with increased volume fraction. Direct comparison revealed the larger effect of strain rate on impact energy for the nanocomposite than for the pure polymer. Based on density measurements, the authors suggested the enhanced capability for crack formation with increasing strain rate for the nanocomposite.
Mantena et al. (2009) considered the compressive response of MWCNT/nylon 6,6 composites at high strain rates of 950 s\(^{-1}\) using Split-Hopkinson pressure bar. Incorporation of 2.5 mass% of MWCNTs resulted in 10–20% improvement in energy absorption and strength.

Gómez-del Río et al. (2014) investigated the strain rate dependent compressive mechanical behaviour of epoxy filled with different types of nanoparticles: (1) rubbery nanoparticles obtained using a block copolymer styrene-b-butadiene-b-polymethylmethacrylate, (2) CNTs, and (3) a combination of both. Significant enhancement of the compressive yield strength was only obtained with CNT/epoxy nanocomposites at impact rates of strain (1000–3000 s\(^{-1}\)) (see Fig. 2.13). Compared to pure epoxy or other nanocomposite compositions, CNT/epoxy nanocomposites showed the largest strain rate sensitivity at high strain rates. However, effects of CNTs on the post-yield behaviour of epoxy were not mentioned by the authors.

![Figure 2.13: Strain rate effect on compressive yield strength for pure epoxy (NR), block copolymer styrene-b-butadiene-b-polymethylmethacrylate modified epoxy (SBM), epoxy reinforced with CNTs (CNT), and a hybrid composite (SBMCNT) (from Gómez-del Río et al. 2014).](image-url)
Numerical investigations of CNT/epoxy or CNT/polymer composites dealing with compressive or dynamic behaviour were mainly seeking to predict elastic instabilities referred to as buckling, or the damping response. Li and Chou (2006) studied the quasi-static compressive behaviour of CNT/polymer nanocomposites using a multiscale model to determine the stress distribution in the matrix and buckling behaviour of the composite. Nanotube and interphase were modelled using the AFEM approach, while the matrix was modelled as a continuum material at the microscale using finite elements (FEs). They showed that the buckling forces are dependent on CNT volume fraction and nanotube length with most effective enhancement achieved with continuous nanotubes.

Namilae and Chandra (2006) performed molecular dynamics simulations to study the axial compressive behaviour of CNTs embedded in polyethylene. Simulation results obtained for a non-bonded interface and bonded interface were compared with the buckling and post-buckling behaviour of neat CNTs. Their simulations predicted marginal differences between neat CNTs and CNTs embedded and non-bonded to the polymer, which indicates that vdWs forces barely affect the critical buckling stress and the CNT buckling behaviour. In contrast, the authors showed that embedded CNTs that are bonded to the polymer possess a significantly reduced critical buckling stress when compared to neat CNTs. The authors attributed the reduction of the critical buckling stress to the introduction of defect sites due to functionalisation leading to deviations from the perfect cylindrical geometry. However, compared to non-functionalised CNTs, and embedded and non-bonded CNTs, a positive effect was found due to significant enhancement of the load-transfer during the post-buckling stage, allowing the compressive stress to exceed the critical buckling stress. Simulations predicted that such chemically bonded CNTs deformed through crushing near the loaded ends in the post-buckling regime.
Rafiee and Moghadam (2012) studied the transient dynamic behaviour of CNT/polymer nanocomposites subjected to impact loading using Rayleigh damping model within the multiscale finite element framework. Weak vdWs interaction between CNT and matrix was modelled. Axial displacement and transverse deflection analyses of the RVE revealed a significant reduction of the post-loading displacements and deflections when compared to the neat resin. 

This reveals an enhanced damping capability of the nanocomposite. Under application of axial loading, the pure resin experiences its maximum displacement and compressive stress in the matrix after a significant amount of time after unloading. In contrast, the CNT reinforced polymer exhibits a maximum displacement when loading is finished and then at the stage of early unloading, the matrix starts to experience tensile stress, indicating a faster dynamic response/response frequency of the nanocomposite. Qualitatively similar results were obtained for the bending mode.

2.4. Multiscale computational modelling of the mechanics of CNT/polymer nanocomposites

Advanced computational modelling of nanocomposites can provide a complementary (to experiments) insight into their behaviour, and also help to optimise their performance. However, predicting nonlinear macroscopic properties of CNT/polymer nanocomposites from their morphology and nonlinear constituent behaviour is a challenge, arising from a complex multiscale deformation mechanism occurring across a wide range of length and time scales.

Two types of multiscale computational modelling approaches are commonly applied for CNT/polymer nanocomposites: (1) sequential (hierarchical) bottom-up schemes and (2) concurrent schemes involving coupling of AFEM and FEM (Wernik and Meguid 2009).
Hierarchical approaches are sequential information-passing methods assuming that the processes at different time and length scale can be separated. On the basis of that, the simulations are running independent from each other in a bottom-up manner (Wernik and Meguid 2009). The advantage is that each scale can be modelled with the most robust method for the given length and time scale. Outputs in form of homogenised quantities of the finer scale are then passed to the coarser scale.

The finest scale methods include ab-initio (or first-principles) simulations based on solving the Schrödinger equation for the motion of electrons and nuclei. Coarser computational methods include MD simulations based on solving the classical Newton’s equation of motion (Vvedensky 2004) to predict motion of atoms. At the other end, continuum methods neglect the atomic structure completely. The material is replaced by a continuous medium. Basic physical principles such as conservation of energy, momentum and mass can be applied to derive continuum partial differential equations, which for example can be solved numerically by using FEM (Wernik and Meguid 2009). A possible hierarchical approach can involve the passing of developed interatomic potentials from ab-initio simulations as input parameter(s) for molecular dynamics simulations. From MD simulations in turn, material properties such as Young’s modulus and Poisson’s ratio of the nanomaterial can be determined assuming an equivalent continuum representation. The value obtained can then be used to specify the constitutive relation of the filler material in a finite element unit cell model in order to determine the macroscopic Young’s modulus and Poisson’s ratio of the nanocomposite.

Concurrent methods, on the other hand, perform the entire multiscale simulation at once, i.e. multiple scales are simultaneously resolved and information is continuously passed from one length scales to the other. Concurrent methods are, therefore, computationally demanding and best suited...
to problems, where different scales significantly depend on each other (Wernik and Meguid 2009).

The coupling of scales, however, involves significant challenges in the formulation of a transition region, which enables transfer of field variables. In MD/FE coupling schemes, those challenges arise from the incompatibility of MD and FE and include for example the generation of phonons in MD, which are not represented in the FE region and might reflect at the FE/MD interface (Fish 2007). The coupling of AFEM and FEM in contrast, which is to the authors knowledge currently the only concurrent multiscale approach applied to polymer/CNT nanocomposites, enables seamless coupling within the transition region/interface without significant challenges due to the compatibility of AFEM and FEM (Wernik and Meguid 2009).

This atomistic-continuum multiscale approach involves a discrete atomistic domain and a continuum domain. Both subdomains, however, are integrated in a continuum model. Multiscale modelling schemes following this approach are very attractive because the AFEM method is a cost saving alternative to MD (Wernik and Meguid 2009).

2.4.1. Discrete-to-continuum modelling of CNTs

In the following sections the main continuum modelling strategies for CNTs are summarised. In atomistic simulations, continuum assumptions are employed in data reduction schemes in order to obtain mechanical properties for continuum theory-based representations of CNTs. Under specific conditions, some of those representations predict correctly the deformation behaviour of single CNTs and, thus, they are meaningful for multiscale modelling approaches. The choice of continuum shell models or structural beam models (see Sections 2.4.1.2 and 2.4.1.3) for example is strongly related to the buckling behaviour of CNTs.
Buckling of structures is characterised by a drop in strain energy within the energy-displacement curve originating from a sudden morphology change at a critical load. The buckling patterns of CNTs strongly depend on type of CNT (e.g. number of walls, aspect ratio) and applied loading conditions. For example, under axial compression, a short aspect ratio CNT undergoes shell-like buckling (see Fig. 2.14a and b) and a long aspect ratio undergoes beam-like buckling (Euler or column buckling) and shell-like post-buckling (see Fig. 2.14c and d). Under bending load, SWCNTs develop a single kink at the compressed side (Similar to Fig. 2.14d) whereas MWCNT exhibit rippling (see Fig. 3 in Section 2.1) resembling the Yoshimura pattern (Shima 2011). For more details on buckling patterns, the reader is referred to the review of Shima (2011).

2.4.1.1. Atomic bond-to-structural beam modelling of CNT bonds

Two similar structural mechanics approaches for representing discrete structural features of CNTs at the continuum level were applied by Li and Chou (2003a) and Odegard et al. (2002). The CNT was replaced by a 3D truss-
like structure within the FE framework. In the method proposed by Li and Chou (2003a), the carbon bonds were represented by beam elements, while the nodes joining the beam elements represented the positions of the carbon atoms of the CNT.

\[ U = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_\omega + \sum U_{vdW} \]

(2.7)

where \( U_r \) refers to bond stretching, \( U_\theta \) to bond angle bending, \( U_\phi \) to dihedral angle torsion, \( U_\omega \) to out-of-plane torsion and \( U_{vdW} \) to vdWs interaction (see Fig. 2.15). The energy contribution due to vdWs forces \( U_{vdW} \) is negligible in a covalent system and the remnant ones can be described as (Li and Chou 2003a)

\[ U_r = \frac{1}{2} C_r (\Delta r)^2, \quad U_\theta = \frac{1}{2} C_\theta (\Delta \theta)^2, \quad U_\phi = U_\phi + U_\omega = \frac{1}{2} C_\phi (\Delta \phi)^2 \]

(2.8)

where \( C_r, C_\theta \) and \( C_\phi \) are the bond stretching force constant, bond angle bending force constant and torsional resistance respectively; \( r, \theta, \phi \) are the atomic distance, bond angle and bond twisting angle respectively. Similarly, classical structural mechanics equations describe the strain energy of a uniform
beam of length \( L \) subjected to loading under tension, bending and torsion. A direct relation between structural mechanics parameters such as tensile resistance \( EA \), flexural rigidity \( EI \) and torsional stiffness \( GJ \) of the equivalent cylindrical beams and force field constants in molecular mechanics were obtained by considering the energy equivalence between the beam and bond deformation (Li and Chou 2003a):

\[
\frac{EA}{L} = C_{r}, \quad \frac{EI}{L} = C_{\theta}, \quad \frac{GJ}{L} = C_{\tau}.
\]  

(2.9)

Such AFEM schemes for the modelling of CNTs are the basis for the concurrent multiscale modelling schemes involving the coupling of AFEM (CNT modelling) and FEM (matrix modelling). Here slight variations exist. While, for example, the originally proposed method by Li and Chou (2003a) applies simple harmonic potentials and it is, therefore, suited to cover the elastic regime of bond deformations, some modified versions account for their nonlinearity by employing the Morse potential (e.g. Tserpes et al. 2008, Wernik and Meguid 2011).

Likewise, the method was often used in sequential approaches. Prior to replacing the whole lattice structure by an equivalent continuum, a single CNT needs to be simulated first. Depending on the equivalent continuum chosen at the next higher scale, specific loading conditions together with continuum assumptions have to be applied in order to determine its effective properties. Ayatollahi et al. (2011) for example replaced the whole CNT by an equivalent continuum beam. Its effective properties such as tensile resistance \( EA \), flexural rigidity \( EI \) and torsional stiffness \( GJ \) were determined from corresponding loading conditions on the structural mechanics model.
2.4.1.2. Discrete-to-structural beam modelling of CNTs

Yakobson et al. (1996) and Iijima et al. (1996) obtained quadratic increase of strain energy of CNTs with bending angle, prior to local buckling (similar to Fig. 2.14d), which is in agreement to Hooke’s law. This suggests that CNTs might be treated as effective beams prior to the onset of local buckling (Quian et al. 2002).

Harik (2002) proposed three non-dimensional SWCNT parameters to limit the validity of the Euler beam assumption for the modelling of CNTs as beams:

- Homogenisation criterion: $l_{o\text{CNT}}/w > 10$
- Aspect ratio criterion: $l_{\text{CNT}}/d_{\text{CNT}}>10$
- Linearity of strains criterion: $(l_{1\text{CNT}}-l_{0\text{CNT}})/l_{0\text{CNT}}<<1$, \hspace{1cm} (2.10)

where $l_{1\text{CNT}}$, $l_{0\text{CNT}}$, $d_{\text{CNT}}$ are the final length, initial length and diameter of the CNT respectively, and $w=0.24$ nm (Harris 1999) is the width of the carbon ring. The homogenisation criterion ensures a minimum number of hexagonal cells along the CNT length, which reduces small scale-effects. One task of the aspect ratio criterion is to exclude CNTs that exhibit shell-like buckling modes (see Fig. 2.14a) and, therefore, cannot accurately be captured by beams. When using data reduction schemes based on the Euler beam assumptions, those criteria need to be satisfied in order to predict the linear elastic initial beam-like buckling (see Fig. 2.14c) correctly.

Govindjee and Sackman (1999) examined the validity of the single-Euler beam model for MWCNTs and concluded that the nested shell structure of MWCNT should not be ignored, when interpreting bending data. The assumption of a continuum cross-section was shown to be valid for MWCNTs composed of more than 201 walls. Ru (2000) proposed a multi-Euler beam model for MWCNTs. Each wall was presented by an individual beam and the radial
deflections of adjacent walls were coupled via vdWs interaction. For relatively stocky short MWCNTs, which may not fulfil the aspect ratio criterion and still exhibit beam-like buckling modes, multi-Timoshenko beam models provided a better estimation of critical buckling loads due to the inclusion of transverse shear deformations (Zhang et al. 2006).

Recent developments in modelling single CNTs include nonlocal elasticity theory, i.e. nonlocal formulations of Euler beam models (Sudak 2003) and Timoshenko beam models (Wang et al. 2006). The classical (local) elasticity theory assumes that the stress at a reference point is a function of strain in that point. In the nonlocal elasticity theory the stress at that point is a function of strains at all other points of the body, which is in accordance with the atomic theory of lattice dynamics and observations of phonon dispersion (Murmu and Pradhan 2009). This renders its application for short CNTs useful, where small scale effects are expected to affect the deformation. More accurate lower estimations of critical buckling strains of relatively short CNTs can be obtained from the local description of the Euler beam model (e.g. see Fig. 1 in Zhang et al. 2009).

Within the context of the equivalent beam concept, one has to point out that the equivalent beam obtained from its rigidities $EA$, $EI$ and $GJ$ does not necessarily have the diameter of the real CNT. Using the structural mechanics approach of Li and Chou (2003a), Papanikos et al. (2008) compared equivalent solid cylindrical and hollow cylindrical beams in capturing the diameter of the real CNT. Hollow cylindrical beams were shown to capture the real diameter much better than solid beams, especially for large diameter CNTs. In contrast, solid beams captured the real diameter of small diameter CNTs only satisfactorily and tend to be significant larger with increasing diameter. One might argue that this effect has no impact when modelling CNTs as beams consisting of 1-dimensional structural elements defined by $EA$, $EI$ and $GJ$, and
superposition to the matrix via node sharing. However, one should be careful when replacing the beam by 2- or 3-dimensional elements with linear elastic and isotropic properties acquired from the beam assumption, because a larger diameter can affect the stress transfer.

2.4.1.3. Discrete-to-isotropic shell (or shell-like) modelling of CNTs

With decreasing length the initial beam buckling (see Fig. 2.14c) transforms into shell-like buckling (see Fig. 2.14a) (Wang et al. 2010). Representation of the tubular structure by a continuum shell is, therefore, better suited in those cases in order to capture the local buckling. Furthermore, Robertson et al. (1992) found that CNTs possess internal strain energy per carbon atom (rolling energy) with dependence on the radius \( r_{\text{CNT}} \) according to \( 1/r_{\text{CNT}}^2 \), which follows classical elasticity theory and suggest the treatment as elastic shells (Pantano 2004). Yakobson et al. (1996) showed that the buckling patterns displayed by MD simulations and critical buckling strains can be predicted by a continuum shell, when special attention is given to the wall thickness \( t_{\text{CNT}} \). The CNT was approximated by a linear elastic isotropic shell with two elastic constants, flexural rigidity \( D \) and in-plane stiffness \( C \). The authors obtained their values from the data in Robertson et al. (1992) and calculated the Poisson’s ratio \( v \) from the diameter reduction of a stretched tube. Classical shell theory renders the connection between flexural rigidity and in-plane stiffness through the shell thickness parameter \( t_{\text{CNT}} \) (Timoshenko and Woinowsky-Krieger 1976):

\[
D = E t_{\text{CNT}}^3 / 12(1-v^2), \quad C = E t_{\text{CNT}}.
\]

(2.11)

Those were used to obtain the complete set of parameters of the linear elastic and isotropic shell as \( E=5.5 \) TPa, \( t_{\text{CNT}}=0.066 \) nm and \( v=0.19 \) (Yakobson et al. 1996). Since then, various continuum shell theories including nonlocal
formulations have been adapted for CNTs. The reader is referred to the review of Rafiee and Moghadam (2014).

However, it must be mentioned that researchers are not consistent in their effective wall thickness results/assumptions. The effective wall thickness equal to the 0.34 nm interlayer spacing of graphite and corresponding Young’s modulus of 1 TPa would for example lead to a flexural rigidity 20–30 times higher than atomistic predictions (Yakobson et al. 1997). Wang and Zhang (2008) shed more light into the large scatter of reported CNT wall thicknesses among different research groups.

A rough guideline for the applicability of continuum shell models is given in Harik et al. (2002). Besides the deemed homogenisation and the linearity of strain criterion (see Eq. (2.10)), applicability is limited to CNTs of radius to thickness ratio greater than 20 (Harik et al. 2002). Additional discussions on applicability of continuum shell as well as beam theory can be found elsewhere (e.g. Zhang et al. 2009, Wang et al. 2004, Peng, Wu et al. 2008, Wang and Zhang 2008, Wang et al. 2010, Arash and Wang 2014).

FE-based equivalent continuum shells have been used to study the deformation of SWCNTs and MWCNTs (Pantano et al. 2004), and remarkable similarities to MD predictions and experiments were found. In terms of SWCNTs those MD predictions include critical buckling loads of SWCNTs under bending (Yakobson et al. 1996), the deformation of SWCNTs due to self-collapse and interaction with a graphite substrate (Gao et al. 1998, Hertel et al. 1998), and for the contact force between two crossing CNTs in a CNT–CNT-substrate configuration (Hertel et al. 1998). A nested shell model was used to model MWCNTs and very good predictions for the buckling wavelength for the rippling pattern (see Fig. 2.16) in bent MWCNTs were obtained.
The buckling wavelength $\lambda_b$ was found to follow the scaling

$$\lambda_b = \sqrt{r_0 h},$$

(2.12)

where $r_0$ is the outermost radius and $h$ is the distance between outermost and innermost shell surface, which was in accordance with experimental observations of Lourie et al. (1998) and Bower et al. (1999).

Hence, in contrast to the beam models, which can be used to model CNTs and beam-like buckling prior to the onset of local buckling, shell models seem to provide an accurate response beyond global beam-like buckling, i.e. including initial local buckling and postbuckling. However, the authors specify four key aspects for a successful continuum shell modelling (Pantano et al. 2004):

1. Using an appropriate set of elastic constants and shell thickness (Young’s modulus of 4.84 TPa, shell thickness of 0.075 nm, Poisson’s ratio of 0.19)
2. Assigning an initial internal stress state that corresponds to the wall curvature
3. Incorporation of a strong normal force between adjacent CNT walls including self-interaction (e.g. flattening of the CNT), and between CNT and substrate if the CNT is in contact with another material.
4. Neglecting the interwall shear resistance, which was shown to be relatively small with 0.48 MPa on average by Cumings and Zettl (2000)
Furthermore, Pantano et al. (2004) observed that a single kink in SWCNTs under bending load was most accurately captured, when the size of the square shell elements equals the height of the hexagonal lattice cell. In case of MWCNTs, bigger elements might miss the buckling wavelength and smaller elements might capture a wavelength that cannot be accommodated (Pantano et al. 2004).

Sears and Batra (Sears and Batra 2004, Batra and Sears 2007) utilised molecular mechanics simulations of SWCNTs in axial and torsional deformation to formulate an equivalent continuum tube (tubular) initially stress-free and with linear elastic isotropic material properties. The obtained torsional rigidity $GJ$ and axial stiffness $EA$ were then used to obtain the wall-thickness for a linear elastic and isotropic equivalent continuum tube by fitting corresponding expression for the shear modulus $G$ and Young’s modulus $E$ in the well-known relation:

$$E = 2G(1+\nu). \quad (2.13)$$

In the case of DWCNTs (Batra and Sears 2007), concentric tubes were interconnected via truss elements to capture vdW's bonding. For infinitesimal deformations, the equivalent continuum tubes were validated against molecular mechanics results by using Euler’s buckling theory applied to equivalent continuum tubes (Sears and Batra 2004, Batra and Sears 2007) and by using FEM (Batra and Sears 2007). Critical buckling strains of equivalent continuum tubes possessing a length to outer diameter ratio exceeding 10 were shown to be in good agreement with molecular mechanics predictions.

Arroyo and Belytschko (2004) developed a finite deformation continuum theory for curved monolayer crystalline lattices and implemented it into a nonlinear finite element formulation for SWCNTs and MWCNTs to capture finite deformations. Their continuum representation of the CNT wall was via a
hyperelastic membrane (membrane-like, i.e. zero thickness but with flexural stiffness). The constitutive model of the membrane was written explicitly in terms of the underlying CNT lattice structure. The key that links the deformation of the lattice vectors to the deformation of a continuum was provided by a fundamental kinematic assumption referred to as exponential Cauchy-Born rule (Arroyo and Belytschko 2002), which extends the Cauchy-Born rule to curved lattice structures. As a result, the deformed bond length and angles were expressed in terms of continuum strain measures, stretch and curvature. By equating the potential energy of a representative cell divided by the area with the strain energy density of the continuum of equivalent area, the Tersoff-Brenner potential was explicitly incorporated into the constitutive relation. Membrane stresses and bending stresses were then obtained by taking the derivative of the strain energy density with respect to strain measures. A continuum version of the vdW's interaction was also implemented. Finite element predictions showed that theory and implementation scheme accurately capture the full non-linear mechanics of SWCNTs and MWCNTs.

2.4.1.4. Discrete-to-solid fibre modelling of CNTs

Shen and Li (2004, 2005) obtained closed-form expressions for the transversely isotropic elastic properties of SWCNTs and MWCNTs by using molecular mechanics. The five independent elastic constants obtained can be directly applied to continuum representation (e.g. using finite elements) of the CNT as an equivalent continuum solid fibre in a bottom-up multiscale approach using e.g. the Representative Volume Element (RVE) approach.

Odegard et al. (2003) used a computational homogenisation approach to represent the CNT, interface and surrounding interphase (local polymer matrix near the nanotube) as an effective continuum fibre with transversely isotropic elastic constants of a coarse-graining (homogenisation) approach. The
homogenisation process was performed with three models (see Fig. 2.17). First, a molecular dynamics RVE model was used to determine the equilibrium structure of the CNT and surrounding polymer. Matrix and CNT were assumed to interact only via secondary vdWs bonding. Based on the equilibrium structure, an equivalent continuum fibre was developed. An equivalent truss model was used to provide the bridge between molecular and equivalent continuum models. The Young’s moduli of the rods, representing primary and secondary bonds, were determined from molecular-mechanics force constants. The total mechanical strain energy of the equivalent truss and equivalent continuum model were equated under identical loading conditions to determine the transversely isotropic elastic properties of the equivalent fibre. Finally, the Mori-Tanaka model (Mori and Tanaka 1973) was used to investigate the macroscopic elastic response of the composite using the equivalent continuum representation of the CNT.

![Figure 2.17](image)

**Figure 2.17**: Three models employed by Odegard (2003) to obtain transverse isotropic elastic constants of an effective continuum fiber that consists of CNT, interface and polymer chains (from Odegard 2003).

Shokrieh and Rafiee (2010a) replaced a long and straight CNT embedded in a cylinder of polymer and its interface by an equivalent solid fibre, which can be
used for the rule of mixture to predict the macroscopic elastic properties of the nanocomposite. In order to obtain the effective elastic properties of the equivalent solid fibre, they employed the AFEM-FEM coupling approach. Due to the simple harmonic inter-atomic potential, the isolated CNT exhibited linear stress-strain behaviour. Timoshenko beam theory was used to represent the carbon bonds. Imperfect bonding was considered by using non-linear spring elements based on the Lennard-Jones potential between the nodes of the CNT (15, 15) and the nodes at the surface of matrix. Due to the highly non-linear variation of vdwS forces with interatomic distance, the vdwS interactions were progressively updated and rearranged during the nonlinear analysis. Under tension a highly nonlinear behaviour of the nanocomposite was shown. Longitudinal, shear and transvers moduli of elasticity of the equivalent solid long fibre were determined by using the rule of mixture inversely. These values may be used in micromechanical equations.

2.4.2. Concurrent multiscale modelling of the nanocomposite

Li and Chou applied this approach to study the stress transfer (Li and Chou 2003b) or the compressive behaviour of CNT/polymer nanocomposites (Li and Chou 2006). The CNT was modelled using the molecular structural mechanics approach and the matrix was considered to be a continuous medium. In the case of weak CNT/polymer interactions, the transition region (interface) was modelled using truss rods, whose non-linear load-displacement curves were based on the Lennard-Jones potential.

The AFEM-FEM coupling scheme was further employed by Wernik and Meguid (2011) to study the nonlinear response of epoxy/CNT nanocomposite. A relatively short cylindrical RVE of 3.5nm length consisting of a continuous CNT (modelled as spaceframe), was connected to the continuous matrix via truss rods at the interface based on the non-linear Lennard-Jones potential (see
Fig. 2.18). In detail, the truss rods linked nodes at the surface of the matrix to nodes of the CNT pairwise and within the cut-off distance of 0.85 nm. In order to account for the nonlinearity of the CNT structure, the C–C bonds were based on the modified Morse potential, which has an additional angle-bending component. Beam elements were used to account for the stretching component, while rotational spring elements were used to account for the angle bending component of the potential. Each carbon atom was, therefore, represented by 3 superpositioned nodes connected via rotational spring elements and with coupled translational and rotational degrees of freedom. The authors found armchair CNTs to be a better reinforcement filler than zig-zag CNTs, which may be attributed to higher stiffness and strength of the armchair configuration. Furthermore, when compared to the properties of the matrix, a volume fraction ranging from 1 to 10% resulted in a 3- to 23-fold increase in Young’s modulus and 27- to 270-fold increase in tensile strength for armchair CNTs.

![Representative Volume Element](image)

**Figure 2.18:** Concurrent multiscale modelling via AFEM-FEM coupling (from Wernik and Meguid 2011).

Shokrieh and Rafiee (2010c) studied the efficiency of load transfer for straight nanotubes of different aspect ratios using an AFEM-FEM approach. CNTs (10, 10) with two hemispherical sections of \( \text{C}_{240} \) molecules were investigated. Secondary vdWs bonding was modelled using non-linear spring elements based on the Lennard-Jones potential, which were progressively rearranged throughout the non-linear simulation. Simulations predicted a negligible
reinforcement effect for CNT lengths smaller than 100 nm. Furthermore, CNTs lengths of 6.75 and 13.5 nm were found to behave like flaws, which reduced the modulus of the nanocomposite. A rapid increase in nanocomposite Young’s modulus with increasing length was obtained for CNT lengths starting from 5616 nm, but almost no further improvement was predicted above 10 μm. FEM results estimated the efficient length of CNTs to be 9072 nm under the assumption of secondary vdWs interface bonding.

It is noteworthy to mention that the concurrent multiscale modelling approach via AFEM-FEM coupling can be integrated in sequential multiscale modelling approaches. Shokrieh and Rafiee (2010a, 2010b) used this modelling scheme to acquire the material properties of an equivalent fibre comprising CNT and interface (see also Section 2.4.1.4). Subsequently, they used the obtained material properties in a sequential multiscale approach.

2.4.3. Sequential multiscale modelling of the nanocomposite

The molecular structural mechanics approach developed by Li and Chou (2003a) was implemented in various Representative Volume Element (RVE) models such as the multiscale shear lag model by Gao and Li (2005) or the multi-scale approach of Tserpes et al. (2008). Gao and Li (2005) homogenised the spaceframe into an effective fibre, incorporated the fibre into an RVE and applied subsequently a shear-lag analysis based on elasticity theory. Tserpes et al. (2008) determined the nonlinear behaviour of isolated CNT from the structural mechanics approach and incorporated the CNT composed of beam elements into a finite element model. Beam elements were superpositioned to matrix elements. Filler/matrix debonding was simulated by prohibiting load transfer through assigning a very small stiffness to the beam elements. Due to the superpositioning of matrix and beam elements, the shear stress cannot be computed directly. Hence, the assumption of constant shear stress along the
beam element together with a force balance approach was used in order to evaluate whether the shear stress exceeded the interfacial shear strength and, thus, debonding occurred.

Recently, Ayatollahi et al. (2011) employed a sequential multiscale modelling approach. Tension, bending and torsion loading modes were first applied to a single CNT, which was modelled following the structural mechanics approach of Li and Chou (2003a). The modified Morse potential was chosen to account for the nonlinearity of the C–C bonds. Simulations were performed until bond breakage occurred at around 20% of CNT strain. Based on the data obtained, the tensile, bending, torsional rigidity was calculated and fitted to three suggested equations. Those were then used to describe the axial modulus, bending modulus and shear modulus as function of strain, (bending) angular deformation and shear strain to develop an equivalent beam element. In a second step, one equivalent beam was incorporated into a cylindrical RVE of the composite, which also assumed an interphase between CNT and polymer.

The effect of a non-uniform spatial distribution due to local variations in CNT volume fraction on the macroscopic elastic behaviour of randomly distributed and oriented CNT nanocomposite was studied by Spanos and Kontsos (2008) using a multiscale Monte Carlo finite element modelling (MCFEM) approach. A multiscale hierarchical scheme was developed, which comprises a series of models. First on the basis of the RVE concept and microscopic images, which display local variations in CNT volume fraction at the microscale, a representative material region corresponding to a portion of the nanocomposite cross-section was identified. Subsequently, this representative material region was used to construct a 2D random field model that discretises the material region into squares and determines for each of the squares the volume fraction based on a distribution function. A corresponding Monte Carlo finite element model was then generated with each finite element representing a square of the
random field model. Prior to the computation of the nanocomposite’s elastic properties under plane-stress assumption, the mechanical properties (Poisson’s ratio and Young’s modulus) of the finite elements were determined by a modified Mori-Tanaka model (Shi et al. 2004) and by using the transversely isotropic properties of an equivalent solid fibre acquired by Odegard et al. (2003). It must be mentioned that the employed modified Mori-Tanaka model accounts for agglomerations, i.e. local variations in CNT volume fraction were additionally introduced at the sub-element level. The authors observed a significant effect of spatial randomness on the macroscopic Young’s modulus, but not on Poisson’s ratio. Further they found that the assumption of a uniform distribution of CNT volume fraction leads to differences in predictions and experimental outcome for large CNT mass fraction (5%) whereas spatial randomness based on a nonsymmetric beta or log-normal distribution were in agreement with the experimental result in this case.

A similar Monte Carlo-based approach was developed by Shokrieh and Rafiee (2010b). However, the AFEM-FEM coupling scheme was used to obtain the properties of an equivalent fibre comprising CNT and interface. Instead of using FEM to obtain the macroscopic properties, the material properties were averaged over the volume of blocks that constituted the representative material region. Prior to that, the equivalent fibre was used in the modified Mori-Tanaka model of Shi et al. (2004) to obtain the (local) material properties of the blocks. Curved CNTs were introduced as straight CNTs of reduced stiffness. In their case, stochastic implementations involve randomness in length, orientation, agglomeration, dispersion and curvature. Random distributions of length and volume fraction were found to be replaceable by their corresponding mean values. In case of CNT volume fraction, this is a sharp contrast to the result of Spanos and Kontsos (2008).
Eslami Afrooz et al. (2012) studied the effect of randomness in spatial CNT distribution on initial yield stress and Young’s modulus using a hierarchical (sequential) multiscale model. The aligned CNTs were presented by truss elements and superpositioned in a 3D RVE via node-sharing. A relative uniform distribution was randomised by increasing the number of nodes available for the positioning of CNTs. This means spatial randomness increases as the number of nodes for the positioning of CNT increases. The authors found that an increased randomness starting from a relatively uniform CNT distribution significantly decreased the nanocomposite Young’s modulus and hardly affected the Poisson’s ratio. The effect is more pronounced for high CNT volume fractions as obtained for a 5% CNT volume fraction with a relative stiffness and yield strength decreasing of around 40%.

Also, Namilae and Chandra (2005) used a hierarchical bottom-up scheme to determine the behaviour of the nanocomposite. In this case, macroscopic properties were obtained from the finite element analysis with a unit cell model, which was enhanced through a cohesive zone interface that captures bonding mechanisms of hydrocarbon groups between CNT and matrix phase. Molecular dynamics simulations of CNT pull-out from a rigid matrix were undertaken. The traction-separation law in shear was derived from the load-displacement curves of forty attachments (40 attachments were identified to carry the main load) between the CNT and the matrix, and their corresponding area on the CNT surface. Resulting traction-separation law is shown in Fig. 2.19.
Jiang et al. (2006) obtained analytically a nonlinear cohesive zone law for CNT/polymer interfaces directly from the Lennard-Jones potential. Their law accounts for the dependence of the shear traction on the normal separation, i.e. tension/shear coupling. Within the scope of hierarchical bottom-up approach the cohesive zone replaces the nanoscaled interface as proposed in the work of Tan et al. (2007).

An important factor limiting the reinforcement efficiency of CNTs is the irregular shape the CNTs can take, when embedded in the polymer. In general, deviation of CNTs from the perfect straight shape is due to structural defects, but may also be introduced during processing due to relatively long aspect ratio and small flexural rigidity (cf. Yaksobson et al. 1996). Using a finite element-based unit cell model in a sequential multiscale approach, Fisher et al. (2002) showed that CNT waviness can decrease significantly the CNT’s effective reinforcing modulus \( E_{ERM} \) (see Fig. 2.20), which was defined through the rule of mixtures as

\[
E_{ERM} = \frac{E_{\text{cell}} - (1-\text{VF})E_m}{\text{VF}},
\]

(2.14)

where \( E_{\text{cell}} \) is the finite element result for the Young's modulus of the cell, \( E_m \) is the Young's modulus of the matrix and \( \text{VF} \) is the CNT volume fraction.
Many studies on CNT waviness followed (e.g. Luo et al. 2007, Shi et al. 2004, Rafiee 2013, Nafar Dastgerdi 2013, Nafar Dastgerdi 2014, Shao et al. 2009, Ginga et al. 2013). However, the assumption of perfect bonding (cf. Fisher et al. 2003, Anumandla and Gibson 2006, Bradshaw et al. 2003, Joshi et al. 2011) overpredicts the stiffness reducing effect of CNT waviness (Nafar Dastgerdi 2014). Similar observations were made by Pantano and Capello (2008). In their sequential multiscale modelling approach, RVEs composed of wavy and aligned CNTs were generated within the FE framework and subjected to uniaxial tension in the direction of CNT alignment. CNTs were modelled as shells following the methodology in Pantano et al. (2004)—interwall interaction and CNT-matrix interaction were modelled via pressure/cohesion depending on separation distance based on the Lennard-Jones potential, i.e. interwall shear resistance was assumed to be zero. Their computational results suggest that in case of poor bonding with absence of shear load transfer, waviness enhances the nanocomposite stiffness. Those enhancements, however, are achieved through the CNT bending energy.

Figure 2.20: Effective CNT reinforcement modulus $E_{ERM}$ as a function of waviness $w$; amplitude $a$, wavelength $\lambda$, ratio of phase moduli $E_{ratio}$, for wavelength ratio $\lambda/d=100$ and $E_{matrix}=1$GPa (from Fisher et al. 2003)
2.5 Concluding remarks

CNTs were shown to possess an outstanding potential as mechanical reinforcement due to their remarkable stiffness and resilience. However, to date the full potential cannot yet be transferred to their nanocomposites. The reasons are related to challenges in the production process that result in imperfections such as CNT agglomerations, incomplete CNT impregnation, CNT waviness, random CNT orientations and insufficient epoxy-CNT bonding. In several studies, it was concluded that those imperfections reduce the stress transfer efficiency or even lead to a void-like behaviour of the filler material in the epoxy matrix.

In the context of impact resistant applications, an efficient stress transfer is necessary for an enhanced stress state within the epoxy matrix that leads to an accelerated plastic deformation. Furthermore, stress concentrations resulting from voids induce premature failure of the nanocomposite and, thus, reduce the energy absorption capability when compared to pure epoxy. Hence, good dispersion and CNT impregnation, as well as an efficient shear stress transfer are essential for impact resistance enhancement of epoxy/CNT nanocomposites caused by their enhanced plastic deformation. With advanced production methods such as CNT functionalisation or high shear mixing, it becomes increasingly possible to overcome those production-process induced imperfections. Experimental studies should, therefore, be performed on samples produced via state of the art production routes. Nevertheless, to date there is still a significant lack in experimental and computational studies investigating the non-linear finite strain response of epoxy/CNT nanocomposites or their behaviour under impact rates of strain.

Advanced material modelling can complement experimental work and assist experimentalists in exploring the relationship between process induced
morphology/imperfections and resulting macroscopic behaviour systematically, for example via changing one factor at a time. Available literature suggests that imperfections such as imperfect epoxy-CNT bonding, CNT waviness, non-uniform CNT distribution, random CNT orientation and CNT agglomeration need to be incorporated in computational models in order to match experimental outcomes. Hierarchical multiscale models are here favoured over concurrent multiscale models because they are computationally efficient and, thus, allow for the incorporation of process induced morphologies with random spatial CNT distributions and orientations.

This work aims, therefore, at developing an experimentally-validated hierarchical multiscale model for the prediction of the nonlinear finite deformation of epoxy/CNT nanocomposites under compressive loading. For model validation, imperfections need to be incorporated into the multiscale modelling scheme. Once the model is validated, effects of those imperfections can be studied, and compared with predictions for perfect systems i.e. those that can eventually be achieved when overcoming process-induced limitations.
Chapter 3

Prediction of energy absorption characteristics of aligned epoxy/CNT nanocomposites

3.1. Objective of computational study

Several researchers used CNTs to improve the damage and failure resistance of CFRP laminates. Various approaches have been pursued. They include enhancement of the mechanical performance of composite matrices (Yokozeki et al. 2007) and the strengthening of the interface between two CFRP pre-preg laminae (Hu et al. 2012). Others have grown them on the microfibre surfaces to produce a stitching effect (Wicks et al. 2010).

In this work it is believed that the incorporation of an epoxy/CNT nanocomposite coating onto the laminate surface can help to enhance overall energy absorption characteristics of the laminates. This is expected to have two different origins: (1) enhanced ductile deformation of epoxy in compression due

1 Parts of this chapter were published in:
to presence of CNTs and (2) CNT crack bridging mechanisms (Gojny et al. 2005, Wernik and Meguid 2010, Zhang, Picu, Koratkar 2007) accompanied by CNT pull-out and interface debonding.

In order to demonstrate the potential of aligned epoxy/CNT nanocomposites towards energy absorption applications, preliminary computational studies were performed. In particular, two case studies were investigated: (1) crack resistance characteristics of the epoxy/CNT nanocomposites with aligned double-walled CNTs (DWCNTs) in the vicinity of a matrix crack, and (2) rate-dependent compressive response of epoxy/CNT systems with aligned single-walled CNTs (SWCNTs). As pointed out in Section 2.3.1, the orientation of CNTs in epoxy can be achieved via external stimuli such as electric (Martin et al. 2005) or magnetic fields (Garmestani et al. 2003), and impregnation of CNT forests with subsequent in-situ polymerisation (Wardle et al. 2008, Dassios et al. 2012).

The influence of mechanical properties of CNT-CNT and epoxy-CNT interface on the normalised total energy release rate at the matrix crack tip and damage propagation along those interfaces were investigated in case (1). In this context, one has to distinguish between ‘interfaces’ and ‘interphases’. The term ‘interface’ refers to the thin transition region between the matrix and CNT, which is in case of weak interactions bridged by weak secondary vdWs bonds. The term ‘interphase’ in contrast specifies a zone of matrix material that surrounds the CNT and has properties different from the bulk material.

In case (2), the nanocomposite behaviour at various strain rates ranging from quasi-static to impact rates was predicted and the effects of CNT volume fraction and CNT aspect ratio on the macroscopic compressive stress-strain response were investigated. Those predictions were compared with the response of unfilled epoxy, and the normalised energy absorption
characteristics of the nanocomposites in the absence of component damage were evaluated.

The simplified modeling approach introduced here in case (2) is also the basis for the development of an advanced multiscale modeling approach presented in Chapter 4.

3.2. Energy absorption characteristics in tension

3.2.1. Modelling approach

An increased impact resistance in the composite areas dominated by tensile stresses is expected to be caused by CNT crack bridging mechanisms, accompanied by CNT pull-out and interface debonding. Hence, a problem of a stationary matrix crack in the vicinity of a DWCNT was studied here to investigate the effect of interface (epoxy-CNT and CNT-CNT) properties on the fracture parameter (energy release rate).

Continuum FEM was applied here as it offers a compromise between accuracy and computational time when compared to molecular simulations. The FE software ABAQUS/Standard was used. An axisymmetric model with a circumferential matrix crack of length \( a \) was used in this work, as shown in Fig. 3.1. This represents a plausible scenario, where a matrix crack approaches a ‘forest’ of aligned (locally or globally) carbon nanotubes, without yet touching of their surfaces. A CNT volume fraction of \( \sim 1.28\% \), defined as volume ratio between an effective solid fibre representation of the CNT and model geometry, was assumed.
A CNT aspect ratio of $l_{CNT}/r_{CNT}=50$ was considered here, where CNT length $l_{CNT}=500$ nm, and CNT radius $r_{CNT}=5$ nm. This aspect ratio is relatively small compared to typical aspect ratios of CNTs. However, it corresponds to a lower reinforcing limit (worst case scenario), where a debonding length and CNT-bridging effect is small. The epoxy matrix was assumed as linear elastic with Young’s modulus and Poisson’s ratio assumed to be 2.5 GPa (see compression tests of pure epoxy samples in Chapter 6) and 0.4 (Reedy Jr 2000) respectively. The Young’s modulus of the CNT was assumed to be 3.36 TPa (Wang and Zhang 2008). The model symmetry resulted in modelling of only one half of the axisymmetric cell. The matrix crack was modelled as a sharp circumferential crack perpendicular to the axis of the CNT. Interfaces were incorporated into the model to account for different CNT-CNT and epoxy-CNT interactions. CAX4 (4-node bilinear axisymmetric quadrilateral elements) and COHAX4
elements (4-node axisymmetric cohesive elements) were used. The stress transfer from the matrix to the top edges of CNT walls was assumed to be negligible, and, therefore, no bonding at the interface between top CNT edges and the matrix was modelled.

CNT-CNT and epoxy-CNT interactions were modelled using the cohesive zone concept through bilinear traction-separation laws (see Fig. 3.2). Those laws include damage initiation, damage propagation and failure. The damage initiation criterion used here is based on the maximum nominal stress value in shear or normal direction. Damage propagation is represented in terms of the stiffness degradation by using a linearly decaying function. The complete set of interface parameters is shown in Table 3.1. It was assumed that fracture modes I and II of the interfaces can be separated. Moreover, damage initiation displacement \( D_i \) and failure displacement \( D_f \) in mode I and mode II were, due to the lack of experimental and computational data, assumed to be of same value, while shear strength, shear stiffness and energy release rate in mode I were assumed to be twice as much as their counterparts in mode II. A doubled shear stiffness corresponds to an isotropic material with negligibly small Poisson’s ratio, such that strain does not result in lateral contraction/expansion.

\[
\begin{align*}
\text{Figure 3.2:} & \quad \text{Bilinear traction-separation law used for nanocomposite interfaces; Energy release rate } G_c, \\
& \quad \text{Shear strength } S, \text{ Shear stiffness } K, \text{ Displacement at damage initiation } D_i, \text{ Displacement at failure } D_f.
\end{align*}
\]
Parameters of the cohesive law for epoxy-CNT interfaces were based on experimental studies reported in the literature. Ganesan et al. (2010) estimated interfacial fracture energies between 50 and 250 MPa-nm from pull-out experiments. From pull-out experiments shear strengths of ~30 MPa for non-functionalised and ~150 MPa for functionalised MWCNTs were found (Barber et al. 2006). Therefore, various combinations of epoxy-CNT interface properties were considered and denoted by letters from A to G (see Table 3.1) to capture the shear strength range (~30–150 MPa) and fracture energy range (~50–250 MPa-nm) as described above.

In addition, a range of mechanical properties for the CNT-CNT interwall bonding reported in the literature is summarised below as follows. Cumings and Zettl (2000) estimated, through controlled and reversible telescopic extension of MWNTs using TEM, the static friction force per contact area as smaller than \(6.6 \times 10^{-15} \text{N/Å}^2\), and the dynamic friction force per contact area as smaller than \(4.3 \times 10^{-15} \text{N/Å}^2\). These values are small and correspond to an interwall shear strength of around 0.5 MPa. In another experimental work, it was shown that the interwall shear resistance can be enhanced through irradiation of MWCNTs, which leads to sp\(^3\)-bonds (Pregler and Sinnott 2006). The grade of irradiation is reflected by the interwall sp\(^3\)-bond density. It is also possible that standard CVD provides MWCNTs with covalent sp\(^3\)-bonding (Barber, Andrews et al. 2005, Barber, Kaplan-Ashiri et al. 2005). Hence, the range of shear stiffnesses reflect variations in the sp\(^3\) interwall bond density, which is defined as the number of sp\(^3\)-bonds divided by the number of carbon atom-pairs in the DWCNT system (Byrne et al. 2010) (see the footnote of Table 3.1). It is noteworthy to mention that those sp\(^3\)-bonds can damage the mechanical performance of CNTs as they can result in defects. However, no effect of the interwall bond density on the mechanical properties (i.e. axial Young’s modulus) of the CNT walls was considered in this work, and CNTs
were modelled as pristine. Various combinations of CNT-CNT interwall bonding considered in this work are denoted by letters from O to R (see Table 3.1).

Table 3.1 Cohesive zone parameters for the interfaces (mode II)

<table>
<thead>
<tr>
<th>Interface</th>
<th>Shear strength, $S$ [MPa]</th>
<th>Shear stiffness, $K$ [MPa/nm]</th>
<th>$sp^3$-bond density*, $f$ [%]</th>
<th>Energy release rate, $G_{IIc}$ [MPa nm]</th>
<th>Damage initiation displacement, $D_i$ [nm]</th>
<th>Failure displacement, $D_r$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>20</td>
<td>-</td>
<td>50</td>
<td>1.5</td>
<td>3.333</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>100</td>
<td>-</td>
<td>50</td>
<td>0.3</td>
<td>3.333</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>100</td>
<td>-</td>
<td>150</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>30</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>0.3</td>
<td>6.667</td>
</tr>
<tr>
<td>E</td>
<td>90</td>
<td>100</td>
<td>-</td>
<td>150</td>
<td>0.9</td>
<td>3.333</td>
</tr>
<tr>
<td>F</td>
<td>120</td>
<td>100</td>
<td>-</td>
<td>150</td>
<td>1.2</td>
<td>2.5</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>180</td>
<td>-</td>
<td>50</td>
<td>0.167</td>
<td>3.333</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td>10</td>
<td>0.00019</td>
<td>2.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>P</td>
<td>25</td>
<td>50</td>
<td>0.00097</td>
<td>12.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Q</td>
<td>250</td>
<td>500</td>
<td>0.00966</td>
<td>125</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>R</td>
<td>2500</td>
<td>5000</td>
<td>0.09659</td>
<td>1250</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

*In this work $sp^3$-bond density $f$ was calculated from $G=G_0f$ for the given shear stiffness $K$ (cases O–R) and the interwall thickness 0.34 nm, where $G_0=1760$ GPa (see Byrne et al. 2010)—values of $f$ in Table 3.1 correspond approximately to 1, 6, 58 and 580 $sp^3$-bonds respectively.

The virtual crack closure technique (VCCT), which is based on assumptions of linear elastic fracture mechanics (LEFM), was used to determine the total energy release rate ($TERR$) for the crack in the epoxy. According to this technique the work necessary to extend the crack from $a+\Delta a$ to $a+2\Delta a$ is the same as the work required to close the crack from $a+\Delta a$ to $a$ (see Fig. 3.3).

![Figure 3.3: Scheme of computation of $TERR$.](image-url)
It is assumed that crack extension from $a+\Delta a$ to $a+2\Delta a$ does not significantly alter
the total energy release rate (Krueger 2004). In general, $TERR$ is obtained from
the energy $\Delta E$ required to close the crack and the area $\Delta A$ of the crack surface
created (Krueger 2004):

$$TERR = \frac{\Delta E}{\Delta A} \quad \text{and} \quad \Delta E = \Delta E_I + \Delta E_{II} + \Delta E_{III},$$

where $\Delta E_I$, $\Delta E_{II}$ and $\Delta E_{III}$ are energy contributions arising from the different
fracture modes I, II and III. Applied tensile loads and model geometry imply
that $TERR$ is equal to the mode I energy release rate $G_I = \frac{\Delta E_I}{\Delta A}$, as no mode II
and III fracture was assumed to be present here. The computation was carried
out at a post-processing stage by calculating $TERR$ at each increment of applied
displacement by

$$TERR = \frac{F_j^2 g_k^2}{\pi \Delta a (2r_{model} - 2a - \Delta a)},$$

which involves the reaction force $F_j^2$ at node $j$ and the displacement $g_k^2$ of node
$k$ in $x_2$ direction.

### 3.2.2. Results and discussion

The effect of the epoxy-CNT interface shear stiffness on $TERR$ for different
combinations of interface properties is shown in Fig. 3.4. The first letter (from A
to G) refers to properties (Table 3.1) of the epoxy-CNT interface and the second
letter (from O to R) corresponds to properties of the interwall interface. The
composite $TERR$ is normalised against $TERR$ of the same axisymmetric model
made of unfilled epoxy containing a stationary crack. The normalised $TERR$ is
then plotted as a function of applied strain to track the evolution of the
normalised $TERR$ with the applied load.
A general trend observed is that the presence of CNTs minimises the value of fracture parameter in the initial stage of loading as compared to unfilled epoxy with a crack.

The shear stiffness of the epoxy-CNT interface significantly affected normalised $TERR$ at the beginning of the loading process until approximately 2% of strain. In this strain range, a higher value of interface shear stiffness produced a lower value of normalised $TERR$, which is directly related to a lower intensity of the stress field ahead of the matrix crack tip. A primary reason for this is the increased stress transfer from the matrix to the nanofiller. Hence, if the matrix crack is in the vicinity of functionalised epoxy-CNT and $sp^3$-bonded CNT-CNT interfaces, the fracture parameter is reduced.

Then, all interface combinations that possess the smallest $sp^3$-bond density (0.00019% for interface O) within the CNT-CNT interwall interface revealed a fracture parameter jump around 1% of strain. The jump was caused by damage (stiffness degradation of cohesive elements) initiated in the interwall interface, which subsequently led to the failure (maximum stiffness degradation, i.e. zero stiffness) of the first cohesive zone element in the interwall layer. Fracture propagation in the interwall phase continued until the onset of failure in a first cohesive zone element in the epoxy-CNT interface—at that stage the entire interwall interface underwent damage of 60 to 70% and (around 2% applied nominal strain) a local minimum of normalised $TERR$ is observed. Then, as damage and failure progressed in the epoxy-CNT interface, the slope of normalised $TERR$ increased with increasing applied nominal strain. At larger applied strains the normalised $TERR$ levelled off at a value of around 1, because of the debonding of the epoxy-CNT interface, and the model behaved as an unfilled epoxy. A value of normalised $TERR$=1 was achieved at around 4.5% of applied strain, which lies out of the investigated range in Fig. 3.4. At this level of strain around 80% of the epoxy-CNT interface failed.
It is noteworthy to mention that the graph reveals a nonlinear relationship between the shear stiffness of epoxy-CNT interface and fracture parameter (normalised TERR). In particular, a significant decrease of normalised TERR was achieved from interface A (20 MPa/nm) to B (100 MPa/nm) (AR and BR), no further significant decrease was found from B (100 MPa/nm) to G (180 MPa/nm) (BR and GR). A similar saturation governs the effect of sp³-bond density—a decrease of the fracture parameter was observed when increasing the sp³-bond density from 0.00019% (interface O) to 0.00097% (interface P). This is shown to be dominant at smaller magnitudes of applied nominal strain (< 2% applied strain). Further increase from 0.00097% (interface P) to 0.00966% (interface Q) or 0.09659% (interface R) did not provide significant improvements.
The decrease in normalised TERR, especially pronounced for BP, BR, GP and GR between applied nominal strain values of 0.005 and 0.013, is probably caused by stress redistribution within the matrix material, which arises from the damaged portion of the epoxy-CNT interface at the CNT end. Prior to the occurrence of damage, the deformation of the matrix material next to this epoxy-CNT interface region were significantly constrained due to the high shear stiffness of the interface. Those constraints on matrix deformation are relaxed due to the localized stiffness degradation of cohesive elements. As a result, further increasing applied strain led primarily to the local straining of the matrix region, while the rest of the model was hardly affected. Temporarily, this led to a less pronounced increase of TERR for the nanocomposite. Normalisation with TERR of pure epoxy resulted then in a local decrease of normalised TERR (see Fig. 3.4). This explanation is supported by less dominant reductions of normalised TERR for epoxy-CNT interface combinations exhibiting a lower shear stiffness of 20 MPa/nm (AP, AQ, AR), which impose less constraints on the matrix material.

Before fracture in the epoxy-CNT interface occurred, the increase in sp³-bond density of the interwall interface provides a larger reduction in normalised TERR when combined with stiff epoxy-CNT interfaces. For example, the reduction of normalised TERR when changing from an AO to an AP-configuration (A corresponds to 20 MPa/nm) is less significant as from GO to GP (G correspond to 180 MPa/nm). This combined effect was further pronounced for BP, BR, GP and GR by a decrease of normalised TERR (explained in the paragraph above) with increasing strain between applied nominal strain magnitudes of 0.005 and 0.013.

The effect of shear strength of the epoxy-CNT interface on normalised TERR is shown in Fig. 3.5a. The range of interface shear strength (considering only the mode II traction-separation law) varied from 30 to 90 to 120 MPa for C, E and F,
respectively. Again, according to the pull-out experiments of Barber et al. (2006), 30 MPa corresponds to non-functionalised CNTs and 120 MPa corresponds to functionalised CNTs.

It was found that the shear strength of the epoxy-CNT interface affected the occurrence of damage in the interwall interface. The interwall damage/fracture occurred only when the interface C (30 MPa) was combined with the weakest interwall interface O (0.00019% sp\(^3\)-bond density), while the epoxy-CNT interface E (90 MPa) exhibited an interwall interface damage in combination with O (0.00019% sp\(^3\)-bond density) and P (0.00097% sp\(^3\)-bond density). The effect of interface shear strength on normalised TERR is shown in Fig. 3.5—for visualisation purposes curves that possess damage in the interwall interface are excluded in Fig. 3.5.

![Figure 3.5](image)

Figure 3.5: Effect of (a) epoxy-CNT interface shear strength and (b) epoxy-CNT fracture energy on normalised TERR.

The graph shows, how the epoxy-CNT interface shear strength influenced the trend of normalised TERR. The minimum value of TERR was reduced and
shifted to larger strain values, with increased epoxy-CNT interface shear strength. A significant reduction of normalised $TERR$ within the applied strain range of 2–3% was obtained by changing the interface configuration from C (30 MPa) to E (90 MPa). However, the difference between E (90 MPa) and F (120 MPa) is negligibly small, which suggests that there will be no significant difference in the stress field ahead of the crack tip. The local minimum of normalised $TERR$ was shifted to larger applied strains, which was caused by the increase in interface shear strength that allowed the interface to last longer as intact. The smaller magnitude of the minimum for larger interface shear strength values (90, 120 MPa) can be attributed to the larger stress that was carried by the CNT. The normalised $TERR$ increased upon reaching the local minimum for all the interfaces (not fully shown for ER and FR in Fig. 3.5a).

The effect of the critical energy of fracture (in mode II) of the epoxy-CNT interface on normalised $TERR$ was studied for three interfaces B (50 MPa·nm), D (100 MPa·nm), and C (150 MPa·nm) and it is shown in Fig. 3.5b. Smaller values of the interface fracture toughness (associated with the smaller displacement at failure—see Table 3.1) resulted in an accelerated interface damage propagation and failure, and caused an increase of stresses at the crack tip, and hence the increase of normalised $TERR$. For all interface combinations, damage (stiffness degradation) in the epoxy-CNT interface started at around 0.5% of applied strain. The start of failure (zero stiffness) was delayed from 1.8% (BP) to 3.0% (DP) and to 4.3% (CP) of applied nominal strain with increasing fracture energy. Additional increase in strain of 0.5% led to a failure (full debonding, i.e zero stiffness) of 38% (BP), 20% (DP) and 14% (CP) of the epoxy-CNT interface. Enhancing the fracture toughness of the interface from 50 to 100 MPa·nm resulted in a significant decrease of normalised $TERR$ between 1.5 and 3% of applied nominal strain.
In summary, the results of cases reported above show that various combinations of mechanical properties (shear stiffness, shear strength and mode II toughness) of CNT-CNT and epoxy-CNT interfaces lead to a reduction of stresses near the tip of a stationary matrix crack when compared with pure epoxy. As expected, the most efficient reduction of fracture parameter is caused by strong interfaces that exhibit a large interface fracture toughness, which leads to an improved stress transfer from the matrix to CNTs during the deformation of the composite, and hence to reduction of stresses at the crack tip.

### 3.3. Energy absorption characteristics in compression

#### 3.3.1. Modelling approach

The ductility of epoxy in compression suggests that the energy absorption characteristics of epoxy/CNT can be improved through a CNT-enhanced nonlinear deformation of the matrix in zones undergoing compression. Hence, in order to understand better the effect of CNT on the nonlinear deformation of epoxy, this study was focused on the prediction of the compressive macroscopic stress-strain response of the epoxy/CNT nanocomposite at strain rates ranging from quasi-static to impact rates. In particular, the emphasis was on the effect of CNT aspect ratio and volume fraction on stress-strain curves and associated energy absorption characteristics. An idealised aligned morphology of CNTs was investigated in this work. A rate-dependent constitutive model for epoxy (Buckley et al. 2004) was implemented into a finite element (FE) framework, and combined with the unit cell and numerical homogenisation. Predictions of nanocomposite behaviour for different rates were compared with pure epoxy, to demonstrate the effect of CNT aspect ratio and CNT volume fraction on energy absorption characteristics of epoxy/CNT nanocomposites.
In order to capture the macroscopic response of the nanocomposite it was assumed that the CNT morphology is globally periodic and that the macroscopic deformation is uniform. This enabled the application of the unit cell concept. A simple axisymmetric unit cell, including a single-walled CNT embedded in an epoxy matrix, was proposed because of its simplicity. However, it must be mentioned that this idealisation concept suppresses CNT bending and columnar buckling as possible deformation mechanisms, which contribute to the energy absorption. The single-walled CNT was modelled as an effective continuum fibre (see Fig. 3.6) of linear elastic and isotropic behaviour. The Young’s modulus of the homogenised continuum CNTs $E_{\text{eff}}^{\text{CNT}}$ were obtained by homogenising tubular versions of SWCNTs (see representation of CNT wall in Section 3.2.1) based on the axial CNT direction, as model and loading conditions used in this study suggest that this is a good approximation. Under axial loading, the homogenised continuum CNT undergoes the same response in terms of quotient of reaction force and strain as its tubular version. Thus, the following relation between their cross-sectional areas $A_{\text{continuum}}$ and $A_{\text{tubular}}$, and corresponding Young’s moduli $E_{\text{eff}}^{\text{CNT}}$ and $E_{\text{CNT}}$ holds:

$$A_{\text{continuum}} E_{\text{eff}}^{\text{CNT}} = A_{\text{tubular}} E_{\text{CNT}}, \quad (3.3)$$

which gives

$$E_{\text{eff}}^{\text{CNT}} = E_{\text{CNT}} \frac{2r_{\text{CNT}} t_{\text{CNT}} - t_{\text{CNT}}^2}{r_{\text{CNT}}^3}, \quad (3.4)$$

where $r_{\text{CNT}}$ is the CNT radius, $t_{\text{CNT}}$ is the CNT wall thickness and $E_{\text{CNT}}$ the Young’s modulus of the CNT, based on a tubular cross-section. A Young’s modulus of $E_{\text{CNT}}=3.36$ TPa (Wang and Zhang 2008) for a discrete (tubular) CNT was used to obtain the effective modulus of the homogenised CNT. This value is higher than commonly used, but it was calculated using elastic shell theory for a smaller (than usual) wall thickness i.e. $t_{\text{CNT}}=0.1$ nm and Poisson’s ratio of
\( \nu = 0.2 \) (Wang and Zhang 2008). The effective Young’s modulus of homogenised CNTs was then calculated as 133.056 GPa.

Figure 3.6 2D Axisymmetric unit cells for aligned epoxy/CNT nanocomposites, (a) periodic structure of the nanocomposite with its axisymmetric repetitive cell, (b) unit cell with (b) tubular fibre with circular cap, (c) homogenised version of B, (d) tubular fibre with straight cap, and (e) homogenised version of D.

It is noteworthy to mention that different geometries of CNTs (tubular and effective fibre, with circular and straight cap) were compared in a preliminary step to investigate the CNT homogenisation and shape of the CNT end (see Fig. 3.6). As a result, negligible differences were found between the stress-strain response of unit cells simulated with tubular isotropic CNT cylinder with circular cap (see Fig. 3.6b) and the response of models employing tubular isotropic CNT cylinders with straight cap (see Fig. 3.6d) and their homogenised versions (see Fig. 3.6c and 3.6e). Thus, the homogenised fibre with a straight cap (Fig. 3.6e) was chosen because of its simplicity and reduction of computational costs.

Perfect bonding between CNTs and the matrix was assumed in this work. Hence, a possible debonding was excluded as possible energy dissipation/absorption mechanism. As a result, nonlinear deformation of the
epoxy matrix was expected to be the major cause of energy absorption for the nanocomposite.

Matrix and CNTs were discretized using up to 3000 CAX8 (8-node biquadratic axisymmetric quadrilateral) finite elements. Uniform displacement boundary conditions were applied to the top edge of the axisymmetric unit cell in the y-direction. In addition, a uniform deformation of the right edge in the x-direction was enforced by setting the corresponding nodal displacements (right edge) as equal to displacement of the top right corner node of the unit cell (using the ABAQUS’ ‘*Equation’ command). The vertical movement (and, thus, rigid body motion) of the unit cell was constrained at the bottom as shown in Fig. 3.6.

Then, the macroscopic true (Cauchy) stresses in the longitudinal direction were predicted based on the sum of reaction forces divided by the current (deformed) cross-sectional area of the unit cell. The normalised energy absorption was calculated as the ratio of areas under the stress-strain curves for the nanocomposite and for pure epoxy up to 13% of applied nominal strain.

3.3.2. Constitutive model for the epoxy matrix

The non-linear and rate-dependent matrix behaviour was represented using a physically-based constitutive model proposed and validated by Buckley et al. (2004) for thermosetting resins. The model accounts for the strain softening and adiabatic heating effect (active upon applied impact loads), and enabled capturing basic phenomena of epoxy matrices subjected to varying strain rates. The mechanical constitutive behaviour was implemented as a user subroutine UMAT (ABAQUS/Standard) (Figiel et al. 2010), with the model parameters obtained by Buckley et al. (2004) for the standard bisphenol A resin.

The model assumes two sources of energy arising from:
• perturbation of interatomic potentials (relaxed by thermally activated flow events)
• entropy-elastic perturbation of molecular conformations (arising from preferred molecular alignment)

The model was described within the framework of continuum, and hence its kinematics is driven by the deformation gradient tensor \( F \). The tensor was decomposed multiplicatively into its volumetric \( F_{\text{vol}} \) and isochoric (deviatoric) \( \bar{F} \) parts (Figiel et al. 2010):

\[
F = F_{\text{vol}} \bar{F} \quad \text{with} \quad \bar{F} = J^{-1/3} F \quad \text{and} \quad J = \det F,
\]

where \( J \) is the volume ratio. The non-linear response is contained within the isochoric part of the deformation gradient (\( \bar{F} \)). Thus, additional measures of deviatoric deformation such as left Cauchy-Green tensor \( \bar{B} \), velocity gradient \( \bar{L} \), rate of deformation \( \bar{D} \) and continuum spin \( \bar{W} \) are defined based on \( \bar{F} \) (Figiel et al. 2010):

\[
\bar{B} = \bar{F} \bar{F}^T, \quad \bar{L} = \dot{\bar{F}} \bar{F}^{-1}, \quad \bar{D} = \frac{1}{2} (\bar{L} + \bar{L}^T), \quad \bar{W} = \frac{1}{2} (\bar{L} - \bar{L}^T),
\]

where the symbol \( \dot{\cdot} \) denotes the material time derivative. Furthermore additive decomposition of the isochoric rate of deformation \( \bar{D} \) into elastic \( \bar{D}^e \) and viscous \( \bar{D}^v \) parts was invoked:

\[
\bar{D} = \bar{D}^e + \bar{D}^v.
\]

There are two deviatoric stress contributions: (1) bond-stretching stress \( \bar{S}^b \) (b-part of the model) and (2) conformational stress \( \bar{S}^c \) (described in terms of isotropic hyperelasticity) (c-part of the model) as a result of the two energy sources stated above.

The total Cauchy stress \( \sigma \) is the sum of these two tensor contributions and the volumetric stress tensor \( \sigma_{\text{vol}} I \) as follows (Figiel et al. 2010):
\[
\sigma = \bar{\mathbf{S}}^b + \bar{\mathbf{S}}^c + \sigma_m \mathbf{I} \quad \text{with} \quad \sigma_m = K_b \ln J ,
\]

(3.8)

where \( \sigma_m, \mathbf{I} \) and \( K_b \) are the mean (hydrostatic) stress, second-order identity tensor and bulk modulus, respectively.

Concerning the \( b \)-part of the model, the objective rate of deviatoric bond-stretch stress is represented as a single relaxation time approximation of the real multi-mode response (Buckley et al. 2004):

\[
\dot{\bar{\mathbf{S}}}^b = 2G^b \bar{D} - \frac{\bar{\mathbf{S}}^b}{\tau},
\]

(3.9)

and \( G^b \) is the shear modulus associated with bond stretching and \( \tau \) is the relaxation time. Taking the objective rate of deviatoric bond-stretch stress \( \dot{\bar{\mathbf{S}}}^b \) as the Jaumann rate, the deviatoric Cauchy \( b \)-stress \( \bar{\mathbf{S}}^b \) is then determined from the following differential equation for the rate of deviatoric bond-stretch stress \( \dot{\bar{\mathbf{S}}}^b \) (Buckley et al. 2004):

\[
\dot{\bar{\mathbf{S}}}^b = \bar{\mathbf{S}}^b + \dot{\mathbf{W}} \bar{\mathbf{S}}^b - \bar{\mathbf{S}}^b \mathbf{W}.
\]

(3.10)

The \( c \)-part of the model applies the physical theory of rubber elasticity due to Edward and Vilgis (1986) neglecting, however, entanglement effects due to high crosslink density of epoxy resins. The deviatoric Cauchy \( c \)-stress \( \bar{\mathbf{S}}^c \) is obtained by differentiating the Edward-Vilgis strain-energy function \( A_c \) (Eq. (22) in Buckley et al. 2004) with respect to elastic network principal stretches \( \bar{\lambda}_i \) (Buckley et al. 2004):

\[
\bar{S}^c_i = \bar{\lambda}_i \frac{\partial A_c}{\partial \bar{\lambda}_i} + p \quad (i \text{ not summed}), \quad \bar{S}^c = \bar{S}^c q_i \otimes q_i ,
\]

(3.11)

where \( \bar{\lambda}^2 \) and \( q_i \) are the eigenvalues and eigenvectors of the left Cauchy Green tensor \( \bar{\mathbf{B}} \), and pressure \( p = -(1/3) \text{tr} (\sigma) \). The model accounts for several features such as strain rate dependence, structural rejuvenation and adiabatic heating.
Strain rate dependence and structural evolution are both driven by the viscous part of the deformation rate tensor, in particular by the relaxation time $\tau$ (Buckley et al. 2004):

$$\tau = a_\sigma \tau_0,$$  \hspace{1cm} (3.12)

where $a_\sigma$ is the time-stress shift factor and $\tau_0$ is the relaxation time in the linear viscoelastic limit. In order to account for the strain rate dependent behaviour, the stress-shift factor $a_\sigma$ is based on a three-dimensional generalisation of the Eyring rate kinetics (Buckley et al. 2004):

$$a_\sigma = \frac{V_s \tau_{\text{oct}}^b \exp(-V_p \sigma_m / RT)}{2RT \sinh(V_s \tau_{\text{oct}}^b / 2RT)},$$  \hspace{1cm} (3.13)

where $\tau_{\text{oct}}^b$ is the octahedral shear component of the bond-stretch stress, $V_p$ and $V_s$ are pressure and shear activation volumes, $R$ is the universal gas constant and $T$ is the temperature.

Using Tool’s fictive temperature concept (Tool 1946), structural rejuvenation, which manifests itself as softening regime in the constitutive model, is incorporated in the $\tau_0$ parameter given by (Buckley et al. 2004)

$$\tau_0 = \tau_0^* \exp \left( \frac{\Delta H_0}{RT} - \frac{\Delta H_0}{RT^*} + \frac{C}{T_{f_\sigma} - T_\infty} - \frac{C}{T_{f_\sigma}^* - T_\infty} \right),$$  \hspace{1cm} (3.14)

and the viscoelastic relaxation time $\tau_0^*$ at some reference temperature $T^*$ and reference structure $T_{f_\sigma}^*$, the Vogel equation constant $C$, the Vogel temperature $T_\infty$, the activation enthalpy $\Delta H_0$ associated with structural change, and the fictive temperature $T_{f_\sigma}$ as measure for the structural state/rejuvenation of the epoxy resin. The latter was assumed to be driven by the sum of the invariants of the viscous strain increments $\bar{\varepsilon}^\nu$ (Buckley et al. 2004):
\[ T_{\text{fc}} = T_{\text{fc0}} + (T_{\text{fc\infty}} - T_{\text{fc0}}) \left[ 1 - \exp \left( -\frac{\tilde{\varepsilon}^v}{\varepsilon_0^v} \right) \right], \]  

(3.15)

where the final fictive temperature \( T_{\text{fc\infty}} \) and the strain range over which rejuvenation occurs \( \varepsilon_0^v \) were taken as material constants.

The thermo-mechanical coupling is based on the following differential equation for the rate of adiabatic heating \( \dot{T} \) (Buckley et al. 2004):

\[
\dot{T} = \frac{1}{\rho c} \left[ \bar{\sigma} : D - \bar{\sigma}^b : D^b \right] - \frac{\phi \Delta c T_{\text{fc}}}{c},
\]

(3.16)

where \( \phi \Delta c \) is the effective specific heat difference, \( c \) is the specific heat, \( \rho \) is the density, \( \bar{\sigma} \) and \( \bar{\sigma}^b \) are the deviatoric Cauchy stress and deviatoric bond-stretching Cauchy stress, respectively.

### 3.3.3. Results and discussion

Predicted compressive stress-strain curves and energy absorption characteristics of epoxy/CNT nanocomposites subjected to different strain rates are discussed in this section. The CNT aspect ratio was changed by varying the CNT length \( l_{\text{CNT}} \), while variations in CNT volume fraction were obtained by changing the dimensions of the unit cell and keeping the distance between adjacent CNTs in the radial direction equal to their distance in the longitudinal direction \( (l_{\text{Model}} - l_{\text{CNT}} / 2 = r_{\text{Model}} - r_{\text{CNT}}) \). It must be mentioned that CNT volume fractions refer to a nanocomposite composed of a hexagonal packing and, therefore, it is slightly smaller than the CNT volume fraction of the CNT unit cell.

Effects of the CNT volume fraction \( (VF) \) and varying strain rates on the stress-strain response are shown in Fig. 3.7. As expected, incorporation of aligned CNTs into epoxy produced a considerable stiffening effect in the linear portion
of the curve—the Young’s modulus of the nanocomposite increased by around 15%, 30%, 46% and 77% compared to pure epoxy for volume fractions of 0.5%, 1%, 1.5% and 2.5%, respectively. Hence, CNT volume fraction exhibited almost a linear effect on the Young’s modulus of the nanocomposite. Just as for the pure epoxy, no change in the nanocomposite Young’s modulus was predicted with increasing strain rate. Experimental data for pure epoxy across a wide range of compressive strain rates for an RTM-6 epoxy system reported in Gerlach et al. (2008) shows that there is no significant change in Young’s modulus up to true strain rates ~ $10^3 \text{s}^{-1}$. The latter is greater than the maximum magnitude of nominal strain rates considered in this work, as the true strain rate $\dot{\varepsilon}_M$ is related to the applied (nominal) strain $\varepsilon_{M(app)}$ through $\dot{\varepsilon}_M = \dot{\varepsilon}_{M(app)} / (1 + \varepsilon_{M(app)})$.

The stiffening effect caused by the CNT volume fraction is also present beyond the elastic limit. In particular, for the given magnitude of applied strain, a gradual increase in the macroscopic true stress with CNT volume fraction was predicted, while the onset of nonlinear deformation was shifted to a slightly lower value of applied strain, with increasing CNT volume fraction. In all cases
the yield stress, defined here as the stress of the transition zone between the elastic and nonlinear behaviour, increased with CNT volume fraction. The post-yield strain softening, typical for the pure epoxy (Buckley et al. 2001), was no longer present macroscopically for volume fractions equal to or greater than 1%. Furthermore, an increase in the CNT volume fraction resulted in an increased post-yield strain-hardening effect (see Fig. 3.7).

Effects of CNT aspect ratio ($AR$) and varying strain rates on the stress-strain response were also investigated (see Fig. 3.8). As expected, the predicted trends were found to be in a qualitative agreement with the effects of varying CNT volume fraction. However, quantitatively, only a slight increase of 3% in nanocomposite modulus was predicted with increasing CNT aspect ratio from 50 to 250. As indicated by different curves, the effect of CNT aspect ratio on the stress-strain response tends to saturate with increasing aspect ratio—less significant improvement of the overall stress-strain response was obtained for aspect ratios greater than 100 within the simulated strain range. However, in general there was an enhanced post-yield behaviour (increasing strain stiffening) with increasing CNT aspect ratio, which suggests that energy absorption characteristic can be enhanced only at large deformations. Again, the major contribution to that comes from the enhanced nonlinear deformation (strain stiffening) of the matrix caused by the presence of CNTs.
Hence, assuming that the energy absorbed by the material system can be represented by the area under the stress-strain curves, it can be postulated that the improved post-yield behaviour of the nanocomposite due to the presence of CNTs can largely contribute to the improved energy absorption of the epoxy/CNT nanocomposite in compression. In order to quantify the energy absorption characteristics, areas under stress-strain curves were evaluated up to strains of ~13%, for the nanocomposites and matrix, at two strain rates ($1\times10^{-3}$ s$^{-1}$ and $1\times10^{3}$ s$^{-1}$), and with different volume fractions and aspect ratios. The predictions are shown in Fig. 3.9 in terms of normalised (with respect to epoxy matrix) energy absorption.

Generally, the normalised energy absorption was enhanced due to the presence of CNTs at both strain rates. In particular, a significant correlation between CNT volume fraction and energy absorption characteristics was found. An increase in CNT volume fraction contributed to a considerable increase in normalised energy absorption under quasi-static loading ($1\times10^{-3}$ s$^{-1}$). This was especially the case for CNT aspect ratios greater than 150. There exists a significant combined effect of CNT volume fraction and aspect ratio. In
comparison, predictions for a volume fraction of 0.5% did not show such a significant increase in the normalised energy absorption with increasing aspect ratio than predictions for a volume fraction of 1.5%.

\[
f(AR, VF) = 0.944 + 61.45VF + 0.2223VFAR - 921ARVF
\]

\[
f(AR, VF) = 0.976 + 48.29VF + 0.08585VFAR - 658.3ARVF
\]

Figure 3.9: Predicted normalised (with respect to epoxy matrix) energy absorption characteristics as a function of CNT aspect ratio (AR) and CNT volume fraction (VF) for quasi-static 1x10^{-3} s^{-1} (a) and high strain rates 1x10^{3} s^{-1} (b). The normalised energy absorption characteristics at the data points (crosses) were used to determine the coefficients of the nonlinear regression functions \(f(AR, VF)\) via the least squares method. Goodness of fit is described by the coefficient of determination \(R^2\).

In summary, these results suggest generally that CNTs can be used to enhance the nonlinear response of epoxies under compression to improve their energy
absorption characteristics. The main contribution comes from the strain stiffening effect occurring in the post-yield regime. The effect is improved with the increasing CNT volume fraction, which should be used for a carefully selected average CNT aspect ratio to maximise the energy absorption of epoxy/CNT nanocomposites. Results of this study holds under the assumption that the nonlinear matrix deformation is the primary energy absorption mechanism.
Chapter 4

General modelling methodology

In this chapter, a 3D modelling approach for the prediction of the nonlinear compressive response of epoxy/CNT nanocomposites is presented. A short general introduction on the multiscale modelling approach used in this work will be first described. Then, a more detailed description of the basic components of the methodology will be presented.

4.1. Multiscale modelling approach

The applied multiscale modelling approach (see Fig. 4.1) involves four distinct length scales:

1) The nanoscale, where mechanical properties of SWCNTs and MWCNTs are derived from molecular mechanics following the work of Shen and Li (Shen and Li 2004, Shen and Li 2005) and properties for CNT-epoxy interfaces are based on molecular dynamics simulations (Frankland et al. 2002),

2) The microscale, where the discrete CNT is represented by a homogenised solid cylinder using the effective fibre concept and where phenomena related to the polymer network are captured by a nonlinear continuum constitutive model for the epoxy matrix (Buckley et al. 2004)

3) The mesoscale, where the nanocomposite morphology is reconstructed using the representative volume element (RVE) concept under assumptions of global periodicity
4) The macroscale, where the nanocomposite stress-strain response is predicted using numerical homogenisation of the RVE response.

![Figure 4.1: Modelling approach (from Weidt and Figiel 2014).](image)

Regarding the two commonly applied multiscale approaches, the hierarchical multiscale scheme is deemed to be computationally more efficient than the coupling of AFEM and FEM. The latter is commonly used in combination with the unit cell concept by modelling a short section of a single CNT as spaceframe that is directly coupled to a continuous matrix via spring elements. The study of more realistic nanocomposite morphologies, however, has to account for a number of full length CNTs randomly distributed within an RVE. Hence, a less demanding hierarchical multiscale approach with homogenised CNT structure and interface was applied here. In so doing, continuum theory was assumed to hold down to the scale at which the nanocomposite morphology can be captured with an RVE. This approach offers a compromise between accuracy of molecular approaches and computational time of numerical continuum methods to study morphology-property relations in the nanocomposites.

The applied continuum approach is nevertheless enhanced by properties coming from the nanoscale and phenomena originating at the molecular level of
polymer chains. Therefore, it was assumed that atomistic time and length scales can be separated from the higher scales, i.e. the model calculations or simulations at the nanoscale are performed independently and the scale-bridging happens via passing of relevant information (CNT and interface properties). At the microscale, phenomena related to the structural evolution of the discrete polymer network are captured by a physically-based constitutive model that is experimentally validated and described within the continuum framework. The parameters captured by each scale are summarised in Table 4.1.

<table>
<thead>
<tr>
<th>Effective scale</th>
<th>Effective length</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano</td>
<td>nm</td>
<td>CNT chirality, atomistic configuration, bond deformations</td>
</tr>
<tr>
<td>Micro</td>
<td>nm/µm</td>
<td>Mechanical properties of CNT (linear elastic, transversely isotropic), CNT aspect ratio, elasto-visco-plastic behaviour of epoxy, relaxation (epoxy), adiabatic heating (epoxy), rejuvenation (epoxy)</td>
</tr>
<tr>
<td>Meso</td>
<td>µm</td>
<td>Nanocomposite morphology, CNT volume fraction, CNT orientation, CNT distribution</td>
</tr>
<tr>
<td>Macro</td>
<td>mm</td>
<td>Mechanical properties of nanocomposite</td>
</tr>
</tbody>
</table>

As mentioned above, the modelling procedure is based on the RVE concept and the first-order homogenisation method. Therefore, determination of an RVE and its size is not a trivial task since an RVE is clearly defined only in two situations (Ostoja-Starzewski 2006):

1) unit cell in a globally periodic microstructure

2) volume containing a very large (mathematically infinite) set of microscale elements (e.g. grains), possessing statistically homogeneous and ergodic properties

Whereas the first point includes the unit cell for real periodic microstructures in a wider meaning of RVE, the second point refers to random microstructures, which renders a more common understanding of RVEs. Generation of an infinite RVE domain is, however, hardly feasible and, thus, a minimal volume
“structurally entirely typical of the whole mixtures on average” (Hill 1963) is used as RVE in practise. It is prone to statistical noise and statistical homogeneity and ergodicity principle ensure that the macroscopic nanocomposite can be statistically represented by an RVE (Ostoja-Starzewski 2006). The implied separation of scales \( L_{\text{micro}} \ll L_{\text{meso}} \ll L_{\text{macro}} \) reveals that the RVE as the mesoscale window should contain enough information about the material structure and be much smaller than the macroscopic body. An additional postulate by Hill’s definition of the RVE is that the “apparent overall moduli must be effectively independent of the surface values of traction and displacement, as long as these values are macroscopically uniform”. This means that using uniform displacement boundary conditions and uniform traction boundary conditions, the constitutive behaviour of the RVE has to converge. An extensive literature on the convergence of the two boundary value problems exists (e.g. Huet 1990, Hazanov 1999, Jiang et al. 2001). However, for some compositions such as soft inclusions/hard matrix, convergence was shown to happen relatively slowly finally leading to very large RVE sizes that are impossible to be studied computationally (Jiang et al. 2001).

Hence, the more practical definition of an RVE by Drugan and Willis (1996) is applied in this work: “It is the smallest material volume element of the composite for which the usual spatially constant (overall modulus) macroscopic constitutive representation is a sufficiently accurate model to represent mean constitutive response.” It is, therefore, considered as lower bound, where finite domains start to behave as the macroscopic material. By dropping the postulate on the RVE independence of the boundary conditions, periodic boundary conditions were shown to obtain a sufficient representation of the macroscopic nanocomposite at small finite domains of the order of 2–3 times the length scale of the inclusion (see Gusev 1997 and Jiang et al. 2001). This was expected to lead to significant computational cost savings throughout this work.
Nevertheless, a finite domain of the nanostructure is considered as RVE when its behaviour converges towards the macroscopic material behaviour. In this context, two types of size effects, namely statistical and deterministic RVE size effects, should be distinguished (Gitman et al. 2007). Deterministic size effects specify the minimum volume of the RVE, provided that they converge with increasing volume element (VE) size, while statistical size effects specify the number of RVE realisations according to the required accuracy. Statistical size effects manifests themselves as decreasing ensemble standard deviation with increasing VE size, while deterministic size effects lead to varying ensemble mean values across VE sizes.

For small ensemble sizes, Welch’s t-test is commonly chosen over Student’s t-test when ensemble standard deviations are unequal. Hence, in the presence of statistical size effects, Welch’s t-test is the more suitable test to conclude about the equality of the ensemble means and, therefore, about the presence of deterministic size effects. The test involves the calculation of the $t^*$ statistics (Ruxton 2006):

$$
t^* = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{s_1^2/n_1 + s_2^2/n_2}},
$$

(4.1)

where $\bar{X}_1$ and $\bar{X}_2$ are the ensemble means, $s_1$ and $s_2$ are the ensemble standard deviations, and $n_1$ and $n_2$ are the ensemble sizes of two VE sizes. In cases of non-normality of one or both of the distributions of the VE sizes, data ranking prior to this calculation is suggested by Ruxton (2006). The degrees of freedom $\nu$ are approximated by the Welch-Satterthwaite equation given as (Ruxton 2006)

$$
\nu = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{(s_1^2/n_1)^2/(n_1 - 1) + (s_2^2/n_2)^2/(n_2 - 1)},
$$

(4.2)

which in general provides a non-integer value that is rounded off. Both values, $\nu$ and $t^*$, can then be used along with Student’s t-distribution to conclude about
the null-hypothesis (H0) on the equality of the means of the two VE sizes in a
two-tailed hypothesis test. In this work this was done via comparison of the
calculated $t^*$-value with $t$-values of t-distribution tables.

The confidence interval width $CIW$ based on student’s t-distribution was used
to quantify the accuracy of RVE predictions based on the ensemble standard
deviation:

$$CIW = 2t^* \frac{s}{\sqrt{n'}}$$

(4.3)

where $n'$ is the ensemble size and the $t^*$-value was obtained from t-distribution
tables based on a significance level of $\alpha=0.05$ and the degrees of freedom, which
are $\nu=n'-1$. Hence, both types of size effects were considered in this work and
results of these studies will be presented in Section 5.3.2.

4.2. Model generator

PYTHON scripts were written in order to automate the generation of the finite
element models. The codes involve several aspects of model generation (see Fig.
4.2): The creation of the nanocomposite morphology, the definition of the
material properties, the controlled meshing of the RVE and the formulation of
the periodic boundary conditions. In detail, after the definition of RVE input
parameters, the complete procedure up to the writing of the INPUT-file was
programmed allowing an automated model generation solely within the
ABAQUS environment.
1. Nanostructure generation

- 3D RVE
- Morphological periodicity
- Fibre geometry

2. Material properties

- Transversely isotropic fibres
- Cohesive interface

3. Meshing

- First meshing step
- Sketching of the meshes
- Second meshing step

4. Periodic boundary conditions

Figure 4.2: Schematic of main model generation steps; three-dimensional morphology generation to account for periodicity of wavy fibre geometries (a detailed description is provided in Section 4.2); definition of the material properties, e.g. transversely isotropic fibres with evolving local coordinate systems along the fibre axis and cohesive interface between fibre and matrix based on vdWs interaction (a detailed description is provided in Section 4.3 and 4.4, respectively); meshing of the RVE using a two-step meshing procedure to obtain identical meshes on opposing RVE faces (a detailed description is provided in this Section 4.2); formulation of periodic boundary conditions (a detailed description is provided in Section 4.6).
Several input parameters were defined at the beginning of the scripts and in this section a description is given on how some of them were used within the RVE generation procedure. The following parameters are used to determine the size of RVEs:

1) Number of CNTs, \( N \)
2) Radius of CNT, \( r_{\text{CNT}} \)
3) Length of CNT, \( l_{\text{CNT}} \)
4) CNT volume fraction, \( VF \)

The side length of the cubic RVE was calculated neglecting the hollow space inside the CNT, i.e. CNTs were herein represented as solid fibres. Then, the RVE side length \( d \) was calculated as

\[
d = \sqrt[3]{\frac{N \pi r_{\text{CNT}}^2 l_{\text{CNT}}}{VF}}. \tag{4.4}
\]

Boolean (ON/OFF) parameters were introduced to have the possibility to account for CNT alignment, transverse isotropy of CNT material properties (see transversely isotropic fibres in Fig. 4.2), or to choose a cuboidal RVE over a cubic RVE.

5) CNT alignment (ON/OFF)
6) Transversely isotropic CNT (ON/OFF)
7) RVE cube (ON/OFF)

Cuboidal RVEs were used in combination with CNT alignment in order to save computational costs related to the required number of CNTs. For example, a cubic RVE populated with CNTs of aspect ratio equal to 50 and a CNT volume fraction of 0.01 would require 255 CNTs in order to possess a minimum edge length of two times the CNT length. In contrast, a cuboidal RVE that exhibits a long side along the direction of CNT alignment can be populated with a
significantly smaller number of CNTs depending on the ratio of the longer to shorter RVE edge. Therefore, the dimension of the side length $d$ of the cuboidal RVE is calculated based on the pre-defined long side $b$ as

$$d = \sqrt{\frac{N \pi r_{CNT}^2 l_{CNT}}{bVF}}. \quad (4.5)$$

A number of scripts were written in order to account for different nanocomposite morphology aspects, such as the inclusion/exclusion of a CNT/epoxy interface and perfectly straight CNTs or wavy CNTs.

Depending on the choice of the script, additional parameters are required to be defined in the input sections of the scripts:

8) Interface thickness $t_{IF}$
9) CNT wavelength $\lambda_{CNT}$
10) CNT amplitude $A_{CNT}$
11) Effective CNT length $L_{eff}$

The interface is located at the lateral surface of the CNT and, thus, its geometry resembles a hollow tube of given interface thickness $t_{IF}$ and its location is concentric to the CNT axis (see cohesive interface in Fig. 4.2). Parameters 9-11 account for the CNT waviness, and they are approximated here by a sine function within restricted domain $D$ as follows (cf. fibre geometry in Fig. 4.2):

$$f(x) = A_{CNT} \sin\left(\frac{2 \pi x}{\lambda_{CNT}}\right), \text{ with } D = [0; L_{eff}]. \quad (4.6)$$

Using Pythagoras’ theorem on an infinitesimal arc length of the curve, the CNT length may be calculated prior to the model generation from

$$l_{CNT} = \int_0^{L_{eff}} \sqrt{1 + \left(\frac{dy}{dx}\right)^2} \, dx = \int_0^{L_{eff}} \sqrt{1 + \frac{4 \pi^2 A_{CNT}^2}{\lambda_{CNT}^2} \cos^2\left(\frac{2 \pi x}{\lambda_{CNT}}\right)} \, dx. \quad (4.7)$$
The quality of the resulting finite element mesh is ensured by two variables which prevent critical arrangements of CNTs within the RVE:

12) Minimum penetration depth variable
13) Minimum distance variable

The minimum penetration depth variable controls indirectly the size of the cells of periodic particles. A periodic CNT crosses the RVE boundary and re-enters the RVE at the opposing RVE face. Thus, the periodic CNT is separated into multiple cells (cf. morphological periodicity in Fig. 4.2). Each cell has to immerge a certain depth towards the RVE centre, which corresponds to the penetration depth variable ‘m’. In detail, this is implemented by an overlap test with an additional cube having the same central point as the original RVE and with side lengths that are 2 times the minimum penetration depth smaller than the RVE side lengths (see Fig. 4.3).

![Figure 4.3: 3D RVE cube and inner smaller cube geometry; ‘m’ corresponds to the minimum penetration depth variable.](image)

Such an implementation will further prevent the generation of periodic or non-periodic particles that are approximately parallel to the faces of the RVE cube and outside the inner smaller cube, which may also lead to a reduction of the mesh quality close to the RVE boundary.

The minimum distance variable controls the minimum distance between particles and RVE boundary and additionally the distance between adjacent
CNTs. The latter case was implemented in the intersection test described in the next paragraph.

A typical acceptance-rejection algorithm was employed to populate RVEs with solid-fibre-like objects representing homogenised CNTs. For this, ‘clash’ tests for intersections with previously generated objects were carried out either resulting in the deletion or inclusion of the newly generated object. However, instead of using actual solid-fibre CNT representations for these ‘clash’ checks, enlarged solid-fibre-like objects accounting for size offsets due minimum distance variable were used. The procedure continued until the requested number of CNTs (corresponding to the required CNT volume fraction) was incorporated. A more precise description is given in the Appendix A.

Besides the above mentioned variables that prevent critical CNT arrangements, filter procedures were performed in order to ensure a sufficient mesh quality. Those procedures include for example the filtering of instances $B'''$ (see Appendix A for denotations of instances) that cannot be meshed using the sweep technique, the filtering of instances $A'''$ that exhibit an edge at the RVE boundary that is 1.75 times larger than the perimeter of the CNT, or the filtering of instances $A'''$ that exhibit cells possessing more than 3 surfaces.

Unfortunately, several bugs in the program code of ABAQUS tend to occur when performing cutting/merging operations with geometric representations of wavy CNTs, interphases or clash test geometries. For example cutting instances $D'$ by wavy instances $A'$, $B'$ or $C'$ occasionally resulted in unmodified instances of $D'$. This led finally to CNT and interphase morphology instances with missing cells or intersecting particles and interphases. Other cases of ABAQUS bugs occurred when merging the instances $A'''$, $B'''$, or $C'''$ with the instances in list $\alpha$, $\beta$, or $\gamma$ respectively, as done for example when creating the final CNT or matrix morphology instances or during the check for intersections with
previously generated objects. Here the operation aborted with an error stating that the operation could not be performed. Hence, several checks were implemented to filter out such unsuccessful operations. Some of these programmed procedures perform tests on cells or whole periodic particles, interphases and clash test geometries before the final morphologies are generated in order to filter out critical geometries in advance.

It can be seen that three instances are generated: CNT morphology instance, the interface morphology instance and the matrix morphology instance. These morphology instances are the building blocks of the RVE, and they were connected using surface to surface tie constraints. The reasons for the choice of using different instances for the morphologies and connecting them via tie-constraints, instead of using one instance representing the RVE, are:

- Reduction of the finite element number due to a possible larger element growth within the RVE

- Incompatible elements such as linear (cohesive) and quadratic elements can be combined within the RVE

- Periodic boundary conditions (PBCs) can be applied following the developed two-step meshing procedure (described below) without experiencing significant mesh distortion

- Better variability in changing the size of elements that are modelled using a UMAT subroutine, which can improve the convergence of the numerical solution

Depending on whether the RVE accounts for an interface, the choice of slave and master surface for those surface to surface tie constraints differs. In the presence of an interface, all surfaces within the matrix domain are used as master surfaces and all interphase surfaces are used as slave surfaces. The
choice of the particle surfaces as slave or master surface depends on the instance of the opposing surface, which can be master in case of an opposing matrix surface or slave in case of an opposing interface surface. For RVEs without interfaces, all surfaces of the matrix domain were used as master surfaces and the particle surfaces were used as slave surfaces.

One of the challenges was the application of periodic boundary conditions (PBCs). They were applied through *EQUATION command, which required identical coordinates of finite element nodes at opposing faces of the RVE boundary. The application of the ABAQUS built-in free-meshing algorithm with tetrahedral elements is the only method which allows the automated meshing of highly complex 3-dimensional geometries. In RVEs that account for randomly oriented and distributed CNT, the matrix phase is a complicated geometry. Main draw-back of this built-in free-meshing algorithm is that obtained meshes at opposing faces of the 3D RVE do not coincide and, thus, the application of PBCs simply through the command *EQUATION is impossible. Furthermore, the complex geometry cannot be partitioned into smaller and less complex geometries by using an automated procedure. However, it is noteworthy to mention that a nanocomposite model composed of continuous and perfectly aligned CNT-like objects would simplify the application of PBCs for 3-dimensional RVEs since the mesh could be swept along the direction of CNT alignment and, thus, produce identical meshes at the faces of the RVE boundary.

To date, a straightforward solution to fulfil this PBCs requirement is not implemented by ABAQUS. Therefore, a two-step meshing procedure was developed to solve this issue. The two steps involved are shown in the following pseudo-code.
STEP 1: Generate mesh on CNT, interphase and matrix morphology instance
From opposing sets of RVE faces take the one that exhibits the largest number of mesh element edges and write out the coordinates of the starting and ending node of each mesh element edge into a list excluding the mesh element edges that touch geometric (RVE) edges
Delete the mesh on CNT and matrix morphology instance
Sketch the same mesh pattern on the opposite face of RVE using the previously generated lists and partition the opposing RVE faces by this sketch
Seed the previously generated edges allowing only one element side per edge

STEP 2: Generate mesh on CNT and matrix morphology instance

It must be mentioned that this two-step meshing procedure generates undistorted meshes only when the different phases, i.e. matrix phase, CNT phase and interface phase, are separated into single instances. The code applied to a multi-phase instance resulted in significant mesh distortions. Additionally, excluding the mesh edges that touch geometric edges in the sketch is necessary because otherwise too many fixed seeds can make the application of the built-in free meshing algorithm impossible.

Prior to the formulation of PBCs, sets of RVE corner vertices, sets of RVE edges excluding RVE corner vertices and sets of RVE faces excluding RVE edges were created. Then, opposing mesh nodes within those sets were searched and PBCs were imposed using the ABAQUS *EQUATION command.

4.3. CNT representation
Various concepts for CNT representations were presented in Section 2.4. A larger number of CNTs need to be modelled within the RVE in order to account for the nanocomposite morphology. Thus, the choice for CNT representation was driven by the computational effort.

Compared to the atomistic finite element approach of Li and Chou (2003a), the concepts of effective (homogenised) representations were deemed to provide a significant reduction of computational effort at the mesoscale. Those concepts,
however, can be further distinguished into partial- and full-homogenisation schemes. Whereas the first one involves the homogenisation of just the CNT-wall, the second one applies a full homogenisation in the transverse direction involving additionally the hollow space and in case of MWCNTs a sequence of interfaces/interphases and CNT walls.

The full homogenisation offers the advantage to study MWCNTs with significant cost savings brought by the decrease of the number of finite elements. For comparison, modelling commercially available MWCNTs that exhibit 10 walls by using the equivalent continuum approach of Sears and Batra (2004, 2007) would require an enormous number of finite elements in order to discretise 10 tubular cylinders and to connect those via truss elements to account for the vdWs interaction.

The equivalent-continuum concept is, therefore, followed by modelling the CNT as effective fibre. In general, an effective fibre is transversely isotropic. Cauchy’s generalised Hooke’s law states

\[ \varepsilon = S_{\text{eff}} : \sigma, \]

where \( \sigma, \varepsilon \) and \( S_{\text{eff}} \) are the second order stress, second order strain and fourth order effective compliance tensor respectively. Using Voigt notation the constitutive relation of a transversely isotropic material may be contracted to (Nye 1985)

\[
\begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
2\varepsilon_{23} \\
2\varepsilon_{31} \\
2\varepsilon_{12}
\end{bmatrix} =
\begin{bmatrix}
S_{11}^{\text{eff}} & S_{12}^{\text{eff}} & S_{13}^{\text{eff}} & 0 & 0 & 0 \\
S_{12}^{\text{eff}} & S_{11}^{\text{eff}} & S_{13}^{\text{eff}} & 0 & 0 & 0 \\
S_{13}^{\text{eff}} & S_{13}^{\text{eff}} & S_{33}^{\text{eff}} & 0 & 0 & 0 \\
0 & 0 & 0 & S_{44}^{\text{eff}} & 0 & 0 \\
0 & 0 & 0 & 0 & S_{44}^{\text{eff}} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2}(S_{11}^{\text{eff}} - S_{12}^{\text{eff}})
\end{bmatrix}
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{31} \\
\sigma_{12}
\end{bmatrix},
\]
where $S_{11}^{\text{eff}}$, $S_{33}^{\text{eff}}$, $S_{12}^{\text{eff}}$, $S_{13}^{\text{eff}}$ and $S_{44}^{\text{eff}}$ are five independent elastic compliance components, axis of symmetry is in the 3-direction and the 1-2 plane being the plane of isotropy. The components can be described in terms of elastic parameters (see Baowan and Hill 2007) as

\[
S_{11}^{\text{eff}} = \frac{3K_p + G_p}{9K_p G_p}, \quad \text{(4.10)}
\]

\[
S_{12}^{\text{eff}} = -\frac{3K_p - 2G_p}{2(3K_p + G_p)} S_{11}^{\text{eff}}, \quad \text{(4.11)}
\]

\[
S_{13}^{\text{eff}} = -\nu_p / E_t, \quad \text{(4.12)}
\]

\[
S_{33}^{\text{eff}} = 1 / E_t, \quad \text{(4.13)}
\]

\[
S_{44}^{\text{eff}} = 1 / G_t, \quad \text{(4.14)}
\]

where $K_p$, $G_p$, $\nu_p$, $G_t$, $E_t$ are the in-plane bulk modulus, in-plane shear modulus, major Poisson’s ratio, longitudinal shear modulus and longitudinal Young’s modulus, respectively.

Using an energy approach based on simple harmonic potentials, Shen and Li (2004) obtained closed-form expressions for those elastic parameters for SWCNTs by analysing four loading conditions: axial tension, torsional moment, in-plane bi-axial tension and in-plane tension-compression. Closed form expressions for those constants for armchair SWCNTs $(n,n)$ are (Shen and Li 2004)

\[
E_{33}^{\text{armchair}} = \frac{4\sqrt{3}C_t}{(r_{\text{CNT}} / 2)^2 \left[ 9 + 3\left(C_t r_0^2 / C_{\theta}\right) / (4\eta) \right]}, \quad \text{(4.15)}
\]

\[
\nu_{31}^{\text{armchair}} = \frac{-1 + \left(C_t r_0^2 / C_{\theta}\right) / (4\eta)}{3 + \left(C_t r_0^2 / C_{\theta}\right) / (4\eta)}, \quad \text{(4.16)}
\]

\[
G_{31}^{\text{armchair}} = \frac{6\sqrt{3}n^2}{\pi^2} \frac{\sin^2(\pi / n)}{2 \left[ 2 + \cos(\pi / 2n) \right]^2 + \left[ 4 - \cos^2(\pi / 2n) \right] \left(C_t a^2 / C_{\theta}\right) / (2r_{\text{CNT}})} \frac{C_t}{r_{\text{CNT}} / 2}, \quad \text{(4.17)}^2
\]

\[
K_{12}^{\text{armchair}} = \frac{\sqrt{3}C_t \left(C_t a^2 / C_{\theta} + 12\eta\right)}{4r_{\text{CNT}} \left(3C_t r_0^2 / C_{\theta} + 12\eta\right)}, \quad \text{(4.18)}
\]

\^ Corrected equation is shown. Typographical error in equation (49) of Shen and Li (2004).
where $C_r = 742 \text{nN/nm}$ (Shen and Li 2004) is the bond stretching force constant, $C_\theta = 1.42 \text{nN-nm}$ (Shen and Li 2004) is the bond angle variation constant, $C_\kappa = 0.0608 \text{nN-nm}^3$ (Shen and Li 2004) is a modified force constant, $r_0 = 0.1421 \text{nm}$ is the C–C bond length, $n$ is the chirality and $r_{\text{CNT}}$ is the radius of the CNT, which can be determined for a general SWCNT $(n,m)$ as

$$r_{\text{CNT}} = \frac{\sqrt{3}r_0}{2\pi} \sqrt{n^2 + mn + m^2}.$$  

Corresponding closed-form expressions for constants for zig-zag SWCNT $(n,0)$ are

$$E_{13}^{\text{zig-zag}} = \frac{4\sqrt{3}C_r}{(r_{\text{CNT}}/2)[9 + 3(C_r r_0^2 / C_\theta)/(2\eta_2)]},$$

$$V_{31}^{\text{zig-zag}} = \frac{-1 + (C_r r_0^2 / C_\theta) / (2\eta_2)}{3 + (C_r r_0^2 / C_\theta) / (2\eta_2)},$$

$$G_{31}^{\text{zig-zag}} = \frac{8\sqrt{3}n^2 \sin^2 (\pi / 2n) C_r}{(r_{\text{CNT}}/2)\pi^2 (6 + C_r r_0^2 / C_\theta)},$$

$$K_{12}^{\text{zig-zag}} = \frac{\sqrt{3}}{4r_{\text{CNT}}} \frac{C_r (C_r a^2 / C_\theta + 6\eta_2)}{3C_r r_0^2 / C_\theta + 6\eta_2},$$

$$G_{12}^{\text{zig-zag}} = \frac{\sqrt{3}C_\kappa}{r_0^2 r_{\text{CNT}}^3},$$

with $\eta_2 = \frac{14 + 12\cos(\pi / n) - 2\cos^2(\pi / n)}{10 + 4\cos(\pi / n) - 6\cos^2(\pi / n)}$.

Those equations can be further used to determine the transversely isotropic properties of DWCNTs and MWCNTs following the further work of Shen and Li (2005). It must be mentioned that two axial loading conditions, tension and

---

3 Corrected equation is shown. Typographical error in equation (36) of Shen and Li (2004).
compression, were considered in this work. Under axial compression, each wall of a DWCNT is assumed to experience the same axial strain. Hence, a uniform end displacement condition was applied by the authors. Under tensile loading, however, the load was applied to the outer wall, which in turn is transferred through the interphase to the inner wall. Compressive and tensile Young’s moduli and Poisson’s ratios are, therefore, distinguished. The complete set of independent elastic constants of a DWCNT is obtained as

$$E_{33}\text{compression} = \frac{2}{\sum_{i=1}^{M} r_i E_{33,i}}$$

$$v_{31} = v_{31,os} - \frac{1}{1 + r_o / r_i + (r_o / K_{12,os} + r_i / K_{12,is})}$$

$$G_{31} = G_{31,os} + \frac{E G_{12,os} (r_o + r_i)}{E (r_o + r_i) + 4 G_{12,os} h}$$

$$K_{12} = K_{12,os} + \frac{E}{E / K_{12,os} + 4 h / (r_o + r_i)}$$

where 'is' and 'os' stands for inner shell and outer shell respectively, $E_{33}$ and $G_{31}$ are the surface longitudinal Young’s modulus and the surface longitudinal shear modulus. Since the

with $A = \frac{1}{2} \left( 1 + \frac{r_o}{r_i} \right) \left( 1 + \frac{r_o}{E_{33,os}} + \frac{2}{r_i E_{33,os}} \right) \frac{E}{h}$

with $\xi = \frac{1}{l_{CNT}} \int_{0}^{l_{CNT}} \left[ 1 - e^{\sqrt{\lambda x}} \left( 1 + e^{2l_{CNT} \sqrt{\lambda}} \right) - e^{-\sqrt{\lambda x}} \left( 1 + e^{-2l_{CNT} \sqrt{\lambda}} \right) \right] dx$,
perimeter is used in their definitions instead of the homogenised cross-sectional area, the use of Eqs. (4.15), (4.17), (4.22) and (4.24) requires multiplying their result by the factor \( r_{\text{CNT}}/2 \). The Poisson’s ratio under compressive loading \( \nu_{31}^{\text{compression}} \) is obtained from Eq. (4.30) \(^4\) for the case of \( \xi=1 \). The only equation that can be used to directly obtain a result for a MWCNT composed of \( M \) walls is Eq. (4.29) for the longitudinal Young’s modulus in compression. For the remnant elastic constants, Shen and Li (2005) proposed a replacement method. For example, for a MWCNT with \( M=3 \) walls/shells the elastic constants of the inner ‘DWCNT’ are calculated first. This inner ‘DWCNT’ is then replaced by a shell that exhibits the same radius as the middle shell of the MWCNT and of effective properties previously obtained. Those are the used in a second calculation for a DWCNT to acquire the properties of the 3-walled MWCNT. The procedure can be continued to obtain the elastic constants for MWCNTs that are composed of many more walls.

### 4.4. CNT/epoxy Interface

Incorporation of interfaces and interphases into modelling approaches can significantly change the stress transfer efficiency (Wan et al. 2005, Hernández-Pérez and Avilés 2010, Li and Chou 2003b) and affect the nonlinear behaviour of the nanocomposite (Barai and Weng 2011, Yang et al. 2013).

In this work it was assumed that the epoxy properties in the vicinity of CNTs are the same as in the bulk, i.e. no interphase is present in the computational models. This seems to be a reasonable approximation for highly crosslinked epoxy matrices, which according to Putz et al. (2008) exhibit a reduced capability of forming interphases within the nanocomposite.

\(^4\) Equation (22) was chosen due to typograpical error in equation (26) for \( \nu_{31}^{\text{compression}} \) of Shen and Li (2005). According to Shen and Li (2005) equation (26) coincides with the equation (22) for \( \nu_{31}^{\text{tension}} \) with \( \xi=1 \).
Weak filler-matrix interaction, however, seems to be commonly present in case of non-functionalised CNTs (see Section 2.3). In order to account for this weak interaction, a bilinear traction-separation law is adapted to capture secondary vdW bonding. The cohesive zone concept based on traction-separation laws is deemed to provide a significant reduction of computational effort when compared to the more common approach of replacing secondary vdW bonds by truss or spring elements based on the Lennard-Jones potential.

The interfacial shear strength as relevant input parameter for the cohesive zone law was chosen to be based on the molecular dynamics study of Frankland et al. (2002). Computational studies have the advantage over experiments as the bonding mechanisms between CNT and polymer can be separated and, thus, the covalent bonding can be excluded or included. In cases of large interface shear strength values that were experimentally obtained, one might speculate whether covalent bonding between CNT and matrix occurred (cf. Cooper et al. 2002, Wagner 1998). In general, a wide range of interfacial shear strength values for non-functionalised CNTs within polymer were obtained experimentally. Wagner et al. (1998) obtained values of the order of 500 MPa. Cooper et al. (2002) obtained values for the average interface shear strength for short embedded lengths between 318-376 MPa. Barber et al. (2006) calculated the maximum interfacial shear strength of 30 MPa. Tsuda et al. (2011) obtained small values between 3.5-14 MPa for an average interface shear strength.

The variations are also significant on the modelling side. Using molecular dynamics, CNT pull-out from a crystalline polyethylene matrix was performed by Chowdhury and Okabe (2007). In case of weak vdW interaction, they obtained average interfacial shear strength values around 250 MPa and 300 MPa depending on the density of the polymer. Further reported values for average interfacial shear strengths of non-covalently bonded CNT within
polymer are 160 MPa (Liao and Li 2001), 133 MPa (Al-Ostaz et al. 2008), 138 and 186 MPa (Wong et al. 2003).

Frankland et al. (2002) performed molecular dynamics simulations to study the interfacial shear strength between the CNT and polyethylene and obtained a substantially lower value of 2.7 MPa for the case of non-covalent bonding between CNT and polymer. In contrast to several reported pull-out simulations from above, the authors applied periodic boundary conditions to their models. Hence, an infinite CNT length surrounded by polymer was modelled and the same force was applied to each and every carbon atom of the CNT. Interfacial shear strength, however, was defined as the total force at which the centre of mass of the nanotube started to move freely, independent of the matrix, and normalised by the CNT surface area within the model.

It is believed that the imposition of periodic boundary conditions led to the substantially lower value of interfacial shear strength when compared to other reported values because it approximates CNT sliding of an infinite CNT—the CNT pulled from one end enters the cell at the opposite end. A molecular mechanics based explanation would be that the total potential energy in this case experiences hardly any changes as for example stated in (Al-Ostaz et al. 2008). When assuming that most of the shear stress transfer happens during pull-out at the CNT ends, as concluded by Li et al. (2011), the significant effect of periodic boundary conditions is the suppression of those end effects. This would also explain the significant larger changes in total potential energy when no periodic boundary conditions are used. Most researchers associated the change in total potential energy with the pull-out energy $E_{\text{pull-out}}$ to obtain the average interfacial shear strength given by (Liao and Li 2001, Wong et al. 2003, Chowdhury and Okabe 2006, Al-Ostaz et al. 2008)

$$\tau_{\text{IF}} = \frac{E_{\text{pull-out}}}{\pi r_e^2}$$

(4.37)
where $l_{emb}$ is the embedded length being pulled-out and $r_o$ is the outer radius of the CNT. It is, therefore, reasonable to assume that the ‘pull-out’ without the use of periodic boundary conditions led to significantly larger values in contrast to the work of Frankland et al. (2002).

Nevertheless the interface shear strength was chosen to be based on the work of Frankland et al. (2002) because those values were of similar small magnitude as obtained experimentally by Tsuda et al. (2011). Computational predictions using this interface shear strength of 2.7 MPa may, therefore, be considered as lower bound for the effects of vdWs interaction.

Using molecular mechanics, Li et al. (2011) performed pull-out simulations of CNTs embedded in polyethylene, which are only interacting through weak vdWs bonding. Effects of CNT characteristics such as CNT length were studied. Their results suggest that the pull-out force is independent of embedded CNT length and fluctuating around a constant value during the pull-out process. This sliding like behaviour can be seen in Fig. 4.4.

![Figure 4.4: Variation of energy change during pull-out of SWCNT(5,5) (from Li et al. 2011).](image)

The change of potential energy $\Delta E$ is due to the work done by the pull-out force (Li et al. 2011). Hence the energy increment can be considered proportional to
the pull-out force. The energy increment $\Delta E_{II}$ of the sliding stage II (see Fig. 4.4) stays approximately constant during the pull-out process. Further results suggest a shear stress transfer length of 2 nm, independent from the length of the embedded CNT. Hence, interfacial shear strength or interfacial sliding stress, when defined as force over this transfer length, can also be considered independent from CNT length and constant during pull out. However, interfacial sliding stress was found to decrease with increasing CNT diameter and to saturate in the case of SWCNTs at 106.7 MPa and in the case of MWCNTs at 128 MPa.

The sliding behaviour was, therefore, captured by constant shear traction within the traction-separation law. However, the study of Frankland et al. (2002) does not provide values for the relative shift of the CNT with respect to the matrix at which the shear stress equals the interfacial shear strength i.e. at the damage initiation displacement. Hence, it was assumed that the damage initiation displacement corresponds to the relative shear shift of two opposing atoms of CNT and epoxy matrix at which a force applied to separate the atoms in shear reaches its maximum. The Lennard-Jones potential can be employed to capture the opposing force $F$ between the two atoms as a function of distance $r$ (Li and Chou 2006):

$$F(r) = 4\frac{\varepsilon}{r} \left[ 12 \left( \frac{\sigma}{r} \right)^{12} - 6 \left( \frac{\sigma}{r} \right)^{6} \right], \quad (4.38)$$

where $\varepsilon$ is the depth of the potential well and $\sigma$ is the distance at which the potential is zero. The atoms are assumed to slide relative to each other on parallel lines that exhibit a distance $2^{1/6}\sigma$ corresponding to the separation of the depth of the potential well $\varepsilon$ (see Fig. 4.5). Hence, the pull-out force $F_{\text{pull}}$ in the CNT direction is opposite to an attractive force component in the sliding direction. $F_{\text{pull}}$ can then be expressed as a function of sliding separation $u$:
\[ F_{\text{pull}}(u) = -4 \frac{\varepsilon u}{u^2 + 2^{\frac{2}{3}} \sigma^2} \left[ 12 \frac{\sigma^2}{(u^2 + 2^{\frac{2}{3}} \sigma^2)^{\frac{5}{3}}} - 6 \frac{\sigma^6}{(u^2 + 2^{\frac{2}{3}} \sigma^2)^3} \right], \quad (4.39) \]

Using the Lennard-Jones parameter \( \varepsilon = 0.4492 \) KJ/mol and \( \sigma = 0.34 \) nm from Meguid et al. (2010), the curve exhibits the maximum pull-out force at a separation distance of around 0.225 nm (see Fig. 4.5). Hence, this value was assumed as damage initiation displacement, i.e. the separation at which the interfacial shear strength in the cohesive zone is achieved.

Figure 4.5: Pull-out force as a function of sliding separation based on Eq. (4.39).

The final traction-separation law was, therefore, based on 2 parameters, the maximum nominal stress value \( S = 2.7 \) MPa and the damage/sliding initiation displacement \( D_i = 0.225 \) nm (see Fig. 4.6). Since the sliding behaviour is described using a linear decaying function, the displacement at final failure was set artificially high, i.e. length of the CNT was used here for convenience. No coupling between the deformation modes (I, II and III) was assumed. Furthermore the traction-separation law was assumed for all deformation modes, however, with a small modification in mode I, where the damage/sliding initiation displacement of the law was reduced in order to
equal the Young’s modulus of the interface with the Young’s modulus of the epoxy matrix. This was meant to prevent interpenetration between CNT and matrix surfaces throughout the deformation.

![Figure 4.6: Traction-separation law with parameter ($S=2.7$ MPa, $D_i=0.225$ nm) based on vdWs interaction.](image)

**4.5. Constitutive model for the epoxy matrix**

The constitutive model introduced in Section 3.3.2 is used to represent the non-linear and rate dependent behaviour of the epoxy matrix.

**4.6. Scale transitions**

The coupling between mesoscale and macroscale is achieved using the nonlinear first-order computational homogenisation approach, which is based on averaging theory (Hill 1963). In this approach, the nanocomposite at the macroscale is represented by an effective homogeneous material, while at the mesoscale, the nanocomposite is modelled as heterogeneous, i.e. consisting of several components such as interface, epoxy and CNT phase. Each macroscopic material point (i.e. an integration point in the macroscopic FE sense) of the macroscopic continuum is associated with an RVE that represents the heterogeneous nanocomposite morphology scale (see Fig. 4.7).
The approach employs a two scale transition scheme: (1) macro-to-RVE and (2) RVE-to-macro scale transition (see Fig. 4.7). The first scale transition is a localisation process in which the strains at the given macroscopic point are transferred as boundary conditions on the RVE level (mesoscale). The second scale transition involves homogenisation of the RVE response obtained from the solution of RVE boundary value problem, and providing a homogenised RVE constitutive law to the macroscopic material point.

In this work it is assumed that the macroscopic deformation is uniform and the nanocomposite is globally periodic, i.e. the RVE is considered to be the building block of the entire nanocomposite. In so doing, the macroscopic behaviour of the nanocomposite can be predicted from a single RVE. The macroscopic strains applied to the RVE produce a stress field within the RVE domain, which can be extracted as macroscopic stress using volumetric averaging techniques. Those require that the averaged mechanical work performed on the RVE is equal to the mechanical work at the macroscale, i.e. the mechanical work calculated using the averaged stresses and strains. This is known as the Hill-Mandel condition or macrohomogeneity condition (Hill 1963) that needs to be satisfied by the RVE and its boundary conditions. It can be shown that periodic boundary conditions conform to this requirement (Kouznetsova 2002).
The nonlinear deformation is described here in terms of the macroscopic deformation gradient tensor $F_{\text{macro}}$, which is transferred as displacement $u_{\text{RVE}}$ onto the RVE level according to

$$u_{\text{RVE}} = \varepsilon_{\text{macro}} X_{\text{macro}} + u_{pc} \quad \text{and} \quad \varepsilon_{\text{macro}} = F_{\text{macro}}^{-1} - I,$$

(4.40)

where $X_{\text{macro}}$ stands for the position vector of a macroscopic point within the undeformed RVE, $\varepsilon_{\text{macro}}$ denotes the macroscopic strain tensor and $u_{pc}$ denotes a fluctuating displacement vector arising from the nanocomposite morphology respectively.

The macroscopic deformation gradient tensor $F_{\text{macro}}$ can be assumed to be equivalent to the volume averaged deformation gradient tensor of the RVE. Integration of the deformation gradient tensor $F_{\text{RVE}}$ over the volume $V_0$ of the undeformed RVE leads to (Kouznetsova 2002)

$$F_{\text{macro}} = \frac{1}{V_0} \int_{V_0} F_{\text{RVE}} dV_0 = \frac{1}{V_0} \int_{\Gamma_0} x \otimes N d\Gamma_0,$$

(4.41)

where the divergence theorem has been used to obtain a surface integral over the undeformed RVE boundary $\Gamma_0$, and $x$ and $N$ denote the position vector of a point on the deformed RVE boundary and corresponding exterior unit normal.

Periodic boundary conditions ensure that the shape and orientation in space of two opposite faces remains identical during the deformation. They also preserve stress continuity across the boundaries due to identical magnitudes of the stress vectors acting on opposing faces opposite in direction. Periodic boundary conditions may be written in general format as (Kouznetsova 2002)

$$x^+ - x^- = F_{\text{macro}} \cdot (X^+ - X^-) \quad \text{and} \quad t^+ = -t^-,$$

(4.42)
where the second equation states the anti-periodicity of the resulting tractions $t^+$ and $t^-$, $X^+$ and $X^-$ are the position vectors of opposing points on the undeformed boundary and $x^+$ and $x^-$ are corresponding position vectors of points on the deformed boundary.

For the RVEs used in this work (see Fig. 4.8), the RVE boundary was separated into corner nodes $J$, faces $F$ and edges $E$. The corner node 1 was constrained in all directions to prevent rigid body movement and the position vectors $x^+$ and $x^-$ on the boundary were linked to the position vectors $x_I$ of relevant corner nodes $I$:

$$x_I^+ - x_I^- = x_I$$ and $x_E^+ - x_E^- = x_I$ and $x_J^+ - x_J^- = x_I$, \hspace{1cm} (4.43)

with

$$x_I = F_{\text{macro}} \cdot X_I,$$ \hspace{1cm} (4.44)

where $X_I$ denotes the position vector of the relevant corner node on the undeformed boundary. A detailed description with nodes involved is provided in Table 4.2. A more general description of Eq. (4.43) is provided in the Appendix B (see Eq. (B.2))
Figure 4.8: Schematics of boundary conditions in 3D RVE (a) and 2D RVE (b) with notations of faces: top (T), bottom (B), left (L), right (R), front (F), rear (RR); edges: top (t), bottom (b), left (l), right (r), topleft (tl), topfront (tf), bottomright (br), bottomrear (brr), leftbottom (lb), leftfront (lf), righttop (rt), rightrear (rrr), frontbottom (fb), frontright (fr), reartop (rrt), rearleft (rrl); and corner nodes (1, 2, . . . 8) (from Weidt and Figiel 2014).

Table 4.2 Boundary conditions for 3D and 2D RVEs applied to relevant nodes

<table>
<thead>
<tr>
<th>Nodes</th>
<th>3D</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Node 1:</td>
<td>constrained in x, y, z</td>
<td>constrained in x, y</td>
</tr>
<tr>
<td>Node 2:</td>
<td>constrained in y, z; negative displacement applied in x</td>
<td>constrained in y, and negative displacement applied in x</td>
</tr>
<tr>
<td>Node 4:</td>
<td>constrained in x, z</td>
<td>constrained in x</td>
</tr>
<tr>
<td>Node 5:</td>
<td>constrained in x, y</td>
<td></td>
</tr>
<tr>
<td>Face nodes:</td>
<td>$x_F^+ - x_F^- = x_I$, with I=2,4,5 for case R-L, T-B, F-RR</td>
<td>$x_E^+ - x_E^- = x_I$, with I=2,4 for case 'r-l', 't-b'</td>
</tr>
<tr>
<td>Edge nodes:</td>
<td>$x_E^+ - x_E^- = x_I$, with I=2 for case 'rrr-rrl', 'br-lb' and 'rt-tl'; I=4 for case 'rrt-brr', 'tf-fb' and 'tl-lb'; I=5 for case 'fr-rrr','lf-rrl' and 'fb-brr'</td>
<td>$x_E^+ - x_E^- = x_I$, with I=2,4 for case 'rrr-rrl', 'br-lb' and 'rt-tl'; I=4 for case 'rrt-brr', 'tf-fb' and 'tl-lb'; I=5 for case 'fr-rrr','lf-rrl' and 'fb-brr'</td>
</tr>
<tr>
<td>Corner nodes:</td>
<td>$x_I^+ - x_I^- = x_J$, with I=2 for 3-4, 6-5 and 7-8; I=4 for case 8-5</td>
<td>$x_I^+ - x_I^- = x_J$, with I=2 for 3-4, 6-5 and 7-8; I=4 for case 8-5</td>
</tr>
</tbody>
</table>

The volume average of the Cauchy stress tensor $\bar{\sigma}_{\text{RVE}}$ can be obtained from the surface integral over the deformed boundary $\Gamma$ as (Kouznetsova 2002)

$$
\bar{\sigma}_{\text{RVE}} = \frac{1}{V} \int_{\Gamma} \sigma_{\text{RVE}} dV = \frac{1}{V} \int_{\Gamma} t \otimes x d\Gamma ,
$$

(4.45)

where $t$ denotes the surface traction and $x$ the position vector. In the 2D case, Kouznetsova et al. (2001) found that Eq. (4.45) can be simplified for periodic boundary conditions and calculated from the force vector $F_i$ which results from the surface tractions $t$, and the position vector $x_i$ of relevant nodes.
\[ \bar{\sigma}_{\text{RVE}} = \frac{1}{V} \sum_{i=1,2,4} F_i \otimes x_i, \]  

(4.46)

For the 3D case, the corresponding relationship is obtained as (Derivation in Appendix B, Eqs. (B.5)–(B.13))

\[ \bar{\sigma}_{\text{RVE}} = \frac{1}{V} \sum_{i=1,2,4,5} F_i \otimes x_i, \]  

(4.47)

for the boundary conditions applied in this work (see Fig. 4.8 and Table 4.2), Eq. (4.47) results in the averaged stress component \( \sigma_{xx} = V^{-1} f_{x(2)} x_{x(2)} \) where \( f_{x(2)} \) and \( x_{x(2)} \) denote force and position of the node 2 (see Fig. 4.8).

The average stress obtained from Eq. (4.47) were used as approximation for the macroscopic Cauchy stress (\( \sigma_{\text{macro}} = \bar{\sigma}_{\text{RVE}} \)). Nemat-Nasser (1999) pointed out that a rigorous route is to calculate the macroscopic Cauchy stress from the averaged nominal stress and the rate of deformation, which are power conjugates.
Chapter 5

Prediction of finite strain compressive behaviour of epoxy/CNT nanocomposites: 2D versus 3D RVE-based modelling

5.1. Objective of computational study

The morphology of CNT/epoxy nanocomposites is quite complex and its reconstruction using RVEs poses significant challenges even when CNTs are simplified as straight and non-bundled short fibres of different distributions and orientations, as is the case in this work. Three-dimensional (3D) RVEs are a natural choice to capture such morphologies, but they require a large number of finite elements and computational resources. On the other hand, two-dimensional (2D) RVEs are computationally more efficient than 3D RVEs, but they can compromise the accuracy of their predictions.

Hence, this chapter seeks to determine the accuracy of 2D RVE-based computational models in capturing the rate-dependent behaviour of the nanocomposite determined from 3D RVE-based models. For this purpose, the influence of material composition, nanocomposite morphology, and strain rate

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5 Parts of this chapter were published in: Weidt, D. and Figiel, Ł. (2014) ‘Finite strain compressive behaviour of CNT/epoxy nanocomposites: 2D versus 3D RVE-based modelling’, Computational Materials Science 82, 298-309.
on the nonlinear compressive response of CNT/epoxy nanocomposites was studied using 2D and 3D RVEs and nonlinear FE-based modelling. Hence, over the unit cell concept pursued previously, this Chapter provides insight into the nonlinear finite compressive behaviour of CNT/epoxy systems on the account of non-uniform CNT morphologies with random CNT distribution and orientation, and particle-particle interaction.

The chapter is structured as follows. Details of the modelling approach are described first. Then, results of a mesh convergence analysis and RVE size study are shown. Subsequently, 2D and 3D RVE-based predictions of the finite strain behaviour of CNT/epoxy nanocomposites are presented and discussed with respect to nanocomposite morphological characteristics, strain rate, computational effort and experimental results.

5.2. Modelling approach

The modelling approach introduced in Chapter 4 is followed by using the model generator (see Section 4.2), nonlinear finite strain constitutive model (see Section 3.3.2) and the first order computational homogenisation approach (see Section 4.6). However, in this chapter, it was assumed that the material behaviour of each effective fibre is isotropic, i.e. can be described by only two elastic constants: Young’s modulus $E_{n}^{11}$ and Poisson’s ratio $\nu_{12}$, where $n$ is the chirality of the CNTs. Zig-zag CNTs of chirality $n=128$, which corresponds to a radius $R\approx5$ nm, were assumed to determine the elastic constants from Eqs. (4.22), (4.23) and (4.27). Young’s modulus and Poisson’s ratio were calculated to be equal to 143.62 GPa and 0.16 respectively. The assumption of isotropy was shown to provide negligible differences in the macroscopic true stress-true strain response when compared to transverse isotropy (see Fig. 5.1). Furthermore, CNTs and epoxy matrix were assumed to be perfectly bonded. A non-contacting distribution of CNTs was enforced by assuming a minimum distance between CNT surfaces, which was
set equal to the CNT diameter of 10 nm. The minimum penetration depth variable was set to 50 nm.

Two types of RVEs were considered and compared here: (a) 2D RVEs assuming the plane strain condition (see Fig. 5.2a and 5.2b) and (b) 3D RVEs (see Fig. 5.2c and 5.2d). 3D RVEs were chosen because of their ability to accurately capture the CNT geometry with two ‘nanometre’ dimensions in the plane of the circular cross-section and one dimension in ‘micrometre’ scale in CNT axis direction. As a consequence, 3D RVEs exhibit the correct ratio of number of CNTs to RVE volume for a given CNT volume fraction. On the other hand, 2D RVEs were chosen for their computational efficiency on the account of the following
assumptions: (a) the third dimension of 2D RVEs under plane strain is neglected (set to unity here), and only one ‘nanoscale’ dimension is captured (i.e. thickness of a CNT)—hence, the CNT shape is captured accurately in the x-y plane only, and the ratio of the number of CNTs to 2D RVE volume for a given CNT volume fraction depends here on the scaling of the CNT dimensions, and (b) the well-known constraint imposed on the out-of-plane strains (in the z-direction here), which is expected to provide a stiffer macroscopic response.

Both, 2D and 3D RVEs assumed two different CNT orientations: (1) aligned (in the x-direction) (see Fig. 5.2a and 5.2c), and (2) misaligned (random) (see Fig. 5.2b and 5.2d). For cuboidal RVEs, the ratio of CNT dimensions to RVE dimension is much smaller in the transverse direction. Hence, the long side of the cuboidal RVE was assumed to be crucial for its size. The lengths of the short edges of the cuboidal RVE were set equal to the short edges in an RVE of 20 CNTs that exhibits a long edge length of $2.5 \times \text{CNT length}$.

Figure 5.2: Schematic sketches of RVEs used in this work: (a) squared 2D RVE of randomly distributed and aligned CNTs, (b) squared 2D RVE of randomly distributed and randomly oriented CNTs, (c) cuboidal 3D RVE of randomly distributed and aligned CNTs, (d) cubic 3D RVE of randomly distributed and randomly oriented CNTs (from Weidt and Figiel 2014).
In the case of 3D RVEs, the matrix material was discretised by 10-node quadratic tetrahedron elements (C3D10) and the CNT by 20-node quadratic brick elements (C3D20). 6-node quadratic plane strain triangle elements (CPE6) were used in 2D RVEs for both, CNT and matrix discretisation.

5.3. Results and discussion

The developed 2D and 3D computational models were used to predict the large strain compressive response of CNT/epoxy for different material compositions and nanocomposite morphologies. The results are presented and discussed in this section. First a mesh convergence study is addressed followed by the determination of the RVE size and ensemble size. Subsequently, the results section is focussed on the investigation of the 2D and 3D modelling approach with respect to the effects of CNT aspect ratio, CNT volume fraction and strain rate effects on the large strain nanocomposite response. For this purpose, stress-strain parameters introduced in Section 5.3.2 were analysed. Furthermore the computational effort of 2D and 3D RVEs is presented and finally the predictions are compared against experimental data from literature.

5.3.1. Mesh convergence

The mesh density can influence FE results significantly, especially when nonlinear FE simulations are performed. Thus, the sensitivity of the stress-strain behaviour to the density of the FE mesh was studied for 2D and 3D models (CNT aspect ratio of 50, CNT volume fraction of 1%). In order to minimise the computational time, relatively small models incorporating only five CNTs were used in the mesh study. 2D models allowed for constant and fine mesh densities due to their computational efficiency (relatively small number of degrees of freedom and element integration points). Therefore, the mesh was refined globally by reducing the average element size. For the sake of
computational cost reduction, 3D models were only refined in regions of interest, i.e. the mesh density of the matrix domain close to the CNTs was enhanced by using more elements along the CNT circumference and also along the CNT axis.

These mesh refinement strategies are denoted here by: (A) one number in 2D, e.g. 11, which stands for the element number along the 2D CNT, and (B) a set of two numbers, e.g. 17;4—the first number refers to the element number along the 3D CNT axis and the second number specifies the element number along the circumference of the 3D CNT.

Additionally, and for completeness, two special cases of mesh refinement were also considered for the 3D model. First, the effect of the size growth parameter for ABAQUS built-in free meshing algorithm on the result was investigated. Apart from the element seeding at the geometric edges (e.g. RVE edges), the user can adjust a size growth parameter for interior elements \( \text{sizeGrowth} \), which affects the element edge lengths inside the geometric volume. The parameter was decreased from \( \text{sizeGrowth} = \text{MAXIMUM} \) to \( \text{sizeGrowth} = \text{MODERATE} \) (case 17;4*). Secondly, the element edge length at the model cube edges was treated as an additional factor and it was changed from \( 0.108 \times \text{CNT length} \) to \( 0.077 \times \text{CNT length} \) (case 17;4**).

The mesh density effect on 2D stress-strain curves are not shown here as the true stress-true strain curves of the two mesh extremes, i.e. mesh densities with 50 and 11 elements along the CNT axis, were coincident. Hence, Fig. 5.3 shows only the results of mesh study for 3D models. Moreover, as it was found that the linear elastic regime and yield peak stress are relatively unaffected by the tested mesh densities in the 3D model, the analysis is focused on the nonlinear portion of the 3D stress-strain behaviour.
In particular, the post-yield behaviour showed a mesh dependence. The number of elements along the CNT axis (see Fig. 5.3a) and along the CNT circumference (see Fig. 5.3b) influences the post-yield behaviour significantly. The effect of size growth parameter and the element edge length at the model cube edges is negligible. The stress-strain curves converge for the case 50;4 as further mesh refinements with more elements along the CNT axis (case 100;4) or along the CNT circumference (case 50;8) brought negligible effects. As a summary, Fig. 5.4 shows the convergence of the overall nanocomposite stress value (for 2D and 3D models at 15% of the overall true strain) when plotted as a function of element number.
Figure 5.4: True stress of the nanocomposite at 15% of true strain as a function of number of elements for 2D and 3D models; (×) in blue are datapoints obtained from 2D simulations (from Weidt and Figiel 2014).

It is noteworthy to mention that premature termination of FE analyses becomes a serious problem when relatively fine meshes are used, as for example obtained for the mesh refinement cases 50;4, 100;4 and 50;8. This is caused by the excessive magnitude of local stresses in the matrix (in the vicinity of CNTs) resulting from the enhanced nonlinear hyperelastic response of the constitutive model, which captures the strain hardening behaviour of the epoxy matrix. This resulted in local stresses rising rapidly with a small increase of strains, leading to convergence problems in the numerical solution. The numerical convergence may be improved by the development of a more robust constitutive tangent. However, as those local stresses exceeded the strength of pure epoxy matrix under macroscopic compression (Buckley et al. 2001), continuation of the analysis would lead to unphysical results. Instead, introduction of a damage variable into the constitutive model for the epoxy matrix will be explored in the future. Therefore, case 17;4 for 3D models was finally chosen as a compromise between accuracy and achievable finite strains, which are nearly twice as much as for the case 50;4.
5.3.2. RVE size and ensemble size

RVE size and the ensemble size (number of RVE realisations per case) are important for accurate predictions of the nanocomposite response. Studies with 2D and 3D RVEs composed of different numbers of CNTs were carried out to investigate deterministic and statistical RVE size effects.

Specific parameters representing subsequent stages of the stress-strain behaviour of CNT/epoxy nanocomposites were selected for the analysis of the RVE size and ensemble size: (a) the Young’s modulus $E$ was defined here as initial slope of the stress-strain response of both, 2D and 3D models; (b) the yield peak stress $\sigma_Y$ (start of material softening) or, in absence of a pronounced yield peak, the yield strength $\sigma_{pl}$ with an offset of 1% of plastic strain; (c) the minimum tangent modulus $T_{min}$ of the whole curve; (d) the softening strain limit $\varepsilon_S$ (the true strain value representing the end of the softening regime and the start of the hardening regime, corresponding to a stress minimum between softening and hardening); (e) the initial hardening modulus $H$ (only for 2D RVEs) defined here as secant modulus between the point (in the hardening regime), where the tangent modulus is equal to $1.5 \times 10^8$ Pa, and the point on the graph determined by adding 0.05 to the true strain value of the first point.

All RVE-size studies were carried out for the CNT volume fraction of 1%, which represents the highest volume fraction considered in this work and, thus, accounts for the maximum CNT-CNT interactions. The influence of the CNT aspect ratio on the RVE size was studied for 2D (aspect ratios of 25, 50 and 100) and for 3D (aspect ratios of 25 and 50) models. Two nanocomposite morphologies were considered: (1) 2D and 3D, with randomly oriented and randomly distributed CNTs, and (2) 3D with aligned and randomly distributed CNTs. RVE-size studies were performed for the quasi-static strain rate of $1 \times 10^{-3}$ s$^{-1}$, as it was assumed that the conclusions will also hold for higher strain rates.
The volume element (VE) size was varied indirectly by changing the number of incorporated CNTs. Thus, the objective was to determine a minimum number of CNTs, and to choose a number of RVE realisations (RVE ensemble size) that ensures an acceptable width of the confidence interval. All stress-strain parameters mentioned above were investigated and the number of realisations varied between 10 (for small VEs) and 3 (for large VEs).

As an example, Fig. 5.5a and 5.5b shows the evolution of $E$ and $T_{\text{min}}$ as a function of CNT number, i.e. VE size. The standard deviations of the investigated parameters of VE ensembles are represented by the error-bars. Deterministic size effects refer to variation of the means across VE sizes, while statistical size effects refer to variation of the standard deviations across VE sizes. Thus, potential deterministic size effects are indicated by effects of CNT number on the investigated parameters.

![Figure 5.5](image)

Figure 5.5: Evolution of (a) Young’s modulus and (b) minimum tangent modulus with increasing CNT number for 2D and 3D models of various CNT aspect ratios (AR); CNT volume fraction of 1%; strain rate of $1 \times 10^{-3}$ s$^{-1}$; standard deviations are represented by error-bars; (c) initial portion of stress-strain curves for 3D RVEs incorporating aligned CNTs with an aspect ratio of 50 (from Weidt and Figiel 2014).

Due to the limited number of VE realisations, parametric Welch’s tests (with and without rank transformation) (Ruxton 2006) were performed to conclude upon the statistical significance of potential deterministic size effects. Unequal
variances were assumed due to statistical size effects that cause the standard deviations to decrease with increasing VE size. The null hypotheses (H0) on the equality of the means of two VE sizes were tested at two significance levels of \( \alpha=0.05 \) (significant) and \( \alpha=0.01 \) (highly significant). The results of the Welch’s tests are shown in Table 5.1. Fig. 5.5c shows how a deterministic size effect shows up in a larger slope in the post-yield regime for 3D VEs with aligned CNTs (CNT aspect ratio of 50), and previously indicated as the effect on \( T_{\text{min}} \) (see Table 3).

**Table 5.1** Results of Welch’s test for 2D and 3D models of various CNT aspect ratios (AR)*

<table>
<thead>
<tr>
<th>Model</th>
<th>AR</th>
<th>Randomly oriented CNTs</th>
<th>Aligned CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>25</td>
<td>-</td>
<td>Not tested</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>( H:30-60(0.05,\text{nrt},\text{rt}) )</td>
<td>Not tested</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>( E:10-30(0.05,\text{nrt}),10-60(0.01,\text{nrt};0.05,\text{rt}); \sigma_{V}:10-20(0.05,\text{nrt}, \text{rt}); \varepsilon_{S}:10-30(0.05,\text{nrt};0.01,\text{rt}),10-40(0.05,\text{nrt},\text{rt}),10-60(0.05,\text{rt}) )</td>
<td>Not tested</td>
</tr>
<tr>
<td>3D</td>
<td>25</td>
<td>-</td>
<td>Not tested</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>( E:9-12(0.05,\text{rt}),9-20(0.05,\text{nrt};0.01,\text{rt}); T_{\text{min}}:9-20(0.05,\text{nrt};0.01,\text{rt}) )</td>
<td>-</td>
</tr>
</tbody>
</table>

*Notation: e.g. \( T_{\text{min}}:9-20(0.05,\text{wrt};0.01,\text{rt}) \), where \( T_{\text{min}} \) is the stress-strain parameter affected by deterministic size effect, 9 and 20 are the two numbers of CNTs corresponding to the two VE sizes that are compared, 0.05,nrt stands for the significance level (0.05) tested without rank transformation (nrt) of data, and 0.01,rt stands for the significance level tested using rank transformed data (rt); '-' means that no deterministic size effect was observed.

Investigation of the strain-hardening behaviour of the nanocomposites was only possible for 2D VEs of CNT aspect ratio of 25 and 50 because of the premature termination of simulations at early stages of the hardening response (see comment in Section 5.3.1).

The results suggest that the minimum number of randomly oriented CNTs of aspect ratio of 50 in 2D RVEs is 60 CNTs or higher due to a deterministic size effect affecting the hardening modulus \( H \). A convergence study of the deterministic size effect on \( H \) was not carried out due to computational constraints. However, in the context of comparison of 2D and 3D RVE approaches, an investigation of the hardening modulus was omitted due to
premature termination of simulations of 3D RVEs. Hence, the selection of a smaller RVE size was deemed to be reasonable. The minimum number of randomly oriented CNTs with an aspect ratio of 100 in 2D RVEs is 20 CNTs. For 3D cuboidal RVEs (with aligned CNTs) a minimum number of 12 CNTs is suggested.

The confidence interval widths (CIW) were calculated for the stress-strain curve parameters for various ensemble sizes (i.e. the number of VE realisations). Ensemble standard deviations were assumed to be equal for various ensemble sizes. Student’s t-distribution was used due to small ensemble sizes. The results for two stress-strain curve parameters are shown in Fig. 5.6. For 3D RVEs composed of randomly oriented CNTs a significant reduction of the CIW of the parameter $\varepsilon_S$ was obtained by increasing the CNT number from 15 to 25 CNTs. An RVE populated with 25 CNTs possesses a normalised CIW of the parameter $\sigma_Y$ of 5% for an ensemble size of 5. Minor improvements were obtained for this parameter by increasing the ensemble size. Hence, an RVE containing 25 CNTs of an acceptable ensemble size of 5 was chosen in the 3D case. In a similar manner, RVEs populated with 20 CNTs and subject to 5 realisations were chosen for the 2D random orientation case, while RVEs containing 20 CNTs with 3 realisations were selected for the 3D aligned case.
5.4. Morphology effects for 2D and 3D

Finite strain compressive behaviour was predicted using the computational model to elucidate effects of CNT aspect ratio, CNT volume fraction, and strain rate on stress-strain parameters (as introduced in Section 5.3.2). Parameter results for the single constituents are presented in Table 5.2. It is important to point out that the Young’s modulus was defined here as initial tangent modulus, which defines the slope of the linear portion of the initial stress-strain behaviour in 2D (plane strain) and 3D. Different assumptions invoked by the 2D (plane strain) and 3D models resulted in the deviation between the initial tangent modulus \( E \) in 3D and its counterpart \( E_{pe} \) in 2D (see Table 5.2), which can be described through the relationship \( E = (1 - \nu^2) E_{pe} \) (Hutchinson and Suo 1992), where \( \nu \) denotes Poisson’s ratio. Throughout this chapter we use the term Young’s modulus to define the initial tangent modulus of the 2D (plane strain) and 3D stress-strain curves.
### Table 5.2 Mechanical properties of CNT phase and pure epoxy (2D and 3D)
(Young’s moduli for pure epoxy were obtained from the initial slope of stress-strain curves)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CNT</th>
<th>2D epoxy</th>
<th>3D epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus $E$ [GPa]</td>
<td>143.62</td>
<td>4.20</td>
<td>3.63</td>
</tr>
<tr>
<td>Yield peak stress $\sigma_y$ [MPa]</td>
<td>138.5</td>
<td>110.2</td>
<td></td>
</tr>
<tr>
<td>Yield strength $\sigma_{p1}$ [MPa]</td>
<td></td>
<td></td>
<td>108.6</td>
</tr>
<tr>
<td>Softening strain limit $\varepsilon_s$ [%]</td>
<td>20.6</td>
<td>28.3</td>
<td></td>
</tr>
</tbody>
</table>

Previously selected RVE sizes (in terms of CNT numbers) and RVE ensemble sizes for randomly oriented CNTs (see Section 5.3.2) were used for RVEs populated with aligned CNTs. For 2D RVEs, the RVE size for randomly oriented and aligned CNTs was assumed to be the same.

#### 5.4.1. Effect of CNT aspect ratio

The effect of CNT aspect ratio is shown in Figs. 5.7 and 5.8. Both figures show results obtained for RVEs containing randomly distributed and randomly oriented CNTs volume fraction of 1% and subjected to quasi-static strain rates ($1 \times 10^{-3}$ s$^{-1}$). Typically, aspect ratios for CNTs are claimed to be larger than 100. However, as CNTs frequently occur in a wavy form, the effective aspect ratios (i.e. those, which allow for an efficient stress transfer) are actually much smaller—thus, three aspect ratios were investigated: 25 (2D and 3D), 50 (2D and 3D) and 100 (2D case only).
As expected, incorporation of CNTs (and their increasing aspect ratio) led to an increase of Young’s modulus $E$ of the nanocomposite of around 4% (5.5%, 8%) for 2D RVEs of aspect ratio of 25 (50, 100) and 7.5% (9.5%) for 3D RVEs of aspect ratio of 25 (50) (see Fig. 5.8a). 2D models predicted a stiffer response (in the linear elastic regime) both for pure epoxy and its nanocomposite, when compared to 3D models (see Fig. 5.7). Therefore, it is concluded that the cause of the stiffer 2D response is the well-known effect of the constraint on the out-of-plane strain caused by the plane strain assumption. The normalised Young’s modulus in the 3D case is slightly larger than in the 2D case, probably caused by the better stress transfer due to larger CNT surface area in 3D and the smaller average CNT distance due to the 3D effect.
Values of the parameter $\sigma_Y$ (yield peak stress) show a difference between 2D and 3D models, which is qualitatively similar to those obtained for pure epoxy under plane strain (2D) and 3D conditions (see Fig. 5.7). However, the CNT presence and the increase in CNT aspect ratio had a negligible effect for 2D RVEs, whereas for 3D RVEs a significant increase from around 4.5% to 7% in $\sigma_Y$ was predicted for the increase in CNT aspect ratio from 25 to 50 (see Fig. 5.8b). The local matrix behaviour of the 2D and 3D models was compared in order to determine the reason for this behaviour. In the averaged true stress-applied strain curves of the matrix, one can observe a slight decrease of the yield peak stress in 2D models and the increase of the yield peak stress in 3D models. This can be explained by comparing the CNT distributions in 2D and 3D models. For the same volume fraction a denser CNT distribution is generated in 3D with a much smaller average CNT to CNT distance—a 3D scaffold of densely packed CNTs is compared against well separated CNTs in the 2D plane (see Fig. 5.9). The dense CNT networks in the 3D RVEs limit the expansion in the lateral directions when the 3D RVEs are subjected to uniaxial loading. Within the matrix, this promotes a bigger volume change as well as an increase in hydrostatic stress when compared to pure epoxy. This led to bigger averaged stresses in the matrix and the nanocomposite—a similar effect is imposed by the plane-strain assumption. In contrast, for 2D models with a bigger average CNT
to CNT distance, the average hydrostatic stress within the matrix around the yield peak was slightly smaller than for the pure epoxy.

Subsequently, a decrease of the magnitude of softening modulus (defined by a reduced softening slope) with increasing CNT aspect ratio was found for 3D RVEs (see Fig. 5.7), while a small increase of the magnitude of softening modulus was predicted for 2D RVEs. Two main effects were identified to contribute to the reduced softening response in 3D. First, the CNT to CNT distance is reduced (as explained earlier), which caused the increase of the averaged hydrostatic stress in the matrix. Secondly, the averaged stress in the CNTs increased well beyond the yield peak within the matrix for the 3D RVE, as shown in Fig. 5.10. In contrast, the averaged stress within the CNTs for 2D RVEs resembled closely the average response of epoxy with regimes such as yield, softening and hardening. The large CNT to CNT distance in 2D RVEs limits the inter-particle interaction and, thus, the averaged stress response of CNTs was mainly governed by the behaviour of epoxy. It is believed that the increased inter-particle interaction in 3D RVEs (because of the smaller CNT to CNT distances) changes an epoxy-like behaviour for the CNTs and, therefore, for the nanocomposite.
It was predicted that increasing CNT aspect ratio accelerates the onset of strain hardening, as indicated by the decreased strain softening limit $\varepsilon_S$ (see Fig. 5.8c). Changing the aspect ratio from 25 to 50 reduced $\varepsilon_S$ both for 2D and 3D models around 20% for 3D, and 7% for 2D models. This difference between 2D and 3D models is a further consequence of the difference in nanocomposite morphology, as explained above.

### 5.4.2. Effect of CNT volume fraction

The effect of CNT volume fraction on the compressive true stress-true strain curves for aligned CNTs and randomly oriented CNTs is shown in Figs. 5.11 and 5.12 using 2D and 3D RVEs. In each case, the predictions are for RVEs with CNT volume fractions of 0.5% and 1% and aspect ratio of 50. They were obtained for the quasi-static strain rate of $1\times10^{-3}$ s$^{-1}$. 
In general, the CNT volume fraction has a qualitatively similar effect on the stress-strain parameters, as the CNT aspect ratio. As expected, the Young’s modulus increased linearly with increasing CNT volume fraction (see Fig. 5.12a). The largest enhancement is associated with 3D nanocomposite morphologies of aligned CNTs with an improvement of ~32% for CNT volume fraction of 1%, while less than half this value was obtained for its 2D counterpart (i.e. ~14% increase of Young’s modulus for CNT volume fraction of 1%). This is again caused by the improved stress transfer due to the larger surface area in 3D and the smaller average CNT distance due to the 3D effect. Significantly smaller differences for the Young’s modulus between 2D and 3D RVEs were found for random CNT orientations.

Figure 5.11: Examples of stress-strain curves from 2D and 3D RVEs incorporating CNTs of various volume fractions (VF); reference stress-strain curves of pure epoxy in 2D and 3D; randomly oriented and aligned CNTs, CNT aspect ratio of 50; strain rate $1 \times 10^{-3}$ s$^{-1}$ (from Weidt and Figiel 2014).
Figure 5.12: Effect of CNT volume fraction (VF) and RVE approaches (2D, 3D) on the normalised stress-strain parameters (a) Young’s modulus, (b) yield peak stress and (c) softening strain limit; RVEs with randomly oriented and aligned CNTs; CNT aspect ratio of 50; strain rate = 1×10^{-3} s^{-1}; standard deviations are represented by error-bars; *value of the normalised yield stress \( \sigma_{p1}/\sigma_{p1e} \) at the strain offset 0.01; **only one realisation considered due to premature termination of simulations (from Weidt and Figiel 2014).

An interesting result was observed regarding the effect of CNT volume fraction on the nanocomposite yield peak. In particular, the volume fraction did not affect the yield peak parameter \( \sigma_Y \) in 2D models (see Fig. 5.12b) (similarly to the effect of aspect ratio in 2D). However, for 3D models there is a linear increase in \( \sigma_Y \) with increased CNT volume fraction. Larger effects were found for 3D nanocomposite morphologies of aligned CNTs (rather than random) with an increase from 15% to 33%. This matches the magnitude of the effect of CNT volume fraction on the Young’s modulus of the nanocomposite. It is noteworthy to mention that in contrast to 3D nanocomposite morphologies of randomly oriented CNTs, this effect did not arise from the increase in the matrix hydrostatic stress. Rather the hydrostatic stress within the matrix was actually smaller than for the pure epoxy at applied strains corresponding to the yield peak stress. Instead, it is believed that the major contribution here was brought by the larger stress, which is carried by the 3D CNTs, as shown in Fig. 5.13, in terms of averaged true stress-applied strain curves for the reinforcement. It is expected that a larger surface area of CNTs within the 3D models contributed to that by promoting a much better stress transfer.
Additionally, it must be mentioned that there is a second averaged CNT stress peak followed by the stress drop located in the hardening regime (at around 35-40% of applied nominal strain) as predicted by 2D RVEs (see Fig. 5.13). It originated from intensive bending and rotation of 2D CNTs, which reduced the stress transfer.

Then, a significant decrease in the magnitude of softening modulus (case CNT volume fraction of 0.5%) and the disappearance of the softening behaviour (case CNT volume fraction of 1%) were predicted by 3D RVEs with aligned CNTs. It is believed that this resulted from the significant increase of the averaged CNT stress in 3D RVEs, as discussed above and shown in Fig. 5.13.

The softening strain limit $\varepsilon_S$ was predicted to decrease with increasing CNT volume fraction (see Fig. 5.12c). The corresponding true strain values were found to be larger for 3D RVEs than for 2D RVEs, and also larger for aligned CNTs than for randomly oriented CNTs: (a) for CNT volume fraction of 0.5%, a reduction of 20-25% in $\varepsilon_S$ was obtained for 2D and 3D approaches of randomly oriented CNTs, (b) decrease of 40% (2D) and 55% (3D) was predicted for aligned CNTs.
5.4.3. Effect of strain rate

The effect of strain rate for aligned CNTs and randomly oriented CNTs is shown in Figs. 5.14 and 5.15 for strain rates of $1 \times 10^{-3}$ (quasi-static strain rate) and $1 \times 10^3$ s$^{-1}$ (impact rate of strain). Both figures show predictions of RVEs containing CNTs of aspect ratio set to 50 and volume fraction equal to 1%. The stress-strain parameters in Fig. 5.15 are normalised against corresponding values of pure epoxy subjected to quasi-static strain rate.

For pure epoxy, the increased strain rate shifted the yield peak stress and the corresponding strain to larger values (see Figs. 5.14 and 5.15a). A conventional explanation is that the time window of material deformation becomes smaller than the relaxation time of the material. Similar trends were predicted for the nanocomposite using 2D and 3D RVEs with aligned and randomly oriented CNTs. As recognised in the previous section, nanocomposite morphologies of aligned CNTs in the 3D case exhibit a larger increase of $\sigma_Y$ or $\sigma_{pl}$ than
morphologies of randomly oriented CNTs. However, the magnitude of this enhancement was larger for impact rates of strain (~55 MPa) than for the quasi-static strain rates (~35 MPa) (see Fig. 5.14).

Considering the softening strain limit parameter $\varepsilon_s$, its normalised value did not show a significant dependency on the strain rate as predicted by 2D RVEs—for pure epoxy it shifted to slightly smaller values of strain with increasing strain rate.

For 3D approaches, the effect of strain rate on $\varepsilon_s$ is shown only for nanocomposites of randomly oriented CNTs because the softening regime was no longer present after CNT alignment. In that case, the normalised parameter $\varepsilon_s$ was significantly reduced from 0.53 to 0.43 when increasing the strain rate from $1 \times 10^{-3}$ to $1 \times 10^{3}$ s$^{-1}$ (see Fig. 5.15b). For the 3D case with aligned CNTs a significantly larger slope of the curve in the post yield regime with increased strain rate was predicted (see Fig. 5.14). It is believed that the enhanced inter-particle interaction in 3D RVEs and CNT alignment caused an improved matrix to CNT stress transfer in the post-yield regime with the increased strain rate. This is confirmed by the increase of average stresses within CNTs, extracted from RVE models, as shown in Fig. 5.16.
Figure 5.16: Average stress-strain curves for the CNT phase; aligned and randomly oriented CNTs, CNT aspect ratio of 50, CNT volume fraction of 1%; quasi-static (1×10⁻³ s⁻¹) and impact rates of strain (1×10⁻³ s⁻¹) (from Weidt and Figiel 2014).

5.5. Computational efficiency

All simulations were performed using a multi-processor supercomputer. 3D RVEs containing 25 randomly oriented CNTs consisted of around 100000 elements and 800000 degrees of freedom. Typical 3D simulations took around 43 hours of wall-clock time with 60 CPUs and a total CPU time reported by ABAQUS of 364 hours (abort at around 21% of true strain). In contrast, 2D RVEs incorporating 20 randomly oriented CNTs consisted of around 14000 elements and 56000 degrees of freedom. In this case the wall-clock time was 1.5 hours using 24 CPUs and a total CPU time reported by ABAQUS was 7 hours (abort at around 36% of true strain).
5.6. Comparison with experiments

Some of the predicted stress-strain trends were qualitatively compared with the available experimental data from the literature. Experimental results of Dassios et al. (2012) were selected, where the authors investigated the large-strain response of aligned CNT mats impregnated with epoxy under quasi-static compressive loading. Similarly to the predictions using 3D RVE based models with aligned CNTs, the authors observed an increase in Young’s modulus and yield peak, and a shift of yielding to larger values of strain for the CNT/epoxy systems, compared to pure epoxy. Due to the relatively large CNT volume fraction of 0.27% and the special arrangement of CNTs in the mat (thickness of the mat is equal to the CNT length), their compression test result represents an upper bound for the current 3D models of aligned CNTs.
Chapter 6

Model validation and effects of CNT waviness and van der Waals bonding on the compressive behaviour of epoxy/CNT nanocomposites

6.1. Objective

Robust multiscale model demands experimental validation to confirm its degree of accuracy and to answer the question whether sufficient detail was included within the multiscale framework. Once a successful validation was carried out for the given material composition, the model can be used to predict the nanocomposite behaviour at other conditions (e.g. other CNT volume fractions or CNT functionalisations) and, thus, replace experimental tests with simulations.

Hence, in this chapter, a combined experimental-computational approach is followed to develop a reliable multiscale model for the prediction of the non-linear finite deformation of epoxy/CNT nanocomposites under compressive loading. Epoxy/CNT samples of low CNT concentrations (maximum CNT mass fraction of 0.6 mass%) and random CNT distribution and orientation were prepared and tested under quasi-static compressive loading. In the previous chapter it was shown that 2D RVEs cannot capture the stress transfer effect and the particle interaction when compared to their 3D counterparts. Thus, the computational section of this chapter involves the study of 3D RVEs of
corresponding nanocomposite morphologies. The predictions also involve RVEs composed of larger CNT mass fractions in order to provide an extended insight into mechanical response of nanocomposites samples, to show their potential in case manufacturing difficulties can be overcome.

The chapter is structured as follows. Details of material preparation, experimental setup and modelling procedure are introduced first. Then, the results of the experimental testing including nanocomposite morphology characteristics are presented. Subsequently, the predictions of the computational model are shown and compared to experimental results.

6.2. Material preparation

Non-functionalised MWCNTs (NANOCYL™ NC3100) were obtained from Nanocyl S.A. (Belgium). The MWCNTs are produced via a catalytic CVD process. The average outer diameter is about 9.5 nm and the average length is 1.5 µm. The purity is above 95 mass%. The number of sidewalls of 18 MWCNTs, which were randomly picked and investigated via TEM, is between 6 and 19. Amino-functionalised MWCNTs (HDPlas™) were obtained from Cheap Tubes (USA). The MWCNTs are produced via a catalytic CVD process and functionalised using a split plasma process. The purity is above 99 mass%. The outer diameter and length ranges between 13–18 nm and 3–30 µm, respectively. The content of amino-groups (NH₂) is 7+/−1.5 mass%. Other functionalities are N–H, O=C–N–H₂.

The resin is a standard diglycidyl ether of bisphenol A (EPON 828). The monomer with a molecular weight of 377 was obtained from Polyscience Europe GmbH (Germany). Glycolitic polypropyleneoxide triamine (Jeffamine T403 hardener) with a molecular weight of 440 was provided by Alfa Chemicals Ltd. (United Kingdom).
Nanocomposite samples and pure epoxy samples (see Fig. 6.1), which will serve as reference material, were produced using two production routes: (1) a non-solvent method and (2) solvent-method using chloroform. Functionalised CNTs were used together with the solvent chloroform, because they are more stable in organic solvents such as chloroform than their non-functionalised counterparts. A relatively time consuming production route was used for the non-solvent method. Preliminary tests showed that adding the whole CNT mass fraction in one step results in a relatively high viscosity mixture, which could not be dispersed successfully. Using the solvent chloroform as dispersion medium enabled the incorporation and dispersion of the whole CNT mass fraction in one step. Hence, the production time was reduced significantly.

Specifics of the samples of the batches are listed in Table 1 (batch notation, functionalisation, solvent, CNT mass fraction). The final cylindrical samples have a length of 20 mm and a diameter of 12.7 mm.

![Figure 6.1: Pure epoxy samples versus nanocomposite sample.](image)
<table>
<thead>
<tr>
<th>Batch</th>
<th>Name</th>
<th>Solvent</th>
<th>CNT functionalisation</th>
<th>CNT mass fraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Epoxy1 (NS)</td>
<td>O</td>
<td>O</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>Epoxy2 (NS)</td>
<td>O</td>
<td>O</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>Nanocomposite (NS,NF) MF=0.1%</td>
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<td>O</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>Nanocomposite (NS,NF) MF=0.2%</td>
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<td>O</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>Nanocomposite (NS,NF) MF=0.3%</td>
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<td>O</td>
<td>0.30</td>
</tr>
<tr>
<td>6</td>
<td>Epoxy1 (S)</td>
<td>X</td>
<td>O</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>Nanocomposite (S,F) MF=0.3%</td>
<td>X</td>
<td>X</td>
<td>0.30</td>
</tr>
<tr>
<td>8</td>
<td>Nanocomposite (S,F) MF=0.45%</td>
<td>X</td>
<td>X</td>
<td>0.45</td>
</tr>
<tr>
<td>9</td>
<td>Nanocomposite (S,F) MF=0.6%</td>
<td>X</td>
<td>X</td>
<td>0.60</td>
</tr>
<tr>
<td>10</td>
<td>Nanocomposite (S,NF) MF=0.3%</td>
<td>X</td>
<td>O</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Nanocomposites produced using the non-solvent method exhibit mass fractions of 0.1%, 0.2% and 0.3% of non-functionalised MWCNTs. 0.1 mass% of CNTs were added first to the epoxy monomer and the mixture was stirred manually for 10min. This was followed by mild water bath sonication for 10 h (see Fig. 6.2, 45 kHz, 150 W). CNT mass fractions of 0.1 and 0.2% were obtained stepwise by adding 0.1 mass% to the dispersed CNT/epoxy mixture followed by a repetition of the sonication process. Between those steps the mixtures was left to rest overnight. In the case of 0.2 and 0.3 mass%, at the start and the middle of the second and the third sonication step the mixture was stirred manually for 15 min in order to break off larger agglomerates at the beaker wall. After obtaining the final CNT mass fraction, the hardener was poured into the beaker containing the CNT/epoxy mixture (resin/hardener-ratio of 100:42). The final mixture was then stirred manually for 25 min followed by two short sonication steps of 15min to degas the mixture. The warmed water was changed in between those sonication steps. Then, the mixture was poured into tubular metal moulds. Those moulds consisted of 2 pieces glued together. The tubular part open at both ends and a cylindrical metal bar slid into it. The open moulds were placed in an oven and the material was cured at 75°C for 2 h at ambient pressure. A post-cure of 2.5 h at 125°C was applied. Pure epoxy reference
samples were produced using the same production route without stirring/sonicating the pure epoxy monomer. Released samples were ground down and polished wet in order to obtain parallel surfaces and their final sample length. The cylindrical samples have a length of 20 mm and a diameter of 12.7 mm.

Nanocomposites produced using the solvent method exhibit mass fractions of 0.3%, 0.45%, 0.6% of functionalised MWCNTs and 0.3% of non-functionalised MWCNTs. Requested final mass fractions of CNTs were first added to chloroform (CNT concentration in chloroform: 2mg/ml). The mixture, placed in air sealed vials, was pre-dispersed for 2 h using mild water bath sonication (45 kHz, 150 W). Then, it was added to the epoxy monomer and manually stirred for 3 min. The open beaker was placed in a water bath at 60°C and sonicated for 4 h to degas the chloroform (45 kHz, 150 W). This was followed by automatic stirring on a hot plate at 65°C and 90 rpms overnight for 12 hours (see Fig. 6.3). Trapped air and possible rests of solvents were degassed in a vacuum oven by applying 4 cycles of vacuum (One cycle: 20 min at 850 mbar, 10 min at 1000 mbar) at 80°C. The mixture was then sonicated (water bath) at 65°C for 2 h in order to counteract possible reagglomeration that might have happened overnight or while applying the vacuum. After addition of the hardener (resin/hardener-ratio 100:42) and manual agitation for 25 min, the material was
poured into the metal moulds and placed in a vacuum oven for 4 cycles (One cycle: 20 min at 850 mbar, 10 min at 1000 mbar) at 35°C. In such a way, possible bubbles incorporated previously by mixing the filled epoxy with the hardener were degassed. The open moulds were placed in an oven and the material was cured at 75°C for 2 h at ambient pressure. A post-cure of 2.5 h at 125°C was applied. Pure epoxy reference samples were produced using the same production route without sonicating the chloroform. Released samples were ground down and polished wet in order to obtain parallel surfaces and their final sample length. The cylindrical samples have a length of 20 mm and a diameter of 12.7 mm.

By using the aforementioned production, nanocomposite samples could be prepared without major difficulties. However, samples with a mass fraction of 0.3% of non-functionalised CNTs exhibit bubbles, which could not be removed via sonication or the application of a vacuum. All other samples are free of visible bubbles. Fig. 6.4 shows the grade of porosity for those samples.
6.3. Experimental setup

Compression tests were performed using a DARTEC 100 KN testing facility (see Fig. 6.5), a 25 mm LVDT (linear variable differential transformer) displacement transducer and the System 6000 Stress Analysis Data System. LVDT displacement transducer and the load-cell of the the DARTEC machine were connected to the System 6000 and calibrated for the force-displacement recording. The parallel sample surfaces were covered by a thin layer of petroleum jelly and the samples were placed between polished metal plates that were attached to the main grip bodies. The DARTEC machine was programmed to test at a constant speed of 0.2 mm/s. The displacement of the upper sample surface was measured indirectly at an angle iron mounted to the main grip body. The load-displacement behaviour was recorded for the subsequent data analysis.
Batch 1 and batch 2 of pure epoxy were produced (non-solvent method) and tested separately in order to evaluate the reproducibility of production process and experimental testing. The averaged stress-strain behaviour of the two batches was found to be nearly identical (see Fig. 6.6), which herein was assumed to confirm their reproducibility. The batches 1, 2–5 and 6–10 were tested on three different days and the samples of these batches were tested in a randomised order.
6.4. Experimental results

Experimental results are presented in this section. First, it is focussed on the stress-strain behaviour and nanocomposite morphologies obtained. Subsequently, the results are discussed and the selection of experimental data for the model validation is explained.

6.4.1. Stress-strain behaviour

Reference samples for pure epoxy, produced by solvent method, exhibit an improved finite strain compressive behaviour over the samples prepared using the non-solvent method. In particular, an increase in yield peak stress and post-yield stresses was found for the epoxy from the solvent method. Hence, in order to investigate the effect of CNTs, one has to compare the results of nanocomposite samples with pure epoxy samples that employed the same manufacturing method, i.e. solvent usage or no solvent usage.

Relatively small enhancements of the Young’s modulus (see Fig. 6.7) were obtained by incorporating CNTs into the epoxy matrix (both for solvent and non-solvent methods). The Young’s modulus was here evaluated as slope between two data points of 10 and 30 MPa true stress. Non-functionalised CNTs show a negligible reinforcement effect (increase in Young’s modulus smaller than 1%) for CNT concentrations of 0.1 mass% and 0.2 mass%. A CNT mass fraction of 0.3% resulted in a significant drop of the nanocomposite Young’s modulus for both preparation methods, which was attributed to poor dispersion. However, the samples produced using the solvent method exhibit a larger Young’s modulus than their non-solvent counterparts indicating a better dispersion state. Functionalised CNTs show a better reinforcement capability than their non-functionalised counterparts. An increase in Young’s modulus of around 2.3% and 1.1% was obtained for samples composed of 0.3 and 0.6
mass% of functionalised CNTs. In contrast, the intermediate CNT concentration of 0.45 mass% shows a negligible reinforcement effect below 0.5%. Again, the decrease of the nanocomposite Young’s modulus is possibly caused by an insufficient state of dispersion, which is confirmed by the morphology characterisation section (see Section 6.4.2).

<table>
<thead>
<tr>
<th>Young's modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy (NS)</td>
</tr>
<tr>
<td>Nanocomposite (NS,NF) MF=0.1%</td>
</tr>
<tr>
<td>Nanocomposite (NS,NF) MF=0.2%</td>
</tr>
<tr>
<td>Nanocomposite (NS,NF) MF=0.3%</td>
</tr>
<tr>
<td>Epoxy (S)</td>
</tr>
<tr>
<td>Nanocomposite (S,F) MF=0.3%</td>
</tr>
<tr>
<td>Nanocomposite (S,F) MF=0.45%</td>
</tr>
<tr>
<td>Nanocomposite (S,F) MF=0.6%</td>
</tr>
<tr>
<td>Nanocomposite (S,NF) MF=0.3%</td>
</tr>
</tbody>
</table>

Figure 6.7: Experimental results for the Young’s moduli of pure epoxy and nanocomposites of various CNT mass fractions (MF) prepared using functionalised/non-functionalised (F/NF) CNTs, and a solvent/non-solvent preparation method (S/NS); pure epoxy samples from the two batches, Epoxy1 (NS) and Epoxy2 (NS) were pooled in Epoxy (NS); error bars show standard error of the mean estimated by dividing the batch standard deviation by the square root of the number of samples.

Qualitatively similar results were obtained for the yield peak stress (see Fig. 6.8). However, the effect of the presence of CNTs on yield peak stress is less significant than on Young’s modulus. A CNT concentration of 0.1 mass% of non-functionalised CNTs resulted in a 1% increase in yield peak stress. Further increase in CNT concentration decrease the yield peak stresses when compared to the previous concentration. Likewise for the case of functionalised CNTs, an enhancement of 1.1% in yield peak stress was obtained for 0.3 mass%. CNT concentrations of 0.45 mass% and 0.6 mass% show negligible enhancements (smaller 1%) of yield peak stresses.
Nanocomposites tend to break at earlier stages of strain than the samples made of pure epoxy (see Fig. 6.9). The general trend is, the larger the CNT concentration the smaller is the true strain at break. This was observed for both types of CNTs, functionalised and non-functionalised. However, a smaller true strain at break was obtained for a CNT concentration of 0.1 mass% than for 0.2 mass% of non-functionalised CNTs. A possible reason can be the small difference in the dispersion state of these batches, which cannot be visualised by electron microscopy and can have a significant effect on the true strain at break due to the induction of stress concentration through agglomerates.

Secondly, it can be possible that the doubled sonication time for the case of 0.2 mass% shortened the CNTs, compared to 0.1 mass%, and, thus, entangled them more effectively, or decreased their tendency to form agglomerates by reducing their specific surface area. Furthermore, when considering the incorporated CNT as pre-existent crack, the CNT length reduction can be linked to a larger stress intensity factor and, thus, to a better toughness.
Figure 6.9: Experimental results for the true strains at break of pure epoxy and nanocomposites of various CNT mass fractions (MF) prepared using functionalised/non-functionalised (F/NF) CNTs and a solvent/non-solvent preparation method (S/NS); pure epoxy samples from the two batches, Epoxy1 (NS) and Epoxy2 (NS) were pooled in Epoxy (NS); error bars show standard error of the mean.

The ultimate compressive strength (UCS) was associated here with the stress at break. The UCS of nanocomposite samples was found smaller than for pure epoxy (see Fig. 6.10), which was decreasing with an increase in CNT content — this trend was a consequence of the trends observed for the strain at break of nanocomposites.

Figure 6.10: Experimental results for the ultimate compressive strengths of epoxy and nanocomposites of various CNT mass fractions (MF) prepared using functionalised/non-functionalised (F/NF) CNTs and a solvent/non-solvent preparation method (S/NS); pure epoxy samples from the two batches, Epoxy1 (NS) and Epoxy2 (NS) were pooled in Epoxy (NS); error bars show standard error of the mean.
The true stress-true strain curves for relevant batch realisations were averaged to investigate the post-yield behaviour of the nanocomposites (see Fig. 6.11), which can largely contribute to the energy absorption capabilities of the nanocomposite. Largest stress enhancements within the post-yield regime at the 30% of true strain were achieved for 0.45 mass% and 0.6 mass% of functionalised nanotubes. In comparison to pure epoxy using the same solvent-assisted preparation method, approximately 3% larger stress values were achieved here. The nanocomposite composed of 0.3 mass% of functionalised CNTs, which exhibited the best result in terms of Young’s modulus and yield peak stress, shows a less significant stress enhancement in the post-yield regime. An improved behaviour (when compared to pure epoxy) for non-functionalised CNTs was only obtained for a mass fraction of 0.1%. Concentrations of 0.2 and 0.3 mass% exhibit smaller stresses within the post-yield regime.

**Figure 6.11:** Averaged experimental stress-strain curves of epoxy and nanocomposites of various CNT mass fractions (MF) prepared using functionalised/non-functionalised (F/NF) CNTs and a solvent/non-solvent preparation method (S/NS).
6.4.2. Morphology characterisation

The Hitachi SU-70 scanning electron microscope was used to study the CNT morphologies. Fractured epoxy/CNT samples were further processed in order to obtain high-quality SEM pictures. In general the samples fractured into two cones and many additional smaller pieces. The cones are a direct result of the friction between metal plates and sample surface, which led to a less deformed conical shape that remains after fracture. It was focussed on the hackle region exhibiting a relatively rough surface that shows crack lines along the crack propagation direction. With the naked eye, the region was easily identified for example on the surface of the cone due to the white colour indicating a large amount of plastic deformation (see Fig. 6.12). Nanocomposites composed of 0.3 mass% of non-functionalised CNTs broke in a more ductile manner and comparable featured surfaces were not found, hence, the fracture surface was picked randomly in those cases. Fracture surfaces were cut out and the opposing side was flattened using a dremel. After cleaning the samples with compressed air, the samples were fixed with carbon tape to the substrate plates. Then, the samples were sputtered with gold for 12 s using a plasma current of 20 mA, resulting in a coating thickness of approximately 30 angstrom.

![Figure 6.12: Schematic of deformation of nanocomposite samples under compressive load (left) and the location of the hackle region (red); SEM micrograph of hackle region (right), pure epoxy batch 1, rough surface morphologies with peeled and plastically deformed features.](image-url)
In case of nanocomposite prepared using non-functionalised CNTs and without solvent, a good dispersion state was achieved for CNT mass fractions of 0.1 and 0.2%, as indicated by isolated CNTs in SEM micrographs (see Fig. 6.13—top left and top right). Within the investigated surface area no CNT agglomerations were found in those cases. Regions of larger CNT concentrations when compared to the general CNT distribution on the fracture surface were observed for the case of 0.2% and 0.3% mass fractions. For the latter concentrations, CNT incorporation clearly resulted in a poor CNT dispersion state with large agglomerations all over the fracture surface (see Fig. 6.13—bottom left). Bridging CNTs and fractured CNTs at opposing fracture surfaces (see Fig. 6.13—bottom right) were observed. In all samples, and especially for CNTs within agglomerations, CNTs tend to be partially pulled out. This indicates poor interfacial bonding between the CNT and epoxy matrix.

Figure 6.13: SEM micrographs of nanocomposites of various CNT mass fractions (MF) prepared using non-functionalised CNTs and a non-solvent preparation method; MF=0.1% (top left) and MF=0.2% (top right): isolated CNTs (white arrows); MF=0.3% (bottom left): CNT rich regions/agglomerations; MF=0.2% (bottom right): fractured CNT after crack bridging mechanism (white arrow); white particles are a result of the post-processing using a dremel.
Using the solvent for the dispersion of a CNT mass fraction of 0.3% of non-
functionalised, it resulted in a slightly better dispersion state of CNTs, when
compared to the non-solvent method. Large CNT agglomerations were still
observed (see Fig. 6.14).

In case of nanocomposites prepared using functionalised CNTs and a solvent, a
good dispersion state was achieved for CNT mass fractions of 0.3%, as
indicated by relatively small CNT-rich regions and isolated CNTs (see Fig.
6.15—top left). In this case, no significant CNT agglomerations were observed.
Many broken CNTs were found close to the fracture surface (see Fig. 6.15—top
left), which indicates a strong interfacial bonding between CNT and epoxy.
Furthermore, crack bridging CNTs were observed (see Fig. 6.15—bottom right).
Besides isolated CNTs and CNT rich regions with well dispersed CNTs, small
agglomerates with incompletely impregnated CNTs and large agglomerations

Figure 6.14: SEM micrograph of nanocomposite with CNT mass fraction MF=0.3% prepared using non-
functionalised CNTs and a solvent preparation method, agglomerations (white boxes), white particles are
a result of the post-processing using a dremel.
were also found for CNT mass fractions of 0.45% and 0.6% (see Fig. 6.15—top right and bottom left).

\[\text{Figure 6.15: SEM micrographs of fracture surfaces of nanocomposite samples of various CNT mass fractions (MF) of functionalised CNTs; MF=0.3\% (top left): good state of dispersion with CNTs broken close to the fracture surface (white arrows); MF=0.45\% (top right): small CNT agglomeration with incomplete impregnation; MF=0.45\% (bottom left): large CNT agglomeration, similar agglomeration sizes obtained for the case MF=0.6\%, MF=0.3\% (bottom right): CNT crack bridging (white arrows).}\]

### 6.4.3. Discussion

In general, one can say that relatively small improvements in Young’s modulus (case CNT mass fraction of 0.1 and 0.2\%), yield peak stress (case CNT mass fraction 0.1 and 0.2\%), and stress response within the post-yield regime (case CNT mass fraction of 0.1\%) were obtained by incorporating non-functionalised CNTs using the non-solvent method. A mass fraction of 0.3\% resulted for both production routes in reduced mechanical performance within the entire stress-strain response. Functionalised CNTs facilitate the dispersion in solvent-assisted preparation methods. They further can become an integral part of the epoxy network due to covalent bonding of the reactive amino-groups that are
acting similar to the hardener. Functionalised CNTs showed a better reinforcement effect with a stress increase of up to 3% at 30% of true strain. However, large CNT mass fractions were not considered in this study due to preparation difficulties. Improved preparation methods are needed to prepare such nanocomposites that enhance the mechanical properties of pure epoxy. All the prepared nanocomposite samples had a tendency to break at earlier stages of strain, possibly due to the presence of cracks/voids/agglomerations and their critical stress concentrations.

Samples produced using chloroform showed less porosity (see Fig. 6.4) and an improved finite strain compressive behaviour (see Fig. 6.7–6.11) than samples produced without the solvent, as shown for the case of non-functionalised CNTs. This can be attributed to the better dispersion state. Agglomerates within the epoxy monomer can influence the mixing with the hardener negatively, because of the larger viscosity localised within the agglomerate. Subsequent stirring of the epoxy/hardener mixture is, therefore, believed to result in less homogenous mixture. The hardener has more difficulties to penetrate into the CNT agglomerations, which can result in localised differences of epoxy-hardener ratios within the CNT agglomerations, and, therefore, in the remnant epoxy. All this is expected to lead to a significant drop of properties as obtained in the case of nanocomposites composed of 0.3 mass% of non-functionalised CNTs prepared without a solvent (see Fig. 6.7–6.11). Furthermore, trapped air within the CNT agglomerations and low attractive secondary bonding via vdWs forces between CNTs may be responsible for agglomerations to act as voids that lower the mechanical properties and provoke early failure, as shown by the decrease of true stresses and strains at failure with increasing CNT mass fraction (see Fig. 6.9–6.10).

Altogether, the reinforcement effect of CNTs on the finite strain compressive properties was shown to be small. Reasons that limit their reinforcement
efficiency are expected to be brought by CNT curvature, CNT defects, CNT misalignment, poor interfacial bonding between CNTs and epoxy, poor dispersions/agglomerations for larger CNT mass fractions.

6.4.4. Selection of experimental data for model validation

Nancomposite samples composed of 0.3 mass% of functionalised CNTs and prepared using a solvent method were chosen for the computational validation. Those samples showed the largest effect of CNT incorporation on the stress-strain response for the highest CNT mass fraction that did not result in significant CNT agglomerations at fracture surfaces. Agglomerations are the features, which cannot be captured by the current computational model.

6.5. Modelling approach

The modelling approach introduced in Chapter 4 was followed here to capture the experimental stress-strain curves. The RVE-based FE model generator (see Section 4.2) was used to create 3D RVEs of randomly distributed and oriented CNTs. However, in contrast to the 3D modelling approach of the previous chapter, the methodology was enhanced by representing MWCNTs as transversely isotropic effective fibres of sinusoidal shape and accounting for a cohesive zone interface. The material data sheet of the CNTs and SEM micrographs of CNTs in powder form were used to determine the CNT-related input variables for the model generator and the calculation of the transversely isotropic properties of the effective fibre. Table 6.2 summarises all the material and geometry characteristics of the effective transversely isotropic and wavy solid CNT fibre.
Table 6.2 CNT to effective fibre transition

<table>
<thead>
<tr>
<th></th>
<th>CNT</th>
<th>Effective fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diameter</strong></td>
<td>13–18 nm (datasheet)</td>
<td>15.5 nm (armchair, n=114)</td>
</tr>
<tr>
<td><strong>Number of walls</strong></td>
<td>18 walls (determined using the inner diameter of 4 nm from the datasheet)</td>
<td>solid cylinder</td>
</tr>
<tr>
<td><strong>Length</strong></td>
<td>3–30 µm (datasheet)</td>
<td>911.87 nm</td>
</tr>
<tr>
<td><strong>CNT wavelength</strong></td>
<td>802 nm</td>
<td>800 nm</td>
</tr>
<tr>
<td><strong>CNT amplitude</strong></td>
<td>103 nm</td>
<td>100 nm</td>
</tr>
<tr>
<td><strong>CNT shape</strong></td>
<td>arbitrary</td>
<td>sinusoidal</td>
</tr>
</tbody>
</table>

A diameter of 15.5 nm was chosen for the effective fibre which lies in the centre of the range mentioned in the datasheet. The inner diameter of 4 nm in combination with the interlayer distance of 0.34 nm provides a wall number of 18, which was used for the calculation of the transversely isotropic material properties. The amplitude and wavelength were determined from SEM micrographs of CNTs in powder form. Those values were assumed not to change significantly when incorporating the CNT into the epoxy matrix. However, it must be mentioned that the determination of amplitude and wavelength is a delicate task because CNT shape in reality is arbitrary and does not follow a sinusoidal curve. A considerable number of 74 CNTs were, therefore, used to determine the mean of amplitude and wavelength. The length used for the calculation of the transversely isotropic properties and the length of the effective fibre was set to 911.87 nm. This value is substantially lower than the values provided in the datasheet. This can be justified though investigation of SEM micrographs as shown in Fig. 6.16.
CNTs tend to be entangled in powder form and the axis, along which the CNT is oscillating due to some arbitrary waviness, is changing orientation dramatically. From SEM micrographs it was observed that the orientation change occurs on average after around one wavelength (800 nm) with axes that are spanning an angle of $90^\circ$–$180^\circ$. Hence a reduced CNT length that is exhibited by a one wavelength CNT was deemed to be a reasonable assumption. This assumption addresses two important aspects. First it prevents overprediction of the load carrying capability due to an accurate effective CNT length, i.e. the length of the path the CNT is oscillating along. Secondly, the jamming limit of the acceptance-rejection algorithm is increased up to values that show significant effects on the mechanical behaviour of the material and, thus, can in general be compared with experimental studies.

The transversely isotropic elastic properties of the effective fibre were calculated from Eqs. (4.15)–(4.21) and (4.28)–(4.36) by applying described earlier replacement method. For that purpose, each wall of the MWCNT was assumed
to exhibit an armchair structure. Furthermore, by using the equations of Shen and Li (2004, 2005), the properties of the effective fibre were calculated assuming perfectly straight CNTs. The CNT wavelength was used as input for the CNT length. Then, the properties were applied within local coordinate systems along the wavy CNT axis. The results are shown in following Table 6.3:

<table>
<thead>
<tr>
<th>Table 6.3 Molecular mechanics results for HDPlas™</th>
<th>Effective fibre (wavy)</th>
<th>Effective fibre (straight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal modulus ( E^{\text{tension}}<em>{33} / E^{\text{compression}}</em>{33} ) [GPa]</td>
<td>687.21/1051.1</td>
<td>713.18/1051.1</td>
</tr>
<tr>
<td>Major Poisson’s ratio ( v^{\text{tension}}<em>{31} / v^{\text{compression}}</em>{31} )</td>
<td>0.12807/0.13686</td>
<td>0.12900/0.13686</td>
</tr>
<tr>
<td>Longitudinal shear modulus ( G_{31} ) [GPa]</td>
<td>204.71</td>
<td>208.77</td>
</tr>
<tr>
<td>In-plane bulk modulus ( K_{12} ) [GPa]</td>
<td>112.11</td>
<td>112.11</td>
</tr>
<tr>
<td>In-plane shear modulus ( G_{12} ) [GPa]</td>
<td>2.0256</td>
<td>2.0256</td>
</tr>
</tbody>
</table>

In ABAQUS, one can define an orthotropic material using the linear elastic engineering constants \( E_{11}, E_{22}, E_{33}, v_{12}, v_{13}, v_{23}, G_{12}, G_{13}, \) and \( G_{23} \). The application of a longitudinal modulus and major Poisson’s ratio in both, compression and tension, however, requires the formulation of a user-defined material (constitutive) model. For convenience, it was assumed that response in tension and compression are equal and, thus, values of longitudinal modulus and Poisson’s ratio in tension were used in simulations. This particular choice was made because it was expected that random CNT orientations lead to CNTs being subjected to mixed (tension and compression) loading conditions, and that a uniform end displacement condition employed to derive the equations in compression may be considered unjustifiable in case of wavy CNTs for which local compression and primarily bending deformation is expected to be...
dominant under compressive loading of the nanocomposite. However, it has to be mentioned that for the CNT under tensile loading, which is applied to the outer wall, the loading of the inner walls through interwall shear stress transfer is accounted for by the effective fibre concept. In the case of localised tensile deformations, which can be especially present for wavy CNTs, the stress transfer length can be significant smaller than the full CNT length, which leads to an overprediction of the CNT stress.

From Eqs. (4.9) and (4.14) one can follow that for transversely isotropic material $G_{11} = G_{13} = G_{23}$ and $G_{12} = G_{21}$. In order to determine the missing linear elastic engineering constants, the following relations for isotropic materials were used (Bower 2011):

$$E_{11} = E_{22} = \frac{9K_{12}G_{12}}{3K_{12} + G_{12}} \quad \text{and} \quad \nu_{12} = \frac{3K_{12} - 2G_{12}}{6K_{12} + 2G_{12}},$$

(6.1)

and the symmetry of the compliance matrix (cf. Eq. (4.9)) was utilised to calculate the remnant Poisson’s ratios based on Eq. (4.12):

$$\nu_{23} = \nu_{13} = \frac{\nu_{11}}{E_{33}} E_{11}.$$  

(6.2)

As a result the complete set of engineering constants $E_{11}$, $E_{22}$, $E_{33}$, $\nu_{12}$, $\nu_{13}$, $\nu_{23}$, $G_{12}$, $G_{13}$, and $G_{23}$ is given as 6.04 GPa, 6.04 GPa, 687.21 GPa, 0.49102, 0.00113, 0.00113, 2.03 GPa, 204.71 GPa and 204.71 GPa (6.04 GPa, 6.04 GPa, 713.18 GPa, 0.49102, 0.00109, 0.00109, 2.03 GPa, 208.77 GPa and 208.77 GPa for straight effective fibres).

In order to account for different CNT surface treatments the model contained cohesive zone interface (with the thickness equal to 2 angstrom) between the lateral surface of effective fibre and epoxy matrix. Two extreme cases of surface treatment were considered: imperfect interfacial bonding and perfect bonding, to compare the model with experimental data. In the first case, the cohesive
zone parameters were chosen to capture secondary vdWs bonding with a sliding-like behaviour (see Section 4.4). For the second case, perfect bonding was modelled using the cohesive zone concept with its parameters associated with the linear elastic properties of the epoxy matrix. Interfacial damage was prevented throughout the simulation by setting interfacial strength artificially high. Such a formulation of the cohesive zone was shown to provide for an RVE the same macroscopic stress-strain response as an RVE modelled without the cohesive zone. The complete set of cohesive zone parameters is shown in Table 6.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Perfect bonding</th>
<th>Imperfect bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 1 stiffness $K_m$ [Pa/Å]</td>
<td>1.23761e+09</td>
<td>1.23761e+09</td>
</tr>
<tr>
<td>Mode 2/3 stiffness $K_s$, $K_t$ [Pa/Å]</td>
<td>4.3500e+08</td>
<td>1.20e+06</td>
</tr>
<tr>
<td>Strength $S$ (All modes) [Pa]</td>
<td>1.0e+12</td>
<td>2.7e+06</td>
</tr>
<tr>
<td>Damage evolution displacement $D_e$ [nm]</td>
<td>9119</td>
<td>9119</td>
</tr>
</tbody>
</table>

Damage evolution displacement $D_e$ corresponds to the failure displacement subtracted by the damage initiation displacement.

The CNT volume fraction $VF$ was calculated from the mass fraction using a rule of mixtures for two immiscible components,

$$VF = \frac{MF / \rho_{CNT}}{MF / \rho_{CNT} + (1 - MF) / \rho_P},$$

based on the densities of CNTs $\rho_{CNT}$ and the polymer $\rho_P$ (see Table 6.5) and the CNT mass fraction $MF$ used in experiments.

The effective fibre density of CNTs $\rho_{CNT}$ was calculated as homogenised density of a tubular CNT and a hollow space within, where the density of the tubular CNT wall was associated with that of graphite $\rho_G = 2.2$ g/cm³ (cf. Anthony et al. 1990). Thus, the effective CNT fibre density was calculated as

$$\rho_{CNT} = \rho_G \frac{r_{in}^2 - r_{os}^2}{r_{in}^2},$$

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where $r_o$ and $r_i$ are the radii of the outer shell and inner shell, respectively. As a result, CNT mass fractions of 0.3%, 0.6% and 0.9% correspond approximately to CNT volume fractions of 0.166%, 0.333% and 0.500%.

The original model parameters obtained for the standard bisphenol A resin epoxy resin reported in Table 1 of Buckley et al. (2004) did not provide a satisfactorily agreement with the current experimental data for Epon 828/Jeffamine T403 epoxy using the solvent method. Therefore, some model parameters were modified according to the current experimental data and they are listed in Table 6.5. Values of the remaining model parameters were used as in the work of Buckley et al. (2004).

### Table 6.5
Constitutive model parameters obtained by comparison to experimental stress-strain data of pure epoxy prepared using the solvent method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Epon 828 / Jeffamine T403</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear modulus $G$ [GPa]</td>
<td>0.87e+9</td>
</tr>
<tr>
<td>Bulk modulus $K$ [GPa]</td>
<td>3.078e+9</td>
</tr>
<tr>
<td>Glass transition temperature $T_g$ [K]</td>
<td>363*</td>
</tr>
<tr>
<td>Density $\rho$ [kg m$^{-3}$]</td>
<td>1140*</td>
</tr>
<tr>
<td>Density of crosslinks $N_c$ [m$^{-3}$]</td>
<td>5.7e+27</td>
</tr>
<tr>
<td>Inextensibility factor of network $\alpha$</td>
<td>0.297</td>
</tr>
<tr>
<td>Final fictive temperature $T_{\sigma\infty}$ [K]</td>
<td>372</td>
</tr>
<tr>
<td>Linear viscoelastic relaxation time $\tau_0$ [s]</td>
<td>2.02e+6</td>
</tr>
<tr>
<td>Rejuvenation strain range $\varepsilon_0^*$</td>
<td>0.339</td>
</tr>
</tbody>
</table>

* Parameters obtained by inference from data with similar materials.

### 6.6. Modelling results and discussion

The comparison between experimental data and the model predictions is addressed in this section. The computational model was validated under quasi-static strain rates and then used to elucidate the effect of CNT mass fraction and the effect of epoxy-CNT interface bonding on the finite strain compressive response of the nanocomposite. Premature termination of the simulation (due to singular behaviour of epoxy model at large strains—see Chapter 5) restricted
the computational study to the evaluation of the macroscopic behaviour up to
the yield peak stress in the case of imperfect bonding, and prior to the onset of
strain softening-strain hardening for the case of perfect bonding. In order to
give an insight into the effect of CNT waviness, RVEs comprising of straight
CNTs were investigated additionally. Both cases, imperfect bonding based on
vdWs interaction and perfect bonding, were considered for those straight
CNTs.

6.6.1. Stress-strain behaviour

The predicted effect of CNT mass fraction on the normalised nanocomposite
Young’s modulus is shown in Fig. 6.17, and compared with experimental
results. The same procedure as for the experimental stress-strain curves was
used to evaluate the Young’s modulus. With increasing CNT mass fraction, the
statistical scatter/ensemble standard deviations in general increased due to the
increasing influence of the randomised CNT morphology with variations in
CNT-to-CNT distances, CNT-to-CNT interactions and matrix-to-CNT stress
transfer. In order to counteract this, the ensemble size was increased for the case
of vdWs bonding, i.e. 3, 4 and 5 RVEs were used for a CNT mass fraction of
0.3%, 0.6% and 0.9%, respectively. In case of perfect bonding, 9, 6 and 6 RVEs
were investigated for a CNT mass fraction of 0.3%, 0.6% and 0.9%, respectively.
Figure 6.17: Effect of CNT mass fraction on normalised nanocomposite Young’s modulus; results obtained from RVEs comprising wavy CNTs, error bars show standard error of the mean.

Increase in CNT mass fraction led to an increase in nanocomposite Young’s modulus for both, perfectly-bonded CNTs and CNTs interacting with the polymer through vdWs forces. In both cases, and within the investigated range of CNT mass fraction, an approximately linear relation between CNT mass fraction and Young’s modulus was obtained. The lack of the perfect linearity resulted from statistical scatter obtained for reconstructed RVE morphologies. Hence, a small preferred orientation of CNTs within an RVE can slightly disturb the output as it was found for the perfectly-bonded model with 0.6 mass% of CNTs (see Figs. 6.17 and 6.18).

To quantify if the preferred orientation exists for a given mass fraction, volume averaging over all CNT orientations was carried out. The study of the preferred average orientation of CNTs requires in general a three-dimensional consideration. However, following the work of Fu and Lauke (1996) (here the CNTs instead of short fibres), only a single angle was used to relate the average CNT orientation within the RVEs to the average Young’s modulus (instead of
the strength (Fu and Lauke 1996)) in the loading direction. For that, the angle $\beta$ between the loading direction $x$ and the average vector $\bar{v}$ of the CNT phase (see Fig. 6.18) was calculated. The latter was obtained by volume-averaging of the vector $v$, which is associated with a CNT axis and defined in terms of direction cosines $k_{3x}$, $k_{3y}$ and $k_{3z}$ — these direction cosines relate the local orientation of a CNT in its axial direction (3-3) and axes $x$, $y$ and $z$ of the global coordinate system. The direction cosines $k_{3x}$, $k_{3y}$ and $k_{3z}$ are the components (row 3, columns 1-3) of the direction cosine matrix (3x3) available in ABAQUS using the member \textit{localCoordSystem} of a field value object that is stored as tensor with respect to a local coordinate system. The complete set of equations involved in the calculation of angle $\beta$ is given as

$$
\beta = \arccos \left( \frac{k_{3x}}{|\bar{v}|} \right) \quad \text{with} \quad \bar{v} = \begin{pmatrix} k_{3x} \\ k_{3y} \\ k_{3z} \end{pmatrix} = \frac{1}{V_{\text{CNT}}} \int v \, dV_{\text{CNT}} \quad \text{and} \quad v = \begin{pmatrix} k_{3x} \\ k_{3y} \\ k_{3z} \end{pmatrix},
$$

(6.5)

where $k_{3x} = e_3 \cdot e_x = |e_x| e_x \cos (\beta_i^{3x})$ (and analogically for $k_{3y}$ and $k_{3z}$), while $e_3$ and $e_x$ are the unit vectors associated with 3-axis and x-axis (see Fig. 6.18), respectively, and $\beta_i^{3x}$ is the angle between axis 3 and $x$ at the i-th integration point within a given CNT. Then, $V_{\text{CNT}}$ in Eq. (6.5) denotes the volume of the CNT phase. Absolute values ($|v|$) of the components of the local orientation vectors were used here to consider the average orientation in the range from 0 to $\pi/2$. In the case of random CNT orientation and for RVE sizes (and, thus, CNT numbers) tending to infinity, one can assume that $|k_{3x}| = |k_{3y}| = |k_{3z}|$ holds, which in turn gives $\beta = \arccos \left( 1/\sqrt{3} \right) \approx 54.74^\circ$. In Fig. 6.18, one can see the distribution of $\beta$ obtained by evaluating Eq. (6.5), from which the arithmetic mean of $\beta$ was found as equal to $\beta_m = 54.12^\circ$, $51.13^\circ$ and $53.26^\circ$ for 0.3%, 0.6% and 0.9% CNT mass fraction, respectively. The reconstructed RVEs contained
CNTs with a preferred orientation for the intermediate mass fraction and, thus, affected slightly the linear relationship between the Young’s modulus and mass fractions (see Fig. 6.17). As one can see from Fig. 6.18, there is an increased fraction of CNTs aligned towards the loading direction for the case of 0.6 mass% CNTs when compared to the other CNT mass fractions as indicated by the concentration on the left side of the distribution.

As a result, the CNT phase carried higher stresses as shown in Fig. 6.19, where the averaged stress within the CNT and matrix components, and the nanocomposite are plotted as a function of applied true strain. In general, an increase in CNT mass fraction resulted in a decrease in stress within the matrix phase. In contrast, when neglecting the previously mentioned case with a slightly preferred orientation towards the loading axis, the average stresses within the CNT phase experienced hardly any changes. VdWs interactions significantly reduce the stress transfer efficiency and, therefore, reduced the

Figure 6.18: Distribution of $\beta$ obtained for RVEs of various mass fractions for perfectly-bonded CNTs (left), length of each bar shows the number of RVEs (hence the total number of RVEs is 9, 6, and 6 for MF=0.3%, 0.6% and 0.9%, respectively), the arithmetic mean of $\beta$ was computed to be 54.12°, 51.13° and 53.26° for 0.3%, 0.6% and 0.9% CNT mass fraction respectively; location of angle $\beta$ is shown on the right.
average stress within the CNT phase by half. The average matrix stresses exceed the stresses of pure epoxy only in the softening regime.

**Figure 6.19:** Averaged stress-strain response of CNT phase (dashed lines), matrix phase (dotted lines), and nanocomposite (continuous lines) obtained from RVEs comprising wavy CNTs.

A zoom into Fig. 6.19 is provided by Fig. 6.20.
VdWs interaction limits the reinforcement efficiency considerably as shown in Fig. 6.17 in terms of normalised Young’s modulus. In general, the simulation results suggest that a three-fold increase in Young’s modulus can be achieved through modification of the interface properties from imperfect (vdWs bonding) to perfect bonding. The computational models predicted an enhancement of the Young’s modulus of around 9% for 0.9 mass% of CNTs, perfectly-bonded to the epoxy matrix. In comparison, the computational study predicted a slight increase (i.e. below 3%) in the case of imperfect bonding.

Young’s modulus predictions by the model with perfect bonding is closer to the experimental results of CNT mass fraction of 0.3% (functionalised CNTs, solvent preparation), as compared with the corresponding case of imperfect bonding. It suggests that the actual interfacial shear strength of CNT-polymer bond is larger than assumed by the imperfect bonding case based on vdWs
interaction. The model with imperfect bonding underpredicted the experimental results. The models predicted an increase of 3% (perfect bonding) and an increase of 1% (vdWs interactions), as compared with 2.3% increase found experimentally.

The effect of CNT mass fraction on normalised nanocomposite yield peak stress is shown in Fig. 6.21.

![Figure 6.21: Effect of CNT mass fraction on normalised nanocomposite yield peak stress; results obtained from RVEs comprising wavy CNTs, error bars show standard error of the mean.](image)

The computational study predicted that an increased CNT mass fraction leads to increased nanocomposite yield peak. However, when compared to the increase in Young’s modulus, the effect of CNT mass fraction on yield peak stress has only half the magnitude (~1.015 versus ~1.03 for perfect bonding and 0.3 mass% of CNTs). Additionally, an interesting effect was observed—the relation between CNT mass fraction and normalised yield peak stress is non-linear with an approximate linear behaviour up to MF=0.6%, further increase in CNT mass fractions resulted in a less pronounced increase in nanocomposite yield peak stress, especially for the case of vdWs interactions. It is believed that
the reason for that is the average stress reduction in the matrix phase (see Figs. 6.19 and 6.20), caused by a drop in the averaged hydrostatic stress of the matrix phase with increasing CNT mass fraction (see Fig. 6.22). This reduction of hydrostatic stress in the matrix counteracted the increase in stress related to the increase in the CNT mass fraction. While the averaged matrix peak stresses of the bond-stretching part of the model decreased approximately linearly with increasing CNT mass fraction, the averaged hydrostatic peak stress was found to decrease non-linearly with the CNT loading (see Fig. 6.22). This led to a non-linear decrease of the average peak stress (total Cauchy stress) within the matrix phase, and hence it is believed that this finally resulted in the non-linear trend of the nanocomposite yield peak stress with CNT loading, as shown in Fig. 6.21.

This effect can be attributed to the waviness of CNTs, as it was found earlier (see Chapter 5)—i.e. for RVEs containing randomly oriented and distributed
straight CNTs, the yield peak stress increases linearly with increasing CNT volume fraction and the hydrostatic stress of the matrix phase is increased when compared to pure epoxy. Similarly, in this chapter, straight CNTs led to an increase in averaged matrix hydrostatic stress (see Fig. 6.23). Thus, a direct comparison of averaged stresses within the different phases of nanocomposites made of straight CNTs versus wavy CNTs is provided in Fig. 6.23.

Material expansion in the lateral directions (as a result of macroscopic compression) can effectively be reduced by a network of straight CNTs but not for wavy CNTs. Straight CNTs oriented in the lateral directions will carry a higher load due to an efficient shear stress transfer and counteract the lateral expansion, which finally leads to an enhanced stress state within the matrix phase (see Fig. 6.23). Wavy CNTs, however, experience a lower stress transfer, and they need to be straightened before their axial modulus can be exploited to the full. Prior to this straightening, the local bending deformation of the CNT occurs under small load, which increases the effective CNT length, i.e. the
length of the end-to-end segment. This is believed to facilitate the lateral expansion that leads to a reduction of the average hydrostatic stress as shown in Fig. 6.22 and to a reduced stress state within the matrix phase (see Fig. 6.23). They will provide an enhanced stress state at later stages of applied strain—see the averaged matrix response in Fig. 6.19, which exceeds the stress response of pure epoxy at larger stages of applied strain.

As in the case of Young’s modulus, changing the assumption from perfect bonding to imperfect bonding based on vdWs interactions led to a considerable property reduction for the yield peak stress. The computational models predicted an enhancement of the yield peak stress around 3% for 0.6 mass% of CNTs perfectly-bonded to the epoxy matrix. In contrast, the computational study predicted a relative increase of around 1% for the case of imperfect bonding at the same mass fraction. The experimental result for the normalised nanocomposite yield peak fell between model predictions for perfect and imperfect bonding. Models predicted an increase of around 0.5% (imperfect bonding) and 1.5% (perfect bonding) of the nanocomposite yield peak stress, in comparison with 1% increase found by experiments.

For both, nanocomposite Young’s modulus and yield peak stress, it was found that the experimentally obtained increase of 2.3% in Young’s modulus and 1.1% in yield peak stress could be approximately predicted by using the cohesive zone parameters in Table 6.6 with an interfacial shear strength of 30 MPa. RVEs with such an interfacial shear strength value predicted a 2% increase in Young’s modulus and a 1% increase in yield peak stress.
Table 6.6 Cohesive zone parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Imperfect bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 1 stiffness $K_{nn}$ [Pa/Å]</td>
<td>1.23761e+09</td>
</tr>
<tr>
<td>Mode 2/3 stiffness $K_{ss}, K_{tt}$ [Pa/Å]</td>
<td>1.33e+07</td>
</tr>
<tr>
<td>Strength $S$ (All modes) [Pa]</td>
<td>3.0e+07</td>
</tr>
<tr>
<td>Damage evolution displacement $D_e$ [nm]</td>
<td>9119</td>
</tr>
</tbody>
</table>

Fig. 6.24 shows the averaged computational predictions and averaged experimental stress-strain response for the pure epoxy and nanocomposites. Computational predictions are only shown for the perfect bonding case as the post-yield response for the imperfect bonding could not be examined due to premature termination of simulations. The predicted Young’s modulus and yield peak stress are relatively close to the experimental data as shown previously. However, the stresses within the softening regime (beyond 10% of true strain) were overpredicted. Possible reasons are the assumption of perfect bonding applied to the computational model and the inaccurate prediction of the softening by the epoxy model. Perfect bonding keeps the stress transfer relatively high throughout the full strain range. In reality however, one can expect that bonds between CNT and epoxy resin can change/break at larger strains and the stress transfer can reduce, and the interactions between epoxy and CNTs can change to the sliding-like behaviour (with friction and vdWs interactions). Then, for a smaller stress-transfer efficiency due to vdWs interaction, a real sample is then believed to change its stress-strain response at larger applied strains towards the behaviour of pure epoxy. Furthermore, one can see that the true strain value, at which the yield peak occurs, is captured inaccurately by the computational model. This may be attributed to the single relaxation time approximation for the real multi-mode response in the constitutive model for pure epoxy. The implementation of a relaxation spectrum is believed to provide a more accurate fit to the pre-yield part of experimental stress-strain curves as shown in Wu and Buckley (2004). Additionally, it may improve the predictions in the softening regime because...
the structural evolution/rejuvenation is incorporated in the relaxation time parameter. However, that multi-mode approach is computationally more expensive.

**Figure 6.24:** Portion of the average non-linear stress-strain response, model predictions for wavy CNTs and experimental results.

### 6.6.2. Effect of CNT waviness and effect of van der Waals forces

Besides agglomeration, waviness and imperfect epoxy-CNT bonding are considered as main factors limiting the reinforcement capabilities of CNTs within nanocomposites. Thus, the effects of waviness and vdWs interaction on the nanocomposite Young’s modulus and yield peak stress were studied for a CNT mass fraction of 0.6%, and compared with the case of straight and perfectly-bonded CNTs, respectively.

Fig. 6.25 shows the effects of vdWs interaction on nanocomposite Young’s modulus and yield peak stress—the results are normalised with respect to corresponding quantities for perfectly-bonded CNTs. The effect of imperfect bonding based on vdWs interaction has the greater magnitude when compared
to the effect of CNT waviness, which is discussed below. Of the two factors limiting the reinforcement efficiency of CNTs (i.e. imperfect interface bonding and waviness), vdWs interaction was found to have the most detrimental effect on nanocomposite Young’s modulus. For RVEs containing wavy CNTs, the Young’s modulus was reduced by 4.5% and for the case of straight CNTs by 7.5%, due to vdWs interaction. Interestingly, vdWs interaction did not affect the yield peak by the same magnitude. The nanocomposite yield peak stress was reduced by 2% for wavy CNTs and by 5% for straight CNTs—a possible reason for that may be the polymer matrix response governing primarily the yield peak behaviour of the nanocomposite, and hence it is less affected by the quality of interface bonding. Therefore, vdWs interaction primarily limited the stress transfer efficiency.

![Figure 6.25: Effect of van der Waals interaction on nanocomposite Young’s modulus (left) and yield peak Cauchy stress (right) for RVEs comprising straight or wavy CNTs.](image)

The effect of CNT waviness is shown in Fig. 6.26—the results are normalised with respect to relevant quantities obtained for straight CNTs. CNT waviness reduced the nanocomposite Young’s modulus by 1.5% for imperfectly-bonded CNTs and by 4% for perfectly-bonded CNTs. It is noteworthy to mention that
the same reductions were obtained, when studying the effect of CNT waviness on the nanocomposite yield peak stress. Waviness limits as well the axial CNT loading by reducing the shear stress transfer, and hence, significantly lower stresses within the CNT phase were obtained for RVEs comprising wavy CNTs (see Fig. 6.23). Moreover, the averaged stress within the CNT phase levelled off prior to the nanocomposite yield strain for wavy CNTs. In contrast, RVEs containing straight CNTs exhibited averaged stresses within the CNT phase that increased beyond the nanocomposite yield peak (see Fig. 6.23). In that case, the efficient stress transfer from the matrix across the perfectly-bonded interface ensures that CNTs carry the load efficiently with increasing deformation. A major effect of CNT waviness was on the total stress state of the matrix. Compared to pure epoxy, straight CNTs increased the averaged matrix stress, while wavy CNTs decreased the averaged matrix stress. Hence, besides the reduced stress transfer efficiency, an additional contribution to the lowered yield peak stresses arises from the reduced total stress state of the matrix. This led finally to an equalised effect on yield peak stress when compared to the effect on Young’s modulus.
Figure 6.26: Effect of CNT waviness on nanocomposite Young’s modulus (left) and yield peak Cauchy stress (right) for RVEs comprising CNTs perfectly-bonded to the epoxy matrix or imperfectly-bonded based on van der Waals interaction.
Chapter 7

Conclusions and Outlook

7.1. Concluding remarks

7.1.1. Prediction of energy absorption characteristics of aligned epoxy/carbon nanotube composites

Computational studies presented in Chapter 3 were performed to investigate the potential of aligned epoxy/CNT nanocomposites towards structural energy absorption applications such as impact-resistant coatings for advanced composite laminates. In particular, two case studies were investigated: (1) crack resistance of the epoxy/CNT nanocomposites with aligned double-walled CNTs (DWCNTs) in the vicinity of a matrix crack, and (2) rate-dependent compressive response of epoxy/CNT systems with aligned single-walled CNTs (SWCNTs). The results of those studies are summarized as follows:

(1) The fracture parameter (total energy release rate) of a stationary matrix crack can be significantly reduced due to the presence of CNTs in the epoxy matrix. The value of that fracture parameter depends on the mechanical properties of CNT-epoxy and CNT-CNT interfaces such as shear strength, shear stiffness and fracture energy. Whereas the shear stiffness significantly reduced the fracture parameter at early stages of applied strain, the interface shear strength and fracture energy contributed to its reduction at larger applied strains. Premature nanocomposite failure due to the existence of matrix cracks can, therefore, be prevented through relevant functionalisations. In particular, the reinforcement of epoxy with CNTs can reduce the crack driving force and promote larger
strains to failure while progressive damage at the CNT-epoxy interface takes place. This might be achieved through enhancements of shear stiffness, shear strength and mode II fracture energy of CNT-epoxy interfaces via CNT functionalisation, and minor increases of low sp³-bond densities in the interwall phase of DWCNTs.

(2) The compressive behaviour of epoxies can be significantly affected by the presence of CNTs at different loading rates (from static to impact). In particular, the initial stiffness and post-yield behaviour of nanocomposites were influenced considerably by CNT volume fraction and aspect ratio. In both cases, increased volume fraction and aspect ratio caused increased strain stiffening. This increased the area under the stress-strain curves, which suggests that energy absorption in compression can be improved by addition of CNTs. The energy absorption characteristics evaluated from the stress-strain curves increased with increasing CNT volume fraction and CNT aspect ratio, both for static and impact rates. Additionally, a combined effect of CNT aspect ratio and CNT volume fraction on energy absorption characteristics was found. This suggests that the average aspect ratio of CNTs should be carefully selected in order to maximize the energy absorption by increasing the CNT volume fraction.

It must be mentioned that this initial modelling approach assumed an idealised nanocomposite morphology containing straight and perfectly bonded CNTs. All this is believed to overpredict the energy absorption capabilities of epoxy/CNT nanocomposites under compressive loading. Therefore, further modelling within this thesis focussed on the finite strain compressive response of epoxy/CNT nanocomposites using more realistic nanocomposite morphologies (e.g. with misaligned and wavy CNTs) and imperfect bonding.
7.1.2. Prediction of finite strain compressive behaviour of epoxy/CNT nanocomposites: 2D versus 3D RVE-based modelling

RVE-based modelling of aligned and misaligned (with random orientations) morphologies of randomly distributed CNTs in an epoxy matrix was carried out in Chapter 5 to investigate the compressive nonlinear, rate-dependent, finite strain response of CNT/epoxy nanocomposites. A particular goal of this work was to compare the 2D RVE-based approach against the 3D RVE-approach to study its accuracy in capturing the behaviour of the nanocomposite and their computational efficiency.

Relatively large differences between predictions of the nonlinear compressive response were obtained from the 2D and the 3D modelling approach. In general, the 2D RVE approach suffers from a lack of inter-particle interaction due to a larger average CNT to CNT distance and the smaller surface area available for the stress transfer from the matrix to CNTs, when compared to their 3D counterparts. As a consequence: (1) the 2D RVE expanded easier in the lateral direction which resulted in an inaccurate prediction of the average hydrostatic stress in the matrix, and (2) the average CNT stress in 2D RVEs was found to be significantly smaller than for 3D RVEs. The larger surface area in 3D RVEs promotes more stress to be transferred into CNTs, which better exploits their mechanical properties. Additionally, in 2D RVEs the averaged stress-applied strain response of CNTs resembled that of the pure matrix. In contrast, a smaller CNT to CNT distance in 3D RVEs increased inter-particle interaction, which resulted in an increase of the averaged stress in the CNT component during the strain softening phase of the matrix.

As a result, the 2D RVEs underestimated the effect of the morphological factors (CNT aspect ratio, CNT volume fraction and CNT orientation) on the salient
parameters of stress-strain curves. In particular, the yield peak stress was found to be nearly unaffected by the presence of CNTs and various changes of the morphological factors in the 2D case. In contrast, 3D models predicted significant effects of morphological factors on the yield peak stress. Therefore, despite obvious demands on substantial computational resources (approximately a 70-fold increase in computational time for 3D models), it is nevertheless advisable to use 3D RVEs for accurate prediction of the nanocomposite response.

The 3D modelling approach predicted that incorporation of CNTs into the epoxy matrix leads to an enhancement of the nonlinear deformation that results in: (1) the increase of yield stress with the CNT aspect ratio, CNT volume fraction and CNT alignment, (2) the change from softening to hardening with the CNT alignment, and (3) the shift of the onset of the strain hardening regime to smaller stages of strain with the CNT aspect ratio and the CNT volume fraction. The CNT alignment was found to have the most significant enhancement effect, especially at high strain rates, which highlights the reinforcement potential of CNTs for impact-resistant applications.

Some of the predicted stress-strain trends obtained in this work were qualitatively compared with the available experimental data from the literature. Similarly to the predictions using 3D RVE-based models with aligned CNTs, those experimental results show an increase in Young’s modulus and yield peak, and a shift of yield peak to larger values of strain for the CNT/epoxy systems compared to pure epoxy (Dassios et al. 2012).
7.1.3. Model validation and effects of CNT waviness and van der Waals bonding on the compressive behaviour of epoxy/CNT nanocomposites

A more holistic 3D computational approach has been developed and reported in Chapter 6. The model accounts for different degree of bonding at the epoxy/CNT interface by considering two limiting cases: van der Waals and perfect bonding. It also takes CNT waviness into consideration. The model was validated with the results of experimental programme carried out for a range of epoxy/CNT nanocomposites subjected to quasi-static uniaxial compression. Generally, the model predicted well the nanocomposite response with functionalised CNTs in terms of experimental Young’s modulus and yield peak stress. It was found that the cohesive zone parameters based on van der Waals interaction provide a relatively accurate prediction of Young’s modulus and yield peak stress, when the interfacial shear strength is increased to 30 MPa.

After validation with experiments, the model was used to predict the effects of CNT mass fraction, waviness and imperfect bonding on the compressive response of the nanocomposite. The computational model predicts a linear increase of the nanocomposite Young’s modulus with increasing CNT mass fraction. The yield peak stress, however, exhibits a non-linear behaviour and was found to saturate for the case of van der Waals bonding at higher mass fractions. This non-linear behaviour is believed to originate from the CNT waviness, which was shown to have a direct effect on the averaged stress within the matrix phase. When compared to the behaviour of pure epoxy, at the nanocomposite yield peak, those averaged stresses decrease non-linearly with increasing CNT mass fraction. This counteracts the increase in stress related to the increase in the CNT mass fraction, which finally results in the non-linear behaviour of the yield peak stress. Under a relatively small load, wavy CNTs oriented in the lateral directions will experience local bending deformation,
which can then lead to CNT straightening and, thus, a significant increase in the effective length of the CNT. This is believed to facilitate the lateral expansion of the RVE (and, thus, of the nanocomposite) that leads to a reduction of the hydrostatic stress and, therefore, to a reduced total stress state within the matrix phase. An enhanced stress state within the matrix is obtained at later stages of strain. In contrast, straight CNTs provide an increased averaged stress within the matrix phase, right from the beginning of the deformation, possibly due to an increase in hydrostatic stress of the matrix phase. This coincides with the findings of the previous chapter for straight CNTs, where additionally a linear relation between yield peak stress and CNT volume fraction was found. Hence, straight CNTs counteract the lateral expansion, which manifests in an increased averaged hydrostatic stress and Cauchy stress within the matrix phase.

At larger strains and within the post-yield regime, the model with perfectly-bonded CNT-epoxy interface and experimental results deviate increasingly, which may be caused by bond breaking at the epoxy/CNT interface, or by the epoxy constitutive model due to the single relaxation time approximation. Premature termination of the analysis with models with imperfectly-bonded CNT-epoxy interface did not allow studying the post-yield behaviour of the nanocomposite—however, it is believed that the predictions of the model with imperfectly-bonded interface would shift towards the experimental results within this regime.

Altogether, a relatively weak effect of CNT incorporation and CNT mass fraction on the mechanical properties was found by experiments. The computational model captured well both quantitatively and qualitatively that weak reinforcement effect of CNTs. This was possible by accounting for the CNT waviness and by varying the bonding degree of the epoxy/CNT interface. Both factors were shown to cause a significant reduction in the nanocomposite
Young’s modulus and yield peak stress. Van der Waals interaction was found to have the most detrimental effect on nanocomposite Young’s modulus.

In terms of energy absorption capabilities, the modelling results suggest to use defect-free and straight CNTs, well-bonded to the epoxy matrix—this combination is expected to lead to a linear relation between CNT mass fraction and yield peak stress. Additionally, straight CNTs are expected to lead to an enhanced hydrostatic stress state within the matrix material and, thus, are believed to lead to an early nanocomposite hardening. Furthermore, those CNTs can effectively increase their stress-load after nanocomposite yield. It is, however, not clear, whether those defect-free CNTs remain straight when embedded in the polymer.

7.2. Outlook

7.2.1. Enhancement of the constitutive model for the epoxy matrix

Premature termination of FE analyses limited the study of the finite strain compressive behaviour of epoxy/CNT nanocomposites to relatively small values of applied true strain (approximately 4%–25%). This was caused by the excessive magnitude of local stresses in the matrix (in the vicinity of CNTs) resulting from the enhanced nonlinear hyperelastic response of the epoxy constitutive model, which captures the strain hardening behaviour. Local stresses rose rapidly with a small increase of strains, leading to convergence problems in the numerical solution. A more robust constitutive tangent may provide improvements, however, as local stresses predicted for the epoxy matrix become large at finite strains (i.e. in the strain-hardening regime), a damage/failure initiation criterion should be considered in future work. A simple isotropic criterion, can involve the comparison of local principle stresses
with the compressive strength of pure epoxy. However, Fig. 6.12 suggests that shear deformations at sample fracture surfaces are dominant. Hence, a more advanced continuum damage model that accounts for shear stresses can be required. Moreover, strain rate and hydrostatic stress effects should also be considered to formulate and implement a more general continuum failure criterion. Special attention would need to be focussed on the numerical implementation of the model, to avoid mesh dependency when using the failure criterion to predict damage evolution and ultimate failure of the nanocomposite. Such a constitutive model that accounts for epoxy damage will further enable capturing of the ultimate strength of the nanocomposite and, thus, enable the validation of the absorbed energy prior to nanocomposite failure.

The inaccurate capturing of the true strain at yield can be attributed to the single relaxation time approximation for the real multi-mode response in the constitutive model for pure epoxy. The implementation of a relaxation spectrum into the constitutive model of the epoxy matrix is believed to provide a more accurate fit to the pre-yield part as well as the true strain at yield of experimental stress-strain curves (Wu and Buckley 2004). Furthermore, improvements of the predictions in the softening regime can be expected, because the structural evolution/rejuvenation is incorporated in the relaxation time parameter.

7.2.2. Enhancement of the modelling approach

The modelling approach pursued in this work considered imperfections such as imperfect epoxy-CNT bonding, CNT waviness, non-uniform CNT distribution and random CNT orientation. An additional factor limiting the reinforcement capabilities of epoxy/CNT nanocomposites at higher CNT volume fractions is the CNTs’ tendency to form agglomerations. Future modelling approaches
should, therefore, include CNT agglomerations. It is, however, hardly feasible to incorporate CNT agglomerations of the size of several micrometres directly into the mesoscale RVE due to its substantial computational effort. Hence, an additional scale needs to be addressed and incorporated into the hierarchical multiscale modelling approach. Homogenised stress-strain behaviour obtained so far from RVEs of varying CNT mass fractions can be used as input (UMAT subroutine) for this agglomeration scale, which might as well employ the RVE concept. Realistic agglomeration morphologies might be obtained by using intersecting spherical inclusions, which, however, correspond to a homogenised epoxy/CNT phase of large CNT mass fraction. The matrix, similarly, represents then a homogenised epoxy/CNT phase of small CNT mass fraction. The macroscopic material behaviour on the account of CNT agglomerations can then be extracted from those RVEs.

Another possible improvement within the modelling scheme addresses the CNT waviness currently approximated by a sinusoidal shape. However, CNT waviness seems to be arbitrary and not well captured by an idealised CNT waviness. Hence, an algorithm needs to be developed to build more realistic CNT morphologies with arbitrary waviness. Such an algorithm may further increase the jamming limit due to the variability of the CNT shape.

### 7.2.3. Modelling of impregnated CNT forests

Very promising effects of CNTs on the finite strain compressive behaviour can be expected from impregnated CNT forests (Dassios et al. 2012). Continuous CNTs are aligned in the loading and when compared to nanocomposites of random CNT orientations, significant larger CNT volume fractions can be obtained (cf. 27% CNT volume fraction). The modelling of such impregnated CNT forests would involve the generation of mesoscale RVEs on the account of continuous and wavy carbon nanotubes randomly distributed and aligned in
the RVE loading direction. The prepared PYTHON scripts are already able to
generate such aligned CNT morphologies, however, small modifications are
necessary, in order to account for continuous effective fibres.

7.2.4. Modelling the impact problem for CFRP laminates

The ultimate goal of the future work is the evaluation of CNTs’ capability to
prevent delamination and catastrophic failure in CFRP laminates. Two main
strategies are suggested for further studies: Improving the impact resistance of
CFRP laminates by using epoxy/CNT nanocomposites as (1) surface coatings
applied onto the composite laminate, and/or as (2) matrix material within the
entire CFRP laminate. In those cases explicit CNT morphologies such as aligned
and epoxy impregnated CNT forests on top of the CFRP laminate, and
randomly oriented and distributed CNTs within the matrix of the composite
laminate can be studied.

The impact problem can be modelled using ABAQUS/EXPLICIT on a macro-
level model of the CFRP laminate. In the case of an epoxy/CNT surface coating,
the CFRP laminate can be modelled as a multi-layer system with prescribed lay-
up properties as a sequence of CFRP plies separated by cohesive zone interfaces
to investigate delaminations. The nanocomposite coating can also be modelled
as a separate layer atop of the laminate, and possibly separated by a cohesive
layer. The macroscopic representation of the coating can then be linked to
RVEs, to study the effect of a given RVE morphology (e.g. aligned CNT forest,
or misaligned CNTs) on the impact response of the coating and the laminate.
Here, one needs to devise computationally efficient macro-to-RVE and RVE-to-
macro scale transitions, which enable transferring macroscopic boundary
conditions onto the RVE to track their deformation. Also, extensions to second-
order computational homogenisation can be required to account for rapid
variations of deformation field due to a very localised nature of impact loads.
As final model validation, drop tower impact tests of nanocomposite-coated CRFP laminates with subsequent damage assessments are suggested.

### 7.2.5. Improving the nanocomposite manufacturing process

Very low mass fractions and associated manufacturing route adopted in this work led to very small or no increases in the mechanical properties of the nanocomposites. Therefore, more advanced manufacturing techniques must be applied in order to obtain enhanced nanocomposite properties for samples of high CNT mass fractions. Dispersion of functionalised CNTs in solvents solely by bath sonication was found to provide a good state of dispersion in the final nanocomposite as well as property enhancements only at low CNT concentrations (0.3 mass%). Hence, more promising production routes via high shear mixing, calendering of more viscous epoxy resins, or impregnation of CNT forests followed by in-situ polymerisation, are worth being considered in future processing of the nanocomposites. Otherwise, when operating with low CNT mass fractions, CNTs that exhibit a minimum number of structural defects should be preferably used in order to obtain a significant effect on the mechanical properties. More advanced processing routes will help to control more efficiently the state of CNT dispersion to help to exploit not only the remarkable stiffness of the CNT, but also draw on their multifunctional properties (e.g. electrical conductivity), to form relevant CNT networks. The latter can be crucial for developing new materials for applications in aerospace such as lightning strike protection, damage sensing or de-icing.
Bibliography


“Experimental characterisation and constitutive modelling of RTM-6 resin under impact loading”, *Polymer*, 49(11), 2728–2737.


Harris, P.J.F. Carbon Nanotubes and Related Structures, Cambridge: Cambridge University Press.


Timoshenko beam theory and using DQM”, *Physica E: Low-Dimensional Systems and Nanostructures*, 41(7), 1232–1239.


Shokrieh, M.M., Rafiee, R. (2010c) “Investigation of nanotube length effect on
the reinforcement efficiency in carbon nanotube based composites”,
Composite Structures, 92(10), 2415–2420.

selective growth of carbon nanotubes and large field emission from
vertically well-aligned carbon nanotube field emitter arrays”, Applied

method for determining mechanical properties of polymer


“Interfacial energy between carbon nanotubes and polymers measured
from nanoscale peel tests in the atomic force microscope”, Composites
Science and Technology, 69(10), 1580–1586.

nonlocal continuum mechanics”, Journal of Applied Physics, 94(11), 7281–
7287.


composite using a nano-pullout method”, Composites Science and Technology, 71(10), 1295–1300.


Appendix A: Acceptance-rejection algorithm

The implementation of the acceptance-rejection algorithm in the RVE generation procedure is shown in the following lines of pseudo-code:

Create parental part A of CNT geometry with origin 0 at point P
Create parental part B of interface geometry with origin 0 at point P
Create parental part C of clash test geometry with origin 0 at point P
Create parental part D of single phase RVE geometry with origin 0 at the centre
Create parental part E of penetration depth test geometry with origin 0 at the centre
Create 27 instances D’ and translate 26 of them flush with the central one (D) (3x3x3 arrangement)
Create 1 instance E’

For the CNT number counting from the first to the last one:
  Set ‘clashtest’ variable equal to 1
  While ‘clashtest’ variable is equal to 1:
    Create the set of instances A’,B’,C’ and randomly orient them and position point P’ within the range corresponding to the space occupied by the central D’ instance
    Create instances A” by trying to cut each of the 27 instances D’ by instance A’ and translate the instances back, i.e. revert the 3x3x3 arrangement for these instances (Repeat for B’ and C’)
    Create instances A’” by cutting the central D’ instance by those previously superpositioned instances A” (Repeat for B” and C”)
    Create instance A’’” by merging instances A’” (Repeat for B’” and C’”)
    If geometry or position of instance A’’” or B’’” will lead to meshing difficulties:
      Go to the beginning of the while loop
    If an ABAQUS bug appeared or is likely to appear during further cut/merge operations involving instance A’’” or B’’”:
      Go to the beginning of the while loop
    If the instance C’’” intersects with one of the previously created periodic instances in list γ:
      Go to the beginning of the while loop
  Else:
    Set ‘clashtest’ variable equal to 0
  Write instance A’’” into list α
  Write instance B’’” into list β
Write instance C''' into list γ

Create CNT morphology instance by merging instances from list α

Create interface morphology instance by merging instances from list β

Create matrix morphology instance by cutting the central D' instance by the CNT morphology instance and interface morphology instance
Appendix B: Derivation of the macroscopic stress

B1. Applied and periodic boundary conditions

3D RVE is subjected to applied displacements as given by Eq. (4.44):

\[
\begin{align*}
    x_1 &= \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \\
    x_4 &= \begin{pmatrix} 0 \\ 0 \\ / \end{pmatrix}, \\
    x_5 &= \begin{pmatrix} 0 \\ 0 \\ / \end{pmatrix}, \\
    x_2 &= \begin{pmatrix} 1/4d \\ 0 \\ 0 \end{pmatrix},
\end{align*}
\]

(B.1)

where \( d \) is the RVE side length, \( x_i \) denotes the position vector applied to relevant nodes \((i=1,2,4,5)\) and "/" indicates the direction in which the node is free to move.

Eq. (4.43) is written in greater detail in relation to Fig. 4.8 as

\[
\begin{align*}
    x_F^+ - x_F^- &= x_F - x_1 \\
    x_E^+ - x_E^- &= x_E - x_1 \\
    x_J^+ - x_J^- &= x_J - x_1.
\end{align*}
\]

(B.2)

With notations provided in Fig. 4.8, Eq. (B.2) can be expanded to

\[
\begin{align*}
    x_R - x_L &= x_2 - x_1 \\
    x_T - x_B &= x_4 - x_1 \\
    x_F - x_{RR} &= x_5 - x_1 \\
    x_{rr} - x_{rl} &= x_2 - x_1 \\
    x_{bs} - x_{bh} &= x_2 - x_1 \\
    x_{tt} - x_{tl} &= x_2 - x_1.
\end{align*}
\]
\( x_{rt} - x_{br} = x_4 - x_1 \)

\( x_{lf} - x_{fb} = x_4 - x_1 \)

\( x_{lf} - x_{lb} = x_4 - x_1 \)

\( x_{lf} - x_{rr} = x_5 - x_1 \)

\( x_{lf} - x_{mr} = x_5 - x_1 \)

\( x_{lb} - x_{br} = x_5 - x_1 \)

\( x_3 - x_4 = x_2 - x_1 \)

\( x_6 - x_5 = x_2 - x_1 \)

\( x_7 - x_8 = x_2 - x_1 \)

\( x_8 - x_5 = x_4 - x_1 \), \hspace{1cm} (B.3)

which can then be rearranged to

\( x_R = x_L + x_2 - x_1 \)

\( x_T = x_{lb} + x_4 - x_1 \)

\( x_F = x_{RR} + x_5 - x_1 \)

\( x_{mr} = x_{ml} + x_2 - x_1 \)

\( x_{br} = x_{lb} + x_2 - x_1 \)

\( x_{lf} = x_{ll} + x_2 - x_1 \)

\( x_{rr} = x_{br} + x_4 - x_1 \)

\( x_{lf} = x_{fb} + x_4 - x_1 \)
\[
x_d = x_{fb} + x_4 - x_1 \\
x_{fr} = x_{mr} + x_5 - x_1 \\
x_{lf} = x_{ml} + x_5 - x_1 \\
x_{fb} = x_{brr} + x_5 - x_1 \\
x_3 = x_4 + x_2 - x_1 \\
x_6 = x_5 + x_2 - x_1 \\
x_7 = x_8 + x_2 - x_1 \\
x_8 = x_5 + x_4 - x_1.
\] (B.4)

**B2. Derivation of macroscopic Cauchy stresses**

The derivation of macroscopic Cauchy stresses is a 3D extension of the approach proposed by Kouznetsova et al. (2001). For the 3D case, the corresponding relationship to Eq. (4.46) is obtained by considering all forces acting on the RVE boundary that result from applied displacements (Eq. B1) and periodic boundary conditions (Eq. (B2)–(B4)). Hence, one has to distinguish between external forces \( F \) at the corner nodes \( I=1,2,4,5 \) and forces \( f_F, f_E, f_J \) and \( f_t \) involved in every tying relation of Eq. (B.2) for faces \( F \), edges \( E \) and nodes \( J \). Each of the constraint (tying) relation satisfies the condition of zero virtual work, i.e.

\[
f_T \cdot \delta x_T + f_B \cdot \delta x_B + f_d^T \cdot \delta x_d + f_1^T \cdot \delta x_1 = 0 \\
f_R \cdot \delta x_R + f_L \cdot \delta x_L + f_2^R \cdot \delta x_2 + f_1^R \cdot \delta x_1 = 0 \\
f_F \cdot \delta x_F + f_{RR} \cdot \delta x_{RR} + f_5^F \cdot \delta x_5 + f_1^F \cdot \delta x_1 = 0 \\
f_m^T \cdot \delta x_m + f_m^T \cdot \delta x_m + f_2^m \cdot \delta x_2 + f_1^m \cdot \delta x_1 = 0
\]

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\[ f_{br} \cdot \delta x_{br} + f_{lb}^{br} \cdot \delta x_{lb} + f_{2}^{br} \cdot \delta x_{2} + f_{1}^{br} \cdot \delta x_{1} = 0 \]

\[ f_{n}^{m} \cdot \delta x_{n} + f_{ul}^{m} \cdot \delta x_{ul} + f_{2}^{m} \cdot \delta x_{2} + f_{1}^{m} \cdot \delta x_{1} = 0 \]

\[ f_{m} \cdot \delta x_{m} + f_{br}^{m} \cdot \delta x_{br} + f_{4}^{m} \cdot \delta x_{4} + f_{1}^{m} \cdot \delta x_{1} = 0 \]

\[ f_{ul}^{n} \cdot \delta x_{ul} + f_{lb}^{n} \cdot \delta x_{lb} + f_{4}^{n} \cdot \delta x_{4} + f_{1}^{n} \cdot \delta x_{1} = 0 \]

\[ f_{br}^{n} \cdot \delta x_{br} + f_{ul}^{n} \cdot \delta x_{ul} + f_{4}^{n} \cdot \delta x_{4} + f_{1}^{n} \cdot \delta x_{1} = 0 \]

\[ f_{lb}^{n} \cdot \delta x_{lb} + f_{ul}^{n} \cdot \delta x_{ul} + f_{4}^{n} \cdot \delta x_{4} + f_{1}^{n} \cdot \delta x_{1} = 0 \]

\[ f_{ul}^{n} \cdot \delta x_{ul} + f_{lb}^{n} \cdot \delta x_{lb} + f_{4}^{n} \cdot \delta x_{4} + f_{1}^{n} \cdot \delta x_{1} = 0 \]

where superscripts have been used to distinguish between tying forces acting on the same edge or node but originate from different tying relations. Substituting Eq. (B.4) into Eq. (B.5) leads to

\[ (f_{T} + f_{ul}) \cdot \delta x_{B} + (f_{T} + f_{4}^{T}) \cdot \delta x_{4} + (f_{1}^{T} - f_{T}) \cdot \delta x_{1} = 0 \]

\[ (f_{R} + f_{ul}) \cdot \delta x_{L} + (f_{R} + f_{4}^{R}) \cdot \delta x_{2} + (f_{1}^{R} - f_{R}) \cdot \delta x_{1} = 0 \]

\[ (f_{F} + f_{RR}) \cdot \delta x_{RR} + (f_{F} + f_{5}^{F}) \cdot \delta x_{5} + (f_{1}^{F} - f_{F}) \cdot \delta x_{1} = 0 \]

\[ (f_{m}^{n} + f_{ml}^{m}) \cdot \delta x_{ml} + (f_{m}^{n} + f_{2}^{m}) \cdot \delta x_{2} + (f_{1}^{m} - f_{m}^{m}) \cdot \delta x_{1} = 0 \]
\[
\begin{align*}
(f_{br} + f_{lb}^{br}) \cdot \delta x_{lb} &+ (f_{br} + f_{2}^{br}) \cdot \delta x_{2} + (f_{1}^{br} - f_{br}) \cdot \delta x_{1} = 0 \\
(f_{n} + f_{dll}^{nt}) \cdot \delta x_{dll} &+ (f_{n} + f_{2}^{nt}) \cdot \delta x_{2} + (f_{1}^{nt} - f_{n}) \cdot \delta x_{1} = 0 \\
(f_{m} + f_{br}^{mt}) \cdot \delta x_{br} &+ (f_{m} + f_{4}^{mt}) \cdot \delta x_{4} + (f_{1}^{mt} - f_{m}) \cdot \delta x_{1} = 0 \\
(f_{tf} + f_{fb}^{tf}) \cdot \delta x_{tf} &+ (f_{tf} + f_{4}^{tf}) \cdot \delta x_{4} + (f_{1}^{tf} - f_{tf}) \cdot \delta x_{1} = 0 \\
(f_{tl}^{h} + f_{lb}^{tl}) \cdot \delta x_{lb} &+ (f_{tl}^{h} + f_{4}^{tl}) \cdot \delta x_{4} + (f_{1}^{tl} - f_{tl}^{h}) \cdot \delta x_{1} = 0 \\
(f_{tr}^{r} + f_{mr}^{fr}) \cdot \delta x_{mr} &+ (f_{tr}^{r} + f_{5}^{fr}) \cdot \delta x_{5} + (f_{1}^{fr} - f_{fr}^{r}) \cdot \delta x_{1} = 0 \\
(f_{fr}^{b} + f_{br}^{fr}) \cdot \delta x_{br} &+ (f_{fr}^{b} + f_{5}^{fr}) \cdot \delta x_{5} + (f_{1}^{fr} - f_{fr}^{b}) \cdot \delta x_{1} = 0 \\
(f_{s}^{(3)} + f_{3}^{(3)}) \cdot \delta x_{4} &+ (f_{3} + f_{2}^{(3)}) \cdot \delta x_{2} + (f_{1}^{(3)} - f_{3}) \cdot \delta x_{1} = 0 \\
(f_{s}^{(6)} + f_{2}^{(6)}) \cdot \delta x_{5} &+ (f_{6} + f_{2}^{(6)}) \cdot \delta x_{2} + (f_{1}^{(6)} - f_{6}) \cdot \delta x_{1} = 0 \\
(f_{7} + f_{8}^{(7)}) \cdot \delta x_{6} &+ (f_{7} + f_{2}^{(7)}) \cdot \delta x_{2} + (f_{1}^{(7)} - f_{7}) \cdot \delta x_{1} = 0 \\
(f_{s}^{(5)} + f_{8}^{(5)}) \cdot \delta x_{5} &+ (f_{8}^{(5)} + f_{4}^{(5)}) \cdot \delta x_{4} + (f_{1}^{(8)} - f_{8}^{(5)}) \cdot \delta x_{1} = 0.
\end{align*}
\]

These relations should hold for any \( \delta x \) and, thus, the relation between the tying forces can be written as

\[
\begin{align*}
f_{T} &= -f_{B} = -f_{4}^{T} = f_{1}^{T} \\
f_{R} &= -f_{L} = -f_{2}^{R} = f_{1}^{R} \\
f_{F} &= -f_{RR} = -f_{5}^{F} = f_{1}^{F} \\
f_{mr} &= -f_{mr} = -f_{2}^{mr} = f_{1}^{mr}
\end{align*}
\]
\[ f_{br} = -f_{fb} = -f_2 = f_1^{br} \]

\[ f_{rt} = -f_{tl} = -f_2 = f_1^{rt} \]

\[ f_{rr} = -f_{br} = -f_4 = f_1^{rr} \]

\[ f_{rf} = -f_{fr} = -f_4 = f_1^{rf} \]

\[ f_{il} = -f_{il} = -f_4 = f_1^{il} \]

\[ f_{li} = -f_{ri} = -f_5 = f_1^{li} \]

\[ f_{if} = -f_{rf} = -f_5 = f_1^{if} \]

\[ f_{fr} = -f_{fr} = -f_5 = f_1^{fr} \]

\[ f_{fb} = -f_{fb} = -f_5 = f_1^{fb} \]

\[ f_1 = -f_1^{(3)} = -f_2^{(3)} = f_1^{(3)} \]

\[ f_5 = -f_2^{(6)} = -f_5^{(6)} = f_1^{(6)} \]

\[ f_7 = -f_2^{(7)} = -f_2^{(7)} = f_1^{(7)} \]

\[ f_8^{(5)} = -f_4^{(8)} = -f_4^{(8)} = f_1^{(8)} , \quad (B.7) \]

which states the antiperiodicity of tying forces on opposing boundaries.

The macroscopic Cauchy stress is defined as

\[
\bar{\sigma}_{RVE} = \frac{1}{V} \int_{V} \sigma \, dV = \frac{1}{V} \int_{V} \nabla \cdot (\sigma^{T} x) \, dV = \\
= \frac{1}{V} \int_{\Gamma} n \cdot (\sigma^{T} x) \, d\Gamma = \frac{1}{V} \int_{\Gamma} t x \, d\Gamma , \quad (B.8)
\]

where \( \Gamma \) denotes the boundary of the RVE, and \( n \) is a unit surface normal vector to RVE faces in the deformed configuration, while \( t \) denotes the vector of surface tractions (i.e. force per unit area) resulting from applied and periodic boundary conditions.
The boundary integral from Eq. (B.8) accounting for all those tractions and relevant position vectors $x$ for nodes, edges and faces can be written as

$$\mathbf{\sigma}_{RVE} = \frac{1}{V} \left( \sum F_i x_1 + F_2 x_2 + F_3 x_3 + F_4 x_4 + F_5 x_5 + \int f_1 x_1 d\Gamma + \int f_2 x_2 d\Gamma + \int f_3 x_3 d\Gamma + \int f_4 x_4 d\Gamma + \int f_5 x_5 d\Gamma \right)$$

$$+ \int f_5 x_5 d\Gamma + \int f_4 x_4 d\Gamma + \int f_3 x_3 d\Gamma + \int f_2 x_2 d\Gamma + \int f_1 x_1 d\Gamma + \int f_6 x_6 d\Gamma + \int f_7 x_7 d\Gamma + \int f_8 x_8 d\Gamma + \int f_9 x_9 d\Gamma + \int f_{10} x_{10} d\Gamma + \int f_{11} x_{11} d\Gamma$$

$$+ \left( \int f_1^1 d\Gamma \right) x_1 + \left( \int f_2^1 d\Gamma \right) x_2 + \left( \int f_3^1 d\Gamma \right) x_3 + \left( \int f_4^1 d\Gamma \right) x_4 + \left( \int f_5^1 d\Gamma \right) x_5$$

$$+ \left( \int f_1^2 d\Gamma \right) x_1 + \left( \int f_2^2 d\Gamma \right) x_2 + \left( \int f_3^2 d\Gamma \right) x_3 + \left( \int f_4^2 d\Gamma \right) x_4 + \left( \int f_5^2 d\Gamma \right) x_5 + \left( \int f_6^2 d\Gamma \right) x_6$$

$$+ \left( \int f_1^3 d\Gamma \right) x_1 + \left( \int f_2^3 d\Gamma \right) x_2 + \left( \int f_3^3 d\Gamma \right) x_3 + \left( \int f_4^3 d\Gamma \right) x_4 + \left( \int f_5^3 d\Gamma \right) x_5 + \left( \int f_6^3 d\Gamma \right) x_6$$

$$+ \left( \int f_1^4 d\Gamma \right) x_1 + \left( \int f_2^4 d\Gamma \right) x_2 + \left( \int f_3^4 d\Gamma \right) x_3 + \left( \int f_4^4 d\Gamma \right) x_4 + \left( \int f_5^4 d\Gamma \right) x_5 + \left( \int f_6^4 d\Gamma \right) x_6$$

$$+ \left( \int f_1^5 d\Gamma \right) x_1 + \left( \int f_2^5 d\Gamma \right) x_2 + \left( \int f_3^5 d\Gamma \right) x_3 + \left( \int f_4^5 d\Gamma \right) x_4 + \left( \int f_5^5 d\Gamma \right) x_5 + \left( \int f_6^5 d\Gamma \right) x_6$$

$$+ \left( \int f_1^6 d\Gamma \right) x_1 + \left( \int f_2^6 d\Gamma \right) x_2 + \left( \int f_3^6 d\Gamma \right) x_3 + \left( \int f_4^6 d\Gamma \right) x_4 + \left( \int f_5^6 d\Gamma \right) x_5 + \left( \int f_6^6 d\Gamma \right) x_6$$

$$+ \left( \int f_1^7 d\Gamma \right) x_1 + \left( \int f_2^7 d\Gamma \right) x_2 + \left( \int f_3^7 d\Gamma \right) x_3 + \left( \int f_4^7 d\Gamma \right) x_4 + \left( \int f_5^7 d\Gamma \right) x_5 + \left( \int f_6^7 d\Gamma \right) x_6$$

$$+ \left( \int f_1^8 d\Gamma \right) x_1 + \left( \int f_2^8 d\Gamma \right) x_2 + \left( \int f_3^8 d\Gamma \right) x_3 + \left( \int f_4^8 d\Gamma \right) x_4 + \left( \int f_5^8 d\Gamma \right) x_5 + \left( \int f_6^8 d\Gamma \right) x_6$$

Then, the relation between the initial two terms/forces of each tying relation (Eq. B.7) can be employed:
\[ \bar{\sigma}_{RVE} = \frac{1}{V} \sum_{i=1,2,4,5} F_i x_i + \int_{r_t} f^T_T(x_t - x_{RT}) d\Gamma + \int_{r_t} f^R_R(x_R - x_{RL}) d\Gamma \\
+ \int_{r_t} f^T_T (x_t - x_{RT}) d\Gamma + (\int_{r_t} f^T_T d\Gamma) x_t + (\int_{r_t} f^R_R d\Gamma) x_t + (\int_{r_t} f_i^T d\Gamma) x_i \\
+ (\int_{r_t} f_i^R d\Gamma) x_i + (\int_{r_t} f_i^T d\Gamma) x_i + (\int_{r_t} f_i^R d\Gamma) x_i + (\int_{r_t} f_i^T d\Gamma) x_i \\
+ (\int_{r_t} f_i^R d\Gamma) x_i + (\int_{r_t} f_i^T d\Gamma) x_i + (\int_{r_t} f_i^R d\Gamma) x_i + (\int_{r_t} f_i^T d\Gamma) x_i \\
+ (\int_{r_t} f_i^R d\Gamma) x_i + (\int_{r_t} f_i^T d\Gamma) x_i + (\int_{r_t} f_i^R d\Gamma) x_i + (\int_{r_t} f_i^T d\Gamma) x_i \\
+ f_3(x_3 - x_4) + f_6(x_6 - x_5) + f_7(x_7 - x_5) + f_8^{(5)}(x_8 - x_5) + f_1^{(3)} x_1 \\
+ f_1^{(6)} x_1 + f_1^{(7)} x_1 + f_1^{(8)} x_1 + f_2^{(3)} x_2 + f_2^{(6)} x_2 + f_2^{(7)} x_2 + f_4^{(8)} x_4 \\
\] 

Substituting Eq. (B.3) into (B.10) gives
\[ \bar{\sigma}_{\text{RVE}} = \frac{1}{V} \left( \sum_{l=1,2,4,5} F_l x_l + \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{1r} x_1 d\Gamma + \int f_{4r} x_4 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

\[ + \left( \int f_{4r} x_4 d\Gamma + \int f_{1r} x_1 d\Gamma \right) \]

By using the remaining relations between the tying forces (Eq. B.7), the boundary integral reduces to

\[ \bar{\sigma}_{\text{RVE}} = \frac{1}{V} \sum_{l=1,2,4,5} F_l \otimes x_l . \]  

The above Eq. can then be simplified to compute stresses in the x-x direction as follows:

\[ \sigma_{xx} = V^{-1} F_{2(3)} x_{2(3)} , \]  

where \( F_{2(3)} \) and \( x_{2(3)} \) denote force and position of the node 2.