Novel glass fibre reinforced hierarchical composites with improved interfacial, mechanical and dynamic mechanical properties developed using cellulose microcrystals

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HIGHLIGHTS

- Cellulose microcrystals based glass/epoxy hierarchical composites were developed.
- Cellulose microcrystals (1–3 wt%) were dispersed homogeneously in the epoxy matrix.
- Glass fibre-matrix interface improved considerably due to cellulose microcrystals.
- Considerable improvements in the composite strength and fracture energy were observed.
- Storage modulus, loss modulus and glass transition temperature increased strongly.

GRAPHICAL ABSTRACT

Abstract

This paper reports the use of cellulose microcrystals (CMCs) for improving fibre-matrix interface, mechanical, dynamic mechanical and thermal degradation behaviour of glass fibre reinforced epoxy composites. An ultrasonic treatment for 1 h was used to disperse CMCs (1–3 wt%) within an epoxy resin, which was subsequently infused through glass fabrics to develop hierarchical composites containing both macro and micro-scale reinforcements. It was observed that CMC dispersion in the epoxy resin was homogeneous at 1 wt% CMC and further increase in CMC concentrations led to linear increase in both agglomerate size and total agglomerated area. Addition of 1 wt % CMC to the composite matrix drastically changed the glass fibre-epoxy interface and led to a maximum improvement of 65% in interlaminar shear strength, 14% in tensile strength, 76% in flexural strength, 76% in flexural strength, 111% and 119% in fracture energy in tensile and flexural modes, 9.4% in impact strength, 13.5% in storage modulus, 21.9% in loss modulus and 13 °C in the glass transition temperature of composites. Therefore, the use of CMCs could be an industrially viable, economical and eco-friendly approach of developing hierarchical glass fibre composites with considerably improved performance.

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1. Introduction

The history of fibre reinforced polymer composites (FRPs) dates back to the work started in the USA in 1940s. FRPs, in which high strength fibres are incorporated within polymeric matrices, show unique properties that are not achievable by either component [1]. Due to a number of advantages including low density, high strength and modulus, good corrosion resistance, easy handling, economic feasibility, easy maintenance, low co-efficient of thermal expansion, high thermal damping capacity, superior durability and tailorability properties, FRPs are finding huge success in different industrial sectors such as automobiles, aerospace, construction, sports, medical, etc. and are considered as the future replacement for metals [1]. Mostly, FRPs are produced in the form of laminated composites, and delamination leading to subsequent failure is one of the ever existing problems with FRPs [1]. Delamination occurs due to poor adhesion between fibres and matrices originating from the difference in their chemical and physical properties. To solve this major issue, many approaches have been reported till date including: use of 3D fabrics (in which different layers are inherently stitched together to avoid delamination), stitching of different layers of 2D fabrics, fibre surface modification (to improve fibre-matrix compatibility), single polymer composites (in which fibres and matrices are made from the same polymer), etc. [1]. Each of the above methods has their own merits and demerits when their performance, cost as well as environmental impacts are taken into consideration.

A great deal of research has been conducted on modifying fibre surface through different physical and chemical techniques such as treatment with plasma, UV, corona, gamma radiation, ozone, alkali, peroxide, permanganate, silane, to name a few [2–4]. Surface treatment is very crucial for plant fibres as they form weak interfaces with polymeric matrices [3]. Glass fibres are also commonly treated with silanes to improve their interfaces with polymeric matrices [4]. More recently, nanofinishing is becoming very popular to introduce different functionalities into composite materials, besides improving fibre-matrix interface and reducing delamination problems. Incorporation of nanomaterials into conventional composites (either on the fibre surface or into the matrix as the second reinforcing phase) led to the development of a new class of composites known as ‘multi-scale’ or ‘hierarchical’ composites, in which reinforcements from different length scales (i.e. macro, micro or nano) have been combined [5–13]. Surface treatment of fibres with carbon and other nanoparticles through spraying, coating, chemical grafting, electrophoretic deposition, growing, etc. strongly improved interfacing, mechanical, dynamic mechanical, thermal and other properties as well as introduced electrical and thermal conductivities and sensing characteristics (such as strain and damage sensing, humidity sensing, etc.) [5–13]. However, high cost, toxicity and environmental issues have been the major barriers in successfully applying these nanofinishes to the composite industries. To summarise, most of the existing fibre surface modification techniques either involve chemical and wet treatments which are non eco-friendly or nanomaterials which are toxic and expensive. Consequently, there exists a huge demand in the composite industry for new eco-friendly and physical techniques that improve interfacing and other properties of composites.

Increasing utilisation of green and sustainable materials has become a key research focus and also an industrial demand in the present time. The use of plant-derived polymers, fibres and nanomaterials in different industrial sectors is steadily increasing [14,15]. Nano and micro materials have been extracted from cellulose, which is abundantly available in nature, in the form of cellulose nanocrystals (CNCs), cellulose nanofibers (CNFs), cellulose microcrystals (CMCs) and cellulose microfibrils (CMFs) [14,15]. Due to outstanding mechanical properties nanocellulose has been widely used as a reinforcement of composite materials and also as a fibre-surface or interface modifier in polymeric or cementitious composites [16–19]. For example, coating of CNF on jute fibres resulted in significantly improved fibre-matrix interface, tensile modulus, flexural strength, fatigue life and fracture toughness of jute fibre reinforced green epoxy composites [17]. Growing bacterial cellulose (BC) on plant-based fibres or BC coating was also found effective in improving interfacing properties and mechanical performance [18]. Very recently, the interface between glass fibres and an epoxy matrix has been improved through nanocellulose coating, resulting in ~69%, ~10%, 10%, 40% and 43% improvements in interfacing shear strength (IFSS), elastic modulus, tensile strength, flexural modulus and flexural strength, respectively [19]. In contrast to nanocellulose, CMCs have been rarely studied in composites and only a few efforts have made recently to incorporate CMCs in various matrices due to their good mechanical properties, low cost, commercial availability and potential for developing high performance composites at an industrial scale [20]. Dispersion of CMCs in polymers or cement resulted in significant improvement in elastic modulus, tensile strength, cement hydration and microstructure, and reduced the cement porosity [21–23]. However, due to highly crystalline structure and low aspect ratio (as compared to nanocellulose) a decrease in the breaking elongation and toughness was noticed in some cases, and this problem has been solved by using a hybrid reinforcement containing both CMCs and carbon nanotubes (CNTs) [24]. Due to a serious lack of research on the use of CMCs as the second reinforcing phase in hierarchical composites, CMCs have been used for the first time in the present study (according to authors’ knowledge), in glass fibre/epoxy composites to improve the fibre-matrix interface as well as mechanical, dynamic mechanical and thermal degradation behaviour of composites. A short physical technique has been used to disperse CMCs within the composite matrix to enhance industrial viability and sustainability of the developed process. The influence of CMC loading and dispersion quality on various properties of developed hierarchical composites have been thoroughly investigated and discussed in detail.

2. Materials and methods

2.1. Raw materials

Glass woven fabrics (square sett plain weave with balanced properties) were purchased from Owens Corning, France. A medium viscosity epoxy resin system (Biresin CR83 resin and Biresin CH83-2 harder) was purchased from Silka®, Germany. CMC (Avicel® PH-101) used in the present work was supplied by Sigma Aldrich (United Kingdom). Morphology of CMC at different magnifications, as studied by a scanning electron microscope (FEG-SEM, NOVA 200 Nano SEM, FEI) using an acceleration voltage of 10 kV and after coating with a 30 nm Au-P film, is provided in Fig. 1. The SEM micrographs showed that CMC crystals were highly agglomerated in the powder form and had different shapes and sizes. The purchased CMC powder was dried at 60 °C for 24 h in an oven before use in order to remove moisture. Some essential properties of glass fibres, CMCs and the cured epoxy resin used in the present study, as per the manufacturer’s data, are listed in Table 1.

2.2. Experimental methods

2.2.1. Dispersion of cellulose microcrystals in epoxy matrix

Prior to dispersion of CMCs in the epoxy resin, required amount of CMCs was dried in an oven at 60 °C for 24 h. After drying, CMC powder was mixed little by little with the resin (part A) and then ultrasonicated (Branson Ultrasonics M series, operated at 40 kHz frequency and 180 W power) for an hour. The ultrasonication conditions and time were selected based on authors' previous studies on CMC dispersion in water and epoxy resins [23,26]. Next, calculated amount of hardener (part B) was mixed with the CMC dispersed resin. The final mixture was then used in the vacuum infusion process to produce hierarchical composites. The schematic of the composite manufacturing process is shown in Fig. 2.
2.2.2. Fabrication of hierarchical composites

Hierarchical glass/epoxy composites with different CMC contents (1 wt%, 1.5 wt% and 3 wt%) along with a neat glass/epoxy composite without CMCs were fabricated using the vacuum infusion technique. Total six layers of glass woven fabrics (0/± layup) were used to fabricate each composite and the fibre volume fraction in the composites was ~55%. The composites were cured at room temperature for 24 h and subsequently, post-cured in an oven at 120 °C for 2 h. The composites had an average thickness of 1.50 mm. The composites were then cut into specific dimensions as required for different characterisations performed later on.

2.2.3. Characterisation of CMC dispersion

The CMC aqueous suspensions prepared using ultrasonication were taken in glass vials and kept standing for 24 h to see the sedimentation behaviour. A small drop was taken from each suspension on a glass slide and studied using an optical microscope to see the suspension homogeneity and CMC agglomeration. Suspensions with different CMC concentrations as well as drop from different parts of each suspension were thoroughly studied using the optical microscope. Besides this qualitative analysis, the optical micrographs were analysed using an image processing software (ImageJ) and the average size of CMC particles and total agglomerated area were calculated as follows:

\[
\text{Average particle size (\mu m^2)} = \frac{\sum_n A_i}{n}
\]

(1)

\[
\text{Total area of agglomerates (\%)} = 100 \times \frac{\sum_n A_i}{A_j}
\]

(2)

where, \(A_i\) is the area of individual CMC agglomerate/particle, \(n\) is the number of identified CMC agglomerates and \(A_j\) is the area of analysed optical micrographs.

Table 1

<table>
<thead>
<tr>
<th>Materials</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass fibre</td>
<td>E-glass, tensile strength: 3445 MPa, compressive strength: 1080 MPa, elastic modulus: 73 GPa, density: 2.58 g/cm³</td>
</tr>
<tr>
<td>Epoxy***</td>
<td>Density: 1.15 g/cm³, tensile strength: 84 MPa, tensile modulus: 2.94 GPa, elongation: 6.7%, flexural strength: 128 MPa, flexural modulus: 3.125 GPa, compressive strength: 107 MPa, impact strength: 93 kJ/m²</td>
</tr>
<tr>
<td>CMC**</td>
<td>Particle size: ~50 μm, moisture content: 3 wt%, solid density 1.54 g/cm³, particle shape: larger fibrous rods to smaller irregular cuboids</td>
</tr>
</tbody>
</table>

Source: *Owens Corning, **Sika Advanced Resins Global, ***Sigma Aldrich, UK.

2.2.4. Characterisation of mechanical properties

Tensile tests of composite samples were carried out according to ASTM D638-03 in a universal tensile testing machine with a load cell of 50 kN and at a crosshead speed of 2 mm/min. For the accurate measurement of elongation, an extensometer was used during testing. In each type, five samples were tested and the average tensile properties have been reported. Flexural tests were performed according to ASTM D790-3 standard in a three-point loading configuration using the universal testing machine with a load cell of 50 kN, crosshead speed of 2 mm/min and a support span of 60 mm. Similar to tensile tests, five samples were tested in each category and the average results have been reported. Fracture energy was calculated from the area under the load-elongation curves using OriginPro software. Izod impact tests were performed according to ASTM D256 using a pendulum impact tester. Prior to testing, a triangle shaped notch with 2 mm depth was introduced at one side of each sample using a notch cutter. At least ten samples were tested from each category and the average results have been reported.

Interlaminar shear strengths (ILSS) of neat glass/epoxy and hierarchical composites were characterized using the short beam shear test according to ASTM D2344 standard. ILSS was calculated as follows:

\[
\tau = \frac{P}{A}
\]

(3)

where, \(\tau\) is the ILSS, \(P\) is the maximum load and \(A\) is the cross-sectional area calculated from the specimen width and thickness. A span length to thickness ratio of 4 was used according to the standard.

The fracture surfaces of samples after tensile tests were characterized using SEM (FEG-SEM, NOVA 200 Nano SEM, FEL acceleration voltage: 10 kV, coating: 30 nm Au-P) to study the adhesion between glass fibres and the epoxy matrix in neat glass/epoxy and hierarchical composites.

2.2.5. Characterisation of dynamic mechanical and thermal degradation properties

The viscoelastic properties of developed composites were studied in a dynamic mechanical analyser (DMA, Hitachi DMA7100) in the three-point bending mode using a sample size of 50 × 14 × 1.5 mm and a gauge length of 45 mm. Tests were performed at 1 Hz frequency in a temperature range of 30–180 °C with a heating rate of 3 °C/min. In each type, three samples were tested and the average results have been reported. The glass transition temperature (\(T_g\)) of composites was calculated from the peak of loss modulus curves.

The thermal degradation behaviour of neat glass/epoxy and hierarchical composites was characterized through thermogravimetric analysis (TGA) in Hitachi STA700 instrument. The sample weights used for testing were in the range of 8–12 mg. The temperature range was
30–900 °C obtained through a heating rate of 20 °C/min under a nitrogen atmosphere (nitrogen flow rate: 20 mL/min).

3. Results and discussion

3.1. Dispersion of CMC in epoxy resin

The results of qualitative and quantitative characterisation of CMC dispersion in the epoxy resin are presented in Fig. 3. The visual observation of the suspensions (Fig. 3a) showed that the suspensions were quite clear without noticeable sedimentation or phase separation. However, the transparency of the suspensions reduced as the CMC concentration was increased.

From the optical micrographs presented in Fig. 3b it is clear that CMC crystals were dispersed as individual particles at low concentrations (i.e., at 1 wt%). As the concentration increased, the size of the observed particles also increased (as can be seen in Fig. 3b, c and d) indicating some degree of CMC agglomeration, which occurred due to inter-particle hydrogen bond formation between numerous hydroxyl groups present in the chemical structure of CMCs [25]. Agglomeration of CMCs in polymers at higher concentrations has been noticed in earlier studies also [26]. Chemical functionalisation of CMCs has been tried by some researchers to improve CMC dispersion and interface with polymers [21]. However, in the present study, only a physical method, i.e. ultrasonication has been used to disperse CMCs to make this process eco-friendly and viable for the industries. The quantitative estimation of agglomerated area and average agglomerate size, as presented in Fig. 3e, also supported the qualitative results. It can be noticed that both agglomerated area and size increased linearly with the increase in CMC concentration. At 1 wt% CMC, the total agglomerated area was only ~3%, which increased up to ~12% at 3 wt% CMC. The average agglomerate size increased from 282 μm² to 451 μm² when CMC concentration was increased from 1 wt% to 3 wt%.

The agglomerated area of CMCs in the epoxy resin achieved in this study was much lower as compared to that (16–25% for 1–5 wt% CMC) achieved when dispersed in water using the same dispersion technique [23]. This could be due to relatively higher viscosity of the epoxy resin which restricted re-agglomeration of dispersed CMC particles that easily occurred in the aqueous medium. The reduced viscosity of dispersion mediums favours nano/micro particle re-agglomeration as previously observed in case of carbon nanomaterials [13].

3.2. Mechanical properties

3.2.1. Strength and fracture energy

The tensile test results of hierarchical and neat glass/epoxy composites are summarised in Table 2 and the load-elongation curves provided in Fig. 4. The results show that the addition of CMCs to glass/epoxy composites significantly improved the tensile strength and fracture energy. A maximum improvement in tensile strength of ~14% was observed by adding 1.0 wt% CMC. Further increase in CMC content reduced the tensile strength. The same trend was also observed in case of fracture energy, which increased up to 111% through addition of 1 wt% CMC and then started to decrease.

Tensile properties of composites are negatively influenced by micro/nano particle agglomerates, as they lead to stress concentration and void formation in composites [27]. The reduction in tensile strength and fracture energy with increase in CMC concentration was mainly attributed to more CMC agglomeration at higher concentrations, as also reported earlier in case of CMC/CNC reinforced composites [26,28]. As shown in Table 2, flexural strength also improved strongly with CMC addition; a maximum improvement of 76% was achieved by adding 1 wt% CMC. Similar to tensile strength, flexural strength also decreased with increase in CMC content due to CMC agglomeration. The fracture energy of composites in the flexural mode increased to a considerable extent owing to CMC addition, improving 119% at 1 wt% CMC. A number of earlier studies also showed significant improvements of strength and
fracture energy of fibre reinforced composites by adding different nanomaterials such as CNTs, nano cellulose, graphene oxide (GO), etc. to the composite matrix [6–13]. According to the published literature, the increased strength and fracture energy of composites due to nanomaterial addition are attributed to the synergy between the macro and nano reinforcements. This occurred due to several reasons: (1) effective stress transfer through nano-modified interfaces due to the higher interfacial adhesion resulting from (a) increased frictional forces and mechanical interlocking [19], (b) higher surface area of nano-modified fibres [19], (c) increased residual thermal stresses [13], (d) chemical bonding between fibres and nanomaterials [6], etc. and (2) tougher interface regions due to nano-reinforcement restricting crack propagation through interfaces [6]. In the present work, a significantly stronger interfacial adhesion was observed between glass fibres and the epoxy matrix due to CMC addition (as discussed in details in Section 3.2.1), resulting in significantly improved tensile and flexural strengths as well as fracture energy. A few studies also reported an improved elastic modulus of composites due to micro/nanomaterial addition in the matrix [13,17]. This improvement mainly resulted from the improved stress transfer through interfaces [13,17]. The predicted elastic modulus of epoxy matrix (calculated according to the ‘Rule of Mixtures’ using elastic modulus of CMCs as 25.4 GPa [29], elastic modulus of the epoxy matrix as 2.9 GPa and a 2D random orientation of CMCs) is presented in Fig. 4c. The predicted modulus of the matrix improved from 2.9 GPa to 3.1 GPa with 3 wt% of CMC addition suggesting a positive effect of CMCs on the matrix modulus.

Previous studies also suggested that CMCs can significantly improve the elastic modulus of epoxy matrices [21]. The predicted and actual elastic moduli of glass/epoxy composites containing 0–3 wt% of CMC is presented in Fig. 4d. The ‘Rule of Mixtures’ was used to calculate the elastic modulus of glass/epoxy composites, using glass fibre elastic modulus of 73 GPa, fibre volume fraction of 0.55 and assuming a bi-axial arrangement of glass fibres (0/90) in the fabric without any crimp. It is clear from Fig. 4d that the effect of CMC addition on the predicted as well as experimental modulus of glass/epoxy composites was insignificant. The insignificant effect of CMC addition on the elastic modulus of composites, as also noticed in earlier studies with other nano/micro particles [9], suggested the absence of the synergistic effect of CMCs on the composite modulus. This could be due to the fact that the role of fibre-matrix interface is expected to be less prominent in the initial elastic region of stress-strain behaviour (i.e., on the elastic modulus of composites) as compared to higher load levels, when the action of the above discussed mechanisms (i.e. fibre-matrix debonding, toughening of interface regions, etc.) becomes predominant influencing strength and fracture energy significantly.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>α (MPa)</th>
<th>% Increase</th>
<th>FE (N.m)</th>
<th>% Increase</th>
<th>αf (MPa)</th>
<th>% Increase</th>
<th>FEf (N.m)</th>
<th>% Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/epoxy</td>
<td>298 ± 3</td>
<td>–</td>
<td>2585</td>
<td>–</td>
<td>290 ± 8</td>
<td>–</td>
<td>429 ± 12</td>
<td>–</td>
</tr>
<tr>
<td>Glass/epoxy + 1% CMC</td>
<td>338 ± 5</td>
<td>14</td>
<td>5467</td>
<td>111</td>
<td>510 ± 6</td>
<td>76</td>
<td>940 ± 16</td>
<td>119</td>
</tr>
<tr>
<td>Glass/epoxy + 1.5% CMC</td>
<td>330 ± 4</td>
<td>11</td>
<td>5314</td>
<td>106</td>
<td>480 ± 7</td>
<td>66</td>
<td>759 ± 13</td>
<td>77</td>
</tr>
<tr>
<td>Glass/epoxy + 3% CMC</td>
<td>313 ± 8</td>
<td>5</td>
<td>3910</td>
<td>51</td>
<td>435 ± 9</td>
<td>50</td>
<td>713 ± 11</td>
<td>66</td>
</tr>
</tbody>
</table>

![Fig. 4. Load-elongation curves of glass/epoxy composites in tensile (a) and flexural (b) modes, the predicted elastic modulus of the epoxy matrix (c) and actual and predicted elastic moduli of glass/epoxy composites (d).](image-url)
3.2.2. Fibre-matrix interface

A drastic change in the fracture surface could be observed when CMCs were added to the matrix of glass/epoxy composites. The fracture surface of neat glass/epoxy composites showed presence of some fibres with smooth surface and holes due to complete fibre pull-out from the matrix (Fig. 5a). This indicates poor adhesion of the epoxy matrix with glass fibres in neat glass/epoxy composites. On the contrary, a very good fibre-matrix adhesion could be observed in hierarchical composites, as shown in Fig. 5b. Fibres were well impregnated and embedded in the matrix with hardly any noticeable pull-out holes. The surface of the fibres protruding from fracture surfaces (partially pulled-out from the matrix during testing) of neat glass/epoxy and hierarchical composites has been further examined and showed in Fig. 5c and d. It can be clearly observed that the surface of glass fibres which were pulled-out from neat glass/epoxy composites was smooth with very low matrix adherance, in contrast to the fibres from hierarchical composites, in which the whole fibre surface was uniformly covered with the matrix. These findings clearly suggest that a much stronger fibre-matrix interface was formed in case of hierarchical composites. Similar observations of improved fibre-matrix adhesion in hierarchical composites with other nano particles (e.g. CNTs, CNCs, etc.) were made earlier by other researchers through fracture surface study [13,19].

The qualitative observation of stronger fibre-matrix interface in case of hierarchical composites has been also supported by the measurement of ILSS, as shown in Fig. 6. It can be noticed that the ILSS increased strongly with the addition of CMCs within the epoxy matrix. The highest improvement of ILSS was observed in case of 1.0 wt% CMC, which showed a 65% increase in ILSS. The improvement of fibre-matrix interface through nanocellulose/bacterial cellulose (BC) coating was previously reported in both polymeric and cementitious composites [17,30]. The coated nanocellulose or BC acted as high-strength links between plant fibres and polymeric or cementitious matrices. Recently, coating of CNCs on short glass fibres improved the interface and mechanical properties of glass/epoxy composites as a result of increased glass fibre surface roughness and chemical compatibility between CNC-coated glass fibres and the epoxy matrix [19]. In the present research, it is believed that one of the main reasons (apart from increased matrix strength and toughness) for the improved interface was the formation of covalent bonds between the silane layer of glass fibres (introduced by the manufacturer) and CMCs as well as between CMCs and the epoxy matrix. The formation of covalent bonds between the silane-coated glass fibres and the epoxy matrix is illustrated schematically in Fig. 7. Previous studies showed that covalent bonds could form between silane and CMCs through condensation reaction when heated at a high temperature [31]. The formation of covalent bonds between CMCs/NCs and epoxy matrices was also evidenced earlier [32,33]. The hydroxyl groups present in CMCs/CNCs could act as nucleophiles in the ring-opening reaction of epoxy molecules, resulting in covalent bond formation with the CMC/CNC surface [33]. Therefore, strong covalent bond formation between the macro-micro reinforcement system and the epoxy matrix during curing of the composites at high temperatures (120 °C) was believed to be main responsible factor for the enhanced interfacial interactions in the developed hierarchical composites.

3.2.3. Impact properties

The impact energies of neat glass/epoxy and hierarchical composites are listed in Table 3. It can be noted that the impact energy improved significantly with CMC addition resulting in a maximum improvement of 9.4% at 1 wt% CMC content. Previous studies also showed significant improvements of impact strength (22.3%) of glass/epoxy composites using graphene nanoplatelets [10]. The improvement of impact energy was due to an enhanced resistance to crack propagation in the
hierarchical composites. During impact testing, cracks could be deflected at the CMC particles (homogeneously dispersed within the matrix) and also hindered to propagate through the interfacial zone due to strong interfacial interactions and matrix toughening by the CMC particles. The crack deflection and toughening mechanisms of epoxy and other polymers using cellulose and other nano/micro particles have been previously discussed [1,6,13]. Nevertheless, most of the previous studies mainly focused on the tensile or flexural fracture modes and therefore, the role of CMCs on the impact performance of polymers has been less understood till date. It has been reported that superior compatibility between dispersed CMCs with polymers could improve their impact strengths [34], whereas poor interface and dispersion of CMCs could result in the deterioration of impact performance [35]. This is in agreement with the present study as it can be noticed that the impact energy improved up to 9.4% using 1 wt% CMC and then decreased at 3 wt% due to the formation of CMC agglomerates. The improvement in impact energy was much lower than the improvement in tensile or flexural properties, as also evidenced in case of GO nanoplatelets [10]. In authors’ previous study, CMC dispersion in an epoxy resin using the same dispersion route (i.e. ultrasonication for 1 h) significantly improved the impact energy of jute fibre/epoxy composites [26]; much higher (~28% using 2 wt% CMC) as compared to the presently investigated glass/epoxy composites. The neat jute composites possessed significantly lower impact energy (~5 times lower than glass/epoxy composites) and therefore, the effect of CMCs on the impact performance of composites was more pronounced.

3.3. Dynamic mechanical properties

The results of DMA characterisation of neat glass/epoxy and hierarchical composites are summarised in Table 4 and the storage modulus, loss modulus and tan delta curves are provided in Fig. 8. It can be observed that the storage modulus of composites, which represents the stiffness, increased with CMC loading and a maximum improvement in storage modulus of 21.9% at 40 °C was achieved with 1.5 wt% CMC. This was attributed to the restriction to the segmental mobility of epoxy molecules by the well dispersed CMC particles, as also reported for other nano materials [12,36]. Good interactions between the CMC particles and epoxy molecules due to a homogeneous dispersion and possible covalent bonding between them improved this effect. A stable improvement of storage modulus over a wide temperature range was observed at 1 wt% CMC due to a homogeneous CMC dispersion. At higher CMC concentrations (i.e. 1.5 wt% and 3 wt%), storage moduli decreased drastically as the temperature increased. This could result from the CMC agglomeration at higher concentrations which reduced the interactions between CMCs and epoxy molecules and the restriction to the segmental mobility. At higher temperatures, this effect became more pronounced due to highly mobile epoxy molecules [12,36].

As compared to storage moduli, the viscous response and energy dissipation of composites (represented by loss modulus and tan delta, respectively) increased more prominently with CMC incorporation. The developed hierarchical composites, therefore, possessed significantly higher damping characteristics as compared to neat glass/epoxy composites. This resulted from the good interactions between CMCs and epoxy molecules leading to considerable frictional energy dissipation during segmental mobility of epoxy molecules [12,36]. Loss moduli increased up to 98% at 40 °C by adding 1.5 wt% CMC and decreased strongly at 3 wt% due to CMC agglomeration. A slight increase in the CMC agglomeration at 1.5 wt% reduced the CMC-epoxy interactions to some extent, facilitating frictional sliding and energy dissipation and therefore, led to an improved loss modulus. However, at 3 wt% CMC agglomeration became high and this led to drastic reduction the interactions resulting in inferior frictional sliding and energy dissipation at the CMC-epoxy molecular interfaces. At high temperatures (~100 °C), the difference in storage moduli became lower, as CMC could not influence the highly mobile matrix molecules, as previously observed for nanocellulose based epoxy composites [36].

On the contrary, the influence of CMCs on loss moduli and tan delta became more prominent at elevated temperatures due to increase in the molecular mobility, resulting in increased viscous and energy dissipation components of composites. It can be seen from Table 4 that glass

Table 3

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Izod impact energy (J)</th>
<th>% Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/epoxy</td>
<td>1.49 ± 0.09</td>
<td>-</td>
</tr>
<tr>
<td>Glass/epoxy + 1% CMC</td>
<td>1.63 ± 0.03</td>
<td>9.4</td>
</tr>
<tr>
<td>Glass/epoxy + 1.5% CMC</td>
<td>1.50 ± 0.16</td>
<td>0.7</td>
</tr>
<tr>
<td>Glass/epoxy + 3% CMC</td>
<td>1.48 ± 0.21</td>
<td>0.6</td>
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</table>
transition temperature ($T_g$) of glass/epoxy composites increased significantly (by ~13 °C) when 1 wt% CMC was dispersed. $T_g$ increased due to the restriction of well dispersed CMCs to the segmental movement of epoxy molecules, as also evidenced by other researchers with nanocellulose and other nanomaterial reinforced epoxy and hierarchical composites [12,17]. Better interaction between CMCs and epoxy molecules due to homogeneous dispersion and strong CMC-epoxy interface were the favourable factors for such an increase in $T_g$. In addition, the cross-linking density of the epoxy matrix could also improve in presence of CMCs due to its accelerating effect, as previously observed with cellulose nanofibres [33], leading to an increase in $T_g$. However, at higher CMC concentrations, CMC bundling and agglomeration could produce defects in the epoxy molecular networks facilitating their segmental mobility and reducing $T_g$ of the composites. Cole-cole plots of the composites presented in Fig. 8d, which are indicative of the homogeneity of the composite systems [34], clearly showed a deviation from the smooth and semi-arc shape in case of 1.5 wt% and 3 wt% CMC based composites. This indicates that these composites were slightly inhomogeneous due to CMC agglomeration at higher concentrations.

3.4. Thermal degradation behaviour

TGA and DTG curves of neat glass fibre/epoxy and hierarchical composites are provided in Fig. 9 and the results are summarised in Table 5. It can be observed that all composites showed similar degradation behaviour with a main degradation stage between 280 °C and 500 °C. This degradation stage resulted from the degradation of epoxy molecules (pyrolysis and decomposition of epoxy molecules and degradation of the amine curing agent) and CMCs (cleavage of glycosidic linkages) present in the hierarchical composites into carbon, hydrocarbons and volatiles [36]. It is interesting to notice that a higher amount of CMC addition (mainly 3 wt%) resulted in the increase of initial and maximum decomposition temperatures of composites. This enhancement in thermal stability of composites can be attributed to the higher cross-linking density of epoxy in presence of CMCs, as previously observed by others with nanocellulose [36]. Moreover, the formation of char from CMCs in the initial degradation stage acted as the insulating layer to the combustible gases produced due to the matrix degradation [36] and reduced the mass release of the volatile gases, resulting in an improved thermal resistance of the composites [36].

It can also be noticed that the residual weight of the composites decreased with the increase in the CMC content. It could be due to less formation of char residue at the final degradation stage owing to change in the decomposition pathway of the epoxy matrix in presence of CMCs. The change in the decomposition mechanism of epoxy and other polymers in presence of various nanoparticles have been previously noticed in earlier studies [37,38]. Nanoparticles can catalyse either the charing reaction or complete degradation forming volatiles, depending on the of nanomaterial or polymer type and degradation conditions [38]. In the present case, good dispersion and interaction of CMCs with epoxy molecular chains is believed to influence the heat transfer to the epoxy matrix, reducing the mass release of the volatile gases.

### Table 4

<table>
<thead>
<tr>
<th>Sample details</th>
<th>$E'$ (GPa)</th>
<th>Increase in $E'$ (%)</th>
<th>$E''$ (GPa)</th>
<th>Increase in $E''$ (%)</th>
<th>$\tan\delta$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/epoxy</td>
<td>17.8 ± 0.3</td>
<td>–</td>
<td>0.51 ± 0.02</td>
<td>–</td>
<td>0.03 ± 0.00</td>
<td>63.1 ± 1.3</td>
</tr>
<tr>
<td>Glass/epoxy + 1% CMC</td>
<td>20.2 ± 0.2</td>
<td>13.5</td>
<td>0.62 ± 0.01</td>
<td>21.6</td>
<td>0.03 ± 0.00</td>
<td>76.3 ± 2.2</td>
</tr>
<tr>
<td>Glass/epoxy + 1.5% CMC</td>
<td>21.7 ± 0.1</td>
<td>21.9</td>
<td>1.01 ± 0.07</td>
<td>98.0</td>
<td>0.05 ± 0.01</td>
<td>54.8 ± 2.5</td>
</tr>
<tr>
<td>Glass/epoxy + 3% CMC</td>
<td>18.1 ± 0.1</td>
<td>1.7</td>
<td>0.60 ± 0.04</td>
<td>17.6</td>
<td>0.04 ± 0.01</td>
<td>51.1 ± 3.4</td>
</tr>
</tbody>
</table>

Fig. 8. Dynamic mechanical properties of glass/epoxy and multi-scale composites: (a) storage modulus, (b) loss modulus, (c) tan delta curves and (d) cole-cole plot.
molecules and their decomposition kinetics, forming a lower amount of char residue. This finding is in agreement with the results of earlier studies on nanocellulose based epoxy composites [39]. However, further research is underway to fully understand the influence of CMCs on the thermal decomposition mechanism of epoxy resins.

3.5. Comparison with previously studied hierarchical glass/epoxy composites

A comparison between the achieved results with those previously obtained for glass/epoxy hierarchical composites fabricated with other nano materials is provided in Table 6. It is clear that the improvements due to different nano/micro materials are different depending on their type and processing methods. CNTs have been mostly used to develop glass/epoxy hierarchical composites and cellulose based nano/micro particles have been rarely used. The incorporation of nanomaterials improved ILSS, in-plane strength and stiffness, fracture properties, Tg as well as dynamic mechanical properties such as storage and loss moduli [5,6,8,11,12,17].

The improvement of ILSS was found to be more when CNTs were applied to the fibre surface as compared to dispersion in the matrix due to the more effectiveness of CNTs present on the fibre surface to improve fibre-matrix bonding. However, CNT incorporation on both fibre surface and in the matrix led to only a marginal improvement in ILSS due to high CNT concentration and agglomeration within the interfacial regions [6]. The improvement in ILSS (65%) achieved in the present study was significantly higher as compared to previous studies with MWCNTs, dispersed within the matrix, probably due to better dispersion of CMCs as compared to CNTs (which present more dispersion problems due to higher surface area and entanglements) in the epoxy matrix. Agglomeration of nano/micro materials reduce their ability to improve fibre-matrix interactions and toughening of matrix in the interface regions, leading to a less ILSS improvement [6]. The improvement of ILSS in the present study was also comparable with that achieved when nanocellulose was coated on the glass fibre surface (69%) [17]. Also, much higher improvements in other mechanical properties (except the composite modulus) were achieved with CMCs as compared to surface-coated nanocellulose. This was expected as the surface coated nanocellulose was more effective in improving the fibre-matrix interface but not the matrix strength and toughness, which strongly influence the strength and fracture properties of composites. In spite of the positive influence on fibre-matrix interface, CMCs did not show any positive influence on the composite modulus probably due to less influence of the fibre-matrix interface on the initial elastic behaviour of composites. The Tg of the composites also improved significantly (by 13 °C) due to CMC addition. However, the improvement was lower as compared to that achieved with the previously studied amine functionalised GO [12]. Although CMCs could form covalent bonding with the epoxy molecules to restrict their segmental mobility, similar to DA-GO, the lower size and higher surface area of GO led to a better molecular confinement and a higher Tg improvement. The thermal degradation temperatures (onset and maximum) improved at high CMC concentrations (3 wt%); the improvement was again significantly lower as compared to that previously achieved with DA-GO [12]. The homogeneously dispersed nano-scale GO platelets formed a tortuous pathway delaying the release of volatile compounds and decomposition rates of composites [12], which was not possible with the micro-scale CMCs. To summarise, the improvements achieved with CMCs in most of the studied properties were comparable or superior as compared to those previously achieved with other nano/micro particles. At the same time, CMCs have significantly lower cost, commercially availability and can be produced from renewable resources and therefore, can be used as a new sustainable reinforcing material to develop glass/epoxy hierarchical composites.

4. Conclusions

In this research, CMC was successfully used to considerably improve the fibre-matrix interface and properties of glass fibre reinforced epoxy composites. Dispersion of CMCs within the epoxy resin was carried out using an ultrasonication treatment for 1 h, which led to an average agglomerate size in the range of 282–451 μm² and the total agglomerated area of 3–11% for 1–3 wt% CMC. The CMC dispersion was homogeneous at 1 wt% CMC, showing dispersion of individual crystals and very less agglomeration. The presence of CMCs in the epoxy matrix significantly improved the fibre-matrix interface, which was believed to be mainly due to chemical bonding between the silane coating of glass fibres and CMCs as well as between CMCs and the epoxy molecules. Incorporation of 1 wt% CMC resulted in a 65% improvement in ILSS, 14% and 76% improvements in tensile and flexural strengths, 111% and 119% improvements in fracture energy in tensile and flexural modes and a 9.4% improvement in the impact strength of composites. In addition, the

Table 5
Summary of TGA results of glass/epoxy and hierarchical composites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Onset degradation temperature (°C)</th>
<th>Maximum degradation temperature (°C)</th>
<th>Residual weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/epoxy</td>
<td>286 ± 0</td>
<td>374 ± 1</td>
<td>78</td>
</tr>
<tr>
<td>Glass/epoxy + 1% CMC</td>
<td>286 ± 1</td>
<td>374 ± 1</td>
<td>73</td>
</tr>
<tr>
<td>Glass/epoxy + 1.5% CMC</td>
<td>287 ± 1</td>
<td>382 ± 1</td>
<td>74</td>
</tr>
<tr>
<td>Glass/epoxy + 3% CMC</td>
<td>292 ± 1</td>
<td>386 ± 1</td>
<td>67</td>
</tr>
</tbody>
</table>

Fig. 9. TGA (a) and DTG (b) curves of neat glass fibre/epoxy and hierarchical composites.
storage modulus, loss modulus and \( T_g \) improved by 13.5%, 21.6% and 13 °C, respectively owing to superior interactions of CMCs with epoxy molecules. The homogeneity of the composite systems decreased at higher CMC concentrations due to agglomeration. Although damping characteristics and thermal degradation behaviour improved at higher CMC concentrations, most of the other studied properties decreased significantly. Therefore, based on the findings it is expected that the developed physical approach of improving interface and performance of glass fibre composites using a green and low-cost commercially available cellulose material can be advantageously used to replace non eco-friendly methods used in the current composite industry.

**Data availability statement**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. The relevant data can be made available on request.

**CRediT authorship contribution statement**

**Shama Parveen:** Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **Subramani Pichandi:** Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **Parikshit Goswami:** Funding acquisition, Writing - review & editing. **Soheil Rana:** Conceptualization, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Writing - review & editing.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**References**


