Topical Review: An Introduction to Polymer Nanocomposites

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Abstract

This topical review presents an overview of the formulation, characterisation and range of applications for polymer nanocomposites. After explaining how material properties at the nanometre scale can vary compared to those observed at longer length scales, typical methods used to formulate and characterise nanocomposites at laboratory and industrial scale will be described. The range of mechanical, electrical and thermal properties obtainable from nanocomposite materials, with examples of current commercial applications, will be outlined. Formulation and characterisation of nanoparticle, nanotube and graphene composites will be discussed by reference to nanoclay-based composites, as the latter are presently of most technological relevance. Three brief case studies are presented to demonstrate how structure/property relationships may be controlled in a variety of polymer nanocomposite systems to achieve required performance in a given application. The review will conclude by discussing potential obstacles to commercial uptake of polymer nanocomposites, such as inconsistent protocols to characterise nanocomposites, cost/performance balances, raw material availability, and emerging legislation, and will conclude by discussing the outlook for future development and commercial uptake of polymer nanocomposites.

1 Introduction: Nanotechnology, composite materials and nanocomposites

This topical review will present an overview of the formulation, characterisation and range of current and emerging applications for polymer nanocomposite materials. These offer significant potential to develop new materials with unique properties that are easier to process than conventional composite materials.

We will begin by defining what ‘nanotechnology’ and ‘composite materials’ are, and briefly explaining how material properties at the nanometre scale can vary compared to those observed at longer length scales. The range of mechanical, electrical, thermal and optical properties obtainable using nanocomposite materials will be outlined, then we will compare the properties of the three main types of nano-reinforcement used to formulate polymer nanocomposites: nanoparticles, layered materials (nanoclays, graphene) and fibres (carbon nanotubes and nanofibres). Some knowledge of standard analytical techniques – thermal analysis, electron microscopy and x-ray diffraction – will be assumed on the part of the reader.

The term ‘nanotechnology’ can be misleading since it is not a single technology or scientific discipline. Rather, nanotechnology is a group of processes, materials, applications and concepts defined by size (Thostenson et al 2005). Nanotechnology involves materials at the nanometre scale,
i.e. within the size range from \( \sim 1 \text{ nm} \) to \( 100 \text{ nm} \) and, as we will see shortly, the physical properties of the same material (e.g. carbon, silicon, metals...) are not the same at the nano scale as at the macro scale. 1 nanometre (\( 1 \times 10^{-9} \text{ m} \)) is one millionth of 1 mm. For comparison, a DNA molecule has a diameter of approximately 2 nm, viruses measure between 10 and 100 nm, red blood cells have a diameter of approximately 5,000 nm and a single human hair measures between 10,000 and 100,000 nm in diameter.

A ‘composite material’ may be defined as an artificially made material that consists of multiple phases. These phases are chemically dissimilar, and there is a distinct interface between the chemical phases present in the material (Callister 2000, p.521). As illustrated in Figure 1, the continuous phase is referred to as the ‘matrix’ and the other phase(s) dispersed in this matrix are referred to as the ‘reinforcement’. Composite – and nanocomposite – materials have been manufactured using a wide range of matrices (e.g. polymers, carbon, metals, ceramics) and reinforcements (e.g. particles, fibres and layered materials); this review will concentrate on polymer matrix composites only as these are of particular technological interest (Thostenson et al 2005, Tjong 2006).

**Figure 1: Layup of a typical fibre-reinforced composite. The terminology used is common to all composite materials.**

At the macro scale, the material properties of a polymer composite are determined primarily by the dimensions of the reinforcement and how it is distributed in the matrix. For example, carbon fibre composites in which the fibres are orientated in different directions in successive laminates, has different mechanical properties to a ‘unidirectional’ composite in which all the fibres are orientated in the same direction (Matthews and Rawlings 1999). Likewise, two otherwise identical composites prepared with carbon fibres of different diameters will exhibit different properties. At the sub-micron scale, the dimensions of the reinforcement and the interface formed between the reinforcement and the matrix – known as the ‘interphase’ – are the dominant influence on the material properties (Thostenson et al 2005). In contrast, as one or more dimensions of the reinforcement approaches the nano scale, it is increasingly the diameter and surface chemistry of the reinforcement that determines the material properties of the final composite material, which is now referred to as a ‘nanocomposite’. The difference in length scales between conventional polymer composites and nanocomposite is significant; for example, the interphase between the fibre and matrix of a typical carbon fibre reinforced polymer composite is larger than an entire nanoparticle.
1.1 Why use nanocomposites?

Though they have come to prominence in recent years, engineered nanomaterials are not actually new. Materials such as zeolites, pigments, carbon black, synthetic amorphous silica, and smectic layered clays, which are nowadays considered to be ‘nanomaterials’, are well known commodity materials (Smart and Moore 1995a). The unique properties of metal colloids have long been known; for example, the vibrant ruby red colours in stained glass windows such as that shown in figure 2 are obtained by adding either copper or gold to the glass during manufacture, which forms colloids in the glass. A remarkable example of such glassmaking is the dichroic glass used to make the Lycurgus Cup, dating from the 4th century A.D. (Freestone et al 2007). This has an opaque green-yellow hue in direct light, but appears ruby red when transmitted light shines through the glass. This effect has been attributed to the presence of nanoparticles of silver-gold alloy in the glass, typically 50 – 100 nm in diameter; it is believed that these nanoparticles formed in situ in the glass during heat treatment following addition of metal salts to the molten glass.

![Figure 2: Stained glass window, Cathedral of the Nativity of the Blessed Virgin Mary, Juneau, Alaska. The colours in the glass arise from the presence of metal colloids in the glass from metal oxides added during its manufacture. At diameters below 100 nm, such colloids may be considered as ‘nanoparticles’ (Photograph courtesy: Kate Murphy).](image-url)
Compared with conventional polymer composites, polymer nanocomposites display improved mechanical and tensile strength, reduced scratch and mar resistance, higher heat distortion temperature and noise dampening. Problems normally associated with high reinforcement content in composites such as decreased toughness, poor optical clarity and higher melt viscosity are less of an issue in nanocomposite production because a nano-reinforcement loading of less than 10 wt% is sufficient to produce high performance polymer nanocomposites.

Nanocomposites may be processed using the same well-established standard methods used to process virgin polymers, such as extrusion, injection moulding, thermoforming, blow moulding and compression or transfer moulding (Bower 2002, Ashby and Jones 2006a). These methods also allow for high throughput which is vital for economic production, e.g. polymer or glass fibre reinforced automotive parts must be produced at a rate of more than one part per minute if they are to be competitive with traditional materials and technologies (Bakewell 2014). Considering that processing accounts for between 2/3 and 3/4 the cost of engineered composite materials, easier processing gives lower overall costs that offsets the higher material costs that may be incurred using nano-reinforcements.

However, nanocomposites are not without their disadvantages too. Compared to virgin polymers, they typically exhibit decreased toughness and poorer optical clarity due to the presence of the nano-reinforcement. They also have significantly higher melt viscosity than virgin polymers, which presents processing difficulties. Nonetheless, manufacturing polymer nanocomposites remains simpler than manufacturing high-performance composite materials using techniques such as autoclave processing or resin transfer moulding with conventional carbon fibre reinforcements. Depending on the nano-reinforcement and matrix used, it is possible to obtain a remarkably wide range of materials properties from polymer nanocomposites; a representative range of these that have already been exploited in commercial applications are presented in Table 1, overleaf.

Nanocomposites are now widely used for applications in packaging, automotive, aerospace, electronics and semiconductors, energy, construction and cosmetics, and the global polymer nanocomposites market is expected to reach a value in excess of $5,100 million by 2020 (Markets and Markets 2015). For comparison, the global market for all nanotechnology products was valued at about $26 billion in 2014 and is expected to reach about $64.2 billion by 2019 (BCCresearch 2014).

The nanomaterial most widely used to prepare nanocomposites on a commercial scale is nanoclay (Uddin 2008). Therefore, the discussion throughout the remainder of this review will take polymer/nanoclay composites as a starting point, and discuss other polymer nanocomposites such as carbon nanotube and nanoparticle reinforced composites by reference to them in the next Section.
Table 1: Examples of commercial applications of polymer nanocomposites (from Paul and Robeson 2008, with permission).

<table>
<thead>
<tr>
<th>Polymer matrix</th>
<th>Nano-reinforcement</th>
<th>Property improvement</th>
<th>Application</th>
<th>Company and/or product trade name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide 6</td>
<td>Exfoliated nanoclay</td>
<td>Stiffness</td>
<td>Timing belt cover: automotive</td>
<td>Toyota/Ube</td>
</tr>
<tr>
<td>Thermoplastic polyolefin (TPO)</td>
<td>Exfoliated nanoclay</td>
<td>Stiffness/strength</td>
<td>Exterior step assist</td>
<td>General Motors</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Carbon nanotubes</td>
<td>Strength/stiffness</td>
<td>Tennis rackets</td>
<td>Babolat</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Carbon nanotubes</td>
<td>Strength/stiffness</td>
<td>Hockey sticks</td>
<td>Montreal: Nitro Hybtonite ®</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>Exfoliated nanoclay</td>
<td>Permeability barrier</td>
<td>Tennis balls, tyres, soccer balls</td>
<td>InMat LLC</td>
</tr>
<tr>
<td>Styrene-butadiene rubber (SBR),</td>
<td>Carbon black (20-100 nm:</td>
<td>Strength, wear and abrasion</td>
<td>Tyres</td>
<td>Various</td>
</tr>
<tr>
<td>natural rubber, polbutadiene</td>
<td>primary particles)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Various</td>
<td>Multi-walled carbon</td>
<td>Electrical conductivity</td>
<td>Electrostatic dissipation</td>
<td>Hyperion</td>
</tr>
<tr>
<td>Unknown</td>
<td>Silver</td>
<td>Antimicrobial</td>
<td>Wound care/bandage</td>
<td>Curad®</td>
</tr>
<tr>
<td>Nylon MXD6, polypropylene</td>
<td>Exfoliated nanoclay</td>
<td>Barrier</td>
<td>Beverage containers, film</td>
<td>Imperm™: Nanocor</td>
</tr>
<tr>
<td>SBR rubber</td>
<td>Not disclosed</td>
<td>Improved tyre performance in winter</td>
<td>Winter tyres</td>
<td>Pirelli</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>Silver</td>
<td>Antimicrobial</td>
<td>Latex gloves</td>
<td></td>
</tr>
<tr>
<td>Various</td>
<td>Silica</td>
<td>Viscosity control, thixotropic agent</td>
<td>Various</td>
<td></td>
</tr>
<tr>
<td>Polyamides: nylon 6, 66, 12</td>
<td>Exfoliated nanoclay</td>
<td>Barrier</td>
<td>Auto fuel systems</td>
<td>Ube</td>
</tr>
</tbody>
</table>

Information from company web pages and industry journal reviews.

1.2 Three categories of nano-reinforcement

The ratio of surface area to volume of nano-reinforcements is key to understanding the structure–property relationships of polymer nanocomposites. Material properties can be very size dependent at the nano-scale, and the surface area/volume ratio is typically three times greater for nano-reinforcements than their micron-sized counterparts. The result is that the surface chemistry of the nano-reinforcement dominates polymer nanocomposites’ properties, as mentioned previously. Nano-reinforcements may be divided into three main categories – particles, fibres and layered materials. These are described in turn below.
**Nanoparticles**

In conventional polymer composites, micron-sized particles are typically added as a reinforcement to increase elastic modulus and yield strength. However, scaling these particle reinforcements down to nanometre scale can give remarkable novel material properties e.g. gold nanoparticles are red in colour, and silver nanoparticles change colour depending on their size and shape (Ledwith et al. 2007), as illustrated in Figure 3.

![Figure 3](image_url)

(a) TEM image of silver nanoparticles (image: Tanushree Bala, University of Limerick); (b) Solutions of silver nanoparticles of average diameter 50 nm; the colour of the nanoparticles varies depending on their shape, which is determined by the conditions under which they are prepared.

**Layered platelet materials**

There are three main types of layered platelet nanomaterials of technological interest for polymer nanocomposites: naturally occurring and synthetic clays – montmorillonite, saponite, mica etc. – graphite, and graphene. Of these, layered montmorillonite clays consisting of nanometre-thick platelets are the most cost-effective nanomaterials, and a wide range of nanoclays modified to be compatible with commodity polymers are commercially available. Montmorillonite is the primary component of bentonite mineral clay, which also contains minerals such as, quartz, mica, feldspar, and zeolite; bentonite is obtained either by quarrying or mining, depending on its source (Kunimine 2015). Nanoclay nanocomposites offer improved stiffness, strength, toughness and thermal stability combined with reduced gas permeability and lower coefficient of thermal expansion (Alexandre and Dubois 2000, Sinha Ray and Okamoto 2003, Paul and Robeson 2008).

Nanoclays exist as layered materials in their bulk form (Smart and Moore 1995a); these layers must be must be separated and dispersed in the polymer matrix to form a nanocomposite material. Several strategies have been developed to formulate polymer nanocomposites using nanoclays, depending on the polymer matrix used, and these are discussed in Section 2. The chemical structures of some naturally occurring nanoclays are shown in Figure 4. It is important to be aware that, even within one type of nanoclay, the physical form and cation (typically sodium) content of the clay can vary depending on its source, as illustrated in Figure 5. Comparable differences arise in synthetic materials such as carbon nanotubes, depending on the method used to synthesise them. These differences can have a significant effect on the formulation of polymer nanocomposites using these nano-reinforcements, and on the properties of the resulting nanocomposites.
Figure 4: Comparison of chemical structures of naturally occurring nanoclays (a) layered smectite nanoclay and (b) layered kaolinite nanoclay. Note also the difference in typical gallery spacing (i.e. the separation between individual clay platelets) between both types of nanoclay.

Figure 5: Comparison of physical structure of commercially available sodium montmorillonite nanoclays observed by scanning electron microscopy (a) Cloisite Na (b) Bentone MA (c) Kunipa F (d) Nanocor PGV. Note that the gallery spacing $(d_{100})$ and the cation equivalent content (CEC) vary appreciably between the nanoclays as well as the physical structure of the clays.
In recent years, graphene has attracted great attention as a promising new nanomaterial (Kim et al 2010). Essentially, graphene is comprised of single sheets of exfoliated graphite. These have similar thickness as exfoliated nanoclay, but offer much improved properties compared to nanoclay platelets. Graphene is still predominantly used in laboratory-scale research, but is proving to be of particular interest for exceptionally high thermal and electrical conductivity. It is discussed further in Section 4.4.

**Nanotubes**

Carbon nanotubes (CNTs) exhibit remarkable electrical and mechanical properties, and have become key components in advanced sensors, electronic and optical devices, catalysts, batteries and fuel cells, and high-strength composite materials (Coleman et al 2006). Arguably, in their purest form - single walled carbon nanotubes (SWCNTs) – carbon nanotubes offer a combination of properties unmatched by any conventional material, as illustrated in Table 2 (Li et al 2011).

**Table 2: Material properties of single walled carbon nanotubes (SWCNTs) compared with conventional materials.**

<table>
<thead>
<tr>
<th>Property</th>
<th>SWCNT</th>
<th>Comparison value</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.33–1.40</td>
<td>2.7</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Elastic modulus (TPa)</td>
<td>1.2</td>
<td>1.2</td>
<td>Diamond</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>2000</td>
<td>276 – 2000</td>
<td>Steel</td>
</tr>
<tr>
<td>electric current carrying capability (amp/cm²)</td>
<td>1 · 10⁹</td>
<td>1 · 10⁶</td>
<td>Copper wire</td>
</tr>
<tr>
<td>Thermal conductivity @ room temperature (W/m K)</td>
<td>6000</td>
<td>3320</td>
<td>Diamond</td>
</tr>
<tr>
<td>Thermal stability (ºC)</td>
<td>2800 (vacuum)</td>
<td>600 – 1000</td>
<td>Metal wires in microchips</td>
</tr>
</tbody>
</table>

However, large scale industrial production of high-quality CNTs is not yet possible. CNTs produced in bulk by all available synthesis methods are of low purity, and additional purification steps are necessary to obtain nanotubes of > 98 % purity. While production of purified CNTs increasing and becoming cheaper, bulk production remains very expensive and it is not possible to produce 1 tonne per day with current technologies. Therefore, it has been suggested that polymer/ CNT nanocomposites are better suited – on the grounds of cost and complexity – to niche high-value
applications that exploit their unique properties such as electrical and thermal properties, rather than for mechanical reinforcement alone, where nano-reinforcements such as nanoclays are more cost-effective (Armstrong and Birkett 2009).

To appreciate how graphite, graphene and carbon nanotubes are related, first consider a piece of graphite, which consists of layers of carbon atoms covalently bonded in a honeycomb-shaped lattice. Imagine taking a piece of pure graphite and peeling off an individual layer of carbon atoms from it: this is a sheet of graphene. Now imagine taking this graphene sheet and rolling it into a tube – this is a carbon nanotube. Because it consists of one layer of graphene, it is called a ‘single-walled carbon nanotube’ (SWCNT). Wrapping a second layer of graphene around this gives a ‘double-walled nanotube’ (DWCNT), and ‘multi-walled nanotubes’ (MWCNTs) have three or more graphene sheets wrapped around each other. The relationship between these materials is summarised in Figure 6. Each graphene layer can be ‘rolled up’ to give different atomic structures, and these different structures give different properties – either metallic or semiconductor – to the nanotube. In reality, graphite, graphene and carbon nanotubes are not prepared like this. In fact, there are several possible routes to prepare each of them, and each route yields material of varying purity with somewhat different properties.

![Image of the relationship between graphite, graphene, and carbon nanotubes.](image)

**Figure 6:** How the structures of graphite, graphene and carbon nanotubes are related.

**Nanowires and Nanofibres**

Compared to nanotubes, as described above, nanowires typically also have diameters of the order of tens of nanometers, but with length scales ranging from microns up to sub-millimetre. A typical carbon nanofibre (CNF) has a larger diameter than a nanotube – typically diameters range from 50–200 nm – with wide-ranging morphologies (Thostenson et al 2005). As we saw in the case of carbon nanotubes, different nanofibre morphology results in different material properties. Vapour grown CNFs have been used to reinforce many polymers, including polypropylene, polycarbonate, nylon,
poly(ether sulfone), poly(ethylene terephthalate), poly(phenylene sulfide), acrylonitrile-butadiene-styrene (ABS) and epoxy. Many of the key challenges associated with the processing, characterization, and modelling of CNF composites, such as dispersion and adhesion, are similar to those for nanotube-, nanoparticle- and nanoclay-reinforced composites, and these are discussed in the following section.

2 How do we formulate a nanocomposite?

As discussed in the Introduction, polymer composite materials reinforced with nanomaterials can achieve high performance at a low loading – <10 wt% – of nano-reinforcement. Problems normally associated with high filler content such as decreased toughness, poor optical clarity and higher melt viscosity are thus less of an issue in nanocomposite production. Furthermore, it is possible to prepare nanocomposites via the same methods used to manufacture conventional plastic parts. To be suitable for scale-up, any proposed route to prepare functionalised nano-reinforcements and formulate nanocomposites from them should meet the following criteria:

- The functionalised nano-reinforcement obtained should have consistent properties and controllable, reproducible morphologies
- They should be easily dispersed in common solvents, and readily incorporated in the polymer resins used to prepare the desired nanocomposite
- Processes used to prepare or modify the nano-reinforcements and nanocomposites should be simple, reproducible, and give a high yield of the desired product under ambient conditions using simple apparatus.

There are three key factors to formulating a nanocomposite: 1) choosing the most appropriate nanoadditive, 2) controlling the morphology of the nanoadditive and finished nanocomposite, and 3) getting the chemistry of the composite formulation right. To control each of these factors, we must start by asking some questions:

1. What type of product – and how much of it – do we want to make?
2. Is the polymer we will use polar or non-polar?
3. Is the polymer (or the monomer from which it is made) miscible with the nano-reinforcement, or
4. Is there a common solvent in which the polymer dissolves and the nano-reinforcement can also be dispersed?

The answers to these questions will lead us to a first choice among three primary processing routes:

1. In-situ polymerisation, if the monomer is liquid and miscible with the nano-reinforcement
2. Solution processing, if there is a common solvent that dissolves the polymer and in which the nano-reinforcement can be dispersed
3. Compounding the nano-reinforcement with the polymer in the molten state, i.e. melt processing.

In general, the aim in formulating a polymer nanocomposite is to achieve a uniform particle size distribution and minimal agglomeration of the nano-reinforcement. Typically, agglomeration of
nano-reinforcements occurs as the volume fraction of nano-reinforcement added to the polymer matrix increases; this results in loss of mechanical and optical properties. Also, the selection of candidate nano-reinforcements and polymer matrices can often be restricted by the intended application, and furthermore the nano-reinforcement may be expected to enhance more than one property of the final material.

Consider the case of nanocomposites intended for use in optical devices (Nguyen 2011). Most polymers used in optoelectronic applications are conjugated polymers (i.e. they have alternating single and double bonds on the polymer backbone, so they behave as semiconductors), which limits the range of matrices available. The nano-reinforcement should have a particle size less than 1/10 the length of visible wavelength (usually < 40 nm) to ensure the nanocomposite remains transparent and does not cause losses due to light scattering, but the nano-reinforcement should also improve the mechanical strength and scratch resistance of the material. In fact, all three primary classes of nano-reinforcement – nanoparticles, layered materials (nanoclays and graphenes), and carbon nanotubes – have found use in optical devices, dispersed in a variety of polymer matrices, demonstrating that more than one solution to a given formulation problem is usually possible. For any given formulation of polymer, compatibiliser and nano-reinforcement, a maximum value for the properties obtained will be found, as illustrated in Figure 7. Achieving an optimal formulation is frequently an empirical exercise involving a combination of skill, experience and trial-and-error on the part of the formulation scientist. If the key factors that affect the formulation can be identified and quantifiable parameters to evaluate its success (or not) can be identified, then statistical design-of-experiments methodologies can often be put to good use to arrive an optimal formulation more efficiently (e.g.: Nouranian et al 2011, Campos-Requena et al 2014). It is also important to be aware that findings for similar nanocomposite formulations published in academic papers and research reports may sometimes appear to contradict each other. When comparing such results, it is instructive to check whether the formulations are actually comparable in terms of the starting materials, preparation and characterisation methods used.

Figure 7: The material properties of any nanocomposite vary with respect to the loading of nano-reinforcement. The critical loading to achieve maximum properties depends on the formulation and processing method used to prepare the composite.
2.1 *In-situ* polymerisation

This was the approach used to prepare the first commercial polymer nanocomposites - nylon/nanoclay composites used to manufacture timing belt covers for the 1994 model year Toyota Camry (Patel and Mahajan 2014). The nano-reinforcement is introduced to the monomer precursor for the desired polymer matrix in the liquid state, dispersed thoroughly, then the monomer is polymerised with the nano-reinforcement *in-situ* to make the final nanocomposite. The experimental approach is similar to surfactant modification of nanoclays, discussed above, and is illustrated for the preparation of a nylon 6,10/nanoclay nanocomposite in Figure 8.

![Caprolactam monomer](image)

![Nylon 6,10](image)

Figure 8: *In-situ* polymerisation of caprolactam monomer in sodium montmorillonite nanoclay to obtain a nylon 6,10 nanocomposite.

2.2 Nanoclays: Surfactant Modification

The nylon/nanoclay example above is unusual in that both the nano-reinforcement and monomer are hydrophilic, and therefore mix readily, whereas most commodity and engineering polymers and monomers are hydrophobic. Naturally occurring nanoclay has positively charged cations (usually sodium or calcium) on the surface of the clay platelets. This makes it hydrophilic – it will not mix with hydrophobic polymers. In this instance, we must modify the clay platelet surface to make it hydrophobic. Typically, the clay is modified with a quaternary ammonium surfactant. The surfactant ions exchange with the sodium ions on the clay platelet surface, as shown in Figure 9, so that the resulting organically modified nanoclay, or ‘organoclay’, becomes hydrophobic. The length of the surfactant’s hydrophobic alkyl chain, or ‘tail’, is chosen to make the organoclay more or less hydrophobic, to better match the hydrophobicity of the organoclay with that of the polymer it is to be combined with. Longer alkyl tails give a more hydrophobic organoclay (Alexandre and Dubois 2000, Sinha Ray and Okamoto 2003).
Surfactant modification of nanoclay with quaternary ammonium surfactant to improve miscibility with hydrophobic polymers by substituting cations on the surface of the nanoclay platelets hydrophobic alkyl chains (‘tails’).

When the platelets are completely separated and dispersed in the matrix, the nanocomposite is referred to as ‘exfoliated’. Exfoliation requires high shear & high temperatures, which can present processing difficulties as degradation of the organic treatment may occur at these higher temperatures. Sometimes, the platelets are not fully exfoliated, but rather, the polymer enters between the surfactant-modified clay platelets, forcing them apart; such nanocomposites are referred to as ‘intercalated’. The process of intercalation and exfoliation of nanoclay platelets is illustrated in Figure 10 and discussed further in case study A, Section 3.

Figure 10: Intercalated and exfoliated layered silicate in a polymer matrix.

2.3 Solution processing

Especially at laboratory scale, solution processing is the easiest approach if both the polymer and nano-reinforcement can be dispersed in a common solvent. A typical procedure is illustrated in Figure 11, and is essentially the same as the method followed for surfactant modification of nanoclays. Preferably, the final nanocomposite should not be miscible in the solvent used, so that the product is easily recovered by filtration or precipitation from the solvent. At larger scale, the main disadvantage of this method is that it is slow, and requires large amounts of solvent and energy.
Melt processing is most appropriate for insoluble or immiscible polymers and nano-reinforcements, and for high-throughput manufacturing. The methods most widely used are comparable to those employed for preparing polymer composites using micron-sized particulate and short-fibre reinforcements. Typically, high shear mixing, (i.e. a twin screw extruder) and a careful choice of polymer resin and compatibiliser is required to achieve adequate dispersion of the nano-reinforcement in the matrix. This is because the nano-reinforcement increases the viscosity of the polymer in the melt significantly compared to the virgin polymer. In fact, achieving complete exfoliation of nanoclay composites by melt mixing, rather than intercalation, poses a significant formulation challenge. A typical procedure to prepare a polypropylene/nanoclay composite is shown in Figure 12.

**Figure 11**: Typical laboratory-scale procedure for solution processing of a polymer/nanoclay nanocomposite.
Figure 12: Typical industrial scale procedure for melt processing of a polypropylene/organoclay nanocomposite. Although the nanoclay is chemically modified with quaternary ammonium surfactant, an additional compatibiliser additive – maleic anhydride – is required to achieve complete exfoliation of the nanoclay in the matrix.

In summary, the properties of nano-reinforcements can vary depending on how they are synthesised (morphology and surface/volume ratio), and how they are functionalised (surface chemistry). Also, the properties of polymer nanocomposites can vary depending on how the nano-reinforcement is functionalised, whether a compatibiliser is used, and how well the nano-reinforcement disperses in the polymer matrix. All these factors must be optimised to formulate a high-quality nanocomposite from a given nano-reinforcement and polymer matrix. The formulation and processing requirements to formulate nanocomposites from the three main types of nano-reinforcement – nanoparticles, nanotubes and layered materials – are compared and summarised in Table 3. How these requirements are balanced in practice to achieve a successful nanocomposite, and how to characterise them, is the subject of the case studies presented next in Section 2. These offer examples of how to functionalise nano-reinforcements and achieve good dispersion in a chosen polymer matrix, how to choose suitable analytical techniques to confirm dispersion of the nano-reinforcements in the polymer, and how to characterise the finished nanocomposites.
Table 3: Summary of formulation and processing requirements to prepare nanocomposites from the three primary types of nanocomposite discussed in Section 1.

<table>
<thead>
<tr>
<th>Processing Method</th>
<th>Material</th>
<th>Particles</th>
<th>Nanorods/ nanotubes</th>
<th>Layered materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Formulation</strong></td>
<td>Good interface formed between polymer matrix and nanomaterial; no agglomerates...</td>
<td>...and polymer must inter-penetrate and exfoliate layers i.e. &gt; 80Å gallery spacing</td>
<td></td>
</tr>
<tr>
<td><strong>goals</strong></td>
<td><strong>Processing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>considerations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>In-situ</strong></td>
<td>Liquid monomer</td>
<td>High shear needed to prevent nanomaterial from agglomerating during mixing</td>
<td>Monomer &amp; clay must have similar hydrophobicity to mix</td>
<td><strong>Case Study C</strong> (Approach 2)</td>
</tr>
<tr>
<td><strong>polymerisation</strong></td>
<td>needed.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>How is it polymerised – heat, UV, catalyst?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Melt</strong></td>
<td>Suits commodity resins, e.g. PP, PC; large scale / high throughput using standard equipment</td>
<td>a. Organic modifications (surfactant, functional groups...) must be thermally stable at processing temperature.</td>
<td>b. Complete intercalation/dispersion difficult to achieve. May give preferred orientation → anisotropic properties.</td>
<td><strong>Case Study A</strong></td>
</tr>
<tr>
<td><strong>compounding</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Solution</strong></td>
<td>Polymer must be soluble but composite must be easily recovered from same solvent</td>
<td>a. More suitable at laboratory scale – slow, small volume.</td>
<td>b. Low loadings produce large quantities solvent waste.</td>
<td><strong>Case Study A</strong></td>
</tr>
<tr>
<td><strong>Processing</strong></td>
<td></td>
<td></td>
<td>c. Supercritical fluid processing easier to recover (SCF evaporates as gas), scalable, environmentally friendly.</td>
<td></td>
</tr>
</tbody>
</table>

3 Case Studies

Case Study A: Comparison of melt processing and supercritical carbon dioxide methods to prepare polyethylene oxide/montmorillonite nanocomposites

As it is extracted from the quarry, montmorillonite nanoclay is polar, and therefore is only compatible with polar solvents and polymers. Hence, nanoclay generally undergoes an organic treatment to make the clay miscible with organic solvents and non-polar polymers of technological interest. The treatment must be chosen to suit to formulation that the nanoclay will be used in.

It can be difficult to achieve a consistent end product when modifying nanoclay via melt processing, especially at laboratory scale where it is difficult to achieve complete mixing of the nanoclay with the polymer or surfactant used to chemically modify it. Chemically modifying nanoclay via solution processing is effective, but slow, and requires a large volume of solvent and is energy-consuming to heat the mixture during processing.
In this case study, the aim was to compare supercritical carbon dioxide (ScCO\textsubscript{2}) fluid treatment with conventional melt processing methods (Armstrong and Fortune 2007). Supercritical fluids are highly compressed gases which combine properties of gases and liquids (Brazhkin \textit{et al} 2012). They are used as a substitute for organic solvents in a range of industrial and laboratory processes.

Poly(ethylene oxide) (PEO) and sodium montmorillonite nanoclay (MMT) are widely used as a model nanocomposite, because these are both polar; this avoids complications in interpreting results from experiments caused by incompatibility between the polymer and nanoclay used. It is known from previous studies that, when PEO/MMT nanocomposites are formulated, once the PEO content of the formulation exceeds 17 wt\%, a bilayer of PEO polymer chains forms in the gallery space between the clay platelets, and these chains adopt a helical structure. Each bilayer of PEO polymer chains increases the height of the MMT’s gallery spacing by ~ 17 Å, so powder x-ray diffraction (XRD) may be used to determine the extent of intercalation achieved by determining the increase in the gallery spacing from Bragg’s law (Smart and Moore 1995b, Cullity and Stock 2001). If the MMT were exfoliated completely, there would be no measurable gallery spacing between adjacent nanoclay platelets, so transmission electron microscopy (TEM) analysis (Williams and Carter 2009) would be required to confirm the nanocomposite was formulated as expected. Also, these helical bilayer structures remain unchanged until the PEO loading exceeds 30 wt\%, so a formulation of 4:1 MMT:PEO (by weight) was used for each experiment to allow direct comparisons between varying molecular weights (400-10,000) and grades of PEO used, and both processing methods.

1.00g PEO and 4.00g MMT were mixed by grinding in a mortar and pestle. For melt processing, this MMT/PEO mixture was pressed into pellets and heated in a laboratory oven at 70ºC for 6 hours. For ScCO\textsubscript{2} processing, the was placed in a gastight pressure chamber, then pressurised to 2800 psi with CO\textsubscript{2} gas, heated to 60ºC, and stirred for 24 hours. After cooling to room temperature, all samples were ground to pass through a 180-micron sieve.

XRD was conducted on each sample prepared to determine the change in gallery spacing, which may be seen as an increase in the d-spacing between the MMT platelets compared to the unmodified MMT, as shown in Figure 13a. The gallery spacing for nanocomposites prepared by ScCO\textsubscript{2} processing were lower than those prepared by melt processing because the PEO polymer chains did not coil in the same manner when plastified as in the molten state. Thermogravimetric analysis (TGA) showed that samples prepared by the ScCO\textsubscript{2} method had lower polymer loading than the equivalent sample prepared by melt processing, as shown in Figure 13b, and the difference in polymer loading (ScCO\textsubscript{2} vs. melt) decreased with increasing PEO molecular weight. No melting transition was observed by differential scanning calorimetry (DSC) for all samples prepared by the ScCO\textsubscript{2} method, i.e. all the PEO present in these samples was amorphous, rather than crystalline. This indicated that the PEO was fully intercalated in the MMT galleries. It was concluded that, rather than acting as solvent for the polymer, ScCO\textsubscript{2} plasticized the polymer, allowing it to intercalate into the MMT galleries in a similar way to melt processing. Any polymer not intercalated into the nanoclay would have been removed from the samples during ScCO\textsubscript{2} processing when the chamber was vented at the end of the procedure, whereas it would have remained as part of the melt-processed samples.

Overall, the results obtained using either method – as compared in Figure 13c – were broadly consistent for each molecular weight of PEO studied, although ScCO\textsubscript{2} processing yielded more homogenous samples. The ScCO\textsubscript{2} technique was found to be most effective when used with PEO of
higher molecular weight (10,000) or fluorinated EO, which is otherwise difficult to process using conventional techniques at laboratory scale.

![Graph](image)

<table>
<thead>
<tr>
<th>PEO grade</th>
<th>Gallery Spacing (Å), by XRD</th>
<th>PEO content (wt%), by TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 000 MW</td>
<td>18.0</td>
<td>21.0</td>
</tr>
<tr>
<td>2 000 MW</td>
<td>17.9</td>
<td>21.2</td>
</tr>
<tr>
<td>400 MW</td>
<td>17.7</td>
<td>24.7</td>
</tr>
<tr>
<td>Fluorinated EO, 164-1423 MW</td>
<td>15.1</td>
<td>22.4</td>
</tr>
<tr>
<td>Unmodified MMT</td>
<td>11.4</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 13: (a): X-ray diffraction patterns for fluorinated PEO/MMT composite (A) and unmodified MMT(B). (b): Comparison of TGA traces showing weight loss due to water and polymer content for unmodified MMT (A), ScCO$_2$ processed PEO/MMT (B) and melt-processed PEO/MMT (C). C: Comparison of properties observed for melt- and ScCO$_2$-processed samples by XRD and TGA. (from: Armstrong and Fortune 2007, with permission).

Case Study B: Functionalised Multi-walled Carbon Nanotubes (MWCNT) for Improved Performance Epoxy Nanocomposites

The aim of this study was to develop a process which allowed carbon nanotubes to be chemically bonded to a polymer, instead of attempting to disperse surfactant-modified nanotubes in the polymer matrix. Here, carbon nanotubes (CNTs) were chemically modified to act as initiators to polymerise a bisphenol A type epoxy resin, as illustrated in Figure 14; the objective was to formulate a lightweight, high strength composite nanomaterial (Armstrong et al 2009).
Figure 14: Polymerisation of epoxy monomer in the presence of functionalised multi-wall carbon nanotubes (MWCNT) to form a nanocomposite.

The synthesis of the functionalised multi-walled carbon nanotubes is described in Armstrong et al (2009); the method used commercially available –COOH functionalised MWCNTs as a starting point and used standard organic chemistry in the intermediate steps of the synthesis so that the method would be easier to scale up in future if required. Commercially available –NH₂ functionalised MWCNTs were also trialled as an initiator.

Confirming that the MWCNTs were correctly functionalised by spectroscopy proved difficult. Typically, organic chemists use Nuclear Magnetic Resonance spectroscopy as a routine tool to determine whether a chemical reaction has proceeded as expected (Williams and Fleming 2008, p.66) but here the nanotubes precipitated out of deuterated chloroform (CDCl₃) solution during the NMR experiments. However, infrared spectroscopy (Williams and Fleming 2008, p.28-30) indicated that they were functionalised with 4,4’-Methylenedianiline, a well-known crosslinking agent used for preparing epoxy resins.

Two routes to prepare the functionalised CNT / epoxy nanocomposites were compared – a standard ‘one pot’ formulation and a two-step ‘masterbatch’ route; these are compared in Figure 15. In industry, masterbatches are often preferred to simplify using nano-reinforcements without the need to handle neat nanomaterials in powder form (emerging health and safety considerations in relation to nanomaterials powders are discussed in Section 4.2). Whereas a typical industrial masterbatch contains a high loading of nano-reinforcement in a polymer matrix, which is subsequently mixed with additional polymer to obtain the final formulation required, here the same starting materials and final nanotube loadings were used for both the one-pot and masterbatch formulations to allow direct comparisons between the finished nanocomposites to be made.
### 'One-pot' formulation

- Bisphenol A propoxylate (1PO/phenol)diglycidyl ether
- + 1 wt% functionalized MWCNT

- Homogenised 60 °C / 30 min
- + 10 wt% hardener #
- Stirred 10 min / 60 °C
- Poured into PTFE mould
- Cured 100 °C / 12 hours

### Masterbatch formulation

**Step 1**
- Bisphenol A propoxylate (1PO/phenol)diglycidyl ether
- + 1 wt% functionalized MWCNT
- + triethylamine accelerator

- Homogenised 60 °C / 30 min
- Stirred 12 h / 100 °C
- Cool to RT

**Step 2**
- + 10 wt% hardener #
- Stirred 10 min / 60 °C
- Poured into PTFE mould
- Cured 100 °C / 12 hours

#4,4’-Methylenedianiline (N2-H), diethylenetriamine (N3-H) or triethylenetetramine (N4-H)

**Figure 15:** Formulation of epoxy/MWCNT nanocomposites by standard and masterbatch methods.

The thermal and mechanical properties of all the formulations prepared were characterised using standard analytical techniques. DSC was used to measure $T_g$, the glass transition temperature (Gabbott 2008, p. 22-26), and the extent of curing (Sichina 2000), of the epoxy nanocomposites. Thermal stability of the nanocomposites was assessed by TGA (Bottom 2008, p. 98-110). Storage modulus ($E’$) and flexural modulus ($E_b$) was determined by Dynamic mechanical analysis (DMA) (Duncan 2008, p. 127-128) and tensile testing (Ashby and Jones 2005), respectively. Ball indentation tests were conducted to determine hardness and rotating disk tests to determine wear resistance. The trends observed for the one-pot and masterbatch methods are presented in Figure 16 and Figure 17 respectively.

For the standard method, it was concluded that the functionalised MWCNT did not form covalent chemical bonds with the epoxy as desired (hence the $T_g$ decreased), but the nanotubes acted as a plasticiser or impurity in the 3D epoxy network. No significant change occurred in the thermal stability of the nanocomposites, as expected. Improvements in $E’$, $E_b$, wear resistance and hardness were observed, but no uniform trend emerged in these changes. The masterbatch method gave broadly similar results upon addition of functionalised MWCNT. Here, covalent bonding was achieved between the nanotubes and epoxy ($T_g$ increased slightly), but the samples did not cure fully. The N3-H hardener and triethylamine accelerator used appeared to have a negative influence on the nanocomposite’s performance and the samples were too soft for wear and hardness testing.

In conclusion, it was possible to improve the epoxy resin’s mechanical and thermal properties by adding 1 wt% of functionalised MWCNT, but no single best route to preparing nanocomposite emerged. Rather, the choice of a preferred processing route depends on which thermal and mechanical properties are considered most important for the application in which the composite would be used. Though functionalised MWCNT can indeed act as initiators and become covalently
bonded to epoxy, optimisation of the nanotubes, accelerator and hardener is required to obtain improved physical properties.

(a) Glass transition temperature, $T_g$

(b) Decomposition temperature

(c) Storage modulus, $E'$

(d) Flexural modulus, $E_B$

(e) Hardness number

(f) Wear resistance

Figure 16: Relative changes in thermal and mechanical properties of epoxy/MWCNT nanocomposites formulated by standard ‘one-pot’ method compared to neat epoxy resin.

(a) Glass transition temperature, $T_g$

(b) Decomposition temperature

(c) Storage modulus, $E'$

Flexural modulus, $E_B$

Figure 17: Relative changes in thermal and mechanical properties of epoxy/MWCNT nanocomposites formulated by masterbatch method compared to neat epoxy resin. These samples were too soft for wear & hardness testing due to their low $T_g$.
Case Study C: Alternative approaches to formulating functional antimicrobial nanocomposites

The rationale behind this study was to functionalise commercially available nano-reinforcements that could add antimicrobial properties to a nanocomposite. Antimicrobial properties are required in a wide range of applications such as consumer products, medical devices, textiles, and engineering materials. From a practical point of view, it is important that the nano-additives can be well dispersed in the polymer matrix using conventional equipment and processes, so that it is suitable to scale up towards commercial production afterwards. Also, the final nanocomposites should demonstrate antimicrobial activity under ‘real world’ conditions that are representative of the intended applications for the material.

Increasing resistance of microbes to antibiotics is a growing problem in areas such as healthcare and food production, so it was decided to use silver as the antimicrobial agent in formulating the nano-additives because it is effective against both primary classes of microbes – Gram positive and Gram negative – and exhibits antimicrobial activity in a variety of physiological settings (Lansdown 2002). The strategy was to incorporate an antimicrobial agent containing silver into contact surfaces to break chain of infection. The antibacterial activity of discs of the materials formulated was evaluated against Gram negative Escherichia coli (E. coli) and Gram positive Staphylococcus epidermidis (S. Epidermidis) using the well-established agar disc-diffusion method (Cappuccino and Sherman 2008, p. 294) Two alternative approaches were studied, i.e.:

Approach 1: Formulation of epoxy–polyester powder coatings containing silver-modified nanoclays (Armstrong et al 2012)

Approach 2: Synthesis of titania–silver and alumina–silver composite nanoparticles and formulation into silicone and epoxy nanocomposites (Bala et al 2011)

Approach 1: Formulation of epoxy–polyester powder coatings containing silver-modified nanoclays

Sodium montmorillonite nanoclay was modified with both silver nitrate and quaternary ammonium surfactant (following the approach described in Figure 9) to achieve antimicrobial properties and mixing with epoxy matrix. The resulting nanoclay was then characterised by XRD to assess the change in gallery spacing (Smart and Moore 1995b) and x-ray photoelectron spectroscopy (XPS) (Moulder et al 1992) to determine whether there were silver ions present on the nanoclay surface as desired. The gallery spacing was found to have decreased from 11.72 Å to 10.44 Å, and elemental analysis of the nanoclay by XPS confirmed that 2.0 atomic % Ag ion was present. To confirm that the nanoclay would not be affected by typical processing conditions, samples of Ag-MMT were annealed at 180 °C for 10 minutes under ambient atmosphere. No thermal degradation was observed. The antimicrobial efficacy of neat and annealed AgMMT was tested against E. coli over 24 hours (Figure 18), and was found to exhibit comparable antimicrobial performance before and after annealing.
A commercial formulation containing equal parts epoxy and polyester resins was used to prepare the powder coatings. 2 wt% of antimicrobial nanoclays was incorporated in each coating, both with and without titanium dioxide (TiO$_2$). TiO$_2$ is typically added to coatings and paints to make them white; it can also act as an antioxidant. Control coatings that did not contain nanoclay or TiO$_2$ were also prepared. The powder coatings were applied to a mild steel substrate using an electrostatic spray-gun and oven-cured at 180 °C for 10 minutes. XRD and TEM of these coatings showed the nanoclay to be mostly exfoliated in the epoxy/polyester matrix. From XPS analysis of the coatings, it was calculated that, at 2 wt% loading of Ag-MMT, the Ag$^+$ content of the coatings was approximately 8.83 x 10$^3$ ppm; the minimum concentration of Ag$^+$ required for antimicrobial efficacy has been reported as 0.1 ppb.

The antibacterial performance of the coatings was evaluated against both Gram negative E. coli and Gram positive S. Epidermidis using the agar disc-diffusion method. Three discs of 6 mm diameter of each material embedded into the surface of agar plates on which the microbes had been grown, to assess how the nanocomposites would perform as surface coatings if these microbes came into contact with the coated surfaces. Unexpectedly, no inhibition of the microbes’ growth was seen, except for a control sample of 10 μL chloroamphenicol antibiotic solution applied to the unfilled coating. Further testing revealed that, even when the coatings were immersed in broth solution containing microbes, no antimicrobial effect was seen even though the Ag-MMT itself had proven effective against Gram positive and negative microbes. The coatings exhibited limited wettability, and it was concluded that this restricted the ability of Ag$^+$ to diffuse from the coating, such that it was not bioavailable to inhibit microbial growth. (Subsequently, the same nanoclays did show good inhibition of microbial growth when added to hydrogels made with poly(vinyl alcohol), which is hydrophilic and, therefore, readily wettable.)

The key conclusion from this case study was that achieving a satisfactory dispersion of the nanoadditive in the polymer matrix is not enough to prepare a successful material. Rather, the
formulation must be chosen and optimised to give the properties and performance necessary for the intended target applications.

**Approach 2: Synthesis of titania–silver and alumina–silver composite nanoparticles and formulation into silicone and epoxy nanocomposites**

Titania–silver (TiO$_2$–Ag) and alumina–silver (Al$_2$O$_3$–Ag) composite nanoparticles were synthesised by a simple, reproducible, wet chemical method under ambient conditions. The surface of the oxides was modified with oleic acid, then silver nanoparticles were grown on the oxide surfaces. XRD showed that crystalline Ag nanoparticles were present in both composite nanoparticles. The Ag nanoparticles were observed by TEM as discrete particles on the surface of the TiO$_2$ particles, as may be seen in Figure 19a. However, the Ag nanoparticles were not well localized on the Al$_2$O$_3$ particles, and unbound Ag nanoparticles were also observed in these samples, as seen in Figure 19b.

![Figure 19](image.png)

**Figure 19:** (a) TEM images of Ag nanoparticles on titania surface; inset: magnified titania nanoparticle having Ag nanoparticles on its surface; (b) TEM images of Ag nanoparticles on alumina surface. (From: Bala et al 2011, with permission).

![Figure 20](image.png)

**Figure 20:** Modes of assembly compared for (a) Titania–silver (TiO$_2$–Ag) and (b) alumina–silver (Al$_2$O$_3$–Ag) composite nanoparticles. The coordination of oleic acid followed different modes on both surfaces: it formed a single layer on titania under acidic conditions (a), but formed a bilayer on alumina under basic conditions (b). The binding strength of the oleic acid layers – and hence the silver nanoparticles – to the oxide surfaces was not equal in both cases. The Ag nanoparticles on titania surface were found to be more site specific and more strongly bound. In contrast, though the inner layer of oleic acid illustrated in (b) was bonded to alumina strongly, the outer layer was less strongly bound. Thus Ag nanoparticles which were anchored to the oxide surface via this outer layer detached easily.
When these composite nanoparticles were analysed further using XPS, FTIR and TGA, it emerged that although the same steps were followed in preparing both TiO$_2$–Ag and Al$_2$O$_3$–Ag, the Ag nanoparticles formed on the oxide surfaces following two different modes of assembly because of differences in the surface chemistry of the titania and alumina particles. These differences are summarised in Figure 20. Here, the key point is that following the same formulation steps using different starting materials does not always necessarily give the same outcome, but rather the end product can be affected by variations in morphology and surface chemistry.

Polymer nanocomposites were formulated with TiO$_2$–Ag and Al$_2$O$_3$–Ag composite nanoparticles by dispersing these composite nanoparticles in silicone and epoxy resin at 1 wt% and 10wt% loading, following a similar approach to the ‘standard method’ described in case study 2. Formulations containing 30 and 50 wt% nanoparticles were also prepared, but these proved too stiff and brittle to use in subsequent testing for antimicrobial activity. In addition, control samples containing 1-50 wt% pristine titania or alumina were prepared. At all loadings prepared, the composite nanoparticles were found to be well-dispersed in the polymer matrices, and the distribution of Ag nanoparticles on the titania and alumina surfaces was unchanged after processing.

Disc diffusion assays against Gram negative *E. coli* and Gram positive *S. epidermidis* using discs of the nanocomposites were conducted as described in Approach 1; an example of these is shown in Figure 21. Preliminary results suggested that these TiO$_2$–Ag and Al$_2$O$_3$–Ag composite nanoparticles have potential as antimicrobial materials suitable for use on contact surfaces; the samples tested and zones of inhibition observed are compared in Table 4. Comparing these outcomes with Approach 1, we can conclude that there is no ‘one size fits all’ solution to preparing functional nanocomposites. Rather, the antimicrobial agent chosen must be tailored to suit the polymer matrix, composite formulation, target microbes and intended application.

![Figure 21: Examples of disc diffusion assays against Gram negative *Escherichia coli* and Gram positive *Staphylococcus epidermidis*. (a) Al$_2$O$_3$ - 10wt% Ag at 50 wt% loading in epoxy; (b) control: 50 wt% alumina in epoxy.](image-url)
Table 4: Results of disc diffusion assays for epoxy composites against Gram positive *Staphylococcus epidermidis* and Gram negative *Escherichia coli*. The diameter of zone of inhibition measured serves as a relative measure of antimicrobial activity between assays conducted under identical conditions.

<table>
<thead>
<tr>
<th>Nano-reinforcement</th>
<th>Diameter of zone of inhibition (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>S. Epidermidis</em></td>
</tr>
<tr>
<td>Alumina</td>
<td>6.97</td>
</tr>
<tr>
<td>Al$_2$O$_3$ - 10wt% Ag</td>
<td>12.25</td>
</tr>
<tr>
<td>Titania</td>
<td>7.03</td>
</tr>
<tr>
<td>TiO$_2$ - 10 wt% Ag</td>
<td>10.00</td>
</tr>
</tbody>
</table>

4  Emerging Issues for Polymer Nanocomposites

We have seen so far that there are several key technical issues to address in formulating a successful polymer nanocomposite. Achieving uniform dispersion of the chosen nano-reinforcements in the polymer matrix is the first step in the processing of nanocomposites, and we have discussed in Section 2 how it can be very difficult to align nanotubes using same processing techniques applied to conventional polymer composites. Finding an efficient, cost-effective, production route is vital if the nanocomposite is to be used in manufacturing, and it should be clear from the case studies that it is necessary to be able to measure the dispersion and alignment of the nano-reinforcement, and the material properties of the finished nanocomposite, consistently.

The field of polymer nanocomposites is still very new, with rapid progress being made in both technical and commercial aspects. At the time of writing, there are, however, several emerging issues – commercial, technical and regulatory – that have the potential to affect the future direction of the field significantly. In the final section of this topical review, we will consider some of these in more detail.

4.1 Development of standard methods to characterise nanomaterials

A recurring issue in sourcing nano-reinforcements as raw materials to prepare polymer nanocomposites is that different commercial suppliers and research laboratories use different methods to determine the quality and purity of their nano-reinforcements and evaluate how well they disperse in polymer matrices (Kingston 2007). How, then, can the buyer compare materials from obtained from different sources reliably? Here, we will consider two pertinent examples: using TGA to measure nanotube purity, and using microscopy to measure nanotube dispersion.

Nanotube purity is frequently reported based on TGA, as illustrated in Figure 22 (Arepalli *et al* 2004). The mean values of $T_o$, the peak oxidation temperature of the sample, and $M_{res}$, the residual mass (i.e. the ash content) remaining at the end of the TGA experiment, are representative of the sample purity (higher oxidation temperature and lower residual ash content are often presented as evidence of higher nanotube purity), and the standard deviations of $T_o$ and $M_{res}$ are representative of the sample inhomogeneity across replicate experiments. However, combustion of the nanotubes during the TGA experiment may cause sudden heat release, resulting in spikes in the recorded weight loss as a function of temperature. (Recall that, in TGA, we measure weight loss of the sample...
as a function of its temperature while heating the sample at a constant rate. Combustion of the sample decreases the values obtained for ash content ($M_{\text{res}}$) and increases the standard deviation of $M_{\text{res}}$ across repeat experiments. Some sample may also be lost due to ejection of smoke particulates from the sample pan. Similar ‘burst expansion’ is observed when characterising graphene by TGA.

To address these shortcomings, and provide a standard test method that can be used to compare nanotube samples with confidence, the US National Institute of Standards and Technology, NIST, has developed a recommended practice guide for conducting TGA of carbon nanotubes (NIST 2008a).

Figure 22: TGA mass loss and its derivative for three separate specimens of (a) purified SWCNT and (b) corresponding raw nanotubes. $T_o$ is the peak temperature at which maximum weight loss of the sample occurs, and $M_{\text{res}}$ is the residual mass remaining at the end of the experiment, i.e. the ash content at 600 °C. (From: Arepalli et al 2004, with permission).

Likewise, NIST have proposed a standard microscopy protocol to characterise SWCNTs (NIST 2008b). This is a top-down approach whereby simpler methods are used to screen samples, and increasing more advanced techniques are used in addition to confirm the dispersion of the nano-reinforcement in the matrix where required – this reduces the amount of effort and cost of analysis required to a practical minimum. For efficiency, samples are prepared for analysis as cast films or thin sections – sample preparation is usually the most difficult and time-consuming stage of microscopic analysis. The protocol may be summarised by the flowchart shown in Figure 23.
Figure 23: Simplified flowchart to assess dispersion of nano-reinforcement in polymer nanocomposite matrices, following NIST suggested microscopy protocol for SWCNTs.

4.2 Safety and toxicity of nanomaterials and nanocomposites

In discussing the technical aspects of polymer nanocomposites, we have already seen that the term ‘nanotechnology’ can be misleading since it is not a single technology or scientific discipline, but a group of processes, materials, applications and concepts defined by size. We have already seen that the physical properties of the same material (e.g. carbon, silicon, metals) are not the same at the nanoscale as at the macro scale. This may apply equally to their behaviour in the body as well as to their materials properties!

At the time of writing, the health and safety effects of new nanomaterials are mostly unknown. Therefore, the risk of accidental exposure to nanomaterials in the workplace is of growing concern as they become more widely used in industry (HSE 2013, ISO 2008). Accidental occupational exposure to nanomaterials can occur:

- During manufacture
- Through incorporation in other materials (e.g. polymer nanocomposites)
- By generating nanoparticles in non-enclosed systems
- During research into their properties and uses
- When cleaning dust collection systems used to capture nanoparticles
- Via incorrect disposal
- Via accidental spillage
The United Kingdom is among the first countries to regulate the usage of nanomaterials. For example, the UK Health and Safety Executive’s guidelines on risk management of carbon nanotubes (HSE 2013) state:

‘Since there is uncertainty about the risks of being exposed to CNTs, the regulatory and safe response is to take a precautionary approach...the toxicity of CNTs has not yet been fully investigated...However it is clear that Safety Data Sheets for CNTs that are based on conventional graphite or graphene will NOT provide suitable adequate information to assess the risk from CNTs.’

Emerging data indicates that when CNTs are breathed in they can cause lung inflammation and fibrosis. Inhaled CNT may have adverse effects at other sites in the body, and CNTs may be able to provoke inflammatory reactions in the skin. The type, shape and surface chemistry of CNT may influence the severity of the response. The UK HSE notes that:

‘...more information is required to properly understand the conditions of exposure that are required to produce such effects...in view of the evidence for lung damage and lack of information on the effects of long-term repeated exposure a high level of control is warranted for CNTs.’

Similar regulations to those in force in the UK are now emerging in other countries now. For example, the French Institut National de Recherche et de Sécurité have published a guide to nanomaterials risk prevention in laboratories (INRS 2012). Also, the European Commission has published two detailed guidance documents on protecting the health and safety of workers who are exposed to nanomaterials (PROGRESS 2013, 2014). These state that because of the uncertainty in relation to manufactured nanomaterials (MNMs), the approach to prevention is based on the precautionary principle. The point is made that new information is becoming available and that those using the guides must take new information into account. A strong emphasis is placed on consideration of exposure, while still trying to prioritise attention paid to MNMs. Inhalation of nanomaterial is regarded as the route of exposure of greatest concern, followed by respiratory and dermal exposure. Exposure by ingestion is considered to be of lower concern.

Another health and safety regulation that may have far-reaching implications for the future use of nanomaterials is Europe is the Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH) regulation (European Commission 2015). REACH is a European Community Regulation, EC 1907/2006, on chemicals and their safe use. Under REACH, manufacturers and importers of chemical substances are required to gather information on the properties of the chemical substances they sell, which will allow their safe handling. This information is registered in a central database run by the European Chemicals Agency (ECHA) in Helsinki. REACH entered into force on 1 June 2007, and its provisions are being phased-in over 11 years. At the time of its launch, nano-scale forms of existing materials were not deemed to be ‘new’ substances; therefore a separate REACH registration was not required for them (Gergely 2012). A key question for nanomaterials is whether nanomaterials will be considered separately to their micro-scale equivalents (e.g. graphite vs. graphene)?
4.3 Reuse and recycling of nanocomposites

In all areas of industry and business, there is an increasing emphasis – both from consumers and regulatory authorities – on reducing waste and reuse or recycling of raw materials and finished products at the end of their useful life. Let us consider two examples of markets where polymer nanocomposites are currently used: electronics and automotive.

Across the European Union, the Waste Electrical and Electronic Equipment (WEEE) directive, 2002/96/EC, requires that producers of electrical and electronic equipment must arrange to collect and reuse or recycle these products at the end of their life (EUR-Lex 2014a). The WEE directive applies to household appliances, IT and telecommunications equipment, consumer goods, lighting equipment, electrical and electronic tools, toys, leisure and sports equipment, medical devices, monitoring and control instruments, and automatic dispensers.

For the automotive industry, European Parliament and Council Directive 2000/53/EC addresses recovery and recycling of end-of-life vehicles. Under this directive, each EU Member State must achieve 95% reuse/recovery by average weight per vehicle by 1 January 2015, to include 85% materials recycling (EUR-Lex 2014b). The car must be recycled in a manner that does not cause environmental pollution, and the vehicle’s owner must not be charged for the cost involved. In addition, under the directive, the use of specified hazardous substances in new vehicles must be minimised.

In both cases, the question for future use of nanomaterials in industry is: how can we develop strategies to recover, separate and recycle polymer nanocomposites in an environmentally sound manner and in compliance with both waste management directives and the emerging health & safety regulations we have already discussed. How will we safely recycle vehicles and electronics built with nanocomposites if nanomaterials are classified as ‘hazardous’?

4.4 Graphene

Graphene, the ‘newest’ nanomaterial, is a layered nanomaterial that consists of individual layers of graphite. It was discovered by Andre Geim and Konstantin Novoselov at the University of Manchester, for which they receive the 2010 Nobel Prize in Physics (Colapinto 2014). Graphene still very much a research material, but it is already proving of particular technical interest for its exceptionally high thermal and electrical conductivity; its material properties are compared with those of single-walled carbon nanotubes in Table 5, overleaf (Kim et al. 2010, Potts et al. 2011).

Graphene is a synthetic material, and since its discovery a range of methods have been developed both to prepare it and to formulate polymer nanocomposites using it (Kim et al 2010, Potts et al. 2011, Singh et al. 2011). In so-called ‘bottom-up’ methods, graphene sheets are grown from carbon-rich gas using similar approaches to growing CNTs, e.g.: chemical vapour deposition (CVD), arc discharge, or chemical reduction of carbon monoxide. Techniques have also been reported to obtain graphene sheets from CNT starting material by ‘unzipping’ the nanotubes. These bottom-up approaches give the highest, most consistent material properties, but they are difficult to scale up from the laboratory toward production.
Table 5: Graphene properties compared with single walled carbon nanotubes (SWCNT).

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphene</th>
<th>SWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density</td>
<td>~ 0.004 g/cm(^3)</td>
<td>1.33–1.40 g/cm(^3)</td>
</tr>
<tr>
<td>Surface area</td>
<td>Up to 2630 m(^2)/g (theoretical limit)</td>
<td>~ 2400 m(^2)/g</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>1 TPa</td>
<td>1.2 TPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>130 GPA</td>
<td>2 GPa</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>6000 S/cm</td>
<td>Varies with chirality</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>5000 W/m K @ room temperature</td>
<td>6000 W/m K @ room temperature</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>&lt; 200 °C (after functionalisation)</td>
<td>2800 °C (vacuum) 750 °C (air)</td>
</tr>
<tr>
<td>Gas permeability</td>
<td>Impermeable to all gases</td>
<td>MMT resistant to (O_2), hydrocarbons</td>
</tr>
</tbody>
</table>

Hence, alternative ‘top-down’ methods more suitable for scale up have been developed. Here, the aim is to separate layers of graphite or graphite oxide starting material to obtain graphene sheets. Exfoliation, followed by chemical reduction, of graphite oxide is the easiest route to scale up, and graphite has an important advantage as a starting material – it is cheap, costing around $825 per tonne. Recently, an intriguing bottom-up method to prepare graphene economically was reported by researchers at Trinity College Dublin (Paton et al 2014): they exfoliated graphene oxide in NMP solvent to obtain graphene sheets using a laboratory scale sonic probe, and have since claimed it is possible to obtain similar results using a kitchen blender and dishwashing liquid. The method has now been licenced and is being further developed for commercial production (Bergin 2015).

Based on our existing knowledge of formulating polymer nanocomposites, it is instructive to consider how these methods to formulate MMT or CNT nanocomposites could be adapted to prepare graphene-based nanocomposites. Recall from our discussion of preparing analogous nanoclay composites that the three principal processing routes available to us are dispersion in solution, in-situ polymerisation, or melt processing.

In solution, graphene oxide (GO) exfoliates easily in water and protic solvents, so it becomes possible to blend GO with a polymer solution. GO can also be exfoliated in aprotic solvent if it is modified with an amine or isocyanate, making it compatible with polymers such as polystryrene, polyurethane and poly(methyl methacrylate). It is possible to remove the solvent after exfoliating the GO, but
compared to exfoliated nanoclays, graphene platelets are more prone to re-aggregation due to the formation of hydrogen bonds between the graphene sheets (Kim et al 2010).

As with nanoclays, in-situ polymerisation processing of graphene may be achieved by intercalating a liquid monomer between the graphene layers, then polymerising it to yield the finished polymer composite. Alternatively, as we saw for the example of an epoxy/CNT composite (Case Study B), monomer or reactive functional groups may be grafted to the graphene sheets, then undergo a cross-linking reaction to form the polymer. Melt processing is also feasible, using the approaches already discussed; for example, PET/graphene melt processed nanocomposite containing 0.07 wt% graphene have been reported (Paton et al 2014). Even compared to other nano-reinforcements, graphene has very low bulk density (see Table 5) and leads to high viscosity melt mixtures, making it difficult to disperse & mix with polymer via melt processing. A detailed review of methods to functionalise graphene surfaces and prepare polymer/graphene nanocomposites in a wide range of polymer matrices was undertaken by Kuilla et al (2011).

5 Outlook: Balancing performance, cost and safety

As nano-reinforcements become increasingly widely accepted and used, it is to be expected that the cost of raw materials will fall in line with increasing demand and larger-scale production. For example, as of February 2015, electric arc grown SWCNTs with carbonaceous purity > 90%, determined according to NIST 2008, were offered at prices starting from $35/g (Carbon Solutions 2015); a decade ago, similar purity SWCNTs typically cost €1500/g. At the same time, MWCNTs typically cost €2.20/g and, at laboratory scale, graphene cost in the order of €130/g for graphene powder and €150/100ml for graphene dispersion. Though these prices have fallen dramatically in the past decade, cost vs. performance is a key consideration in all commercial materials applications. For comparison, as of February 2015, representative carbon black costs ranged from €5/kg to €15/kg for highly conductive grades, and nanoclays cost €1.30 - €3.50/kg depending on their source and chemical functionalization.

Ironically, perhaps one indicator that nano-reinforcements are on their way to becoming commodity materials is that at least one significant manufacturer has withdrawn from the market. Bayer Materials Science had manufactured ‘Baytubes’, since 2007. Baytubes were micron-sized agglomerates of MWCNTs designed for dispersion in thermoplastic and thermoset polymers. As of 2010, Bayer operated a pilot plant with the capacity to produce 200 tonnes of Baytubes per year. However, they announced the closure of this plant and the end of research projects in the area of CNT products during 2013 (Broadwith 2013).

Taking the health and safety concerns around exposure to nanomaterial powders we have previously discussed into account, these MWCNT agglomerates were easier to handle than powder form nanotubes because they could be handled and processed in the same manner as conventional micron-sized reinforcements. In fact, nano-reinforcement manufacturers have put much research effort into developing new products and formulations that avoid the need to handle neat nanomaterials for this reason. Alternative approaches include masterbatches of high loadings of nanoclay, nanotube or nanoparticle already dispersed in a range of engineering polymers, or off-the-shelf polymer nanocomposites ready for processing into finished articles (e.g. ‘PLASTICYL’™).
masterbatches of 15-20% CNTs dispersed in thermoplastic resins (Nanocyl 2015) or ‘nanoMax’® nanoclay-polyolefin resin masterbatches (Nanocor 2015) which contain contains 50 wt% organically modified montmorillonite.)

Though it is now twenty years since the first polymer nanocomposites found commercial application, the field continues to grow at a remarkable rate, with the combination of new nanomaterials, processing methods and characterisation techniques leading to higher performance materials, new applications and lower costs. Even as this review was being prepared, the UK’s first ‘graphene-enhanced’ consumer product was launched – a lightbulb containing a filament-shaped LED coated with graphene (Stoye 2015). This is produced by Graphene Lighting, a company formed by the University of Manchester and the UK’s National Graphene Institute. Almost simultaneously, researchers based in South Korea and the USA published reported bright visible light emission from single-monolayer-thick graphene devices suspended between electrodes (Kim et al 2015, Wogan 2015) – effectively these are graphene light-emitting diodes. The authors also created arrays of graphene light emitters by chemical-vapour-deposition, which may provide a starting point to develop graphene-based on-chip optical communications. It is worth noting that these applications made use of graphene nanoplatelets, whereas many of the laboratory-scale prototype applications reported for graphenes to date have made use of graphite oxide (Potts et al 2011).

By analogy to nanoclays, graphite oxide may be thought of by as intercalated graphene platelets rather than fully exfoliated graphene. At the time of writing, Haydale Composite Solutions have announced that they are working with Alex Thomson Racing to investigate adding functionalised graphene nanoplatelets into carbon fibre reinforced plastics, polyester and epoxy resins for use in ocean racing yachts. Potential applications include reducing weight in hulls and structural components, bearings and friction points, protecting against delamination of composite materials and thermal heat management (Haydale 2015). With the potential to incorporate such novel functionality into polymer matrices waiting to be exploited, the future for polymer nanocomposites certainly looks bright!

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