

REPORT

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**Review of Methods for the
Characterisation of the
Dispersion of Nanoparticles
in Polymer Nanocomposites**

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SUMMARY

Polymer nanocomposites are attracting increasing attention due to their potential benefits in improved performance, for example in enhanced barrier properties for packaging applications and better conductivity for electromagnetic field (EMF) shielding applications. However, without proper dispersion of the nanoparticles within the polymer matrix the potential property enhancements of the nanocomposites will not be fully realised. Currently, methods for assessing the dispersion of particles in polymers are not suited for quality control. This review assesses the potential of rheological and thermal methods for characterising the extent of dispersion of nanoparticles in polymer nanocomposites. Furthermore, it discusses some of the issues that affect the reliability of data obtained using established "imaging" techniques, principally transmission electron microscopy (TEM) and X-ray diffraction (XRD), for assessing nanocomposites dispersion.

Recommendations for future research work include:

- Establish and standardise key descriptors for quantifying dispersion state from analysis of microscopy images.
- Development of appropriate rheological tools for quantification of dispersion quality of nanoparticles in polymeric media, and their validation.
- Develop understanding of underpinning science of the effect of nanoparticles on thermal properties of polymers (e.g. glass transition temperature and crystallisation temperature) potentially leading to additional tools for the assessment of dispersion quality.

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1 INTRODUCTION

There is significant growth potential for the use of nanoparticles in polymers, thus forming polymer nanocomposites (PNCs). Significant improvements in properties of polymers on the inclusion of nanoparticles have been reported. Utracki [2004] commented that significant benefits of PNCs are in terms of increased modulus, strength, elongation at break, impermeability and flame resistance, with disadvantages of higher viscosity and cost. Significant improvements in barrier properties can also be achieved using nanoclays: a key issue in packaging where, for example, exclusion of oxygen from the product is important to extend its shelf life.

However, the degree of dispersion is a key issue to the future success of nanocomposites. Gacitua et al [2005] concluded that *"one of the main issues in preparing good polymer matrix nanocomposite samples is the good dispersion of the nanoparticles in the polymer matrix"*. Similarly, Vermogen [2005] commented that the limiting factor for the development of nanocomposites is the control of exfoliation, dispersion and orientation. Kotsilkova [2007], on thermoset nanocomposites, commented that both dispersion and particle-polymer interaction are important factors in achieving good PNCs. Without proper dispersion of the filler in the matrix, polymer nanocomposites will not achieve their full potential, for example their significantly improved barrier properties. However, current measurement methods for assessing dispersion are unsuitable or inadequate for quality control of materials.

This report reviews the current state of the art for characterising the quality of the dispersion of nanoparticles in polymer nanocomposites, focusing on the use of rheological and thermal test methods. The review also discusses some of the issues with transmission electron microscopy (TEM) and X-ray diffraction (XRD). These two techniques are widely used for imaging the structure of PNCs as they provide valuable information on nanoparticle structure and distribution in PNCs on appropriate length scales.

2 POLYMER NANOCOMPOSITES

Utracki [2004] defined a nanocomposite as a matrix material having particles dispersed within it that have at least one dimension that is not more than 10 nm. For polymer nanocomposites (PNCs) the matrix material is a polymer. The nanoparticles can be categorised in terms of their geometry, being either spherical (e.g. silica), rod (e.g. carbon nanotubes (CNT) or carbon nanofibres (CNF)) or platelet (e.g. clay) in form. Examples of nanoparticles of each of these geometries are given in Table 1.

The small particle size and high aspect ratio of nanoparticles (the latter obviously for non-spherical particles only) results in a high surface area to volume ratio of the filler. Broughton [2006] commented that polymer nanocomposites are also characterised by high particle densities. These factors contribute to the existence of short inter-particle separations that are comparable to the radius of gyration of polymer molecules. Thus there is significant potential for a very large number of particle-polymer and particle-particle interactions, with resultant low percolation thresholds corresponding to the formation of three-dimensional (3D) networks. These interactions have the potential to influence significantly the properties of the PNC. A small concentration of nanoparticles in a polymer, typically up to 5 wt%, can have a significant effect on its

mechanical, thermal, rheological and barrier properties. However, to achieve these benefits strong interactions of the nanoparticles with the polymer molecules are considered necessary, which is often achieved through surface treatment or 'compatibilisation' of the nanoparticles. Organoclays, for example, are organically modified clays where the hydrophilic clay surface has been modified with organic surfactants to facilitate dispersion in the polymer.

Polymer nanocomposites cover a wide range of materials: some of those studied in the scientific literature are identified in Table 2. Probably the most successful commercialised polymer nanocomposites are organoclay filled nylons, largely due to their compatibility. Although organoclays have attracted the greatest attention in the literature, carbon nanotubes have attracted considerable attention recently for their electrical and mechanical properties. This review has focused on these two types of nanoparticles in particular. In comparison, the literature on spherical nanoparticle based PNCs is relatively sparse and is reflected by the number of papers reviewed on them herein.

Tjong [2006] commented that a clay platelet is of the order of 0.94 nm thick, and a non-expanded tactoid has a repeat distance of 0.96 nm. Basal spacings for different types of organoclay, i.e. organically modified, were quoted by Tjong [2006] in the range 1.85 nm to 3.23 nm, and by Ratinae [2006] from 1.43 nm to 5.6 nm. Tjong [2006] commented that the aspect ratios of layered silicates (montmorillonite) were approximately 100 to 200. In comparison Utracki [2007] commented that the aspect ratio of exfoliated clay platelets ranged from 10 to 2000, as was echoed by Kotsilkova [2007]. However, Utracki [2007] added that higher aspect ratio platelets are more difficult to intercalate, as intercalation is a diffusion controlled process, but offer better potential properties gains.

Tjong [2006] commented that carbon nanotubes have aspect ratios typically of ≈ 1000 , with single wall carbon nanotube (SWCNT) diameters typically 1 nm to 2 nm, multi-walled carbon nanotube (MWCNT) diameters typically 3 nm to 10 nm, and carbon nanofibre (CNF) diameters typically 50 nm to 200 nm.

Given the particle sizes certain researchers have attempted to predict percolation threshold values. Utracki [2005] reported that the maximum packing volume fraction ϕ_m related to overlapping of particles and thus potential particle interactions, is given for discs ($\phi_{m,d}$) by

$$\frac{1}{\phi_{m,d}} = 1.55 + 0.0598p \quad [1]$$

and for rods ($\phi_{m,r}$) by:

$$\frac{1}{\phi_{m,r}} = 1.38 + 0.0376p^{1.4} \quad [2]$$

where p is the aspect ratio of the particles. However, the reported figures yielded by these expressions are significantly less than generally observed experimentally for the establishment of 3D network structures. Using equation 1 with an aspect ratio of 500, volume fractions of 0.00032 for platelets and 0.00004 for rods were reported (It is

noted, however, that equations 1 and 2 actually yield values that are 100 times greater than these quoted values, which would make these expressions closer to experimentally observed values for percolation. Cassagnau [2008] reported that King [2007], on a similar basis that the percolation threshold for clay nanocomposites was based on overlap of randomly oriented clay tactoids, predicted a percolation threshold of 0.6 vol% (≈ 1.4 wt% based on a density of $\rho \approx 2.35$ g/cm³)¹, which is reasonably consistent with rheological data.

For fibres, Huang YY [2006] reported an expression for the volume fraction at which the fibres overlap, i.e. an estimate of the percolation threshold:

$$\phi_c \approx d^{7/5} \ell_p^{-3/5} L^{-4/5} \quad [3]$$

where d is the fibre diameter, L is the length and ℓ_p the tube persistence length ($0.5 \mu\text{m} - 1 \mu\text{m}$), giving a mass fraction in their case of 0.5 wt% to 1.5 wt% ($\rho \approx 2.1$ g/cm³).

These models thus give, as a first approximation, an indication of the threshold values for percolation but they are based on a particle-particle interaction assumption and as such do not take into account the role of particle-polymer interactions in percolation development.

Although the building blocks for a polymer nanocomposite are simple, when combined to form a polymer nanocomposite the resultant structure is potentially complex comprising of individual particles and agglomerates of nanoparticles forming, for example, microparticles or complex 3D network structures. In the case of nanoclays the particles are also in the form of tactoids (i.e. stacks of individual platelets).

Table 1: Nanoparticle types and dispersions

Geometry	Dispersion state	Examples
Spherical	Agglomerated or aggregated Dispersed Structured	Carbon Silica Polyhedral oligomeric silsesquioxanes (POSS) Magnetite
Rod	Agglomerated or aggregated Dispersed Structured	Single-walled carbon nanotubes (SWCNT) Multi-walled nanotubes (MWCNT) Carbon nanofibres (CNF) Sepiolite
Platelet	Agglomerated or aggregated Intercalated Exfoliated Dispersed	Clays (montmorillonite, organoclay)

¹ <http://webmineral.com/data/Montmorillonite.shtml>

3 DISPERSION OF NANOPARTICLES IN POLYMERS

3.1 DEFINITIONS OF DISPERSION

Hackley [2001], in their NIST Recommended Practice Guide on the use of nomenclature in dispersion science and technology, define dispersion as "*a two-phase system in which discontinuities of any kind (solid, liquid, gas) are dispersed in a continuous phase of a different composition or state*" and well-dispersed as "*a stable suspension in which the minimum particle size has been achieved*".

The first of these definitions applies well to polymer nanocomposites, but perhaps the second does not go far enough. For a well-dispersed nanocomposite there must also be uniformity in the concentration of particles per unit volume to ensure uniformity of properties of the PNC. However, and as will be seen later, optimal properties may not necessarily be achieved from an ideally well-dispersed system. For example, electrical properties may be enhanced by the formation of structured 3D networks [Alig, 2007], which on a small enough scale will not appear uniformly distributed. Cassagnau [2008], in comparing spherical silica with platelet clays, commented that the percolation threshold will decrease with increasing exfoliation of the nanoclay, but will increase with increasing dispersion of the silica, leading to the warning that the use of methods to assess dispersion state must account for the geometric form of the particles. Thus the length scale on which the PNC is assessed to be uniformly well-dispersed is critical in assessing its quality. For quantitatively assessing the dispersion of particles, Broughton [2008] described statistical models that can be used for spherical and rod particles.

Hackley [2001] defines aggregation as particles forming *a cohesive mass or cluster* and agglomeration as the *formation of aggregates in a suspension through physical or electrostatic forces*.

3.2 STRUCTURE IN POLYMER NANOCOMPOSITES

The structure of polymers filled with nanoparticles is likely to be varied and complex, Figures 1 and 2. For semi-crystalline polymers this will be not only in terms of the nanoparticles structure but of their crystallinity (type and level of crystallinity) that is likely to be effected by the nanoparticles. Indeed, to assign a few terms in an attempt to reliably describe the structure of the nanoparticles alone is over-simplistic in the least. However, and for the purposes of convenience, the structures range from fully dispersed where individual particles are dispersed uniformly through the matrix, to agglomerations or aggregations, where clusters of nanoparticles exist, to 3D structured arrays of particles.

A classification for the range of dispersion states for each of the principal particle forms is given in Table 1, consisting of 'agglomerates or aggregates of nanoparticles', and 'structured', 'intercalated' and 'exfoliated' nanoparticles. The term 'dispersed' is also presented to describe the spatial distribution of the particles, and is considered to be complimentary to the other terms in that it can be applied in addition to those terms rather than instead of.

Aggregated or agglomerated particles are where individual particles have formed, for example, bundles (for rod particles) or stacks (for platelet particles), i.e. the

nanoparticles are not separated into individual particles. Such agglomerates may provide property enhancement in the conventional macro-scale composites sense, Figure 3.

The term “structured” as used in Table 1 refers to a non-random arrangement of nanoparticles. There is ample evidence in the literature supporting the formation of 3D networks, as is particularly evident for CNTs through TEM images and the measurement of electrical conductivity. Kotsilkova [2007] suggested that 3D networks might be formed in nanocomposites due to particle-particle interactions or polymer-particle interactions, the latter with bonding of the polymer molecules to the particles' surfaces. The formation of such 3D structures will affect the mobility and relaxation processes of the polymer molecules and thus their rheological and thermal properties. Cassagnau [2008] commented that *"a fractal structure of fillers is required to get the best balance of reinforced properties"*.

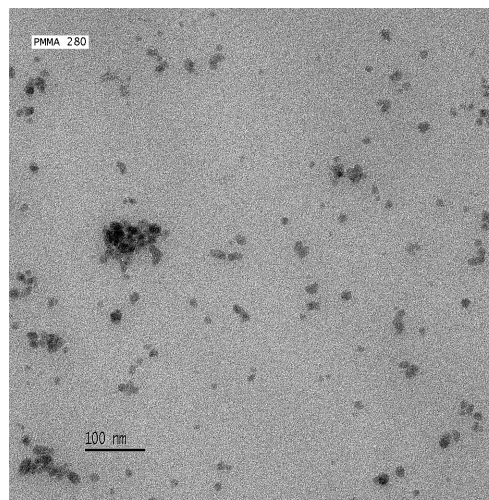


Figure 1: TEM image of silica particles in PMMA

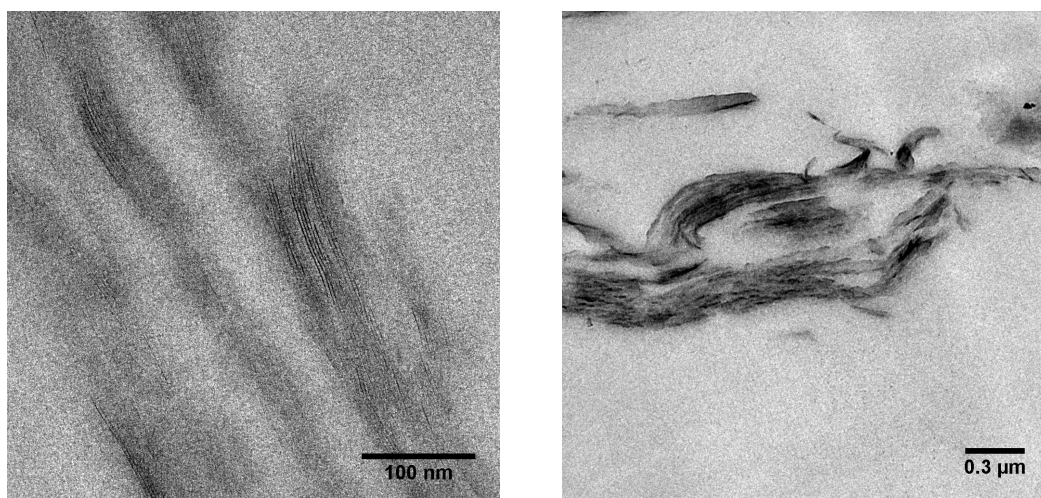


Figure 2: TEM images of polymer nanocomposite with nano-clay

Exfoliation and intercalation are terms used to describe platelet configurations. Intercalation refers to where molecules have penetrated between adjacent platelets resulting in a well-ordered multi-layer structure with molecules penetrating into the gallery space between platelets, resulting in an increase in the interlayer spacings, Figure 3. Utracki [2004] commented that the aims of intercalation are to expand the clay platelet spacing to 3 nm to 4 nm, reduce platelet-platelet interactions increase clay-polymer interactions, the latter through making the clay organophilic. Utracki [2004] defined an intercalated material as layered platelets, separated by molecules, with an interlayer spacing of at least 1.5 nm.

In comparison, exfoliation refers to where the platelets are separated, often significantly, and interspersed potentially by a large number of polymer molecules, Figure 3. Utracki [2004] defined an exfoliated layered material as one where the distance between the platelets is greater than 8.8 nm and where the platelets are either oriented forming tactoids or randomly dispersed. Thus, by the definitions of Utracki [2004], tactoids can be either intercalated or exfoliated. This latter point may not be a universally used view - the process of describing TEM images being usually subjective - but the advantage of the definitions of Utracki [2004] is that they are unambiguous. Tjong [2006] commented that in practice fully exfoliated systems do not occur, as materials will exhibit a mix of aggregated, intercalated and exfoliated states.

Tjong [2006] commented that clay intercalation occurred due to the affinity of the polymer molecules for the organoclay surfaces thereby moving into the gallery spacings, and that exfoliation of the tactoids occurs due to shearing.

Eckel [2004] classified, perhaps more simply, the structure of nanoclays as (i) exfoliated (individual platelets having no systematic orientation or position relative to neighbouring platelets), (ii) tactoids (sheets stacked face to face, from just a few layers to up to 100 layers, with the space between sheets being called the interlayer or gallery spacing) or (iii) agglomerated tactoids. This, however, does not differentiate between intercalated and non-intercalated tactoids, where intercalation is a key step along the processing route to exfoliation.

Schematics representing conventional, intercalated and exfoliated states are presented in Figure 3.

The dispersion of nanoparticles in polymer matrices is not a static state however. Annealing of well-dispersed magnetite nanoparticles grafted with PMMA brushes in PMMA homopolymers resulted in the formation of aggregates [Xu, 2008]. Aggregation was observed to occur on annealing the sample at 185 °C for 4 days. The occurrence of aggregates was explained by dry and wet brush theory, where aggregation occurred for particles in the dry brush state in which the matrix polymer chains did not penetrate the grafted brushes of the nanoparticles due to their molecular weight being higher than that of the brushes. Interestingly, string-like aggregates were observed without a hypothesis as to the mechanism, but the authors commented that such string-like aggregates were also observed by Lan [2007]. They also showed migration of nanoparticles to the film surface. Although the conditions used for annealing are considered to be extreme² the

² Extreme on the basis that the Tg of PMMA is approximately 105 °C [Krevelen, 2000] and, assuming a doubling of rate per 10 °C, an estimate of the equivalent duration at 105 °C is of the order of 7 years, and in excess of a thousand years at ambient condition temperature.

work of Xu [2008] and Alig [2007] clearly show that migration of nanoparticles can occur to form aggregates, some with string-like 3D form.

It is clear that the implications of the dynamic state of dispersion, i.e. the ability of particles to migrate, must be taken into account when developing and using test methods that probe the material in its melt-phase. Migration of particles will potentially complicate the execution and interpretation of such tests. However, the extent of migration occurring over the time durations and temperatures to which PNC are normally exposed in testing and processing is unclear.

Finally, particle orientation is likely to be important in determining the PNC properties [Broughton, 2008]. However, the study of orientation of high aspect ratio nanoparticles in PNCs has, in comparison with dispersion, received little attention in the literature. This is presumably due, in part, to the difficulty in characterising the orientation distribution of particles. This topic is largely outside the scope of this review. However, its potential contribution to results, image analysis results in particular, should be considered.

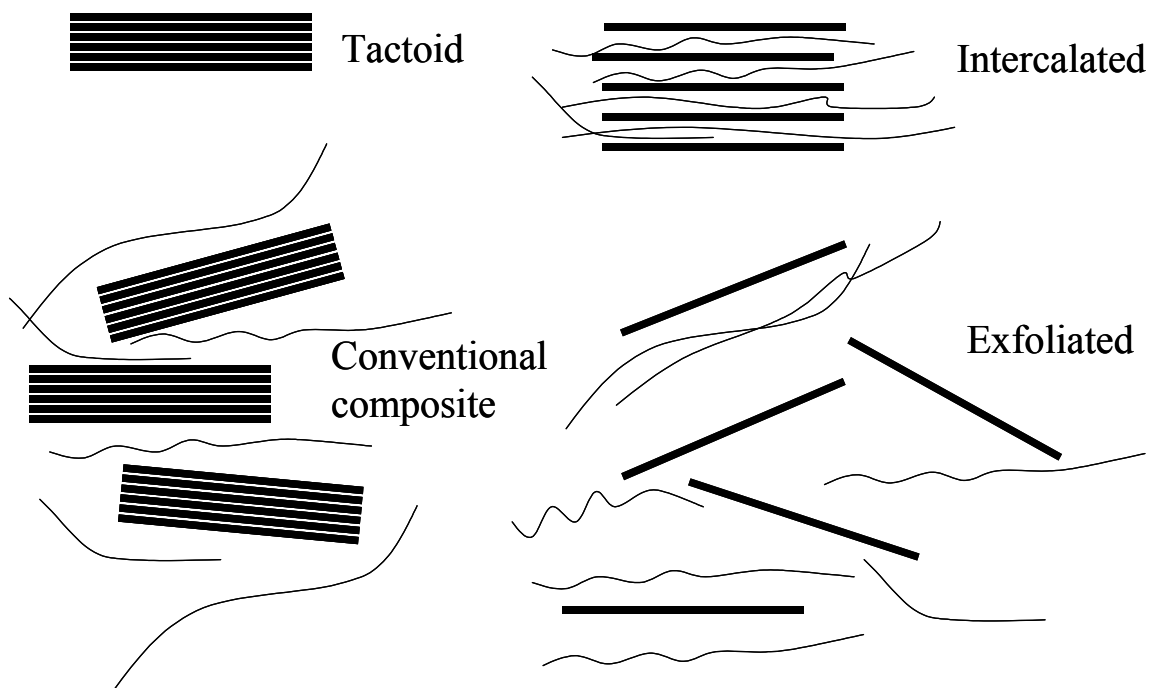


Figure 3: Schematic representation of platelet structures

3.3 PROCESSING OF POLYMER NANOCOMPOSITES

There are three principal methods for producing polymer nanocomposites reported in the literature: in-situ polymerisation, solution casting/processing and melt processing:

- In-situ polymerisation - monomers diffuse into platelet galleries, followed by polymerisation.
- Solution casting – nanoparticles dispersed with polymer in solution, followed by removal of solvent.
- Melt processing (mixing) – melt compounding of nanoparticles and polymer using an extruder or compounder.

Chastek [2005] commented that melt blending is the most economic method for preparing polymer nanocomposites, but is challenging due to the non-polar nature of polymers compared with the polar nature of commercially available clays. Thus compatibilisers are used to improve miscibility of the particles with the polymer but these, as seen later, can introduce additional problems.

Horsch [2006] similarly commented that of melt mixing, solution casting and in-situ polymerization, melt mixing is likely to be the most viable commercial process. As melt mixing is not ideal, they investigated the use of supercritical CO₂ to aid achieving good dispersion in melt mixing. For supercritical CO₂ processed nanoclay-PDMS materials, shear storage moduli and zero-shear steady shear viscosity values were found to be significantly increased for the nanocomposites compared with the unfilled PDMS, but the cross-over of the shear storage modulus G' and the shear loss modulus G'' (i.e. $G' = G''$) and the shear modulus-angular frequency plot gradients were similar. The authors commented that the use of supercritical CO₂ improved the level of dispersion of the nanoclay, but that it was dependant on the level of the clay's CO₂-philicity.

Durmus [2007] commented that graft ratio, molecular weights of the compatibiliser and polymer matrix, miscibility, compatibiliser/filler weight ratio and processing conditions are important for achieving good dispersion. Somewhat in contrast, Ryu [2005] related the degree of dispersion, characterised by XRD and TEM, to the residence (mixing) time in a twin-screw extruder. They commented that for clay-LLDPE nanocomposite exfoliation could be achieved without compatibiliser providing appropriate processing equipment and conditions were used.

Chastek [2005] commented that modification of natural clays is achieved by exchanging the native cations with cationic surfactants. However, both Chastek [2005] and Tjong [2006] commented that the thermal stability of the surfactants used for intercalation is an important criterion for melt mixing at high processing temperatures as this can cause these modifiers to be lost through degradation. Similarly, Utracki [2004] commented that due to thermal/oxidative degradation of the intercalant re-aggregation of exfoliated clay during melt-phase processing has been observed, e.g. for quaternary ammonium intercalant above approximately 165 °C. Pogodina [2008] commented that melt-phase test results are complicated by the thermal degradation of the polymer. When oscillatory testing at low frequencies the test duration increases

dramatically (due to the use of the low frequencies), and degradation is likely. This could potentially cause complications in studying the melt-phase properties of PNCs, for example rheology and thermal analysis, but if testing conditions are controlled to be similar to processing conditions then valuable information can be achieved on the effect of processing on the material's properties.

On mixing of carbon nanotubes PNCs, Lee [2008] reported on the effect of different PNC preparation methods for MWNT in poly(styrene-*ran*-vinyl phenol) copolymer (PSVPh): namely melt mixing and solution/precipitation casting processes. The authors concluded that the melt mixing resulted in more reproducible mechanical properties and was more effective at creating polymer-MWNT interactions than the precipitation routes, as inferred from FTIR measurements of intra- and inter-associated hydroxyl group vibrations. Increased interactions between the MWNTs and the polymer were used to infer improved dispersion of the MWNT. However, no direct 'imaging' techniques, e.g. TEM and XRD, were used to support these conclusions.

Bose [2008] studied the dispersion of CNT in PA-6/ABS blends, varying the route by which the CNT are melt-mixed: initially either with the PA-6 as a "masterbatch" or the ABS as a "masterbatch" and then blended with the other component, or when all three components are blended simultaneously. They concluded that the CNT migrate to the PA-6 phase when blended with ABS first, or stay within the PA-6: the PA-6 had the lower viscosity. They also commented on CNT migration during melt mixing and processing and the formation of a skin-core structure.

It is clear that there are many issues that affect the resultant level of dispersion in polymer nanocomposites, particularly where that material has been produced by a melt mixing or compounding route. Compatibilisation of the nanoparticles with the polymer is a key element in achieving well-dispersed PNCs. Furthermore, once that material has been converted into a product or form (e.g. film) it is far from certain that the level of dispersion achieved after conversion will be the same as in the raw material form, e.g. pellet, prior to conversion.

4 ASSESSMENT OF THE QUALITY OF DISPERSION OF NANOPARTICLES IN POLYMER NANOCOMPOSITES

4.1 IMAGING TECHNIQUES

4.1.1 Introduction

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), optical microscopy and X-ray diffraction (XRD) have been used to 'image' the structure of polymer nanocomposites materials, e.g. Durmus [2007], Samyn [2008], Horsch [2006] and Zhang [2008]. TEM and XRD feature most commonly in the literature and provide valuable information on the degree of dispersion. Although not ideally suited for quality control purposes they potentially provide valuable reference information. In TEM only miniscule quantities of the sample, of the order of $< 10^{-18}$ kg, are imaged and is thus not necessarily representative of the bulk material. Furthermore TEM images are time consuming and expensive to obtain, and interpretation of them is not straightforward. XRD data provide a potential wealth of information on the structure of polymer nanocomposites, but interpretation of the data can be difficult due to the likely

complex and spatially variable structure of polymer nanocomposites. AFM has been used, for example, by Xu [2008] and Yeh [2004] but in both cases the surface information obtained appeared to be of relatively limited value for understanding the nanostructure compared with TEM and XRD.

This part of the review examines some of the issues with using TEM and XRD, in particular, for characterising PNCs.

4.1.2 Microscopy methods: TEM, SEM and optical

One of the key issues in using TEM, SEM and optical microscopy is in the interpretation of the images produced by these methods: qualitative visual perception can be misleading with variations in interpretation between different persons. The TEM images presented by Durmus [2007] demonstrate the difficulty in drawing reliable undisputed conclusions from such images: the few images presented, in the opinion of this author, do not clearly support some of the conclusions drawn. However, it is expected that the image presented formed only a part of a larger library on which the conclusions were founded.

Luo [2008/2] described methods used for quantification of dispersion from microscopy images, as follows.

(i) Particle size measurement: measure clay particle length and tactoid thickness, used to determine how many platelets in a tactoid, and the correlation length (i.e. interparticle spacing) between tactoids. From the aspect ratio of the tactoid a measure of the dispersion can be determined. However this approach does not differentiate between different exfoliated systems and orientation effects.

(ii) Particle density measurement: determination of number of particles (or tactoids) in an area, with the higher value indicating greater dispersion. This approach does not differentiate between systems with local variations in particle density within the measurement zone.

(iii) Linear intercept distance measurement: average particle (or tactoid) spacing along orthogonal grid lines. However, this is dependant on the loading and exfoliation.

To improve on these methods Luo [2008/1&2] presented an interesting and reportedly "*unambiguous*" dispersion quantification of CNF and CNT filled PNCs using TEM. Analysis of the images was carried out to determine the free path length distribution between particles along orthogonal grid-lines superimposed on the image (using ImageJ freeware program), from which the probability of the free-path length being within 10% of the mean free-path length $D_{0.1}$ is calculated. They recommended that at least three "representative" TEM images are analysed. The authors claimed that the dispersion parameter $D_{0.1}$ is independent of filler shape, size or loading. Although this claim is not necessarily agreed, there are, however, the usual image analysis problems that exist which are not discussed therein. Examples of these include identifying digitally what is and what isn't a particle (i.e. contrast issues), and how clusters of particles are handled.

Ratinac [2006] pointed out that quantification of TEM images, the only true direct observation of nanocomposite structure, is essential. Methods involve intersection analysis of particles with lines, interlayer distance measurement, and analysis of spacing of maxima and minimum in intensity, and combinations of manual and automated analysis of images by counting and sizing particles and determining their separations. The authors commented on Vermogen [2005] who analysed images at

different length scales characterising agglomerates, tactoids and individual platelets thus capturing local variations in structure of the composites and overcoming some of the issues with statistical sampling sizes. Ratinac [2006] used 7100 $\times$ and 110000 $\times$ magnification, although the latter with semi-manual analysis was used as baseline data for exfoliation that would not be visible using the lower magnification. The authors used a variety of measured parameters to characterise the micro- and nano-structures and then a number of derived parameters that describe specific features of the structure, including exfoliation factor, degree of exfoliation and agglomeration factor. They concluded the most valuable parameters for quantifying micro- and nano-structure were the particle density and degree of exfoliation parameters.

Vermogen [2005] considered the following representative descriptions of the clay particles: micron sized agglomerates, middle sized tactoids, intercalated and non-intercalated small size tactoids (5-15 platelets), intercalated or exfoliated sheets (3-5 platelets), and individual exfoliated platelets. A statistical approach was then used, analysing a large number of images and assigning one of these categories to each individual particle, thus yielding a frequency distribution of occurrence for each of these forms for a given material. The authors commented on difficulties in determining tactoids length, the results of which were a factor of five lower than expected (100 nm c.f. 500 nm). They concluded that multi-scale analysis and characterisation is essential to fully understand the structure, using TEM and optical, the latter to observe agglomerates not apparent in the very small scale TEM images.

To address the issue of scale of the analysed image, it is essential that TEM is used in combination with SEM and even optical microscopy to assess the quality of dispersion on several, preferably overlapping scales. The resolution of optical microscopy tends to approximately 0.2 μm , SEM between 1 nm and 20 nm, and TEM sub-nanometre resolution: these values are dependent on the specific instrument used.

Utracki [2004] commented on the use of TEM at lower resolutions to check on the uniformity of dispersion. Reporting on Dennis [2000, 2001] he described a method to subdivide the TEM image into a square grid and the number of platelets per square were counted: the number per grid being used as a measure of dispersion (the variation being a measure of the variability in dispersion). This method could be taken a stage further where the size of the area used for the counting is varied and the variation in number of platelets per unit area used as a further estimate of uniformity and method reliability, and to identify the optimal size of the counting area used.

Eckel [2004] assessed dispersion using particle density and linear intercept measurements (average distance between particles along an array of parallel lines: a smaller value indicating better dispersion. With highly aligned systems they used lines perpendicular to the orientation of the platelets only. However, they commented that the linear intercept measurement is affected by particle orientation, as perfect alignment is unlikely to ever exist in real cases. Eckel [2004] further highlighted the issue of platelet orientation on TEM imaging, commenting that single platelets can only be image edge on. Similarly, the orientation of rod shaped particles is likely to also have an effect on the assessment of their dispersion. They reported that an exfoliated structure has a linear intercept value of less than 0.1 μm . They considered the linear intercept measurement to be preferable as it is independent of particle length (presumably for a given volume loading), is easier to perform, and can be compared with the theoretical value for

idealised (aligned) system, although they reported that due to stereological errors there will be a discrepancy that increases with specimen thickness and smaller particles.

Eckel [2004], commenting on imaging of agglomerations, reported that because an agglomeration can be larger than the thickness of the TEM specimen (80 nm in Eckel [2004]), the actual size of the agglomerate may be larger than that imaged by TEM thereby presenting a false representation of the structure. Similarly, Vermogen [2007] highlighted the errors associated with TEM sample preparation to thicknesses less than 100 nm impacting on the measured aspect ratio of the clay platelets, as observed through a thickness-dependant aspect ratio. They concluded that it might be better to use the tactoids thickness, interparticle spacing and platelet density as improved measures of dispersion.

On TEM, Wagener [2003] commented that the sample volume that is probed is very small and that sample preparation is difficult and expensive in both time and costs, and thus not appropriate for routine characterisation. In TEM the observable area is typically of the order of 1 micrometres squared ($1 \times 10^{-12} \text{ m}^2$) and is thus not representative of gram, let alone kg or tonne scale production. Furthermore, Causin [2005] emphasized that great care must be exercised in selecting "representative" TEM images. Samyn [2008], for example, presented typical TEM images of organoclay, reporting that this was based on careful analysis of at least 50 images taken from different parts of the sample.

Similarly Vermogen [2007], commenting on their earlier TEM work, reported that the image analysis procedure had limitations in terms of how representative the analysed volume was of the sample. They commented that wide-angle X-ray scattering (WAXS) and TEM are the most commonly used methods for structure characterisation, although adding that the structure is usually complex. They commented that Liu [1999], Yang [1999] and Liang [2002] observed a nanoparticles concentration limit below which the material was exfoliated and above which the material had a mixed exfoliated/intercalated structure. Vermogen [2007] commented that TEM or WAXS alone are insufficient to reliably describe the dispersion in nanocomposites, adding that the use of different techniques, e.g. rheology, NMR, SAXS and TEM has been successful in quantifying orientation and dispersion. Their study suggested that SAXS tactoids thickness distribution was in good agreement with TEM image analysis, leading credence to their volume analysis method.

Gilman [2005] referred to the use of a laser scanning confocal fluorescence microscope with a cationic dye modified organo-montmorillonite clay to study bulk, meso-scale dispersion in nanocomposites, presumably from the fluorescence intensity signal. This potentially provides an imaging technique with 3D capability provided the matrix is transparent and the concentration of clay is not too high.

ISO 11332-1 and BS3406-4 provides guidance on image analysis for particle size analysis but require relatively ideal samples requirements that are not likely to be easily achievable for PNCs, in particular for rod or platelet PNCs with their overlapping particles, or for agglomerated spherical particles forming complex fractal shapes.

In summary, it is clear that microscopy imaging techniques provide valuable information on the structure of PNCs but considerable care needs to be exercised, in

particular, in the analysis of the images and in sampling procedures, preferably using a range of overlapping length scales, to ensure that the descriptive parameter values obtained are representative of the dispersion of the whole sample.

4.1.3 XRD methods

X-ray diffraction and scattering techniques rely on there being a regular structure within the material that diffracts or scatters the X-rays to produce patterns that are characteristic of the structure of the material. As such it is largely limited, in the context of nanoparticles dispersion, to the study of clay-based PNCs. Indeed only one paper that was reviewed used it for another filler (Boehmite nanoparticles, Coiai [2008]) but found the technique unsuccessful.

X-ray diffraction is based on the Bragg equation

$$\lambda = 2d \sin \theta$$

where λ is the wavelength of the X-rays, typically 0.154 nm [Durmus 2007, Lim 2003]. The technique identifies regular spacings, d , in layered structures from the angles between the incident and scattered rays. The interlayer spacing in a platelet structure is also known as the d -spacing or basal spacing, d_{001} .

Utracki [2004] commented that XRD was the principal method for studying intercalation and exfoliation of polymer nanocomposites, classifying the technique into two categories: small angle x-ray scattering (SAXS) and wide angle X-ray scattering (WAXS). The boundary between SAXS and WAXS is at an angle of $2\theta \approx 2^\circ$ (≈ 4.4 nm), although WAXS can be used down to $2\theta \approx 1^\circ$ (≈ 8.1 nm). Utracki [2004] commented that SAXS and SANS have been used with angles down to $2\theta \approx 0.05^\circ$ (≈ 180 nm) and WAXS up to $2\theta \approx 10^\circ$ (≈ 0.9 nm). Small angle neutron scattering (SANS) can be used for small angles (spacings of up to 80 nm are reported) with greater sensitivity than SAXS.

In considering XRD data, Pogodina [2008] commented that the derived d -spacings provide limited information as they are averaged values for the sample, hiding detail concerning the whole structure. In comparison, he commented that rheology can be used to detect differences in the dispersion state of agglomerates and thus they are complementary in the data they provide.

Tjong [2006] commented that nanoparticle dilution, peak broadening and orientation can result in errors in interpretation of XRD spectra, similarly adding that TEM is a complimentary technique.

Eckel [2004], on XRD, commented about the effect of mixed layering affecting the peak diffraction angles, and also that changes in the diffraction patterns from that of the neat clay can be difficult to interpret. Furthermore, particle size, defect density, strain effects and mixed layering can affect the peak widths. Similarly, peak heights can be affected by flow-induced orientation of platelets or concentration effects (i.e. interactions). They concluded that XRD is suitable for determination of intercalation by the increase in spacing of the basal reflections, and exfoliation by the absence of the clay basal peak. However, other factors can contribute to these effects, leaving open the

potential to misinterpret XRD spectra. Wagener [2003] commented that the disappearance of an XRD peak should not be inferred as proof of full exfoliation of the clay platelets as other changes in physical state of the tactoids could be responsible for the loss of XRD peaks, but with elucidating further.

Similarly, Causin [2005] commented that factors such as particle size, defect density, strain effects, mixed layering and experimental parameters can affect the WAXS data (reportedly the most frequently used technique). Furthermore, because of the low angle limit of WAXS, exfoliation cannot be guaranteed because of the absence of the clay basal peaks. Similarly, Lim [2003] commented that the use of WAXD is not suitable for where the periodic structure, e.g. that associated with intercalated platelets, is lost. Causin [2005] claimed that good agreement between TEM and SAXS was obtained for structural descriptors (number of clay layers) using their new analysis in their comparison, and highlighted the difficulties associated with adjacent "face-to-face" tactoids of clay platelets appearing as a single tactoid in TEM but not in WAXS.

Utracki [2004] commented that XRD has been used to estimate the degree of exfoliation from the relative areas of the peaks for the PNC sample and for the same material with (only) intercalated clay. He commented that peak broadening is due to exfoliation, although the peak position remains unchanged, but that broadening can be due to other factors such as imperfections in the structure of the clay tactoids e.g. different spacings and imperfections in the tactoids. However, these latter factors would need to change on processing, for example, for them to result in a broadening of the peak.

Ratinac [2006], studying PMMA clay nanocomposites using TEM and wide angle X-ray diffraction, investigated the use of parameters to quantify the dispersion. Comparison of WAXD data against analysis of TEM images demonstrated limitations in using WAXD as a sole measure of the nanocomposites structure. They reported that WAXD has an effective upper limit of 6 nm for layer separation due to the background noise, and thus are not able to detect partially exfoliated structures or individual platelets, and due to data interpretation issues, cannot differentiate between well-separated small tactoids and agglomerated tactoids.

Commenting on FTIR and Raman and the limitations of XRD, Utracki [2004] stated that FTIR and Raman are suitable for study of exfoliated systems that do not scatter in XRD due to large spacings, albeit providing different information. On NMR, Utracki [2004] commented that it is only suited for clays containing paramagnetic Fe^{3+} , thus limiting its suitability for study of PNCs.

Samyn [2008] commented that XRD, SEM, TEM and melt rheology give useful information for describing the dispersion of the nanoparticles in PNCs. SEM was used to check for sub-micron dispersion by the absence of agglomerates. NMR measurements were also performed but they concluded that the flame retardant particles interference distorted the results yielding underestimates. They commented that typically less than 10 wt% of nanoparticles is required to achieve improved properties, although 5% of organo-modified montmorillonite was used in their reported work. Samyn [2008] reported that agglomerates exhibited intercalation to some extent at higher magnifications, with *d*-spacings estimated from the images of 2.6 nm compared with 3.3 nm from XRD measurements (1.7 nm for pure OMMT [Pogodina, 2008]).

In summary, it is clear that X-ray diffraction and scattering techniques provide valuable information on the structure of PNCs but considerable care needs to be exercised in the analysis of the spectra. It is noted that such data are averaged and therefore do not provide easy access to spatial variation information.

4.1.4 Comparison of microscopy and XRD methods

In comparing microscopy and XRD techniques it is clear that both have their advantages, disadvantages and limitations. TEM, SEM and optical microscopy can provide information on spatial variations in micro- and nano-structure, whereas XRD provides averaged information on structural parameters at the nano-scale. Exfoliation has been inferred, in the literature, on the basis of an absence of XRD peaks, but this inference has attracted criticism as such absence of peaks can be due to other experimental factors. In comparison, XRD is well suited to studying intercalation processes. Of the microscopy techniques, exfoliation can only be reliably determined from TEM, but it is on very small sample sizes and thus how representative the sample is of the bulk is a important issue that is time consuming to address experimentally using microscopy. Due to their different strengths, XRD and, in particular, TEM should be considered as complimentary rather than alternative techniques.

4.2 RHEOLOGICAL STUDIES OF POLYMER NANOCOMPOSITES

4.2.1 Introduction

Utracki [2004] reported that "*the knowledge of the thermodynamics and rheology of nanocomposites is very limited*"; adding that widely varying responses were observed. He suggested using rheological characterisation to quantify the thermodynamic interactions of particles with polymers.

Similarly, Kotsilkova [2007] reported on a rheological approach for thermosetting plastics, but there was very limited imaging information on the degree of exfoliation and intercalation of the materials. Kotsilkova [2007] commented that factors such as dispersion, polymer-clay interaction and clay content are expected to be factors in determining the rheological response of PNCs. He concluded that low deformation rates in rheological measurements provide the most sensitive measures for nanocomposites characterisation, whereas high strain, high rate testing should be used for data generation for process simulation.

Oscillatory rheometry is a technique that can provide low shear strains and low shear strain rates. It has been used to investigate changes in shear storage modulus G' or complex viscosity η^* at low frequencies by, for example, Durmus [2007], Samyn [2008] and Horsch [2006] for clay-based PNCs, by Zhang [2008] and Huang YY [2006] for carbon nanotube based PNCs, and by Cassagnau [2008] for fumed silica based PNCs. These papers are reviewed along with others later in this report.

Thus, it would appear that rheology offers a potential route for qualitatively assessing the mix or dispersion quality of polymer nanocomposites, in particular identifying network formations that were likely to be critical to the development of enhance performance properties promised by polymer nanocomposites.

The review presented below is structured on the basis of materials form: (i) platelets, dominated by organoclays, (ii) fibres consisting of carbon nanotubes and nanofibres and (iii) spherical particles.

4.2.2 Nanoclays

The majority of papers on nanoclays in the literature reported the use of low frequency oscillatory rheometry for the study of polymer nanocomposites. However, a few reported on steady shear flow methods that tend to be at comparatively higher deformation rates.

Utracki [2004] suggested that end-tethered polymer-nanoparticle systems tend to exhibit 3D network formations at approximately 0.5 wt% loadings of clay, resulting in solid-like (yield-stress) behaviour at low deformation rates, and shear thinning with oriented platelets in high shear rate flows. To observe these networks, Pogodina [2008] commented on the need for small amplitude (small strain) oscillatory shear measurements so that the 3D networks formed by the nanoparticles are not destroyed by the measurements themselves: measurements must therefore be carried out in the linear viscoelastic regime, assuming that such a regime exists and is achievable using current instruments.

Durmus [2007] commented that low frequency rheology offers a route for assessing dispersion quality, in particular on network formation (percolation threshold). An increase in shear storage modulus G' or complex viscosity η^* at low frequencies with frequency independence yielding "solid-like" behaviour was explained by the formation of 3D networks of nanoparticles. The storage moduli G' increased by up to 3 decades over the unfilled polymer. They commented that shear forces in mixing are important in dispersing clay particles. For compounds with low shear viscosity, e.g. due to low molecular weight compatibiliser, insufficient shear forces may be generated to facilitate dispersion of nanoparticles thus offsetting the potentially better compatibility of the compatibiliser. The effect of the low molecular weight, low viscosity compatibiliser was also apparent in the high frequency ($\omega > 5$ rad/s) results where the lubricating effect of the higher loading of compatibiliser due to the higher clay loading was apparent. They also commented on the use of the strain limit of linear viscoelastic behaviour, determined using a strain sweep (strain at which G' is 90% of its plateau value), suggesting that the shear strain limit is due to network formation, the alignment of the clay particles, and rupture of particle-particle interactions. However, the discriminatory ability of this approach seems relatively poor. Durmus [2005] proposed the use of the shear rate thinning exponent n as a measure of dispersion (values reported were in the range $0.03 < n < 0.83$, where n was determined over the range $0.01 < \text{angular frequency (rad/s)} < 0.1$). Durmus [2007] also presented shear storage modulus G' values (at 0.01 rad/s) against the volume fraction in an attempt to determine the percolation threshold, observing that it was in the range 1 vol% to 2 vol% and was dependent on the compatibiliser type. The authors then used this to determine the aspect ratio of the clay tactoids/particles using

$$A_f = \frac{3\phi_{pR}}{4\phi_p}$$

where A_f is the average aspect ratio of the particles, ϕ_{pR} is the percolation threshold volume fraction for randomly packed spheres (Durmus [2007] used 0.3) and ϕ_{pR} is the experimentally obtained value for the material. This yielded values for A_f of ≈ 21 and ≈ 13 for the two materials with different compatibilizers investigated.

Vermogen [2005], studying PP-clay nanocomposites, concluded that rheology, WAXS and TEM showed different nanocomposite morphologies. They commented that WAXS can give a misleading and incomplete interpretation of the nanostructure. They reported that Bafna [2003] used WAXS and SAXS for orientation studies, and found that there was non-homogenous orientation of clay: the agglomerates and intercalated platelets were orientated in the shear flow direction whereas there was no orientation of unmodified clays tactoids. Oscillatory rheometry revealed higher viscosities for better dispersion states. The authors stated "*the increasing order of compounds viscosity at low frequency lets one class the compounds as a function of their dispersion state*", and also that the gradients of the G' and G'' curves at low frequencies were indicative of the nanocomposite behaviour.

Kashiwagi [2004], in studying the flame retardant properties of nylon-6 clay nanocomposites, suggested the formation of a sample-spanning network for a 5 wt% loading of clay nanoparticles, as indicated by a high elastic component of modulus (G') at very low frequencies and frequency independent moduli measured using oscillatory rheometry. This was also observed by Durmus [2007], reported above. However, this was not the case for the 2 wt% sample. The importance of the higher viscosity in suppressing bubble formation during burning, contributing to the improved fire resistance, was suggested. XRD and TEM were also used to characterise the micro- and nano-structures.

Samyn [2008], in also studying the flame retardant properties of various polymer nanocomposites, reported on dynamic rheological testing, although only complex viscosity data were plotted. The authors suggested that the shear thinning³ behaviour of the complex viscosity correlated to the extent of exfoliation, intercalation and agglomeration, the first having the highest and the last the lowest degree of shear thinning. However, it is not clear that this correlation is correct from the evidence presented, although Samyn [2008] suggested that there might be interaction of the fire retardant particles with the nanoparticles that complicated the interpretation of behaviour. The absence of G' data, or the ability to generate them from the data provided, is noted and may, if the behaviour is strongly characterised by its elastic response, prove critical in understanding the rheological behaviour.

Pogodina [2008] used both rheology, light attenuation, TEM and XRD to study dispersion in OMMT (3 wt% - 5 wt%) filled poly(lactic acid). They concluded that percolation was detected as a step (significant) increase in the low frequency elastic modulus G' , with melt elasticity increasing with mixing energy and associated with the improved dispersion of the clay platelets as evidenced by TEM imaging. Both the light attenuation and rheology showed significant variations with clay dispersion, with a reasonable linear correlation ($r = 0.88$) between the loss tangent ($\tan \delta$)⁴ and the light

³ 'Shear thinning' was the term used by the authors to describe the angular frequency dependence of viscosity.

⁴ The loss tangent, $\tan \delta$, is the ratio of the shear loss modulus G'' to shear storage modulus G' .

attenuation (where $\tan \delta$ was determined at a low frequency, lower than that giving a maximum in $\tan \delta$).

Huang W [2006], in their studies of organoclay in a liquid crystalline polymer, commented that hydrogen bonding between the polymer and the surfactant on the organoclay, a hydroxyl polar group, helped achieve a high degree of dispersion. The authors concluded that *"rheological measurements, when properly interpreted, can be used as a powerful tool for a better understanding of the dispersion characteristics of organoclay nanocomposites"*.

Using this principal in an interesting approach for assessing the compatibility of nanoparticles with organic materials, Chastek [2005] investigated the dispersion of synthetic clays, functionalised with organic surface groups, in both solvents and PS. The solvents were used for a quick visual and rheological assessment of the compatibility of the clays with polymers. They observed that the clays formed gels in aromatic and branched alkyl solvents, exhibiting high elastic modulus G' with a plateau at low frequencies. In the gels, network formation occurred at approximately 0.5 wt% (approx 0.2 vol%), requiring an aspect ratio of approximately 190 for percolation to occur. They commented that the formation of a network might inhibit exfoliation of excess clay platelets when higher concentrations above the percolation threshold were used. They also used the strain dependence of G' – the strain at which G' decreased to 80% of its value – as a measure of gel strength. The G' plateau values were consistent with SAXS and TEM data which showed that better dispersion and higher aspect ratio correlated with the higher G' plateau samples.

Pogodina [2008] referred to a model developed initially for gelation by Winter and Mours [1997]. At the critical gel point, it is stated, the low frequency dynamic moduli exhibit power-law behaviour. A consequence of this is that the loss tangent, $\tan \delta$, is frequency independent at the gelation point. The authors argued that high plateau (frequency independent) values of G' indicated a solid-like network of percolating nanoclay. Pogodina [2008] also referred to van Gurp plots in which the loss angle δ is plotted as a function of the complex modulus G^* : the gel point corresponds to the plateau region at low G^* values. The authors suggested that this plot indicated different micro/nanostructures of the percolation network of differently processed materials. The authors also showed a strong increase in complex viscosity with decreasing angular frequency, compared with the plateau region for the unfilled material: again further evidence of the formation of a network and solid-like behaviour.

As commented previously, steady shear methods have been used, but minimally compared with low frequency oscillatory measurements. Lim [2003] observed that the steady shear viscosity and power-law index (shear thinning exponent), obtained by fitting a Carreau model, increased with improved dispersion quality as achieved through ultrasonication at 28 kHz in the solution stage of sample preparation (nanoclay in PEO). Also, the shear rate value at the onset of shear thinning decreased with improved dispersion quality. The differences in steady shear viscosity (by up to $\times 7$ difference) were most noticeable at the lowest rate of 0.01 s^{-1} . At the highest shear rate, the best dispersed system had the lowest shear viscosity of all the nanoparticles filled materials, and thus was most suited to high rate processing methods. The oscillatory rheometry evidence presented appeared insufficient to support the comments concerning solid-like behaviour at low frequencies made by the authors, but their suggestion was that

individual particles and tactoids in well dispersed systems are constrained by neighbouring particles from rotating freely during shearing. The authors commented that ultrasonification targets the individual platelets in tactoids and agglomerates of tactoids thereby improving dispersion.

Ratnayake [2006] studied PP homopolymer based clay nanocomposites processed by melt mixing using TEM and XRD, using maleic anhydride-grafted PP (PP-MA) compatibiliser and amide-type slip additives to enhance dispersion. The authors commented on the extent to which dispersion and exfoliation in the various systems could be achieved. Following Zhu et al [2004], they used melt flow rate testing, commonly used in the polymer industry to characterise the flow properties, utilising its low shear rate characteristics to probe the nano-structure, and using equivalent unfilled polymer system to normalise the data. Reported melt flow rates for the nanocomposites were up to 50% lower compared with the non-compatible PP, corresponding to an equivalent increase in viscosity. The authors concluded that it is an appropriate parameter for characterising nanocomposites.

Wagener [2003] commented that pronounced shear thinning (at high rates) and solid-like behaviour (at low rates) are features of well-dispersed nanocomposites, speculating that the latter was possibly due to edge-to-face interactions of platelets and tactoids. However, the relationship of the shear thinning response to the degree of dispersion is confused by the fact that, as commented by the authors, it is also dependant on the concentration of filler. As a consequence they held the concentration constant at 4 wt% in their studies to remove this sensitivity. The authors demonstrated that oscillatory rheometry can induce alignment in the clay nanocomposites, reducing complex viscosity after performing a high amplitude strain sweep up to 600%. However, the effects of structure breakdown [Alig, 2007] and thermal degradation do not appear to have been considered in their suggesting that thermal randomisation of platelet orientation occurred on holding the nanocomposite sample at 240 °C for 1 hour.

4.2.3 Carbon nanotubes and fibres

Research on carbon nanotubes and fibres has focused on their addition as fillers to thermoplastics and thermosetting plastics, as well as in solution form. The major difference in the reported testing, compared with nanoclays, is the use of dielectric and electrical testing and, not too surprisingly, the complete absence of XRD.

Xie [2005] commented that the "*critical challenge ... is to enhance dispersion and alignment of CNTs in the matrix*". He remarked that CNTs have a strong tendency to agglomerate, bundle and entangle due to van der Waals forces, ionic interaction and hydrogen bonding, with the consequence that the poor dispersion and entanglement led to significant reductions in mechanical properties. They discussed the purification, disentangling (cutting) and activation of CNTs prior to chemical treatment. In reviewing papers on CNTs, they commented that the use of only 1 wt% of CNTs increased the T_g by 25 °C for an epoxy based composite. They concluded that good dispersion can be achieved by high power dispersion and melt blending techniques with compatibilizers and surfactants. They reported that very large increases in storage modulus (1135% at 90 °C), glass transition temperature T_g (40 °C) and electrical conductivity (10 decades, with 0.1 wt% loading) above that of the matrix were observed: other mechanical properties were improved to a significantly lesser degree than storage modulus highlighting its value as a sensitive measure of dispersion. The

change in T_g was accounted for by the CNTs acting as nucleating sites, increasing crystallization and the melting temperature. Furthermore, they also reported that significant improvements in properties can be achieved by orienting the CNTs, e.g. induced through flow or the application of magnetic or electric fields.

Pegel [2008] concluded that sedimentation behaviour of aqueous dispersions of MWNT in water/surfactant solutions can be used as a simple means of estimating the dispersability of MWNT: higher sedimentation rates corresponding to less well dispersed system (more, larger agglomerates). They commented, similar to Xie [2005], that during melt mixing high shear forces are required to disentangle the MWNT and prevent agglomeration due to the high van der Waals forces and physical entanglements, adding that Lin et al [2006] discussed the efficiency of mini-mixers. Agglomeration was observed to occur during mixing at high temperatures and low shear rates. However, structured agglomerations can aid the formation of an electrical percolation network. Pegel [2008], commenting on earlier work, said that annealing at temperatures well above the melt temperature can give very significant increases in the conductivity of the PP/MWNT samples – though the term annealing in this context is perhaps misleading. They also commented on a simple model for agglomeration [Alig, 2007] concluding that prolonged mixing time does not necessarily increase dispersion: secondary agglomeration formation is related to the level of shearing forces. They also commented that conductivity recovered after shearing ceased in combined rheological and conductivity measurements, suggesting agglomeration destruction during shear and re-formation thereafter.

Dan [2009] observed that significant increases in viscosity, of the order of 2-3 decades at a shear rate of 0.1 s^{-1} , were observed on adding 1 wt% surfactant to 0.3 wt% to 0.4 wt% of SWNT in water. The authors commented that the mechanisms for this are not entirely clear, but that the effect was due to the formation of weakly associated network structures. This may be due either to changes in the surfactant micellar structure or depletion flocculation of the SWNTs: effects which are degraded at higher shear rates. These effects in solution are, presumably, similar in nature to those in polymers. Although of value, it is not expected that the results from the studies of aqueous systems by Pegel [2008] and Dan [2009] will be anything more than indicative of the behaviour of the CNTs in high molecular weight polymers.

Huang YY [2006] commented on the need for a minimum time to achieve satisfactory dispersion of MWCNT in PDMS, the time being dependant on the CNT concentration and the shear stress in mixing. They are, perhaps unjustifiably, critical of SEM in that it is a surface technique and that preparation of the sample by etching to reveal the CNTs allows them to aggregate. Significant, multi-decade changes in dynamic viscosity and elastic modulus were observed for different loadings and mixing times. Importantly, for the 7% loading changes in elastic moduli were observed with time after mixing, referred to as "ageing" or the reverse process of dispersion. Thus time delays between sample mixing and testing may have a significant effect on measured properties. They noted that for a low loading of 1% "ageing" was not observed, hypothesized to be due to the insufficient Brownian motion to agglomerate remote, non-interacting particles.

Zhang [2008] reported on the use of dynamic rheological behaviour to estimate the dispersion of carbon nanotubes (0-5 wt%, diameter 20 nm) in polystyrene prepared by emulsion polymerisation, using MWNTs with and without surface functionalization.

Dispersion was assessed using TEM and SEM. They observed that the addition of nanoparticles had a significant effect on the dynamic properties, increasing with decreasing frequency: the material loses its Newtonian plateau at low frequencies and is replaced by increasingly higher complex viscosity η^* and shear storage modulus G' values and thus a more solid-like response. This was accounted for by the formation of networks of nanotubes, with a more homogeneous dispersion giving a stronger solid-like response and less temperature dependence at elevated temperatures compared with the unfilled polymer. Although differences due to the nanoparticles loadings were clearly visible below angular frequencies of 10 rad/s, the most significant differences were observed at the lower limit of frequency used of 0.01 rad/s where differences in both G' and η^* in excess of 100 $\times$ were observed. It was reported that the viscous G'' data exhibited a similar trend to elastic G' data, however no results were presented. Analysis using presented η^* and shear storage modulus G' data revealed that the effect of filler on G' was of the order of 10 times greater than that on G'' : G' values increased by approximately 340 $\times$ for the untreated MWNT, and 1200 $\times$ for the treated (carboxylated) MWNT, whereas G'' changed by 40 $\times$ and 130 $\times$ respectively. This clearly indicates that the elastic component is more sensitive to the addition of MWNT compared with the viscous component G'' ($\tan \delta$ decreased on adding increasingly higher loadings of MWNTs). On the basis of TEM and SEM studies, although evidence was limited and open to interpretation, the authors commented that the surface functionalised MWNTs were more dispersed and formed networks. Furthermore, they concluded that these networks constrained the long-range molecular movement of the polymer chains, and is thus apparent in the low frequency rheological behaviour.

Alig [2007] presented results on the effect of shearing on dielectric analysis of CNT filled polycarbonates. They observed decreases in conductivity of the samples on shearing, linked to the breakage of the percolation network. However, a strong recovery of the percolation network on cessation of shearing was observed on annealing at 230 °C over a period of two hours (T_g estimated at approximately 120 °C, Krevelen [2000]). Although a rotational rheometer was used to provide the controlled shearing, results of rheological measurements were not presented. These observations were supported by TEM images showing MWNT aggregation consistent with increased electrical conductivity.

Isayev [2008] concluded that the use of ultrasound reduced the loading of CNFs (diameter: 70 nm - 200 nm, length 50 μ m - 100 μ m, although the modal length after processing was of the order of 3 μ m - 4 μ m) in PEI needed to reach the percolation threshold, identified by volume resistivity measurements. However, a seemingly high value of 15 wt% (e.g. compared with 5 wt% by Zhang [2008]) was reported in the ultrasound case. However, a ball-milled sample exhibited lower CNF percolation concentration of 4 wt%, accounted for by the presence of long and aggregated fibres forming a better-interconnected network, even though they were reportedly poorly dispersed with the polymer matrix. This obviously complicates the interpretation of resistivity results. Thermal conductivity measurements showed an increase in value (0.25 W/(m.K) to 0.5 W/(m.K)) with increasing CNF concentration, but the trends were not clear with the untreated CNF having values approaching the mean of the materials. SEM was used to identify bundles of CNFs (diameter 10 μ m - 50 μ m) in the material indicating, by their absence, a good dispersion. Dynamic rheometry results again showed a large (500 $\times$) effect on the shear storage modulus and a smaller (10 $\times$) effect on the shear loss modulus of the addition of up to 20 wt% CNF, the effect being largest at

the lowest angular frequency (10 rad/s). Mechanical testing indicated an improvement in modulus by up to a factor of 2×, strength relatively unchanged, and elongation at yield and break and toughness decreasing significantly with increasing CNF concentration. The ultrasound treatment generally had a small effect compared with that of varying the CNF concentration. It is considered, however, that the loadings reported here are significantly higher than values reported elsewhere in the literature that were necessary to achieve percolation threshold.

Kashiwagi [2007] used UV-vis spectroscopy and optical confocal microscopy to measure the dispersion of single walled carbon nanotubes in PMMA, with dispersion being determined by image analysis of 100 images to obtain a “relative dispersion index” (RDI) and absorbance. The authors commented that a quantitative descriptor of spatial dispersion is necessary to understand the structure-performance relationship as good spatial dispersion is essential for realising the full potential of CNTs, referring to the quadrant method of Morishita [1959] for quantitative analysis. Additional methods were presented for analysis, with results shown to be sensitive to the analysis domain size. Samples were prepared using the coagulation method (solution based) to produce varying levels of dispersion. They observed correlations of electrical conductivity, storage modulus and flammability with RDI. The authors commented that uncertainties in the RDI determination included: the inability to image small bundles of CNT or individual CNTs using confocal microscopy (an area 92 micrometres square was imaged), large scale non-uniformity, threshold value selection for identification of CNTs in the imaging process, and inability to separate (overlapping) tube bundles - the authors suggested that intensity information may be useful to address the latter issue. Variations in dispersion resulted in changes of up to four decades in storage modulus and eight in conductivity. Again the occurrence of solid like response inferred through G' at low frequencies was observed, in this case for 0.5 wt% nanocomposites but not for all the prepared dispersed systems. The authors commented that the wide range in percentage weight of CNTs needed to achieve percolation in electrical conductivity or storage modulus, as reported in the literature and commented on above, may well be due to agglomeration of the particles thus preventing adequate dispersion from being achieved.

Battisti [2008] studying CNT filled unsaturated polyester resins commented that re-agglomeration of the CNTs can be expected during the curing process due to the strong attractive forces between the particles, signifying the need to assess dispersion in the product as well as the unprocessed material. They commented that horn sonification is recognised as one of the most effective methods for achieving good dispersion, but commented that there was not a "direct" standard method for quantifying the level of dispersion. Dispersion in the liquid state was assessed using an optical microscope, and in the solid form by SEM (TEM was used on the original, unused fibre sample). Rheological measurements were performed using steady shear with a cone and plate geometry, with the Carreau viscosity model⁵ used to determine the shear thinning parameter. Large variations in the shear thinning parameter were observed to occur with ultrasonic energy input that was qualitatively compared with optical microscopy assessment of agglomeration. Electrical measurements were found to be very sensitive to temperature (≈ 60 %/°C), thus requiring instantaneous temperature correction in

⁵ Carreau model: $\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) (1 + \lambda^2 \dot{\gamma}^2)^{-N}$ where λ is a relaxation time, η_0 and η_{∞} the limiting shear viscosities at very low and very high shear rates and N a shear thinning exponent.

order to produce useful data. The shear thinning parameter was chosen by the authors as the preferred parameter to qualitatively characterise dispersion, and correlated well with ultrasonic mix energy input and with electrical resistance. The decrease in the latter, by three to four decades, was accounted for by the development of a percolating system (albeit with some clusters, indicating the complexity of the system). Potential evidence was presented that indicated damage to the CNTs by excessive ultrasonification (also see [Isayev, 2008]), leading to an increase in electrical resistivity and thus complex correlation with the degree of dispersion.

4.2.4 Nanospheres

Tang [2007] used FTIR and XPS to assess the extent of grafting onto ZnO nanoparticles (40 nm diameter), and the effect of that grafting on improving the dispersion in polystyrene using SEM and TEM. The improved dispersion was in qualitative agreement with inferences from DSC measurements showing an increase in T_g (by 15 K) and improved thermal stability by thermogravimetric analysis (TGA). However the assessment of the improved dispersion was qualitative and not conclusive on the evidence presented.

In studying silica filled systems, Cassagnau [2008] used linear and non-linear rheological measurements, observing the increase in solid-like behaviour of the low deformation properties as widely observed for the nanoclay based PNCs (e.g. high plateau G' values at low frequency and low strain compared with the unfilled PS, and smaller Newtonian plateaux in steady shear measurements). He concluded that two mechanisms resulted in the solid-like behaviour: the principal mechanism for fumed silica PNCs was particle-particle interactions, whereas for colloidal silica PNCs it was particle-polymer interactions (for clay-based nanocomposites he suggested it was particle-particle interaction) although in all cases these interactions were moderated by surface treatments, e.g. grafting.

4.2.5 Modelling of effect of nanoparticles on rheological properties

The effects observed in the rheological behaviour reported in the previous sections have led to various models being proposed for describing the data. Many have their basis in previous work, for example in describing yield phenomena and gelation behaviour.

Cassagnau [2008], in reviewing papers in the literature, reported on the use of linear and non-linear rheology for studying polymer nanocomposites, the former determined using oscillatory rheometry, arguing that both are strongly affected by nanostructure. He added that the rheology of elastomers and thermoplastics are, however, quite different due to the differences in viscoelastic properties of the matrix. Cassagnau [2008] finally commented that transient shear methods are often used and best suited for clay based nanocomposites (i.e. probing the effect of the flow history), whilst dynamic non-linear methods are preferred for silica based nanocomposites which are primarily elastomer based systems due to their complex, strong elastic behaviour.

Cassagnau [2008] commented that the modelling by Sarvestanti [2004, 2005, 2007] provided "*powerful*" predictions of the linear viscoelastic behaviour. Sarvestani [2004] predicted that the solid like behaviour due to the interaction between the polymer and the nanoparticles is greater in G' than G'' data, and is greatest at low frequency. Sarvestani [2004] also predicted steady shear flow behaviour, commenting that the

observed response, agreeing with that in the literature, is controlled by the polymer attachment and de-attachment rates: at high shear rates the de-attachment rate is greater and the material exhibits shear thinning behaviour that is independent of the filler content.

On clay nanocomposites, Cassagnau [2008] commented that increasing filler content increased the solid-like behaviour, but suggested that the effects of compatibiliser, molecular weight and the role of interfacial properties are less clear. The author added that use of rheometry to infer quantitative measures of dispersion is scarce due to the difficulty of modelling the effects of dispersion and exfoliation. Reporting on Lertwimolnum [2006], a somewhat empirical approach was adopted, using a Carreau-Yasuda constitutive model for complex viscosity η^* that included a yield stress term.

$$|\eta^*(\omega)| = \frac{\sigma_o}{\omega} + \eta_o \left(1 + (\lambda\omega)^a\right)^{(n-1)/a} \quad [4]$$

where σ_o is the yield stress, η_o the zero shear viscosity λ the relaxation time, a the Yasuda parameter, n is the power-law index and ω the angular frequency. The yield stress values, based heavily on the low frequency solid-like response of the material, were used for quantitative comparison of materials.

Cassagnau [2008] suggested that because of the similarities of the reported 3D network formation in nanocomposites, modelling based on sol-gel transitions and percolation theory (e.g. Kanai [1992], Rueb 1997]) might be appropriate. At the sol-gel percolation threshold the shear storage G' and loss G'' moduli have the same power-law angular frequency dependence

$$G'(\omega) \propto G''(\omega) \propto \omega^x \quad [5]$$

where x is the relaxation exponent. Furthermore, The author commented that above the gel transition the loss tangent, $\tan \delta$, is constant and given by $\tan(\Delta\pi/2)$. Furthermore, he noted that above the percolation threshold the zero shear rate viscosity η_o , given by

$$\eta_o = \lim_{\omega \rightarrow 0} G''(\omega) / \omega \quad [6]$$

and the equilibrium elastic modulus G_o , given by

$$G_o = \lim_{\omega \rightarrow 0} G'(\omega) \quad [7]$$

have been fitted by:

$$G_o \propto (\phi - \phi_c)^y \text{ for } \phi > \phi_c \quad [8]$$

and

$$\eta_o \propto (\phi_c - \phi)^s \text{ for } \phi < \phi_c \quad [9]$$

respectively and showed good agreement albeit on the basis of limited comparisons (ϕ is the volume fraction and ϕ_c the percolation threshold volume fraction).

For silica nanocomposites, Cassagnau [2008] reported that the elastic modulus has been shown in the literature to be related to the volume fraction ϕ by

$$G_o \propto \phi^m \quad [10]$$

adding that this form is dependant on particle-particle interactions. Values of the power-law exponent m were reported in the range from 3 to 6 for clay nanocomposites and 3 to 7 for silica based systems.

Cassagnau [2008] suggested that a fractal structure, consisting of disperse and aggregated particles is likely to be important for achieving a balance of properties of PNCs. Although clearly applicable for describing spherical particle systems, where the percolation threshold is observed to increase with increasing dispersion, its applicability to platelet systems is less apparent and simplistic if platelet-platelet interactions dominate. A fractal approach to describing the form of agglomerated particles and relating that parameter to the equilibrium modulus G_o was adopted, but large discrepancies were reported making the approach problematic. Following a similar route, Cassagnau [2008], reporting on modelling by Vermant [2007], commented on the model

$$G_o \propto \phi^{(3+x)/(3-d_f)} \quad [11]$$

where x is related to the filler volume fraction (ϕ) and aggregate structure, and d_f is a fractal dimension representing the structure. The terms of this expression have been used to quantify the dispersion of nanoclays.

Cassagnau [2008] also reported on the potential for non-linear rheology to provide information on the state of dispersion. The argument is that the breakdown of structure (i.e. of the 3D nanoparticles networks) at a limiting shear strain results in the reduction in moduli from their plateau values. The author proposed that the limiting shear strain is given by

$$\gamma_c \propto \phi^{-\gamma} \quad [12]$$

where γ was observed to vary from 0.7 to 4. Shih [76] predicted that the non-linearity limit is given by:

$$\gamma_c \propto \phi^{-(1+x)/(3-d_f)} \quad [13]$$

This, in combination with equation 11, can be used to determine the values of x and d_f by solving them simultaneously. However, the author commented that the onset of non-linearity of dynamic data (equivalent to shear thinning behaviour) is difficult to identify unambiguously. For nanoclay dispersions, Casagnau [2008], on Lertwimolnum [89] and Vergnes [55], reported that the non-linearity onset and amplitude of the storage modulus was affected by the degree of exfoliation, and implied a dependence on

particle-particle interactions. In support of this, Cassagnau [2008] indicated that transient methods for investigating thixotropy and recovery of properties have been used to study structural changes in PNCs, and commented that inter-particle interactions are the dominant driving force for recovery and also control thixotropic behaviour: not Brownian motion or particle-polymer attraction. Interestingly, Cassagnau [2008] also noted the breakdown of the 3D network on thermal expansion of the polymer at the melting transition.

Kotsilkova [2007] proposed various models for interpreting the rheological data of polymer nanocomposites, addressing increasingly complex issues. For elucidation of the dispersion, he proposed the use of the shear thinning response identified by the power-law parameter n :

$$\eta = A\dot{\gamma}^{n-1} \quad [14]$$

where η is the shear viscosity and $\dot{\gamma}$ the shear rate, and the gradients of the shear storage G' and loss G'' moduli, m and n respectively, at low frequencies, i.e.

$$G' \propto \omega^m \text{ for } \omega \rightarrow 0 \quad [15]$$

and

$$G'' \propto \omega^n \text{ for } \omega \rightarrow 0 \quad [16]$$

as being meaningful. The values of constants m and n for fully relaxed polymer have theoretical values of $m = 2$ and $n = 1$, whereas in practice values are lower than these. They tend to zero for G' and G'' for solid-like and "extreme shear thinning" behaviour respectively. The steady shear flow and dynamic data are fitted using the appropriate equations 14 - 16 at the lowest shear rates or frequencies to determine the power-law exponent values. These values can then be used to compare materials, provided they are of the same volume fraction of nanoparticles. Similarly Wagener [2003] used the power-law equation

$$\eta = A\omega^n \quad [17]$$

to model viscosity (η) versus angular frequency (ω) data of nanoclay-PBT PNCs where χ is a constant. Using logarithmic axes the gradient is equal to n and the pre-exponent factor A by the value at an angular frequency of $\omega = 1 \text{ s}^{-1}$, with the plot fitted to the lower rate data about $\omega = 1 \text{ s}^{-1}$ if a non-linear plot was obtained. Values for n were -0.02 for the base resin and -0.04 for the purified montmorillonite PNC, but significantly higher at -0.56, -0.67 and -0.86 for the organically modified montmorillonite PNC. The author correlated the large negative values with well-exfoliated materials. Their observation that the viscosity was not very temperature dependant at low rates, but more so at high rates, supported the explanation for the shear thinning where the low angular frequency (equivalent to low shear rate) end is dominated by platelet-platelet (or tactoids) interactions. The author concluded that the shear thinning exponent n is a semi-quantitative measure of the degree of exfoliation and delamination, but it is considered that not all of their conclusions are valid due to the loading dependence of shear thinning.

Kotsilkova [2007], in a similar manner to Cassagnau [2008], proposed that the filler volume dependence, μ , of the storage modulus can be used as a measure of the strength of the filler structure

$$G_o' \propto \phi^\mu \quad [18]$$

where G_o' is determined at a frequency less than 0.5 s^{-1} . In comparison, Cassagnau [2008] suggested this should be determined in the limit of diminishing angular frequency. Kotsilkova [2007], on Krishnmoorti [1997, 2001], commented that the power-law dependence of G' and G'' in the terminal (low frequency) region decreased with increasing loading, and related the terminal pseudo-solid response to polymer-particle interactions. Furthermore, the relative viscoelasticity in dynamic testing, when $G' > G''$, and yield behaviour in steady shear might be indicative of the filler structure.

Kotsilkova [2007] proposed fitting the Casson equation to steady shear data, with extrapolation to zero shear rate to obtain the yield stress σ_o :

$$\sigma^{1/2} = \sigma_o^{1/2} + \eta^{1/2} \dot{\gamma} \quad [19]$$

where σ is the stress, η the viscosity and $\dot{\gamma}$ the shear rate. However, this latter approach relies on the need for accurate extrapolation to low shear rates.

Kotsilkova [2007] proposed a further method for studying the structure of PNCs that identifies whether the structure is represented by cluster-cluster aggregation (1st percolation threshold) or by a 3D network (2nd percolation threshold). Both are quoted as volume content values. The first percolation threshold is determined by the intercept of plots using equation 15, where the exponent changes value rapidly across the percolation threshold: it is therefore determined from the intercept of two power-law curves fitted to the data, one fitted above and the other below the first threshold. Between the first and second percolation thresholds the material becomes increasingly viscoelastic but still $G' < G''$. The second percolation threshold is defined by the existence of a terminal zone in G' (i.e. $m \approx 0$), $G' > G''$, a rapid increase in viscosity, and a yield stress $\sigma_o \square 0$. The second threshold is determined as the percentage volume content for the cross-over of G' and G'' (i.e. $G' = G''$), each measured using a frequency of 0.1 s^{-1} . The author commented on other rheologically-based definitions of percolation threshold in the literature, including the extrapolation of data of various loading levels using equation 17 to the percolation level for which $m \approx 0$ (equation 15) indicating solid-like behaviour.

Finally, Kotsilkova [2007] proposed a method for studying the polymer-nanofiller interactions based on relaxation-time spectra, where the relative mean relaxation time $\tau_{m,r}$ is characteristic of the polymer-nanofiller interactions and is given by the equations

$$\tau_m = \frac{\sum_{i=1}^n G_i \tau_i^2}{\sum_{i=1}^n G_i \tau_i} \quad [20]$$

and

$$\tau_{m,r} = \frac{\tau_m}{\tau_{m,0}} \quad [21]$$

G_i and τ_i are the relation spectrum coefficients, τ_m is the mean relaxation time, $\tau_{m,0}$ is the mean relaxation time of the unfilled polymer, and $\tau_{m,r}$ is the relative mean relaxation time. An increase in the relative mean relaxation time is related to increased interactions between the polymer and filler, resulting in reduced mobility and thus increased relaxation times. However, evidence was only presented for varying filler content and not degree of dispersion and thus its value as an assessment of the latter was not demonstrated.

Kotsilkova [2007], on the nanoparticle concentration dependence of viscosity, referred to Utracki [2004] where the relative viscosity⁶ is given by

$$\eta_r = 1 + [\eta]\phi \quad [22]$$

where

$$[\eta] = 2.5 + a(pb - 1) \quad [23]$$

and ϕ is the volume fraction, a and b are constants found experimentally and p is the aspect ratio of the particles. He also referred to Jeon [2003] who used a modified Krieger-Dougherty equation

$$\eta_r = \left[1 - \frac{\phi}{\phi_{m,e}} \right]^{-[\eta]\phi_{m,e}} \quad [24]$$

where $\phi_{m,e}$ is the effective maximum packing volume fraction determined experimentally. How this approach handles different degrees of dispersion and exfoliation is unclear. It is likely that this approach is most suited to high rate rheological testing to assess the concentration dependence of viscosity, as at high rates shear alignment of anisotropic particles and disruption or breakage of networks is likely thus resulting in the conventional reinforcement effect of particles for which this equation is more likely to be valid. Furthermore, this model was found to fit data well above a volume fraction of 0.2 which is usually much higher than for polymer nanocomposites.

For determining the aspect ratio of the particles, and thus a measure of their exfoliation, Utracki [2002] used the intrinsic viscosity dependence on the aspect ratio

$$[\eta]_{disk} = 2.5 + a(1 - p^b)$$

⁶ The relative viscosity η_r is the ratio of the dispersion (or solution) viscosity to the continuous phase (or solvent) viscosity. The intrinsic viscosity $[\eta]$ is the value of the relative viscosity as the concentration tends to zero, Walters [book].

where a and b are constants and determined a priori using different aspect ratio materials, presumably using the same filler loading. Good agreement was obtained with values of the aspect ratio calculated on the basis of permeability of the unfilled and nanoparticles filled polymers.

4.3 THERMAL ANALYSIS STUDIES OF POLYMER NANOCOMPOSITES

As commented earlier, polymer nanocomposites are typified by short inter-particle separations that are comparable to the radius of gyration of polymer molecules [Broughton, 2006]. Thus it is reasonable to hypothesize that, even without polymer-particle interactions, the mobility of the polymer molecules is likely to be constrained by the nanoparticles, the extent of which will be dependent on the level of dispersion, and that this constraint will be apparent in thermal transitions, for example the glass transition temperature T_g . Thermal analysis thus provides a potential complementary quality control route to rheology for assessing dispersion quality.

Gacitua [2005] reported that glass transition temperatures were affected by the inclusion of nanoparticles. Kotsilkova [2007] commented that T_g has been observed to decrease significantly for exfoliated PNCs but increase for intercalated nanocomposites. This would potentially account for apparently inconsistent observations of increasing or decreasing T_g as the response is dependant on the state of the filler: the T_g of a material with both intercalated and exfoliated particles will increase, decrease or remain unchanged compared with the unfilled polymer, depending on the relative extent of exfoliation. Following Jordan et al [2005], Gacitua [2005] commented the glass transition temperature was affected by the addition of nanoparticles but that the crystallinity of semi-crystalline and crystalline materials was not affected by much.

Gacitua [2005] commented that nanoparticles may only affect the polymer molecules in close proximity (few nanometres) to the filler. Oh [2009] commented that Tsagaropoulos [1995] observed the formation of two glass transition temperatures for strong nanoparticle-polymer chain interacting systems, one due to the polymer chains remote from the nanoparticles and a larger T_g due to polymer chains near the nanoparticles: the relaxation of the latter are slower due to the perturbation by the grafted nanoparticles. They commented that even in the absence of strong interactions, the T_g increased along with the longest relaxation times and thus the system viscosity. It is suggested that for some systems the breadth of the measured glass transition might increase and shift in peak position, rather than the formation of two distinct peaks.

Sizeable effects on T_g have been observed. Oh [2009] observed changes in T_g of up to 10 K for PS containing PS-grafted gold nanoparticles for less than 1 wt% of nanoparticles. They accounted for the observed behaviour using wet and dry brush theory, commenting that the properties of the nanocomposite can be controlled by controlling the degree of polymerisation of the grafted and matrix polymers, particle size weight fraction of particles and the particle's surface grafting density. An increase in T_g was observed for nanoparticles with high molecular weight chains grafted to the nanoparticles whereas a decrease was observed for low molecular weight grafted chains. In the latter a dry-brush system is formed where the matrix molecules do not interpenetrate the shorter grafted molecules. Oh [2009] used broadband dielectric spectroscopy to study molecular dynamics (relaxation processes), and used DSC and

capacitive measurements to study T_g , the latter as a measure of thermal expansion that revealed the glass transition. TEM measurements used to assess dispersion suggested the formation of agglomerates at higher loadings of nanoparticles, accounting for potential suppression of the effect of the nanoparticles on T_g .

Glotzer [2003], on Mackay [2003] commented that the addition of spheres, formed by cross-linking linear polystyrene molecules, into the same linear polystyrene resulted in lower viscosity and glass transition temperature compared with the matrix material: the latter as also seen in ultrathin polymer films of less than 100 nm thickness. Mackay [2003] presented data showing a decrease in T_g by up to 8 °C for a 0.5 mass fraction, but more typically by 3 °C at lower loadings. It was speculated that this might be due to an increase in free volume and certain molecular configurational changes, resulting in greater molecular dynamics in the vicinity of the nano-sized sphere. However, the authors stated that for larger particles, including nanoclays for which the particle size in two directions was significantly greater than the polymer molecule, this reduction in viscosity did not occur.

Clayton [2006] commented that, on adding CNTs to poly(4-methyl-1-pentene) (PMP), higher storage modulus G' values, higher T_g (via DMTA) and higher crystallinity levels (via DSC) were obtained, although the modulus changes near the glass transition temperature were less. They reported on dispersion optically, commenting on agglomeration and the uniform dispersion of the nanotubes – highlighting differences in interpretation of dispersion. In comparison, Sprenger et al [2004] found that the glass transition temperatures of epoxy adhesive systems were not altered by adding SiO_2 nanoparticles.

Kádár [2006] investigated the surface characteristics of clay-based nanocomposites, using XRD to study nanocomposite structure, and nitrogen adsorption and inverse gas chromatography (for surface tension) to study particle and surface characteristics. They commented that excessive surfactant in the polymer nanocomposite, dissolved in the polymer, may affect the glass transition temperature thereby making such properties more tenuous for monitoring dispersion. Furthermore, surfactant, necessary to reduce agglomeration and improve exfoliation through reducing the surface free energies, will reduce mechanical properties, e.g. tensile yield stress.

Gacitua [2005] commented on the use of NMR (providing very limited quantification on the level of exfoliation in polymer nanocomposites), XRD (due to availability and simplicity), TEM (for qualitative structural assessment), DSC (to understand T_g crystallization behaviour), FTIR (to detect functional groups) and dynamic mechanical analysis. They commented that for good particle-polymer interaction the glass transition temperature increased with decreasing particle size for amorphous polymers, and decreasing particle concentration for crystalline materials. For a poor particle-polymer interaction, T_g decreased for amorphous materials.

Utracki [2007] and Tjong [2006] reported that crystallisation behaviour of polymers was affected by adding nanoparticles, with the nanoparticles either enhancing or inhibiting crystallisation. On clay-based PNCs, Utracki [2004] commented, along with a rider to the effect that it is impossible to generalise, that crystallisation rate is usually increased yielding a less stable crystalline form along with increased crystallisation and melting temperatures, with the level of crystallinity either increasing or decreasing.

In a review of the mechanical properties of polymer nanocomposites with structural characterisation by TEM and XRD, Tjong [2006] commented that for clay-based nanocomposites, the nanoclay always acted as a nucleating agent for spherulites, with the consequence that for a disperse system this will result in a reduction in spherulite size. However, high loadings of nanoparticles (> 5 wt%) may hinder the molecular mobility and thus the crystallisation process. The author commented that crystallisation has been observed to be enhanced for nanoclay filled PA, PE, PET, PBT, PS and PVDF, but not for PEO. The crystallisation behaviour of nanocomposites with spherical inorganic particle, e.g. calcium carbonate and silica (SiO_2), is similar to that for clay particles, but at high loadings (10 wt%) the particles agglomerate and hinder crystal growth.

Billotti [2008] studied sepiolite, a needle-shaped nanoclay particle (hydrated magnesium silicate) thought to disperse more easily than platelet clay because of its, reportedly, lower specific surface area for the same aspect ratio, reducing its propensity to agglomerate. They explicitly commented that the nanoparticles can affect the crystalline structure and level of crystallinity of the matrix polymer thereby affecting its properties. The authors, reviewing other works [Pukanszky 1998, Pozsgay 2002], commented that the nucleating effect of calcium carbonate on PP increased with decreasing particle size and consequently increasing particle aggregation, and that the nucleating effect of nanoclay platelets was dependent on the interlayers, rather than the surfaces. This was supported by Svoboda [2002] who observed an increase in crystallisation temperature for systems containing clay tactoids but not for those of well-dispersed clays. Billotti [2008] suggested that the nanoparticles may also affect the crystalline structure that is formed on crystallisation. They observed up to an approximately 25°C increase in crystallisation temperatures T_c on adding nanoparticles, the increase being dependent on the compatibiliser. They concluded that the well dispersed system has an initial increase in T_c with filler content, but reaches a limit at 1 wt%, whereas the poorly dispersed system continues to increase T_c with higher loadings, suggesting either that agglomerates are better nucleating sites, or because of their compatibiliser the nucleating efficiency of the dispersed particles is reduced.

Coiai [2008] reported that the onset and peak crystallisation temperatures increased for both the untreated and treated Boehmite particle, indicating their effect as a nucleating agent for PP, with a shift in the temperatures by up to 10°C . They commented however that functionalization of the Boehmite particles with an organic material reduced their nucleating effect. However the level of crystallinity was not affected by the addition of the nanoparticles. XRD was carried out to investigate the effect of the nanoparticles on the crystalline structure of the PP. DMTA testing identified that the $\tan \delta$ peak shifted to higher temperatures (by up to 7.5°C) on the addition of the nanoparticles, indicating a loss of mobility of the molecular chains.

In summary, it is clear that the addition of nanoparticles to polymers can have a significant effect on their glass transition temperatures, crystallization temperatures and levels. However, the magnitude and direction of that effect appears to be dependent on many factors including nanoparticle and/or agglomerate size and concentration and compatibiliser type. Thus these parameters are less likely to be suitable for unambiguous assessment of the degree of dispersion of nanoparticles in PNCs

5 SUMMARY

It is clear that polymer nanocomposites are complex materials with structures that can vary from agglomerates to disperse particles, and for clays - the most commonly used particulate for PNCs - added complexity in the extent of intercalation and exfoliation of the clay platelets. TEM and XRD are the most widely reported methods for 'imaging' the structure of PNCs, providing valuable information on the structure of PNCs, but it is clear that these methods and the interpretation of their data are problematic. In addition these methods are not ideally suited for quality control. The need to image PNCs on several length scales, using TEM, SEM and even optical microscopy is highlighted as being important in order to assess the spatial variation in nanoparticles dispersion and agglomerations occurring. It is necessary to use appropriate methods for analysis of the microscopy images to enable reliable measures of the degree of dispersion, intercalation and exfoliation to be obtained, and such methods need to be standardised. XRD is largely limited to the study of clays having a platelet form: it has, almost without exception, been used only for nanoclay based PNCs in the literature surveyed. Furthermore, the data obtained are averaged for the sample and therefore do not provide easy access to spatial variation information. Additionally, care needs to be exercised in the analysis of the XRD spectra. Despite these issues the various forms of microscopy and XRD techniques provide invaluable information on the extent of dispersion of particles in PNCs.

Various test methods have been used to assess the performance of PNCs, e.g. rheology, thermal, electrical, mechanical and permeability. These data have been related, to varying extents, with the nano- and micro-structure of the material. Rheological techniques appear to be a suitable route with low frequency, low strain amplitude dynamic testing providing very high sensitivity to the development of 3D 'percolation' networks. On development of such a network the low frequency, low strain shear storage (elastic) modulus increases dramatically, and is indicative of solid-like behaviour. Additional but less dramatic changes in the behaviour have been observed in the Newtonian viscosity behaviour at low shear rates in steady shear flow, where the viscosity magnitude and onset of non-Newtonian behaviour are both effected, and also the onset on non-linearity in oscillatory strain sweep measurements.

Rheology is a method that appears suitable for all types of PNCs; is directly linked to the mechanical performance of materials; tests significantly larger sample volumes than are examined by TEM or SEM; and is suitable for quality control. However, high temperatures and long tests durations are necessary for testing PNCs in the melt phase and at low frequencies (respectively), and these may lead to degradation of the polymer and surfactants that are used in the intercalation process for nanoclays. Such effects therefore may complicate the interpretation of rheometry results, and testing should be tailored to minimise the thermal exposure and oxidation degradation effects.

Various models have been used in the literature for fitting the experimental data, for example the onset of solid-like behaviour as observed by low frequency oscillatory rheometry, with some approaches based on fractal descriptions of the particle structure. However, there appears to be a division between those who consider that the observed solid-like behaviour, considered important for achieving the enhancement in properties of PNCs, is due to polymer-particle interactions or particle-particle interactions. This suggests that for a PNC whose behaviour is controlled by particle-particle physical

interactions then the need for compatibilisation would simply be to obtain a well-dispersed system. Limited FTIR studies reportedly provide evidence for polymer-particle interactions for nanoclays and CNTs. In further support of polymer-particle interactions, a theoretical network model [Sarnestani, 2004] based on polymer-particles attachment and detachment dynamics provided realistic predictions of PNC rheological behaviour, including the onset of solid-like behaviour. Given the complexity of the structure of PNCs, it is likely that both particle-particle and polymer-particle interactions will each have a role and be dependant on the material system. However, how significant each of these mechanisms is for all systems and all degrees of dispersion is not clear.

The suitability of thermal methods, for example the onset of crystallisation and the glass transition temperature, for assessing dispersion is not clear with different trends being observed for different PNC systems. No doubt nanoparticles do affect the thermal transitions of polymers. However, the effects appear to be dependant on a number of factors, for example nanoparticle and/or agglomerate size and concentration and compatibiliser type, that may be difficult to isolate successfully. In combination with rheological assessment thermal analysis could potentially provide a more robust systematic approach than a single method on its own, but it is unlikely that thermal methods alone will provide a robust universal approach for a wide range of PNCs.

Evidence in the literature has clearly identified the occurrence of nanoparticle migration and 3D nanoparticle structure breakdown on shearing with high strains. However, the effect has only been observed on exposure of the samples to high temperatures for long durations: significantly longer than one would normally expect a polymer to be subjected to during processing. The extent of these effects in processing is not certain and is perhaps a source of the variability in results reported in the literature, for example due to different sample preparation routes.

It is clear that no one technique will be sufficient on its own to understand the dispersion of nanoparticles in PNCs. Rheology appears to provide a sensitive measure of the formation of percolation networks that is important to the development of the enhanced properties that are sought after from PNCs. The development of a systematic, validated approach to assessing the quality of PNCs based on rheological methods is proposed, although this must not be done in isolation from other techniques, in particular TEM, SEM and XRD, that are necessary for validation purposes over a range of length scales. However, these imaging techniques themselves need to be used with caution.

The development of suitable quality control tools will enable the full potential of polymeric nanocomposites to be consistently achieved. It will facilitate the usage of such materials, particularly in high value products where performance reliability is key e.g. medical devices.

The availability of validated quality control tools will result in greater confidence in nanocomposites through improved quality of materials, with consequent benefits in improved products, product cost savings and reduced environmental impact through reduced material usage and weight. It will also enable more reliable assessments to be made of other performance properties of PNCs as this is currently limited by a lack of understanding of the dispersion quality of the materials.

6 RECOMMENDATIONS FOR FUTURE WORK

The recommendations for immediate metrology-based research are to:

- **Establish and standardise key descriptors for quantifying dispersion state from analysis of microscopy images.**

Although unambiguous (albeit seemingly arbitrary) definitions of intercalation and exfoliation of platelets have been proposed by Utracki [2004] the same is not true of dispersion. In analysing 2-D images (e.g. TEM) many quantitative measures of the dispersed states have been proposed and used in the literature. It is necessary to rationalise these measures by identifying the key ones, establishing more appropriate new measures if appropriate, and standardising their usage. This will enable greater comparability of research and will help to clarify inconsistencies reported in the literature, for example of widely ranging percolation threshold values.

- **Develop appropriate rheological tools for quantification of dispersion quality of nanoparticles in polymeric media, and their validation.**

Rheological properties appear to provide a consistent qualitative measure of dispersion in polymer nanocomposites, and are potentially applicable to all polymer nanocomposite systems due to their probing the polymer-particle interactions. However, in order for rheology to be used as a quality control tool to provide quantitative measures of dispersion quality of polymer nanocomposites, the preferred rheological methods and procedures need to be established.

The procedures will need to be validated using a range of formulated materials of varying key parameters (e.g. surface treatment, process conditions (mix energy), particle size and shape) by comparison with imaging techniques e.g. TEM, SEM and optical microscopy and XRD, and performance characteristics.

For electrically conducting polymer nanocomposites - a primary application for carbon-based nanoparticle filled polymers - simultaneous rheological-dielectric measurements would provide a powerful tool for their study, enabling independent determination of percolation threshold values.

The applicability of the methods for different types of polymer nanocomposite needs to be demonstrated, for example with respect to nanoparticle shape (i.e. platelet, rod or spherical).

Furthermore, it would be of value to also:

- **Develop the scientific understanding of the effect of nanoparticles on thermal properties of polymers (e.g. glass transition temperature and crystallisation temperature), potentially leading to the development of additional tools for the assessment of dispersion quality.**

It is clear that thermal properties can be influenced, sometimes significantly, by the addition of nanoparticles. However, the phenomenon is not well understood and different trends are reported in the literature. A clear understanding of the effect of nanoparticles on thermal properties is required for materials and product design purposes, for example, but also to assess whether thermal methods could reliably be used to characterise dispersion quality.

Subsequent to these essential underpinning activities, further research should focus on:

- **Investigation of the migration of nanoparticles in polymers due, for example, to ageing, stress and annealing.**

Migration and agglomeration of particles due to processing and ageing could have significant implications for product performance, e.g. electrical conductivity. Understanding these factors is critical to the success of polymer nanocomposites as functional or engineering materials.

- **Development of techniques for characterisation of nanoparticle orientation.**

The understanding of the effect on nanoparticle orientation on performance properties is very limited. Techniques to characterise nanoparticle orientation need to be developed and assessed, in order to provide the tools required to develop an understanding of the structure-property relationships for polymer nanocomposites.

It is proposed that some of these activities would be best undertaken within the framework of the Versailles Project on Advanced Materials and Standards (VAMAS) that addresses pre-standardisation issues for materials testing.

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8 ABBREVIATIONS

ABS	Acrylonitrile-butadiene-styrene
AFM	Atomic force microscopy
ATR-IR	Attenuated total reflection infrared spectroscopy
CNF	Carbon nanofibres
DMA	Dynamic mechanical analysis
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
EVA	Ethylene-vinyl acetate copolymer
FT-IR	Fourier transform infrared spectroscopy
IR	Infra-red spectroscopy
LLDPE	Linear low density polyethylene
MMT	Montmorillonite
MW	Molecular weight
MWNT/MWCNT	Multi-walled carbon nanotube

NMR	Nuclear magnetic resonance
OM	Optical microscopy
OMMT	Organically modified montmorillonite
PA6	Polyamide 6
PBT	Poly(butadiene terephthalate)
PC	Polycarbonate
PDMS	Poly(dimethyl siloxane)
PE	Polyethylene
PEI	Poly-ether-imide
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PP-g-MA	Maleic anhydride-modified polypropylene,
PS	Polystyrene
PSVPh	Poly(styrene- <i>ran</i> -vinyl phenol) copolymer
SAXS	Small-angle X-ray scattering
SEM	Scanning electron microscopy
SWNT/SWCNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermo-gravimetric analysis
UV	Ultra-violet
WAXD/WAXS	Wide-angle X-ray diffraction / scattering
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

9 REFERENCES

- Alig [2007] Alig I., Skipa T., Engel M., Lellinger D., Pegel S. Pötschke P., Electrical conductivity recovery in carbon nanotube-polymer composites after transient shear, *Physica Status Solidi (b)*, Special issue: Electronic Properties of Novel Nanostructures 244 No.11, p 4223-4226 (2007).
- Bafna [2003] Bafna A, Beaucage G., Mirabella, F, Mehta, S, *Polymer*, 2003, 44 pp1103-1115.
- Battisti [2008] Battisti A., Skordos A.A., and Partridge I.K., Monitoring dispersion of carbon nanotubes in a thermosetting polyester resin, *Composites Science and Technology* in press 2008.
- Bilotti [2008] Bilotti E., Fischer H.R., Peijs T., Polymer nanocomposites based on needle-like sepiolite clays: Effect of functionalized polymers on the dispersion of nanofiller, crystallinity, and mechanical properties, *J. Appl. Polym. Sci.*, Jan 2008, 107 (2), pp.1116-1123.
- Bose [2008] Bose S., Bhattacharyya A.R., Kodgire P.V., Kulkarni, A.R., Misra, A., Specific interactions induced dispersion and confinement of multi-walled carbon nanotubes in co-continuous polymer blends, *J. Nanosci. Nanotechnol.*, Apr 2008, 8 (4), pp.1867-1879.

- Broughton [2005] Broughton WR, Crocker LE and Lodeiro MJ, Characterising micro and nanoscale interfaces in advanced composites: a review, NPL Report DEPC-MPR 055, September 2006, ISSN 1744-0270.
- Broughton [2008] Broughton WR, Characterization of nanosized filler particles in polymeric systems: a review, NPL Report MAT 12, January 2008, ISSN 1754-2979.
- Cassagnau [2008] Cassagnau Ph., Melt rheology of organoclay and fumed silica nanocomposites, *Polymer* 49 (2008) 2183-2196.
- Causin [2005] Causin V., Marega C., Marigo A., Ferrara G., Assessing organo-clay dispersion in polymer layered silicate nanocomposites: A SAXS approach, *Polymer*, Nov 2005, 46 (23), pp.9533-9537.
- Chastek [2005] Chastek T.T., Stein A., Macosko C., Hexadecyl-functionalized lamellar mesostructured silicates and alumino silicates designed for polymer-clay nanocomposites. Part II: Dispersion in organic solvents and in polystyrene, *Polymer*, May 2005, 46 (12) pp. 4431-4439.
- Clayton [2006] Clayton LM., Gerasimov T.G., Cinke M., Meyyappan M., Harmon JP., Dispersion of single-walled carbon nanotubes in a non-polar polymer, *J. Nanosci. Nanotechnol.*, Aug 2006, 6 (8), pp.2520-2524.
- Coiai [2008] Coiai S., Passaglia E., Augier S., Narducci P., Ciardelli F., Organophilic boehmite nanoparticles by ATRP methacrylates polymerization: Synthesis, characterization and dispersion in polypropylene, *J. Nanosci. Nanotechnol.*, Apr 2008, 8 (4), pp.1803-1811.
- Dan [2009] Dan B, Irvin GC, Pasquali M., Continuous and Scalable Fabrication of Transparent Conducting Carbon Nanotube Films. *ACS Nano*. 2009 Apr 8.
- Durmus 2007] Durmus A., Kasgoz A., and Macosko C.W., Linear low density polyethylene (LLDPE)/clay nanocomposites. Part I: Structural characterization and quantifying clay dispersion by melt rheology, *Polymer*, 48 No. 15, July 2007, pp.4492-4502.
- Eckel [2004] Eckel D.F., Balogh M.P., Fasulo P.D., Rodgers W.R., Assessing organo-clay dispersion in polymer nanocomposites, *J. Appl. Polym. Sci.*, Aug 2004, 93 (3) pp 1110-1117.
- Gacitua [2005] Gacitua W., Ballerini, A., Zhang J., (2005) Polymer Nanocomposites: Synthetic and Natural Fibers a Review, *Madera. Ciencia y Tecnologia*, 7(3).
- Gilman [2005] Gilman J.W., Davis R.D., Bellayer S., Maupin P.H., Raghavan D., Langat J., Bourbigot S., Flambar X., Fox D., Trulove P., De Long HC., Use of optical probes and laser scanning confocal fluorescence microscopy for high throughput characterization of dispersion in polymer layered silicate nanocomposites, *Abstr. Pap. Am. Chem. Soc.*, Mar 2005, 229 Part 2, pp.100-PMSE , PG 1. Abstract only available.
- Glutzer [2003] Sharon C. Glutzer, *Nature Materials* 2, 713 - 714 (2003), Nanoscale science: Complex rules for soft systems.

- Hackley [2001] Hackley V.A. and Ferraris C.F., NIST Recommended Practice Guide Special publication 960-3, The Use of Nomenclature in Dispersion Science and Technology, NIST Feb 2001
- Horsch [2006] Horsch S., Serhatkulu G., Gulari E., Kannan R.M., Supercritical CO₂ dispersion of nano-clays and clay/polymer nanocomposites, *Polymer*, Oct 2006, 47 (21), pp.7485-7496.
- Huang W [2006] Huang W., Han C.D., Dispersion characteristics and rheology of organoclay nanocomposites based on a segmented main-chain liquid-crystalline polymer having side-chain azopyridine with flexible spacer, *Polymer*, May 2006, 47 (12), pp.4400-4410.
- Huang YY [2006] Huang Y.Y., Ahir S.V., Terentjev E.M., Dispersion rheology of carbon nanotubes in a polymer matrix, *Phys. Rev. B*, Mar 2006, 73 (12), AR 125422, PG 9.
- Isayev [2008] Isayev A.I., Jung C., Gunes K., Kumar R., Ultrasound assisted single screw extrusion process for dispersion of carbon nanofibers in polymers, *Int. Polym. Process.*, Sept 2008, 23 (4), pp.395-405.
- Jeon HS [2003] Jeon HS, Rameshwaram JK, Kim G, Weinkauff DH, *Polymer* 2003 44, 19 5749.
- Jordan [2005] Jordan J., Jacob K., Tannenbaum R., Sharaf M., Jasiuk I., *Experimental Trends in Polymer-Matrix Nanocomposites - A Review*, *Maat. Sci. & Eng.* 2005, A 393, 1-11.
- Kádár [2006] Fruzsina Kadar, Laszlo Szazdi, Erika Fekete, Béla Pukanszky *Langmuir* 22(18), 7848-7854, American Chemical Society, 2006. Surface characteristics of layered silicates: influence on the properties of clay/polymer nanocomposites
- Kanai 1992] Kanai H, Navarrete RC, Macosko CW, Scriven LE, *Rheol. Acta* 1992, 31, pp333-344.
- Kashiwagi [2004] Kashiwagi T., Harris R. H., Zhang X., Briber R. M., Cipriano B. H., Raghavan S. R., Awad W. H., and Shields J. R., "Flame Retardant Mechanism of Polyamide 6 – Clay Nanocomposites", *Polymer*, 45: 881-891 (2004).
- Kashiwagi [2007] Kashiwagi T., Fagan J., Douglas J. R., Yamamoto K., Heckert A. N., Leigh S. D., Obrzut J., Du F., Lin-Gibson S., Mu M., Winey K. I., Haggemueller R., Relationship Between Dispersion Metric and Properties of PMMA/SWNT Nanocomposites. *Polymer*, Vol. 48, No. 16, 4855-4866, July 2007.
- King [2007] King Jr HE, Milner ST, Lin MY Singh JP, Mason TG, *Phys Rev E*, 2007, 75: 021403 [1-20]
- Kotsilkova 2007] *Thermoset nanocomposites for engineering applications*, Ed. R. Kotsilkova, Smithers Rapra 2007.
- Krevelen [2000] Van Krevelen, D.W., *Properties of polymers*, Elsevier, 2000.
- Krishnamoorti [2001] Krishnamoorti R, Silva AS, *Polymer-Clay Nanocomposites*, Ed. Pinnavaia TJ and Beall GW, John Wiley & Sons, 2001.

- Krishnamoorti, 1997] Krishnamoorti R, Giannelis EP, *Macromolecules* 1997, 30, 14, 4097.
- Lan [2007] Lan Q, Francis, L.F., Bates, F.S., *J. Polym Sci., Part B: Polymer Physics* 2007, 45(16) pp.2284-99.
- Lee [2008] Lee C.U., Dadmun M.D., Improving the dispersion and interfaces in polymer-carbon nanotube nanocomposites by sample preparation choice, *J. Polym. Sci. Pt. B-Polym. Phys.*, Aug 2008, 46 (16), pp.1747-1759.
- Lertwimolnum [2006] Lertwimolnum W, Vergnes B, *Polym. Eng. Sci.* 2006, 46, pp314-23.
- Li [2007] Li Z.M., Li S.N., Xu X.B., Lu A., Carbon nanotubes can enhance phase dispersion in polymer blends, *Polym.-Plast. Technol. Eng.*, Feb 2007, 46 (2), pp.129-134.
- Lim [2003] Lim S.T., Choi H.J., Jhon M.S., Dispersion quality and rheological property of polymer/clay nanocomposites: Ultrasonification effect, *J. Ind. Eng. Chem.*, Jan 2003, 9 (1) pp.51-57.
- Lin [2006] Lin B., Sundararaj U., Pötschke P., Melt Mixing of Polycarbonate with Multi-Walled Carbon Nanotubes in Miniature Mixers, *Macromolecular Materials and Engineering* 291 (2006) 227-238.
- Luo [2008/2] Luo Z.P., Koo J.H., Quantification of the layer dispersion degree in polymer layered silicate nanocomposites by transmission electron microscopy, *Polymer*, Apr 2008, 49 (7), pp.1841-1852.
- Luo. [2008/1] Luo Z.P., Koo J.H., Quantitative study of the dispersion degree in carbon nanofiber/polymer and carbon nanotube/polymer nanocomposites, *Mater. Lett.*, Jul 2008, 62 (20), pp.3493-3496.
- Mackay [2003] Michael E. Mackay, Tien T. Dao, Anish Tuteja, Derek L. Ho, Brooke Van Horn, Ho-Cheol Kim & Craig J. Hawker, *Nature Materials* 2, 762 - 766 (2003), Nanoscale effects leading to non-Einstein-like decrease in viscosity.
- Morishita [1959] Morishita M, *Memories of the faculty of science series E, Biology*, vol 2, Fukuoka, Japan, Kyushu University, 1959, 215.
- Movahed [2009] Movahed SO, Ansarifar A, Song M, Measuring dynamic properties of rubbers filled with silanized silica nanofiller, *Rubber World*, March 2009, pp23-31.
- Oh [2009] Hyunjoon Oh and Peter F Green, *Nature Materials*, 8 Feb 2009 139-143 Polymer chain dynamics and glass transition in athermal polymer/nanoparticle mixtures.
- Pegel [2008] Pegel S., Pötschke P., Petzold G., Alig I., Dudkin S.M., Lellinger D., Dispersion, agglomeration, and network formation of multiwalled carbon nanotubes in polycarbonate melts, *Polymer* 49 (2008) 974-984.
- Pogodina [2008] Pogodina N.V., Cercle C., Averous L., Thomann R., Bouquey M., Muller R., Processing and characterization of biodegradable polymer nanocomposites: detection of dispersion state, *Rheol. Acta*, Jul 2008, 47 (5-6), pp.543-553.
- Pozsgay [2002] A. Pozsgay T. Frater L. Papp I. Sajo and B. Pukanszky *J Macromol Sci-Phys B41* (2002), p. 1249.

- Pukanszky [1998] Pukanszky B, Fekete E. Aggregation tendency of particulate fillers: Determination and consequences. *Polymer Composites* 6: 313-322 (1998).
- Qu [2004] Qu L.W., Lin Y., Hill D.E., Zhou B., Wang W., Sun X.F., Kitaygorodskiy A., Suarez M., Connell J.W., Allard L.F., Sun Y.P., Polyimide-functionalized carbon nanotubes: Synthesis and dispersion in nanocomposite films, *Macromolecules*, AUG 2004, 37 (16) pp 6055-6060.
- Ratinac [2006] Ratinac K.R., Gilbert R.G., Ye L., Jones A.S., Ringer S.P., The Effects of Processing and Organoclay Properties on the Structure of Poly (Methyl Methacrylate) – Clay Nanocomposites”, *Polymer*, 47, pp.6337-6361 (2006).
- Ratnayake [2006] Ratnayake U.N., Haworth B., Polypropylene-clay nanocomposites: Influence of low molecular weight polar additives on intercalation and exfoliation behaviour, *Polymer Engineering and Science*, 46 (8), pp.1008 - 1015
- Rueb 1997] Rueb C.J., Zukoski C.F., *J. Rheol.* 1997, 41, pp197-218.
- Ryu [2005] Ryu S.H., Chang Y.W., Factors affecting the dispersion of montmorillonite in LLDPE nanocomposite, *Polym. Bull.*, Nov 2005, 55 (5), pp.385-392.
- Samyn [2008] Samyn F., Bourbigot S., Jama C., Bellayer S., Nazare S., Hull R., Fina, A., Castrovinci A., Camino G., Characterisation of the dispersion in polymer flame retarded nanocomposites, *Eur. Polym. J.*, Jun 2008, 44 (6), pp.1631-1641.
- Sarvestani [2007] Sarvestani A.S., Jabbari E., *Macromol. Theory Simul.*, 2007, 16, pp.378-385.
- Sarvestani [2004] Sarvestani A.S., Picu C.R., *Polymer* 2004 45, pp7779-7790.
- Sarvestani [2005] Sarvestani A.S., Picu C.R., *Rheol. Acta*, 2005, 45 pp132-141.
- Sprenger [2004] Sprenger S., Eger C., Kinloch A. J., Taylor A., Lee J. H. and Egan D., Nano-modified ambient temperature curing epoxy adhesives, *Adhesion: Special Edition*, Vol. 3, Kleben & Dichten, 2004.
- Svoboda [2002] Svoboda P., Zeng C., Wang H., Lee L.J. and Tomasko D.L., *J Appl Polym Sci* 85 (2002), pp. 1562–1570.
- Tang [2007] Tang E.J., Liu H., Sun L.M., Zheng E.L., Cheng G.X., Fabrication of zinc oxide/poly(styrene) grafted nanocomposite latex and its dispersion, *Eur. Polym. J.*, Oct 2007, 43 (10), pp.4210-4218.
- Tsagaropoulos [1995] Tsagaropoulos G. and Eisenberg A., Direct observation of 2 glass transitions in silica-filled polymers—implications for the morphology of random ionomers, *Macromolecules* 28 (1995), pp. 396–398.
- Tjong [2006] Tjong S.C., Structural and Mechanical Properties of Polymer Nanocomposites, *Materials Science and Engineering*, R 53, 2006, pp 73-197.
- Utracki [2002] Utracki L.A., and Lyngaae-Jørgensen J., Dynamic melt flow of nanocomposites based on poly-ε-caprolactam, *Rheol. Acta*, 41 No. 5, 2002.

- Utracki [2004] Utracki L.A., Clay-containing polymeric nanocomposites, Rapra Technology Limited, 2004.
- Utracki [2007] Utracki L.A., Mechanical behaviour of polyamide-based nanocomposites – a round robin tests of the VAMAS TWA-PNC, 2007 (private communication).
- Vermant [2007] Vermant J, Ceccia S, Dolgovskij MK, Maffettone PL, Macosko CW, J. Rheol. 2007, 51, pp429-450.
- Vermogen [2005] Vermogen A., Masenelli-Varlot K, Seguela R Duchet-Rumeau J Bouchard S, Prele P Macromolecules 2005, 38(23) pp.9661-9669.
- Vermogen [2005] Vermogen A., Masenelli-Varlot K., Seguela R., Duchet-Rumeau J., Boucard S., Prele P., Evaluation of the structure and dispersion in polymer-layered silicate nanocomposites, Macromolecules, Nov 2005, 38 (23), pp.9661-9669.
- Vermogen [2007] Vermogen A., Masenelli-Varlot K., Vigier G., Sixou B., Thollet G., Duchet-Rumeau J., Clay dispersion and aspect ratios in polymer-clay nanocomposites, J. Nanosci. Nanotechnol., Sept 2007, 7 (9), pp.3160-3171.
- Wagener [2003] Wagener R., Reisinger T.J.G., Polymer 44 (2003) 7513–7518, A rheological method to compare the degree of exfoliation of nanocomposites
- Winter [1997] Winter HH, Mours M, Rheology of polymers near liquid-solid transition. Adv. Polym. Sci., 134, 1997, pp165-248.
- Xie [2005] Xie X.L., Mai Y.W., Zhou X.P., Dispersion and alignment of carbon nanotubes in polymer matrix: A review, Mater. Sci. Eng. R-Rep., May 2005, 49 (4), pp.89-112.
- Xu [2008] Xu C., Ohno K., Ladmira V., Composto R.J., Dispersion of polymer-grafted magnetic nanoparticles in homopolymers and block copolymers, Polymer, Jul 2008, 49 (16), pp.3568-3577.
- Yeh [2005] Yeh J.M., Hsieh C.F., Jaw J.H., Kuo T.H., Huang H.Y., Lin C.L., Hsu M.Y., Organo-soluble polyimide (ODA-BSAA)/montmorillonite nanocomposite materials prepared by solution dispersion technique, J. Appl. Polym. Sci., Mar 2005 95 (5) pp1082-1090.
- Zanetti [2004] Zanetti M., Bracco P., and Costa L., Polym. Degrad. Stab., 85 (2004) 657-665, Thermal degradation behaviour of PE/clay nanocomposites.
- Zhang [2008] Zhang Q.H., Fang F., Zhao X., Li Y.Z., Zhu M.F., Chen DJ., Use of dynamic rheological behavior to estimate the dispersion of carbon nanotubes in carbon nanotube/polymer composites, J. Phys. Chem. B, Oct 2008, 112 (40), pp.12606-12611.
- Zhu [2004] Zhu L and Xanthos M, J. Appl. Polym. Sci. 93 1891 (2004).
- Liu [1999] Liu L, Zongneng QI, Xiaoguang Z, J. Applied Polym. Sci., 71 (1999) pp1133-1138.
- Yang [1999] Yang Y, Zhu ZK, Yin J, Wang XY, Qi ZE, Polymer, 40, No.15 (1999) pp4407-4414.
- Liang [2002] Liang ZM, Yin J, Xu HJ, Polymer 44 (2003) pp1391-1399.

Table 2: Methods used for assessing the dispersion of nanoparticles in polymeric matrices

Author, year	Polymer matrix	Nanoparticle filler	Characterisation methods	Comments
Alig 2007	PC	MWCNT 0.875 wt%	TEM, dielectric	Observed recovery of percolating electrical network
Battisti 2008	Unsaturated polyester resin	CNT 0.25 wt%	Steady shear cone and plate rheometry, electrical resistivity, optical microscopy, SEM, TEM	Shear thinning parameter good indicator of dispersion
Bilotti 2008	PP-g-MA, PP-acid, PP-PEO (a di-block copolymer)	Needle-like sepiolite clays 1-5 wt%	SEM, TEM, WAXS (crystallinity), DSC (crystallinity), Tensile testing	Melt compounding using a mini-extruder
Bose 2008	Blends of PA6 /ABS	MWNT + reactive modifier: sodium salt of 6-amino hexanoic acid (Na-AHA) 5-7 wt%	Dielectric, electrical conductivity, SEM, TEM, RAMAN	Melt mixed Percolation threshold at 0.5 wt% MWNT
Cassagnau 2008	Various	Organoclay Fumed silica	Rheology	Review
Causin 2005	PP	Organo-clay	SAXS, TEM	Melt mixing
Chastek 2005	Organic solvents and PS	Synthetic clays 1-23 wt%	Oscillatory rheometry, SAXS, TEM, visual	Percolation threshold at 0.5 wt%
Clayton 2006	poly(4-methyl-1-pentene) - a non-polar polymer	SWCNT pre-treated with polar solvent N,N-Dimethyl-formimide (DMF) 0.5 wt%	DSC, DMA, micro-hardness, optical microscopy, XRD	Solution preparation
Coiai 2008	Isotactic PP + functionalized PP	Boehmite alumina nanoparticles 2 wt%	ATR-IR – functionalization, TGA – functionalization, SEM, XRD, DSC, DMTA	Melt blended
Dan 2009	Solution	SWCNT 0.1-3 wt%	Viscosity, SEM, AFM. Electrical	Polymer wrapping of CNTs
Durmus 2007	LLDPE	Organoclay 1-10 wt%	Oscillatory rheometry, XRD, TEM, WAXD	Melt processing
Eckel 2004	Urethane PA	Organoclay	TEM, XRD	Melt processing
Gacitua 2005	Various	Various	Various	Review

Author, year	Polymer matrix	Nanoparticle filler	Characterisation methods	Comments
Horsch 2006	PDMS	Organoclays 15 wt%	WAXD, SEM, TEM, rheology	Use supercritical carbon dioxide to disperse nanoparticles
Huang YY 2006	PDMS	MWCNT – untreated, 0.5-7 wt%	Oscillatory rheometry	
Huang W 2006	liquid-crystalline polymer PABP	Organoclays: 3-5 wt%	XRD, WAXD TEM, FT-IR oscillatory rheometry, DSC, polarised optical microscopy	Solution blending
Huang YY 2006	PDMS	MWCNT, 0.5 – 7 w%	Oscillatory rheometry	Melt mixing
Isayev 2008	PEI	CNF, 1 - 20 wt. %	Die pressure, electrical (volume resistivity), thermal conductivity, rheological, SEM morphology, mechanical (tensile)	Ultrasonically assisted single screw extrusion process: suggestion that ultrasound improves properties
Kádár 2006	PP	Clay	XRD	
Kashiwagi 2004	PA6	Clay, 2% wt and 5% wt	TEM, XRD, oscillatory rheometry, TGA	Commercially available grade
Kashiwagi 2007	PMMA	SWCNT, 0.5 wt%	UV-vis spectroscopy, optical confocal microscopy, TGA, oscillatory rheometry, electrical conductivity, flammability	Coagulation (solution) method, quantitative analysis of images – relative dispersion index
Kotsilkova 2007	Thermosets	Various	Various	Review
Lee 2008	poly(styrene- <i>ran</i> -vinyl phenol) (PSVPh) copolymer	MWNT 5 wt%, having various surface (oxidation) treatments	FTIR for intramolecular bonding between MWNTs and PSVPh to infer dispersion, DMA	Melt mixing better than precipitation (more bonding & more stable properties).
Li 2007	Copolymers: EVA/PE PC/PE	MWCNT 5 wt%	SEM phase morphological observation	Master batching by solution-phase processing, then melt-mixed with PE

Author, year	Polymer matrix	Nanoparticle filler	Characterisation methods	Comments
Lim 2003	Poly (ethylene oxide)	Organophillic montmorillonite 9 wt%	TEM, SEM, WAXD, TGA, Rheometry: steady shear and oscillatory	Solvent casting. Effect of ultrasonification on dispersion and properties
Luo 2008/1	Epoxy, PA11, PA12, TPE, TPU, cyanate ester thermoset, phenolic thermoset	CNF CNT 3-5 wt%	TEM combined with analysis to yield dispersion parameter	High-shear mixing or twin-screw extrusion preparation.
Luo 2008/2	Polyester polycaprolactone, PA11, PA12, cyanate esters, epoxy	Nanoclays 0.5-10 wt%	TEM	Analysis of TEM images
Movahed 2009	Poly(styrene – butadiene) copolymers	Silica	DMA, DSC	Mixing
Oh 2009	PS	Gold NP grafted with PS, 0.3-5 wt%	Rheology, dielectric spectroscopy, capacitive dilatometry, DSC, SEM, TEM	Solution preparation method
Pegel 2008	PC	MWNT 0.5-5 wt%	Optical microscopy, TEM, dielectric spectroscopy	Melt mixing of masterbatch
Pogodina 2008	PLA	OMMT 3-5 wt%	Rheology, Light attenuation, XRD, mechanical (tensile),	Melt compounding: miniature twin-screw extruder & internal batch mixer.
Qu 2004	Polyimide	SWNT MWNT 15-30 wt%	UV/vis/near –IR Raman, NMR TGA, SEM, TEM	Functionalisation with low molecular weight polyimide
Ratinac 2006	PMMA	Organoclays 5 wt%	TEM, WAXD	Extensive quantitative analysis of images
Ratnayake 2006	PP	Organoclay 2-6 wt%	TEM, XRD, MFI	Effect observed in low rate MFI results
Ryu 2005	LLDPE	Montmorillonite 1-5 wt%	gas permeability, tensile modulus, XRD, TEM	Twin screw extruder and internal mixer under various processing conditions

Author, year	Polymer matrix	Nanoparticle filler	Characterisation methods	Comments
Samyn 2008	PP, PBT & PA6 with 3 phosphorus based flame retardants	Organoclay 5 wt%	XRD, SEM, TEM, EDX, oscillatory rheometry, NMR	Extrusion prep. NMR results affected by flame retardants.
Sprenger 2004	Epoxy	SiO ₂ , 1-25 wt%	Mechanical	Masterbatch
Tang 2007	Latex	zinc oxide particles with poly(styrene) grafted	TEM, SEM, FT-IR, XPS, TGA, DSC UV-vis absorption	Solution route
Tjong 2006	Various	Clay, SiO ₂ , CNT	TEM, XRD, mechanical testing	Review
Utracki 2004	Various	Clays	Various	Review
Vermogen 2005	PP	Organoclay 5 wt%	WAXS, oscillatory, TEM	Melt compounding
Vermogen 2007	PA6 PE	Organoclay 5 wt%	Image analysis procedure based on TEM/optical microscopy, WAXS, SAXS	Melt compounding
Wagener 2003	PBT	Montmorillonite & OMMT 4 wt%	Oscillatory rheometry, SEM, tensile	Melt compounded and in-situ polymerisation
Xie, 2005	Various	CNT	Various	Review
Xu 2008	PMMA homopolymers, PS-b-PMMA block copolymer	Spherical magnetite NPs grafted with PMMA brushes 1-16 wt%	TEM of microtomed 50 nm thin slices. AFM (in acoustic mode) for surface morphology of films. TEM for magnetite particle sizing	Solution preparation. Aggregation after annealing observed.
Yeh 2005	Polyimide (PI)	Organoclay 3 wt%	FTIR, powder-XRD TEM, AFM, electrochemical corrosion, gas permeability, UV-vis transmission	Solution preparation
Zanetti 2004	PE	Organoclay 5 wt%	WAXS, TGA, FTIR	Melt processing, EVA compatibiliser. Flame retardancy.
Zhang 2008	PS	MWCNT (untreated and surface treated) 1.25 wt% and 5 wt%	TEM, SEM on fracture surfaces, oscillatory rheometry, FTIR for surface chemistry of MWNT.	Solution preparation