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Nanocomposites for Vehicle Structural Applications

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1. Introduction

Fiber-reinforced composites are a type of engineering material that has exhibited high strength–weight and modulus–weight ratios, even compared with some metallic materials. In the last two decades, some studies have shown the potential improvement in properties and performances of fiber reinforced polymer matrix materials in which nano and micro-scale particles were incorporated. This technology of nano and micro-scale particle reinforcement can be categorized into inorganic layered clay technology, single walled and multi-walled carbon nanotube, carbon nanofiber technology, and metal particle technology. To date, nanoparticle reinforcement of fiber reinforced composites has been shown to be a possibility, but much work remains to be performed in order to understand how nanoreinforcement results in major changes in material properties. The understanding of these phenomena will facilitate their extension to the reinforcement of more complicated anisotropic structures and advanced polymeric composite systems.

Large quantity of nanomaterials (such as carbon nanotubes, nanofibers, SiO_2 and montmorillonite) is presently available due to the establishment of well-developed manufacturing technologies such as chemical vapor deposition method, ball milling and electrospinning. With ease to manufacture in bulk, fiber-reinforced polymer nanocomposites are finding increasingly more practical applications (for example, in the manufacture of composite structures microelectronics). The improvements that are being identified for the high performance structures and payloads are related with the type of property that is expected to be modified primarily mechanical, thermal and electrical properties. In reality, the high performance structures and payloads are multi-functional elements with various design drivers that cannot be separated, due to the vehicular limited size and weight. High performance structure design imposes a number of restrictions on the properties of materials to be used. It also follows that lighter, thinner, stronger and cheaper structures are very important goals of materials science and engineering nowadays. The restricted parameters could be seen as a subset of the design parameters. Formulation and establishment of the design parameters build up a process of certification.

Fiber-reinforced composites are very sensitive to intrinsic damage, such as delamination (in particular), matrix cracking and fatigue damage. Several approaches are adopted to tackle these, which include: (i) improving the fracture toughness of the ply interfaces of the fiber-

matrix including resin blends and (ii) reducing the mismatch of elastic properties (and stress concentrations) at the interfaces between the plies. However, these materials lack other required functional properties like high electrical/thermal conductivities to account for electrostatic dissipation and lightening strike protection. Currently, it is believed that the best route to achieve multi-functional properties in a polymer is to blend it with nanoscale fillers. The fundamental basis behind this idea is the three main characteristics that define the performance of polymer nanocomposites:

i. nanoscopic confinement of matrix polymer chains;
ii. nanoscale inorganic constituents and variation in properties; that is, many studies have reported that mechanical, conductive, optical, magnetic, biological and electronic properties of several inorganic nanoparticles significantly change as their size is reduced from macro- to micro- and nano-scale levels and
iii. nanoparticle arrangement and creation of large polymer/particle interfacial area.

One of the technology drawbacks is that the mechanical reinforcement by the application of nanoparticles as a structural element in polymers is quite difficult to realize and still remains a challenging task. An efficient exploitation of the nanoparticles properties in order to improve the materials performance is generally related to the degree of dispersion, impregnation with matrix and to the interfacial adhesion. The advantage of nano-scaled compared to micro-scaled fillers is their enormous surface-to-volume ratio, which can act as interface for stress-transfer. The methods published so far on the improvement of mechanical properties of polymer composites have mainly focused on the optimization of the manufacturing process of the composites, i.e. with the use of prepared nanofillers. The property and performance enhancements made possible by nanoparticle reinforcement may be of great utility for carbon or glass fiber-epoxy composites that are used for the high performance and high temperatures applications such as aerospace engine components and nacelle, storage of cryogenic liquids, and motorsports. Then again, precautionary measures should be observed in high temperatures since the structure and properties of these materials can change radically when they are exposed to extreme temperatures, especially in a cyclical fashion.

Better dispersion of nanosized, silicate-based filler in matrice systems is expected to yield improved materials properties in several areas. Various mechanical properties, specifically improved fracture toughness, as well as improved flame-retardant effects are of interest. A key objective of the ongoing worldwide research is investigating whether a nano-modified matrix yields improved delamination resistance in a fiber-reinforced laminate compared to a laminate with neat polymer as matrix material. It is necessary, however, to evaluate the damage resistance characteristics of three-phase nanocomposite laminates for the enhancement of their applicability to the structural elements. Further, as lamented earlier on, another complication is that the microstructure of semicrystalline polymer matrices is influenced not only by the processing history but also by the presence of nanofillers. The addition of various types of carbon nanotubes, nanofibers or nanoclays to polymers has already been observed to influence the crystallization kinetics and resulting morphology. Such changes in matrix morphology need to be considered when evaluating the nanocomposite performance with regard to the intrinsic filler properties. The effects of nanoparticles on such oriented polymer systems, although significant, have not yet been

fully established. In addition, as mentioned earlier on, it should be noted that the presence of additives such as coloring pigments has been shown to influence matrix morphology during fiber spinning, whilst there is the whole technology of nucleating agents which are deliberately added to influence crystalline microstructure.

2. Strength and stiffness properties

Material used for crashworthy structural application, traditionally have been metals, due to their plastic deformation characteristics that enable them to absorb impact energy in a controlled manner. Polymer composite materials, contrasting metals, do not typically exhibit plastic deformation. However, their stress–strain relationships may show signs of other types of nonlinearities, but they are superior to metals for specific energy absorption. Nanoreinforced polymers have focused the attention, because of their potential to exhibit impressive enhancements of material properties compared to the pure polymers (Sun et al., 2009). For example, enhancement of materials strength and stiffness properties compared with the unreinforced material. The most important parameter which affects these properties is the load transfer between the composite phases, realized via shear stress induced in the interface region. If high-modulus filler is added into low-modulus matrix, the stress in the composite is transferred into the stiffer phase, causing higher loads to be carried by the filler. That is why efficiency of the stress transfer across composite phases depends on quality of the interfacial region. This includes interfacial strength and stiffness (Zhang et al., 1993). If weak coupling exists between the phases, then the load transfer is poor and the properties of the composite are dominated by the matrix. Enhancement of interfacial properties causes that the load is transferred more efficiently, leading to an increase in composite modulus and strength.

An important influence on the properties of the interfacial region is the aspect ratio of the reinforcement. The higher the aspect ratio of the reinforcement is, the bigger the load carrying area, and the higher the composite modulus and strength. This phenomenon explains the unique properties of the materials reinforced with nanoparticles. Large number of small particles in nanocomposite increases the available interfacial area leading to significant enhancement of the mechanical properties. The effectiveness of nanofillers in reinforcing polymeric materials depends on several factors, which are defined and summarized here after.

2.1 Filler size

It is well known that incorporation of rigid micro-fillers usually increases composite stiffness, but at the cost of reduced ductility. This is caused by the stress concentration regions that exist in close proximity of the reinforcement. In case of nanofillers the stress concentrations are significantly reduced. Therefore, composite ductility can be maintained at the constant level or even improved, in relation to the net polymer.

The size effect of TiO_2 particles on mechanical properties of the epoxy resin was investigated by Ng *et al*. (Ng et al., 1999). The authors studied tensile properties of the epoxy material reinforced with nano (32nm) and micro (0.24μm) particles, at constant 10% weight fraction. The obtained results show, that incorporation of micro-particles increased the modulus of the epoxy resin, but decreased its strain to failure. On the other hand, incorporation of nanoparticles increased both, the modulus and the strain to failure. The effects of

nanoparticles on mechanical properties of polyurethane/clay (PU/MMT) nanocomposite foams have also been investigated in the literature. It is well known that H-bond formation among urethane groups, greatly contributes to the strength and modulus of PUs. The overall performance of PU nanocomposite foams depends on the competition between the positive effects of clay on polymer reinforcement and foam morphology, and the negative effects on H-bond formation and network structure.

Effect of particles size on the mechanical properties of polyurethane foams was studied by Javni *et al*. (Javni et al., 2002). Incorporation of nanosized filler was found to increase the compression strength of the foam, and to decrease its rebound resilience. On the other hand, the addition of micro-sized fillers was found to lower the hardness and compression strength, at the same time leading to an increase in rebound resilience. In another development, (Njuguna *et al. 2008)* fabricated and characterised a series of nanophased hybrid sandwich composites, based on polyurethane/montmorillonite (PU/MMT). Polyaddition reaction of the polyol premix with 4,4'-diphenylmethane diisocyanate was applied to obtain nanophased polyurethane foams, which were then used for fabrication of sandwich panels. It has been found that the incorporation of MMT resulted in higher number of PU cells with smaller dimensions and higher anisotropy index. The obtained materials exhibited improved parameters in terms of thermal insulation properties. Importantly, these foams can also be selectively stiffened to meet specific requirements.

2.2 Volume fraction of fillers

Another important factor which can have significant impact on the stress-strain behavior of nanocomposites is the filler content. In contrast to microparticles, which reduce composite strength at high filler content, the nanoparticles offer an increase in both modulus and strength, with rising fraction of the filler. However, bad dispersion of particles or existence of agglomeration regions may cause stress concentrations, which initiate local cracks, resulting in reduced ductility of the composite. This phenomenon is especially augmented at high filler loadings where agglomerations are more likely to occur (Javni et al., 2002).

The enhancement of mechanical properties due to the high filler content is associated with inter-particle distance. If the distance between particles is below the critical value, then a three dimensional network of interphase region is created across the particles and the matrix. Within this region the properties of the composite can be assumed as a gradual transition from that of the particle to that of the matrix. Value of the inter-particle distance τ is closely related to the concentration φ and average size of the particles d, what can be described using equation (1), assuming ideal dispersion of the particles (Zhang et al., 2006).

$$\tau = d \cdot \left[\left(\frac{\pi}{6\varphi} \right)^{1/3} - 1 \right] \tag{1}$$

Zhang *et al*. (Zhang et al., 2006) found, that if inter-particle distance is smaller than the average particle size d, then composite performances increase significantly, as it is presented in Figure 1. Similar conclusions were drawn by Wetzel *et al*. (Wetzel et al., 2006) who compared experimental fracture toughness with theoretical data presented in (Evans, 1972).

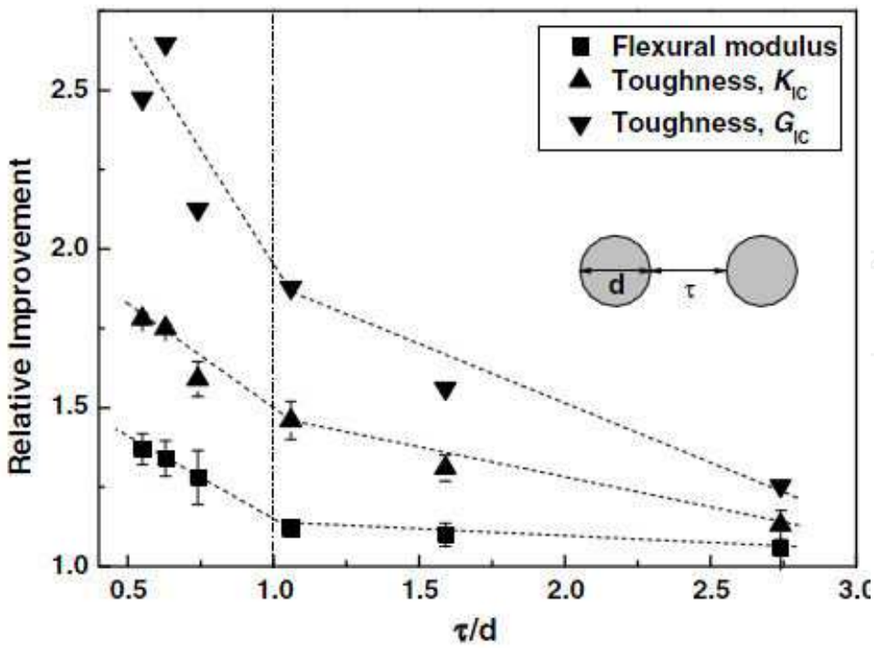


Fig. 1. Correlation between inter-particle distance and mechanical properties of SiO_2 /epoxy nanocomposites (Zhang et al., 2006).

2.3 Filler shape

The surface-area-to-volume ratio of the filler has the biggest influence on the mechanical properties of a nanocomposite, which is closely related with its shape. Figure 2 shows three typical geometries, which can be used as reinforcement in nanocomposites. Each of them possesses different aspect ratio, which can be expressed using equations (2-4) (Crosby & Lee, 2007).

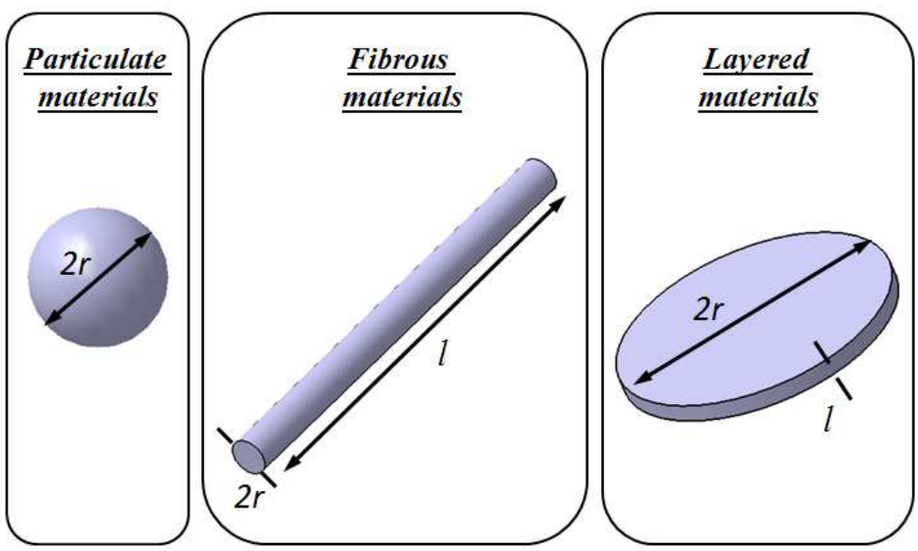


Fig. 2. Various reinforcement geometries.

- Particulate materials

$$\frac{A_s}{V_s} = \frac{4\pi r^2}{4/3\,\pi r^3} = \frac{3}{r} \tag{2}$$

- Fibrous materials

$$\frac{A_f}{V_f} = \frac{2\pi r^2 + 2\pi rl}{\pi r^2 l} = \frac{2}{r} + \frac{2}{l} \qquad l > r \tag{3}$$

- Layered materials

$$\frac{A_l}{V_l} = \frac{2\pi r^2 + 2\pi rl}{\pi r^2 l} = \frac{2}{r} + \frac{2}{l} \qquad r > l \tag{4}$$

If we compare surface-area-to-volume ratios of the particulate and cylindrical materials we obtain the following relation:

$$\frac{SV_p}{SV_c} = \frac{3}{2(1 + r/l)} \tag{5}$$

If the filler is in the form of plates ($r>l$) or short rods ($l<2r$), then its surface-area-to-volume ratio is bigger than that of a spherical particle. On the other hand, spherical particles have bigger surface-area-to-volume ratio in relation to long fibers ($l>2r$). Influence of r/l ratio on aspect ratio of the filler is shown in Figure 3.

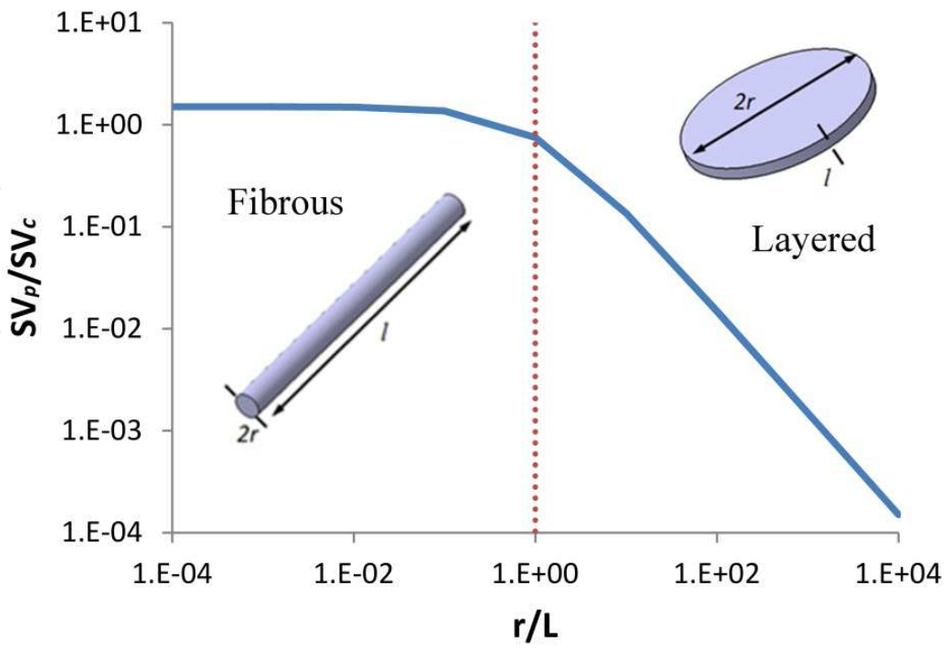


Fig. 3. (SV_p) to (SV_c) ratio as a function of particle radius (r) to length (l) ratio.

Summarizing, we can note that the best surface properties can be achieved using plate geometries. However, the mechanical properties of nanocomposites depend on various factors, i.e. size, dispersion and volume fraction of the filler. That is why it is difficult to directly compare different shapes of fillers in experiment. For example, cylindrical fillers are difficult to disperse in a homogeneous manner, at high volume fraction. Therefore, mechanical properties of the non-homogeneously dispersed filler of the one shape are not directly comparable with properly dispersed filler of the other shape, even at a constant volume fraction.

3. Impact resistance and energy absorption performance

Advanced vehicle structures must be able to withstand severe impact loads, at the same time providing safety of the occupants. That is why structural materials, used for crashworthy applications for instance, must be characterized by the energy absorption capability. In order to ensure survivability of the accident, structure has to dissipate energy in a controlled manner. This is limited by the two factors: induced decelerations (controlled by the strength of structure) and maintaining of a survival space for occupants during a crash. Traditionally metallic materials have been applied for the crashworthy structures, due to their ability to sustain plastic deformations. In contrast, composite materials do not exhibit plastic deformations as they are usually brittle. However, if they are properly designed they can absorb high amounts of impact energy by the progressive crushing and delamination.

For light weight constructions, among various nanocomposites, much attention has been paid to polymer/silica nanocomposites, because of the enhanced mechanical properties, high thermal stability and high flame-retardants. According to (Lux Research, 2004; Business Communications Company [BCC], 2006) nanoclays are accounting approximately 70% of the total volume of nanomaterials commercially used. In the automotive and packaging sector nanoclays are widely used, mainly due to their low cost and availability. PMMA-epoxy-nanoclay composites (Hyun Park & Jana, 2003), polypropylene-nanoclay composites (Galgali et al., 2004), polyvinylidene fluoride-nanoclay nanocomposites (Dillon et al. 2006) and nanoclay-modified rigid polyurethane foam (Widy & Macosko, 2005) have shown exhibit improved properties when compared to their bulk polymer constituents and conventional macro-composite counterparts. Numerous studies have reported the improvement of energy absorption of nanoclay/polymer nanocomposites (Chen & Evans, 2008; Sterky et al., 2010; Iqbal et al., 2009; Njuguna et al., 2008). For example, John *et al.* (John et al., 2010) have shown that the incorporation of 2 and 4 vol. % of nanoclay respectively improves the tensile modulus of cyanate ester syntactic foams by 6 and 80%.

Damages results from low-velocity impact events weaken the structure of composite materials, due to a continuous service load (Figure 4).

Furthermore, the impact may generate different types of flaws before full perforation, i.e. sub-surface delamination, matrix cracks, fiber debonding or fracture, indentation and barely visible impact damage (BVID). Over time, these effects can induce variations in the mechanical properties of such composites structures (the primary effect of a delamination is to change the local value of the bending stiffness and of the transverse-shear stiffness), leading to possible catastrophic failure conditions (Capezzuto et al., 2010).

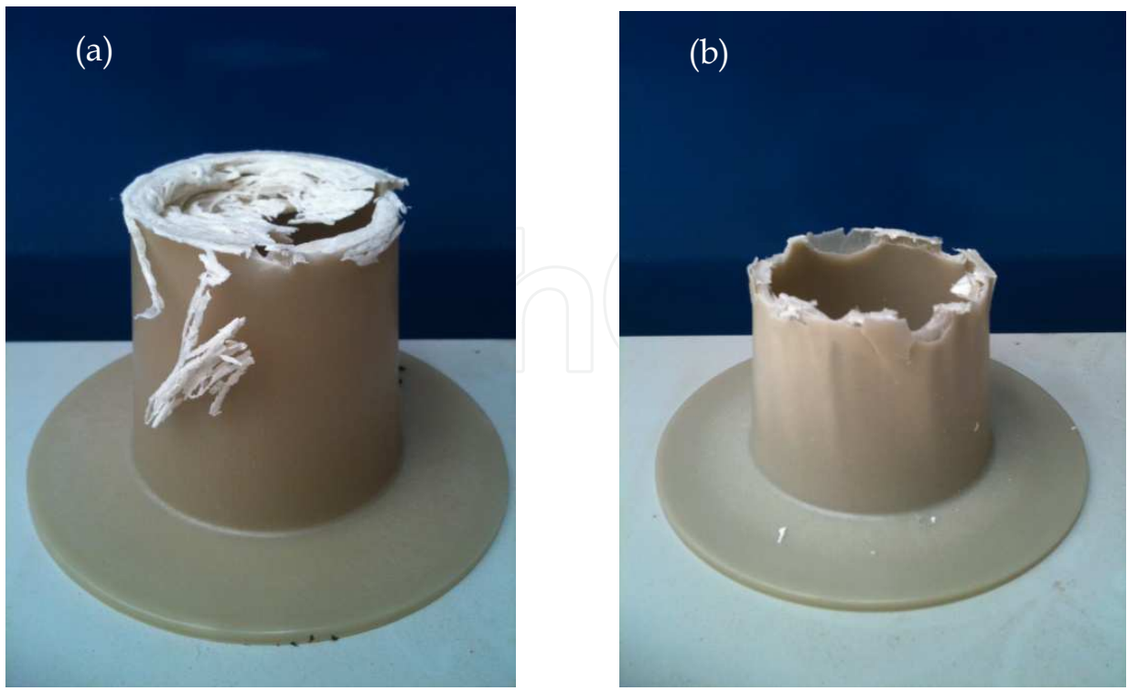


Fig. 4. 1kJ impact on (a) Glass-fiber/nanoclay reinforced Polypropylene Glass-fiber/ nanosilica reinforced Polyamide 6.

Numerous studies have investigated the impact behaviour of polymer nanocomposite and are listed in Table 1.

It has been reported that the energy absorption capability and related properties of polymer matrices can be engineered by adding nano-scale fillers. For example, rigid nanosized particles such as SiO_2, TiO_2, $CaSiO_3$, Al_2O_3 powder, carbon nanotubes (CNTs) and clay nanoplatelets have been used, and some important findings are summarised in this section.

3.1 Effects of particle stiffness

Viana (Viana, 2006) has shown that the particle stiffness influenced the properties of the polymer matrix. While soft/elastic fillers improved the impact toughness, at the same time those fillers reduced the modulus of elasticity of the polymer blend. However, increasing the amount of hard/rigid fillers improved both the impact toughness and the modulus of elasticity. For instance, the addition of nanoclay (less than 5 wt. %) into a polyurethane foam matrix, significantly improved the failure strength and energy absorption of the foam, with over a 50% increase in the impact load carrying capacity when compared to the unenforced matrix (Mohamme, 2006). Another example is the addition of rigid $CaCO_3$ (Ø 600 nm, 0.2 vol. %) in high density polyethylene (HDPE), which improved the impact strength by more than 200 % (Liu, 2002).

Such exorbitant improvements are not typically observed for composites reinforced with conventional micro-particles. Subramaniyan *et al.* (Subramaniyan & Sun, 2007) reported that core shell rubber (CSR) nanoparticles having a soft rubber core and a glassy shell improved the fracture toughness of an epoxy vinyl ester resin significantly more than nano-clay particles, having the same weight fraction. However, hybrid blends of CSR and nanoclay

Matrix material	Nanofiller	Ref.
Carbon fiber reinforced plastics	Multi-wall carbon nanotubes	(Kostopoulos et al., 2010)
Polystyrene	Cu_2S nanoparticles	(Capezzuto et al., 2010)
Polystyrene	Ammonium-treated montmorillonite clay	(Chen & Evans, 2008)
Nylon 6	Organoclay	(Lim et al., 2010)
Polyvinyl chloride	Organically modified montmorillonite	(Sterky et al., 2010)
Polyoxymethylene	Zinc oxide	(Wacharawichanant et al., 2008)
Epoxy matrix	Poly(acrylonitrile-co-butadiene-co-styrene) (ABS), clay (layered nanofiller) and nano-TiO_2	(Mirmohseni & Zavareh, 2010)
Carbon fiber–epoxy	Octadeclyamine modified montmorillonite s	(Iqbal et al., 2009)
Polyacrylate (PA), polyimide(PI) and polypropylene (PP)	Silica	(Li, 2008)
DGEBA (diglycidyl ether of bisphenol A) epoxy resin	TiO_2	(Bittmann et al., 2010)

Table 1. Studies investigating impact behaviour of polymer nanocomposite.

were found to yield the best balance of toughness, modulus and strength. The same investigators highlighted that when the nanoclay particles were used to enhance the polymer matrix in a conventional glass fiber-reinforced composite, the interlaminar fracture toughness of the composite was less than that of the unreinforced composite. As a possible reason for this result the arrangement of the nanoclay particles along the fiber axis was suggested.

Two factors dominate the capacity of rigid particles for energy dissipation at high loading rates (Dubnikova et al., 2004):

- the ability of the dispersed particles to detach from the matrix and to initiate the matrix local shear yielding in the vicinity of the voids and
- the size of the voids.

Therefore, the optimal minimal rigid particle size for polymer toughening should assure two main requirements:

- be smaller than the critical size for polymer fracture and
- have a debonding stress which is small compared to the polymer matrix yield stress.

3.2 Effects of particle geometry

Typical fillers for the reinforcement of polymer matrices are particles e.g. silica or aluminum oxide particles, tubes e.g. nanofibers or nanotubes and plates e.g. nanoclay platelets.

Significant enhancement of impact strength of polymeric nanocomposites was achieved by adding amino-functionalized multi-wall carbon nanotubes (MWCNTs) or small amounts of single-wall carbon nanotubes (SWCNTs) (Donclero & Gorga, 2006). Furthermore, the impact toughness of PMMA (polymethyl-methacrylate) has been improved considerably by the addition of CNTs and the toughness and modulus of MWCNTs reinforced PP exhibited a maximum at 1 wt.% CNTs (Donclero & Gorga, 2006). Additionally, the impact toughness and stiffness of CNT–reinforced polymer matrix have been found to be functions of the Young's modulus of the nanotubes (Kireitseu et al., 2008). The impact toughness of polymers containing inorganic nanofillers such as MMT (montmorillonite) nanoclay, based polymer composites was found to decrease (Viana, 2006), whereas adding Al_2O_3 nano-whiskers, glass fibers and wollastonite in a polymer resin improved the fracture toughness, KI_C, compared with that of the unreinforced resin (Yilmaz & Korkmaz, 2007)

3.3 Effects of inter-particle distance and volume fraction of fillers

The toughening of particle modified semi-crystalline polymers is related to the inter-particle distance *s*, independently of the type of added particles (Figure 5). The distance *s* relates both to the concentration *u*, and the average size d of the particles. Zhang *et al.* (Zhang et al., 2006) reported that the toughness improves significantly when the inter-particle distance *s* becomes smaller than the particle diameter, *d*. Qi *et al.* (Qi et al., 2006) showed that the fracture toughness and modulus of DGEBA epoxy resin increased with increasing volume fraction of nano-clay particles.

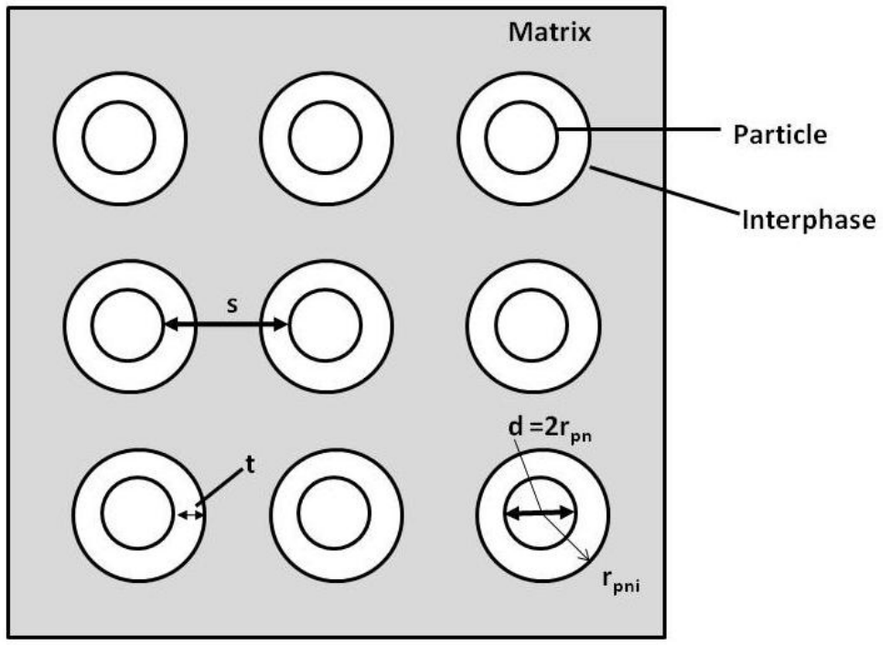


Fig. 5. Geometric parameters in nanoparticle-reinforced composites.

For nanophased hybrid sandwich composites based on polyurethane/montmorillonite (PU/MMT) shows that nanophased sandwich structures are capable of withstanding higher peak loads than those made of neat polyurethane foam cores when subject to low-velocity impact despite their lower density (Fig. 6).

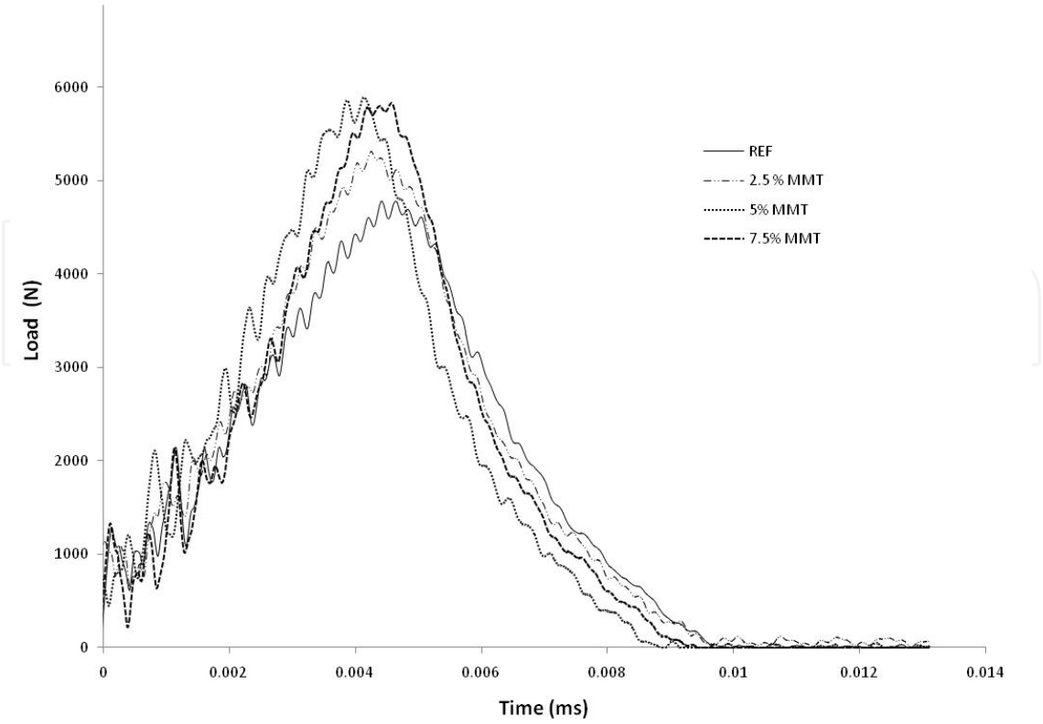


Fig. 6. Load vs time graph obtained from impact test.

This is especially significant for multi-impact recurrences within the threshold loads and energies studied by Njuguna *et al.* (Njuguna et al. 2010). Feasible applications for these lightweight structures are in energy absorbing structures or as inserts in hollow structures.

3.4 Effects of particle size

To investigate different toughening or energy absorption effectivenesses for fillers with micro- and nano-scale size, *d*, Wacharawichanant *et al.* (Wacharawichanant et al., 2008) measured tensile and impact properties of POM/ZnO (71 nm) and compared them with those of composites having micron- size ZnO (0.25 μm). It was shown that the nanocomposite has a higher mechanical properties e.g. tensile strength, Young's modulus and impact strength than the microcomposite. Fu *et al.* (Fu et al., 2008) investigated the mechanical behavior of polypropylene (PP)/$CaCO_3$ nanocomposites; the particle size varied from 10 nm, 80 nm, 1.3 to 58 μm. The study has shown that the composite strength increases with decreasing particle size due to higher total surface area for a given particle loading. This indicated that the strength increased with increasing surface area of the filled particles through a more efficient stress transfer mechanism. Furthermore, the Izod toughness was also found to increase with decreasing particle size.

3.5 Effects of stochastic variation of particle size and strength

Due to individual stochastic variation in the strength, different carbon nanotubes may have direct effect on the fracture mechanisms as in micro-based fiber composites. Xiao *et al.* (Xiao et al., 2008) measured the relation between individual CNT and CNT bundle strengths and proposed a method for determining the tensile strength distribution of individual CNTs or

CNT sub-bundles from experimental measurements on CNT bundles. The Weibull shape and scale parameters of the tensile strength distribution of CNTs were found to have wide variability of strength.

Tomar *et al*. (Tomar & Zhou, 2005) highlighted, that a microstructure less prone to fracture showed higher variations in fracture response when compared to the one which offers least resistance to crack propagation. Additionally, for a particular micro-structural morphology, the levels of variations in the crack surface area generated and the variations in the energy release rate were of the same order as the levels of variations in constituent properties.

3.6 Effects of polymer matrix and fillers types

The energy absorbent of nanocomposites depends on the polymer-clay affinity. For example, leads the reinforcement of polyacrylate (PA), polyimide (PI) and polypropylene (PP), with silica to striking variation in impact toughness behavior under identical processing conditions. The maximum stress intensity factor of PA-based enhanced significantly as compared with PI and PP based composites. Additionally the steady state fracture toughness of PA composite is approximately 45% and 25% higher than pure polyacrylate and both PP-based and PI-based hybrid specimens (Lin, 2008).

3.7 Effects of interfacial adhesion

Hybrid organic–inorganic composites usually exhibit enhanced mechanical properties compared to those of their separate components. The dispersion of the inorganic components into the inorganic matrices affects the mechanical performance of the materials. Hence, homogeneous despaired filler components are desirable. The employment of inorganic bulk fillers that can be exfoliated into well organized nano size fillers in the polymer matrices is one method to get well dispersed inorganic reinforced organic matrix nanocomponent. For example, Park *et al.* (Park, 2009) confirmed that silane-treated MMT could be successfully intercalated and dispersed in the epoxy matrix. The experimental results show that silane coupling agent (SCA) treatments cause an increase in both the specific component (due to the epoxide ring and amine group) and the dispersive component (due to the increase of the specific molecular volume). It was considered that the presence of SCAs leads to an increase of the interfacial adhesion between the MMTs and epoxy resin, which results from the improvement of the polar functional groups or of the specific component of the surface free energy of the MMTs. This enhances the mechanical interfacial strength between the MMTs and the epoxy matrix.

Hamming *et al.* (Hamming et al., 2009) studied the quality of dispersion and the quality of the interfacial interaction between TiO_2 nanoparticles and host polymer on properties such as glass transition temperature (T_g), elastic modulus and loss modulus. T_g is an attractive target property because of its high sensitivity to chain mobility and its use as a benchmark in other studies. The results showed that as the degree of dispersion improved (finer scale agglomerations) the T_g was depressed for samples of unmodified TiO_2 nanoparticles in PMMA and increased for samples of modified TiO_2 nanoparticles in PMMA. These results indicate that the quality of dispersion shifted T_g. However, the direction of shifts depended on the interfacial interaction of the nanoparticles with the matrix. This study indicated that the bulk properties of nanocomposites were highly sensitive to the quality of the interfacial interaction and quality of dispersion of the nanoparticles.

3.8 Distribution status of fillers

A number of experiments have shown that fracture toughness improved with addition of clay nano-platelets to epoxy when the clay nano-platelets were not fully exfoliated, and intercalated clay nano-platelets were present (Xidas & Triantafyllidis, 2010). Xidas *et al.* (Xidas & Triantafyllidis, 2010) showed that quaternary alkylammonium ion-modified organoclays (C18 alkylammonium ion and hydrogenated tallow ammonium ions) provided highly intercalated structures, which led to significant increase of tensile strength and strain at break.

4. Thermal properties

The deterioration of materials depends on the duration and the extent of interaction with the environment. Degradation of polymers includes all changes in chemical structure and physical properties of polymers due to external chemical or physical stresses caused by chemical reactions, involving bond scissions in the backbone of the macromolecules that lead to materials with characteristics different (usually worsened) from those of the starting material (Fig. 7). As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties, the article becomes brittle and the life of the material becomes limited. Thus, any polymer or its (nano) composite, which is to be used in outdoor applications, must be highly resistant to all environmental conditions.

Research indicates that the modified epoxy nanocomposites possess better flame retardance than conventional composites. By the Kissinger method, the activation energies of thermo-oxidative degradation for the epoxy nanocomposites are less than those of the pure epoxy in the first stage of thermo-oxidative degradation. However, the activation energies of thermo-oxidative degradation for epoxy nanocomposites are generally higher than those of the pure epoxy in the second stage of thermo-oxidative degradation. For example, the main mechanism of layered silicate is a barrier formation influencing the flame spread in developing fires. Several minor mechanisms are significant, but important fire properties such as flammability or fire load are hardly influenced. Hence combinations with aluminum hydroxide and organo-phosphorus flame-retardants need to be evaluated. It has been shown that carbon nanotubes could surpass nanoclays as effective flame-retardant additives if the carbon-based nanoparticles (single- and multi-walled nanotubes, as well as carbon nanofibers) form a jammed network structure in the polymer matrix, such that the material as a whole behaves rheological like a gel (Kashiwagi et al., 2005).

The thermal degradation of nanoclay nanocomposites depends on the clay loading, and structure and the nature of the ambient gas. Leszczyńska *et al.* (Leszczyńska et al., 2007) have reviewed thermal stability of various polymer matrices improved by montmorillonite clay, and their influencing factors in detail. For the majority of polymers, owing to their hydrophobic character, the clay must be modified with a surfactant in order to make the gallery space sufficiently organophilic to permit it to interact with the polymer. In fact, several factors were found to govern the thermal stability of nanocomposite materials, such as intrinsic thermal resistance of polymer matrix, nanofiller content, chemical constitution of organic modifier and chemical character of polar compatibilizers as well as an access of oxygen to composite material during heating. For surface modification of clay, the surfactant is usually described as an 'onium' salt, but in fact ammonium salts are most commonly used. The quaternary ammonium ion is nominally chosen to compatibilize the layered silicate with a given polymer resin. However, the molecular structure (length and number of alkyl chains and unsaturation) is also the determining factor of the thermal stability of the polymer/MMT nanocomposites.

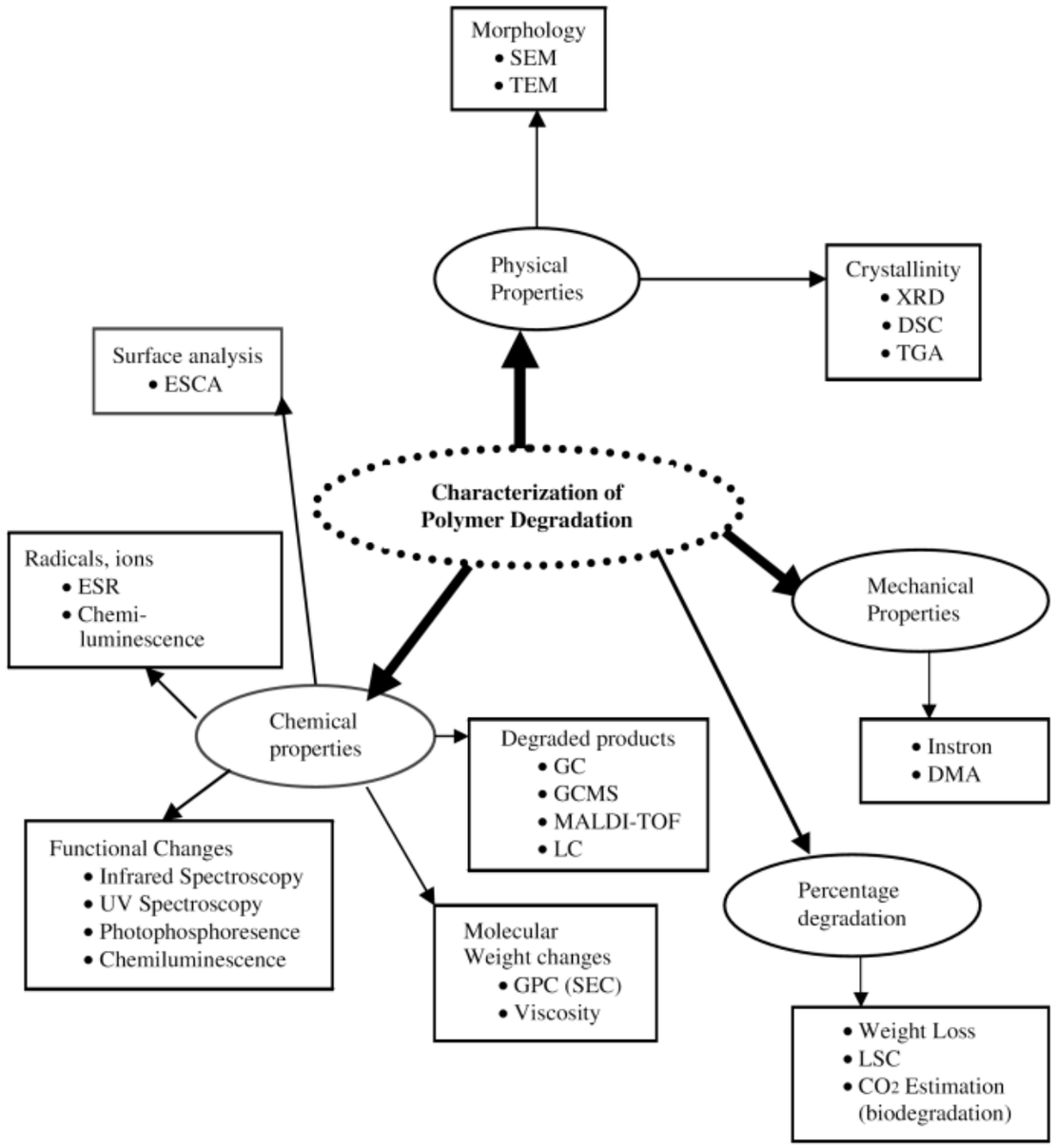


Fig. 7. Schematic representation of different degradation and stabilization processes in polymers (Pandey et al., 2005).

The possible mechanism for degradation of modifiers in silicates by among others Hwu *et al*. (Hwu et al., 2002), Leszczyńska et al. (Leszczyńska et al., 2007) and research has shown that surfactants degrade between 200 and 500 °C. The amount of surfactant lost during thermogravimetric analysis of various organoclays indicates that surfactants with multiple alkyl tails have greater thermal stability than those with a single alkyl tail. It has been proposed that the organic modifiers start decomposing at temperature around 200 °C, and the small molecular weight organics are released first while the high-molecular weight organic species are still trapped by organic layered silicate matrix. With the increase of temperature, the high-molecular organic polymer chains may still exist between the

interlayers until the temperature is high enough to lead to their further decomposition. The incorporation of silicate layers with high-aspect ratio decomposed/charred material on the clay surface act as carbonaceous insulators. The silicate has an excellent barrier property that prevents against permeation of various degraded gaseous products.

The addition of clay enhances the performance by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. The clay acts as a heat barrier, which could enhance the overall thermal stability of the system, as well as assisting in the formation of char during thermal decomposition. In the case of the nanocomposite, the temperature at which volatilization occurs, increases as compared to the case of the micro-composite. Moreover, the thermal oxidation process of the polymer is strongly slowed down in the nanocomposite with high-char yield both by a physical barrier effect, enhanced by ablative reassembling of the silicate, and by a chemical catalytic action due to the silicate and to the strongly acid sites created by thermal decomposition of the protonated amine silicate modifier.

The polymers that show good fire retardancy upon nanocomposite formation exhibit significant intermolecular reactions, such as inter-chain aminolysis/acidolysis, radical recombination and hydrogen abstraction. In the case of the polymers that degrade through a radical pathway, the relative stability of the radical is the most important factor for the prediction of the effect that nanocomposite formation has on the reduction in the peak heat release rate. The more stable the radical produced by the polymer is; the better the fire retardancy is, as measured by the reduction in the peak heat release rate, of the polymer/clay nanocomposites.

The presence of MWNTs improves the thermal stability of PA6 under air obviously, but has little effect on the thermal degradation behavior of PA6 under nitrogen atmosphere. The thermal degradation mechanism of PA-6 has been proposed by Levchik *et al.* (Levchik et al., 1999). Vander Hart *et al.* (VanderHart et al., 2001.) observed that in the presence of clay the α-phase of PA 6 transforms into the γ-phase. The effect of modifier on the degradation of nanocomposite was studied by ^{13}C NMR. In the presence of modifier (dihydrogenated-tallow ammonium ion) the nylon nanocomposite begins to degrade at 240 °C, whereas the virgin polymer does not. They concluded that the organic modifier is less stable. The combination of shear stress and temperature may lead to extensive degradation of the modifier and the extent of clay dispersion may not depend on the modifier.

Davis *et al.* (Davis et al., 2003) have studied the thermal stability of injection moulded PA-6 nanocomposites by ^{13}C NMR. The virgin PA 6 and its nanocomposites were injection moulded at 300 °C. PA 6 did not degrade at processing temperature, whereas there was significant decrease in molecular weight in nanocomposites in the same conditions. It was observed that the degradation might depend upon the percentage of water in the nanocomposites, which might cause hydrolytic cleavage. Fornes *et al.* (Fornes et al., 2003) found color formation with polymer matrix degradation after twin-screw extrusion of polymer nanocomposites. The researchers reported that degradation of the nanocomposites depends on the type of nylon-6 materials as well as the chemical structure of the surfactant in the organically modified MMT (OMMT). Hydroxy-ethyl groups in the surfactant, as opposed to methyl groups, and tallow substituents, as opposed to hydrogenated tallow substituents, produced more colors in nanocomposite, which was related to unsaturation in the alkyl ammonium surfactant causing considerable polymer degradation. The kinetic parameters of PA-6 clay nanocomposite decomposition have also been studied.

5. Future trends

5.1 Numerical modeling for material properties

It is well known that interactions between nanofiller and matrix have a significant impact on the mechanical behavior of nanocomposites (Ajayan et al., 2003). That is why modeling of these materials becomes a challenging task, due to the wide range of length scales that need to be considered in the analysis. The most common used numerical methods for modeling nanocomposites include: Molecular Dynamics (MD); micro-mechanical, macro-mechanical and multiscale modeling. MD methods consider interaction at atomistic scale, and apply principles of quantum mechanics and molecular dynamics. These methods allow the determination of mechanical properties at nanoscale by solving equations of motion of interacting atoms within inter-atomistic potentials (Rapaport, 2004). MD simulations have been successfully applied in investigation of crack propagation and fracture of individual single and multi-walled carbon nanotubes (CNTs) (Belytschko et al., 2002; Namilae, 2005) and predicting the elastic properties of CNTs (Cornwell & Wille, 1997). However, these techniques are computationally expensive, and therefore, they are limited to studies of individual particles and polymer chains (Fisher, 2006). Link to the modeling of larger structures is currently unavailable. For a larger scale structures, continuum mechanics and micromechanics based finite element (FE) methods can be applied. General description and main challenges associated with these techniques are presented hereafter.

5.1.1 Macroscopic modeling

Macroscopic modeling is a simplified approach where micro or nano-scopic interactions between matrix and reinforcement are neglected. Properties of the composite are homogenized before the analysis, producing anisotropic and homogenous continuum (Aboudi, 1990). Effective properties like stress-strain curve and yield point are then obtained by using mechanical testing.

A big challenge when composite materials are considered is modeling of yield and failure under multiaxial loading. Most of the existing models, implemented into commercial FE packages, are developed for metals, and therefore, they are based on von-Misses criterion. In this approach yielding occurs at the same point in tension and compression, and it is specified by the value of effective stress. These assumptions are not necessarily correct for polymer composites. Contrary to metals, polymers yielding and failure are dependent on hydrostatic pressure, which is omitted in von Misses theory. Several experiments confirmed that hydrostatic part of stress tensor increases polymers yielding (Rabinowitz et al., 1970; Pae & Mears, 1968; Pugh et al., 1971) and failure (Ol'khovik, 1983) stress. That is why several modifications of Tresca and von Misses criteria were proposed to properly predict polymers behavior in the literature (Bowden & Jukes, 1972; Quinson et al., 1997; Sternstein & Ongchin 1969). These formulations take into account both hydrostatic and deviatoric components of the stress tensor. The yield stress is then calculated as a linear or nonlinear function of the hydrostatic pressure. In case of polymers under low pressure the linear representation is in good agreement with the experimental results, while the nonlinear characteristic is valid for the polymers under high pressure (Altenbach & Tushtev, 2001).

While selecting the material model for polymer composites it is also important to consider existence of nonlinear elastic region and strain rate effect. Some polymers exhibit significant rate dependency of modulus while others do not. That brings additional complications to modeling process, as not all material models are capable to represent these effects.

Application of the rate independent model to rate dependent material leads to an important error in stiffness prediction (Lobo, 2007).

5.1.2 Micro and multiscale modeling

In micro-scale modeling, each phase of a composite is considered separately. Loading and boundary conditions are applied both to the matrix and the reinforcement. The overall macroscopic properties of the material are then averaged and calculated as a function of the constituents properties, using a homogenization method or direct FE representation of Representative Volume Element (RVE). In contrast to the macroscopic approach multiscale modeling is able to provide information about stresses in phases, and it allows the definition of per-phase failure. Moreover, with this formulation, influence of the filler content on the composite properties can be predicted and investigated without performing an expensive material testing, for each configuration. An important drawback of this method is the larger computation time, in relation to the macroscopic approach, where material properties are calculated 'off line' (Aboudi, 1988).

However, the main principle of micro-mechanical modeling is the concept of RVE. The RVE is defined as a volume V of heterogeneous material, which must be large enough to correctly reflect statistical fluctuations of the composite properties. It must ensure an accurate prediction of the effective properties like Young's modulus or Poison's ratio (Kanit et al., 2003). Furthermore, it must contain all the data which can influence the composite behavior e.g. volume fraction, size and distribution of the filler.

In order to predict mechanical properties of the composite materials, various homogenization models can be applied. The most widely used models are Mori-Tanaka (Mori & Tanaka, 1973) and Halpin-Tsai (Ashton et al., 1969; Halpin, 1969) which are based on Eshelby's equation (Eshelby 1957; Eshelby 1961). Good description of these models can be found in (Tucker & Liang, 1999).

In order to predict the response of composite structures, taking into account its microstructure, a multiscale analysis can be applied. In this approach calculations are conducted at both macro and micro levels. At micro level, a finite number of constituents are defined, and each is described by its own constitutive model and material properties. The constitutive relation and the effective properties of composite at macro level are then calculated using a homogenization method. Once the effective properties are known a conventional FE analysis can be performed, giving macroscopic strain tensor ε at each point x, which at the micro level is viewed as a centre of the RVE. Subsequently, knowing the macro values of stress and strain tensor it is possible to compute approximated values at the micro level, in each phase.

Micromechanical models have been applied in several studies to predict elastic properties of nanocomposites (Luo & Daniel, 2003; Fornes et al., 2003; Wu et al. 2004; Wilkinson et al., 2007; Chavarria & Paul, 2004) as well as damage and failure (Fornes et al., 2003; Chen et al., 2003; Chen et al., 2007; Boutaleb et al., 2009). Luo *et al*. (Luo & Daniel, 2003) studied properties enhancement of epoxy matrix reinforced with silicate clay particles. A three-phase model, including the epoxy matrix, the exfoliated clay nano-layers and the nano-layer clusters was developed to account for partial exfoliation of nano-layers. The Mori-Tanaka method was applied to predict elastic properties of the material. Various parameters including the exfoliation ratio, clay layer and cluster aspect ratios, intra-gallery modulus, matrix modulus and matrix Poisson's ratio were taken into account. The exfoliation ratio

was investigated using TEM micrographs and the estimated value (10%) was included in the model. Predicted values of elastic properties were found to be in close agreement with the experimental results. That is why influence of various parameters on mechanical properties of the composite was further studied using the same method.
Boutaleb *et al*. (Boutaleb et al., 2009) extended micromechanical model based on Eshelby's formulation to predict stiffness and yield stress of silica reinforced polymer nanocomposites. The presented model took into account an interphase region around the nanoparticles and calculated its elastic modulus as gradual transition from that of the naoparticle to that of the matrix. The third phase centred around the particle is assumed to be inhomogeneous. Each phase was described by the own elastic stiffness tensor *C*. The dispersion of the filler and the interphase region in the matrix was assumed to be random. The yield function of the composite was calculated using the averaging procedure derived by Ju *et al*. (Ju & Sun, 2001).
The numerical results obtained by the authors are in good agreement with the experiment. A dominating role of the interphase region on the composite yield stress is observed. For the small particle size the stiffness of the interphase is relatively strong. Increase in size of the particle leads to a softening of the interphase region. This indicates that process of debonding is dominating in this case.

5.2 Natural fiber-reinforced nanocomposites

At present the awareness of environmental pollution has increased. Carbon footprint, global warming and greenhouse gases are the main keywords related to this topic and the industrial and social attitude towards a "cleaner" future is omnipresent. Therefore, one of the most promising structures as component in nanocomposites are cellulosic nanofibrillars, due to their renewable and environmentally being nature and their outstanding mechanical properties. Cellulose nanofibers are obtained from various sources such as flax bast fibers, hemp fibers, kraft pulp, and rutabaga, by chemical treatments followed by innovative mechanical techniques. The nanofibers thus obtained have diameters between 5 and 60 nm. However, the key issues of concern for applications in which cellulosic nanocomposites are either intended or destined for long term use remains the durability. Although cellulosic nanocomposites proven to have superior properties, it remains a challenge to guarantee to the end user that such properties are reliably achieve during industrial scale processing. Furthermore, the degradation of properties over time cannot be assessed and secured at present (Hubbe et al., 2008).

5.3 Age and durability performance

Durability of the nanofiber layers can be affected by many different characteristics of the ultimate material composite. Therefore, each step towards the fabrication of the final composite material must be considered. Furthermore, durability depends to a great extent on structural elements and phenomena which are effective at micro- but most important at nanoscale.
Pramoda *et al.* (Pramoda et al., 2003) observed that the temperature of onset of degradation for PA-6 and 2.5% clay filled nanocomposites was higher than other compositions (neat polymer, 5% and 7.5%), respectively. Gilman *et al.* (Gilman et al., 1997) proposed that with the higher loading of clay, temperatures of onset of degradation remain unchanged, which was attributed to agglomeration in nanocomposites. The presence of organoclay (for PA6 – 2.5 wt. % clay nanocomposite) increased the activation energy for degradation, E_a,

compared to the neat PA-6 under N_2. The major evolved gas products were cyclic monomers, hydrocarbons, CO_2, CO, NH_3 and H_2O for PA-6 and PA-6/clay nanocomposites. During flammability measurements on the calorimeter in conjunction with an FTIR spectrometer in real time, changes in the condensed phase of PA-6 and a PA-6/clay nanocomposite have revealed that the spectra obtained during the burning are of sufficiently high quality to show the progression of the material in contact with the probe from molten polymer to thermal degradation products. The spectral features are consistent with the evolution of formation of caprolactam as a result of depolymerization.

Compared with pure PA6, the PA6/clay nanocomposite has higher activation energy, lower thermal decomposition rate constants and better thermal decomposition stability (VanderHart et al., 2001). The activation energy (E_a) of PA6/clay nanocomposites containing 1.2% and 3.5% clay are 174.47 and 309.175 kJ/mol, respectively, and that of pure PA6 is only 143 kJ/mol. Using ^{13}C NMR, they observed that in the presence of modifier (dihydrogenated-tallow ammonium ion) the nylon nanocomposite began to degrade at 240 °C, whereas the virgin polymer did not. They concluded that the organic modifier was less stable. The combination of shear stress and temperature may lead to extensive degradation of the modifier and the extent of clay dispersion may not depend on the modifier.

In an intumescent EVA-based formulation, using PA-6 clay nanocomposite instead of pure PA6 (carbonization agent) has been shown to improve the fire properties of the intumescent blend. Using clay as "classical" filler enabled the same level of FR performance to be obtained in the first step of the combustion as when directly using exfoliated clay in PA-6. But in the second half of the combustion, the clay destabilized the system and increased the flammability. Moreover, a kinetic modeling of the degradation of the EVA-based formulations showed that adding clay to the blend enables same mode of degradation and the same invariant parameters as for the polyamide-6 clay nanocomposite containing intumescent blend. The increase in the flammability by the K-10 in the second half of the combustion showed the advantages of using nanoclay rather than micronclay in an intumescent system (Levchik et al., 1999).

Organically modified clay-reinforced polyamide 6 was subjected to accelerated heat aging to estimate its long-term thermo-oxidative stability and useful lifetime compared to the virgin material (Kiliaris et al., 2009). Changes in molecular weight and thermal and mechanical properties were monitored and connected to the polymer modification encountered during aging. Generally, the strong interaction between the matrix and the clay filler renders the polymer chains, mainly that adjacent to silicates, highly restrained mechanically, enabling a significant portion of an applied force to be transferred to the higher modulus silicates. This mechanism explains the enhancement of tensile modulus that the non-aged clay-reinforced PA6 exhibited (1320 MPa) with regard to the neat polymer (1190 MPa), as shown in Figure 8.

The effects of hydrothermal ageing on the thermo-mechanical properties of high-performance epoxy and its nanocomposites are also reported in the literature (Njuguna et al., 2010). It was found that the storage modulus and relaxation behavior were strongly affected by water uptake, while the fracture toughness and Young's modulus were less influenced. Dependence of tensile strength and strain at break on water uptake was found to be different in neat epoxy and epoxy–clay systems. Further improvement of the flame retardancy using combinations of the nanofiller and traditional FR-additives (e.g. aluminum trihydrate) was observed. The nanocomposites based on nanofillers and aluminum trihydrate passed the UL 1666 riser test for fire-resistant electrical cables (Beyer, 2005).

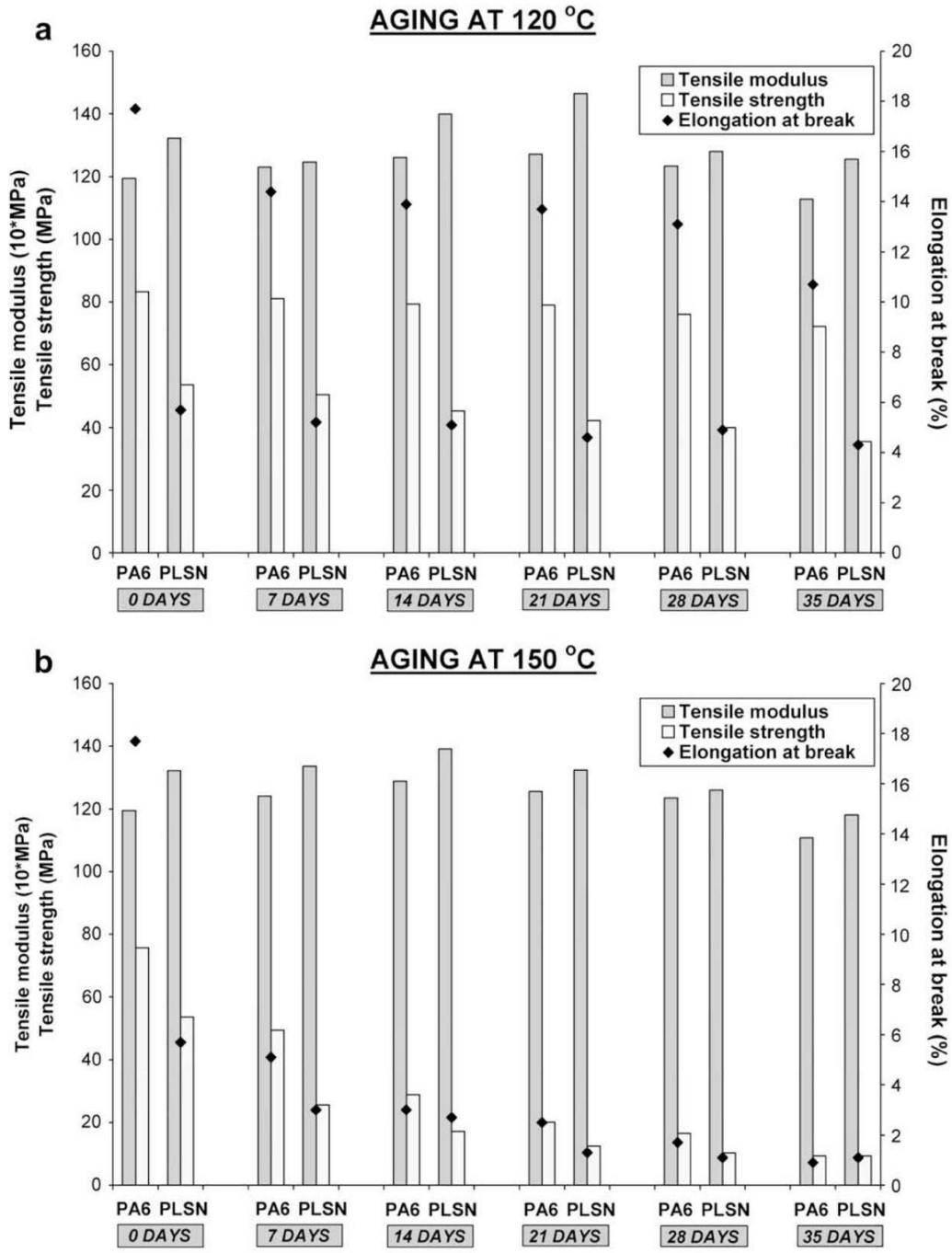


Fig. 8. Tensile properties of PA6 and PA6 nanocomposite, oven-aged at (a) 120 °C and (b) 150 °C (Kiliaris et al., 2009).

There are two factors which have opposite influences on the thermal stability of epoxy–clay nanocomposites. First factor is that the addition of clay to epoxy decreases the curing reactivity of epoxy resin. Lower reactivity of the resin generally results in lower cross-linking density of the cured resin and the longer polymer chains among the cross-linking

points. It is known that a longer polymer chain is less stable thermally than a shorter chain, so both the nanocomposites are easier to degrade than the pristine epoxy resin. Secondly, silicate layers have good barrier to gases such as oxygen and nitrogen, they can insulate the underlying materials and slow the mass loss rate of decomposition products. Moreover, exfoliated nanocomposites have better barrier properties and thermal stability than intercalated ones. In the case of intercalated nanocomposites (10 wt. % clay), the first factor is dominant, whereas for an exfoliated nanocomposites (2 wt.% clay), the second factor is dominant. Becker *et al.* (Becker et al., 2004) have found that the water uptake (in aquatic environment) was considerably reduced in epoxy nanocomposites with a particular clay loading percentage.

5.4 Electrical properties

In the conventional fiber-reinforced polymers (FRPs), fiber-orientation is usually in-plane (*x*- and *y*-direction) resulting in fiber-dominated material properties in these directions, whereas matrix dominates in the *z*-direction. Therefore, FRPs are very sensitive to intrinsic damage, such as delamination (in particular), matrix cracking and fatigue damage. Moreover, their usage as structural materials in aerospace applications has evolved from less than 5% by structural weight to 50% (mainly due to the necessity to reduce weight and gain fuel savings), which leads to many issues related to their functionalities like vibration/acoustic damping, tribological behavior, and hygroscopic properties. Therefore, for enhanced structural stability, durability and performance, it is necessary to address and accommodate these undesirable issues.

Several approaches have been adopted to tackle these problems independently, which include (a) using epoxy/elastomer blends at ply interfaces, (b) incorporating interleave viscoelastic layers, (c) reducing the mismatch of elastic properties (and stress concentrations) at the interfaces between the laminated plies, and (d) using carbon filaments in place of interleaves. These approaches have their own positives and negatives as these materials are 'functional' rather than 'structural' and their high cost, low stiffness/stiffness, compatibility/adhesion with the FRP laminates, or poor processability always result in a compromised situation.

A specific area of interest is tuning the interleave material to achieve the desired multi-functionalities or to have an enhanced effect on the desired properties compared to FRPs without interleaf layers.

For the concept of non-destructive evaluation, damage sensitivity and reinforcing effect of carbon nanocomposites could be obtained from the electrical volume and contact resistivity measurement with acoustic emissions techniques. Adding conductive particles to an isolating polymer can result in an electrically conductive composite, if the particle concentration exceeds the percolation threshold, which is the particle volume fraction required to form a conductive network through the bulk polymer. Because of their aspect ratio and strong tendency to reagglomerate, CNTs are very effective fillers concerning the implication of electrical conductivity into polymeric matrices. Percolation thresholds as low as 0.0025 wt. % have been reported using MWNTs in an epoxy matrix (Sandler et al., 2003). The percolation threshold for the materials and the dispersion process used in this work was found to be below 0.1 wt. % (Gojny et al., 2005). Conductivities of up to 2×10^{-2} S/m could be achieved with unfunctionalised CNTs. The functionalisation of CNTs with amino-groups usually increases the percolation threshold and decreases the maximum achievable

conductivity, because the graphitic structure of the nanotubes becomes more defected during the functionalisation process.

Furthermore, the average nanotube length is reduced, which explains the increasing percolation threshold (Gojny et al., 2005). Park *et al.* (Park, 2003) explored this concept by applying electro-micromechanical technique to obtain the fiber damage and the reinforcing effect of carbon nanocomposites with their content. The sensitivity for fiber damage such as fiber fracture, matrix deformation and fiber tension was highest for 2.0 vol. % CNT composites. They suggested that damage sensitivity by electrical resistance measurement might be related to closely three-dimensional network structure. For CNT composites, mechanical properties and apparent modulus indicating the reinforcing effect increased with CNT content. The researchers confirmed that, apparent modulus measurement by electro-micromechanical test could be applied to evaluate mechanical properties of fiber reinforced composites. Reinforcing effect of 2.0 vol. % CNT obtained from mechanical properties and apparent modulus measurements was the highest. In 2.0 vol. % CNT case, percolation structure was observed when compared to 0.1 and 0.5 vol. % CNT cases. Morphological trends were found consistent with the result of damage sensitivity based on electrical properties.

The optimal use of sensor technology is in itself crucial in the design, manufacturing, maintenance, and proper functioning of a number of aerospace and defense related adaptive structures and other strategic equipment. Electrode materials with carbon nanotubes resulted in better behavior than traditional carbon electrodes including good conducting ability and high chemical stability. Another possible application entails the inherent multifunctionality of CNT-based materials that lead to designs which are self-sensing - sensor skins capable of probing the environment around the vehicle could be designed so that they are part of the vehicle itself. Their multifunctionality arises from the ability of the nanotubes to be either metallic or semi-conducting based on their chirality. Due to this property, SWNT have been used to fabricate several nanoscale devices, such as field-effect transistors and molecular logic devices. Furthermore, simply changing the environment around a nanotube can change its conducting behavior. This phenomenon is being exploited in order to create sensors capable of measuring several parameters related to vehicle structural health (i.e. strain, pressure, temperature, etc.). In the context of aerospace systems, innovative lighter weight and smaller volume sensors will allow carrying out enhanced real-time prognostic health monitoring and diagnosis of aerospace and military structures, strategic tactical transportation and weapon systems. However, as lamented earlier on, there are concerns that presently used maintenance techniques cannot meet the growing demand for high reliability and readiness. New advanced built-in diagnostic techniques have to be developed which can perform damage diagnosis automatically, avoiding human error; provide advanced warning of structural failure to pilots or operators; minimize unnecessary downtime for scheduled maintenance; maintain reliability and improve safety of aging structures; reduce maintenance costs; and enhance combat readiness.

Structural Health Monitoring (SHM) is the process of implementing a damage detection and characterization strategy for engineering structures. Here damage is defined as changes to the material and/or geometric properties of a structural system, including changes to the boundary conditions and system connectivity, which adversely affect the system's performance. The SHM process involves the observation of a system over time using periodically sampled dynamic response measurements (Hiem et al., 2004).

5.5 Health and safety aspects of nanoparticles

Numerous studies have focused on studying the potential health risks of the ultrafine- and nanoparticles, in the past few years (Maynard & Aitken R, 2007; European Agency for Safety and Health at Work [EU-OSHA], 2009). The European Union funded several projects dealing with the toxicological effect of nanoparticles. The NANOTOX (Impart- Nanotox, 2010) and NEPHH (Nanomaterial Related Enviormental Pollution and Health Hazard Throughout their Life cycle [NEPHH], 2010) projects both deal with the toxicological impact of nanoparticles on human health and the environment. To do so, the properties of different nanoparticles must be characterized and a sufficient amount must be sampled for toxicological investigations. A major risk of those projects is that the nanoparticles cannot be detected, and hence cannot be examined on their toxicological impact. Particles in those size ranges are suspected to enter the human cells more easily than micro sized particles, via respiratory, dermal or oral absorption. The high biological activity can be explained by the large surface-to-volume ratio; hence many types of nanoparticles have shown toxic impact (European Agency for Safety and Health at Work [EU-OSHA], 2009; Dreher, 2004). Despite limited knowledge about the risks associated with the exposure to and the release of nanoparticles in the environment, the development of mass production of products and materials has begun (Business Communications Company [BCC], 2006).

Crucial for the assessment of the potential environmental and health risks of ultrafine- and nanoparticles are the understanding of the exposure mechanism. In relation to toxicological studies, investigation of all physical and chemical parameters of engineered nanoparticles would be ideal, but represents a major workload. A significant number of parameters can therefore be retained as a minimum for successfully conducting meaningful toxicological studies (Murdock et al., 2008). These would include:

- Particle size and distribution,
- Specific surface area,
- Crystalline structure,
- Surface reactivity and composition,
- Purity.

Therefore, attention will have to be paid to the characterization of the different properties and hence the need for feasible and reliable measurement and characterization equipment for nanosized particles is fundamental.

At present, a standard procedure to measure airborne particles in workplaces and environment is to measure the aerosol mass concentration. The simplest approach is to use a filter-based sampler comprising some form of inertial particle pre-selector. This conventional pump based filter sampling of aerosols is not the best solution for exposure assessment for airborne nanostructures. There are two reasons for that: Firstly, mass concentration, is not necessarily well-suited to the toxicity assessment of inhaled nanoparticles. Toxicity studies show that particle toxicity increases as they become smaller (Oberdörster et al., 2005); Secondly none of the existing instruments used for monitoring give specific information about particle concentration below 1 µm aerodynamic diameter (European Agency for Safety and Health at Work [EU-OSHA], 2009).

More relevant parameters for describing airborne nanostructures are criteria to relating to their size and shape. Some of the equipments developed around these indicators allow a continuous measurement. The sections 6.2 and 6.3 of ISO Standard TR 27628 include a

classification of each instrument based on continuous measurement of size, number and surface area parameters for the collected aerosol. These parameters *X*, can be described as a function of the time *t*, as shown in equation (1):

$$X=f(t) \tag{1}$$

X involves the whole aerosol or one of its particle size distribution fractions (European Agency for Safety and Health at Work [EU-OSHA], 2009). Table 2 summaries the currently available instruments on the market, to measure airborne nanoparticles.

Instrument Type	Measured Parameter (X)	Size Range (µm)	Concentration Range (particles/cm³)	Response Time (s)	Sample Flow Rate (l/min)
CPC	Number Concentration	0.003-.025	10^4-10^3	4	0.3-3
SMPS	Size Distribution, Number Concentration	0.0025-1	1-10^8	30 to 600	0.2-4
FMPS	Size Distribution, Number Concentration	0.0056-.56	10^6	1	10
ELPI	Size Distribution, Number Concentration	0.03 -10	n/a	< 5	10 or 30
APS	Aerodynamic size distribution	0.5 to 20	10^3-10^4	n/a	5
TEOM	Mass Concentration	2.5-10	1.5 µg/m³	0.5	0.5–5

APS, Aerodynamic Particle Sizer; CPC, Condensation Particle Counter; FMPS, Fast Mobility Particle Sizer; SMPS, Scanning Mobility Particle Sizer; ELPI, Electrical Low Pressure Impactor; TEOM, Tapered Element Oscillating Microbalance

Table 2. Instrument for measuring of Airborne Particles.

The instruments available at present on the market are capable to characterize airborne nanoparticles. The instruments are adequate to characterize nanoparticle properties such as particle size and concentration, as well as mass concentration. However, those instruments have several limitations and drawbacks, as low volume flows, background noises and particle losses. Furthermore, the lack of standardization makes the comparison of results obtained in different studies, which use different instruments, rather challenging. The high financial investment and the required specialist skills additional limit the different instruments. These different considerations require foreseeing a universal instrument for aerosol measuring, which would have the ability to record various parameters permitting optimum, simultaneous evaluation of (Maynard & Aitken, 2007):

- aerosol numerical, surface and mass concentration;

- an ultrafine fraction (which indeed requires definition as well as conventional respirable, inhalable and thoracic fractions who are defined in standard ISO 7708);
- Rapidly collected data and their storage for later use.

A universal instrument should be portable. At present all the instruments monitoring continuously a single parameter can be used static, because of their weight. Furthermore, concentration enriched systems, for direct exposure of cells with airborne particles needs further development in order to avoid sampling of particles with ESPs or filter, which leads to contamination and might change the original physical properties of the airborne particles.

For instance, low velocity impact of PU/MMT nanocomposites generated nanoparticles, which can be seen in the increasing of total number of particles for the period after the impact (Fig. 9). The particle increased for the first 15min after impact, after this period particle concentration decreases until it reached a normal ambient level again. Decrease of particle concentration is caused by three factors: Firstly, larger particles deposit due to gravitation; Secondly, airborne particles agglomerate to larger particles which is demonstrated by the increase of particles size over the time period; And thirdly, decrease of particle concentration is caused by the volume flow of the SMPS+C (0.3 l/min).

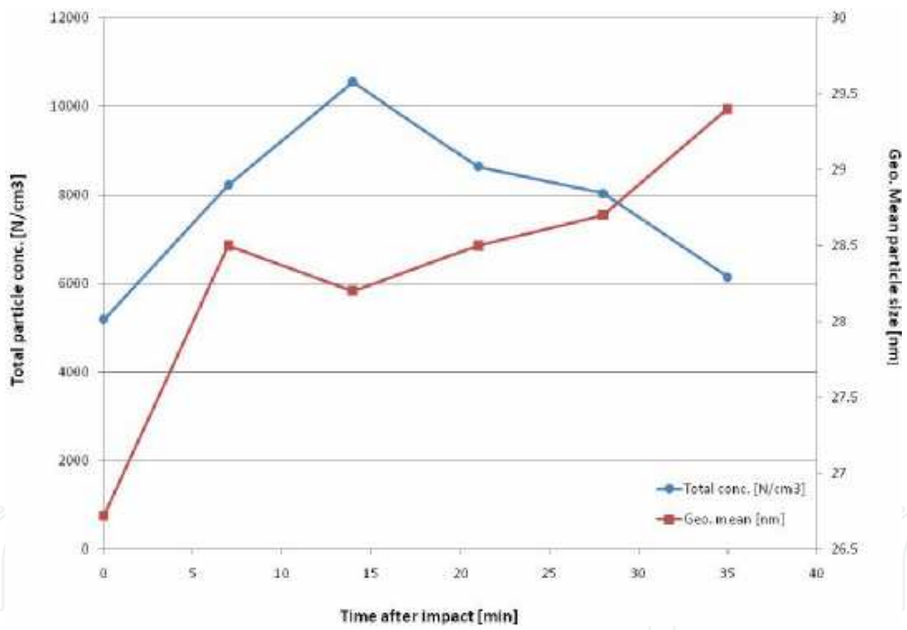


Fig. 9. Geometric mean particle size and total dependency of time after impact.

6. Applications in vehicle structures

Toyota researchers reported in the early 1990s, work based on true nylon-6–clay thermoplastic nanocomposites technology. Their results showed significant improvement of mechanical properties, with small amount (4.2wt%) filler loading. The strength increased more the 50%, the modulus doubled and additional improvement of thermal properties were obsereved (Oriakhi, C.O. 1998; Kozima, 1993). Since then, polymer nanocomposites are manufactured commercially for diverse structural vehicles applications. The consumption of

clay-based polymer nanocomposites will increase to 181,094 metric tons and 692.3 million USD by 2014. (Business Communications Company [BCC], 2006). For example, one of the leading automotive manufacturers is using 300000 kg of nanoclay composites annually for various automotive exterior part/panel applications at present (Keles et al., 2009). However, other nanofillers have found applications for exterior vehicle panels. Carbon nanofibres have been used in automotive exterior panels for weight reduction, in bumpers and fenders. Figure 10 shows the potential application of for nanoclay and carbon nanofibers in automotive applications. As shown in figure 10 the opportunities of clay Nanocomposite lay in the increased stiffness and reduced density, which will lead to thinner wall stock and lower part weight. Additionally improved scratch resistance and reduced thermal sensitivity can be achieved. The incorporation of carbon nanofibers in sheet moulded compounded body panels, improves surface quality and can be used for improved toughness and thinner panels.

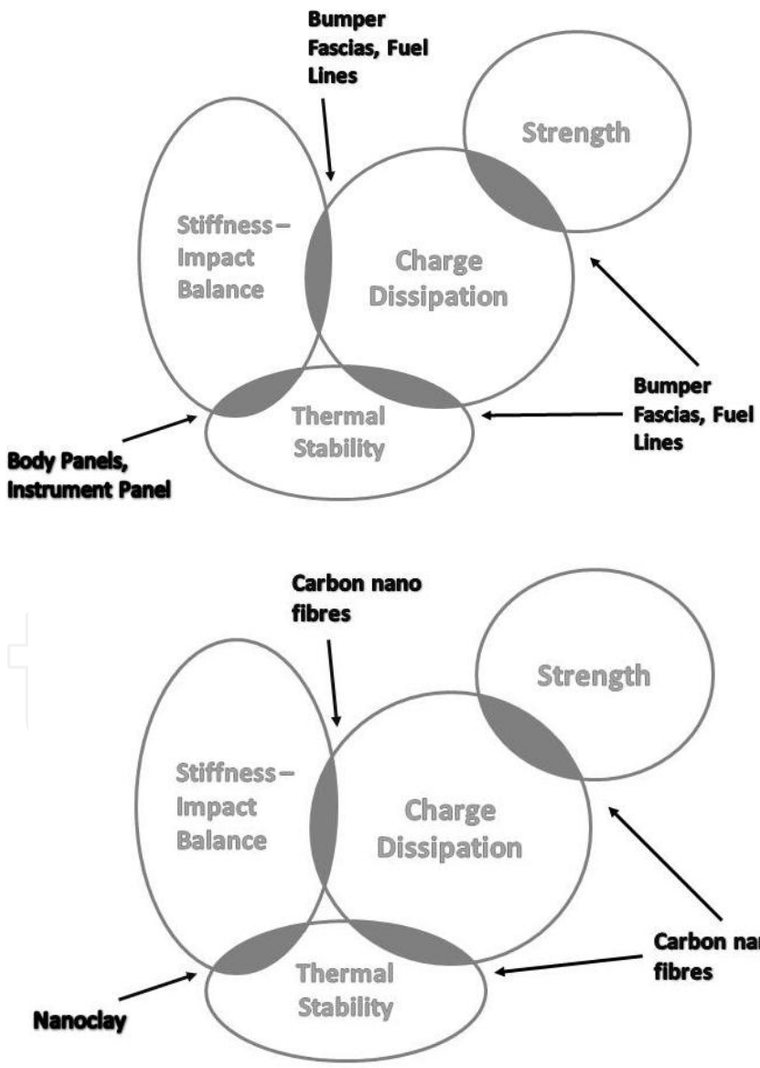


Fig. 10. Potential Automotive Applications of Nanocomposites.

Nevertheless, the nature of the constrained region as the mechanism of reinforcement has yet to be satisfactorily explained and property improvements have yet to be confirmed on commercially available nanocomposites using standard processing techniques. In automotive applications such as side mouldings, trim and panels in General Motor's vehicles, nanoclay compounds have advantages including reduced weight, a wider processing window, improved colourability and improved scratch and mar resistance. A consequential research focal point that has emerged relates to the known deleterious effects of the automobile exhaust air pollutant NO_x on nylon-6, in efforts to protect the nanocomposite from degradation (Njuguna et al., 2009).

7. Conclusions

Numerous studies have demonstrated that nanofiller have potential in improving both stiffness and energy absorption of polymer and/or conventional fiber-reinforced polymer composites. Tube crushing experiments have been widely used for measuring energy absorption in conventional structural composites over large displacement ranges. Energy absorption of nanocomposites as characterized by quasi-static fracture or low-speed impact energy absorption is caused by different energy absorption mechanisms in nanocomposites. The influence of some key control parameters such as shape and size of nanofillers, mechanical properties of nanofillers and matrix materials, interfacial adhesion, interphase characteristics, as well as the volume fraction and dispersion of fillers in the matrix. The complex mechanisms and numbers of control parameters make it difficult to obtain an ideal nanocomposite.

Due to numerous potential applications such as crashworthy transportation vehicle structures, protective armor, noise and vibration control, fracture-resistant structures, and multifunctional materials and structures, further research on energy absorption capacity of nanocomposites is crucial. Overall there is essential requirement to investigate the durability of these nanocomposites in different environmental conditions to extend the applicability of these hybrid materials. Further, the current limited knowledge of the degradation mechanism of polymer nanocomposites has led to development of more efficient stabilizers for improving the product performance on one hand and on the other, development of sensitizers to produce degradable polymers and to preserve the environment.

Further, through nanoparticles reinforcement, an electrically conductive matrix could provide enhanced feasibilities including stress–strain monitoring or damage detection. The application of an electrical field is known to orient the nanoparticles in the in-field-direction, which may result in an increased efficiency of the *z*-reinforcement of the laminates. As a further benefit, the electrical conductivity in *z*-direction should be increased with this approach. Nanoparticles and especially CNTs provide a high potential for the modification of polymers. They are very effective fillers regarding mechanical properties, especially toughness. Besides, they allow the implication of functional properties, which are connected to their electrical conductivity, into polymeric matrices. The electro-micromechanical technique had been studied as an economical non-destructive evaluation method for damage sensing, characterization of interfacial properties, and non-destructive behavior because conductive fiber can act as a sensor in itself as well as a reinforcing fiber.

The degradation of polymers has harmful aspects as well as beneficial aspects. If unchecked it can play havoc with a polymer nanocomposites performance, if uncontrolled it can lead to safety hazards of fire and toxicity, but if properly harnessed it can be used for producing

new and better materials. It will be worthwhile to focus further studies with nanoparticulates such as clay, carbon nanotubes, metal oxides, metal salts in the aspect of degradation in an environment where they are to be utilized in specific aerospace and military applications. Fundamental to the success of nanotechnology is its perceived safety by the public. Many concerns have been aired concerning the use of manufactured nanoparticles.

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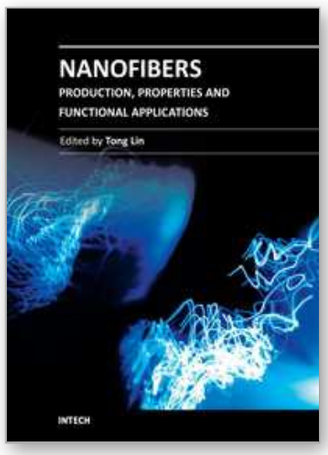
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As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with a number of novel properties for advanced applications. This book is a compilation of contributions made by experts who specialize in nanofibers. It provides an up-to-date coverage of in nanofiber preparation, properties and functional applications. I am deeply appreciative of all the authors and have no doubt that their contribution will be a useful resource for anyone associated with the discipline of nanofibers.

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