DURABILITY AND MECHANICAL PROPERTIES OF POLYMER-LAYERED SILICATE NANOCOMPOSITES

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ABSTRACT

Chemically treated layered silicates (clays) can be mixed with polymer materials to form a nanocomposite in which clay layers are evenly distributed throughout the material. These high aspect ratio clays have been reported to alter the properties of the polymer by a number of mechanisms; increasing the strength and fire resistance and reducing permeability. The objective of this paper is to present an introduction to nanocomposites and investigate the potential for nanocomposites to be used in adhesives. Tensile, compressive and permeability tests are reported and show that the possible advantages of nanocomposites depend on the properties of the base resin or adhesive. Mechanical property advantages may be achieved with more elastomeric polymers while little improvement is generated in highly glassy materials. The durability of some adhesives may be improved by reducing the permeability of the polymer; however, the type of adhesive and ingressing agent have a large influence on the attainable reductions.

KEYWORDS

Adhesives, durability, nanocomposites, mechanical testing.

INTRODUCTION

Nanocomposites are a new and developing area that has a wide range of potential application. Their use was first demonstrated during the early 1990’s when they were incorporated into thermoplastic resins. The technology has progressed through to thermosets, fibre composites and adhesives. There has been a wide range of claims made about the property improvements that these materials can generate, focussing on the mechanical, permeability and fire resistance properties. Many of these claims have been contradictory and property advantages are far from constant between different types of polymer. This paper presents an introduction to nanocomposites and investigates the application of nanocomposite technology into adhesive polymers.

Clay Types and Structure

The clay used in nanocomposites are:

- of high strength and stiffness along their length, reported to be higher than glass fibres (Luo & Daniel 2003).
- of high aspect ratio enabling large surface areas (700m²/g) to be in contact and bond with the polymer.
- modified more easily than most other types of clay; this high level of intercalation chemistry enables the clays to be chemically altered to aid their bonding and dispersion in the polymer.
- naturally occurring and can be purified at a relatively low cost.

These sheets are 0.96nm thick and typically about 250nm in length and width. The large surface area makes them exceptional at altering the properties of a polymer. Between the layers is a gap known as the “gallery layer”; unmodified clays have a small gallery layer. The spacing can be modified when used in nanocomposites, the way in which this gap changes and the final size of the gallery layer will influence the properties of the resulting nanocomposite.

Chemical Modification

Clays are naturally hydrophilic and are immiscible in organic liquids; therefore, the clay must be altered to become organophilic, this modification is known as compatibilisation. The most common compatibilisation
process is onium-ion modification; a small hydrocarbon chain (surfactant) is bonded to the surface of the clay layer that enables it to be wetted by and mix with organic liquids.

**TYPES OF POLYMER-LAYERED SILICATE NANOCOMPOSITES (PLSN)**

The way in which the clay layers are dispersed in the polymer will influence their level of interaction with the polymer, affecting the material properties. There are three distinct types of clay dispersion that can be formed by the introduction of these clay layers.

**Conventional Composites:** If the clay layers and polymer are not compatible, the surface energies are incompatible for wetting, and consequently no polymer will penetrate the gallery layer. There will be no, or very little, bonding between the clay and the polymer; therefore, the clay will provide little mechanical reinforcement.

**Intercalated Nanocomposites:** An intercalated nanocomposite is formed when the clay layers are separated by a fixed amount. The clay layers will reinforce the polymer, although the fixed layer separation is unable to provide the optimum level of reinforcement.

**Exfoliated Nanocomposites:** An exfoliated nanocomposite is formed when the clay layers are dispersed in the polymer with random separation and orientation. The clay layers will be sufficiently separated and randomly orientated to allow full interfacial bonding and to contribute all their strength to improve the properties of the nanocomposite.

**PROPERTY IMPROVEMENTS**

The property improvements generated by the inclusion of nanoparticles in polymers have been well researched since the first nanocomposites were produced by Toyota researchers (Okada *et al.* 1993) using polyamide-6 in the late 1980s and early 1990s. The majority of polymers have been used to construct nanocomposites and all have shown improvements in mechanical properties to varying degrees. Recent research has focussed on the use of thermoplastic resins, as these types of nanocomposites are commercially viable for small-scale products such as food packaging. However, many thermosets have also been used; epoxy resin systems typically used are amine cured Bisphenol A and F resins.

The increase in mechanical properties can be attributed to the high strength and stiffness clay layers acting as short randomly dispersed fibres, transmitting stress through the specimen. The mechanism responsible for the improved barrier resistance is due to the increased path length through the nanocomposite that must be taken to negotiate around the clay layers (Neilson 1967). The tortuous path that an ingressing agent must take can be made longer or shorter depending upon the clay loading applied to a nanocomposite.

**NANOCOMPOSITE RESEARCH**

The majority of research work undertaken to date relating to nanocomposites has been mainly associated with pure polymers, but investigations are now being extended to fibre-matrix composites and adhesives. Some work has been carried out into glass fibre/epoxy nanocomposites (Haque *et al.* 2003, Subramaniyan *et al.* 2003). Most research conducted in the early evolution and assessment of polymer-clay nanocomposites was carried out by chemists and material scientists. This led to production, characterisation and property evaluation of the nanocomposites, with little application of the technology.

**NANOCOMPOSITE ADHESIVES**

Previous researchers have shown that most nanocomposites can improve the mechanical and barrier properties of the polymer in which they are applied, whether thermoplastic or thermosetting polymer. The transfer of this technology to adhesives would represent an efficient way of improving the durability of adhesively bonded joints while potentially improving their mechanical performance. However, the high viscosity of adhesives presents a challenge with respect to the processing of these materials. In order to attain a high level of property improvement an exfoliated or partly exfoliated/intercalated structure must be formed. This can be achieved relatively easily in liquid epoxy resins where the processing can be performed on a basic resin with few additives. However, commercially available adhesives are highly viscous and contain many additives to improve in-service properties. The use of solvents or high temperature processing would be required to apply the organoclay to the base part of an adhesive polymer. The adhesive could then be applied as normal with the
organoclay within the adhesive. However, the formation of an adequate clay morphology may not be created due to the high viscosity of the adhesive during cure, investigation into this aspect would be required.

EXPERIMENTAL INVESTIGATION

Provided the organoclay could be introduced into the adhesive and an adequate clay structure obtained the improvements in the properties would be similar to those in a non-adhesive type polymer. The basic mechanical and barrier properties of two different epoxy systems were investigated to discover the way in which organoclays can modify the properties of polymers. Due to the difficulties in the processing of adhesives a basic epoxy resin and two different curing agents, representing each extreme in the glassy-elastomeric state to cover all types of adhesives were used to produce nanocomposites to test the mechanical and permeability properties.

Materials

The resin component of the nanocomposite was a low molecular weight DGEBA with no diluents or additives. Two curing agents were used to attain results from two different systems, a high performance glassy system (Ethacure 100, diethyltoluenediamine) and the other a more elastomeric lower performing system (Polypox H205, poly(oxypropylene)diamine). The organoclay used was Nanomer I.30E from Nanocor, a leading distributor in organoclays. This nanoclay was selected after a trial with a number of different organoclays to select the one that would form the best clay structure.

Nanocomposite Preparation

The morphology of a nanocomposite is dependent upon temperature, time and shearing rate of the mixing. Direct mixing methods alone will not break down the primary clay particles to form a uniform material. The nanocomposites formed still retains a micro-aggregated structure, similar to all direct mixing methods. Uniform nanocomposites can only be achieved through high-shear mixing techniques such as high-speed dissolvers, extensive ultra-sonics, grinding or high pressure mixing (Liu et al. 2005).

Nanocomposites were processed as follows;
- resin and organoclay were mixed together by hand in the required quantities until the clay was roughly mixed.
- resin and organoclay were stirred at 750rpm for 4 hours at 80-90°C.
- resin and organoclay were mixed in a vertically stirred grinding media mill with 2mm glass beads for 3 hours at 2000rpm until all large clay particles had been removed.
- the resin was fully degassed, the curing agent was added and cured.

TENSILE PROPERTIES

Tensile tests were conducted using 125x12x6mm specimens reduced to 10mm in the central 50mm of the specimen; specimens were tested at 1mm/min until failure. Polypox and Ethacure specimens of 0, 5 and 10wt% I.30E nanoparticles were manufactured by the method described above.
The results from the tensile tests are summarised in Figures 1 and 2, showing the relative ultimate stress and modulus of the nanocomposites compared to the pristine polymer. The Polypox nanocomposites achieved a 14.2 and 28.6% increase in tensile modulus at 5 and 10wt% organoclay loading respectively. However, the increase in ultimate stress was smaller and did not increase proportionally with increasing clay content. The increase in ultimate stress was 12.2 and 4.4% at 5 and 10wt% clay loading respectively. The high clay loading at 10wt% leads to a slightly premature failure that is not experienced at 5wt%.

The Ethacure system performed less well with the organoclay providing a modest improvement in tensile modulus but reducing the ultimate tensile stress. The Polypox system is more easily reinforced than the Ethacure due to the low density of cross-linking creating a more elastomeric material. The Ethacure material is a highly glassy densely cross-linked system in which any small impurity will generate high stress concentrations and lead to premature rupture of the material.

**COMPRESSIVE PROPERTIES**

Compression tests were carried out on 14mm diameter cylinders 28mm long, loaded at 0.5mm/min. Polypox specimens of 0, 2, 5 and 10wt% and Ethacure specimens of 0 and 5wt% I.30E nanoparticles were manufactured by the method described above. The relative properties of the Polypox nanocomposites are shown in Figure 3. The Polypox nanocomposites achieved an increase of 5.3 and 25.9% in compressive ultimate stress and compressive modulus respectively. While the compressive modulus increased with direct proportionality to the clay loading the ultimate compressive stress appears to reach a critical loading between 2.5 and 5wt%. After this critical value, little increase in ultimate compressive stress can be achieved with increasing clay loading.

These increases were much higher than those of the more glassy Ethacure nanocomposites in which increases of 3.9 and 4.5% were found for the ultimate compressive stress and compressive modulus respectively. In a similar way to the tensile properties the level of reinforcement that can be obtained depends on the relative degree of glassy-elastomeric characteristic of the resin system.

The mechanical properties that may be achieved with any form of polymer or adhesive nanocomposites will depend on the physical nature of the base material. If the polymer or adhesive is highly glassy there will be little improvement in the physical properties of any nanocomposite produced. However, if the polymer or adhesive is of a slightly more elastomeric type system some reasonable improvements in the physical properties may be achieved.

**PERMEABILITY**

Permeability tests were undertaken to gain an understanding of the way that organoclays can alter the permeability of polymers. Gravimetric tests were used to monitor the uptake of agents into different types of polymer system. Specimens of 125x12x6.4mm were prepared; although not standard, this specimen geometry was chosen so that flexural tests could be performed on the specimens after saturation. Specimens of Polypox

![Figure 3. Relative compressive properties of Polypox nanocomposites.](image-url)

(●) Compressive modulus and (▲) ultimate compressive stress.
and Ethacure containing 0, 5 and 10wt% 1.30E organoclay were produced, three specimens of each type being
tested. Unmodified clay of the same type that is used  in the organoclay was used to prepare 5wt% clay filled
composites using the Polypox system. Two different ingressing agents, water and one solvent were used to
assess the specimen permeability. Distilled water and acetone were selected and placed with the specimens in
test tubes for the duration of the tests. The specimens in water were maintained at 50°C and the acetone at room
temperature. Specimens were removed for their test tube, surface dried and weighed on a 0.1mg precision
analytical balance periodically.

The uptake of acetone into Polypox specimens can be seen in Figure 4. There appears to be only a small
reduction in the acetone uptake in the Polypox specimens and little difference between the 5 and 10wt%specimens. The average overall acetone uptake of both 5 and 10wt% nanocomposites is about 0.85 times that of
the pristine polymer. The specimens produced from the unmodified clay absorbed the solvent much faster and
broke up long before the pristine and nanocomposite specimens. The clay layers in the unmodified specimen are
not separated and have no polymer between the clay laye rs. These spaces between the clay layers can be taken
up by the solvent, increasing the amount of acetone absorbed by the specimens.

The uptake of acetone into Ethacure specimens can be seen in Figure 5. The rate of acetone uptake of the
nanocomposites is vastly reduced compared to the pristine polymer. The pristine polymer has reached
equilibrium uptake after 2700 hours, while the nanocomposite specimens, assuming the rate of uptake remains
constant, should reach equilibrium at around 5000 and 8800 hours for 5 and 10wt% respectively. The average
overall rate of acetone uptake (before reaching equilibrium) for the 5 and 10wt% specimens is 0.47 and 0.28
times that of the pristine material. These values are close to the theoretical values predicted by Neilson’s tortuous
path model, 0.34 and 0.2 times for 5 and 10wt% nanocomposites respectively for a perfectly exfoliated
nanocomposite with a clay aspect ratio of 200.

The uptake of water into Polypox specimens can be seen in Figure 6. The nanocomposites do not appear to have
altered the amount of water absorbed. The 5wt% unmodified specimens have again absorbed almost twice the
amount of water as the other specimens for the same reasons as those highlighted above. The uptake of water
into Ethacure specimens (Figure 7) was also not improved by the organoclay. Although the clay morphology is
the same in all Ethacure specimens in both water and acetone the affect of the organoclay is very different. The
permeability reductions attainable in layered silicate nanocomposites are often stated to be dependant solely
upon clay morphology due to creation of a tortuous path. However, the clay morphology in all the Ethacure
specimens was the same but the permeability reductions obtained for water and acetone are dissimilar. The
permeability of the nanocomposites must be affected by more than just the clay morphology. The reductions in
permeability that can be achieved are heavily dependant upon the interaction between the ingressing agent and
the polymer. Therefore, potential permeability reductions will depend on the specific polymer and ingressing

Figure 4. Uptake of acetone into Polypox specimens. (●) 0wt%, (▲) 5wt%, (●) 10wt% and
(+) 5wt% unmodified clay.

Figure 5. Uptake of acetone into Ethacure specimens. (●) 0wt%, (▲) 5wt% and (●) 10wt%.
agent, with some polymers achieving a permeability decrease while others would be unaffected. However, the presence of a solvent is not a common occurrence and the majority of ingressing agents occurring during the service life of a component are water based. This will require further research with different polymers to establish the types of polymer in which permeability reduction in water could be achieved.

CONCLUSIONS

The properties of any nanocomposite are dependant upon the base properties of the resin or adhesive system used. The mechanical properties will depend on the position of the material within the glassy-elastomeric property range. The barrier properties will also depend on the base material; the affinity the material has with the ingressing agent appears to affect whether any reduction in permeability can be achieved. This may result in permeability reductions being achievable in some and not other polymer or adhesives depending upon the specific types of chemicals found within the system. This would mean that any new material used to form a nanocomposite would have to be tested to determine whether barrier improvements could be achieved for the specific agent that the component will be exposed to during service. This series of tests, although not carried out using a standard adhesive, displays the general types of properties that can be developed with any form of epoxy amine cured polymer. Research will continue into commercially available adhesives to discover if exfoliated nanocomposites can be achieved and explore the resulting properties of any adhesive nanocomposite generated.

REFERENCES