The Effect of Hybrid Nanoparticle Additives on Epoxy-Nanocomposite Behavior and Morphology

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ABSTRACT: Amine modified polyhedral oligomeric silsesquioxane (POSS-NH$_2$) was used to modify sodium montmorillonite (MMT) nanoclays for improved dispersion in epoxy resin. The dispersion of the clay particles was inspected using scanning electron microscopy, energy dispersive spectroscopy (EDS) and X-Ray diffraction and the thermal properties compared using differential scanning calorimetry (DSC) and thermogravametric analysis. The introduction of the amine-POSS was found to have a positive effect on the dispersion of the MMT clays and prevented agglomeration. The absence of clay agglomerates lead to an increase in glass transition temperature (T_g) from 44°C in the samples with the untreated clay up to 54°C in the samples with 10% additional POSS-NH$_2$. The addition of POSS-NH$_2$ initial increase of the weight loss ($T_{d\ 5\%}$) but slowed down the rate of degradation due to the formation of an inert silica layer and eventually leading to an increased charyield. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3212–3216, 2011

Key words: epoxy; nanocomposites; POSS; montmorillonite; structure-property relations

INTRODUCTION

Nanocomposites of epoxy resin materials are a popular material choice for the engineering industry due to their unique organic-inorganic characteristics and enhanced physical properties such as improved thermal stability, dielectric breakdown strength, tensile strength, hardness, and many other attributes.[1–6] Montmorillonite (MMT) clay is a popular nano-additive because it is readily available, environmentally friendly and low cost, but its efficacy as a nanocomposite constituent is dependant on the dispersion of the clay in the epoxy matrix. Poor dispersion can result in agglomeration and worse rather than improved properties. MMT clays consist of stacked silicate layers with a typical thickness of 10 Å[6] which unmodified are hydrophilic and tend to form self-assembled multilayer intercalated structures which have a tendency to agglomerate.[4] To create a well-dispersed exfoliated structure, the MMT clay needs to be treated to reduce its polarity and make it compatible with most polymer matrices. Surface treatment can be used to open up the interlayer space allowing more movement of polymer in between the layers and improve the miscibility of the clay and the epoxy matrix.[7] Organic ammonium has been used to create a cation exchange effect on the clay surface to improve the dispersion, but using such surfactants often has a detrimental effect on thermal properties.[8]

Polyhedral oligomeric silsesquioxane (POSS-NH$_2$) nanoparticles (Fig. 1) are organic-inorganic hybrids with the empirical formula R(SiO$_{1.5}$)$_n$ where n is an even number and R the organic chain. Significant property enhancements have been found for some epoxy-POSS systems.[9,10] Additionally it has been reported that POSS can positively affect the dispersion of MMT nanoclays in various polymer systems.[1,8–12] Being silicate based the POSS family of materials also impart good thermal stability.

In this study, a commercial DGEBA epoxy resin was used, cured as standard with a diamine curing agent. Additional Na$^+$-MMT clay were added with varying amounts of POSS-NH$_2$ and characterized for the effects of the nano-additives on the thermal properties and morphologies of the resulting nanocomposites.

EXPERIMENTAL

Materials

Clay nanopacticles Cloisite 15A, were obtained from Southern Clay Products and the Hunstman CY219 DGEBA based epoxy resin and HY5160 curing agent were used as the matrix. The hybrid organic/inorganic POSS-NH$_2$ nanoparticles (hereafter described as POSS) were produced our laboratories via a process described previously.[13]

TABLE I
A Summary of the Thermal Properties

	T_g (°C)[a]	$T_{d\ 5\%}$ (°C)[b]	$T_{d\ 50\%}$ (°C)[c]	Char yield %[d]
Ref epoxy	49	313	400	5.4
3% Clay	46	307	402	10.2
3% Clay 1% POSS	28	338	408	12.7
3 % Clay 3% POSS	43	277	403	11.3
3% Clay 10% POSS	40	259	426	18.9
10% POSS	51	220	412	13.2

[a] Glass transition temperature.
[b] 5% degradation temperature.
[c] 50% degradation temperature.
[d] Char yield at 800°C.

Nanocomposite preparation

The commercial epoxy and curing agent were used in the recommended formula and any included amine containing POSS was in addition to those in the original system. To mix the components, the hardener was heated to 40°C and POSS and clay were added separately, and the mixture was stirred mechanically for 30 min. The epoxy resin was then added, and the stirring was continued for $\sim$ 15 min. The composite mix was cast into a mould. Samples were heat treated at room temperature for 12 h and held at 60°C post curing for 24 h to enable the removal of residual solvents.

Microscopy

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis were carried out using a JEOL JSM-5900LV scanning electron microscope equipped with a OXFORD Isis spectrometer with germanium detector. The fracture surface of the cured resin nanocomposite was investigated with SEM for morphological characterization. EDS mapping of silicon, carbon, and oxygen was carried out over the same area as imaged.

Thermal analysis

Small samples were cut from the cast composites for thermal analysis. Thermogravametric analysis (TGA) was carried out on a Perkin Elmer TGA 7 instrument under a nitrogen atmosphere at a heating rate of 20°C/min from 49 to 850°C. Sample mass was between 12 and 17 mg. Selected samples were also run at 10°C/min and showed no evidence of thermal lag. Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer Pyris 1 to verify that there was no residual unreacted matter and determine the glass transition temperature (T_g). Samples of 4–5 mg were used in standard aluminium pans. Heating from −20 to 200°C, followed by holding isothermally for 2 min and cooling from 200 to −20°C,

was repeated twice at 10°C min^{-1} under nitrogen atmosphere. The gas flow rate was 40 mL/min. The T_g was measured during the second heating ramp.

X-ray diffraction (XRD)

XRD spectra were collected on a −5000 X-ray diffractometer with monochromatic CuKα radiation over the Theta range of 2 to 12°.

RESULTS

Microscopy

SEM and EDS mapping were carried out on the fracture surface of each sample to inspect the fracture mechanisms and determine if any agglomeration was evident. The EDS inspection mapped the distribution of silicon, which is present in low amounts in the epoxy and is a major constituent of the POSS and clay nanoparticles.

The neat epoxy exhibits a smooth fracture surface indicative of brittle fracture behavior typical of an unfilled epoxy. The sample containing 10% POSS without additional clay also exhibits the same smooth fracture surface indicating that the POSS was evenly distributed in the epoxy matrix.

The fracture surface (Fig. 2) of the samples containing clay has considerably different fractographic features, it can be observed from the surface roughness that the crack propagation was deflected and perturbed because of the presence of clay nanoparticle agglomerates. These agglomerates can be observed in the EDS map of Si. Such crack deflection would indicate an increase in fracture toughness of a material. In some places, microvoids can be seen. The clay agglomerates are likely to act as stress concentrator sites which could lead to de-bonding of the
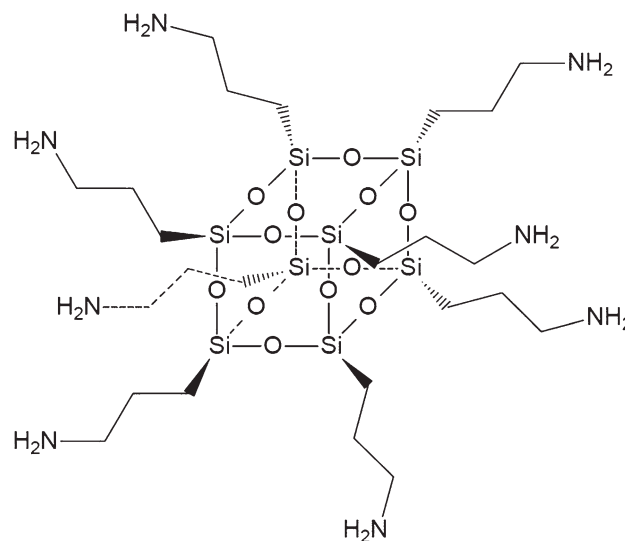
Figure 1 Chemical structure of POSS-NH$_2$ monomer.
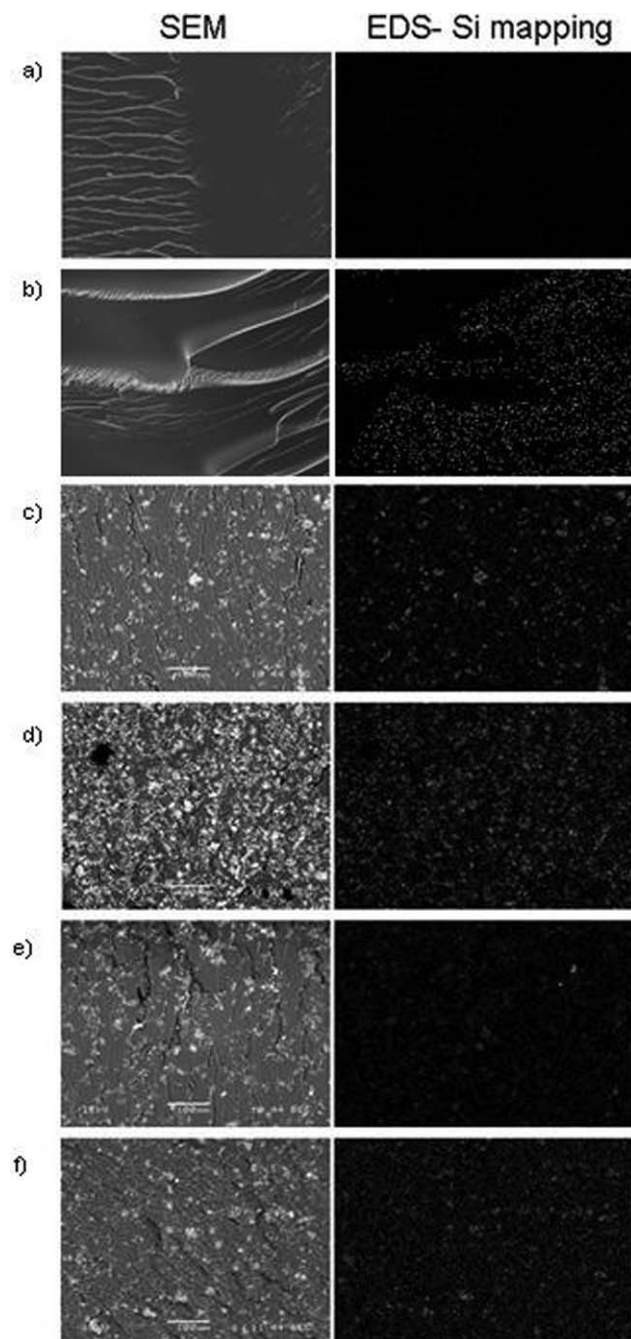
Figure 2 SEM images and energy dispersive spectroscopy mapping of facture surfaces of (a) neat epoxy, (b) epoxy 10% POSS (c) epoxy 3% MMT clay, (d) epoxy, 3% MMT clay, 1% POSS, (e) epoxy, 3% MMT clay, 3% POSS, (f) epoxy, 3% MMT clay, 10% POSS. All images are shown at ×200 magnification.

epoxy matrix–clay interface or break up or delaminate the clay agglomerates, both of which would lead to the formation of microvoids.

XRD

Figure 3 represents the XRD patterns of the samples containing nanoclay and varying amounts of POSS.

In the sample containing clay and no POSS a reflection peak at 5.1° 2θ which is assigned to the (001) basal plane indicating that the clay particles are aligned in a layered intercalated structure within the epoxy matrix. This is symptomatic of the agglomerates observed in the SEM. With the addition of POSS to the epoxy nanoclay system, the reflection peak reduces in intensity, indicating that the nanoclay is becoming increasingly dispersed in the matrix forming a more exfoliated structure (as shown schematically in Fig. 4). The results show that the addition of 3% POSS reduces the degree of intercalation, but the addition of 1% has a greater effect and 10% effectively creates an almost entirely exfoliated structure. It can be noted that the peak position does not significantly alter with addition of POSS indicating the d-spacing, and therefore the distance between the platelets is largely unaffected. This implies that the POSS functions improve the miscibility of the MMT clay layers rather than increasing the interlayer distance.

DSC

DSC was used to measure the glass transition temperature of the samples after curing. The results (shown in Fig. 5 and Table 1) show that the reference sample has a T_g around 49°C. Other articles[14] have reported that the addition of clay restricts the chain movement increasing the T_g, however in this case the addition of 3% clay slightly reduced the T_g of 46°C due to the poor distribution of the clay and the resulting agglomerates acting in a small extant as a plasticizer.[15] The effect is even more pronounced with the addition of 1% POSS decreasing the T_g to 28°C.

With addition of POSS to the system, we have introduced an increased number of crosslinking sites
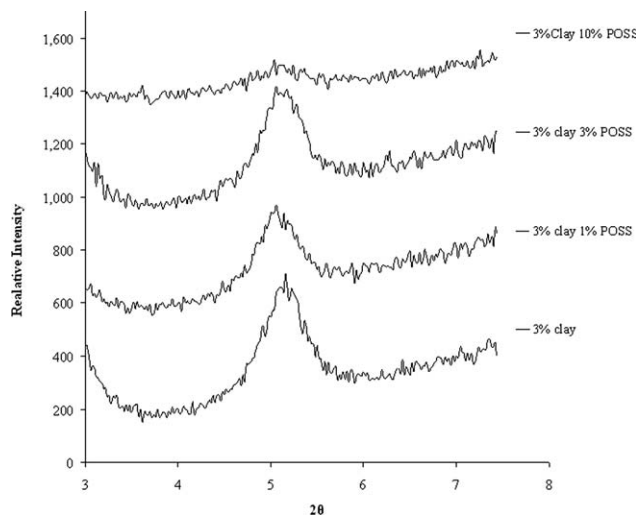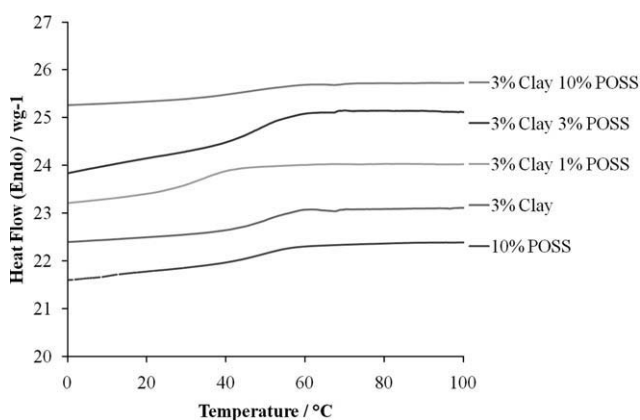

Figure 3 XRD spectra.
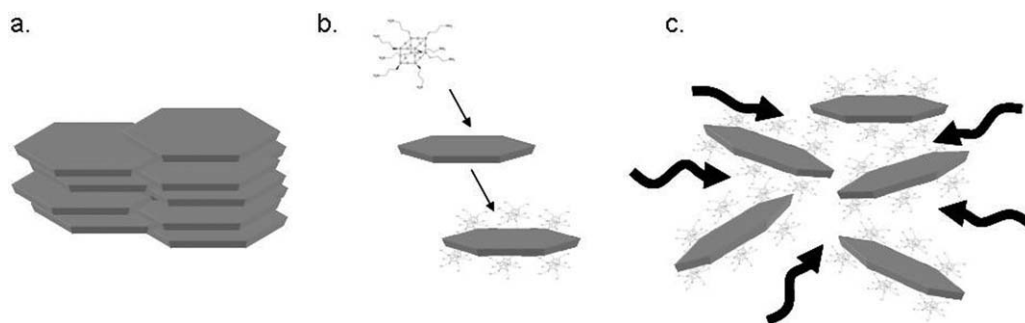
Figure 4 Schematic illustration of the mechanism of dispersion. (a) Untreated nanoclay platelets form intercalcated stacks, (b) surface treatment with POSS –NH$_2$ reduces the surface polarity, (c) the treated surface is more organophilic and allows permeation of the epoxy matrix.

to the network, this would contribute greatly to a stiffer network with a high T_g.[16] However, the epoxy system has only a limited number of reactive sites meaning that at higher POSS concentrations the free epoxy reactive sites will be saturated and the addition of more POSS will not effect the crosslinking density further. This is demonstrated by the sample with 10% POSS without clay, which despite the manifold increase in amine groups in to the system has only a marginal increase in T_g to 51°C. Whilst also affecting the crosslinking density, the addition of POSS is improving the clay dispersion and the well dispersed clay nanoparticles retards chain movement more effectively. Thus leading to a further increase in the network stiffness and T_g.

TGA

Thermogravimetric analysis was carried out on each sample to measure the effect of nanoparticle additives on the thermal stability of the epoxy matrix. The TGA weight loss plots are shown in Figure 6 and the summary of results in Table 1. The addition of 3% clay did not make a discernable difference to the thermal stability of the material

when compared with the neat epoxy giving $T_{d\ 5\%}$ 307.5 and 313.9°C, respectively. However, the final char yield was increased due to the additional clay content from 5.41% for the neat epoxy and 10.24% for the clay as we know from the product data sheets that the cloisite clay is stable up to temperatures exceeding this test range. The sample containing 10% POSS does show initially poorer thermal stability and a $T_{d\ 5\%}$ of 220°C, significantly lower than the reference sample. Although the initial thermal stability is worsened, the rate of degradation at higher temperatures is actually slower than that of the reference material resulting in a $T_{d\ 50\%}$ which is an improvement compared to the reference and the epoxy clay system.

The addition of 1% POSS to the clay/epoxy matrix increased $T_{d\ 5\%}$ to 338.5°C and this could be due to the increase in crosslink density. The higher char yield is again due to the additional clay and silicate from the POSS. The samples treated with 3 and 10% POSS had a lower $T_{d\ 5\%}$ at 277.7 and 259°C, respectively. This implies that the addition of POSS

Figure 5 DSC thermograms.
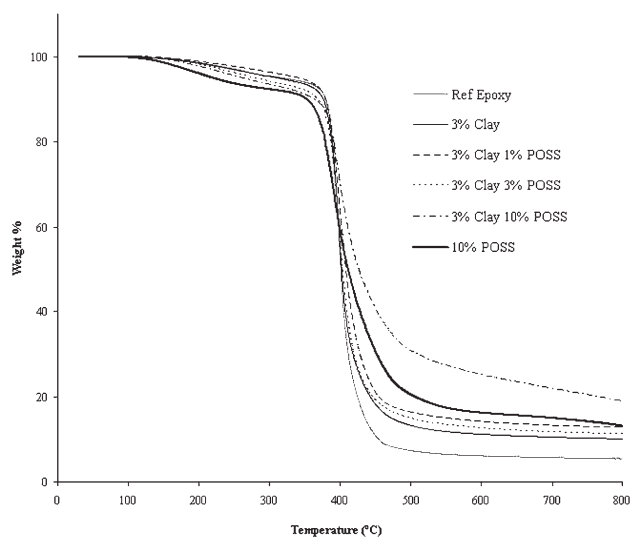
Figure 6 Thermo gravimetric analysis (TGA) curves.

nanoparticles aids the thermal stability of the epoxy clay systems.

When POSS degrades, it leaves an inert silica layer which can form a protective layer on the surface of the material preventing further oxidation of the inner part of the matrix.[4,17,18] Earlier reports[19,20] have suggested that 10% POSS loadings were sufficient to form a silica layer that could cover the material surface thus explaining why the decomposition of the 10% POSS occurred at the slowest rate.

CONCLUSIONS

The effect of amine-POSS on the morphology and thermal properties of epoxy-clay nanocomposites were investigated. Using SEM, EDS, and XRD, we have determined that the NH_2-POSS had a positive effect on the dispersion of the nanoclay platelets in the epoxy matrix. DSC revealed that with increasing POSS content the T_g of the epoxy clay rises due to the improved chain retardance from the better dispersed clay platelets. Furthermore, TGA revealed that the addition of POSS had an effect on the thermal stability of the system, initially decreasing the $T_{d\ 5\%}$ but slowing down the rate of degradation due to the formation of an inert silica layer, and eventually leading to an increased charyield.

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