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Structure–property relationships and modeling of the mechanical properties of a high-temperature resistant thermoset nanocomposite

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ABSTRACT

In this study we report thermo-mechanical properties of organo-clay based nanocomposites with a high-temperature resistant thermoset resin. Nanocomposites up to 5 wt% of clay were prepared by a solution casting method and dispersed by ultrasonication. The structure and thermo-mechanical properties were characterized by X-ray diffraction (XRD) and dynamic-mechanical analysis (DMA) respectively. The characteristics of dispersion and influence of the preparation process on the structure of nanocomposites are critically discussed. XRD measurements indicate imperfect exfoliation and an anisotropic dispersion of clay particles in the nanocomposites. The elastic modulus and heat deflection temperature are systematically improved upon increasing the concentration of clay particles. The Halpin–Tsai model is used to fit the experimental data for describing the mechanical properties. Both the XRD results and the Halpin–Tsai model analysis indicate that the degree of exfoliation decreases with increasing concentration of clay particles. The capability of the model to explain the reinforcing mechanism in nanocomposites is discussed.

1. Introduction

Nanocomposites of polymer and layered-silicate particles are the subject of considerable interest in recent years because of their superior properties [1,2]. Addition of the particles leads to a significant improvement of mechanical properties [3]. The reinforcement of polymers by the incorporation of nano-clay particles is achieved at very low loading levels of the clay compared to their counter part micro-composites [4]. This advantage of lower filler levels for the enhanced stiffness has been exploited to prepare light-weight components. This is a desirable feature in many applications, especially in transportation, where fuel efficiency is important. Moreover, nanocomposites exhibit a negligible loss in other matrix properties, e.g. fracture toughness, ductility and surface finish [5]. The aviation industry is in search for high-temperature resistant matrices for high-performance composites, to meet the future demands of high speed and fuel efficiency. In this regard composites of Bismaleimides are getting attention due to their high temperature resistance, high dimensional stability, good resistance to chemicals and reasonable mechanical strength [6–9]. The processability of Bismaleimides is as easy as epoxy but its performance is much better than that of epoxy. Bismaleimides are thermosets which release very low amounts of volatiles during curing [10]. In contrast, the high-temperature resistant polyimides are cured by a condensation-type polymerization process involving the release of volatiles, which leads to void formation, which compromises performance [10]. Bismaleimides have a balanced combination of properties, processability and affordability. Brittleness is one of the major concerns for Bismaleimides, which leading to low damage tolerance. Different strategies have been adopted to improve its toughness with minimum loss of the thermal properties [8–11].

High-temperature resistant thermoset nanocomposites are rarely reported in the literature. However, the importance of these materials warrants thorough investigation. Hence, we were motivated to study Bismaleimide nanocomposites. We have selected a recently developed pre-polymer resin of Bismaleimide, which is claimed to be high-temperature resistant. It is a one-component system, in contrast to commonly used two-components Bismaleimide systems. It is challenging to find an optimal processing route for this resin to incorporate the filler. Moreover, a thorough characterization and fundamental understanding of the effects of nano-filler is needed to tailor it for the desired applications. In our previous study on the same polymer we used carbon nanofiber as filler and a melt blending technique to mix the filler with the matrix. It turned out that this did not lead to significant improvement of the mechanical properties [12]. In the present study we have adopted a different processing strategy and also used an organically modified nano-clay as the filler.

The reinforcing effect of the fillers depends on various filler parameters, such as shape, aspect ratio, modulus, volume fraction, interfacial adhesion, surface characteristics and orientation [13–16]. Thus, many factors could potentially influence the

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stiffness of the final nanocomposite, and a better understanding of the effects of each filler property is needed. Over the years the effect of various parameters on the mechanical properties of nanocomposites have been studied, and micromechanical models have been proposed to explain the reinforcing effect [13,15,17,18]. These micromechanical models are based on conventional composite theory, which assumes that each individual phase keeps the same properties as if the other phase were not there. These models and experimental studies indicate that the filler aspect ratio is an important parameter affecting the stiffness of a nanocomposite. Van Es [19] concluded that the stiffness of nanocomposites to a large extent is determined by the particle aspect ratio. The better the degree of exfoliation, the higher the effective aspect ratio, the larger the effect of the nano-filler on mechanical properties.

The Halpin–Tsai model has been found to explain the mechanical properties of the nanocomposites reasonably well. Fornes and Paul [13] modeled the mechanical behavior of nanocomposites using the Halpin–Tsai and Mori-Tanaka models, and found that an exfoliated platelet structure with a high aspect ratio provides superior reinforcing effect. The heat distortion temperature obtained by model predictions and experiment were in good agreement. The model predicts the heat distortion temperature (HDT) to increase with increasing aspect ratio. Picken et al. [18] modeled the mechanical behavior of nanocomposites using the Halpin–Tsai model for different filler geometries and found that the modulus increases with increasing aspect ratio. Weon and Sue [15] studied the effect of clay aspect ratio and orientation on mechanical behavior of nanocomposites. The modulus and heat distortion temperature improved with high aspect ratio and alignment of the filler. Another group of researchers [20] used two types of clay particles with different aspect ratios and investigated their effect on thermo-mechanical properties. Nanocomposites prepared with high-aspect-ratio clay particles exhibited better mechanical reinforcement despite having an intercalated structure as compared to low aspect ratio particles of clay with an exfoliated structure. This reinforcement was well explained by the Halpin–Tsai model.

The present study aims at preparation of high temperature-resistant thermoset nanocomposites, characterization and modeling of their mechanical properties. A reasonable reinforcing efficiency and good thermal stability was achieved by the addition of nano-clay particles. The Halpin–Tsai model is applied to explain the mechanical properties of the nanocomposites.

2. Experimental

2.1. Materials

The resin used was a pre-polymer of Bismaleimide with trade name of "Homide 250" supplied by Hos-technik, Austria, in the form of a yellow powder. Organically modified clay, Cloisite 30B, was obtained from Southern Clay Products, USA. It is Montmorillonite (MMT) modified with bis-(2-hydroxyethyl) methyl tallow alkyl ammonium cations. The solvent N-Methyl-2-pyrrolidone (NMP) was obtained from Sigma Aldrich.

2.2. Nanocomposite preparation

A pre-polymer resin solution of 30 wt% concentration in NMP solvent was prepared by magnetic stirring. An ultrasonication probe Sonotrode UIS-250LS (460 W, 50–60 Hz) by Hielscher Ultrasonics, GmbH was used to disperse the clay in NMP in a plastic vial of 25 ml. The clay and NMP solution was sonicated for 2 h to prepare a master batch dispersion with 5 wt% clay. After that the master batch was diluted to 2.5 wt% and ultrasonicated for 1 h. Then both the diluted clay dispersion and resin solutions were mixed in appropriate proportions to prepare a resin clay mixture with various concentrations of clay particles. The resin clay solution mixture was magnetically stirred for 8 h. After that, the mixture was poured in a glass dish. The dish was placed in a vacuum oven at 80 °C for 3 h to evaporate the solvent and remove any entrapped air. In the mean time, the mixture was stirred intermittently with a spatula to avoid skin formation. The solvent was evaporated and the mixture dried to an extent that it could be easily poured into a mold. We used silicone-rubber molds with slots of dimensions length 25 mm, width 3 mm, and a depth 1 mm. After filing the mold, the samples were cured for 1 h at each of the following temperatures: 80 °C, 120 °C, 140 °C, 160 °C, 180 °C and 200 °C. The samples were removed from the molds after curing, and post cured at 220 °C for 4 h. The samples were finished by removing the overflowed material and burrs using sand paper.

2.3. Characterization

In order to assess the state of dispersion of the clay platelets in the nanocomposites we used X-ray diffraction (XRD). The measurements were performed on a Bruker AXS D8 Discover X-ray diffractometer equipped with a Hi-Star 2D detector using Cu Kα-radiation ($\lambda = 0.154$ nm) filtered by cross-coupled Göbel mirrors at 40 kV and 40 mA. The sample was placed at a distance of 10 cm from the detector and the range of the cone angle 2θ was 1.7–23.7°. Both radial and azimuthal integrations were performed on the X-ray diffraction data.

Storage and loss moduli of the nanocomposites were measured using a Perkin Elmer DMA 7-e dynamic mechanical analyzer in a three point bending mode at a frequency of 1 Hz. The distance between the supports was 10 mm. The controlled oscillating strain applied was 0.15%. The temperature was scanned from 25 to 325 °C at a heating rate of 2 °C/min. The sample dimensions were $15 \times 3 \times 0.6$ mm^3.

3. Results and discussion

3.1. X-ray diffraction

3.1.1. Intercalation/exfoliation characterization

X-ray diffraction is a common technique to probe the degree of exfoliation in polymer clay nanocomposites. Stacks of clay particles consist of platelets arranged like a deck of cards with regular interplatelet spacing. The X-rays are diffracted from the regular planes of the platelets and interfere, resulting into high intensity sharp peaks in the X-ray diffraction pattern. The interlayer distance is calculated from the 2θ value of these peaks using Bragg's law. If the clay platelets are completely separated and disordered upon mixing with the polymer matrix, the characteristic 001 d-spacing peak of clay platelets disappears from the X-ray diffraction pattern. The XRD results of composites are shown in Fig. 1. For the dry powder Cloisite 30B the 001 d-spacing peak position is at an angle of $2\theta \approx 4.84°$ corresponding to a basal spacing of 18.2 Å. Furthermore, a peak at $2\theta \approx 20°$ relates to the internal structure of the clay platelets [21]. The unmodified resin showed a broad peak with a maximum at approximately $2\theta \approx 18°$, which shows that the cured material has an amorphous structure, as expected for a thermosetting polymer [21]. In the case of nanocomposites, the 001 d-spacing peak at $2\theta \approx 4.84°$ has disappeared, indicating that the stacks of platelets have fallen apart and that the platelets inside the nanocomposites are fairly well exfoliated. The peak at $2\theta \approx 20°$ is present for all the samples, as the internal structure of the clay platelets has not changed. It is worth to point out here that for 5% composite