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Graphene has received much attention recently as a material for improvement of polymeric nanocomposite properties due to its outstanding strength, stiffness, high thermal and electrical conductivity and gas impermeability. Recent investigations of cyanate ester resins as high temperature resin materials for space and propulsion applications have brought attention to the need for high temperature composite materials with improved stiffness, strength, hot/wet performance and high maximum use temperatures. The incorporation of grapheme in polycyanurate matrices should result in composites with improvement on one or all of these properties. Additionally, different forms of grapheme, such as grapheme oxide, offer the potential of improved interaction between filler and polycyanurate matrix. Graphene oxide was prepared from graphite and dispersed in commercially available bisphenol E dicyanate (LECy) in 1, 2 and 5 wt% loadings. The resulting properties of oxygen functionalized grapheme sheets dispersed in polycyanurate matrix will be presented.

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Cyanate Ester Graphene Composites

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Graphene has received much attention recently as a material for improvement of polymeric nanocomposite properties due to its outstanding strength, stiffness, high thermal and electrical conductivity and gas impermeability. Recent investigations of cyanate ester resins as high temperature resin materials for space and propulsion applications have brought attention to the need for high temperature composite materials with improved stiffness, strength, hot/wet performance and high maximum use temperatures. The incorporation of graphene in polycyanurate matrices should result in composites with improvement on one or all of these properties. Additionally, different forms of graphene, such as graphene oxide, offer the potential of improved interaction between filler and polycyanurate matrix. Graphene oxide was prepared from graphite and dispersed in commercially available bisphenol E dicyanate (LECy) in 1, 2 and 5 wt% loadings. The resulting properties of oxygen functionalized graphene sheets dispersed in polycyanurate matrix will be presented.

Cyanate Ester Graphene Oxide Composites

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Introduction

Graphene, an allotrope of carbon, is an atomically thick monolayer of carbon atoms arranged in a honey-comb lattice. Interest and research of this material has grown rapidly in recent years due to its unusual properties. Graphene is the strongest material measured to date[1] and can display exceptionally high thermal conductivity,[2] electrical conductivity[3] and gas impermeability[4] making it a potential next generation nanomaterial for property improvement in polymeric nanocomposite materials. Unlike the other allotropes of carbon (fullerenes, carbon nanotubes and diamond) graphene can be isolated as individual sheets from relatively inexpensive graphite.[5] The superior properties and relative low cost of graphene combined with the ability to change the structure and properties of graphene to match anticipated applications make it a material of choice for polymer composites. Recent investigations of cyanate ester resins as high temperature resin materials for space and propulsion applications have brought attention to the need for high temperature composite materials with improved stiffness, strength, hot/wet performance and high maximum use temperatures.[6,7] Dispersion of graphene oxide in cyanate eater resins will likely provide these property improvements

Experimental

Materials. Nonylphenol (technical grade) was purchased from Aldrich, copper (II) acetylacetonate was purchased from ROC/RIC and 1,1'-bis(4-cyanato) ethane ("LECy") was obtained from Lonza. All materials were used as received. Graphite (xGnP-M-25) was purchased from XG Sciences.

Sample Preparation. Graphite oxide was prepared by the Hummers method of oxidation.[5] Batches of catalyst comprised of 30 parts by weight nonylphenol to one part by weight of copper (II) acetylacetonate were prepared by mixing the ingredients in a vial and heating to 60 °C while stirring vigorously until complete dissolution took place (typically one to two hours). Silicone molds (R2364A, Silpak Inc., mixed at 10:1 by weight with R2364B platinum-based curing agent and cured overnight at room temperature, followed by post-cure at 150 °C for 1 hour) were prepared by degassing for 60 minutes at 25 °C and 300 mm Hg. LECy / graphite oxide composites were prepared by mixing 2phr with LECy and graphite oxide. Graphite oxide was dispersed in LECy by high shear mixing for 1 hour followed by ultrasonication for 1 hour. Samples of 1%, 2% and 5% graphite oxide in LECy were prepared. The mixture was degassed at 90 °C and 300 mm Hg for 30 minutes then placed in an open mold under flowing nitrogen and cured at 150°C for 1 hour and 210°C for 24 hours. The temperature ramp rate during cure was 5 °C/min.

Test Procedures. Dynamic mechanical analysis (DMA) was performed with a TA instruments Q800. Rectangular samples with typical dimensions 60x13x2.5mm were analyzed in dual cantilever mode and ramped at 5°C/min from 25°C to 350°C at a frequency of 1Hz and amplitude of 10μm. Dispersions of graphene oxide in water were spin-cast on freshly cleaved mica for AFM imaging. AFM images were obtained using a Veco Digital Instruments Nanoscope IV in tapping mode. SEM images of fractured surfaces were obtained with a FEI Quanta 600 SEM in high vacuum mode. Samples were gold sputtered prior to imaging.

Results and Discussion

Graphene oxide sheets prepared by the Hummers method of oxidation were characterized by AFM (Figure 1). Typical dimension of the sheets were 1-5 μm diameter and a thickness of 1 nm.

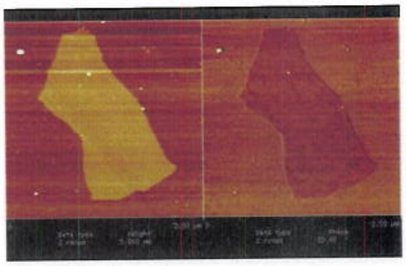

Figure 1. AFM height (left) and phase (right) images of graphene oxide deposited on mica from a suspension in water. Images are 2μm x 2μm.

LECy polycyanurates containing 1, 2 and 5 wt% graphene oxide were characterized by DMA and compared to that of LECy polycyanurate without filler (Figure 2,3). The polycyanurate with 1wt% graphene oxide displayed an increased storage modulus over the neat LECy resin (Figure 2). The storage modulus increased futher with the addition of 2 wt% graphene oxide, however, the storage modulus of 5 wt% graphene oxide was lower than the 1 and 2 wt% samples and only slightly higher than neat LECy polycyanurate. The tan delta curves for the composite materials show no decrease in Tg for the 1 wt% material and a slight decrease in T_g for the 2 and 5 wt% samples (Figure 3).

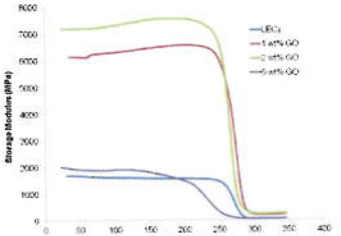

Figure 2. Storage moduli of 1, 2 and 5 wt% graphene oxide in LECy polycyanurate.

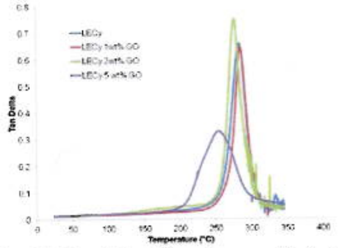

Figure 3. Tan delta of 1, 2 and 5 wt% graphene oxide in LECy polycyanurate

A typical SEM image of the fracture surface of the LECy / graphene oxide composites is shown in Figure 4. The surface topology of the polycyanurate samples in which graphene oxide was dispersed displayed a characteristic roughness that was not present in the fracture surface of neat LECy polycyanurate. Areas of the fracture surface where graphene oxide sheets were found protruding from the surface also typically had high aspect ratio voids where the graphene oxide sheets had pulled out of the polycyanurate matrix.

The storage modulus of the 1 and 2 wt% LECy / graphene oxide composites indicates that there is load transfer of the polycyanurate matrix to the stiffer graphene oxide filler. Theoretically the load transfer may be occurring through covalent bonding between the graphene oxide sheets and the polycyanurate matrix. It is known that the surface of graphene oxide contains hydroxyl and oxirane functionalities,[8] both of which are known to react with aryl cyanate esters.[9] However, SEM micrographs of the fractured

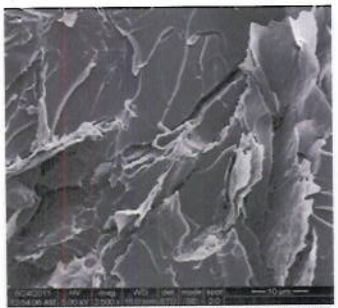

Figure 4. SEM image of the fractured surface of 2wt% graphene oxide in LECy polycyanurate.

surface of these materials show locations where graphene oxide has pulled out of the surface. Furthermore, the polycyanurate resin does not appear to "coat" the graphene oxide protruding from the surface. Therefore, the SEM imiges suggest that this load transfer is most likely due to intermolecular interactions rather than covalent bonding.

Conclusions

The incorporation of graphene oxide at 1, 2 and 5 wt% loading into LECy polycyanurates resulted in a significant increase in storage modulus at loadings of 1 and 2 wt%. Further increase of graphene oxide content resulted in a decrease in storage modulus which was only slightly higher than neat LECy polycyanurate. SEM images of the fracture surface of composites suggest that the interaction between graphene oxide filler and polycyanurate matrix is due to intermolecular attraction rather than covalent bonding.

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