Nano-reinforcement of Epoxy Adhesives with POSS

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ABSTRACT

The reinforcement of epoxy adhesives with polyhedral-Oligomeric-SilSesquioxane (POSS) was studied. Shear performance of the nano-filled adhesive was evaluated as a function of filler content using the single-strap bonded joint configuration. It is found that maximal stress and maximum shear strain both increase with the POSS loading. X-ray diffraction (XRD) analyses indicated that aggregation and crystallization of POSS occurred over the curing cycle. Dynamic mechanical analyses (DMA) showed an increased storage modulus with the addition of POSS and decreased loss modulus, hence enhanced network elasticity. The increased chain relaxation enhanced the polymer/aluminum interaction at the interface, resulting in increased interfacial strength and toughness, which was evident from the observed shift in failure mode from adhesive to cohesive for the bonded joints with increased POSS content.

Keywords: epoxy adhesives, mono-epoxide-POSS, nano-reinforcement, bonded joints

INTRODUCTION

The strength and serviceability of adhesive-bonded joints are mainly the result of the play of forces of intermolecular interaction between the adhesive and the substrate. Newly modified adhesives characterized by high adhesion strength, lower curing temperature, high fracture toughness, and other functionalities, such as heat/moisture resistance and noncombustibility is of great practical interest.

The process of achieving high adhesion strength is hindered by a number of phenomena that accompany the formation of adhesive bonded joints. First, an intermediate layer of undercured polymer can be formed when adhesives are used on high-energy substrates due to the absorption of reagents by the solid surface. Second, in the course of setting of the adhesive, its volume decreases due to volatilization of solvents, polymerization or physical structuring. As a result of the adhesion interaction of the adhesive and the substrate, the film can contract only in thickness. The film extends while contraction stresses appear in the substrate. Rapid growth of stresses tends to reduce the length of the film[1]. In addition, thermal stresses caused by differences of the coefficients of linear thermal expansion of the adhesive and the substrate appear in the course of heating or cooling of the adhesive-bonded joint.

Introducing finely dispersed mineral filler with lyophilic or lyophobic surface character into polymer composition (adhesive) was found to increase the polymer-substrate adhesive bond strength, as migration of low molecular weight impurities, including low molecular weight fractions formed during curing, to the polymer-metal substrate boundary decreased as a result of their physiosorption to the filler surface, thus allowing the formation of a less defective boundary layer[1]. However, the internal stresses in the coating grow as the filler content increases, since modified filler simultaneously displays effects of restriction of mobility and polymer structural plasticization in the boundary layer due to the presence of long chain modifier molecules. Increased internal stresses result in reduced strength of the coating-metal substrate adhesive bond. On the other hand, widely used methods for decreasing the internal stresses relate to increasing their rate of relaxation, for example, by decreasing the modulus of elasticity when adding plasticizers to adhesives or when they are combined with elastomers. But the decrease of adhesive rigidity commonly results in decrease of its heat resistance and stress-strain behavior stability, and decrease of strength limits under bending, contraction, and shear due to the lower cohesion strength of the modified adhesive itself [1].

Reinforcement of polymer systems with well-defined nano-sized inorganic clusters, for example Polyhedral-Oligomeric-SilSesquioxane (POSS) has been given considerable attention recently. Functionalized POSS reagents combine a hybrid inorganic-organic composition with nanosized silica-like cage structures having dimensions comparable to those of most polymeric segments or coils[2] and can be covalently bound to the polymer, leading to reinforcement of the system on molecular level. Due to the large surface area, only small amounts are needed to cause significant changes in properties of the matrix. Interestingly, recent study on methacryl-POSS indicates POSS may have the potential to behave like a filler particle or a plasticizing molecule, depending on the degree of dispersion at molecular level[3]. Incorporation of POSS into a wide range of polymers such as polysiloxane[4], polymethacrylate[5], polystyrene[6], polyurethane[7] and epoxy thermosets[2] and has shown improvements in mechanical and rheological properties, including increased glass-transition temperature and modulus, reduced flammability, increased gas permeability and decomposition temperature. Nonetheless, improved

mechanical properties in the context of bulk nanocomposites will not necessarily translate into an increase of polymer/substrate adhesion strength and adhesion toughness in the context of adhesive bondline as the presence of solid surface often affects the formation of polymers. In addition, incorporation of multi-functional POSS to polymers has been found to increase the network chemical crosslink density, which may lead to slowing down of the polymer chain relaxation process[2]. In sight of the latter, POSS with monoepoxide functionality (E1-POSS, see Figure 1 for the chemical structure) was used as the reinforcing element in a common two-part epoxy adhesive system in our study with the aim of a strong and tough bondline. Upon cure, the E1-POSS units are expected to covalently bind to the network chain as pendant units without an increase of chemical crosslinks. The weight percentage of nanofiller was kept below 5wt% in consideration of economic viability of future application.

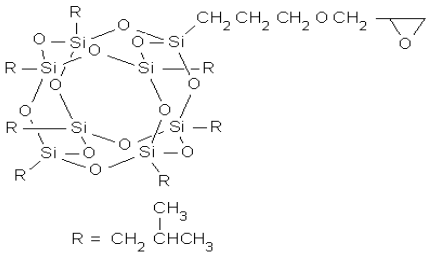

Figure 1. Structure of E1-POSS

EXPERIMENTAL

Mono-epoxide-POSS (PSS-(3-Glycidyl)–Heptaisobutyl substituted, E1-POSS, purchased from Sigma-Aldrich) was added to the epoxy monomer (Araldite GY502 from Vantico, a diglycidyl ether of bisphenol A based resin). A series of mixtures containing different weight percentages of POSS (0-5wt.%) were prepared and heated to 60˚C. At this temperature, POSS can fully dissolve in epoxy and form a solution. The solution was allowed to cool. At room temperature, the POSS/epoxy emulsion was mixed with the polyamidoamine curing agent (Aradur 955-1 US from Vantico) at a weight ratio of 100 to 27 (epoxy/amine) to form the adhesive.

Aluminum bars (75mm x 20mm x 3.2mm) were degreased with trichloraethane (Sigma-Aldrich) and etched in Nochromix®/sulfic acid solution for 30 minutes. They were then rinsed with tap water for around 20 minutes and dried at 100˚C for 40 minutes. At room temperature, the adhesive was applied on the aluminum bars and single strap bonded joints were made. The joints were allowed to stay 8 hours at room temperature to remove the micro bubbles within the adhesive layer. Four hours curing at 90°C followed. Uniform pressure was applied during the making of joints to keep a consistent thickness of the bondline.

Shear tests of prepared bonded joints were performed on an MTS 810 under displacement control mode (0.2mm/sec). For each adhesive, seven joints were tested. The failure surface of bonded joints (adhesive layer) was subject to X-ray diffraction (XRD) analysis to obtain information about network morphology. Specimen of 17.5mm x 12.7mm x 3.0mm of cured adhesives were made in aluminum foil and dynamic mechanical thermal analyses (DMTA) were performed on a DMA Q800 V3.13 Build 74 under 1Hz 3 point bending mode and a temperature ramp of 2°C/min.

RESULTS AND DISCUSSION

Figures 2 and 3 are plots of static performance of aluminum joints versus the E1-POSS content in the adhesive based on statistical treatment of experimental data. Clearly, the incorporation of E1-POSS nanoparticles into the adhesive layer increased epoxy/aluminum adhesion strength as indicated by the increasing stress at failure in Figure 2. As is shown in Figure 3, addition of 5wt% E1-POSS nearly tripled the adhesive toughness. Visual examination of the failure surfaces shows that cohesive failure was achieved for POSS content higher than 1.0 wt.%, indicating an enhanced polymer/metal interface.

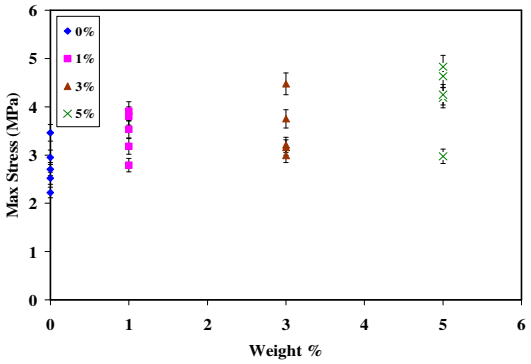

Figure 2. Adhesion Strength vs POSS Content

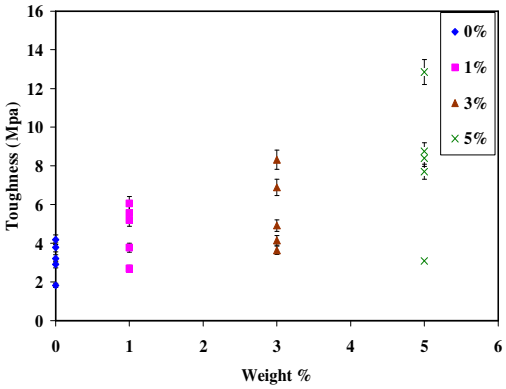

Figure 3. Adhesion Toughness vs POSS Content

Morphology of E1-POSS-modified epoxy network was studied using XRD technique. XRD results of failed adhesive surface are shown as Figure 4 in comparison of the spectrum of pure E1-POSS particles. It appears that the E1-POSS crystal structure was not affected by its incorporation in the epoxy network, as is indicated by the existence of a sharp peak around 2θ=7.8˚ for all E1-POSS concentrations. That is to say, even at very low concentrations, E1-POSS was not dispersed in the network at molecular level. As authors have pointed out, the POSS units in polymers tend to aggregate or even form crystallites [8]. In light of the strain increase of the bondline with the addition of E1-POSS, we infer that a loose transition region of two thermodynamically incompatible phases of formed before POSS crystallization took place. The existence of a loose POSS rich transition region may lower the density of macromolecular packing, which results in decrease of shrinkage during the network formation. This loose transition region in the system may also provide for an increased free volume and lead to higher mobility of the

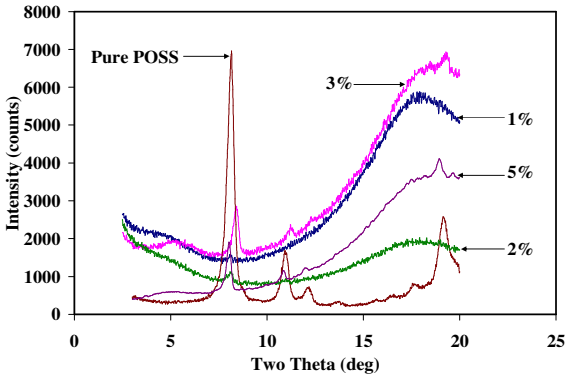

Figure 4. XRD Spectra of E1-POSS/Epoxy

chain segments between the crosslinks of the network. Decrease of internal stress in turn contributes to the formation of a less defective adhesive/metal interface[1]. From the perspective of fracture mechanics, the presence of loose transition region can both initiate and limit the growth of crazes. A large number of small crazes rather than a small number of large cracks are formed and in this case the energy dissipates in a much great volume.

Results of DMTA measurements presented as Figures 5 and 6 show that the bending storage modulus (E') of POSS/epoxy increased with the POSS content for the range 0- 5wt%. As can be seen in Figure 5, the equilibrium rubbery modulus of E1-POSS-modified network at a temperature above breaking of crystalline domains is close to that of the POSS-free network. It can be inferred that the reinforcing effect of POSS disappears at a high temperature and E1-POSS has very insignificant effect on the permanent chemical crosslinking density, based on the theory of rubber elasticity [9]. Namely, reinforcement of the E1-POSS epoxy network is mainly caused by the formation of physical crosslinks between pendant POSS units rather than the increase of chemical crosslinking density.

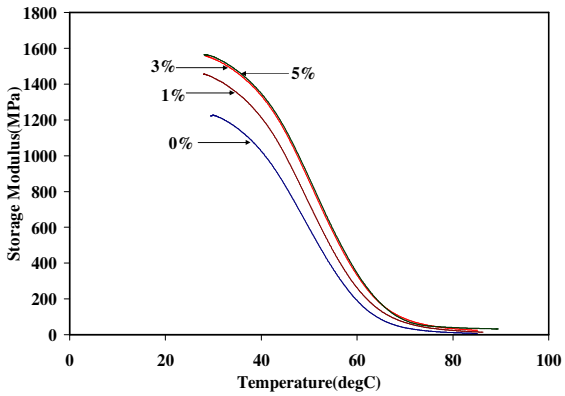

Figure 5. Storage Modulus vs Temperature

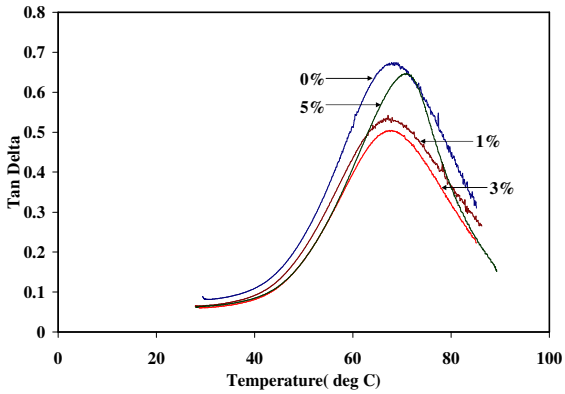

Figure 6. tan δ vs temperature curves

As is shown in Figure 6, the glass transition temperature T_g (defined as the temperature at which tanδ peaks) was not affected by the presence of POSS at low POSS concentrations (<3 wt%). This corresponds to the formation of a loose POSS transition region. As a result, the breadth and amplitude of tanδ peaks both decreased with increasing POSS concentration. Notably, further incorporation of E1-POSS (5 wt%) led to a substantial increase of T_g (5˚C), indicating restricted chain segmental mobility and the emergence of a rigid network at high POSS concentrations. This observation also echoes XRD results, which clearly show that the degree of crystallization of E1-POSS increased with the POSS content in the network. Conceivably, an increase of E1-POSS content causes a decrease of the distance between dangling units, hence stronger POSS-POSS interaction. Zheng et al.[8] suggested the existence of critical POSS concentration above which POSS-POSS interactions percolate through the system. As a result of large-scale crystallization, the fraction of mobile free network chains may be considerably reduced. Together with the inertia effect of a large mass POSS molecule, this leads to a decrease of network flexibility and the retardation of chain relaxation process, which contribute negatively to the mechanical performance of the network as a bondline. In addition, tight POSS agglomerates or crystals can act as areas of stress concentrations from the perspective of mechanics.

Therefore, integrating large mass of POSS to epoxy adhesives is not likely to further strengthen the bondline.

CONCLUSIONS

Incorporation of a mono-epoxide POSS in suitable amount can effectively enhance the mechanical performance of epoxy adhesives. Interactions of pendant POSS units covalently bound to the polymer chains form physical crosslinks and lead to increased modulus and increased cohesive strength of the adhesive. When the POSS concentration is low, thermodynamically incompatible components form a loose transition region, which may generate free-volume and promote the chain relaxation process. With the presence of aluminum, interactions between dangling E1-POSS units percolates at a POSS concentration around 4-5wt% and crystallization occurs over a large scale, leading to an increased T_g, which may lead to a decrease of the bondline deformability and limit further enhancement of adhesive performance.

ACKNOWLEGEMENT

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