Mechanically Reinforced Glassy Epoxy Nanocomposites Using a Lamellar Mesostructure

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Abstract. A glassy epoxy polymer has been mechanically reinforced using a lamellar mesostructured silica, MSU-SA. MSU-SA silica was synthesized via a supramolecular assembly pathway using a cost-effective sodium silicate as a silica source and dodecylamine as a structure-directing agent. The as-made MSU-SA silica exhibited a typical lamellar structure with 4.0nm d-spacing ($2\theta = 2.20°$) and high order reflections ($2\theta = 4.46°$ and $6.80°$) in its X-ray diffraction pattern. The lamellar mesostructured silica was readily dispersed in an epoxy resin (EPON 826) and the epoxy/MSU-SA mixture was cross-linked with Jeffamine D-230 (α,ω-diamine) to form thermoset epoxy polymer nanocomposites. The storage modulus of the nanocomposites was systematically enhanced relative to the pristine polymer at relatively low MSU-SA loading over the range of 1-3 wt%. The nanocomposite containing 3 wt% MSU-SA silica exhibited 13% increment of storage modulus (3126MPa at 40°C) relative to pristine polymer (no filler). Due to monofunctional dodecylamine the tan δ ($\sim T_g$) value of the nanocomposites decreased by 6°C at 3wt% silica loading.

Keywords: polymer nanocomposite, epoxy, mesostructure, exfoliation, mechanical property, oxygen permeability.

1. Introduction

The applications of thermoset epoxy polymers are extensive including coatings, adhesives, and electrical (and thermal) insulators.[1,2] Layered silicate clays (*e.g.* montmorillonite) have been widely investigated as reinforcing agents in order to improve the mechanical,[3] thermal,[4] and barrier[5] properties. For exfoliation (nanolayer separations >10nm) of clay nanolayers in a polymer matrix, the gallery of the clays typically are needed to be hydrophobic, so that the clays usually were modified by exchange reaction with organic molecules.[6]

As well as the smectite clays, mesostructured materials such as MCM-41, MSU-J, and MSU-F have been used for the mechanical reinforcement of engineering polymers.[7-9] The mesostructured silicas prepared through supramolecular assembly exhibit relatively large pore size (>4nm) and hydrophobic surfactant tail groups in the pore. For example, addition of the MSU-F silica (9wt%) improved the tensile modulus of a rubbery epoxy polymer by up to 3.7 times.

MCM-50 silica is a lamellar mesostructured material synthesized via a supramolecular assembly pathway. The MCM-50 has been used as a reinforcing agent for a polypropylene grafted with maleic anhydride moieties (PP-*g*-MA) because the lamellar framework structure of MCM-50 is identical to smectite clays.[10] Although exfoliation of the lamellae of MCM-50 silica was shown in XRD patterns and TEM images, any improved properties (*e.g.* mechanical, thermal, and barrier) of the PP-*g*-MA have not been

reported. However, lamellar mesostructured silicas still possess advantages including no need for organic modification relative to layered silicate clays.

In the present study we examine the epoxy polymer reinforcing properties of a lamellar mesostructured silica, denoted MSU-SA.[11] Although MSU-SA silica possesses identical framework structure to that of MCM-50, it is synthesized from a primary amine surfactant (dodecylamine) unlike MCM-50 from a quaternary ammonium surfactant (*e.g.* cetyltrimethylammonium bromide). The storage modulus of the epoxy/MSU-SA nanocomposites was systematically enhanced relative to the pristine polymer at relatively low MSU-SA loading over the range of 1-3wt%. The nanocomposite containing 3wt% MSU-SA silica exhibited 13% increment of storage modulus relative to pristine polymer. Due to monofunctional dodecylamine the tan δ (~T_g) value of the nanocomposites decreased by 6 °C at 3wt% silica loading. It is interesting that the oxygen permeability of the nanocomposites also increases with the MSU-SA content due to more permeable corona formation around the silica particles and micropores of the amorphous silica framework.

2. Experimental

Epoxy resin EPON826, a diglycidyl ether of bisphenol (Resolution Performance Products), was used to prepare epoxy/MSU-SA nanocomposites. The α,ω-diamine polypropylene oxide $H_2NCH(CH_3)CH_2$ $[OCH_2CH(CH_3)]_xNH_2$ was obtained from Aldrich under the trade name, Jeffamine D-230 (x~2.6). To synthesize MSU-SA, sodium silicate (NaOH = 14%, SiO_2 = 28%, Aldrich) was used as a silica source and dodecylamine (>98%, Aldrich) was used as a structure-directing agent.

MSU-SA silica was synthesized by slightly modifying a recipe from a previously published US Patent[11]. The surfactant solution was prepared by adding 0.58mg of dodecylamine to 10mL water and 10mL of 0.5M acetic acid was then added to the solution. After 10min a 2.7g quantity of sodium silicate in 30mL of water was added to the surfactant-acid mixture. The reaction mixture was stirred at ambient temperature for 20h. The resulting powder was recovered by filtration and dried in ambient condition.

To prepare the epoxy polymer nanocomposites, a pre-determined amount of the as-made MSU-SA silica was added to the epoxy resin (EPON 826) and mixed at 50°C for 10min. A stoichiometric amount of the Jeffamine D-230 curing agent was then added to the mixture and mixed at 50°C for another 10min. The resulting slurry was out-gassed under vacuum and transferred to a silicon mold. Pre-curing of the nanocomposite was conducted at 75°C for 3h, followed by an additional 3h cure at 125°C to complete the crosslinking.

The powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-2500 diffractometer equipped with Cu K_α X-ray radiation and a curved crystal graphite monochromator operating at 45kV and 100mA. The dynamic mechanical properties were determined using a dynamic mechanical analyzer (TA instrument, DMA 2980). The sample was subjected to dual-cantilever bending with amplitude of 0.2% at a frequency of 1Hz. The temperature was increased at a heating rate of 2°C/min in the range of 30°C to 150°C. Oxygen permeability data were recorded on a MOCON OX-TRAN 2/21 oxygen permeability instrument with a test gas containing 100% oxygen, nitrogen (containing 2vol% hydrogen) as a carrier gas. Film samples with a thickness between ~60μm, area of 0.785cm^2, were cast from an aluminum disk mold, and were loaded in the testing cells with adhesive aluminum foil masks.

3. Results and Discussion

3.1. Synthesis of MSU-SA and preparation of epoxy/MSU-SA nanocomposites

MSU-SA silica was prepared from a previous reported patent except amount of acetic acid. When the amount of NaOH in the sodium silicate solution is neutralized with acetic acid, the resulting mesostructure exhibits a HMS-type wormhole framework structure.[11] In the pH neutral region dodeylamine is partially protonated so that the curvature of the surfactant micelle head becomes small. Thus the framework silica forms cylindrical structure matching the micelle head structure. However, at high pH values dodecylamine head groups are deprotonated resulting in a mesophase with little or no curvature. In a typical synthesis, 9.5mmol of NaOH is present in 2.7g of sodium silicate solution but only 5mmol of acetic acid was added to

the surfactant solution. Fig. 1A shows a XRD pattern of the as-made MSU-SA silica. Three 00l reflection peaks (1st order = 4.0, 2nd order = 2.0 and 3rd order = 1.3nm) in the pattern indicate the typical lamellar structure of the as-made MSU-SA.

XRD patterns of the composites were also obtained and demonstrated in Fig. 1B. As soon as the as-made MSU-SA silica was mixed with the epoxy resin, the XRD reflections disappeared despite a small peak approximately at 2θ ~3 (Fig. 1B(a)). It is because EPON826 molecules may be solvated in the gallery of layered smectite clays.[12] The cured epoxy/MSU-SA nanocomposites exhibit an identical XRD pattern as shown in Fig. 1B(b). Presumably the lamellae of the MSU-SA silica were exfoliated in the epoxy polymer matrix as reported in MCM-50 nanocomposites.
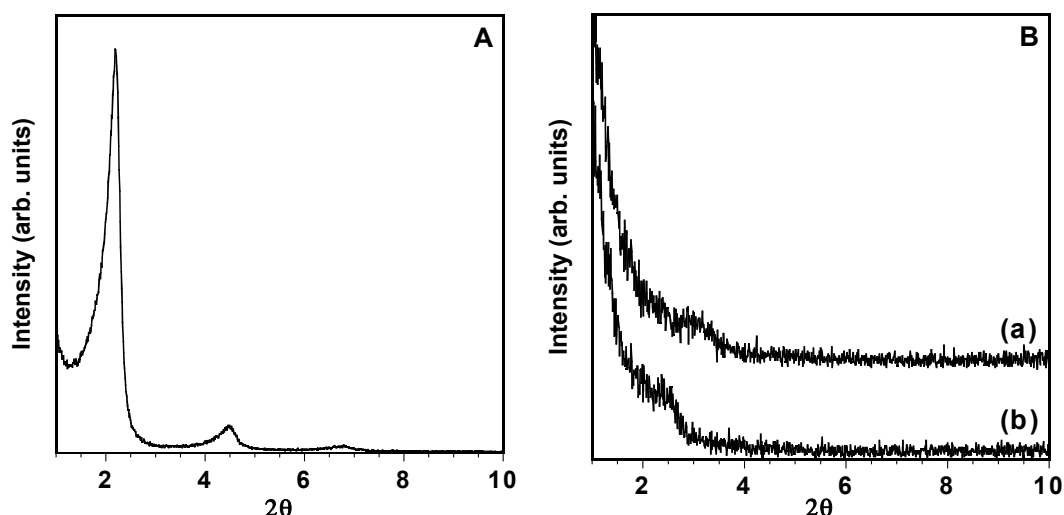

Fig. 1: X-ray diffraction patterns of A. as-made MSU-SA and B. epoxy/MSU-SA nanocomposites; (a) epoxy resin (EPON826) and MSU-SA mixture, (b) cured epoxy/MSU-SA nanocomposite containing 3wt% MSU-SA.

3.2. Epoxy/MSU-SA nanocomposites; mechanical property

The mechanical performance of the epoxy/MSU-SA namocomposites is improved relative to the silica-free pristine epoxy polymer. The storage modulus curves are shown in Fig. 2. Only at 3wt% silica loading, the storage modulus increases by 13% (40°C, see Table 1). In the rubbery region (>T$_g$) the storage modulus is also enhanced by 30% (120°C). According to the simple rule of mixture, the higher improvement of the modulus in the rubbery region is rational due to low modulus of the pristine rubbery epoxy polymer. As-made MSU-SA contains approximately 50% of dodecyamine so that the 3wt% loaded composite actually contains 1.5wt% of silica. More than 10% increment of storage modulus at 1.5wt% silica loading level is a remarkable result even for a stiff glassy epoxy polymer.

Despite the enhancement of the storage modulus the tan δ decreases with the increase of silica loading. For complete crosslinking, we need at least two amine groups at the end of a curing agent. However, dodecylamine is a monoamine so that the dangling alkyl chain of the cured dodecylamine renders the thermoset epoxy polymer flexible.

Table 1. Storage modulus and tan δ for the pure epoxy polymer and epoxy/MSU-SA nanocomposites.

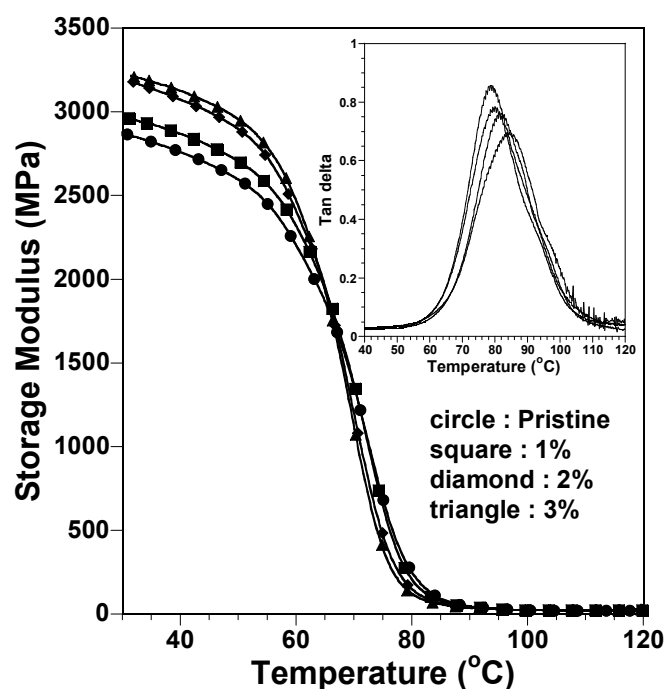| Filler Content (%)	Storage Modulus (MPa)		tan δ (^{o}C)
	40°C	120°C	
0	2762	20	84.4
1	2870	22	81.5
2	3074	24	80.0
3	3126	26	78.6

Fig. 2: Dynamic mechanical analysis curves for the pure epoxy polymer (●: no filler) and the epoxy/MSU-SA nanocomposites (■: 1%, ♦: 2%, and ▲: 3%). (inset) Tan δ profiles.

3.3. Epoxy/MSU-SA nanocomposites; oxygen permeability

Table 2 presents the O_2 permeability of the epoxy/MSU-SA nanocomposites as a function of as-made and MSU-SA silica loadings. A steady increase in oxygen permeability occurs with increase of the silica loading. The oxygen permeabilities of polymer nanocomposites formed from platelet particles (smectite clays) generally have improved barrier property of the polymer matrix as expected for high aspect ratio of the layers. However, the composites formed from MSU-SA show relatively high oxygen permeability despite its lamellar framework structure. Like the composites formed from as-made MSU-J [8] a corona or more permeable polymer around the silica particles provides a pathway for enhanced oxygen permeability. Because only 3wt% silica loading cannot provide a percolation pathway, an abrupt or significant increase in oxygen permeability is not observed in this report. Porosity of the amorphous silica could be another explanation for the enhanced permeability as well as the corona formation around the silica particles. Several previous reports have shown micropore formation in the amorphous silica synthesized via sol-gel reaction. [13,14] In the literature, silica shell at polymer beads resulted from sol-gel reaction preserve the spherical silica structure after calcination of the beads. It indicates that thermally decomposed volatile organic species escape through the pore of the silica shell.

Table 2. Oxygen permeability data of polished films prepared from cured pristine epoxy polymer and epoxy/MSU-SA nanocomposites.

Samples	O_2 Permeability (cc mil m^{-2}day^{-1})
Pristine (Epon 826/D230)	92.8
1 %	110
2 %	111
3 %	116

4. Acknowledgements

5. References

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