Effect of Alumina Platelet Reinforcement on Dynamic Mechanical Properties of Epoxy

Dharmendra Kumar Shukla, Rachit Kumar Srivastava

***Abstract*— Fillers are used to improve various mechanical properties of polymers. However, conventional micro-sized fillers cause adverse effect on strength and ductility. In the present work, composites of epoxy are synthesized with non-functionalized and functionalized alumina platelets of polygonal shape having a thickness of 200nm and size in the range of 5-10μm as reinforcement by in situ polymerization technique. The platelets were functionalized using 3-glycidoxypropyltrimethoxysilane (GPS). Good dispersion of the platelets inside the matrix was observed through scanning electron microscopy (SEM) images. Formation of Si-O-Al bond was indicated in Fourier Transform Infra-red (FTIR) Spectroscopy of the composites having functionalized alumina platelets. Dynamic mechanical analysis of the prepared samples was performed to find out the dynamic moduli of the epoxy-alumina platelet composite. The inclusion of as received alumina platelets in epoxy matrix improves the storage modulus and the glass transition temperature of the polymer whereas the improvement in storage modulus and glass transition temperature was moderate in case of composites having functionalized alumina platelets.**

Index Terms— Dynamic mechanical analysis, epoxy resin, functionalized reinforcement, polymer composites

I. Introduction

IT has been a usual practice to reinforce polymers with rigid particles in order to increase the stiffness and fracture toughness. But these reinforcements come with a negative impact on tensile strength and ductility [1-4]. Recently, a lot of work on nano-sized filler has been reported. These have reported increase in tensile strength for a limited loading of filler material [5-6]. But dispersion of nanosize reinforcement is a difficult task to achieve.

In our earlier work, in order to combine the effect of micro and nano size fillers authors studied the effect of mixed length scale fillers with an aspect ratio in the range of 25-50 on epoxy polymer matrix [4]. At low volume fractions of reinforcement, there was moderate reduction in tensile strength but the decrease was significant at higher volume fractions. The negative impact on tensile strength was attributed to the poor bonding between the alumina platelet and the epoxy matrix. Functionalization of alumina platelets was carried out before preparation of composite specimen in order to improve the bonding between reinforcement and matrix [7]. Alumina platelets were functionalized using 3-glycidoxypropyltrimethoxy silane. In the present work, dynamic mechanical properties of composites having uncoated as well as coated alumina platelets was determined. Material characterization was done using Scanning Electron Microscopy (SEM). The effect of functionalization of platelet surface with GPS on dynamic mechanical properties was then studied.

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II. Experimental

A. Material System

The matrix material used for the present study was epoxy (Bisphenol-A) prepared from Araldite LY556® having density 1.17 gm/cc at 25^0C and Hardener HY951® having density 0.98 gm/cc at 25^0C supplied by Vantico Performance Polymers Pvt. Ltd. India. Chemical structure of uncured epoxy is shown in Fig.1.

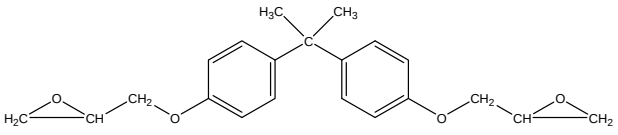

Fig.1 Chemical Structure of uncured epoxy

Alumina platelets used in this study were supplied by Advanced Nanotechnology Ltd. Australia. These platelets having density 3.97 gm/cc were having a thickness of 200 nm and in plane dimension in the range of 5-10 μm. It can be seen from the SEM image of alumina platelets (Fig.2) that these platelets are of irregular polygonal shape. To functionalize the alumina platelets, 3-Glycidoxypropylmethoxysilane (GPS) (Dow Corning ® Z-6040, 500 ml, purity 98%, density 1.07 g/cc at 25^0C) supplied by Dow Corning Chemicals was used. Chemical structure of GPS is shown in Fig. 3.

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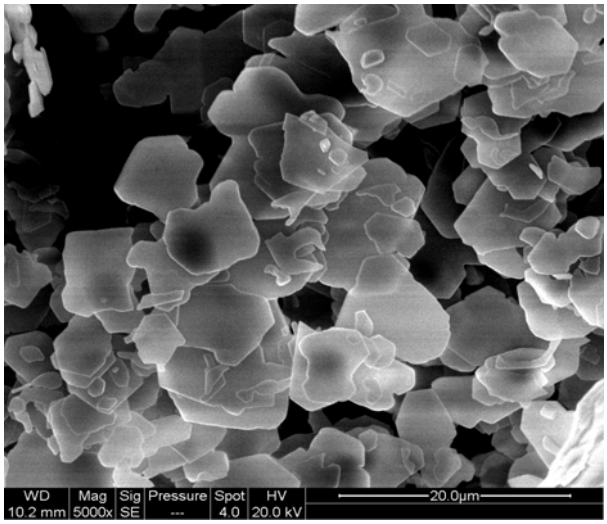

Fig.2 SEM photograph of alumina platelets

Composites were fabricated with both uncoated and silane coated alumina platelets for volume fractions 1, 2 and 5 %.

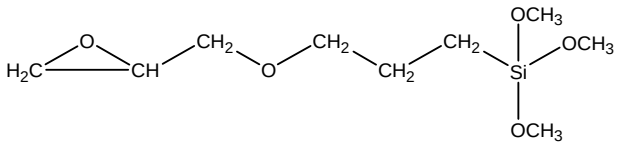

Fig.3 Chemical structure of GPS

B. Composite Preparation

Composites with Uncoated Platelets

Epoxy alumina platelet composite was prepared by mechanical exfoliation / in-situ polymerization. The required amount of alumina and epoxy was mixed mechanically for 10 min. Then, the mixture was sonicated for 30 minutes using a 13 mm diameter acoustic probe and Sonics Vibra Cell® ultrasonic processor (Ti-probe, frequency 20 KHz, intensity 100 W/cm^2). The mixing was carried out at 75% amplitude in the pulsing mode (5 s on and 9 s off). To avoid rise in temperature during sonication the mixing beaker was kept in a mixture of ice and water. Temperature of the mixture was not allowed to rise beyond 60 ^{0}C. After sonication the mixture was kept in vacuum of 20 mm Hg for 45 minutes to remove the air bubbles entrapped during mechanical mixing and sonication process. Then hardener HY951 was gently mixed with the mixture in the ratio of 1:10 by weight of resin. The final mixture was poured into vertical acrylic moulds and was allowed to cure at room temperature for 24 hours. After this the composite was taken out of the mould and post cured at 100 ^{0}C for 4 hours. The composite was allowed to cool to room temperature in the oven itself.

Composite with Coated Platelets

3-Glycidoxypropylmethoxysilane (GPS) was used as the coupling agent to functionalize the platelets. The required amount of GPS was mixed drop by drop in a solvent made of 95% absolute ethanol and 5% de-ionized water while the solvent was getting sonicated. The pH value of the solvent was initially adjusted to 4.5 using acetic acid. The GPS and solvent mixture was sonicated for 15-20 minutes in order to get complete hydrolysis of GPS [8, 9]. Then the required amount of alumina platelets was added to the mixture. Subsequently the mixture was sonicated for one hour. After complete evaporation of solvent the coated platelets were washed with hexane to remove any excess quantity of silane.

The GPS treated platelets were then dispersed in epoxy by 30 minutes of effective sonication and the composite was fabricated in the same way as in the case of uncoated platelets.

C. Characterization

To examine the dispersion of alumina platelets in epoxy matrix, samples of size 10 mm*5 mm*6.5 mm were cut from the composite sheets. One of the faces of each sample was finely polished and then gold coated. Images of the gold coated face were taken using a Scanning Electron Microscope (SEM, Quanta 200, FEI). As the sheets (120 mm*120 mm*6.5 mm) of composites were molded in vertical acrylic molds and the epoxy has a gelation time of 30 minutes, there is a chance that the platelets may settle down due to gravity. Hence, specific gravity measurements were also carried out to determine if there is settlement of platelets due to gravity. Ten samples were cut from different locations along the height of the mold and specific gravity was measured by hydrostatic weighing.

To investigate the chemical changes at the platelet surface, Fourier Transform Infrared Spectroscopy (FTIR, Vertex 70, Bruker, Germany) was performed at different stages of composite preparation. The samples required for FTIR spectroscopy were prepared by mixing 95% of KBr powder with the composite (solid) in a pestle and subsequently grinding them into a uniform fine powder. The sample pellet is prepared by pressing the powder into a disc. In case of liquid samples, a drop of the liquid sample was sandwiched between two KBr pellets. The KBr disc was then kept in a spectrometer disc holder and mounted in the spectrometer and scanned for wave number ranging from 400 cm^{-1} to 4000 cm^{-1}.

Dynamic mechanical analysis tests were performed using Dynamic Mechanical Thermal Analyzer. The dimension of DMA test specimen was 60×10×3 mm^3. The tests were performed on a frequency of 1 Hz at a heating rate of 3^{0}C. The temperature range was from 25^{0}C to 250^{0}C.

III. Results and Discussions

The density of composite for each volume fraction was measured by taking samples from different location along the height of the mold. No variation in the density was observed. This indicates that platelets did not settle due to gravity. To ensure proper dispersion of platelets in the epoxy matrix SEM images were taken for each volume fraction. Fig. 4 shows the dispersion of platelets in

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composites having 1 % and 5 % alumina platelets by volume. It was observed that the platelets were distributed uniformly in each case.

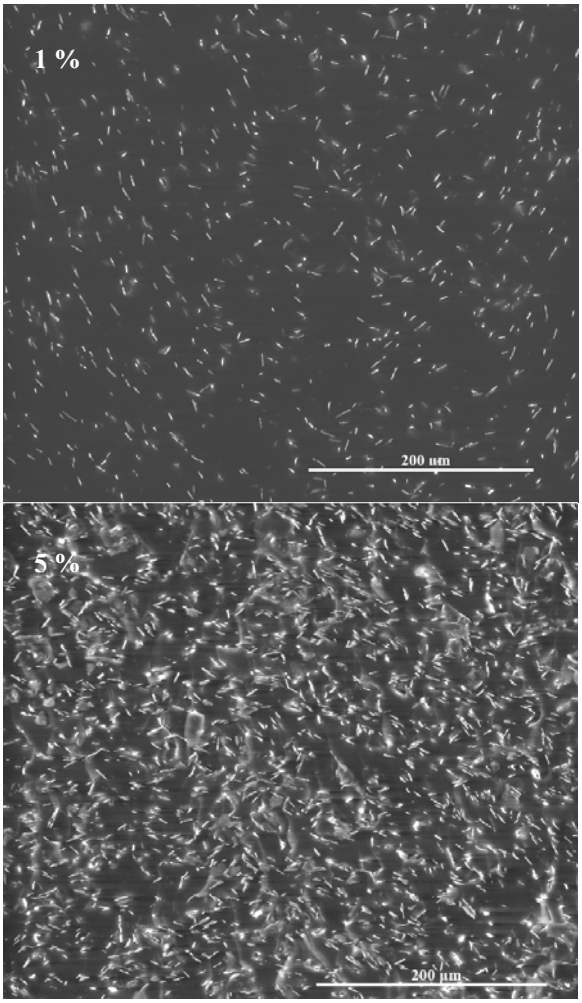
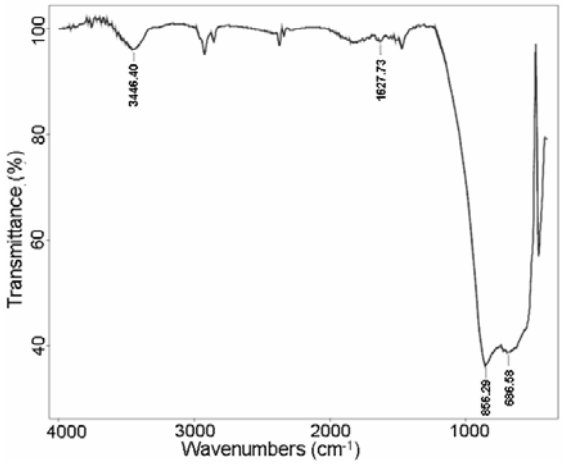


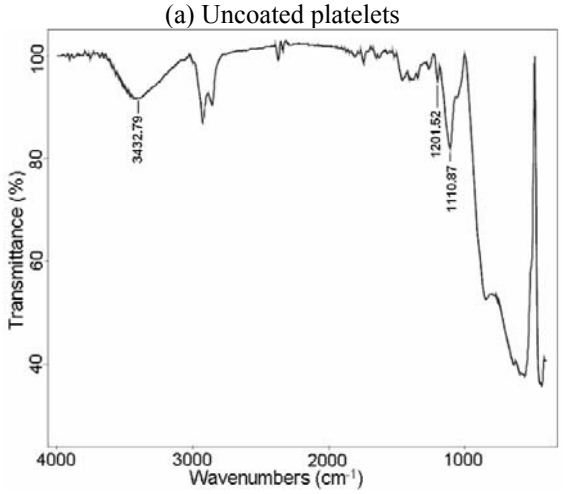
Fig.4 SEM micrographs showing the distribution of platelets in epoxy

FTIR analysis was done to ensure that indeed a Si-O-Al bond has formed in the composite between alumina and GPS. Figure 5 shows the FTIR spectra of uncoated alumina platelets after heating and the FTIR spectra of GPS coated alumina platelets. The FTIR spectrum of uncoated platelets showed a broad peak at around 3446.40 cm^{-1} which is recognized to be due to the hydroxyl groups on the surface of the alumina platelets that are hydrogen bonded either to absorbed water molecules or to each other [10, 11]. The FTIR spectrum of GPS coated alumina platelets (Fig. 5 b) indicates an additional peak at 1110.87 cm^{-1}, which is not present in the FTIR spectrum of uncoated platelets. This peak is due to the formation of Si-O-Al bond.



i. 3446.40 cm^{-1} corresponds to O-H group stretching vibration (surface hydroxyl groups of the platelets, and hydroxyl groups of absorbed water molecules)
ii. 856.29 cm^{-1} corresponds to stretching vibration of Al-O in tetrahedral coordination
iii. 686.58 cm^{-1} corresponds to stretching vibration of Al-O in octahedral coordination.

(a) Uncoated platelets



i. 1459.95 cm^{-1} corresponds to asymmetrical deformation of CH_3 and scissoring deformation of CH_2.
ii. 1201.52 cm^{-1} corresponds to epoxide ring vibration.
iii. 1110.87 cm^{-1} broad peak corresponds to asymmetrical Si-O stretch (from Si-O-H, Si-O-Al and Si-O-Si).

(b) GPS coated platelets

Fig. 5: FTIR spectrum of (a) Uncoated Platelets (b) GPS coated platelets

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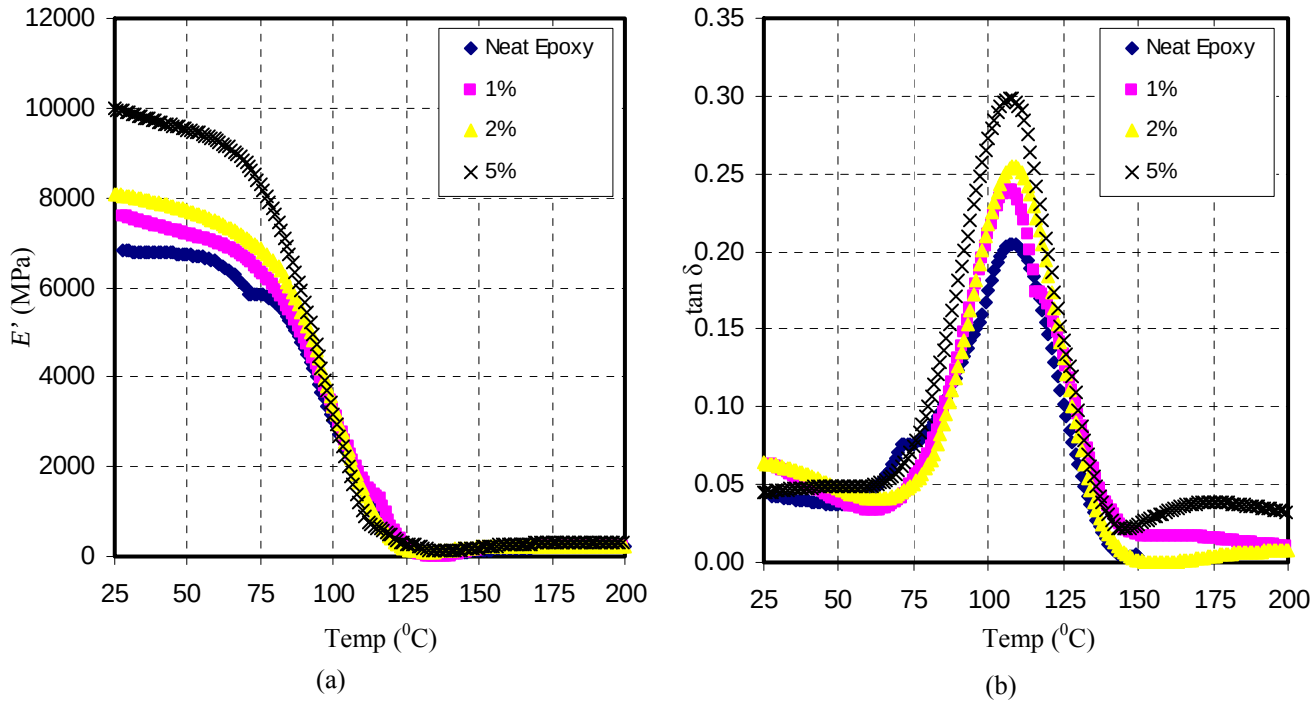

Fig. 6: The plots of (a) storage moduli and (b) tan δ as a function of temperature for epoxy and composites having 1, 2 and 5 % uncoated alumina platelets by volume

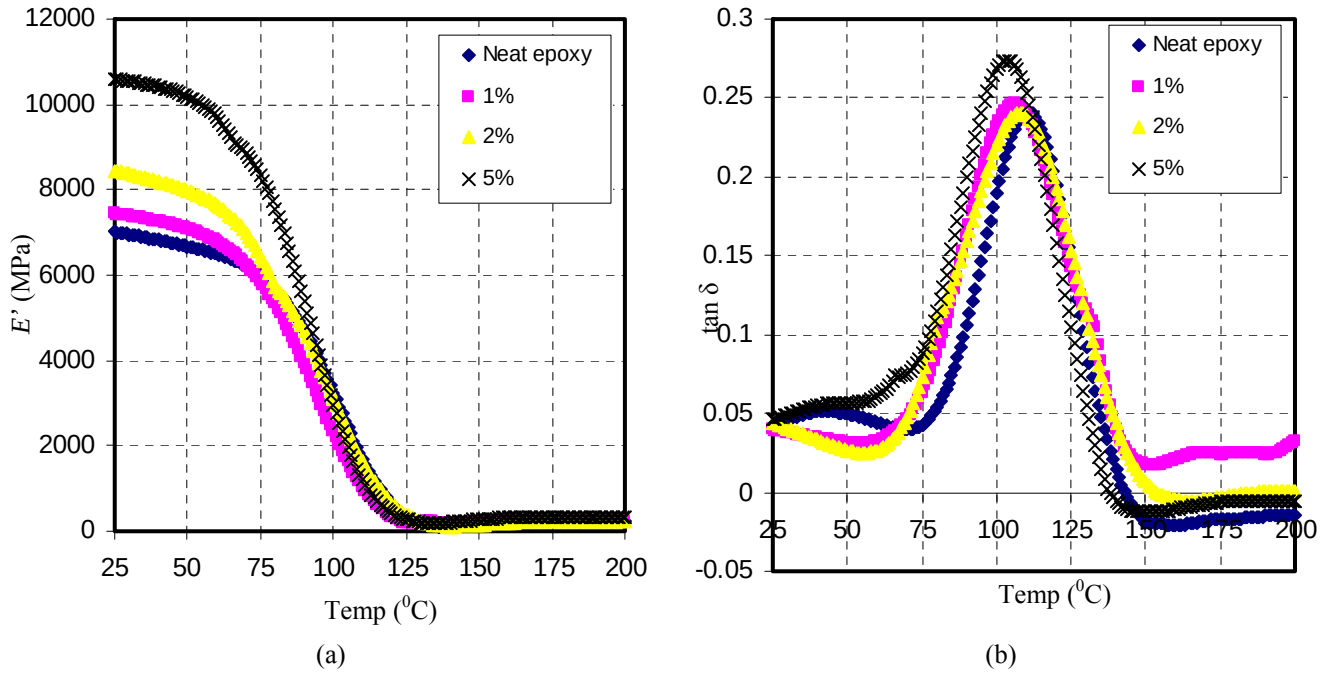

Fig. 7: The plots of (a) storage moduli and (b) tan δ as a function of temperature for epoxy and composites having 1, 2, and 5 % functionalized alumina platelets by volume

Figure 6 and 7 shows the plots of DMA for storage moduli and tan δ as a function of temperature for neat epoxy and composites having 1, 2 and 5 % of uncoated and coated alumina platelets by volume. The tan δ values for the platelet composites were obtained by dividing the loss modulus by corresponding storage modulus of the composites. It is clear from fig. 6 (a) and 7 (a) that the storage modulus of the composite increases with the increase in the alumina platelets volume fraction for both the coated and uncoated platelets in the glassy region and the increase is more pronounced in case of composite having silane coated platelets. The constraint imposed by the rigid alumina platelets on the mobility of local matrix material gives rise to the increase in the storage modulus both in the case of uncoated and coated platelets. In case of silane coated platelets the restriction on the local matrix deformation field increases due to the formation of covalent bond between epoxy and alumina platelets giving rise to the higher improvement in the storage modulus. The increment in the storage modulus in the

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rubbery region is insignificant in comparison to increment in the glassy region.

The tan δ value for the composites increases with the increase in the volume fraction of both coated and uncoated alumina platelets. The increase in the case of composites having uncoated platelets is more pronounced in comparison to composites having coated platelets. The inclusion of alumina platelets increases the energy dissipation from matrix resulting in an increase in loss modulus.

IV. CONCLUSIONS

In the present work, the effect of uncoated alumina platelets and silane coated alumina platelets on dynamic mechanical properties of epoxy was studied. Dispersion of alumina platelets in the epoxy resin was achieved by ultrasonication. A good dispersion of alumina in epoxy was shown by the SEM micrographs. Platelets were functionalized using 3-glycidoxypropyltrimethoxysilane (GPS). The formation of Si-O-Al bond was confirmed by the FTIR spectroscopy performed at different stages during the synthesis of composites. Improvement in storage modulus and tan δ values of composites was observed as an effect of alumina platelet reinforcement in epoxy.

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