J Mater Sci (2008) 43:6992–6997
DOI 10.1007/s10853-008-3023-1

LETTER

Observation of two α-relaxation peaks in a nanoclay-filled epoxy compound

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Received: 19 June 2008 / Accepted: 26 September 2008 / Published online: 18 October 2008

Introduction

For over 10 years, the effect of nanosilicate layers on glass transition temperature of epoxy resins has been studied by various research groups. Unfortunately, there appears to be no consensus in the literature regarding the role of nanoclay addition on α-relaxation peak (T_g-peak) in montmorillonite (MMT)-filled epoxy compounds [1–8]. Several studies reported an increase in the overall glass transition temperature (T_g) of MMT-filled epoxies compared to the neat epoxy [1–3], while other studies claimed suppression of the T_g in these nanocomposites [4–6]. There are even some results indicating that the addition of nanoclay has no effect on α-relaxation peak of epoxy resins [7, 8]. Table 1 contains a description of the materials investigated in these studies. The following sections contain discussions of glass transition behavior in several types of nanoclay-filled epoxies.

Messersmith and Giannelis [1] reported broadening of the tan δ peak in the glass transition region and a slight increase in the T_g of mica-filled epoxy compound with the interlayer distances larger than 100 Å. The glass transition temperature was characterized using a dynamic mechanical analyzer (DMA). The increase in T_g was attributed to the strong interactions between silicate platelets and epoxy network that restrict molecular motion of polymer segments near the silicate layer surface.

Regarding the observations of T_g depression, several hypotheses have been proposed. Chen et al. [4] attributed this phenomenon to the presence of interphase region between the silicate layers where the surface modifiers of clay act as plasticizer in epoxy resin. They predicted the effective size of interphase region in the order of 50 Å [4]. It was reported that the glass transition temperature decreased as the volume fraction of the interphase region inside the galleries increased by increasing the interlayer distance between silicate platelets [4]. However, Jackson and McKenna [9] found that confining organic liquids (1,2-diphenylbenzene and benzyl alcohol) in both surface treated and untreated nano-size pores resulted in similar T_g suppression.

Becker et al. [5] believed that the presence of unreacted epoxy monomers leads to T_g depression in clay nanocomposites. Specifically, it was claimed that the drop in the T_g can be ascribed to the lower crosslink density of epoxy network between silicate layers, i.e. in the galleries [5].

The purpose of this letter is to report an observation on the effect of nanoclay fillers on the α-relaxation in an epoxy resin. This observation, which is a small portion of a more detailed study on MMT-filled epoxies, provides useful insight on glass transition processes in nanoclay-filled epoxy composites.

Experimental procedure

Materials

In this investigation, intercalated-exfoliated clay–epoxy compounds were synthesized by swelling an organophilic montmorillonite in an aromatic epoxy resin and subsequent

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Table 1 Summary of materials investigated in the referred studies

Reference	Materials	d-spacing	T_g
Messersmith and Giannelis [1]	Diglycidyl ether bisphenol A (DGEBA) Nadic methyl anhydride (NMA) Boron trifluoride monoethylamine (BTFA) Benzyldimethylamine (BDMA) Methylenedianiline (MDA) Octadecyl ammonium treated mica	WAXS and TEM: >100 Å (exfoliation)	DMA (110 Hz) and DSC: increase
Lu and Nutt [2]	DGEBA 4,4′-Diaminodiphenyl sulfone (DDS) Bis-2-hydroxyethyl methyl tallow ammonium treated MMT	WAXS: 45–54 Å (intercalation)	DSC: increase
Chen et al. [4]	3,4-Epoxycyclohexylmethyl-3,4 epoxycyclohexane carboxylate Hexahydro-4-methylphthalic anhydride (HHMPA) Bis-2-hydroxyethyl methyl tallow ammonium treated MMT	WAXS (63 Å—no peak) and TEM (combination of intercalation and exfoliation): dependent on MMT content	DMA (torsion mode, 1 Hz): decrease
Becker et al. [5]	DGEBA Triglycidyl p-amino phenol (TGAP) Tetraglycidyldiamino diphenylmethane (TGDDM) Aromatic diethyltoluene diamine (DETDA) Octadecylammonium treated MMT	WAXS: 20 Å—no peak (combination of intercalation and exfoliation, dependent on MMT-epoxy system and MMT content)	DMA (dual cantilever bending, 1, 3, and 10 Hz) and DSC: broadening and decrease
Liu et al. [6]	Tetraglycidyl tetradiaminodiphenylmethane (TGDDM) 4, 4′-Diaminodiphenyl sulphone (DDS) Octadecylammonium treated MMT	WAXS (no peak) and TEM (35–60 Å): (intercalation)	DMA (1 Hz): decrease
Hutchinson et al. [7]	DGEBA Poly(prophylene glycol) diamine Octadecylammonium treated MMT	SAXS: 37 Å (intercalation)	DSC: no change
Yasmin et al. [10]	DGEBA Anhydride Bis-2-hydroxyethyl methyl tallow ammonium treated MMT	SAXS and TEM: no peak (disordered intercalation)	–
Velmurugun and Mohan [13]	DGEBA Triethylenetetramine (TETA) Alkyl quaternary ammonium treated clay	WAXS: $d > 70$ Å (combination of Intercalation and exfoliation)	DMA (3-point bending, 20 Hz): tow distinct T_gs

WAXS wide angle X-ray scattering, *SAXS* small angle X-ray scattering polymerization. The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA), EPON 828, with an equivalent weight of 184–190 g/eq from Hexion Specialty Chemicals. This epoxy resin was cured with piperidine, obtained from Sigma–Aldrich. Nanomer® I.30E. An octadecyl amine treated montmorillonite from Nanocor was chosen as the nanofiller in this study.

Epoxy compounds preparation

For preparation of the epoxy compound, the organoclay powder was mixed with the appropriate amount of resin for 2 h at 80 °C using a mechanical stirrer at 300 rpm. Then, 5 parts curing agent per 100 parts epoxy resin was mixed for 15 min at the same temperature. Note that the curing agent was injected gently into the bottom of the resin using a syringe to avoid vaporization. Vacuum was then applied with continued stirring for another 15 min to degas the mixture. Then, the mixture was poured into a preheated aluminum mold and cured at 120 °C for 16 h. A similar process was used to prepare the neat resin.

Characterization techniques

Dispersion of organoclay in the epoxy matrix was investigated using wide angle X-ray scattering (WAXS: Philips PRO Xpert with Cu-K$_\alpha$ radiation) and transmission electron microscopy (TEM: field emission gun Philips CM200, at an accelerating voltage of 200 kV in bright field mode).

In order to investigate the α-relaxation behavior of MMT-filled epoxy compound, dynamic mechanical thermal analysis (DMTA) was performed on 50 × 10 × 3 mm test specimens using an ARES Rheometrics RDA-2 with a temperature sweep from 25 to 150 °C at 5 °C per step, a frequency of 5 Hz, and sinusoidal strain amplitude of 0.2% under torsion mode.

Results and discussion

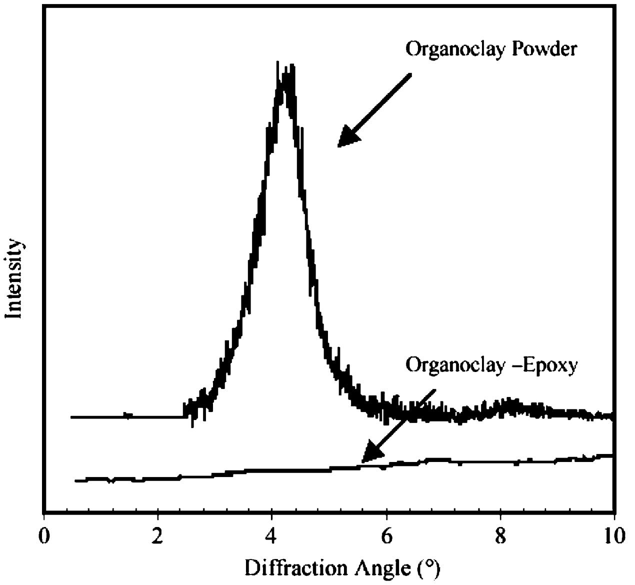

Fig. 1 X-ray diffraction patterns of the organoclay powder and the epoxy compound containing 1.5 wt% organoclay

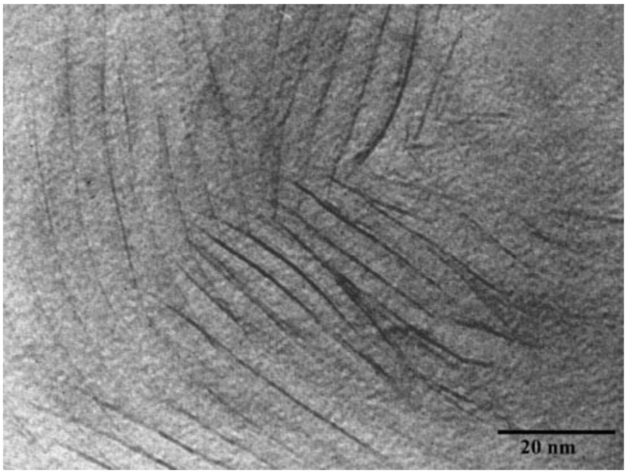

Fig. 2 TEM micrograph taken from the epoxy compound containing 1.5 wt% organoclay

Figure 1 depicts the X-ray diffraction (XRD) patterns of the organoclay powder and the epoxy compound containing 1.5 wt% organoclay. The XRD pattern of the organoclay powder shows a significant peak in the range of 2.5–5.5° corresponding to *d*-spacing of 16–35 Å representative of crystalline/ordered structure of the organoclay, while X-ray analysis of the MMT-filled epoxy compound does not show any peak in the scan range, which suggests random/disordered dispersion of silicate layers in the epoxy resin, i.e. exfoliation. Despite the XRD results, TEM revealed intercalation of silicate layers in the epoxy resin with the interlayer distances about 85 Å (see Fig. 2). This is in agreement with recent studies which reported either intercalation or combination of intercalation-exfoliation of clay platelets in epoxy resins based on TEM observations while no diffraction peak was detected using either wide angle X-ray scattering (WAXS) or small angle X-ray scattering (SAXS) analyses when the *d*-spacing is larger than 45 Å [4, 6, 10]. However, the absence of Bragg scattering in an XRD pattern has been considered as evidence for an exfoliated morphology by some researchers [5, 11, 12]. This indicates that both XRD and TEM examinations are required to determine dispersion state of clay layers in a polymeric matrix whether exfoliation was achieved.

Figures 3–5 contain the DMA results for the neat epoxy and the epoxy compound containing 1.5 wt% organoclay. The DMA spectra (G'' and tan δ curves) of the organoclay-filled epoxy compound show two distinct relaxation peaks that suggest the presence of two T_gs. The smaller relaxation peak at 75 °C occurs at a temperature that is lower than the T_g of the neat epoxy. The larger relaxation peak occurs at 100 °C, which is the same temperature of the α-relaxation peak of the neat epoxy. Both these relaxation peaks satisfied the Williams–Landel–Ferry (WLF) relationship in terms of the effect of frequency on the peak position, which proves the presence of two glass transition temperatures in this compound. The observation of two T_g peaks in this study agrees with Velmurugan and Mohan [13] who reported two distinct T_g transitions and broadening of tan δ peak in MMT-filled epoxy nanocomposites. These researchers attributed the two relaxation peaks to soft and hard segments in the epoxy [13]. Hard segments were attributed/correponded to the segments arrested at the neighborhood of clay–epoxy interface. No explanation was given for the occurrence of the soft segments with a T_g lower than the neat epoxy. The shifting and the broadening of the tan δ peak(s) were attributed to the partial mixing between soft and hard segments. The materials used by Velmurugan and Mohan [13] are described briefly in Table 1.

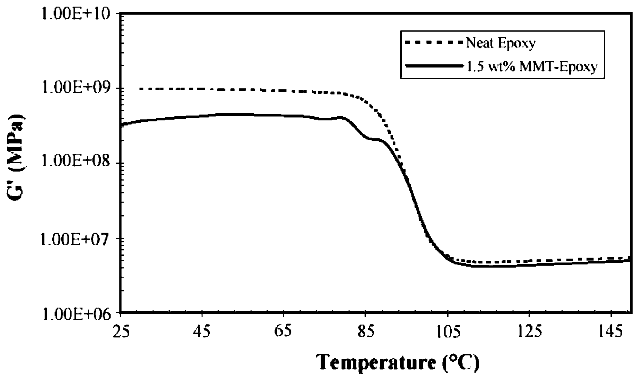

Fig. 3 Variation of shear storage modulus versus temperature in the neat epoxy and the epoxy compound containing 1.5 wt% intercalated-exfoliated MMT

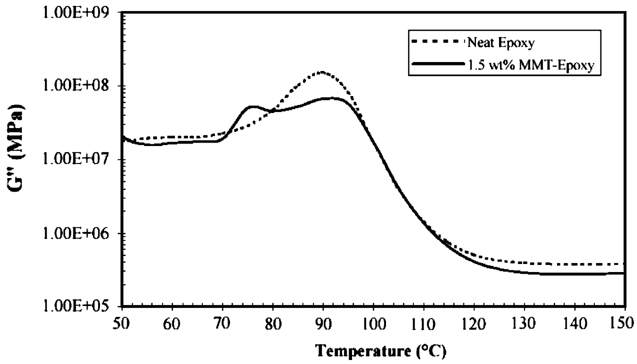

Fig. 4 Variation of shear loss modulus versus temperature in the neat epoxy and the epoxy compound containing 1.5 wt% intercalated-exfoliated MMT

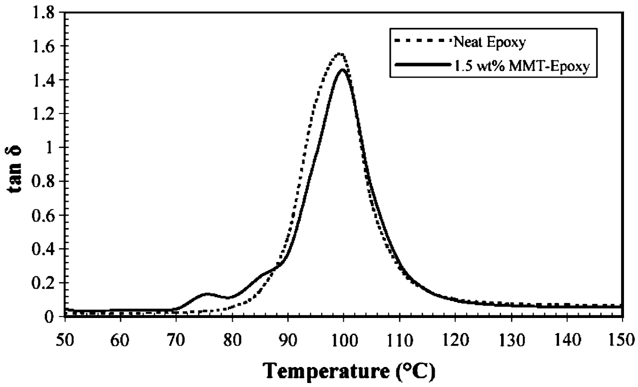

Fig. 5 Variation of tan δ versus temperature in the neat epoxy and the epoxy compound containing 1.5 wt% intercalated-exfoliated MMT

The observation in this study can be explained using the coarse-grained domain relaxation model proposed by Lu and Nutt [2] as well as the analogy between thin films and nanocomposites in thermomechanical responses [14, 15]. The coarse-grained domain relaxation model proposed by Lu and Nutt [2] considers three possible relaxation domains for intercalated clay–polymer nanocomposites. The interphase region near the surface of the clay layers is said to have the slowest relaxation rate. The fastest relaxation rate corresponds to central area between clay layers inside the galleries, hence only exists for intercalated particles. The modest relaxation rate corresponds to bulk material domain, where the polymer chains have the normal segmental mobility.

The coarse-grained domain relaxation model by Lu and Nutt [2] proposes that α-relaxation occurs at different time scales in the three different domains that exist in intercalated clay-filled nanocomposites. Unfortunately, multiple T_gs in intercalated nanocomposites were not detected using differential scanning calorimetry (DSC) in their study [2]. See Table 1 for the description of the epoxies used by Lu and Nutt [2]. The observation of two glass transitions using DMA in the present study is similar in some respect to the coarse-grained domain relaxation model by Lu and Nutt [2], who propose different relaxation time scales in three different domains. However, only two distinct domains were detected in the current study and the authors believe that the low T_g domain is the interphase region near the surface of the clay layers.

Segmental mobility in the interphase region depends on the strength of the interactions between the solid surface and the polymer chains. Bansal et al. [14] and Mayes [15] made the analogy between nanocomposites and ultrathin polymer films. Depending on the nanofiller/polymer interactions, the polymer chains can either relax faster in the vicinity of the nanofiller surface when the interactions are weak or relax slower when the interactions are strong. This analogy can be used to explain the glass transition shift in the present study. The silicate surfaces can act as free surface and provide a region with higher degree of freedom compared to the bulk material in the case of weak interaction between silicate platelets and epoxy. Thus, the interphase around the silicate layers favors polymer segments mobility in this area and local rearrangement can take place at lower temperatures, while the crosslink density is same as the bulk domain. In the case of strong interactions between polymer chains and nanofiller surface, lack of mobility of adsorbed polymer chains retards the relaxation process.

Therefore, the observation of the T_g below the bulk glass transition can be attributed to the higher motion ability of epoxy segments located in the interphase outside the galleries compared to the polymer segments in the bulk. The weak adhesion between epoxy and silicate layers let the motion and local rearrangements of segments in the interphase at lower temperature and far from the silicate layer decay in the relaxation process.

Another possible explanation is that organic-based surfactants on the surfaces of MMT platelets form an interphase region where the surfactant-rich region is plasticized by the presence of the surfactants and hence lead to T_g depression. This may be more effective due to plasticized interphase outside the galleries rather than this region effect inside the galleries, while Chen et al. [4] believed that formation of an effectively plasticized interphase inside the galleries due to clay surfactants results in the reduction of glass transition temperature in MMT-epoxy nanocomposites.

Besides the two given interpretations, some other reasons may be claimed to explain the occurrence of the lower T_g in this study. These include the effects of small molecules (unreacted epoxy oligomers/prepolymers, unreacted curing agent molecules, and decomposed clay surfactants), migrated excess amount of clay surfactants in epoxy matrix, and lower crosslink density of epoxy.

The claim, which proposes T_g depression due to presence of small molecules, can be refuted at least in the present work. The cure schedule (16 h at 120 °C) used in our work provided enough time to complete the cure reaction and the low cure temperature minimizes possible decomposition of clay surfactants. Also, please note that only 5 phr curing agent was used in this study. Using small amount of curing agent decreases the probability of glass transition changes that resulted from the remaining unreacted curing agent molecules between silicate platelets, although existence of any kind of small molecules possibly cause local variations.

Regarding the possibility of plasticization effect of migrated excess amount of clay surfactants into the bulk epoxy and plasticizing the bulk epoxy, this cannot be placed in this study since two glass transition peaks, lower and at the same temperature range as the neat resin, are observed here.

As mentioned, it may also be argued that the observation of the lower α-relaxation peak resulted from the presence of epoxy network with lower crosslink density. It has been described in the literature that the organoclay may change the chemistry of the polymerization reaction and indeed clay surfactants may catalyze homopolymerization of the epoxy resin [16]. This can form an epoxy network with lower crosslink density compared to the neat resin. Therefore, a decrease in T_g can be expected due to less crosslink density of organoclay-filled epoxies [5, 6]. Homopolymerization due to catalytic effect of surfactants can place inside and outside the galleries. Considering the interlayer distance between intercalated silicate layers (about 85 Å) and length of the epoxy molecule between two tie points (approximately 26 Å), it is more likely the formation of either linear epoxy chains in two dimensions within the galleries instead of a polymer network in three dimensions or an epoxy network with a chain length containing maximum three epoxy segments across the *d*-spacing between clay platelets. In addition, it is possible bond formation between only one epoxy oligomers/prepolymers and surfactants inside the galleries. This can make local areas/zones with higher degree of freedom, which can result in easier local motions. Although questions should be addressed are how much the presence of organoclay can affect crosslink density of an epoxy resin and how much change in crosslink density (inside the galleries) may affect α-relaxation process in nanoclay-filled epoxies. In this study, the idea of affecting the crosslink density of bulk polymer due to the presence of clay layers cannot be proper, since the glass transition region in the temperature range of the neat resin is observed. Comparing the interphase size and the spacing between silicate layers in intercalated nanocomposites proposes that the occurrence of glass transition process below the bulk value might be more likelihood due to interphase effect specially outside the galleries than the effects of lower crosslink density and small molecules.

Based on the results, it can be concluded that the observation of two T_g transition regions implies different temperature dependences of molecular motions in different length-scale. The lower glass transition suggests presence of domains, which provide easier molecular motions for polymer segments. According to the nanocomposite structure, it seems that polymer chains/segments located at the interphase have more mobility compared to the molecular mobility both between the silicate platelets in the galleries and in the bulk epoxy. Therefore, it may be appreciated the significance of interphase on segmental motions in clay–epoxy nanocomposites.

Conclusion

In this study, the dynamic mechanical relaxation behavior of an intercalated-exfoliated nanoclay-filled epoxy compound was investigated. The presence of two glass transition temperatures in the nanocomposite was found. One relaxation peak was located at lower temperature range and another relaxation peak occurred over the same temperature range of α-relaxation transition in the neat epoxy. The occurrence of lower T_g may be attributed to faster segmental motions in the interphase.

Acknowledgement The financial support from ARKEMA, Iranian Gas and Petrochemical Institute and Sharif University of Technology is gratefully acknowledged.

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