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Comparative study of different polymerically-modified clays on curing reaction and thermal properties of epoxy resin

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ABSTRACT

polymerically-modified clays including polystyrene-co-methyl acrylate modified clay (PSMA-clay) and polystyrene-co-acrylic acid modified clay (PSAA-clay), which contain either ester groups or carboxylic acid groups, were prepared by cation exchange and used to prepare diglycidyl ether of bisphenol A (DGEBA)/clay composites. The curing reaction of DGEBA/clay composites was investigated using DSC and FT-IR. The morphology and thermal properties of DGEBA/clay composites were characterized using XRD, TEM, TGA and DSC. DSC and FT-IR analyses demonstrated that there is a reaction between epoxy groups and carboxylic acid groups besides the curing reactions between epoxy groups and the curing agent, 4,4′-diaminodiphenylmethane (DDM) for DGEBA/PSAA-clay composites. XRD and TEM results indicated that the reaction between epoxy groups and carboxylic acid groups in the inter-gallery of PSAA-clay facilitated the clay dispersion in the epoxy matrix. Improved thermal properties due to the addition of reactive clay were also achieved for DGEBA/PSAA-clay composites.

1. Introduction

Epoxy resins have been widely used as adhesives [1–3], coatings [4], laminates [5], casting materials [6], and a matrix resin for composites [7,8] because of their excellent mechanical properties, low price, good adhesion, and chemical stability. However, properties of epoxy resin, such as heat resistance and moisture resistance, need to be improved for its applications in manufacturing materials such as circuit boards, liquid crystal displays (LCD), field emission display (FED), and plasma display panels (PDP) [9]. One of the methods to improve the thermal properties and moisture resistance of the epoxy resin is preparing hybrid composites using clay [10–12], and this improvement depends on the dispersion of clay in the polymeric matrix. Researches indicated that well-dispersed and exfoliated clay could enhance the properties of the polymer matrix in most cases [13–16].

Generally, to have good compatibility with the epoxy matrix, clay needs to be organically modified. Surfactants containing alkylammonium ions have been commonly chosen to modify the clay interlayer to improve the compatibility between the clay and polymer matrix [17–22]. Becker described that the octadecyl ammonium modified smectite clay could form intercalated and ordered exfoliated layered silicate structure, and the equilibrium water uptake of all nanocomposites was reduced compared to the neat epoxy [23]. Nigam used the octadecyl ammonium to modify clay and the mechanical properties of the obtained epoxy/clay composites were improved while the thermal stability and glass transition temperature (T_g) of epoxy/alkylammonium modified clay composites were unexpectedly reduced due to the presence of octadecyl ammonium species in the organic clay [24]. Wang et al. proposed a method using acidic onium ions-modified clay as interlayer crosslinking agent through the reaction between –COOH and epoxy group to facilitate the polymerization–delamination process, and an intercalated with partial exfoliation clay structure was obtained [25].

It is well known that the curing reaction temperature could be as high as 250 °C, which is high enough to degrade the long-chain alkyl ammonium modifier of clay and this degradation may lead to the further degradation of polymer matrix [26,27]. The styrene-based polymerically-modified clays, which are thermal stable, polarity and *d*-spacing tunable, could be a right choice to replace the long-chain alkyl ammonium to modify clays in the preparation of epoxy/clay composites [28–33].

In this work, polystyrene-co-acrylic acid modified clay (PSAA-clay) and polystyrene-co-methyl acrylate modified clay (PSMA-clay) will be used to prepare diglycidyl ether of bisphenol A (DGEBA)/clay composites. The dispersion of clay and the influence of different polymerically-modified clays on curing reaction and thermal properties of epoxy resin will be explored.

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2. Experimental

2.1. Materials

The epoxy resin used was a commercial grade of diglycidyl ether of bisphenol A (DGEBA) with an epoxy value of 0.44 mol/100 g from Baling Petrochemical Company Ltd. (Yueyang, China). The hardener, 4,4′-diaminodiphenylmethane (DDM), was purchased from Honghu BMI Resin Factory (Hubei, China). Pristine sodium montmorillonite was provided by Southern Clay Products, Inc. (cationic exchange capacity (CEC) = 90 meq/100 g). Styrene (St), acrylacid (AA), vinylbenzylchloride, methacrylate (MA), 30% trimethylamine aqueous solution, and N,N′-azobis (isobutyronitrile) (AIBN) were purchased from Shanghai Shanpu Chemical Reagent (Shanghai, China) and used without further purification. Tetrahydrofuran (THF) was purchased from Yueyang Chemical (Yueyang, China) and distilled before using.

2.2. Instrumentation

Fourier transform infrared spectroscopy spectra (FT-IR) were recorded on a WQF-200 instrument in a transmission mode (KBr pellets, 32 scans, resolution 4 cm^{-1}). For all clays, measurements were carried out using conventional KBr pellets. In the case of the DGEBA/clay liquid blends, the samples were loaded on potassium bromide pellets. X-ray diffraction (XRD) patterns were collected from 0.5 to 10° using a step size of 0.02° on a Bruker-D8 instrument (Karlsruhe, Germany) using monochromatic CuKα radiation. The curing process of DGEBA/clay composites was measured from 20 to 200 °C under nitrogen atmosphere and 15 °C/min scan rate using a differential scanning calorimeter (Netzsch DSC200F3). The glass transition temperature (T_g) of cured epoxy composites were also characterized on the DSC fitted with a liquid nitrogen cooling system. Specimens (8–12 mg) were cut as powder to avoid effect of the heat transfer as far as possible and then encapsulated in the aluminum pans. Two consecutive heating and cooling runs were performed using 10 °C/min heating and cooling rates respectively. Thermogravimetric analysis (TGA) was conducted from 30 to 800 °C and 20 °C/min scan rate on a Netzsch STA409PC instrument under nitrogen atmosphere with a 20 mL/min flow speed. All TGA results are averages of a minimum of three determinations; temperatures are reproducible to ±1 °C, while the error bars on the non-volatile material are ±1%. Transmission electron microscopy (TEM) was performed on a JEOL-1230 instrument (Tokyo, Japan) under an accelerating voltage of 100 kV. The samples were ultra-microtomed with a diamond knife at room temperature to give thin sections which were approximately 70 nm. The sections were transferred from the knife edge to 600 hexagonal mesh Cu grids.

2.3. Preparation of polymerically-modified clays

In general, the polymerically-modified clays were prepared by cation exchange of the sodium ions in the Na-MMT with the corresponding polymeric quaternary ammonium salts. The polymeric quaternary ammonium salts were prepared from the reactions of trimethylamine with the corresponding polymers, which were synthesized by free-radical copolymerization of styrene, monomers, and vinylbenzylchloride (the mass ratio: 85:10:5). The method for preparing polymerically-modified clays was reported in our previous work [34,35].

The structures of polymeric modifiers are shown in Fig. 1. The molecular weight and molecular weight distribution of polymeric modifiers determined by GPC and the organics content in PSAA-modified clay and PSMA-modified clay based on TGA data are summarized in the Table 1. All the clays were grinded and sieved with a 320-mesh sieve, and then dried at 100 °C under vacuum for 12 h before use.

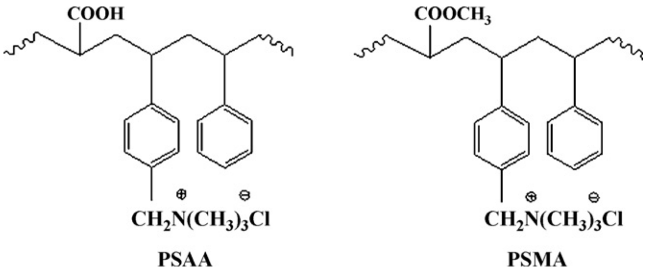

Fig. 1. The structure of two polymeric modifiers.

2.4. The preparation of the cured DGEBA and DGEBA/clay composites

The cured composites based on DGEBA, DDM and polymerically-modified clays were prepared from the stoichiometric proportion of DGEBA and DDM. The clay loadings in these systems were 3 wt%. If a polymerically-modified clay with 50% of organic content was used, it means actually 6 wt% of organic clay would be added in the system. The calculated amount of clay was added into 30 g of DGEBA. Subsequently, this system was homogenized for 1 h at 130 °C using a high-speed disperser at a speed of 2000 r/min, ultrasounded for 30 min, and degassed under vacuum for 30 min to remove the entrapped air. Then the mixture was blended with DDM at 90 °C for 10 min and a uniform mixture was obtained. The resin was injected into a 6-mm PTFE mold (length 150 × width 50 (mm)), sandwiched between two steel plates. PET films were inserted between the steel plate and sample to allow easy removal of the samples. Samples were cured following the sequence below: (a) 95 °C for 1 h (including degassing under vacuum); (b) 115 °C for 1 h; (c) 140 °C for 1 h; and (d) a post-cure temperature of 180 °C for 3 h. Sample of pure DGEBA was processed in the same way and used for comparison.

3. Results and discussion

3.1. Characterization of the polymerically-modified clays

FT-IR analysis has been used to obtain the chemical structural information of the modified clays. In Fig. 2, one could see the characteristic absorption bands for Na-MMT in spectrum a: the absorption bands at 1035 cm^{-1} and 800–400 cm^{-1}, which are assigned to Si–O–Si and the silica–oxygen tetrahedral/aluminum–oxygen octahedral sheet, respectively. Apparently, it is observed that there is an absorption band at 1730 cm^{-1} which is attributed to the ester group in Fig. 2(b) and an absorption band at 1710 cm^{-1} which is attributed to the carboxylic acid group in Fig. 2(c) besides the characteristic absorption bands for Na-MMT. All these above evidence indicated that polymerically-modified MMTs (PSAA-clay and PSMA-clay) have been achieved.

The *d*-spacing of the polymerically-modified clays was determined by XRD. Their XRD traces are shown in Fig. 3. The prinstine clay shows an apparent peak at $2\theta = 7.40°$, which is corresponding to a *d*-spacing of 1.2 nm, while the PSAA-clay (Fig. 3(b)) shows

Table 1
The structure parameters of polymeric modifiers.

Material	Mn	Mw	Mw/Mn	The organics content of clay/%
PSAA	2560	6001	2.3	53.1
PSMA	2518	6215	2.5	51.1

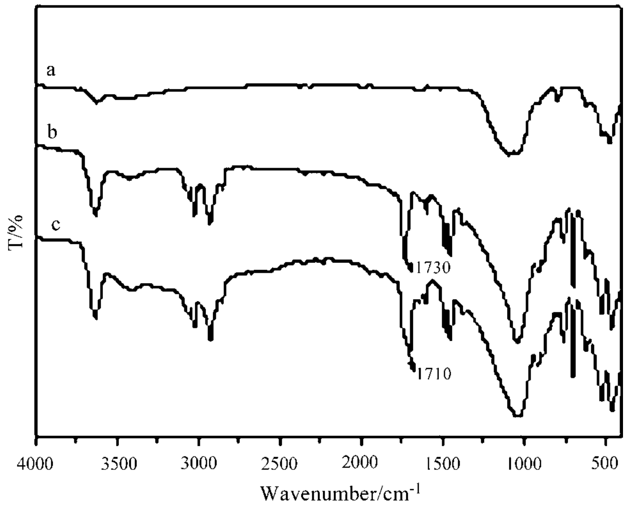

Fig. 2. FT-IR spectra obtained from: (a) pure clay; (b) PSMA-clay; and (c) PSAA-clay.

a weak peak at $2\theta = 1.87°$, a d-spacing of 4.72 nm and PSMA-clay (Fig. 3(c)) shows a weak peak at $2\theta = 2.10°$, a d-spacing of 4.20 nm. XRD results indicated that the d-spacing of clay has been well expanded after modification, and could facilitate the incorporation of the epoxy precursor and curing agent.

3.2. Characterization of the curing reaction of DGEBA/polymerically-modified clay composites

DSC was used to monitor the thermal curing behaviors of the DGEBA/polymerically-modified clay/DDM blends, and DSC traces were shown in Fig. 4. Only one exothermic peak was observed for the DGEBA/DDM (curve a), DGEBA/DDM/pure clay (curve b), and DGEBA/DDM/PSMA-clay (curve c), indicating one curing reaction for all these blends. In contrast, there is an additional weak shoulder peak at 130 °C for the DGEBA/PSAA-clay/DDM composite (curve d). It provides information that the thermal cure of the investigated DGEBA/DDM/PSAA-clay composite is probably accelerated by the active groups in the galley of PSAA-clay. DSC monitoring experimental data of thermal curing reaction of DGEBA and polymerically-modified clay blends without DDM were shown in Fig. 5. An obvious exothermic peak was observed at 130 °C for DGEBA/PSAA-clay system while no exothermic peak for other blends without DDM. It indicated that the exothermic transition of the small shoulder peak region in Fig. 4(d) results from the curing reaction between DGEBA and PSAA-clay and the drastic exothermic transition at the peak temperature were due to the polymerization heat of the reaction between the epoxy matrix and DDM. In addition, from DSC studies, it is also found that the peak temperature of DGEBA/DDM, DG EBA/DDM/pure clay, DGEBA/DDM/PSMA-clay, DGEBA/DDM/PSAA-clay is 174.1 °C, 176.0 °C, 178.7 °C and 174.1 °C, respectively. The occurrence of delayed peak temperature in the present of pure clay and PSMA-clay is due to the superior thermal insulation of the silicate layers which is depending on the dispersion of clay [36]. For the PSAA-clay composites, in contrast, this thermal insulation might be counteracted by the accelerative effect of the active groups –COOH in the galley of PSAA-clay [37].

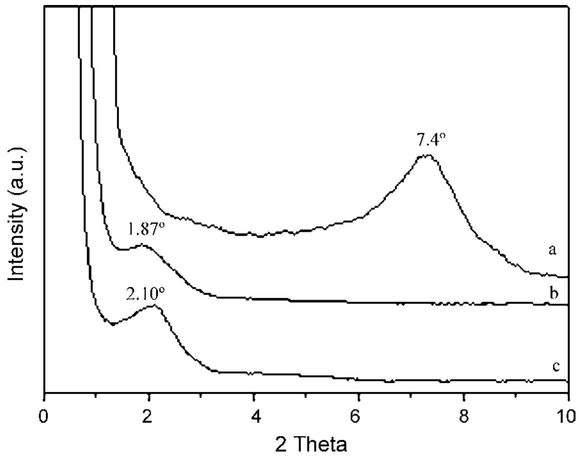

Fig. 3. XRD traces obtained from: (a) pure clay; (b) PSAA-clay; and (c) PSMA-clay.

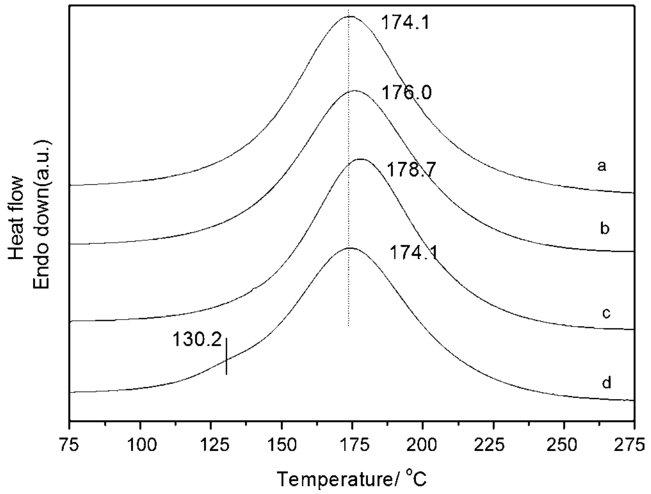

Fig. 4. DSC traces obtained from: (a) DGEBA/DDM; (b) DGEBA/DDM/pure clay; (c) DGEBA/DDM/PSMA-clay; and (d) DGEBA/DDM/PSAA-clay.

In order to further illustrate the change of the chemical groups caused by curing reactions between DGEBA and PSAA-clay, the FT-IR experiments of the samples before and after heating at 130 °C of DGEBA/PSAA-clay without DDM were performed. The FT-IR spectra are shown in Fig. 6. The absorption band at 1710 cm^{-1} in spectrum b is attributed to the carboxylic acid groups of the PSAA clay. After the mixture was heated, the absorption band at 1710 cm^{-1} shifted to 1730 cm^{-1}, which is attributed to the ester carbonyl groups (C=O) formed from the thermal curing reaction. Considering of both DSC experimental and FT-IR experimental data, one could have a conclusion that the exothermic transition of the small shoulder peak region in DGEBA/DDM/PSAA-clay composite is due to the reac-

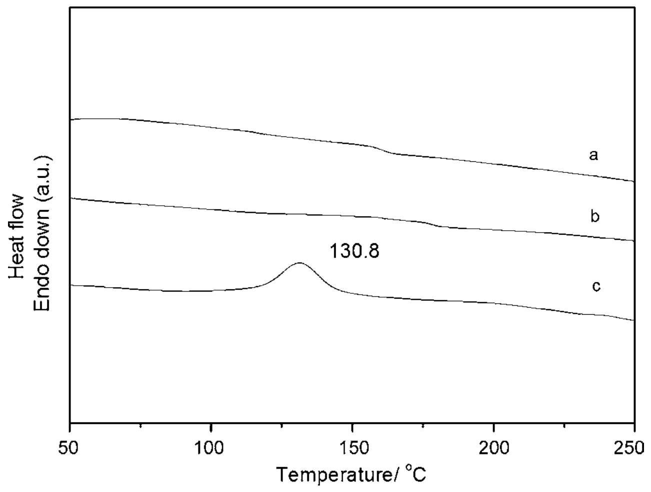

Fig. 5. DSC traces obtained from: (a) DGEBA/pure clay; (b) DGEBA/PSMA-clay; (c) DGEBA/PSAA-clay.

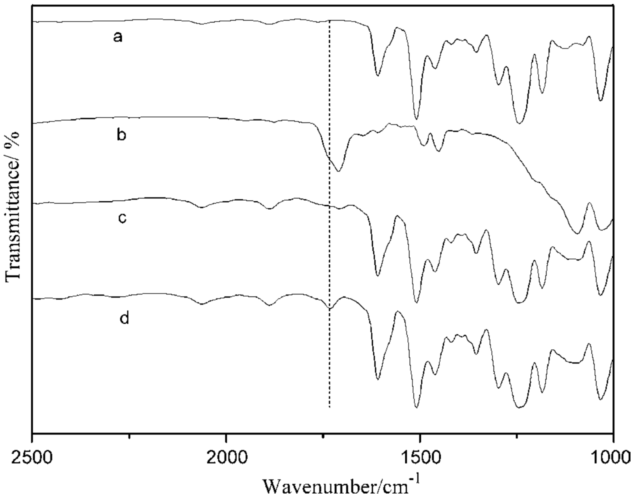

Fig. 6. FT-IR spectra obtained from: (a) DGEBA; (b) PSAA-clay; (c) DGEBA/PSAA-clay before heating; (d) DGEBA/PSAA-clay after heating.

tion happening between the carboxylic acid groups in PSAA-clay and epoxy groups in DGEBA (Fig. 4(d)). In addition, this reaction occurred in the lower temperature compared to the polymerization reaction between the epoxy matrix and DDM, which will improve the dispersion of clay in the DGEBA [25].

3.3. *The morphology of DGEBA/polymerically-modified clay composites*

The structures of the polymeric surfactants in the polymerically-modified clay are expected to have an effect on the dispersion of clay in the DGEBA. Fig. 7 shows the XRD patterns obtained from DGEBA/clay composites. Apparently, DGEBA/PSMA-clay composites reveals a peak at $2\theta = 0.72^\circ$ corresponding to a *d*-spacing of 12.2 nm. This indicates that an ordered intercalated structure is formed. However, there are no significant peaks that could be observed from the XRD traces of epoxy/pure clay composite and DGEBA/PSAA-clay composite. These results suggested that the clay platelets are probably exfoliated or completely disordered. These results alone cannot confirm this premise as the observed absence of scattering could be due to geometry effects or lack of sensitivity at the low level of clay loading.

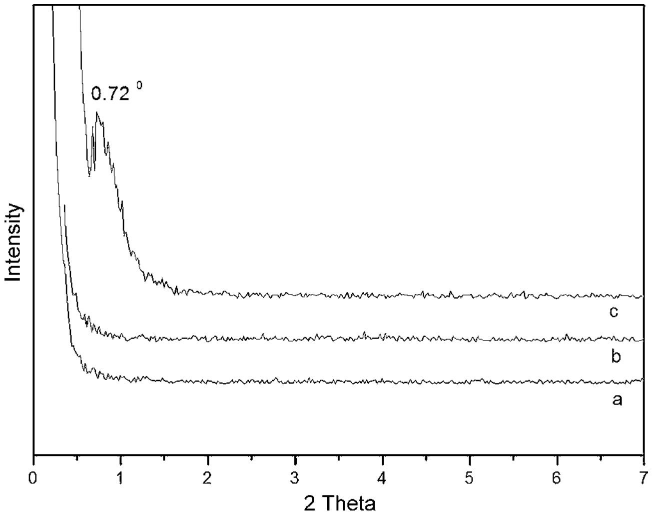

Fig. 7. XRD patterns obtained from composites: (a) pure clay; (b) PSAA clay; (c) PSMA clay.

Table 2
The thermal degradation data of DGEBA and DGEBA/clay composites.

Composites	Parameters of thermal degradation		
	T_{10}/°C	T_{50}/°C	Char/%
Epoxy	379	419	16
Epoxy/pure clay	378	421	18
Epoxy/PSMA clay	381	423	19
Epoxy/PSAA clay	388	424	17

To confirm the structure of DGEBA/polymerically-modified clay composites, TEM experiments were performed. TEM images of polymerically-modified clays composites are shown in Fig. 8. It is obvious that the composites formed from pristine clay contain many aggregates of clay as shown in Fig. 8(A1), while most of the particles in the PSAA-clay composites (Fig. 8(C1)) are much smaller than that observed in pristine clay composite and PSMA-clay composite (Fig. 8(B1)). This indicated that PSAA-clay is better dispersed in the epoxy resin than pure clay and PSMA-clay which is due to the existence of reactive groups in the gallery. However, 'tactoid' particles in DGEBA/PSAA-clay are still present. A comparison of the high images among three composites is shown in the Fig. 8(A2), (B2) and (C2). It can be seen that the clay galleries of polymerically-modified clay are enlarged. In addition, it also can be seen that the dispersed plates for PSAA-clay composite are more irregular compared to the pure clay, while PSMA-clay composite has an ordered intercalated structure, which is agree with XRD results of composites.

3.4. *The thermal properties of DGEBA/polymerically-modified clay composites*

The T_gs of DGEBA and the DGEBA/clay composites were evaluated by DSC. Fig. 9 shows T_g traces obtained from cured DGEBA and DGEBA/clay composites. It can be seen that the composites with clays have higher T_g values than the pure DGEBA because of the confinement of the silicate layers and their ability to hinder the motion of the molecular chains and network junctions. As for the DGEBA composites with various clay, it can be seen that the composite with PSAA-clay shows the higher T_g than those with pure clay and PSMA-clay. This could be attributed to the formation of the chemical bond through the reaction and the confinement of the silicate layers of the clay, which is consistent with DSC and FT-IR results. Compared with that of the pure clay, however, the slight decrease in T_g of PSMA-clay is observed. This is due to the addition of polymerically-modified surfactant exerted plasticization effects [33].

The thermal stability of DGEBA and its composites have been evaluated using TGA. Generally, information obtained from TGA analysis includes: the 10% weight loss temperature (T_{10}), a measure of the onset degradation; the 50% weight loss temperature (T_{50}), the midpoint of the degradation process; and the char. The decomposition parameters of cured DGEBA and its composites were summarized in Table 2. One step decomposition was observed in all the samples. It can be seen that the onset degradation temperature of DGEBA/PSAA-clay composite is 9 °C, 10 °C and 7 °C higher than the pure epoxy, DGEBA/pure clay composite and DGEBA/PSMA-clay composite, respectively. This is also related to the formed chemical bond and network between epoxy and PSAA clay. In the case of DGEBA/pure clay, the slight decrease in the onset temperature compared to the pure epoxy has been observed which is attributed to the lowered crosslink density due to the addition of clay [22]. One can see the onset temperature of the DGEBA/polymerically-modified clay composites was all higher than the DGEBA/pure clay. This is contributed the better dispersion of polymerically-modified clay composites compared to the pure clay in the epoxy [33].

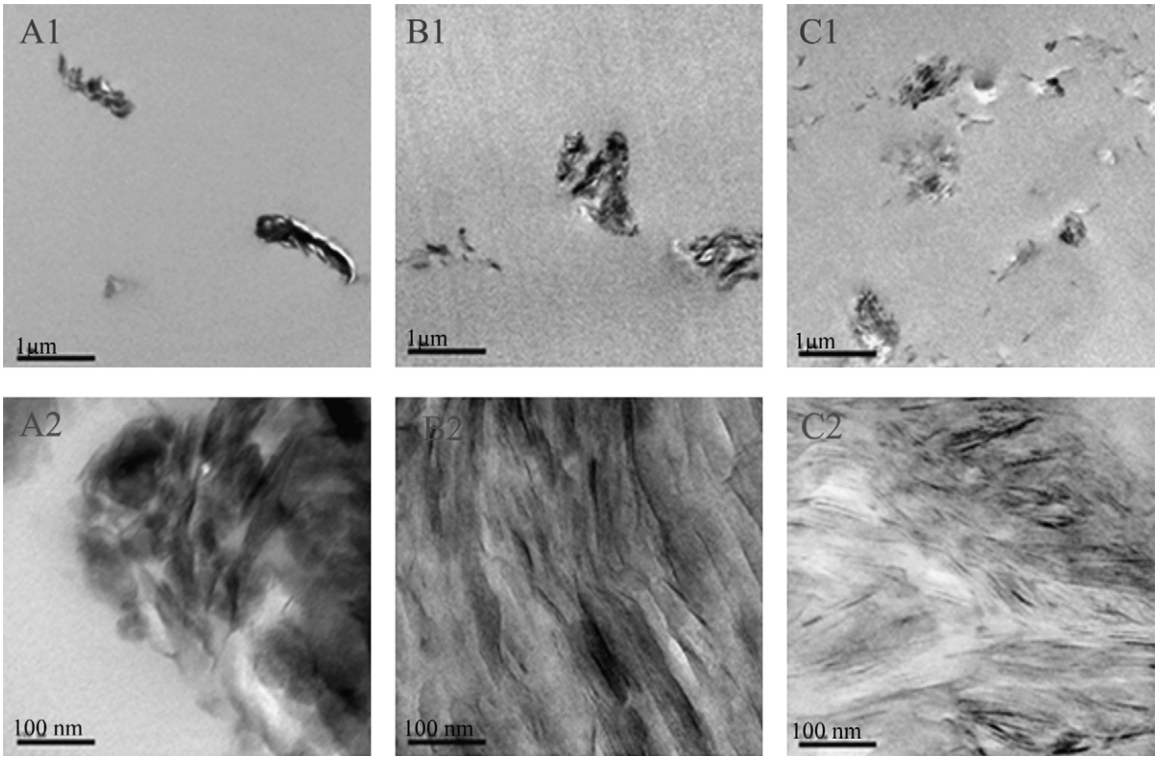

Fig. 8. TEM images for pure clay (A), PSAA-clay composites (B) and PSMA-clay composites(C); (1) low magnification, (2) high magnification.

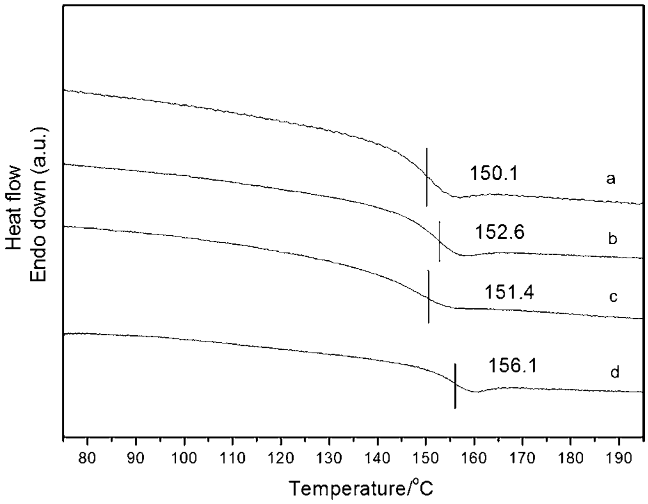

Fig. 9. T_g curves of cured epoxy resin filled with clays: (a) epoxy; (b) pure clay; (c) PSMA clay; (d) PSAA clay.

4. Conclusions

A comparative study on the curing reaction and thermal properties of DGEBA/clay composites prepared from polymerically-modified clays has been performed. Experimental results have indicated that curing reaction and thermal properties of the composites are dependent on the chemical structure of modifiers used in the preparation of clays. The reaction occurred between epoxy groups and carboxylic acid in the inter-gallery of PSAA-clay which could facilitate to clay dispersion in the epoxy matrix and improve the thermal properties of DGEBA.

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