Effect of external shearing force on exfoliation structure and properties of high-performance epoxy/clay nanocomposites[①]

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Abstract: To further investigate the influence of organic modifiers (primary amine with catalytic hydrogen and quaternary alkylammonium salt) on exfoliation behavior of clay tactoids, high-speed emulsifying and homogeneous mixing(HEHM) and ball milling were used to exert external shearing force on two organic clay tactoids (termed as MMT_{DDA} and MMT_{DBDA}, respectively), which were organically modified with DoDecyl Amine(DDA) and Dodecyl Benzyl Dimethyl Ammonium chloride(DBDA), respectively. The effects of external shearing force on microstructure and properties of both resultant nanocomposites were investigated by X-ray diffractometry(XRD), transmission electron microscopy(TEM) and thermogravimetric analysis(TGA). The results show that whether the clay tactoids are organically modified with catalytic primary amine or quaternary alkylammonium salt, the large agglomerates will not be finely dispersed or exfoliated by conventional mixing (magnetic stirring). After being vigorously sheared by HEHM or ball milling, the dispersion and exfoliation of clay tactoids are increasingly promoted for both MMT_{DDA} and MMT_{DBDA}, and the mechanical properties of the high-performance epoxy/clay nanocomposites are enhanced. For epoxy/MMT_{DDA} nanocomposites, impact strength can be increased up to 44.5 kJ/m² from 32.1 kJ/m², which is about 39% higher than that of pristine matrix, and the flexural strength is enhanced by about 4%. A similar enhancement for epoxy/MMT_{DBDA} nanocomposites has also been achieved. Improvement on thermal stability of epoxy/clay nanocomposites is dependent on the exfoliation of clay layers and molecular structure of the modifiers. The onset temperature is increased with the clay loading decreasing from 5% or higher content to 3%(mass fraction), and the DBDA modifier with the heat-resistant benzyl may also improve the stability of epoxy/MMT_{DBDA} nanocomposites.

Key words: shearing force; exfoliation; nanocomposites; epoxy; clay

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1 INTRODUCTION

Over the last decade, a new approach to improve the polymer performance with incorporation of layered silicate clay has been established. Compared with conventional filled composites, the nanoscale clay layers, typically ranging between 1 and 100 nm, will offer a variety of new and enhanced properties for polymer/clay nanocomposites, including high modulii, increased strength and heat resistance, reduced gas permeability and water uptake, resistance to flammability etc[1,2]. Now, the application of such polymer/clay nanocomposites has been extended into many commercial polymer fields, ranging from commodity plastics to advanced aerospace systems.

For advanced materials, extensive research on aerospace epoxy/clay nanocomposites has been carried out[3,4]. As it is well known, when the layered silicates are mixed with epoxy resin, two typical morphologies can be achieved: 1) intercalated nanocomposites and 2) exfoliated nanocomposites.

It is generally believed that the improvement of many properties of such nanocomposites strongly depends on the dispersion and exfoliation of clay particles in the polymer matrix, and achieving a disordered exfoliation of clay particles in viscous epoxy resin, therefore, will be our major objective. Substantially, exfoliation behavior of clay layers in epoxy resin may be determined by many factors such as length and number of modifier chain, nature of clay, curing agent, curing conditions (temperature, time of curing), viscosity and functionality of resin matrix[5-8]. It has been suggested that well-dispersed and fully exfoliated clay layers may result from the intergallery self-polymerization promoted by the catalytic role of acidic primary alkylammonium[9], consequently, how to control and balance the reactivity between inter- and extra-gallery may be the key point during the processing of epoxy/clay nanocomposites.

When summarizing previous major reports, most of relative research results only show an intercalated or partially exfoliated structure. How to

achieve a real fully-exfoliated structure is still a technical challenge. Although improved mechanical properties for dynamic modulus have been involved[10, 11], nearly no improved static mechanical properties such as impact strength or flexural strength for the high-performance epoxy/clay nanocomposites have been successfully achieved. We suggest that dispersion process will be one of the most significant and important influences on the exfoliation of clay tactoids. As we know, the commonly used dispersing methods are direct mixing or solution mixing. Due to the preferred face-to-face stacking in agglomerated clay tactoids, it is difficult to break the tactoids down into the scale of individual particles in the conventional dispersion process such as magnetical stirring. During the curing of the systems, whether the clay layers can be pushed out to yield exfoliation will inevitably depend on the size of clay tactoids. With the formation of polymer network, the exfoliation of clay layers in larger agglomerated tactoids will be much more difficult to shift to the outside than that of small clay particles. So the partially exfoliated structure is generally formed.

For melt intercalation, the study[12] of both the practical experiments and Monte Carlo simulation method has demonstrated that the shearing force produced by processing devices such as extruder and kneading mixer can promote the exfoliation of silicate layers. Although the preparation process for thermoset polymers is different from thermoplastic polymers, exerting similar shearing force when mixing aerospace epoxy resin with clay particles will be a powerful driving force to induce clay tactoids homogeneously dispersed. Now, a three-roll mill has been used by Yasmin and coworkers[13] as a means of applying external shearing forces to disperse and exfoliate the silicate clay layers, however, the static mechanical properties are still not reported.

Until now, the exfoliation mechanism has attracted great attentions, but is still not well understood. Our previous report[14] has suggested that the dispersion and pulverization of clay agglomerates by exerting vigorous shearing force during mixing clay with thermoset resin are more significant and important than influence of how to control other factors or even balance the reaction rate of inter- and extra-gallery. In this paper, we still use the optimized processing methods to prepare the epoxy/clay nanocomposites, i. e. the high-speed emulsifying and homogeneous mixing(HEHM) and ball milling were used to exert shearing force on agglomerated clay tactoids to promote their dispersion and exfoliation. The effect of two organic modifiers (primary amine and quaternary alkylammonium salt) on exfoliation behavior of clay tactoids is further investigated.

2 EXPERIMENTAL

2. 1 Materials

Na^+-Montmorillinite (MMT) used in this study, provided by Zhejiang FENGHONG Clay Chemicals Co Ltd, was industrially purified, and the cation exchange capacity (CEC) is $80-90$ mequiv/100g. Dodecyl benzyl dimethyl ammonium chloride (DBDA) and dodecyl amine(DDA) were obtained from Beijing Chemical Reagents Company. Epoxy resin(E-51) was the diglycidyl ether of bisphenol A (DGEBA), provided by Wuxi Resin Factory. And it was cured by Diaminodiphenyl-sulfone (DDS) which is purchased from Suzhou Yinsheng Chemicals Co Ltd.

2. 2 Preparation of organic clay

10 g natural MMT was suspended in 200 mL distilled water and stirred vigorously by high-speed emulsifying and homogeneous mixing(HEHM) for a period of time at room temperature and then transferred to a three-necked flask. DBDA or DDA was added to the suspended solution with stirring and continuously stirring for about 6 h at 80 ℃. The reaction mixture was filtered and washed repeatedly with distilled water to remove the chloride ions, and then dried in a vacuum oven at 80 ℃ for about 10 h. The dried products, termed as MMT_{DBDA} and MMT_{DDA}, respectively, were ground and sieved with a particle size about 38 μm.

2. 3 Preparation of aerospace epoxy/clay nanocomposites

1) Conventional mixing: Certain amount of organic clay was dispersed into 100 g DGEBA, stirred with magnetic bar for 4 h at $70-80$ ℃, and then a stoichiometric amount of curing agent was mixed thoroughly with the DGEBA/MMT hybrid at 120 ℃ for about 30 min. The mixture was cast into the glass mold covered with Polytetrafluoroethylene(PTFE) film and then degassed in a vacuum oven for 40 min. Samples for mechanical testing were cured at 140 ℃ for 2 h and 180 ℃ for 4 h.

2) High-speed shearing mixing by HEHM: Certain amount of organic clay was dispersed into 100 g DGEBA at $70-80$ ℃, and vigorously sheared for a period of time by HEHM, the following steps are the same as the above-mentioned conventional mixing.

3) Ball milled mixing: In order to exert more vigorous shearing force on MMT, the DGEBA-MMT mixture was dissolved in ketone and continued to be pulverized for a long time by ball milling. Ketone in DGEBA/MMT solution was eliminated under vacuum, and the following steps are the

same as the above-mentioned conventional mixing.

2. 4   Measurement and characterization

Room temperature X-ray diffraction spectra were collected on a Rigaku DMAX-RB 12 kW X-ray diffractometer (Cu K_a Radiation, λ= 1. 540 6 Å) with a tube voltage of 40 kV and tube current of 150 mA. The state of dispersion and exfoliation for clay particles in nanocomposites was inspected using a HITACHI H-800 transmission electron microscopy(TEM) with an acceleration voltage of 150 kV, and the ultrathin samples with a thickness of less than 1 μm were microtomed in liquid nitrogen using LKB Bromma 2088 cutter. Thermo-gravimetric analysis was carried out using SDT 2960 DTA-TGA, made by TA instrument under nitrogen atmosphere. Impact strength and flexural strength test were performed on Charpy Impact Tester (XCJ-400) and ZMGi 250 machine, respectively. At least ten samples were used for impact measurement and five for flexural measurement. The average value of each test group is employed for subsequent analysis.

3   RESULTS AND DISCUSSION

3. 1   XRD analysis

The XRD patterns of MMT_{DDA} and MMT_{DBDA} are shown in Fig. 1(a). It is clear that the diffraction peak (d_{001}) of both MMT_{DDA} and MMT_{DBDA} is shifted to the low degree (2θ), and the corresponding clay interlayer d-spacing is swollen up to 17. 589 Å and 16. 598 Å (2θ= 5. 02° and 5. 32°), respectively, compared with the original d-spacing, 12. 51 Å (2θ= 7. 06°). This results indicate that enough modifier molecules have been intercalated into the gallery of MMT. However, it is important to point out that the d-spacing of MMT_{DDA} is a little larger than that of MMT_{DBDA}. This may be caused by the different molecular structures of modifier chains, and the larger spatial distribution of DBDA chains with benzyl group will prevent much more DBDA from being intercalated into MMT gallery. Therefore, as indicated in previous literature[15], the DDA chains will be more liable to reorient from their initial monolayer to lateral bilayer, or inclined paraffin structure than DBDA chains. Fig. 1(b) shows the XRD patterns of epoxy/MMT_{DDA} and epoxy/ MMT_{DBDA} nanocmoposites. We can see that the diffraction peaks of both nanocomposites have been shifted to the low degree less than 2°, indicating that the averaged gallery spacing is swollen up to > 44. 1 Å or the clay layers are finely exfoliated.

3. 2   Morphology of epoxy/ clay nanocomposites

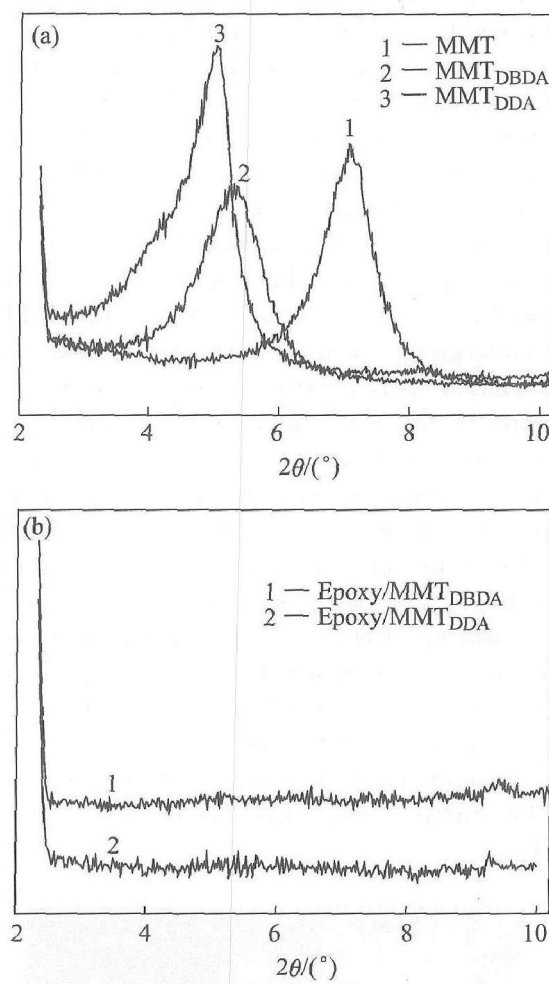Previous study[16, 17] has demonstrated that the

Fig. 1   XRD patterns of MMT and organically modified MMT(a), and epoxy/organically modified MMT nanocomposites(b)

acidic hydrogen in modifier chains (e.g. DDA) will serve to catalyze intragallery polymerization reactions, and the curing agent with low reactivity such as DDS can also delay the extragallery gelation. Consequently, by enhancing the intragallery polymerization rate relative to the bulk polymer, the delamination of clay tactoids in the polymer matrix can be facilitated and the exfoliated structure will be liable to be formed easily; while the clay tactoids organically modified with quaternary ammonium surfactant such as DBDA still remain an intercalated structure. Our study has shown that conventional mixing methods such as magnetical stirring cannot induce MMT_{DBDA} finely dispersed and intercalated. Moreover, the MMT_{DDA} tactoids still remain mostly intact, and only partially exfoliated layers for small clay particles or the external layers can be achieved, as shown in Fig. 2. We suggest that this may be caused by the poor dispersion and pulverization of agglomerated clay tactoids. The driving force during curing cannot induce the layers of large clay tacoids finely exfoliated. So, the mixing methods are optimized, i. e. exerting external shearing force (vigorously stir-

ring by HEHM) on clay tactoids. A typical TEM image has been provided in Fig. 3. For epoxy/ MMT_{DDA} nanocomposites, the interlayer distance is dramatically increased compared with that of clay tactoids dispersed by conventional stirring. Furthermore, the surface layers are finely exfoliated, and the internal layers can also be well expanded and tend to be exfoliated. It is confirmed that exerting external shearing force can promote the exfoliation of clay layers. Although MMT_{DBDA} with undergoing shearing force of HEHM cannot be exfoliated also, exerting external shearing force can improve the intercalation effect compared with conventional stirring. Based on this point, the effect of external shearing force on exfoliation behavior of agglomerated MMT_{DDA} and MMT_{DBDA} particles is further investigated by varying the mixing method, i.e. ball milling with much more vigorous shearing effect is used to finely disperse and pulverize the agglomerated clay particles. A satisfactory result is achieved for both MMT_{DDA} and MMT_{DBDA}, as shown in Fig. 4. The large clay tactoids are effectively dispersed and the clay layers can be further separated layer by layer for MMT_{DDA}.

Fig. 2 Microstructure of epoxy/ MMT_{DDA} nanocomposites dispersed by conventional mixing

It is worth noting that the clay layers of MMT_{DBDA} are more finely dispersed and exfoliated in epoxy matrix than those of MMT_{DDA}, which indicates that the acidic catalysis of DDA is not the key factor to influence the exfoliation. Whether the clay layers can be exfoliated will directly depend on the dispersion and pulverization of agglomerated clay tactoids. We also can see that although some of clay layers are obviously fractured, the clay layers are not infinitely stiff and most of them can bend, which will improve the strengthening and toughening of aerospace epoxy/ clay nanocomposites.

3.3　Mechanical properties

The effect of external shearing force, induced by different mixing devices, on impact strength and flexural strength for epoxy/ MMT_{DDA} and ep-
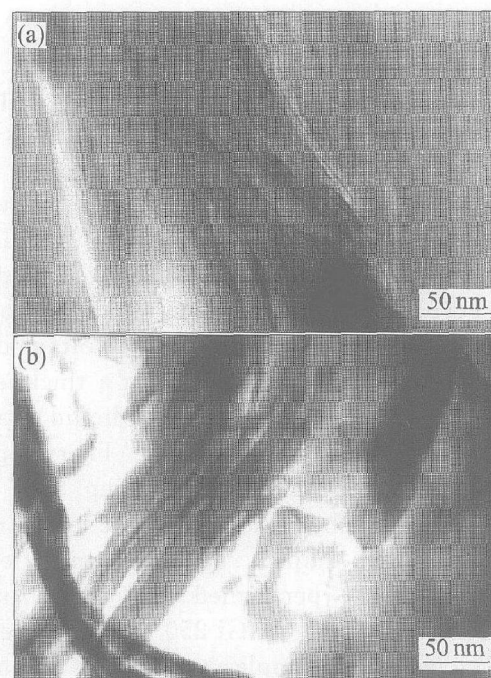

Fig. 3 Microstructures of epoxy/ clay nanocomposites dispersed by HEHM
　(a) —Epoxy/ MMT_{DDA} nanocomposites;
　(b) —Epoxy/ MMT_{DBDA} nanocomposites
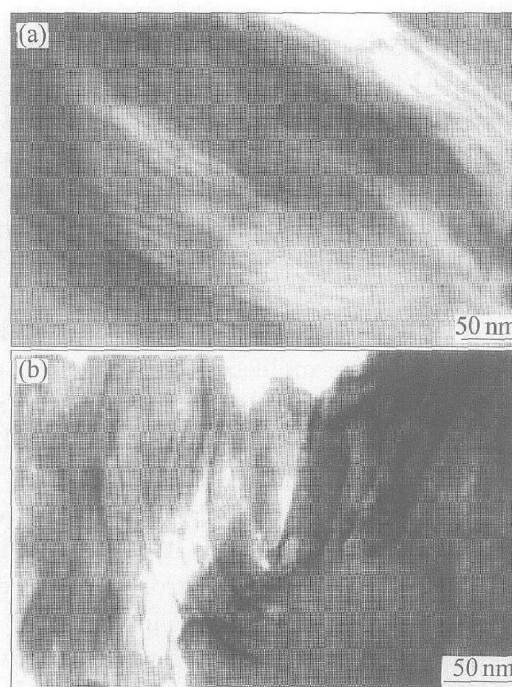

Fig. 4 Microstructures of epoxy/ clay nanocomposites dispersed by ball milling
　(a) —Epoxy/ MMT_{DDA} nanocomposites;
　(b) —Epoxy/ MMT_{DBDA} nanocomposites

oxy/ MMT_{DBDA} nanocomposites (3% clay loading, mass fraction) are shown in Fig. 5. It is observed that the addition of MMT_{DDA} and MMT_{DBDA} in epoxy by conventional mixing will lead to a sharp decrease for both impact strength (by about 16% and 17%, respectively) and flexural strength (by
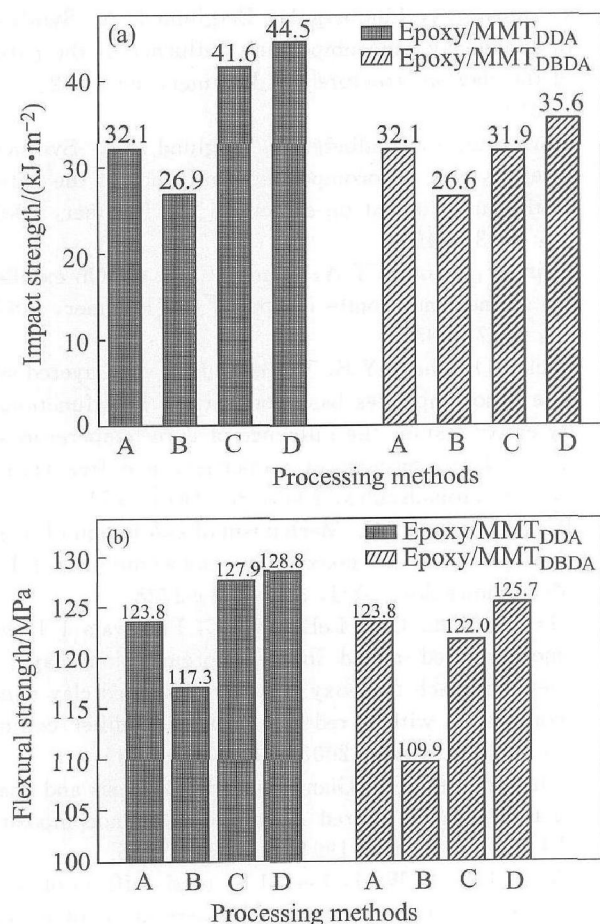
Fig. 5 Mechanical properties of epoxy/clay
nanocomposites prepared by different processing
(a) —Impact strength; (b) —Flexural strength
(A —Blank epoxy sample; B —Magnetic stirring;
C —Sheared by HEHM; D —Sheared by ball milling)

about 5% and 11%, respectively), which may be caused by the bad dispersion and exfoliation of agglomerated clay tactoids. This result is in good agreement with what observed in TEM image. After exerting external shearing force on epoxy-solvated clay by vigorous stirring of HEHM, the mechanical properties can be improved for both epoxy/MMT_{DDA} and epoxy/MMT_{DBDA} nanocomposites. The impact strength of epoxy/MMT_{DDA} nanocomposites can be increased up to 41.6 kJ/m² from 26.9 kJ/m², which is about 55% higher compared with the conventional mixing and is nearly about 30% higher than that of blank epoxy resin. The flexural strength also has a great improvement, which is about 9% and 3% higher than that of the conventional mixing, respectively. For epoxy/MMT_{DBDA} nanocomposites, although both the impact strength and flexural strength have an improvement by about 20% and 11%, respectively, compared to the conventional mixing, it is still lower than that of blank epoxy resin. However, the same system is continuously sheared for a period of time by ball milling, and a significant improvement can be typically achieved. The impact

strength of epoxy/MMT_{DBDA} nanocomposites is increased up to 35.6 kJ/m² from 32.1 kJ/m², which is unexpectedly 11% higher than that of blank samples, and the flexural strength also has a comparable enhancement. Mostly important, the impact strength of epoxy/MMT_{DDA} nanocomposites can be further increased up to 44.5 kJ/m², which is about 39% higher than that of blank epoxy resin, and the flexural strength is also increased by about 4%. It is important to point out that the enhancement of MMT_{DBDA} layers is slightly lower than that of MMT_{DDA}, and this may be due to the different structure of DBDA and DDA chains. Many amine groups in DDA molecules may react with the epoxy matrix and the interfacial interaction between MMT_{DDA} layers and epoxy matrix, therefore, is highly improved.

3.4 Thermal stability

It is generally believed that the clay layers can act as barriers to minimize the permeability of volatile degradation products out from the material and to improve the thermal stability. However, most previous reports[18-20] have shown that the thermal stability of epoxy/clay nanocomposites is lower than that of pure epoxy. In our study, we attempt to improve the thermal stability by optimizing the mixing method to achieve much more finely exfoliated structure. The TGA curves are shown in Fig. 6, in which it can be seen that the onset temperature of Epoxy/MMT_{DDA} nanocomposites with 3% clay loading also have a slight decrease for about 5 ℃. With the clay loading increasing, the onset temperature is rapidly decreased to 368 ℃ from 394 ℃. However, it is noteworthy that the thermal stability of epoxy/MMT_{DBDA} nanocomposites can be improved and a little higher onset temperature is observed. This may be mainly attributed to the heat-resistant benzyl group in DBDA chains. On the other hand, the high concentration
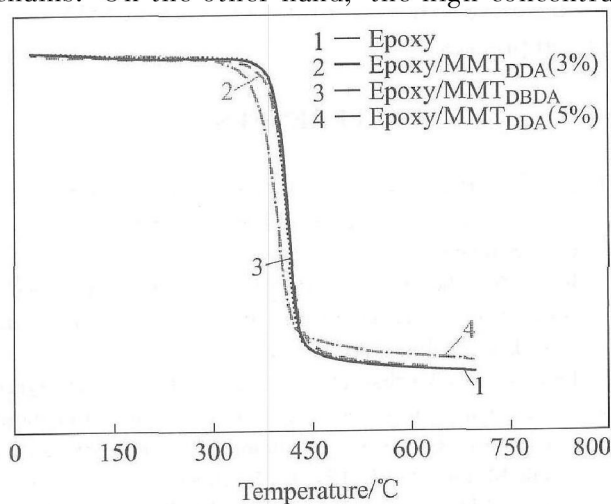

Fig. 6 TGA curves for epoxy and
epoxy/clay nanocomposites

of amine group in DDA chains will react with the matrix resin and form more 'dangle chain' in the crossing linking structure than that of DBDA, which results in a low cross-linking density of cured epoxy resin. Therefore, whether the thermal stability of epoxy/clay nanocomposites can be improved will be determined by many competitive factors such as layer barrier, modifiers, and much more attention should be paid on the study of the degradation mechanism.

4 CONCLUSIONS

The exfoliation of clay layers in epoxy resin is strongly dependent on the dispersion and pulverization of clay tactoids, and exerting shearing force by HEHM or ball milling has a profound effect on improving the exfoliation of clay tactoids. Whether the organic modifiers have catalytic acid hydrogen are not the key influence on the exfoliation of clay tactoids. Compared with the conventional mixing, the mechanical properties for both epoxy/MMT$_{DDA}$ and epoxy/MMT$_{DBDA}$ nanocomposites can be highly improved after being sheared by HEHM and especially by ball milling. The impact strength of epoxy/MMT$_{DDA}$ nanocomposites can be increased up to $41.6 \, kJ/m^2$ from $26.9 \, kJ/m^2$, which is about 55% higher than that of the conventional mixing and is nearly about 30% higher than that of blank epoxy resin. The flexural strength also has a great improvement, which is about 9% and 3% higher than that of the conventional mixing, respectively. A further improvement for mechanical properties can still be achieved by ball milling. The thermal stability of epoxy/clay nanocomposites is related to the exfoliation of clay layers and molecular structure of modifiers. Decreasing clay loading and improving the exfoliation of clay tactoids can increase the onset temperature of decomposition, and DBDA modifier with the heat-resistant benzyl may also improve the stability of epoxy/MMT$_{DBDA}$ nanocomposites.

REFERENCES

[1] LeBaron P C, Wang Z, Pinnavaia T J. Polymer-layered silicate nanocomposites: an overview[J]. Applied Clay Science, 1999, 15: 11 − 29.

[2] Ray S S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing [J]. Prog Polym Sci, 2003, 28: 1539 − 1641.

[3] Brown J M, Curliss D, Vaia R A. Thermoset-layered silicate nanocomposites —quaternary ammonium montmorillonite with primary diamine cured epoxies[J]. Chem Mater, 2000, 12: 3376 − 3384.

[4] Koerner H, Jacobs D, Tomlin D W, et al. Tuning polymer nanocomposite morphology: AC electric field manipulation of epoxy-montmorillonite(clay) suspen-

[5] sions[J]. Adv Mater, 2004, 16(4): 297 − 302.

[5] Kornmann X, Lindberg H, Berglund L A. Synthesis of epoxy-clay nanocomposites: Influence of the nature of the clay on structure[J]. Polymer, 2001, 42: 1303 − 1310.

[6] Kornmann X, Lindberg H, Berglund L A. Synthesis of epoxy-clay nanocomposites. Influence of the nature of the curing agent on structure[J]. Polymer, 2001, 42: 4493 − 4499.

[7] Chin I J, Thomas T A, Kim H C, et al. On exfoliation of montmorillonite in epoxy[J]. Polymer, 2001, 42: 5947 − 5952.

[8] Becker O, Cheng Y B, Varley R J, et al. Layered silicate nanocomposites based on various high-functionality epoxy resins: the influence of cure temperature on morphology, mechanical properties, and free volume [J]. Macromolecules, 2003, 36: 1616 − 1625.

[9] Park J H, Jana S C. Mechanism of exfoliation of nanoclay particles in epoxy-clay nanocomposites [J]. Macromolecules, 2003, 36: 2758 − 2768.

[10] Triantafillidis C S, LeBaron P C, Pinnavaia T J. homostructured mixed inorganic-organic ion clays: a new approach to epoxy polymer-exfoliated clay nanocomposites with a reduced organic modifier content [J]. Chem Mater, 2002, 14: 4088 − 4095.

[11] Messersmith P B, Giannelis E P. systhesis and characterization of layered silicate-epoxy nanocomposites [J]. Chem Mater, 1994, 6: 1719 − 1725.

[12] Yoon J T, Jo W H, Lee M S, et al. effects of comonomers and shear on the melt intercalation of styrenics/clay nanocomposites[J]. Polymer, 2001, 42: 329 − 336.

[13] Yasmin A, Abot J L, Daniel I M. Processing of clay/epoxy nanocomposites by shear mixing[J]. Scripta Materialia, 2003, 49: 81 − 86.

[14] Lu H J, Liang G Z, Ma X Y, et al. Epoxy/clay nanocomposites: further exfoliation of newly modified clay induced by shearing force of ball milling [J]. Polymer International, 2004, 53: 1545 − 1553.

[15] Lan T, Kaviratna P D, Pinnavaia T J. Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites [J]. Chem Mater, 1995, 7: 2144 − 2150.

[16] Kong D, Park C E. Real time exfoliation behavior of clay layers in epoxy-clay nanocomposites[J]. Chem Mater, 2003, 15: 419 − 424.

[17] LÜ J K, Ke Y C, Qi Z N, et al. Study on intercalation and exfoliation behavior of organoclay in epoxy resin [J]. J Polym Sci: Part B: Polym Phys, 2001, 39: 115 − 120.

[18] Triantafillidis C S, LeBaron P C, Pinnavaia T J. Thermoset epoxy-clay nanocomposites: the dual role of -diamines as clay surface modifiers and polymer curing agents[J]. J Solid State Chemistry, 2002, 167: 354 − 362.

[19] Becker O, Varley R J, Simon G P. Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites[J]. European Polymer Journal, 2004, 40(1): 187 − 195.

[20] Gu A J, Liang G Z. Thermal degradation behavior and kinetic analysis of epoxy/montmorillonite nanocomposites[J]. Polymer Degradation and Stability, 2003, 80: 383 − 391.

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