ELSEVIER

Journal of University of Science and Technology Beijing
Volume 15, Number 3, June 2008, Page 320

Materials

Influence of clay concentration on the morphology and properties of clay-epoxy nanocomposites prepared by in-situ polymerization under ultrasonication

Jinwei Wang, Xianghua Kong, Lei Cheng, and Yedong He

Beijing Key Laboratory for Corrosion, Erosion and Surface Technology, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

(Received 2007-11-05)

Abstract: To investigate the effect of clay concentration on the structures and properties of bisphenol-A epoxy/nanoclay composites, three composites with organoclay concentrations of 2.5wt%, 5wt%, and 7.5wt% of the epoxy resin were prepared by in-situ polymerization under mechanical stirring followed by ultrasonic treatment. The clay aggregates on micro-scale indicate the absence of fully exfoliated nanocomposites. The layer space decreases with the increase of clay concentration, which suggests that the exfoliation would be constrained if more clay is added as the ultrasonic force is exerted. The thermal decomposition temperature remains almost unchanged with the increase of clay concentration. The glass transition temperature of the composites decreases slightly with the increase of clay concentration, whereas the storage modulus increases with the increase of clay concentration.

Key words: nanocomposite; thermal properties; mechanical properties; clay concentration; ultrasonication

1. Introduction

Polymer-clay composites have been widely studied because of the possibility to build a nanostructure from a polymer and organophilic clay, which known as nanocomposites. Nanocomposites were prepared by dispersing or exfoliating intercalated clay into a host polymer [1]. The intercalation expanded the platelets to the point where individual platelets could be separated by mechanical shear. Many researchers have performed investigations in the field of polymer nanocomposites based on epoxies [2-4], polyurethane [5], polyethylene [6], PMMA [7], *etc.*

The attractive feature of polymer/nanoclay composites was the obvious improvement in some of its properties with the addition of only a small amount of nanoclay as most of the literatures reported. Lan *et al.* reported more than a ten-fold increase in strength and modulus in a rubbery epoxy matrix with only 15wt% of delaminated organoclay. An increase in tensile modulus of 30% of a partially delaminated unsaturated polyester-clay nanocomposite with 5vol% of clay was also reported [3]. With a clay loading of 10 wt%, the compressive yield strength and the modulus of elasticity were increased by 17% and 27%, respectively; a total delamination of the clay was required to obtain these improvements [8]. With the addition of only 4.5 phr of clay, the strain energy release rate of the epoxy-clay nanocomposites based on tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) cured with diaminodiphenyl epoxy increased 5.8 times from the original value, and there was also significant reduction in the diffusivity and the maximum water uptake [9]. However, some other researches showed that the improvements in the properties of the nanocomposites were rather limited with the addition of a small amount of nanoclay due to the limited dispersion of layered silicates in polymer matrix if the processing conditions were also considered [4,10].

In our previous study, with constant clay content in the composites, the ultrasonic effect on their structures and properties were studied [11]. At an optimum ultrasonic time, the effect of clay concentration on the morphology, structure, and properties of nanocomposites based on bisphenol-A epoxy was continuously studied in this article. The dependence of layer space

---

Corresponding author: Jinwei Wang, **E-mail:** wangjw@mater.ustb.edu.cn

and clay aggregation on the clay amount was characterized by small-angle X-ray diffraction (SAXRD) and scanning electron microscopy (SEM). The thermal and mechanical properties were studied by thermogravimetric analysis (TGA) and dynamic mechanical analyzer (DMA).

2. Experiment

The bisphenol-A diglycidyl ether (D.E.R.332, from Dow Chemical) was put into a 500 mL beaker that was heated to 80°C, followed by the addition of curing agent 4,4'-diaminodiphenylsulphone (from Merk-Schuchardt) under mechanical stirring at 400 r/min for approximately 30 min until the curing agent dissolved. The epoxy resin with an organophilic clay (I.30E, from Nanocor Inc.) concentration of 2.5wt%, 5.0wt%, or 7.5wt% was then put into the beaker under continuous mechanical stirring at 400 r/min for 1 h at 80°C. The mixture was transferred to a capped bottle, which was then immersed in an ultrasonic bath (JAC ultrasonic 1505) under ultrasonic stirring for 2 h. Then, the mixture was degassed at 120°C followed by precuring at 170°C for 5 h and postcuring at 200°C for 2 h. The SAXRD analysis was performed by using Shimadzu XRD-6000 X-ray diffractometer with Cu radiation (λ=0.1542 nm) with a scanning speed of 0.05°/min and a scanning range from 0.01° to 1.5°. TGA were measured in air using Perkin Elmer TGA-7 with a heating rate of 10°C/min and the temperature ranging from 50 to 650°C. Mechanical properties were measured by DMA 2980 Dynamic Mechanical Analyzer from 50 to 240°C at a frequency of 1 Hz and a rate of 5°C/ min under nitrogen atmosphere.

3. Results and discussion

The cross section morphology of the epoxy-nanoclay composites are presented in Fig. 1. For composite with 2.5wt% organoclay concentration (Fig. 1(a)), two distinct particle sizes are apparent: large aggregates, surrounded by smaller ones, which indicates that with less organoclay concentration in the epoxy resin, the clay aggregates could be separated into smaller ones as the ultrasonic force is exerted. At a higher organoclay concentration (5.0wt%, Fig. 1(b) or 7.5wt%, Fig. 1(c)), there is a departure from this trend. Large clay aggregates could be obviously observed, and this implies that as the organoclay concentration increases, the amount of dissociation of alkylammonium ions also increases; hence, more homopolymerization reactions of epoxy monomers with alkylamines resulting from the dissociation of alkylammonium ions result in the further increase in viscosity; under such circumstances, part of the force exerted has to overcome the increase in viscosity and as a result the dispersion and exfoliation are restricted [3].

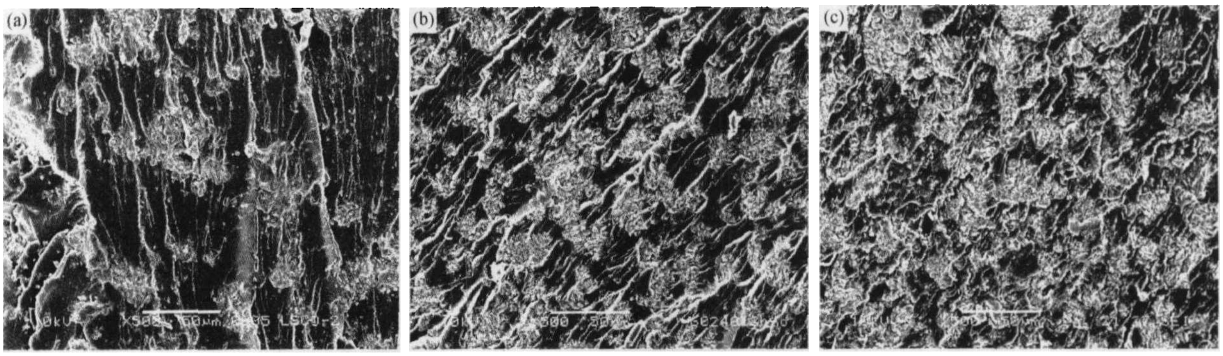

Fig. 1. SEM cross section image of nanocomposites with different clay content: (a) 2.5wt%; (b) 5wt%; (c) 7.5wt%.

Fig. 2 shows the small-angle X-ray diffraction profiles of epoxy and nanocomposites with clay concentrations of 2.5wt%, 5wt%, and 7.5wt%, respectively, where the epoxy exhibited amorphous holo, while the peaks positions at 2θ equal to 0.0525°, 0.07005°, and 0.08225° corresponded to the overall layer spaces of clay, *d*, equal to 29.4, 21.9, and 18.7 nm, respectively. The layer space of clay particles decreased with the increase of clay concentration, and this may be due to the degree of exfoliation of the clay layers, which depends on the extent of homopolymerization of epoxy monomers between clay layers [12]. As the organoclay concentration increases, the viscosity also increases, and hence the separation of clay layers became more difficult. The higher intensity of the peaks for composites with more clay content suggested the existence of more clay aggregates (Fig. 1).

Fig. 3 presents the changes in weight loss with temperature for clay, epoxy, and composites. The thermal decomposition temperatures (T_d) at a weight loss of 10% are almost the same for epoxy and the nanocomposites, except for the pure clay. The much lower T_d of the organoclay than those of the composites and epoxy implies that the presence of alkylammonium ions, which are small organic molecules that could be easily decomposed, would lower the T_d of the nanocomposites [11]. As the organoclay concentration increases, the amount of alkylammonium ions presented in the system also increase; alkylammonium ions participate in the chemical reaction with epoxy groups before the addition of curing agent, and more branched polymer chains would be formed instead of cross-linked polymer chains, in which case the T_d would be lower [3]. However, as discussed earlier, the increase in particle aggregation and the decrease in layer space with the addition of more clay would reduce the probability of the reaction of alkylammonium ions in the clay with epoxy group, as a result of which the T_d would be higher. It seemed that these controversy trends were in a balance under this ultrasonic processing condition, and hence, clay concentration had no effect on their thermal stability.

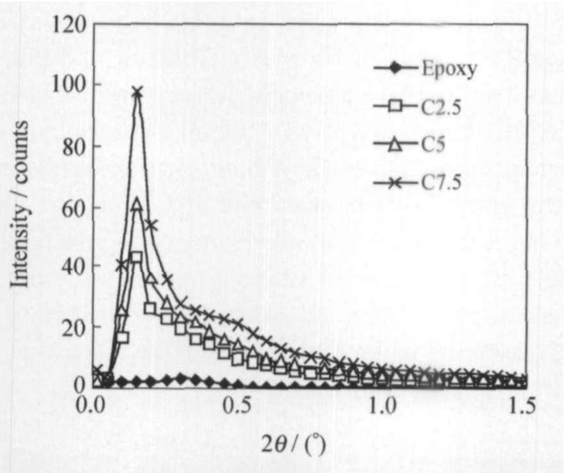

Fig. 2. SAXRD patterns of epoxy and nanocomposites with clay concentrations of 2.5wt% (C2.5), 5wt% (C5), and 7.5wt% (C7.5).

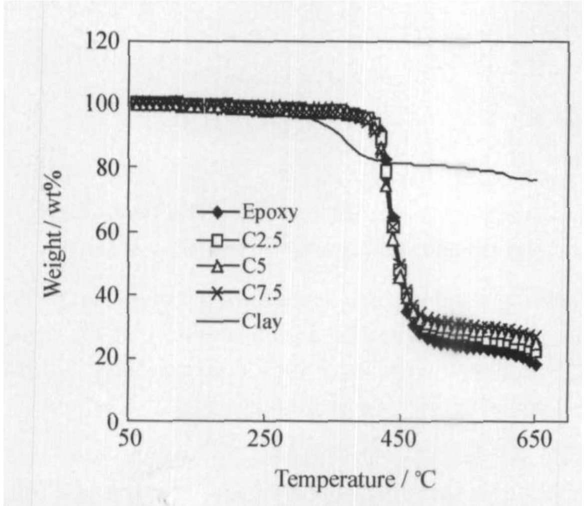

Fig. 3. Thermogravimetric analysis of clay, epoxy and nanocomposite with clay concentrations of 2.5wt% (C2.5), 5wt% (C5), and 7.5wt% (C7.5).

Fig. 4 shows the changes in tanδ of the clay, epoxy, and composites with temperature. The peaks at 229, 222, 217, and 217°C corresponded to the glass transition temperatures (T_g) for epoxy and the nanocomposites with clay concentrations of 2.5wt%, 5wt%, and 7.5wt%, respectively. All the composites have a lower glass transition temperature than epoxy. Moreover, the T_g of the system decreases (not significant) with increasing clay concentration until a point where the clay concentration did not lead to a further decrease in the T_g. T_g is dependent on the cross-linking density of the system [11]; the reaction of alkylammonium ions with epoxy monomers during swelling results in the presence of unreacted curing agent in the system and hence lowered the T_g [3]. However, with the addition of more clay (above 5wt%), there was more aggregation of clay particles, and the layer spaces can not be separated further as the ultrasonic force is exerted, the cross-linking density remains unchanged, and as a result the T_g does not decrease further.

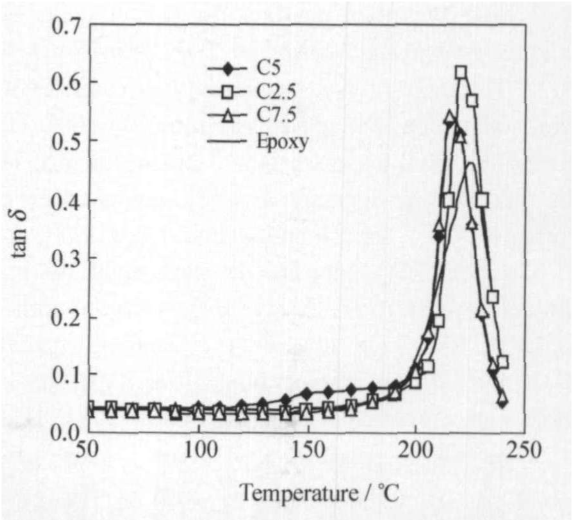

Fig. 4. Dynamic mechanical tanδ for epoxy and nanocomposite with clay concentrations of 2.5wt% (C2.5), 5wt% (C5), and 7.5wt% (C7.5).

Fig. 5 presents storage modulus of the epoxy and the composites with varying concentrations of clay.

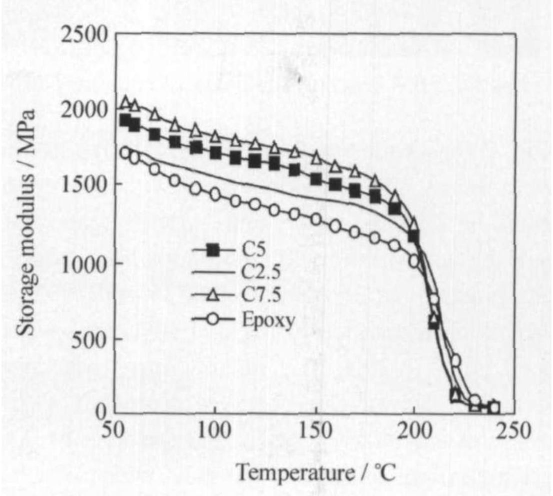

Fig. 5. Dynamic mechanical storage modulus for epoxy and the nanocomposites with clay concentrations of 2.5wt% (C2.5), 5wt% (C5), and 7.5wt% (C7.5).

The storage modulus of the epoxy-nanoclay composites is higher than that of epoxy at any temperature. As the clay concentration increases, the storage modulus also increases. This is the characteristic of a material reinforced with stiff filler material [11]. As observed from Figs. 1 and 2, the ultrasonic force in this study could not exert obvious effect on the clay dispersion and exfoliation at higher concentrations (above 5wt%), and the results of storage modulus indicate that the clay in the composites mainly exhibited stiff filler reinforcement with partial exfoliation [10].

4. Conclusion

Ultrasonication is an effective method for the dispersion of clay into the polymer matrix and for the separation of clay layers. However, the effect of ultrasonic force on the structures and properties exhibits a strong dependence on clay concentration, and it is very difficult to achieve complete exfoliation under ultrasonic force. At a lower clay concentration, the clay can be dispersed more evenly and the layer space can be expanded effectively; however, at a higher clay concentration, clay particles aggregate severely and the enlargement of layer space is restricted due to the increase in viscosity. Clay concentration does not exhibit obvious effect on the thermal properties of the nanocomposites, while the increase in storage modulus of the composites with the increase in clay content reveals that the improvement is due to stiff filler reinforcement with partial exfoliation.

References

[1] A. Usuki, Y. Kojima, M. Kawasumi, *et al.*, Synthesis of nylon 6-clay hybrid, *J. Mater. Res.*, 8(1993), p.1179.

[2] M.S. Wang and T.J. Pinnavaia, Clay-polymer nanocomposites formed from acidic derivatives of montmorillonite and an epoxy resin, *Chem. Mater.*, 6(1994), p.468.

[3] T. Lan and T.J. Pinnavaia, Clay-reinforced epoxy nanocomposites, *Chem. Mater.*, 6(1994), p.2216.

[4] C.K. Lam, K.T. Lau, H.Y. Cheung, *et al.*, Effect of ultrasound sonication in nanoclay clusters of nanoclay/epoxy composites. *Mater. Lett.*, 59(2005), p.1369.

[5] A. Pattanayak and S.C. Jana, Synthesis of thermoplastic polyurethane nanocomposites of reactive nanoclay by bulk polymerization methods, *Polymer*, 46(2005), p.3275.

[6] J. Morawiec, A. Pawlak, M. Slouf, *et al.*, Preparation and properties of compatibilized LDPE/organo-modified montmorillonite nanocomposites, *Eur. Polym. J.*, 41(2005), p.1115.

[7] J.H. Park and S.C. Jana, The relationship between nano- and micro-structures and mechanical properties in PMMA-epoxy-nanoclay composites, *Polymer*, 44(2003), p.2091.

[8] Z. Wang, J. Massam, and T.J. Pinnavaia, Epoxy-clay nanocomposites, [in] *Polymer-Clay Nanocomposites*, New York: Wiley, 2001, p.57.

[9] W.P. Liu, S.V. Ho, and M. Pugh, Organoclay-modified high performance epoxy nano-composites, *Compos. Sci. Technol.*, 65(2005), p.307.

[10] H.S. Jeon, J.K. Rameshwaram, G. Kim, *et al.*, Characterization of polyisoprene-clay nanocomposites prepared by solution blending, *Polymer*, 44 (2003), p.5749.

[11] J.W. Wang and S.C. Qin, Study on the thermal and mechanical properties of epoxy–nanoclay composites: The effect of ultrasonic stirring time, *Mater. Lett.*, 61(2007), p.4222.

[12] I.J. Chin, T.A. Thomas, H.C. Kim, *et al.*, Exfoliation of montmorillonites in epoxy, *Polymer*, 42(2001), p.5947.