ELSEVIER

Polymer 42 (2001) 5947–5952

polymer

www.elsevier.nl/locate/polymer

On exfoliation of montmorillonite in epoxy

In-Joo Chin[a,1], Thomas Thurn-Albrecht[a], Ho-Cheol Kim[a], Thomas P. Russell[a,*], Jing Wang[b]

[a]*Polymer Science and Engineering Department, University of Massachusetts, Room 701, Box 34530, Amherst, MA 01003-4530, USA*
[b]*Aspen Systems, Marlborough, MA 01752, USA*

This paper is dedicated to Roger S. Porter whose pioneering efforts on the mechanical and rheological properties of polymers have taken us a step closer in establishing the relationship between structure and property.

Received 28 December 1999; accepted 6 March 2000

Abstract

Nanocomposite formation of octadecyl amine treated montmorillonite clays in epoxy was investigated by small-angle X-ray scattering and atomic force microscopy. When diglycidyl ether of bisphenol A (DGEBA) was cured with equimolar or higher amounts of meta-phenylene diamine (MPDA), only intercalated nanostructures were obtained. Exfoliated nanocomposites were formed with DGEBA cured with less than stoichiometric amounts of MPDA or with auto-polymerization of DGEBA without curing agent. Extragallery crosslinking appeared to be favored with higher curing agent concentrations. Differential scanning calorimetry analyses of the exfoliated nanocomposites indicated that the reaction need not be complete in order to attain exfoliation in the DGEBA/montmorillonite mixture. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: DGEBA/montmorillonite mixture; Exfoliated nanocomposite; SAXS

1. Introduction

Polymer nanocomposites containing layer-structured, inorganic nanoparticles have attracted much attention since the Toyota research group [1–4] showed the tensile properties and the heat distortion temperature of the nylon-6 nanocomposites were greatly improved. Nanocomposites have been demonstrated with many polymers of different polarities including polystyrene [5], polycaprolactone [6], poly(ethylene oxide) [7–9], polyamide [2–4], polyimide [10–13], epoxy [14–20], polysiloxane [21], and polyurethane [22]. Modeling studies of the melt intercalation of polymer into layered silicates have been reported [23,24], and recently the phase-behavior of the polymer/clay nanocomposites has been treated theoretically [25,26].

Nanoscale layered clays with very high aspect ratios and high strength can play an important role in forming effective polymer nanocomposites owing to their intercalation chemistry. Montmorillonite has been particularly important in polymer nanocomposites. Montmorillonite is a crystalline, 2:1 layered clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets [27]. The layers are continuous in the *a* and *b* directions and are stacked one above the other in the *c* direction. The gallery is a term used to describe the stacked array of clay sheets separated by a regular spacing. A particular feature of the montmorillonite structure is that water and other polar molecules can enter between the unit layers because of the relatively weak forces between the layers, causing the lattice to expand in the *c* direction. Due to the substitution of ions of different valence there is a charge deficiency on the sheet surface, and this charge is typically balanced by exchangeable cations adsorbed between the unit layers and around their edges. Usually, montmorillonite clays are modified by an onium ion substitution reaction with surface sodium ions, rendering the normally hydrophobic silicate surface organophilic, which enables insertion of organic materials including many polymers. The alkyl ammonium cations provide functional groups that can react with the polymer or initiate polymerization of monomers [1,2,6,14].

When the nanoparticles are dispersed in the polymer matrix, two types of nanocomposite structures can be obtained [15,20]. Intercalated nanocomposites are formed when there is limited inclusion of polymer chain between the clay layers with a corresponding small increase in the

---

* Corresponding author. Tel.: +1-4130-545-0433; fax: +1-413-577-1510.

E-mail address: russell@iskra.pse.umass.edu (T.P. Russell).

[1] Permanent address: Department of Polymer Science and Engineering, Inha University, Inchon 402-751, Korea.

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00898-3

interlayer spacing of a few nanometers. On the other hand, exfoliated structures are formed when the clay layers are well separated from one another and individually dispersed in the continuous polymer matrix. Because exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart, the exfoliated structure is more desirable in enhancing the properties of the nanocomposites. However, it is not easy to achieve complete exfoliation of clays and, indeed with few exceptions, the majority of the polymer nanocomposites reported in the literature were found to have intercalated nanostructures.

The nature and mechanism of the exfoliation process of the surface treated montmorillonite nanoparticles in the epoxy network derived from diglycidyl ether of bisphenol-A (DGEBA) crosslinked with m-phenylene diamine (MPDA) has been of recent interest. Lan et al. [15] found for the MPDA cured DGEBA epoxy nanocomposites containing 5% C_{18} ammonium exchange montmorillonite that the clays with primary and secondary onium ions formed exfoliated nanocomposites, whereas those with tertiary and quarternary onium ions retained an intercalated structure. It was argued that acidic alkyl ammonium ions tend to favor exfoliation by facilitating the intragallery epoxide polymerization. However, Messersmith and Giannelis [14] found DGEBA cured with the primary and secondary amines such as methylene dianiline yielded little or no increase in layer separation with silicate d-spacings of 30–40 Å or less. This was attributed to either the bridging of the silicate layers by the bifunctional amines which prevent extensive layer expansion or the strong polarity of the N–H groups in the primary and secondary amines that causes a reaggregation of dispersed silicate layers.

During the reaction of DGEBA with MPDA in the presence of alkyl ammonium treated montmorillonites, extragallery and intragallery polymerization occur. As long as the intragallery polymerization occurs at a rate comparable to the extragallery polymerization, an exfoliated nanocomposite structure can be formed [15]. However, if the extragallery polymerization is more rapid than the intragallery diffusion and polymerization or if intragallery polymerization is retarded, an intercalated structure will result.

In this article the structural evolution of epoxy-montmorillonite nanocomposites was examined by time-dependent small-angle X-ray scattering using synchrotron radiation. X-ray scattering using a conventional X-ray source and atomic force microscopy (AFM) were used to investigate the static structure and differential scanning calorimetry (DSC) was used to measure the reaction kinetics. It was found that the structure of the nanocomposite was affected by the amount of the curing agent and that exfoliation was suppressed when the molar ratio of MPDA–DGEBA was equivalent or higher.

2. Experimentals

2.1. Nanocomposite preparation

Octadecyl amine treated montmorillonites (Nanomer 1.30 E, Nanocor) were used as received. DGEBA (epoxide equivalent weight = 178 g) was provided by Shell (EPON 828), and MPDA was used as curing agent for DGEBA. The mixture of DGEBA and montmorillonites was prepared by dispersing montmorillonite powders in DGEBA with stirring, followed by sonication for about 30 min and degassing in vacuum. Predetermined amounts (5, 14.5, and 25 phr (parts per hundred resin), respectively) of the curing agent were added to the DGEBA/montmorillonite mixture at 60°C with vigorous stirring. The DGEBA/montmorillonite/MPDA mixture was heated for 2 h at 80°C and for an another 2 h at 135°C, which is similar to the curing condition for the equimolar mixture of DGEBA and MPDA recommended by Shell. The same curing procedure was applied to the mixtures without the curing agent.

2.2. Characterization of nanocomposite

The layer spacing of the montmorillonite was measured using a wide angle X-ray diffractometer (D500 Siemens). Small-angle X-ray scattering using a Rigaku 18 kW rotating anode operated at 8 kW with Ni–filtered Cu radiation with Siemens HiStar area detector was employed to characterize the epoxy nanocomposites. Samples were supported between two Kapton windows (50 μm thick) separated by 1 mm. Time-resolved X-ray scattering studies were performed at the Brookhaven National Synchrotron Light Source (Beamline X27C equipped with 1-D detector) to investigate the in situ exfoliation with high resolution. Thermal transitions associated with the polymerization reaction were measured by DSC (DSC2910, Du Pont). The topology of the exfoliated nanocomposites was investigated by AFM (Dimension 3000 SPM, Digital Instruments) in the tapping mode.

3. Results and discussion

The change in the interlayer spacing of montmorillonite powders upon swelling in DGEBA was measured. Organically modified montmorillonite powders showed a strong X-ray diffraction peak (Fig. 1a) with a characteristic interlayer spacing of about 23 Å. However, when the montmorillonites were swollen in DGEBA, the interlayer spacing increased to about 39 Å (Fig. 1b), indicating an intercalation of the clay by the epoxy. These spacings are comparable to the values reported by others. For example, the basal spacing of the air-dried $CH_3(CH_2)_{17}NH_3^+$ exchanged montmorillonites was reported to be 18.0 Å and that of the DGEBA solvated clay was 36.7 Å, which was very close to the spacing calculated by assuming an all trans configuration of gallery cations oriented vertically to

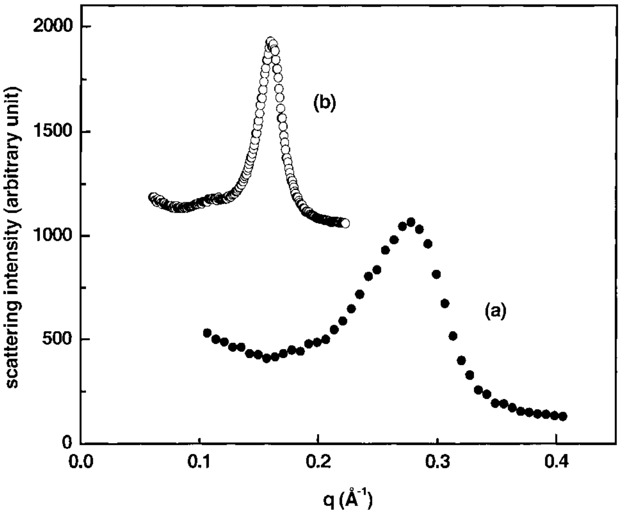

Fig. 1. X-ray scattering patterns of (a) octadecyl amine treated montmorillonite powders and (b) montmorillonite swollen in DGEBA.

the clay layer [15]. Messersmith and Giannelis [14] reported a layer spacing of the dry silicate treated by predominantly octadecyl ammonium of 17 Å, and a DGEBA/silicate mixture showed the layer spacing of 35 Å both at room temperature and 90°C.

The structural development of the epoxy nanocomposites with cure was examined by the small angle X-ray scattering. The spacing of the initial DGEBA/MPDA/clay mixtures was between 34 and 39 Å, independent of the curing agent concentration (between 5 and 25 phr) and it was comparable to those of the DGEBA solvated montmorillonites. When heated for 2 h at 80°C, the spacing remained constant, regardless of the curing agent concentration. However, the interlayer spacing of the nanocomposites heated for an additional 2 h at 135°C varied dramatically with the curing agent concentration. Fig. 2 shows the small angle X-ray scattering profiles of DGEBA epoxies containing 1% clay heated with different amounts of the curing agent for 2 h at 80°C and for an additional 2 h at 135°C. When DGEBA was cured with an excess amount of curing agent (Fig. 2a), the final interlayer spacing was 34.5 Å, which is close to that of the DGEBA solvated montmorillonites, showing no indication of exfoliation. For the mixture that was heated with stoichiometrically equivalent amount of the curing agent the interlayer spacing was 40.5 Å (Fig. 2b), showing that exfoliation was suppressed by the reaction involving the curing agent. As the curing agent concentration decreased further to well below the stoichiometric amount, the layer spacing increased extensively to approximately 180 Å, as shown in Fig. 2c. This means that the individual layers of montmorillonite were well separated in a regular manner and they were clearly exfoliated. An even better ordered structure was formed without any curing agent, as will be discussed below. The lower the curing agent concentration, the higher was the extent of exfoliation of clay observed. An excess amount of the curing agent resulted dominantly in the extragallery crosslinking of DGEBA and MPDA with insufficient diffusion of materials into the intragallery regions. The rapid rate of extragallery crosslinking in comparison to the slower intragallery diffusion limited the exfoliation.

To further understand the role of montmorillonite clays in forming the nanocomposite structure only DGEBA was heated with the clay, effectively eliminating the extragallery reaction of DGEBA. It has been shown that direct polymerization of epoxy, in the absence of curing agent, in the galleries of various montmorillonites could result in polyether nanocomposites [18,19], though the mechanism and kinetics of the exfoliation process are not well understood. Wang and Pinnavaia [18] obtained powders of a polyether/clay mixture, suggesting that some acidic onium ions on the montmorillonite clays facilitated the auto-polymerization and the exfoliation at high temperatures around 200°C. Lan et al. [19] also observed the self-polymerization of DGEBA when heated with acidic onium ion exchanged forms of montmorillonite to form polyether/clay nanocomposites. They found that the protonated primary amine cations on the exchanged sites of the montmorillonites acted primarily as acid catalysts rather than as curing agents.

DGEBA/montmorillonite mixtures were subjected to the same reaction conditions as the DGEBA/MPDA/montmorillonite mixtures. They were heated for 2 h at 80°C and for an additional 2 h at 135°C. Fig. 3 shows the progressive change in the layer spacing calculated from the maximum in the scattering profile of montmorillonites. Once the clay was solvated in DGEBA, there was virtually no expansion in the layer spacing of montmorillonites with time at 80°C up to 2 h, regardless of the clay concentration. Upon heating

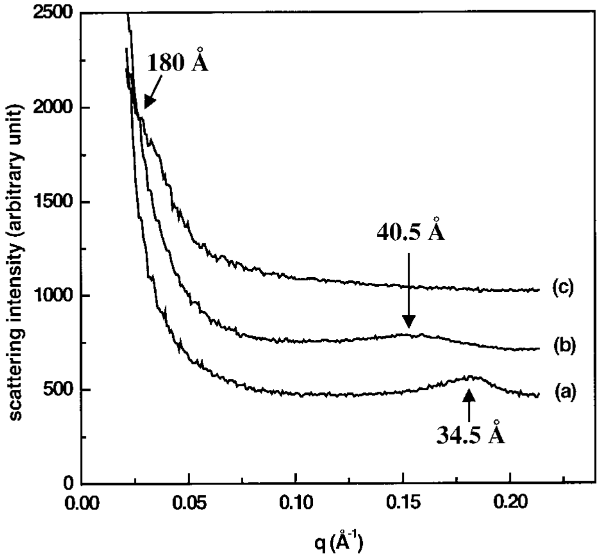

Fig. 2. Small angle X-ray scattering patterns of 1% montmorillonite containing DGEBA epoxy cured with (a) 25 phr MPDA, (b) 14.5 phr MPDA, (c) 5 phr MPDA. (The scattering with the corresponding d-spacings are indicated by arrows.)

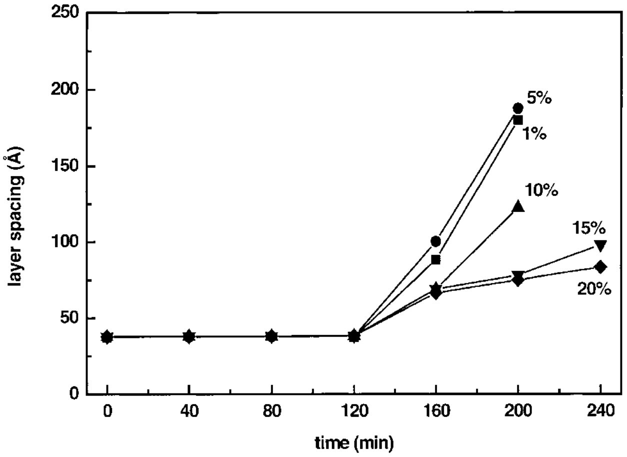

Fig. 3. Change in the layer spacing of montmorilonite in DGEBA with time as obtained from SAXS. (The numbers indicate the weight concentration of clay.)

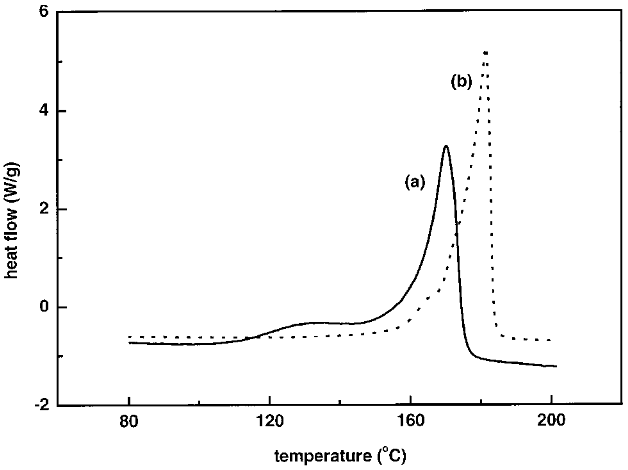

Fig. 4. DSC curves of (a) exfoliated DGEBA/montmorillonite mixture, (b) fresh DGEBA/montmorillonite mixture.

to 135°C the d-spacing of all the mixtures increased with time, but at different rates. The higher the clay concentration, the lower was the rate of increase in the basal spacing. As the concentration of the montmorillonites increased from 1 to 20%, the maximum spacing obtained decreased. After 80 min at 135°C the scattering maximum of the mixtures that contained 10% or less montmorillonites virtually disappeared, indicative of a highly exfoliated structure with a layer spacing greater than about 200 Å (the detection limit of the instrument). On the other hand, the spacing of the mixture containing 20% clay was about 80 Å. All the samples were transformed into powder with considerable volume increase, which is consistent with the findings by others [18,19]. If we assume that the exfoliation of clay is simply due to space filling by epoxy, the maximum interlayer spacing of the fully exfoliated clay nanocomposite can be predicted.[2] The calculated maximum spacing for 1, 5, 10, 15 and 20% clay are about 1700, 330, 155, 88, and 69 Å, respectively. Our experimental results for 1, 5, and 10% clay were larger than 200 Å, while the layer spacings of the mixtures containing 15 and 20% clay were ~98 and 83 Å, which are in reasonable agreement with the calculated maximum values.

In forming an exfoliated structure for the polyether/clay mixture one should be concerned with the diffusion of DGEBA into the gallery in addition to the intragallery polymerization of DGEBA. Exfoliated epoxy nanocomposites containing 5% clay that had been heated for 2 h at 80°C and for another 3 h at 135°C were examined by DSC. Fig. 4a shows an exotherm at ~170°C with a shoulder at ~130°C. The amount of heat evolved in the exothermic process was ~309 J/g. The total heat of the exothermic process of the DGEBA/clay mixture containing 5% clay was found to be ~517 J/g, as determined by a DSC scan of the fresh mixture from room temperature to 200°C (Fig. 4b). Thus, some 40% of the total ΔH available for the mixture was consumed in the exfoliation process. Major contribution to the exothermic process includes the polymerization of DGEBA with the aid of the catalytic activity of the montmorillonite surface [28]. The fact that only 40% of the total ΔH available for the mixture was consumed in forming an exfoliated nanocomposite means that some 60% of the total ΔH can still be exploited for further reaction. Consequently, exfoliated structures can be realized without the completion of the reaction and a reaction may not be necessary to complete exfoliation. It should be noted that the mixture was not completely transformed into powder, which may indicate that the reaction was not completed. In fact, a simple calculation based on the constant diffusion coefficient of DGEBA confirmed that DGEBA can diffuse into the gallery between neighboring clay plates in a relatively short time (well within 1 h).

To obtain topological information of the nanocomposite surface AFM was used in the tapping mode. Fig. 5 is an AFM phase image of the polyether/clay nanocomposite containing 5% clay, which was shown to have an exfoliated structure by small angle X-ray scattering. The mixture of DGEBA/clay was confined between two Kapton films while heating, and one Kapton film was removed to expose the exfoliated nanocomposite intact for the AFM observation. Many stacks of high aspect ratio clay sheets with a remarkable regularity are clearly evident. The average distance between each stack was determined to be 200 Å, which

---

[2] Assuming that the clay sheets are stacked uniaxially on top of each other and that the interlayer space is filled completely with epoxy, the volume fraction of clay will be $t_1/(t_1 + t_2)$, where t_1 is the thickness of the individual clay sheet ((10 Å), and t_2 is the maximum interlayer spacing of the completely exfoliated nanocomposite. The volume fraction of the clay can also be calculated from the density (d) and the weight fraction (w) of clay (subscript 1) and DGEBA(subscript 2) to be $(w_1/d_1)/[(w_1/d_1) + \{(1 - w_1)/d_2\}]$. Thus, $t_2 = t_1 \times [(1 - w_1)/d_2]\,[d_1/w_1]$.

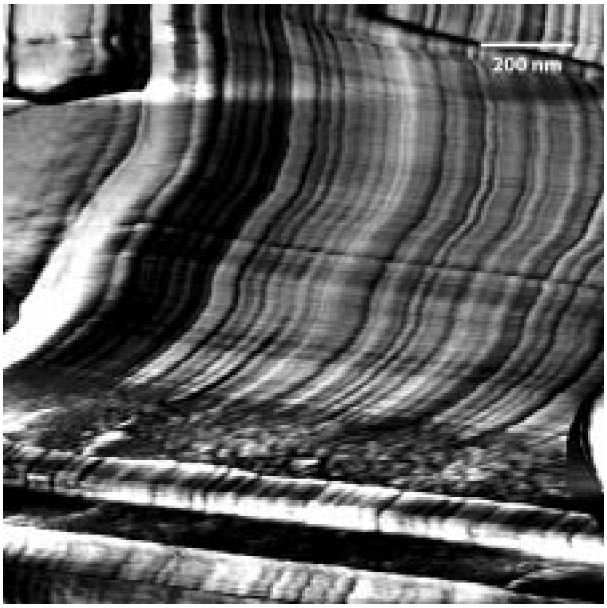

Fig. 5. AFM phase image of exfoliated montmorillonite in DGEBA.

agrees with the layer separation obtained by the X-ray scattering measurement.

Time-dependent small-angle X-ray scattering was used to follow the structural development in the intermediate stages of exfoliation. Because the layer spacing of the DGEBA/montmorillonites mixture remained virtually constant for 2 h at 80°C (as discussed earlier), only the scattering patterns at 135°C were collected. The sample was preheated at 80°C for 2 h. While the scattering data was collected, the sample was held at 135°C. Fig. 6 shows the evolution of the scattering profiles as a function of time obtained in situ for a DGEBA/montmorillonite mixture containing 5% clay. The position of the scattering maximum of the X-ray pattern seemed to decrease continuously with time, corresponding to a monotonic increase in the basal spacing. However, when the scattering profiles were carefully analyzed, during the intermediate stages two distinct reflections were evident. As shown in Fig. 7, one reflection corresponding to a smaller layer spacing persisted throughout the intermediate stage (up to ~105 min), whereas the other reflection corresponding to a larger spacing continuously shifted to smaller q (larger spacing) with time. The smaller spacing was found to be ~35–39 Å, essentially identical to the spacing of the clay swollen in DGEBA. After 105 min only one reflection was observed characteristic of the exfoliated structure, indicating that the exfoliation of the gallery occurs in a serial manner. The presence of the reflection corresponding to the initial structure is more clearly seen in the inset of Fig. 6. The scattering peaks at earlier stages were relatively sharp and narrow, becoming broader as the exfoliation proceeded. The apparent initial increase in the spacing (up to 25 min) results from the superposition of the reflection at ~35–39 Å and the reflection at larger spacing corresponding to the structure as it is exfoliating. At 195 min the d spacing reached about 120 Å, characteristic of a volume filled exfoliated morphology. It appears that until the intermediate stage of the reaction some clays remained only swollen in DGEBA, whereas the others already began to exfoliate from the earlier stage.

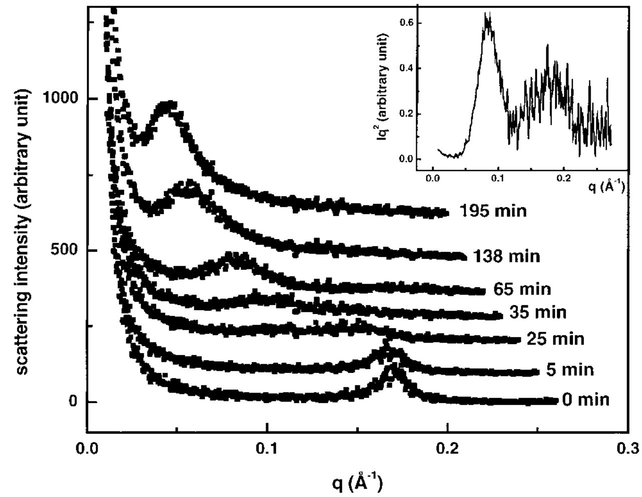

Fig. 6. Time-dependent small angle synchrotron X-ray scattering patterns of the DGEBA/montmorillonite mixture at 135°C. The inset shows the data for 75 min analyzed in more detail to emphasize the presence of the higher q reflection.

4. Conclusions

Formation of exfoliated nanocomposite was confirmed by small-angle X-ray scattering and AFM, when DGEBA was auto-polymerized with montmorillonites. Exfoliated nanocomposites were also observed with DGEBA cured with MPDA of less than equimolar concentration. As the curing agent concentration increased, the extragallery crosslinking

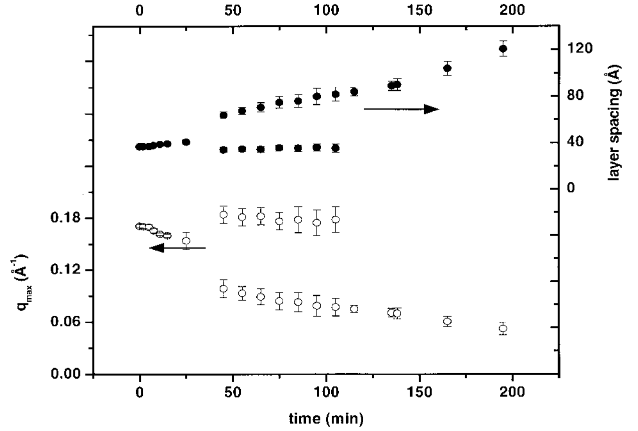

Fig. 7. Time-dependent change in the scattering maximum of the DGEBA/montmorillonite mixture at 135°C. Q_{max} was obtained from the plot of Iq^2 vs. q plot of data in Fig. 6. The layer spacing corresponds to the Bragg spacing of the peak position. Error bars are indicated.

dominated, resulting in intercalated nanocomposites. Time-dependent synchrotron X-ray scattering showed two different layer spacings in the intermediate stages of auto-polymerization with montmorillonites. By evaluating the exothermic heat evolved in the exfoliation and reaction, it could be concluded that exfoliated nanocomposite could be achieved without the completion of the reaction in the DGEBA/montmorillonite mixture. During the intermediate stages of the structural evolution, two distinct reflections in the X-ray scattering profile were found, each corresponding to the layer spacing of the clay swollen in DGEBA and the spacing of the exfoliated structure, respectively. At the later stage there was only one reflection characteristic of the exfoliated structure, indicating that the exfoliation of the gallery occurs in a serial manner.

Acknowledgements

This work was performed with support from the Materials Research Science and Engineering Center funded by the NSF under contract DMR 9809365, and from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG 02-96ER45612). T.T.A. acknowledges support from DFG.

References

[1] Usuki A, Kawasumi M, Kojima Y, Okada A, Kurauchi T, Kamigaito O. J Mater Res 1993;8:1174.
[2] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O. J Mater Res 1993;8:1179.
[3] Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O. J Mater Res 1993;8:1185.
[4] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O. J Polym Sci, Part A: Polym Chem 1993;31:983.
[5] Vaia RA, Jandt KD, Kramer EJ, Giannelis EP. Macromolecules 1995;28:8080.
[6] Messersmith PB, Giannelis EP. J Polym Sci, Part A: Polym Chem 1995;33:1047.
[7] Aranda P, Ruiz-Hitzky E. Chem Mater 1992;4:1395.
[8] Vaia RA, Sauer BB, Tse OK, Giannelis EP. J Polym Sci, Part B: Polym Phys 1997;35:59.
[9] Harris DJ, Bonagamba TJ, Schmidt-Rohr K. Macromolecules 1999;32:6718.
[10] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. J Polym Sci, Part A: Polym Chem 1993;31:2493.
[11] Lan T, Kaviratna PD, Pinnavaia TJ. Chem Mater 1994;6:573.
[12] Yano K, Usuki A, Okada A. J Polym Sci, Part A: Polym Chem 1997;35:2289.
[13] Tyan HL, Liu YC, Wei KH. Chem Mater 1999;11:1942.
[14] Messersmith PB, Giannelis EP. Chem Mater 1994;6:1719.
[15] Lan T, Kaviratna PD, Pinnavaia TJ. Chem Mater 1995;7:2144.
[16] Phillip G, Schmidt H. J Non-Cryst Solids 1986;82:31.
[17] Lan T, Pinnavaia TJ. Chem Mater 1994;6:2216.
[18] Wang MS, Pinnavaia TJ. Chem Mater 1994;6:468.
[19] Lan T, Kaviratna PD, Pinnavaia TJ. J Phys Chem Solids 1996;57:1005.
[20] Wang Z, Pinnavaia TJ. Chem Mater 1998;10:1820.
[21] Langley NR, Mbah GC, Freeman HA, Huang H, Siochi EJ, Ward T, Wilkes GJ. Colloid Interface Sci 1991;143:309.
[22] Wang Z, Pinnavaia TJ. Chem Mater 1998;10:3769.
[23] Krishnamoorti R, Vaia RA, Giannelis EP. Chem Mater 1996;8:1728.
[24] Vaia RA, Giannelis EP. Macromolecules 1997;30:8000.
[25] Lyatskaya Y, Balazs AC. Macromolecules 1998;31:6676.
[26] Ginzburg VV, Balazs AC. Macromolecules 1999;32:5681.
[27] Grim RE. Clay mineralogy. New York: McGraw-Hill, 1953.
[28] May CA, editor. Epoxy resins. 2nd ed. New York: Marcel Dekker, 1988.