General Approach to Nanocomposite Preparation

Hatsuo Ishida,* Sandi Campbell, and John Blackwell

*NSF Center for Molecular and Microstructure of Composites (CMMC),
Department of Macromolecular Science and Engineering, Case Western Reserve University,
Cleveland, Ohio 44106-7202*

A novel approach to nanocomposite preparation utilizing a swelling agent, a monomer or polymer known to intercalate/exfoliate smectite clay, has allowed the preparation of several new nanocomposites. Present in small amounts, the swelling agent serves to swell the clay layers, allowing the organic matrix to be virtually any polymer. Twenty-four polymers are used in this study, varying in solubility parameter, molecular weight, and polarity. Many of these polymers do not yield a nanocomposite structure by simple melt mixing of the clay and polymer. Although some polymers are capable of partial intercalation or exfoliation without the addition of a swelling agent, addition of 2 wt % of this additive results in either complete intercalation/exfoliation or an increased percentage of nanocomposite formation, in comparison to the clay–polymer mix. The evidence of a nanocomposite structure is provided by a shift in, or the absence of, clay reflections in X-ray powder diffraction patterns.

Introduction

The field of polymer nanocomposites has attracted considerable attention as a method of enhancing polymer properties and extending their utility, by using molecular or nanoscale reinforcements rather than conventional particulate filled microcomposites.[1] Okada et al.[2] have demonstrated that nylon 6 clay hybrids exhibit substantial improvements in mechanical, thermal, and rheological properties, making possible new material applications of the nylon polymer. Epoxy–clay nanocomposites have also shown greatly improved tensile modulus and strength.[3]

Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale regime. These materials exhibit behavior different from conventional composite materials with microscale structure, due to the small size of the structural unit and the high surface-to-volume ratio.[4] The properties of composite materials are greatly influenced by the degree of mixing between the two phases. In conventionally filled polymers, the constituents are immiscible, resulting in a coarsely blended macrocomposite with chemically distinct phases. This results in poor physical attraction between the organic and inorganic components, leading to agglomeration of the latter, and therefore, weaker materials. In addition, the micrometer size particles act as stress concentrators. In nanocomposites, chemically dissimilar components are combined at the nanometer scale and are too small to be stress concentrators. Stronger interactions between the polymer and silicate clay produces improved materials with increased mechanical properties. The structure of the composite depends on the extent to which the organic and inorganic components are made compatible.[5]

Clays are used as additives because they are composed of layered silicates that can intercalate organic molecules. The morphology of the clay particles has been described in several papers.[6,7] Analysis of smectite clay has shown that there are several levels of organization within the clay minerals. The smallest particles, primary particles, are on the order of 10 nm and are composed of stacks of parallel lamellae with an average of 10 sheets per particle. Microaggregates are formed by a lateral joining of several primary particles, and aggregates are composed of several primary particles and microaggregates. However, the lack of affinity between the hydrophilic silicate and the hydrophobic polymer makes it difficult to achieve a homogeneous mixture. Compatibility between the silicate clay layers and the polymers is therefore achieved by ion exchange reactions. While the interlayer cations of silicate clays are usually Na^+, Ca^{2+}, or K^+; exchange reactions with an organic cation increases the organophilicity of the clay layer surface. This lowers the surface energy and improves wetting with the polymer matrix.[5]

Two particular characteristics of layered silicate particles are exploited in nanocomposite preparation. The first is the fact that the silicate particles can be dispersed into individual layers, with a thickness of ~1 nm, and the second is the ability to fine-tune their surface chemistry through the exchange reactions with organic and inorganic cations. To prevent agglomeration

* Corresponding author.
(1) Burnside, S. D.; Giannelis, E. P. *Chem. Mater.* **1995**, *7*, 1597.
(2) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1185.
(3) Wang, Z.; Lan, T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2200.
(4) Gonsalves, K.; Chen, X. In *Materials Research Soc. Symposium Proceedings*; Materials Research Society: Warrendale, PA, 1996; Vol. 435, p 55.

(5) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
(6) Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* **1995**, *28*, 8080.
(7) Akelah, A.; Salahuddin, N.; Hiltner, A.; Baer, E.; Moet, A. *Nanostructured Mater.* **1994**, *4*, 965

Table 1. Polymers Reported as Nanocomposite Matrices and the Observed Nanostructure

polymer	nanocomposite structure	ref(s)
poly(methyl methacrylate)	intercalated	7
polypropylene	intercalated	5
poly(ethylene oxide)	intercalated	8, 9
polyvinylpyrrolidene	intercalated	10
nitrile copolymer	intercalated	11
poly(butadiene/ acrylonitrile)	intercalated	12
polyoxymethylene	intercalated	9
polystyrene	intercalated	13, 14
poly(dimethylsiloxane)	exfoliated	1
epoxy	exfoliated	15
nylon 6	exfoliated	16
polycaprolactone	exfoliated	17
polyacrylonitrile	exfoliated	10

and stabilize the surface of the ultrafine particles, repulsive interparticle forces are essential, and ionic surfactants are used for this purpose.[4] The cation exchanged silicates are easily dispersed in an organic matrix and may form nanocomposites of two types: intercalated structures in which the separation between the silicate layers is increased but relatively constant, or exfoliated nanocomposites in which the unstacked mineral blocks are highly dispersed throughout the polymer, with random interlayer distances and orientation.[8] In intercalated nanocomposites, extended polymer chains are intercalated between host layers in a crystallographically repeating manner, resulting in a well-ordered composite, although these structures are only a few molecular layers wide. The host layers of an exfoliated nanocomposite are dispersed in a continuous polymer matrix, the clay layers being separated by average distances that depend on loading.[9]

Several methods of nanocomposite preparation have been utilized resulting in both intercalated and exfoliated nanostructures. Suspension in a solvent such as water, acetonitrile, or dimethylacetamide (DMAC) has resulted in intercalated hybrids of poly(ethylene oxide)[10,11] and polyoxymethylene oligo(oxyethylene).[11] Melt methods have led to the intercalation of polystyrene[12] and exfoliated nanocomposites of epoxy,[13] via melt/interlayer polymerization. Interlayer polymerization has also produced intercalated polystyrene,[14] poly(ε-caprolactone),[15] and poly-6-amide[16] nanocomposites. Other approaches such as the sol–gel process,[17,18] and monomer/polymer grafting to clay layers[14,19] have also resulted in polymer–clay hybrids. Although several successful approaches have been demonstrated, a major barrier to nanocomposite preparation is that not all polymers can be successfully introduced into clay galleries. Table 1 lists several reported polymers that have

been reinforced by nanometer level dispersion of silicate clays, as well as the structure of the resultant nanocomposite.

The purpose of this paper is to investigate the efficiency of a monomer or polymer additive as an aid to nanocomposite preparation. The additives used are different from the polymer matrix and known to intercalate or exfoliate silicate clay. Okada et al.[20] have reported using a polyolefin oligomer with polar telechelic hydroxyl groups to prepare a polypropylene clay hybrid. One criterion of this oligomer is its miscibility with the polymer. Therefore, the extent of nanocomposite formation as a function of solubility parameter, of the polymer and additive, is investigated. Several other parameters affecting nanocomposite formation will also be discussed, such as polymer molecular weight, the structure of the organic exchange ion, the concentration of the swelling agent, mixing time, and mixing rate.

The ability of a swelling agent to expand the clay layers and permit various types of polymers to form a nanocomposite allows a wide variety of materials to be prepared for specific uses. Also, changing mixing time or additive concentration, in some cases, allows for both intercalated and exfoliated nanocomposites to be prepared from the same polymer.

Experimental Section

Materials. Bentolite-L (bentonite) clay was obtained from Southern Clay products. Epoxy monomer, derived from the diglycidyl ether of bisphenol A (EPON 825), was obtained from Shell. The structure of this monomer is shown in Chart 1, where *n* is 0 or 1. Poly(dimethylsiloxane) (PDMS) was purchased from Huls Petrarch Systems. Poly(styrene-acrylonitrile) (PSAN), nylon 12 (N12), poly(vinyl alcohol) (PVOH), and polyvinyl acetate (PVAc) were purchased from Polysciences Inc. Specimens of poly(1-butadiene), poly(1-butene), poly-(chloroprene), poly(isoprene), poly(isobutylene), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly-(methyl methacrylate) (PMMA), polyoctadecyl methacrylate (POdMA), polyethylene (PE), polystyrene (PS), polycarbonate (PC), polycaprolactone (PCL), poly(ethylene glycol) (PEG), poly-(tetrafluoroethylene) (PTFE), polypropylene (PP), nylon 6 (N6), polyvinyl imidazole (PVI), polypoly(vinyl chloride) (PVC), and polyoxymethylene (PA) were purchased from Aldrich. Polystryrene standards with molecular weights of 1.86×10^5, 10.2×10^4, 4.39×10^4, 1.03×10^4, and 5.40×10^3 and a PDI $\approx$ 1.02, were purchased from Toyo Soda. Ion exchange materials, 12-aminododecanoic acid, and hexadecylamine, were purchased from Aldrich. All chemicals were used as received, with the exception of PVC which was blended with Mark1900 tin stabilizer from Witco.

Sample Preparation. The protonated form of 12-aminododecanoic acid was prepared by dissolving the amine (1.07 g, 5 mmol) in 450 mL of a 0.005 M aqueous HCl at 60 °C. Bentonite clay (5 g) was dispersed in the solution and the resultant mixture was stirred at 60 °C for 1.5 h. The solution was filtered and the clay was washed thoroughly with water at 60 °C. The clay treated with 12-aminododecanoic acid, abbreviated as B12, was then dried overnight in a vacuum oven at 100 °C. The same procedure was followed to prepare clay that is ion exchanged with hexadecylamine (1.21 g, 5 mmol), abbreviated as B16.

Polymer, clay, and epoxy were mixed in the melt in the following amounts: polymer (0.88 g), clay (B12, 0.10 g), and epoxy (0.02 g), unless otherwise stated. Each polymer was heated above its devitrification or melting point, the minimum

(8) Carrado, K.; Xu, L. *Chem. Mater.* **1998**, *10*, 1440.

(9) Lan, T.; Pinnavaia, T. J. *Chem. Mater.* **1994**, *6*, 2216.

(10) Vaia, R. A.; Sauer, B. B.; Tse, O. K.; Giannelis, E. P. *J. Polym. Sci. Part B, Polym. Phys.* **1997**, *35*, 59.

(11) Wu, J.; Lerner, M. M. *Chem. Mater.* **1993**, *5*, 835.

(12) Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Chem. Mater.* **1996**, *8*, 2628.

(13) Wang, M. S.; Pinnavaia, T. J. *Chem. Mater.* **1994**, *6*, 468.

(14) Akelah, A.; Moet, A. *J. Mater. Sci.* **1996**, *31*, 3589.

(15) Messersmith, P. B.; Giannelis, E. P. *Chem. Mater.* **1993**, *5*, 1064.

(16) Fukushima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. *Clay Miner.* **1988**, *23*, 27.

(17) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.

(18) Ellsworth, M. W.; Novak, B. M. *Chem. Mater.* **1993**, *5*, 839.

(19) Keener, B. D. Masters Thesis, Case Western Reserve University, 1998.

(20) Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* **1997**, *30*, 6333.

Chart 1
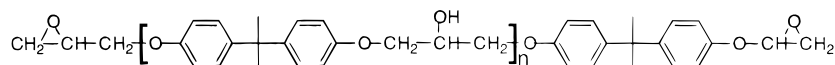
temperature being 75 °C. Clay and epoxy were added, and the mixture was mixed manually for 30 min, during which time the sample was sheared or "kneaded" with a spatula or a pestle. The same procedure was followed using 0.90 g of polymer and 0.10 g of B12, in an attempt to prepare nanocomposites in the absence of epoxy. Representative samples were prepared using PDMS in place of epoxy, for comparison as a function of solubility parameter, δ. Samples prepared with epoxy using poly(isobutylene), poly(butadiene), poly(1-butene), and poly(isoprene) were heated, after stirring for 30 min, at 140 °C in a vacuum oven overnight. For the purpose of this investigation, a relatively high clay loading (10 wt %) was used so differences in X-ray peak intensities were pronounced.

The effect of the alkylammonium ion on hybrid formation was demonstrated by preparing nanocomposites of B16 with PS and POdMA matrices. The dependence of hybrid formation on the mixing rate and time was demonstrated by mechanically mixing PE, 2 wt % epoxy and 5 wt % B12, in a Banbury mixer (Brabender Plasticorder) at speeds of 40 and 60 rpm for 10 min to 2 h. The samples prepared in this study to simply show the feasibility of nanocomposite formation with any polymer were mixed manually for 30 min. Although mixed manually, the reproducibility of the extent of nanocomposite formation was within ±3%. This was determined by preparing 3 samples each of N12, PE, PSAN, and poly(1-butene), with epoxy, and calculating the extent of nanocomposite formation for each sample.

X-ray Analyses. X-ray powder diffraction patterns were obtained using a Philips XRG 3100 X-ray diffractometer with Ni-filtered Cu Kα radiation. Samples were ground into powder, and the data were recorded in the reflection mode in the range of $2\theta = 2-15°$, using a scanning speed and step size of 0.3°/min and 0.05°, respectively. A slit size of one-half inch was used. Since no internal reference was used, absolute intensity of the X-ray diffraction was compared by preparing the nanocomposite samples to have the same size and thickness, thus containing the same amount of clay.

A shift in the first clay peak at $2\theta = 5.5°$ indicates the formation of an intercalated structure, whereas disappearance of that peak, or reduction in its intensity without any shift, indicates an exfoliated structure. The percentage of intercalation and/or exfoliation is calculated from XRD patterns using the equation: $1 - [(\text{clay peak area with epoxy})/(\text{clay peak area without epoxy}) \times 100]$. Intensity measurements were made assuming a linear background, introducing ~5% error into the calculation of percent nanocomposite formation. In all XRD data, only the peak at $2\theta \leq 05.5°$ corresponding to the clay. Any other peak is due to the polymer.

Results and Discussion

The XRD pattern in Figure 1 illustrates the effect of swelling the clay by 20 wt % epoxy monomer in the absence of a polymer matrix. The characteristic peak for clay B12 appears at $2\theta = 5.5°$ ($d = 1.6$ nm). For B12 swollen with epoxy, this peak is broadened and shifted to $2\theta = 3.8-4.7°$ ($d = 2.3-1.9$ nm), suggesting the clay is swollen to a range of d spacings. Epoxy typically forms an exfoliated composite; however, when used in a small amount relative to the amount of clay, the epoxy only swells the clay layers.

To investigate which polymers are able to form a nanocomposite on the addition of a swelling agent, a variety of polymers were used, including rubbers and thermoplastics of varying δ, polarity, and molecular weight. It will be seen that both intercalated and
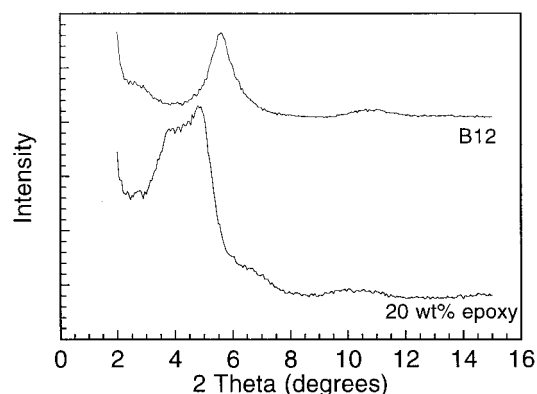

Figure 1. X-ray diffraction patterns of B12 and B12 swollen with epoxy.

Table 2. List of Each Polymer Used, the Percent of Nanocomposite Formation, the Polymer Molecular Weight, and the Nanocomposite Structure for Both Epoxy and PDMS Swelling Agents

polymer	δ	percent (%) formation		molecular weight	structure
		epoxy	PDMS		
PTFE	6.2	89	51	unknown	exfoliated
poly(isobutylene)	7.2	39	81	500 000	exfoliated
PP	7.4	77	56	unknown	int. (epoxy)/ exf. (PDMS)
poly(1-butene)	7.6	26	18	185 000	exfoliated
poly(isoprene)	8.0	26		410 000	exfoliated
PE	8.0	68	15	125 000	int. (epoxy)/ exf. (PDMS)
poly(1-butadiene)	8.1	23		420 000	exfoliated
POdMA	8.3	0		170 000	intercalated
PBMA	8.7	66		337 000	intercalated
PEMA	8.9	50	51	515 000	exfoliated
PMMA	9.1	50		120 000	exfoliated
N12	9.2	99		unknown	exfoliated
PEG	9.4	82		10 000	intercalated
PCL	9.4	54		15 000	exfoliated
PS	9.5	54		45 000	exfoliated
PVAc	9.6	70	71	60 000	exfoliated
poly(chloroprene)	9.6	81		188 000	exfoliated
PVI	9.8	73		unknown	exfoliated
PVC	9.9	100		unknown	exfoliated
N6	10.1	100		unknown	exfoliated
PA	10.5	70		unknown	exfoliated
PVOH	10.6	80		2 000	exfoliated
PC	10.7	64		29 000	exfoliated
PSAN	10.8	85	87	185 000	int. (epoxy)/ exf. (PDMS)

exfoliated samples have been prepared, the nanocomposite structure being dependent on the polymer used, the epoxy concentration, mixing time, and amine exchange ion. Table 2 lists each polymer, percent nanocomposite formation, molecular weight, and the nanocomposite structure formed with both epoxy and PDMS swelling agents. Figures 2 and 3, show the XRD patterns of clay/epoxy specimens with polymer matrices of PSAN and N12, respectively, prepared with and without epoxy pretreatment. Figure 2 shows a peak corresponding to the original clay d spacing as well as a second peak at a smaller diffraction angle, suggesting a partially intercalated nanocomposite. In Figure 3, the intensity of the initial clay peak decreases on the
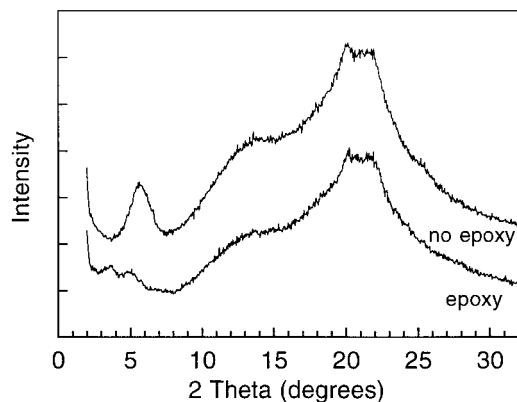
Figure 2. X-ray diffraction patterns of PSAN with and without epoxy.
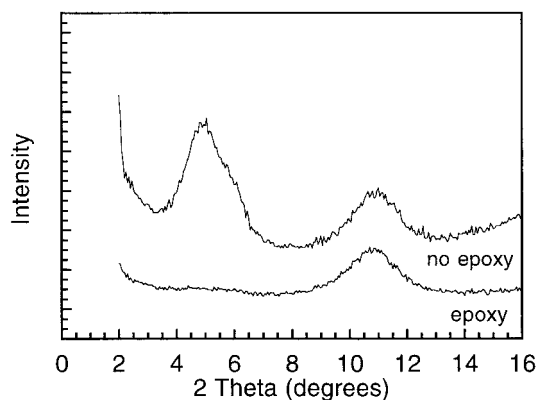

Figure 3. X-ray diffraction patterns of N12 with and without epoxy.

Figure 4. X-ray diffraction patterns of PEG with and without epoxy.
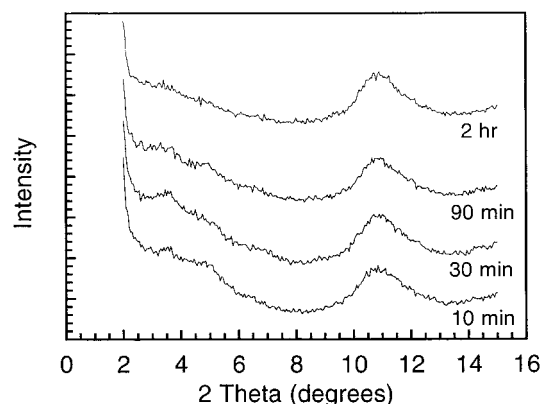
Figure 5. X-ray diffraction patterns of PE at increasing times with stir rate of 40 rpm.

addition of epoxy indicating exfoliation of the clay by the nylon matrix.

The observed changes in clay structure can be attributed to the presence of polymer within the clay layers. The weight of epoxy in each sample is only 20% that of the clay, or 2 wt % of the total composite, and the data in Figure 1 shows that epoxy alone does not exfoliate the clay. Rather, the initial intercalation of the epoxy facilitates penetration by the polymer at the edges of the clay particles, leading to improved dispersion. Therefore, with an exfoliated structure, there is no doubt that the exfoliation of the clay is due to the presence of the polymer within the clay. However, XRD of the epoxy-clay composite with 20 wt % epoxy has already shown intercalation of the monomer.

Figure 4 shows XRD data for PEG. In the absence of epoxy, there are two distinguishable peaks at $2\theta = 3.0°$ and 5.5°, corresponding to intercalated and unintercalated clay, respectively. On addition of epoxy, the intensity of the peak due to unintercalated clay ($2\theta = 5.5°$) decreases while that for the intercalated clay ($2\theta = 3.0°$) increases. Since the latter peak is also observed on intercalating PEG in the absence of epoxy, it seems likely that the polymer is within the silicate layers when epoxy is present. Had a new peak been observed in the range of $2\theta = 3.8-4.7°$, as in Figure 1, then it could have been concluded that only epoxy was within the clay layers.

Other polymers such as PP, PSAN (Figure 2), and PE (Figure 5) do not intercalate in the absence of epoxy. Figure 5 also shows that by increasing the mixing time,
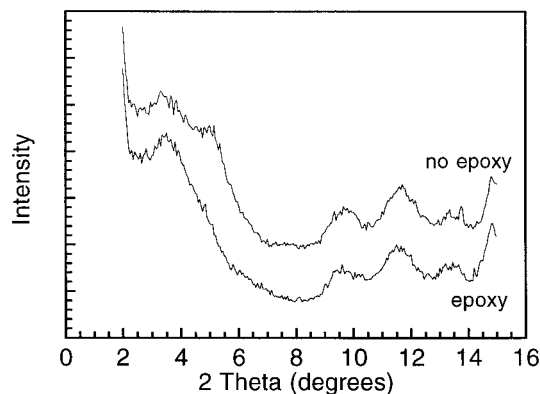
the PE will both intercalate and exfoliate the clay. After mixing with clay and epoxy for 30 min, XRD peaks are observed at $d = 1.7$ and 2.5 nm for all three polymer systems. As previously mentioned, the d spacing of B12 is 1.6 nm, and on addition of 20 wt % epoxy, the clay swells by 16−30% to $d = 1.9$ and 2.3 nm. However, for the specimens containing PP, PSAN, and PE, we observe a peak at $d = 2.5$ nm, indicating a greater swelling than obtained for epoxy alone. This requires the presence of polymer within the clay, unless there has been a redistribution of the epoxy. Increasing the mixing time of 20 wt % epoxy and pure clay leads to X-ray data similar to that in Figure 1, i.e., only swelling of the clay. However, as seen in Figure 5, mixing clay, epoxy, and PE for the increased time results in an exfoliated nanocomposite. Since increasing mixing time will lead to exfoliation in the presence of the polymer but not in the epoxy/clay system, it is probable that the polymer chains are intercalated into the clay structure.

Rate of Nanocomposite Formation, Effect of Mixing Time. The amount of time necessary for hybrid formation to occur depends on the polymer and the preparation method used. PS has been shown to intercalate in an extruder within 4 min.[21] Mechanically mixing PE at increasing rates and times demonstrates

(21) Vaia, R. A.; Giannelis, E. P *Macromolecules* **1997**, *30*, 7990.

(22) Blumstein, A.; Malhotra, S. L.; Watterson, A. C. *J. Polym. Sci. Part A-2* **1970**, *8*, 1599.

(23) Jeon, H. G.; Jung, H. T.; Lee, S. W.; Hudson, S. D. *Polym. Bull.* **1998**, *41*, 107.

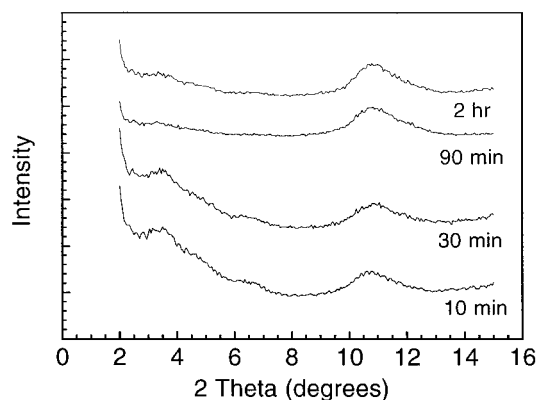(24) Vaia, R. A.; Ishii, H.; Giannelis, E. P. *Chem Mater.* **1993**, *5*, 1694.

Figure 6. X-ray diffraction patterns of PE at increasing times with stir rate of 60 rpm.
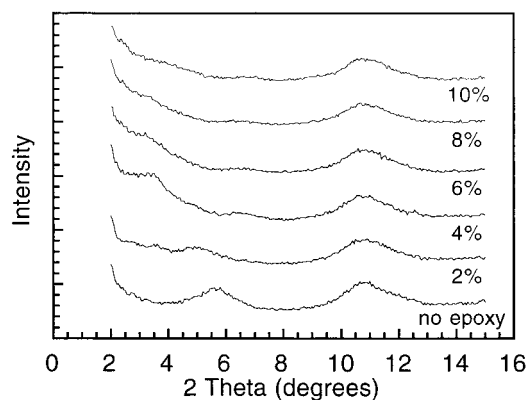

Figure 7. X-ray diffraction patterns of PE with increasing epoxy concentration, from 2 to 10%.

the dependence of nanocomposite formation on such parameters. Figures 5 and 6 show the intercalation and exfoliation of the silicate by PE mixed with 2 wt % epoxy at rates of 40 and 60 rpm. While both figures show intercalation and exfoliation, the difference is the time needed for the nanocomposite to form. At a rate of 40 rpm, an original clay peak ($2\theta = 5.5°$) is still evident after 10 min of stirring. However, after 10 min at 60 rpm, the clay is completely intercalated by PE. In both cases, the intensity of the clay peak is very small by 2 h, indicating that the clay is exfoliated.

Since mass transport into the silicate interlayer is the limiting step to hybrid formation, the degree of constituent mixing is critical for rapid hybrid formation.[6] Increasing the mixing time allows both intercalated and exfoliated nanocomposites to be prepared with the same polymer, by giving the polymer more time to diffuse into the silicate layers. A second method of easing this diffusion is to increase the concentration of the swelling agent.

Increased Epoxy Concentration in Clay/Polymer/ Epoxy Systems. At low epoxy concentrations, PE (Figure 7) shows two peaks by X-ray diffraction, due to incomplete intercalation of the polymer into the clay. As seen in the figure, on increasing the epoxy concentration, the peak intensity of the intercalated structure increases, while the intensity of the original clay peak decreases, until the polymer is completely intercalated.
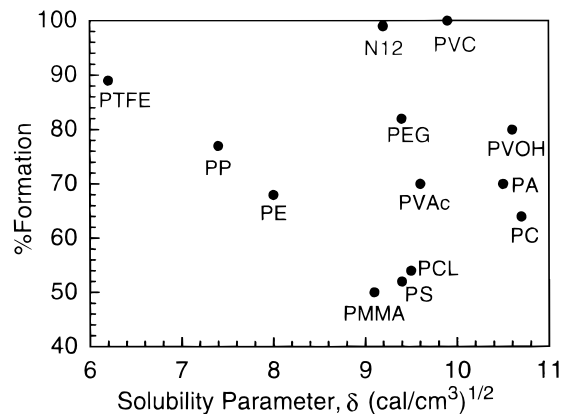
(25) Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1179.
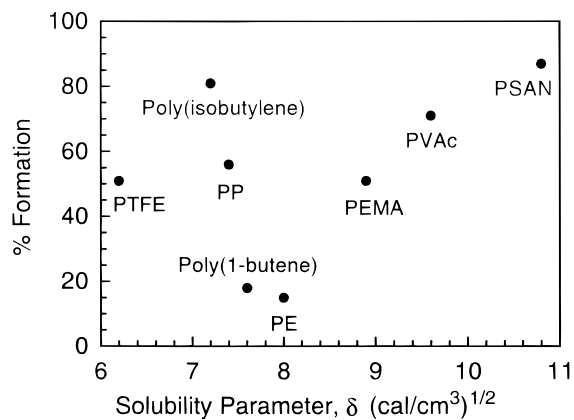

Figure 8. Percent nanocomposite formation vs δ using epoxy swelling agent.

On further increasing the epoxy concentration, the peak intensity due to the intercalated structure becomes almost undetectable, suggesting exfoliation at higher concentrations of epoxy. From Figure 7, the *d* spacing of the peak corresponding to intercalated clay at 2 wt % epoxy corresponds to an interlayer separation larger than that attributed to swelling by epoxy, suggesting intercalation of PE. However, at 5 wt % epoxy, the concentration of the swelling agent with respect to clay is 50 wt %, and mixing just clay and epoxy results in a diffraction peak at $2\theta = 3.4°$ ($d = 2.6$ nm). The diffraction peaks at 4 wt % and 6 wt % epoxy plus PE have similar *d* spacings to the clay swollen by 5 wt % epoxy without PE. Therefore, from these data alone, it is unclear as to whether PE is intercalated at higher epoxy concentrations. However, increasing the epoxy concentration has led to an increase in the degree of exfoliation by PSAN and poly(1-butene). As shown in Figure 2, PSAN with 2 wt % epoxy yields a partially intercalated nanostructure; however, addition of 5 wt % epoxy to the PSAN sample (not shown) results in a completely exfoliated nanocomposite. To cause exfoliation, the PSAN must be penetrating the clay. As shown in Table 2, poly(1-butene) exfoliates 26% of the clay when 2 wt % epoxy is used. On addition of 5 wt % epoxy, the polymer exfoliates 87% of the clay.

While increasing the mixing time or the epoxy concentration has been shown to yield completely intercalated and exfoliated nanocomposites, Table 2 shows that for several polymers, mixing with clay and 2 wt % epoxy for 30 min results in a partial nanocomposite structure. Therefore, the efficiency of the swelling agent was investigated in terms of its miscibility with each polymer.

Solubility Parameter, δ. Epoxy was chosen as the swelling agent in this study because it is known to exfoliate silicate clay, and epoxy has a high boiling point in comparison to other organic monomers. PDMS was selected as the second swelling agent because it has been used in nanocomposite preparation, and the large difference of δ compared to that of epoxy allows comparison of the percentage of nanocomposite formation as a function of polymer δ. Matrix polymers of a range of different solubility parameters were chosen.

Figure 8 shows the percent of nanocomposite formation versus the δ of the polymer matrices, using the epoxy monomer swelling agent. In Figure 8, only

Figure 9. Percent nanocomposite formation vs δ using PDMS swelling agent.

Figure 10. X-ray diffraction patterns of PTFE after mixing with B12 and epoxy for 3, 5, and 10 min.

Figure 11. X-ray diffraction patterns of N12 after mixing with B12 and epoxy for 3, 5, and 10 min.

polymers with a MW < 150 000 were plotted to exclude effects of high MW on nanocomposite formation. This figure shows a relatively linear region between $\delta = 6-9$ and a curved region between $\delta = 9-11$ with a maximum corresponding to $\delta_{polymer} = \delta_{epoxy}$. Therefore, the curve suggests that as the solubility parameter of the polymer approaches that of the swelling agent, the two materials are miscible and yield a higher percent nanocomposite formation. As $\delta_{polymer}$ moves away from $\delta_{swelling\ agent}$ the percent nanocomposite formation decreases. Once a minimum in the curve is reached, $\delta \approx 9$, there is a gradual increase in the percent of formation. These data imply that a larger extent of immiscibility is more favorable to nanocomposite formation than partial miscibility. The general shape of this plot is reproduced in Figure 9, using the PDMS swelling agent. However, the curve now has a maximum at $\delta = 7.2$, where $\delta_{polymer} = \delta_{PDMS}$. This curve decreases to a minimum at $\delta \approx 8.0$, and between $\delta = 8-11$ there is a gradual increase in the percent nanocomposite formation as the immiscibility of polymer and PDMS increases.

Since a high degree of nanocomposite formation is achieved when polymer and swelling agent are very miscible or very immiscible, the initial stages of change in clay structure are examined by XRD using polymers of varying miscibility with epoxy. We propose the clay is dispersed by separate mechanisms that depend on δ of the swelling agent and polymer matrix.

To investigate the initial stages of nanocomposite formation with a polymer that is immiscible with epoxy, a polymer was chosen that has a δ very different from that of the swelling agent, corresponding to the gradually increasing region in Figure 8, $\delta = 6-9$. Figure 10 shows the XRD patterns of PTFE mixed with B12 and epoxy for 3, 5, and 10 min. As seen in the figure, there is a shift in the clay peak as it is swollen with epoxy. While the three components are mixed at the same time, due to the immiscibility of polymer and epoxy, the epoxy can preferentially enter the clay, swell the interlayer galleries, decrease interlayer interactions, and allow penetration of the polymer in a second step. This weakening of the interlayer interactions by the epoxy is critical, since mixing PTFE and clay in its absence does not yield a nanocomposite. In the case of PTFE, the polymer does not flow freely, therefore the silicate layers may disaggregate by mechanical force and/ or adhesion to the rubbery polymer. Since PTFE does not
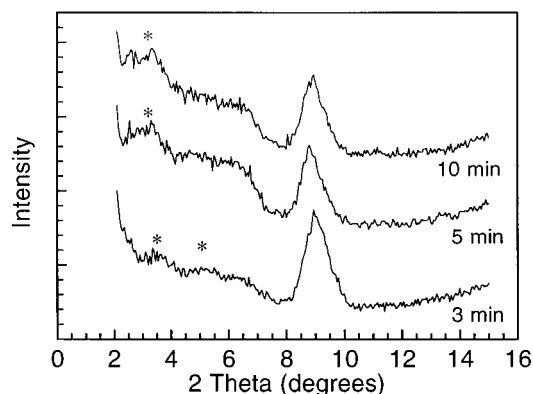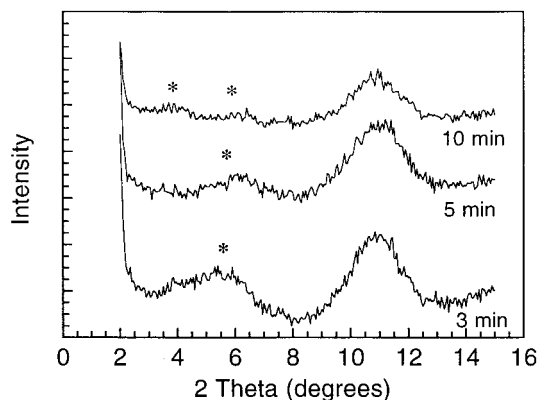
melt or flow at 150 °C, further detailed study is needed to determine the structure of the nanocomposite. However, the nanocomposite formation is representative of a two-step process and is also seen on mixing PP and epoxy for the same time intervals.

When the swelling agent is completely miscible with the polymer, which corresponds to the curved region of Figure 8 ($\delta = 9-11$), the nanocomposite may form in one step. This is illustrated in Figure 11, where N12 is mixed with B12 and epoxy for 3, 5, and 10 min, and examined by XRD after each interval. In this case, at 3 and 5 min, there is no evidence of swelling of the clay, rather the clay peak intensity simply decreases. At 10 min, there is a small peak at $2\theta = 3.5°$, corresponding to swollen clay. However, exfoliation of the majority of the clay prior to the observed swelling implies the clay layers are exfoliated in one step, without preliminary swelling of the silicate galleries. Mixing PP with PDMS ($\delta_{PP} \approx \delta_{PDMS}$) also follows the trend of a gradually decreasing clay peak as exfoliation proceeds.

PMMA has 50% nanocomposite formation and is located at the minimum of the curve in Figure 12 ($\delta = 8.9$). Mixing PMMA with B12 and epoxy for 3, 5, and 10 min intervals did not change the structure of the clay. However, mixing for 1 h results in 90% nanocomposite formation. When there is partial miscibility, the swelling agent is only partially dissolved in the polymer; therefore, intercalation cannot proceed in one step. However, due to the partial miscibility the intercalation may not take place in two discrete steps, since there is only slight preferential swelling of the clay by epoxy. The clay may not be swollen enough to facilitate further penetration
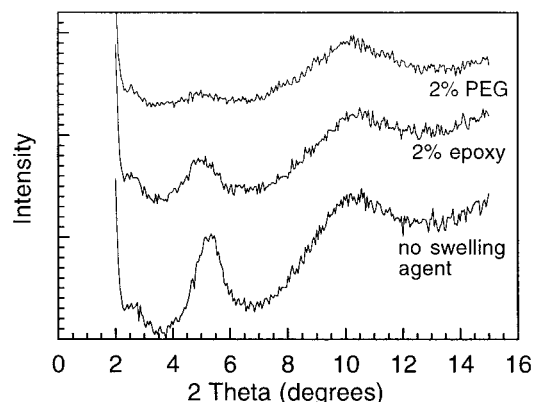
Figure 12. X-ray diffraction patterns of PS with and without epoxy and with PEG.

Figure 13. Percent formation vs PS molecular weight using B16.

Figure 14. Percent formation vs PS molecular weight using B12.

of the polymer, suggesting that when there is partial miscibility, a longer mixing time may be necessary to achieve the higher extents of nanocomposite formation.

In all three regions of the plots in Figures 8 and 9, the intercalation/exfoliation process is thermodynamically driven,[21] the difference in each case is in the kinetics of the process. PS and PMMA both have a percent of nanocomposite formation falling at the minimum of the curve in Figure 8, i.e., partial miscibility with epoxy. With PMMA, we have demonstrated that increasing the mixing time to 1 h results in a higher extent of nanocomposite formation. This is not necessarily the best method, however, due to the increased possibility of polymer degradation. A better option is to find a swelling agent of appropriate δ. As mentioned earlier, PEG partially swells the clay without the addition of epoxy. Since $\delta_{PEG} = \delta_{PS}$, 2 wt % PEG was used as a swelling agent in a PS matrix. As shown in Figure 12, the high miscibility of the two polymers results in a high extent of exfoliation.

Although we have gathered some circumstantial evidence which suggests the occurrence of separate processes of nanocomposite formation depending on the miscibility of polymer and swelling agent, further investigation is necessary to rule out other possible mechanisms. For example, it may be that, on some scale, each polymer follows a two-step process, regardless of miscibility. Even when miscible, some amount of swelling agent, especially in the case of epoxy because it is a small molecule, may still preferentially enter and swell the clay.

Molecular Weight. While δ yields information about percent formation as a function of chemical structure, it does not account for variations due to polymer molecular weight. Poly(isobutylene), has a molecular weight of 500 000 and 39% exfoliation is calculated from the XRD data. PEMA, has a similar molecular weight, 515 000, but shows 50% exfoliation because it flows more easily. As mentioned earlier, the epoxy monomer simply swells the clay; however, the polymer must diffuse into the clay layers. This becomes more difficult, and takes longer if the polymer has a high molecular weight or high viscosity.

When using the epoxy swelling agent, high molecular weight polymers, MW >150 000, tend to exfoliate to a lesser extent than their low molecular weight counterparts. The majority of high MW polymers used were rubbers, many of which have a δ value less than 8.0,
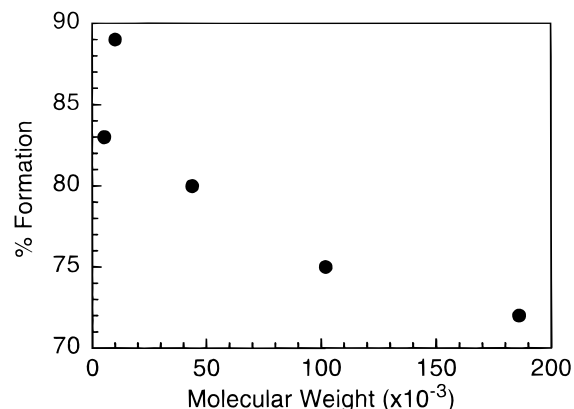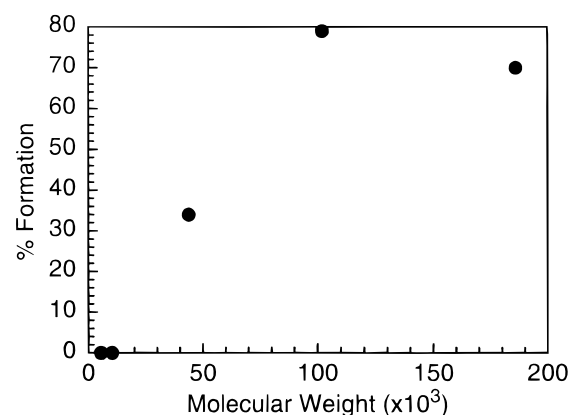
making them immiscible with epoxy. However, from what was concluded earlier, a very different δ value should result in a high degree of nanocomposite formation. When δ values are similar, the two materials should mix, and diffusion of the polymer into the clay is aided by the swelling agent. When the δ values are very different, this diffusion is dependent on the flow of the polymer. In general, rubbers and polymers of high MW have a higher viscosity than those of a low MW, thus impairing their ability to flow and hindering diffusion into the clay. Therefore, although the majority of high MW polymers are very immiscible with epoxy, they do not intercalate or exfoliate to degrees comparable to the low MW polymers. Using PDMS as the swelling agent, where δ_{PDMS} is similar to δ of the high MW polymers, the PDMS is miscible with the polymer and aids diffusion into the clay. In this case, MW does not seem to be a factor in the extent of nanocomposite formation. Similarly, polychloroprene rubber, MW = 200 000, and PSAN, MW = 185 000, both have a high percent nanocomposite formation with epoxy due to their miscibility with this monomer.

It has been reported[6] that as the molecular weight of a polymer increases, the percent of nanocomposite formation decreases, if conditions remain the same. Figure 13 exhibits this trend. In this case, the structure of the alkylammonium ion is changed and B16 is used with epoxy and monodisperse PS standards. However, Figure 14 shows that using B12 and epoxy, as the molecular weight of the PS standards is varied from 5400 to 186 000 g/mol, the percent of exfoliation in-

creases, and at lower molecular weights there is no evidence of nanocomposite formation. The reason for the trend observed in Figure 14 needs further study. However, the difference between B12 and B16 is in the ability of the carboxylic acid group of the amine in B12 to hydrogen bond with the silicate. This hydrogen bonding essentially holds the silicate layers together more strongly than the van der Waals interactions present in B16. Also, in the case of B12, when epoxy enters the clay, it could hydrogen bond with the amine, whereas in B16 hydrogen bonding would be between epoxy and silicate. The trend of increasing nanocomposite formation on increasing PS molecular weight, using B12, is not observed when the swelling agent is changed to PDMS or PEG. Since both these polymers may hydrogen bond to clay or amine, their difference from epoxy is in their viscosity and solubility parameters. Therefore, while the swelling agent allows nanocomposite preparation using a variety of polymer matrices, the structure of the alkylammonium ion is clearly an important parameter.

Effect of the Alkyl Ammonium Ion. As shown in Table 2, using B12 and epoxy, all polymers show some increase in the percent of nanocomposite formation, with the exception of POdMA. POdMA partially intercalates into B12 both with and without epoxy; however, on addition of the swelling agent, there was not any further intercalation. However, using B16, on addition of epoxy the size of the original clay peak is decreased, and 56% of the clay is intercalated by the polymer. An attractive feature of nanocomposites has always been the ease of surface modification of the clay by changing the structure of the alkylammonium ion. Therefore, while using an amino cation with a structure similar to the polymer matrix does not guarantee a nanocomposite can be prepared, the structure of the alkylammonium ion should not be ignored.

Conclusions

Both monomers and polymers that are known to intercalate or exfoliate smectite clay have been used to aid in swelling the silicate clay layers allowing a polymer that typically will not interact with clay to form a nanocomposite, or increase the degree of such formation. Intercalated or exfoliated composites have been prepared with 24 different polymers using 2 wt % epoxy and a clay loading of 10 wt %. A decrease in the ratio of the clay peak area of samples containing epoxy to the clay peak area of samples without epoxy indicates the increase in the dispersion of the clay within the polymer matrix. Several factors including molecular weight, epoxy concentration, mixing rate, mixing time and the alkylammonium ion affect the efficiency of nanocomposite formation as well as the structure of the nanocomposite. Therefore, while intercalation and/or exfoliation is not complete with all the polymers used, a lower clay loading, longer mixing time, and higher swelling agent concentrations may result in completely intercalated or exfoliated nanostructures.

CM990479Y