Macromolecules **2005,** *38,* 6533−6543

Relationship between the Solubility Parameter of Polymers and the Clay Dispersion in Polymer/Clay Nanocomposites and the Role of the Surfactant

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Received April 26, 2005; Revised Manuscript Received June 1, 2005

ABSTRACT: Nanocomposites were prepared of polymers having different solubility parameters and pristine or organically modified clays, and the dispersion of clay in the polymer was evaluated using X-ray diffraction and transmission electron microscopy. The solubility parameters of both the polymers and surfactants of interest were calculated according to the group contribution method and correlated with the clay morphology. A close relationship between the solubility parameter of the polymer and the clay morphology was observed. The clay has a very polar group, so the higher is the solubility parameter of the polymer, the larger is the *d* spacing of the clay that can be achieved. This can explain why in-situ polymerization shows better dispersion than does melt-blending. It appears that the modification of the surfactants is less important than modification of the polymer. However, an enlarged *d* spacing by the surfactant enables the insertion of the monomer into the gallery space by in-situ polymerization and allows the polymer chain having a high solubility parameter to penetrate the gallery space of the clay during melt-blending.

Introduction

Since the introduction of polymer/clay nanocomposites,[1] the study of the formation of nanocomposites has been a very active area of research because very small amounts of clay bring about a large enhancement of the mechanical properties,[2−6] thermal and fire properties,[7−9] and gas permeability.[10,11] The clay consists of stacked aluminosilicate layers that can be separated, but the clay layers, which are held together by electrostatic forces,[12] cannot be broken into separate layers by simple shear. Thus, organic modification of the clay is necessary to achieve separation of the stacked clay layers. To obtain a larger *d* spacing, many studies on nanocomposite formation have focused on the modification of clay by introducing organic molecules into the clay layers through a cation-exchange reaction. Hence, there have been many attempts at the organic modification of clay either using organic cations, such as ammonium, imidazolium,[13] phosphonium,[14] stibonium,[15] tropylium,[16] etc., or introducing different organic groups onto these cations. The objective of the modification of the clay is to provide hydrophobic characteristics to the hydrophilic surface of clay layer, which may permit the entry of organic polymers; at the same time, the *d* spacing of the clay is increased from 1 to 2 nm or higher.

The in-situ polymerization method has been most frequently utilized because it usually provides good nanodispersion of the clay compared to other methods. The preparation of polymer/clay nanocomposites via melt-blending is important for many polymers, and it is the most preferred method from the industrial point of view. The solution-blending method may be a good method to obtain good nanodispersion of the clay in a polymer matrix, but it may also present environmental problems. For these reasons, the melt-blending method for the preparation of polymer/clay nanocomposites draws much interest.

While the *d* spacing of polymer/clay nanocomposites prepared by in-situ polymerization with modified clays increases, compared to that of organically modified clay, the melt-blending method does not provide consistent results in terms of the *d* spacing of the clay in a polymer matrix. Since the prominent properties of polymer/clay nanocomposites are observed when either delamination (preferably) or intercalation is achieved, many models and theories have been developed to predict the dispersion of clay and phase behavior in a polymer matrix.

Vaia and Giannelis[17,18] proposed a mean-field lattice model of polymer−melt intercalation in organically modified layered silicate (polymer/surfactant/silicate system). Considering the layer separation and polymer intercalation, the total free energy change associated with the entropy and enthalpy components were expressed as a function of the gallery height (*d*-spacing). Immiscible, intercalated, and delaminated morphologies were explained in terms of the free energy changes using this model, and it was suggested and proven by experiment that the intercalated and delaminated structures are obtained in systems with either somewhat weak polymer−clay interactions or favorable polymer−clay interactions, respectively. On the basis of this model, the modified clay should be designed to maximize the configurational freedom of the functionalized chain and the potential interaction site.

Lyatskaya and Balazs[19] presented an Onsager model to predict the morphology of the platelet by assuming the clay layer as a rigid disk (polymer/clay system). The model predicts that an increase in chain length of the polymer (N) requires a decrease in the Flory−Huggins interaction parameter (χ) and the delaminated structure is only possible for low N and positive χ, and they showed that a very small volume fraction of clay in a polymer/clay composite may exhibit the delaminated morphology due to the high aspect ratio of clay layer. Then they expanded the system to polymer/organically modified clay by introducing numerical self-consistent-field (SCF) calculations.[20,21] How features of the surfactants and polymer melt can be designed to yield the desired phase behavior by controlling χ, the chain length

10.1021/ma0508909 CCC: $30.25

of surfactant (N_{gr}), and the chain length of polymer matrix (N) were examined. Density functional theory was combined with this SCF model to consider concentration effects. This model indicates that longer chain lengths of the surfactant promote intercalation of the clay.

Kim et al.[22] extended the SCF theories used by Balazs et al. to a four-component system: clay, short-chain intercalant (surfactant), long-chain end-functionalized compatibilizer, and host polymer. There is strong clay−clay interaction in the absence of compatibilizer and the minimum surface fractions of each component for good dispersion of clay were estimated.

The numerical analyses based on these theories were carried out under limited conditions. The dispersion behavior of the clay layers was explained under the condition of $-0.02 \leq \chi \leq 0.02$ and $N \leq 400$, which conditions are expected to give compatibility between the components, and the Flory−Huggins interaction parameter (χ) between components and the chain length (N) of the polymer are out of these ranges in many real cases.

Vaia et al.[18] prepared polymer/clay nanocomposites by powder mixing followed by pressing at 70 MPa and static annealing at temperatures greater than the glass transition temperature of the polymer in a vacuum. Because no shear was applied to the sample and the temperature may be not high enough to have sufficient mobility for the polymer chain to penetrate the gallery of clay, some experimental results may not reflect the real morphological behavior of the polymer/clay systems prepared through melt-blending or in-situ polymerization.

All the above articles dealing with the interaction parameter (χ) provide useful information about the morphology of polymer/clay nanocomposites under certain conditions, but if one wants to view the extended systems or systems having a large interaction parameter between the components, it may be difficult to obtain a practical idea on the design of systems because the estimation model becomes complicated as the nanocomposite systems are extended. While the previous work on the polymer/clay nanocomposites was based on the clay dispersion and morphology, the solubility parameter may be used to explain the clay morphology in a polymer matrix.

Burnside[23] obtained Hansen's solubility parameters (the contribution of dispersion, polarity, and hydrogen bond for the solubility)[24] for the several organically modified clays by measuring the turbidity and viscosity (swelling) in various solvent, and these values were used to predict nanocomposite formation between polymer and organically modified clays by comparing solubility parameters; however, its prediction did not provide consistent results.

Ho and Glinka[25] investigated the effect of Hansen's solubility parameters on the dispersion of organically modified clay in various solvents using small-angle neutron scattering (SANS) and wide-angle X-ray scattering (WAXS). It was found that the dispersion force of the solvent is the principal factor determining whether the organically modified clay layers remain suspended in the solvent, whereas the forces of polarity and hydrogen bond affect the tactoid formation/structure of the clay in solution.

Ishida et al.[26,27] prepared polymer/clay nanocomposites using swelling agents (compatibilizer) for the organically modified clay, such as an epoxy and/or poly(dimethylsiloxane). A variety of polymers were evaluated, and the extent of nanocomposite formation as a function of solubility parameter was evaluated. The swelling agents, which have a solubility parameter range that facilitates entry of both the swelling agent and polymer matrix between the clay layers, were successfully applied for the preparation of intercalated and/or delaminated polymer/clay nanocomposites. The authors focused on the effect of the swelling agents on the formation of nanocomposites without considering the relationship between the polymer and clay.

It appears that the dispersion of the clay layers may depend on the solubility parameter of polymer matrix. The above articles on the solubility parameter deal with the clay morphology in specific systems, such as a static annealed sample,[23] a liquid solution,[25] and a melt-blended sample.[26] It may be preferable to use Hansen's solubility parameters for the polymers used in polymer/clay/surfactant system when considering interaction between polymer/surfactant and polymer/clay. However, there are not enough and consistent data for the Hansen's solubility parameters (HSP) of the polymers of interest in the literature[28] and the obtaining each polymer's HSP by the swelling method of the polymers in various solvents is out of the scope of this study. Therefore, in this study, the calculated solubility parameter is introduced to correlate the dispersion of the clay in the polymer matrix. First, the effect of surfactant on the clay dispersion is considered in terms of solubility parameter of the surfactant and polymer for the nanocomposite samples prepared by in-situ polymerization as well as melt-blending. Then, based on these results, the correlation between the clay dispersion with the solubility parameter of polymer was established. It should be noted that this approach describes only a part of the enthalpic contributions and ignores entropic effects.

Solubility Parameter and Methodology

There are several ways to predict and explain the miscibility in multiple phase system using thermodynamics,[29,30] including the solubility parameter, the lattice theory, and the equation-of-state. Among these methods, the solubility parameter (SP, δ), which is the square root of cohesive energy density (energy of vaporization per unit volume), was used in this study. Since it is not possible to obtain the molar vaporization energies for polymers, indirect methods, which are obtained from swelling and viscosity measurements in various solvents, and calculations based on group contributions, are used for the solubility parameters of the polymers. The solubility parameter of the polymer depends on the polarity of solvents used, the molecular weight of polymer, the density, tacticity, etc.; in many cases, the solubility parameters of the specific polymers are given not as a specific value but over a range. The solubility parameter is a function of pressure and temperature,[31] so each component of interest needs to have its own solubility parameter at the desired temperature. There are several different tables[32] showing molar attraction constants that can be used for the calculations of the solubility parameters. Nonetheless, it is said that accurate predictions are made when the calculated, rather than experimental, values are used for the predictions.[30]

To compare the solubility parameters of each component in a simple and consistent way, the solubility

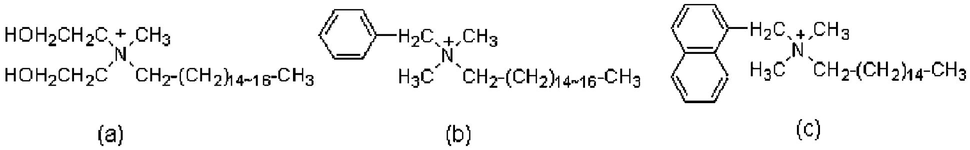

Figure 1. Structures of the ammonium ions: (a) methyl hydrogenated tallow bis(2-hydroxyethyl)ammonium, 30B; (b) dimethylbenzyl hydrogenated tallow ammonium, 10A; (c) dimethylnaphthenate hexadecylammonium, Np.

parameters of polymers and surfactants were calculated on the basis of the following equation, using Hoy's table[33,34] for the molar attraction constant of the specific functional groups. For the simplicity, room temperature is used as the standard condition.

$$\delta = (\rho \sum F)/M \tag{1}$$

where δ, ρ, F, and M are the solubility parameter, density, molar attraction constant, and molecular mass of the repeating unit, respectively. The units of the solubility parameter are given as $J^{1/2}/cm^{3/2}$.

The maximum solubility parameter difference for complete miscibility between the two components was calculated using the following equations

$$\chi_{AB} = 0.5(1/x_A{}^{1/2} + 1/x_B{}^{1/2})^2 \tag{2}$$

$$(\delta_A - \delta_B)^2 = \chi_{AB} RT/V_r \tag{3}$$

$$(\delta_A - \delta_B)^2 \approx 6\chi_{AB} \tag{4}$$

where χ_{AB} is the Flory–Huggins interaction parameter of polymers A and B, x is the degree of polymerization (the number of repeating unit), R and T are the gas constant and temperature, and V_r is a reference volume, which is the molar volume of the smallest repeat unit. If V_r is conveniently taken to be 100 cm^3/mol at room temperature, then eq 4 is obtained.

To correlate the relationship between the polymer solubility parameter (SP) and clay dispersion, many previous results on the clay dispersion in a polymer matrix have been investigated and classified according to the calculated solubility parameter: low SP polymer, medium SP polymer, and high SP polymer. Four different polymers are used as model polymers for this study: polystyrene (PS), poly(styrene-*co*-acrylonitrile) (SAN), polyamide 6 (PA6), and polyacrylonitrile (PAN). Regarding the clays, the pristine clay (sodium montmorillonite) and three different organically modified clays were utilized. Thus, PS is classified as a low SP polymer, SAN as a medium SP polymer, and PA6 and PAN are sorted as high SP polymer. Two things should be noted; first, all of the equations and calculations are approximate, and the proposed classification on the dispersion of clay and the role of surfactants may not match some specific polymer/clay systems; these should be used only as a guide. Second, only the interactions between the surfactant and the polymer are calculated herein; the interactions between polymer and the inorganic clay itself are speculated on the basis of the clay morphology results in a polymer matrix.

Experimental Section

Materials. Polystyrene (PS) and polyamide 6 (PA6) were purchased from the Aldrich Chemical Co., and poly(styrene-*co*-acrylonitrile) (SAN) was provided by Cheil Industries Inc.; the mass ratio of styrene/acrylonitrile in SAN is 75/25. For the emulsion polymerization of polyacrylonitrile (PAN), acrylonitrile, potassium persulfate, sodium dodecyl sulfate, and 2-acrylamido-2-methylpropanesulfonic acid were purchased from Aldrich. Three differently organically modified montmorillonite clays were used: Cloisite 30B clay (Southern Clay Products, containing 30% organic modifier (methyl hydrogenated tallow bis(2-hydroxyethyl)ammonium) and 70% inorganic clay), Cloisite 10A clay (Southern Clay Products, containing 30% organic modifier (dimethylbenzyl hydrogenated tallow ammonium) and 70% inorganic clay), and Np-clay (prepared in this laboratory,[35] containing 30% organic modifier (dimethylnaphthenatehexadecylammonium) and 70% inorganic clay). The structures of ammonium salts used for the modification of clay, the surfactants, are shown in Figure 1. The pristine clay, sodium montmorillonite (Na-clay), was provided by Southern Clay Products Inc. All the above materials were used as received without further purification.

Preparation of Polymer–Clay Composites. Polystyrene (PS), poly(styrene-*co*-acrylonitrile) (SAN), and polyamide-6 (PA6) were melt-blended with the Na–clay and the organically modified clays in a Brabender mixer for 10 min at 200–210 °C for PS and SAN and 230–240 °C for PA 6. The inorganic clay contents for polymer/clay composites for PS, SAN, and PA6 are 3.0 and 5.0 wt %. Since PAN–clay nanocomposites cannot be processed via melt-blending, PAN–clay composites are prepared by emulsion polymerization. A 5.2 g portion of Na–montmorillonite (Na–clay) was dispersed in 150 g of deionized water for 24 h at room temperature. A solution containing 100 g of acrylonitrile, 1.0 g of sodium dodecyl sulfate, and 1.0 g of 2-acrylamido-2-methylpropanesulfonic acid was premixed in 100 g of deionized water. The Na–clay solution and acrylonitrile solution were charged to a 1000 mL reactor equipped with a mechanical stirrer and a reflux condenser. Then, the temperature of the reactor was raised to 60 °C with stirring, and 1.0 g of potassium persulfate dissolved in 50 g of deionized water was added to the reactor, which was maintained at 60 °C for 3 h to complete the polymerization. For the polymerization of virgin PAN, the same amounts of reactants and deionized water were used without clay, following the same procedure as described above. The synthesized PAN and PAN/clay composite were washed with water, filtered, and dried in a vacuum oven.

Characterization of Polymer–Clay Nanocomposite. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the dispersion of clay and the formation of nanocomposites. XRD patterns were obtained using a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu Kα generator (λ = 1.5404 Å); generator tension was 50 kV, and the current was 20 mA. TEM images were obtained at 60 kV with a Zeiss 10c electron microscope; the samples were microtomed using a Richert-Jung Ultra-Cut E microtome.

Results and Discussion

The Choice of Surfactants Used in This Study. A wide variety of surfactants have been described and used to prepare polymer–clay nanocomposites, as described in the introductory section of this paper. Of the common surfactants, only Cloisite 30B clay contains a functional group. All of the other commonly used materials have only long alkyl chains; thus, Cloisite 30B was chosen as an example of a functionalized surfactant. Cloisite 10A clay contains a benzyl group, and one might expect enhanced compatibility between an organic polymer, such as polystyrene, and a surfactant which

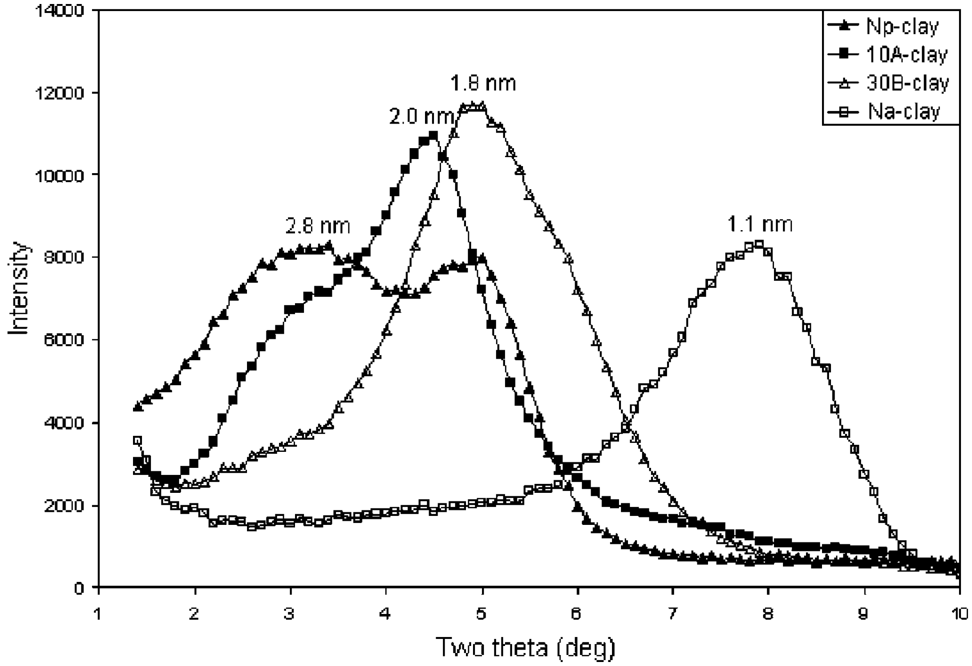

Figure 2. XRD patterns for the pristine clay and organically modified clays. Inset number denotes the d_{001} of clay.

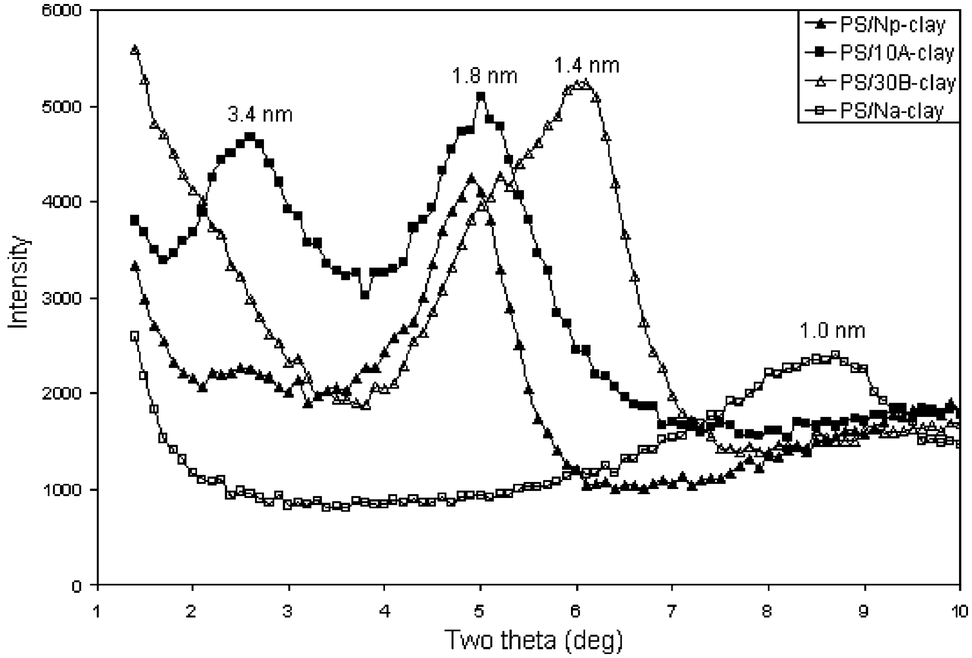

Figure 3. XRD patterns for the melt-blended PS/clay composites having 5% inorganic clay content. Inset number denotes the d_{001} of clay.

contains an aromatic moiety. In previous work from this laboratory, the naphthenate-containing clay (Np−clay)[35] has been described, and quite good dispersion of the clay in polystyrene has been observed by in-situ bulk polymerization.

Characterization of the Clay Dispersion. The formation of a nanocomposite between the polymers and various types of clays was observed by XRD and then confirmed with TEM images. Figure 2 shows XRD patterns of the sodium and the organically modified clays. The unmodified Na−clay has a *d* spacing (d_{001}) of 1.1 nm. For the modified clays, Np−clay exhibits peaks at both 2.8 and 1.8 nm; it is presumed that 2.8 is d_{001}, the 10A-clay shows d_{001} at 2.0 nm with some intensity also at 2.8 nm, and the 30B-clay shows the d_{001} at 1.8 nm. (The supplier reports a *d* spacing of 19.2 Å for 10A, 18.5 Å for 30B, and 11.7 Å for the sodium clay.) All these clays are melt-blended with PS, SAN, and PA6 at 3.0 and 5.0 wt % inorganic clay content, and the XRD results of each formulation having 5.0 wt % in organic clay content are shown in Figure 3 (PS−clay), Figure 4 (SAN−clay), and Figure 5 (PA6−clay).

XRD curves of the materials prepared by the melt-blending of PS and the various clays are shown in Figure 3. The sample formed using the 10A clay exhibits an increased *d* spacing at 3.4 nm, but there is also a considerable intensity at $d_{001} = 1.8$ nm, which means some amounts of clay layers have a decreased *d* spacing after melt-blending. The *d* spacing of the 30B clay is decreased from 1.8 to 1.4 nm after melt-blending. In the

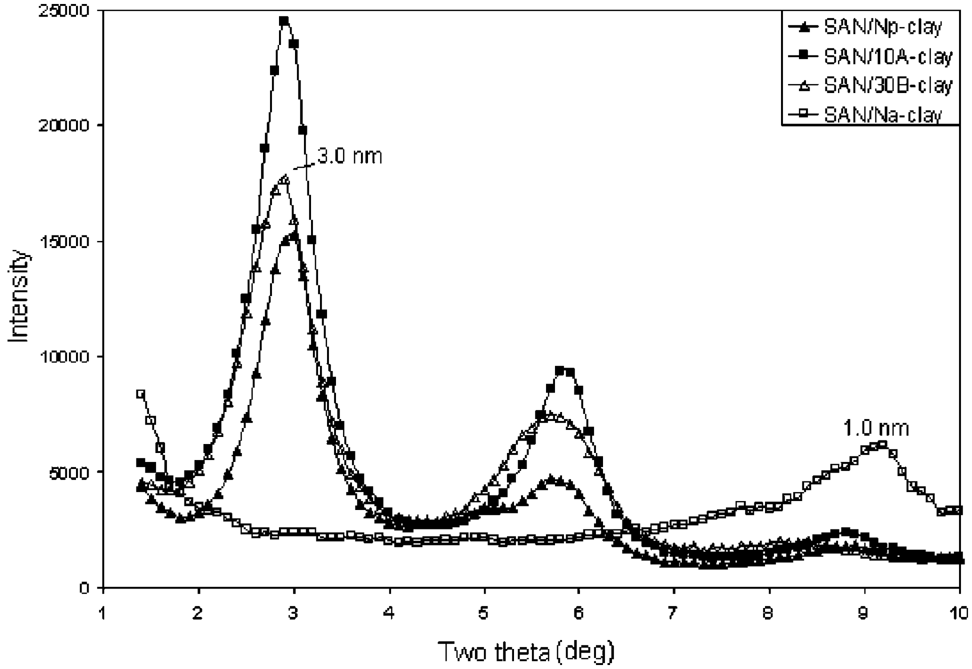

Figure 4. XRD patterns for the melt-blended SAN/clay having 5.0% inorganic clay content. Inset number denotes the d_{001} of clay.

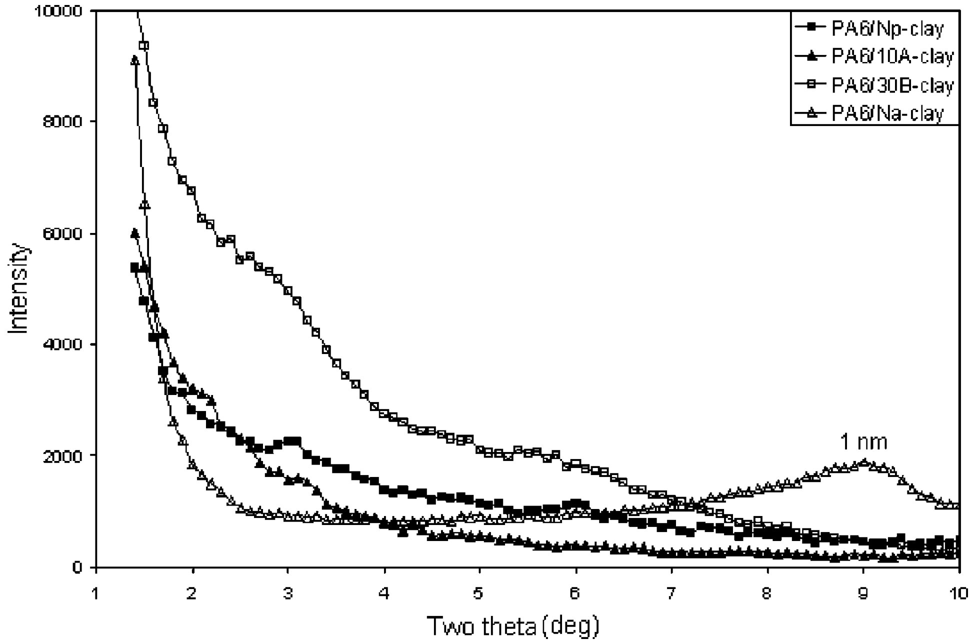

Figure 5. XRD patterns for the melt-blended PA6/clay having 5.0% inorganic clay content. Inset number denotes the d_{001} of clay.

case of Np−clay, d_{001} is reduced from 2.8 to 1.8 nm. Although there is some difference in the *d* spacing with the surfactant, a considerable amount of clay in the modified clays and even the pristine clay exhibit a smaller *d* spacing compared to those of the original clays. Even though the surfactants in the modified clays provide some effect on the changes of *d* spacing, as in the case of polystyrene/10A clay, generally they do not lead to nanodispersion and the formation of intercalated or delaminated structures by melt-blending. From the XRD data, the morphology of the clay is not nanodispersed but rather microdispersed, with, perhaps, some partial intercalation.

On the other hand, SAN/modified-clay composites exhibit a well-developed intercalated morphology in the XRD patterns, as shown in Figure 4. All SAN/modified-clay composites show peaks at the 2θ values of 2.9°, 5.9°, and 8.8°, which correspond to the (001), (002), and (003) planes, implying an intercalated morphology. In the case of SAN/Np−clay, a peak at 4.9° was observed in low intensity, implying that some amount of the Np−clay was not well-mixed during the preparation of the nanocomposites, while the SAN/Na−clay composite shows a decreased *d* spacing from the XRD trace of the clay alone as in the PS result, simply a microcomposite. If modified clays are used in the preparation of SAN/clay nanocomposites via melt-blending, irrespective of the surfactant used, the clay exhibits a highly ordered structure, and the *d* spacing increases to a value of 3.0 nm for these nanocomposites. In the case of SAN, the

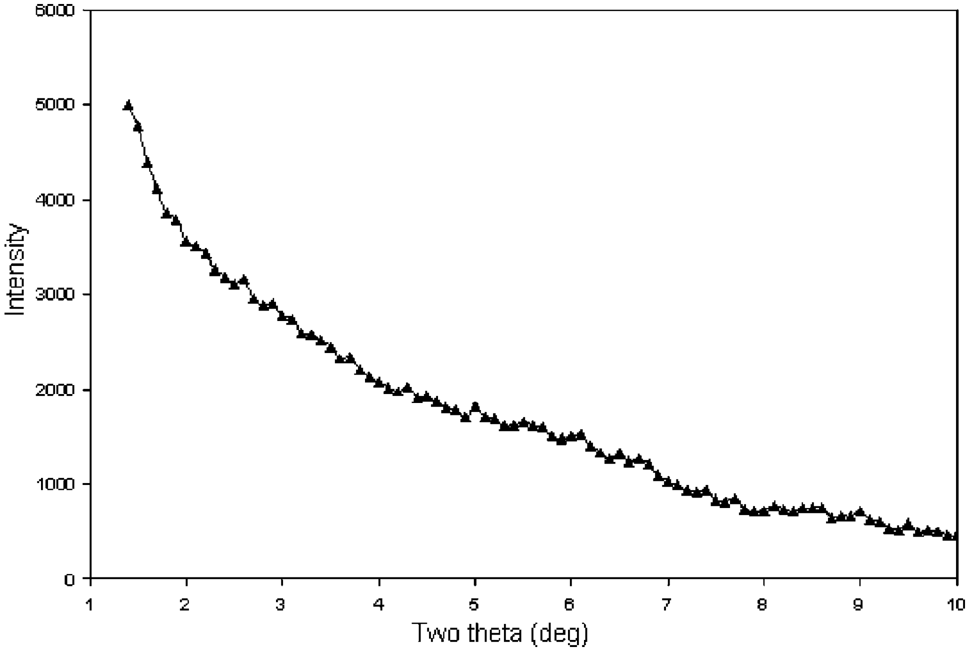

Figure 6. XRD patterns of in-situ polymerized PAN/Na-clay having 5.0% inorganic clay content.

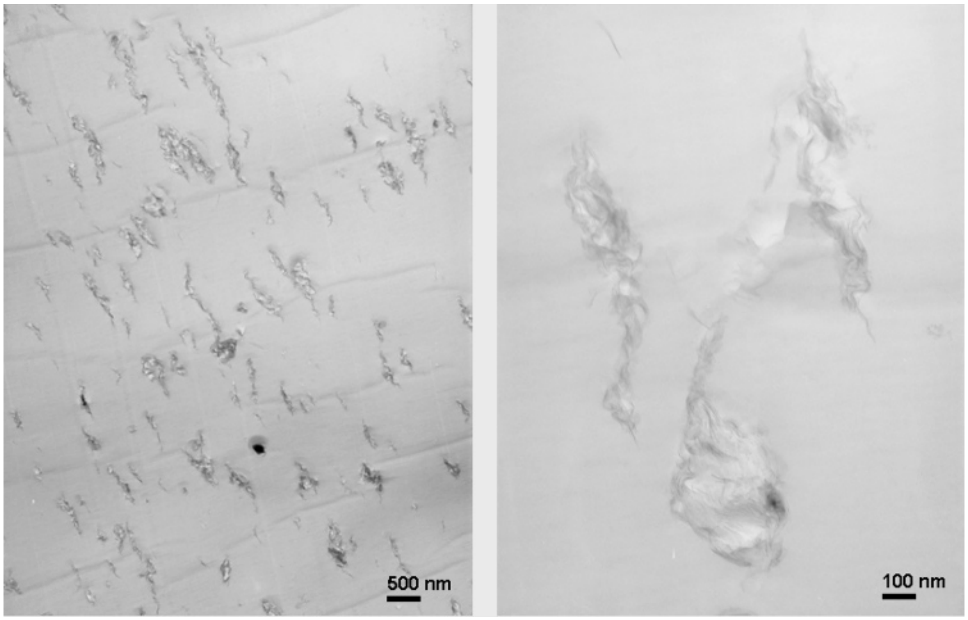

Figure 7. TEM images of polystyrene/10A-clay having 3.0% inorganic clay content at low magnification (left) and high magnification (right).

intercalated morphology of clay is readily obtained by melt-blending with the modified clay, which is consistent with the work of Morgan et al.[36]

The composites of PA6/modified clays do not exhibit significant peaks in the XRD traces (Figure 5). The presence of small peaks around 3° and 6° imply that there is some intercalated clay portion, along with the predominant delaminated structure. The PA6/Na−clay composite exhibits a peak at 9°, which indicates that no polymer has entered the clay, in the case of pristine clay. It is known that polyamide 6 can readily form delaminated nanocomposites by simple melt-blending with organically modified clays.[37,38] The in-situ polymerized sample of PAN/Na−clay exhibits no peaks as shown in Figure 6, implying a delaminated morphology.

Since the clay morphology in the polymer/clay systems does not exhibit any significant changes with the type of surfactant, the nanocomposites using 10A-clay were selected as representative formulations for each polymer. The TEM images for each polymer/clay composition are shown in Figures 7−10.

In the case of the PS nanocomposites, good dispersion is evident at the microscale from the low-magnification image, but clusters of clay are clearly seen in the high-magnification image, as shown in Figure 7. The TEM of the SAN nanocomposite shows the well-dispersed intercalated structure.[39] Bourbigot et al.[40] showed similar results for SAN−clay nanocomposites prepared by melt-blending. Finally, polyamide 6 and PAN apparently show a delaminated morphology. The TEM images for PA6 show several white regions, which are where the sample was microtomed.

Through the XRD and TEM study, it was shown that the dispersion of clay exhibits different morphologies

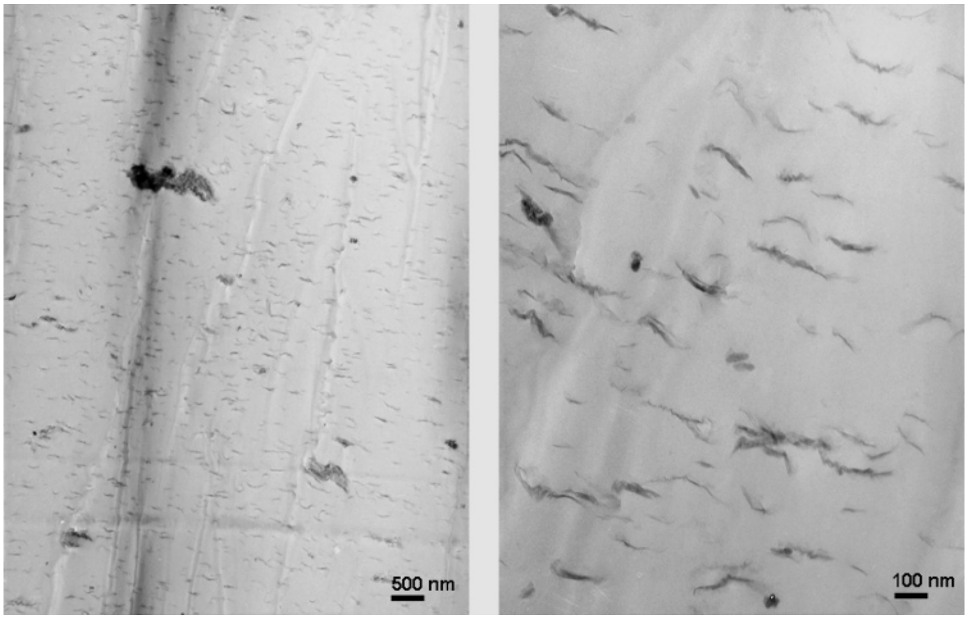

Figure 8. TEM images of poly(styrene-*co*-acrylonitrile)/10A-clay having 3.0% inorganic clay content at low magnification (left) and high magnification (right).

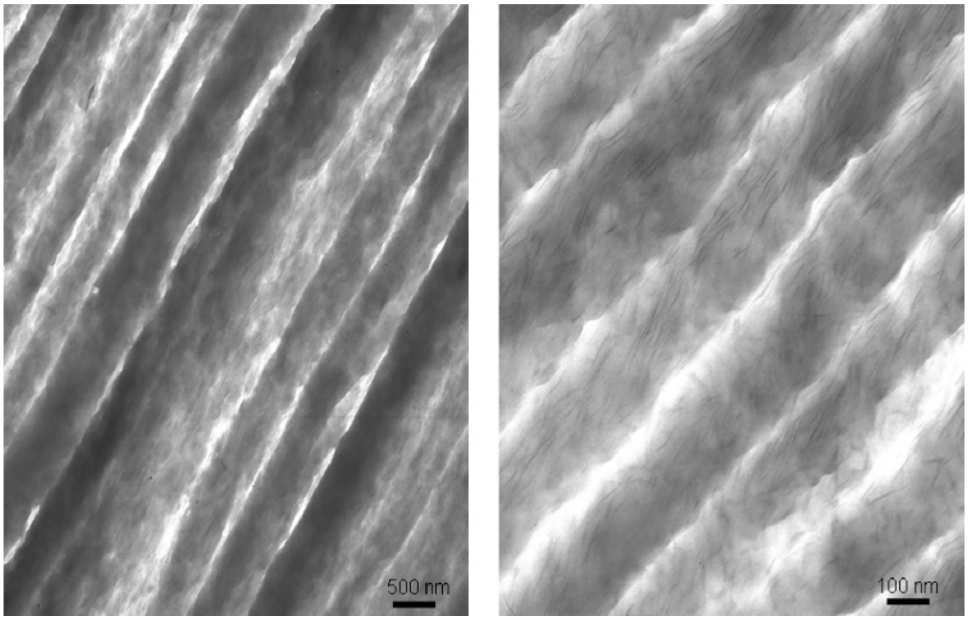

Figure 9. TEM images of polyamide 6/10A-clay having 3.0% inorganic clay content at low magnification (left) and high magnification (right).

with different polymers, using the same set of clays; it appears that the structure of the surfactants does not significantly affect the dispersion of the clay in the polymer/clay nanocomposites.

Solubility Parameter of the Polymer and Morphology. There are a large number of procedures available to obtain the solubility parameter. These are tabulated at room temperature, and there is some question as to the validity of using room-temperature values for systems that have been processed at about 200 °C. Utracki has explained the process of converting from room temperature values to temperatures above the glass transition temperature, which is a more reasonable temperature, since melt-blending occurs above this temperature.[41] The conversion from room temperature to higher temperature has the effect of decreasing the solubility parameter; for instance, for polystyrene the value at 25 °C is 22.4 while it falls to 19.5 at 300 °C, and the tabulated value is 18.7. In general, the values taken from a listing of the solubility parameters show better agreement with the values at high temperature than they do with the room temperature values computed by Utracki and Simha.[31] The intention of this paper is not to correlate the absolute values of the solubility parameter with other properties but rather to sort polymers into classifications, which can be done as well with the room temperature values. Accordingly, the solubility parameters of the surfactants and polymers were calculated on the basis of eq 1, using Hoy's molar attraction constant table.[33,34] To calculate the solubility parameters of the surfactants through group contributions, several assumptions were made. Since the surfactants, which are ammonium salts, are connected to the clay layers electrostatically, it is assumed that the longest chain in the surfactant structure dominates the solubility parameter and the

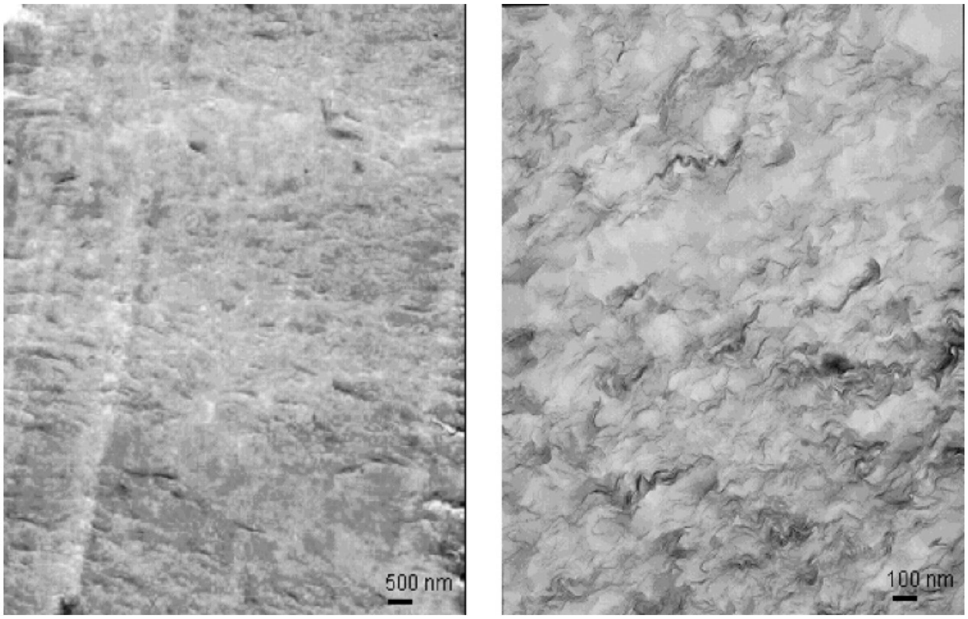

Figure 10. TEM images of polyacrylonitrile/Na-clay having 5.0% inorganic clay content at low magnification (left) and high magnification (right).

Table 1. Calculated Solubility Parameters of Polymer and Surfactant Using the Group Molar Attraction Constants of Hoy[34] (in $J^{1/2}/cm^{3/2}$)

sample	calcd SP
polystyrene (PS)	18.6
styrene−acrylonitrile copolymer (SAN)	20.3
polyamide 6 (PA6)	23.8
polyacrylonitrile (PAN)	26.1
methyl hydrogenated tallow bis(2-hydroxyethyl)ammonium (30B)	16.8
dimethylbenzyl hydrogenated tallow ammonium (10A)	16.2
methyl naphthenate hexadecylmethylammonium (Np)	16.5

other substituents are considered as part of the longest chain, and the ammonium moiety is excluded in the calculation of the solubility parameter. The calculated solubility parameters for the polymers and surfactants are shown in Table 1. If only the longest chain in the surfactant is assumed to determine the solubility parameter, then the solubility parameter of the surfactant is very similar to that of polyethylene (SP: 16.3) because most of the surfactants used for the preparation of polymer/clay nanocomposites consist of linear aliphatic chains, such as hydrogenated tallow, hexadecane, octadecane, etc.

The maximum difference of solubility parameters between the two components for miscibility was calculated according to eqs 2 and 3. Assuming that the degree of polymerization (the number of repeating unit) of the surfactant is 20 and that of polymer is 1000, the maximum solubility parameter difference for complete miscibility between the surfactant and polymer is calculated as 0.9 $J^{1/2}/cm^{3/2}$. Comparing the solubility parameters in Table 1, the differences between the solubility parameters of the polymers and surfactants are much larger than this. Hence, miscibility between the surfactants and polymers is not expected.

As a model polymer, polystyrene was used and melt-blended with various clays. PS is classified as a low solubility parameter (SP) polymer, and its composite with the modified clays exhibits only microdispersion. The *d* spacing does not increase but decreases after melt-blending in most cases, as shown in Figure 3. In this laboratory, significant work has been performed on the formation of nanocomposites of low SP polymers such as polyethylene[42] (SP 16.3), polypropylene[43] (SP 16.6), polystyrene[44] (SP 18.6), and poly(methyl methacrylate)[45] (SP 18.8) via melt-blending. These result in a mixed immiscible/intercalated morphology for the polymer−clay nanocomposites. However, there has been no significant increase in the *d* spacing of clay after melt-blending compared to the *d* spacing in the organically modified clay. In the case of polyethylene and polypropylene, the solubility parameters of the polymers are not very different from those of the surfactants in the modified clays because the surfactant usually consists of a long aliphatic chain that is similar to a polyolefin. Despite this agreement in solubility parameters, the *d* spacing in a polyolefin nanocomposite was not increased after melt-blending, which implies that the compatibility between the polymer and surfactant does not play an important role in enlarging the *d* spacing in the polymer/clay composites by melt-blending.

Galvin and co-workers[46,47] introduced quaternary ammonium end-functionalized polystyrene to clay by ion-exchange and made nanocomposites with polystyrene; to promote intercalation, styrene-modified clays having five different molecular weights were used, but no further intercalation was observed in any cases after processing. It was explained that the high levels of modification resulted in dense polymer brushes on the clay surfaces, preventing further intercalation by the PS matrix; when the two polymer brushes come close together, the free melt chains can be expelled between the two layers, which implies an attraction between the sparsely grafted surfaces.[48] In this case, since the longest chain of surfactant has the structure of polystyrene, its solubility parameter must be the same as that of polystyrene, and the interaction parameter (χ) between surfactant and polymer matrix must be zero, and complete miscibility is expected. These results imply that the chemical affinity between the matrix polymer and the clay may be more important than that between the polymer and surfactant. There are features of the interactions that cannot be understood only from the

Table 2. Solubility Parameter of Polymer and the Dispersion of Clay

	low SP polymers	medium SP polymers	high SP polymers
solubility parameter	−19	19−23	23−
polymers	polyethylene, polypropylene, poly(methyl methacrylate), polystyrene, etc.	poly(styrene-*co*-acrylonitrile), poly(ethylene terephthalate), poly(vinyl chloride), polycarbonate, etc.	polyamide 6, poly(vinyl alcohol), poly(acrylonitrile), etc.
dispersion of clay	melt-blending: *d* spacing does not increases; in-situ polymerization: *d* spacing increases	melt-blending: *d* spacing increases; in-situ polymerization: often delaminated morphology	melt-blending: often delaminated morphology; in-situ polymerization: delaminated morphology
modification of clay by surfactant	necessary	necessary	melt-blending: necessary; in-situ polymerization: not necessary

solubility parameters of the polymers and surfactants.

On the other hand, if low SP polymer/modified-clay composites are prepared via in-situ polymerization, intercalated and/or partially delaminated structures are observed more readily, and the clay layers exhibit an increased *d* spacing (an intercalated structure) or a delaminated structure after in-situ polymerization.[49−54] It must be noted that the materials that have been prepared by in-situ polymerization are not at thermodynamic equilibrium, and if they are subjected to melt-blending, they can revert to an intercalated morphology. The summary of low SP polymer/clay nanocomposites is shown in Table 2.

The medium SP polymers, such as poly(vinyl chloride) (PVC, SP 19.7), SAN (SP 20.3), polycarbonate (PC, SP 21.1), and poly(ethylene terephthalate) (PET, SP 22.9), show a different behavior than that observed in the low SP polymers. In this study, the melt-blending of SAN and organically modified clay provides an increased *d* spacing, and an intercalated morphology is obtained irrespective of the type of modified clay used. Similar results have been seen in PVC/modified-clay,[55,56] PC/modified-clay,[57] and PET/modified-clay composites,[58,59] using melt-blending. The *d* spacing of the clay increases after melt-blending between the medium SP polymers and the organically modified clays. When in-situ polymerization is used for the preparation of nanocomposites between medium SP polymers and organically modified clays, a partially or fully delaminated clay morphology is obtained.[60−66]

In the case of the high SP polymers, such as PA6 (SP 23.8), PAN (SP 26.1), and poly(vinyl alcohol) (SP 29.7), a delaminated morphology is obtained through not only in-situ polymerization but also melt-blending[67,68] with organically modified clays. If in-situ polymerization is utilized for the preparation of the nanocomposite, even the pristine inorganic clay may provide the delaminated morphology for the high SP polymers, as shown in the result for the in-situ polymerized sample of PAN/clay in this study.

For the preparation of polyolefin/clay nanocomposites by melt-blending, good nanodispersion of clay is achieved by introducing polar groups into the polymer chain; typically maleic anhydride (SP 27.8) is grafted to polyethylene[69,70] or polypropylene[71] (polyolefin-*g*-MA) in small amounts (less than 1 wt %), and the oligomer of polyolefin/maleic ahhydride[72] is used as a compatibilizer. These formulations show either an intercalated or a delaminated morphology by melt-blending. Since the amount of maleic anhydride used is very small, the calculated solubility parameters of the modified polymers are not much different from those of the polyolefin, so they do not follow the classification summarized in Table 2.

Another exception is the poly(ethylene-*co*-vinyl acetate) (EVA) system. Camino et al.[73] prepared an EVA/30B-clay nanocomposite, which showed a delaminated morphology, along with some intercalation. Considering the calculated solubility parameter of EVA (17.4 $J^{1/2}/cm^{3/2}$), it should be difficult to obtain an increased *d* spacing by melt-blending, according to Table 2. This result may be caused by a hydrogen bond between EVA and the clay. An alcoholic band at 3460 cm^{-1} was detected in the IR spectrum of EVA in low intensity.[74] Hence, it is speculated that this small amount of hydroxy group in EVA may be instrumental in the nanodispersion of clay. Combining the EVA result and the polyolefin-*g*-MA results, it is suggested that the introduction of a polar group to the side or end chain of a low SP polymer is very effective to permit nanodispersion between the low SP polymers and organically modified clays.

The relationship between the dispersion of clay and the solubility parameter of the polymer is summarized in Table 2. Since the solubility parameters calculated using Hoy's molar attraction constant are approximate and the extent of dispersion may depend on the processing condition, some exceptions from what is shown in Table 2 may be expected.

Organic Modification of Clay and the Role of the Surfactant. Clay is inherently hydrophilic, and it is commonly felt that the pristine inorganic clay is completely delaminated in water. Although it is not possible to obtain the solubility parameter of the clay, it can be considered to be a highly polar material, with hydrophilic structural groups. Referring to Table 2, the results on the dispersion of clay in the polymer matrix are generally consistent with the solubility parameter of the polymer. Melt-blending involves the polymer chain, so the compatibility between each component may be very important to obtain a well-dispersed clay morphology in the polymer/clay system.

In the low SP polymer/clay nanocomposites, the *d* spacing of the clay generally decreases after melt-blending irrespective of the structure of surfactant, as described in the previous section. These results imply that in order to obtain a well-dispersed nanocomposite, especially with low SP polymers, an increase in the *d* spacing by introducing bulky surfactants into the clay may be more important than improving the compatibility between the surfactant and the polymer matrix. Gilman et al.[50] compared the clays modified with dioctadecyl-substituted ammonium and that modified with monooctadecyl-substituted ammonium through melt-blending with polystyrene; the former yields a nanocomposite with an intercalated structure, while the latter gives only a microcomposite. In the case of in-situ polymerization, the increase in the *d* spacing by the organic modification of the clay enables the monomer to penetrate into the gallery space and polymerize, so an increase in the *d* spacing is advantageous for a polymerization process.

Considering the miscibility range between solvent (monomer) and polymer, the calculated maximum solubility difference ($\Delta\delta$) using eq 4 for complete miscibility between the two components is 3.6 $J^{1/2}/cm^{3/2}$, assuming that the degree of polymerization for polymer is 1000, $\Delta\delta$ is 0.2 $J^{1/2}/cm^{3/2}$ for polymer−polymer system, and it increases to 7.1 $J^{1/2}/cm^{3/2}$ for the monomer−monomer system. This calculation suggests that a low molecular weight compound is more miscible than high molecular weight material. The clay is assumed to be a polar compound having a very high solubility parameter. Thus, in the case of low SP polymers, monomer as well as polymer is not compatible with the clay, so even the monomer cannot enter the gallery space if the clay is not organically modified, but the increased *d* spacing obtained by the introduction of surfactants may allow the low SP monomer to enter the gallery space and polymerize, which results in an intercalated morphology. The modification of clay with various surfactants is necessary for the preparation of polymer−clay nanocomposites. However, it is still difficult for low SP polymer to achieve a delaminated morphology, even through in-situ polymerization, probably because only small molecules can enter the gallery space, and the miscibility window in terms of solubility parameter becomes smaller as polymerization proceeds. As the solubility parameter of the polymer increases, the monomer or polymer can enter the gallery space, and finally, a delaminated morphology can be obtained. Therefore, in the preparation of high SP polymer/clay nanocomposites, it may not be necessary to use organically modified clay for in-situ polymerization, but it is common practice to do so.

Although complete compatibility between the long chain of the surfactant and the polymer matrix may be preferable for better dispersion of clay, it appears that the modification of clay by introducing surfactants to obtain better compatibility is less important than the modification of polymer matrix by introducing polar groups. The role of the surfactant is to enlarge the *d* spacing to make room for the monomer or polymer to penetrate into the gallery space during the preparation of polymer/clay nanocomposites.

One must also consider the thermal stability of the surfactant that is used with the clay. The common ammonium-based surfactants begin to undergo thermal degradation by a Hofmann elimination reaction at temperatures close to 200 °C, and this will dramatically change the nature of the surfactant and hence of the putative nanocomposite.

Conclusion

The relationship between the solubility parameter of the polymer and dispersion of clay was examined through the study of model polymers having different solubility parameters and by including previously reported results. By calculating the solubility parameter of polymers and surfactants, polymers were classified and correlated with the dispersion of clay. The increase in *d* spacing of the clay is closely related to the solubility parameter of polymer rather than the surfactant. Since the clay is highly polar, the dispersion of the clay depends on the solubility parameter of polymer. The type of surfactant is less important as long as the introduction of surfactant to the gallery space enlarges the *d* spacing of the clay. The enlarged *d* spacing obtained by introducing surfactants assists the insertion of the monomer into the gallery space during in-situ polymerization and enables the entry of the polymer chain having a high solubility parameter between the clay layers during melt-blending.

Acknowledgment. This work was supported, in part, by the Office of Naval Research under Grant N00014-03-1-0172. We gratefully acknowledge the help of Leszek Utracki, who very patiently taught us about the solubility parameter.

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MA0508909