Study of the Factors Influencing the Exfoliation of an Organically Modified Montmorillonite in Methyl Methacrylate/Poly(methyl methacrylate) Mixtures

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ABSTRACT: The factors that affect the dispersion of exfoliated organically modified montmorillonite in a solution of poly(methyl methacrylate) in methyl methacrylate are explored. Exfoliation of montmorillonite in the solution is achieved with the assistance of ultrasound, and rheological measurements indicate a very significant increase in the viscosity, a dramatic shear thinning behavior, and a finite yield stress, all of which are direct consequences of the exfoliated state of the clay platelets. A number of factors, including the sonication power, clay loading, use of a swelling agent, and moisture content of the modified montmorillonite, are found to influence the exfoliation process. The effect of addition of a range of titanate coupling agents (LICA-01, 12, 38, 44, and 97) on the viscosity of the nanoclay dispersions was investigated. It was found that LICA-44 had the effect of reducing the viscosity of the exfoliated montmorillonite dispersion without apparently influencing the extent of the exfoliation. Molecular modeling, UV–visible and Fourier transform infrared spectrometry were used to investigate the possible reasons for efficacy of this LICA. The LICA appears to act through a combination of steric effects and the presence of certain charges on the organic molecule. The magnitude of the negative charges on elements of the LICA appears to influence its ability to bind to the clay and also its ability to reduce the viscosity of the nanoclay. This article indicates how the apparently conflicting requirements of achieving a highly exfoliated state and also maintaining a viscosity low enough for processing can be effectively addressed. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2614–2626, 2006

Key words: methyl methacrylate; montmorillonite; rheology

INTRODUCTION

Exfoliated dispersions of organically modified clays incorporated into polymer systems can improve their thermal stability,[1,2] change their barrier properties,[3–5] modify their tensile strength,[6,7] and increase their elongation at break.[8] In a previous paper, we reported the use of ultrasound to aid the exfoliation of organically modified montmorillonite (OMMT) in low molar mass poly(propylene glycol).[9] It was shown that in low viscosity media, high shear by itself may not be sufficient to achieve exfoliation. The additional use of ultrasound has been shown to provide an effective route to the dispersion of the OMMT platelets at a nano level.

The creation of dispersions of clay at a nano level, "nanocomposites", can be achieved by dispersion of the exfoliated or intercalated clay platelets in a polymer melt or monomer prior to polymerization. Dispersed in a melt or monomer, exfoliated clay platelets exhibit rheological properties similar to those of other thickening agents.[10] They form a transient structure, which can strongly enhance the viscoelasticity far beyond that of the expected matrix effects alone.[11] In contrast, when the clay is present in a nonexfoliated form, it exhibits a featureless Newtonian fluid behavior.[12] However, the large surface area of an exfoliated OMMT allows yield stress behavior to be observed at low weight fractions of OMMT, indicative of the creation of a structured fluid.[13] For example, studies of montmorillonite clay dispersed in xylene[13] indicate that with the aid of ultrasound it is possible to achieve a highly exfoliated state, as reflected in the loss of the characteristic X-ray scattering peak from the gallery structures. The rheological properties of these dispersions are sensitive to the degree of ultrasonic irradiation and this has been attributed to the extent to which a transient structure is formed in the fluid.

In particular, such behavior has been ascribed to a shift of the normal shear-dependent characteristics of the polymer to lower shear rates as a result of the interaction of the polymer with the clay.[14] However, this explanation is not appropriate for a dispersion in a liquid such as xylene that does not have an inherent shear thinning capability.[13] In our previous paper,[9] the possibility of edge-to-face interactions arising from

electrostatic interactions was proposed. Under the influence of shear, this "house of cards" structure is broken down and the platelets align parallel to the direction of flow, resulting in shear thinning behavior.

In this article, rheological studies on dispersions of an organically modified smectic clay, Cloisite 30B, in a solution of poly(methyl methacrylate) (PMMA) and methyl methacrylate (MMA) are reported. This type of solution is used for thin barrier film formation using a photocuring process. Incorporation of a nano-dispersed clay should, in principle, allow improvement of the gas barrier characteristics of such films, but for this to be achieved, it is essential that the reaction mixture contains clay in a truly exfoliated state, and this creates a pseudonematic state under shear. Accordingly, we prepared these dispersions by ultrasonication. Ultrasound as a method of obtaining a good dispersion of nanoparticles has been used previously,[15,16] and, in particular, has previously been used to disperse smectic clays in MMA.[17] This article attempts to control the rheological properties by influencing the edge-to-face interactions, allowing viscosities appropriate for thin film coating prior to photo-curing.

EXPERIMENTAL

Materials

PMMA (MW, 120,000 g mol^{-1}), MMA (purity, 99%), and laurylmethacrylate (LMA; purity, 96%) were purchased from Aldrich (Gillingham, UK). Cloisite 30B, a mica-type silicate modified with bis(2-hydroxy ethyl) methyl tallow (predominantly C_{18} hydrocarbon), was obtained from Southern Clay Products Inc. (Gonzales, TX). As part of the study, five titanate coupling agents were investigated. The titanates used were provided by Kenrich Petrochemicals Inc. (Bayonne, NJ) and were neopentyl(diallyl)oxy trineodecanonyl titanate (LICA-01), neopentyl(diallyl)oxy tri(dioctyl)phosphato titanate (LICA-12), neopentyl(diallyl)oxy tri(dioctyl)pyro-phosphato titanate (LICA-38), neopentyl(diallyl)oxy tri(N-ethylenediamino) ethyl titanate (LICA-44), and neopentyl-(diallyl)oxy tri(m-amino)phenyl (LICA-97). Solutions of the titanate coupling agents were prepared by dissolving the solid in xylene (purity, 98.5%; Aldrich). Solutions for UV–visible (UV–vis) spectrometry were prepared using propan-2-ol (Fluka, Buchs, Switzerland) as solvent.

Preparation of samples

Solutions were prepared in mass; 5 g of PMMA was dissolved in 45 g of MMA. For certain studies 1.25 and 5 g of LMA were used as part of the monomer component. The LMA was added to explore whether this was able to assist the exfoliation process. The PMMA was dissolved in the MMA by placing the components in a sealed jar in an oven at 50°C for 48 h. The PMMA

was added to the monomer to enhance the viscosity to a level that would aid exfoliation and control the viscosity required for thin film formation. To the base solution, Cloisite 30B was added at concentrations of 3–10% (w/w) to form a series of suspensions. The suspensions containing the Cloisite 30B were produced by adding an appropriate mass of the clay to the monomer–polymer solution and stirring the mixture for 15 min at 200 rpm with a Eurostar IKA-WERKE stirrer. The mixture was sonicated while being mixed, using a Cole-Parmer Ultrasonic Processor CPX 750 with a 1/4 inch tapered titanium sonic probe. The suspension was placed in a small water bath, around which there was running cold water, to cool the solution during sonication. The power output from the sonic probe was measured by observing the temperature rise produced by the probe operating for a fixed period of time when immersed in a known volume of deionized water. The temperature rise observed was typically about 8°C and it was assumed that the density and heat capacity were constant over this temperature interval. The output varied between 7.16 and 26.06 W at a frequency of 20 kHz. For samples containing LMA, the Cloisite was swollen with LMA at 50°C for 24 h prior to addition to the PMMA/MMA solution.

Coupling agents

Two different methods for the addition of the titanate coupling agents were used. Method one involved the prior dissolution of the LICA in MMA. This solution was added to the PMMA/MMA/Cloisite mix after sonication and the fluid was stirred at 200 rpm for 1 min. Method two involved the direct addition of LICA to the PMMA/MMA/Cloisite mix before sonication. Prior to using titanate coupling agents, all glassware was washed with a 3% (w/w) solution of the appropriate LICA in xylene, as recommended by the manufacturer's reference manual.[18] The LICA-97 wash was carried out with a 3% (w/w) solution of LICA-97 in propanol-2-ol, as LICA-97 is insoluble in xylene.

Analytical methods

Rheological measurements

Rheological measurements were performed using a CSL2 500 Carri-Med rheometer (TA Instruments, Leatherhead) operating in cone and plate geometry with a 4-cm, 2° steel cone. The temperature of the plate was held at 25°C for all the measurements. To determine the flow curve of the solutions, the sample under test was carefully placed between the platens, the shear rate was then increased from 0.3 s^{-1} to 1260 s^{-1}, and the shear stresses (and consequently the viscosity profile) were monitored.

To determine the extent of recovery of the viscosity after shearing, the samples were first deformed as mentioned earlier. After the final measurement at 1260 s^{-1}, the measurement cycle was immediately repeated. The solution was then left under quiescent conditions for 10 min before once more performing a set of shear stress measurements using the previously described shear rates. To explore the stability of the dispersions, shear stress was observed after performing a scan from 0.3 s^{-1} to 1260 s^{-1} and the rate was then held constant at 1260 s^{-1} for 5 min and the shear stress monitored.

In a further set of experiments, the shear stress was set at a fixed value (in a suitable range to determine yield stress), and the shear rate (and consequently the viscosity profile) was monitored over a 5- or 10-min period.

UV–vis spectrometry

Spectra for solutions of the various coupling agents in propan-2-ol or MMA were obtained using a Helios-β UV–vis spectrophotometer over the wavelength range of 190–790 nm using a 10-mm quartz cell.

Fourier transform infrared analysis

Infrared spectra of the coupling agents in various MMA/PMMA/Cloisite mixtures were obtained using a Mattson 5000 FTIR spectrometer.

Wide angle X-ray diffraction

Wide angle X-ray diffraction was carried out in the range 0°–50° using a Siemens D500 high-resolution diffractometer with Cu Kα wavelength. The machine was operated at 40 kV and 20 mA. The viscous monomer fluids and the Cloisite 30B powder were placed in a sample holder and their surface was smoothed using a glass microscope slide to provide a smooth surface flush with the sample holder surface.

Molecular modeling

Molecular modeling calculations were performed using a Spartan 5.0 package on a Silicon Graphics computer. Semiempirical PM3 (TM) calculations were used to optimize the geometry, followed by single point energy calculations.

RESULTS AND DISCUSSION

Clay loading

The measured shear stress and calculated viscosity of samples containing 3–10% (w/w) of Cloisite 30B are shown in Figure 1. The stress profile is unusual, in that for most polymer solutions, the shear stress would increase monotonically with shear rate. However, these are suspensions in a polymer solution, and here the stress increases, passes through a maximum, and falls before starting to rise again. This behavior suggests that the structure at high shear rates (platelets approximately aligned with the flow) is different from that at low rates (house of cards). The stress data appear to fall into three distinct regions. The 4, 5, and 6% (w/w) samples have very similar stress profiles, whereas there is a large jump in measured stress between the 6 and the 7% (w/w) sample. This change between 6 and 7% (w/w) Cloisite 30B is further emphasized in Figure 2, which shows that there are two sections of linear increase of viscosity with clay loading: one from 4 to 6% (w/w), then another from 6 to 10% (w/w). A similar trend has been reported in the literature.[19] The origin of this behavior lies not in the degree of exfoliation but rather in the phase structures developed by the exfoliated clay platelets.

That exfoliation of clay platelets in MMA is achievable can be seen in the wide-angle X-ray diffractograms illustrated in Figure 3. The diffractogram for Cloisite 30B shows an intense scattering peak originating from stacked platelets. In contrast, the diffractograms for different loadings of Cloisite 30B in MMA postsonication are relatively featureless, indicating high levels of exfoliation for all the samples. The nature of the dispersion postpolymerization has been characterized by transmission electron microscopy and will be the subject of a future communication.

The clay particles have a high aspect ratio, being ~1 nm thick and of the order of 200–400 nm in length. Below some critical value, the exfoliated platelets will exist in the fluid as essentially noninteracting entities, and their enhancement of the viscosity will essentially be that of a particulate solid and described by the usual Einstein enhancement relationship $\eta = 2.5nv_m$, where n is the number of particles and v_m is the volume occupied by the particle. Strictly, the factor 2.5 is incorrect, as it applies to a spherical particle, but nevertheless, the enhancement in the viscosity for isotropically dispersed platelets will be significantly smaller than when a three-dimensional "house of cards"-like structure is created throughout the fluid. Accordingly, the transitions we see in Figures 1 and 2 essentially represent structural transitions associated with platelet–platelet interactions. The possible phase structure that can be created in such situations has been considered theoretically by Balazs and coworkers.[20–23] The theory indicates that at some critical concentration, which depends on the interaction parameter between the fluid and platelets, order will be created and the isotropic distribution will change to a nematic type of order. This model does not allow for the specific interactions between the platelets that would create the "house of cards" type of structures

(a)

(b)
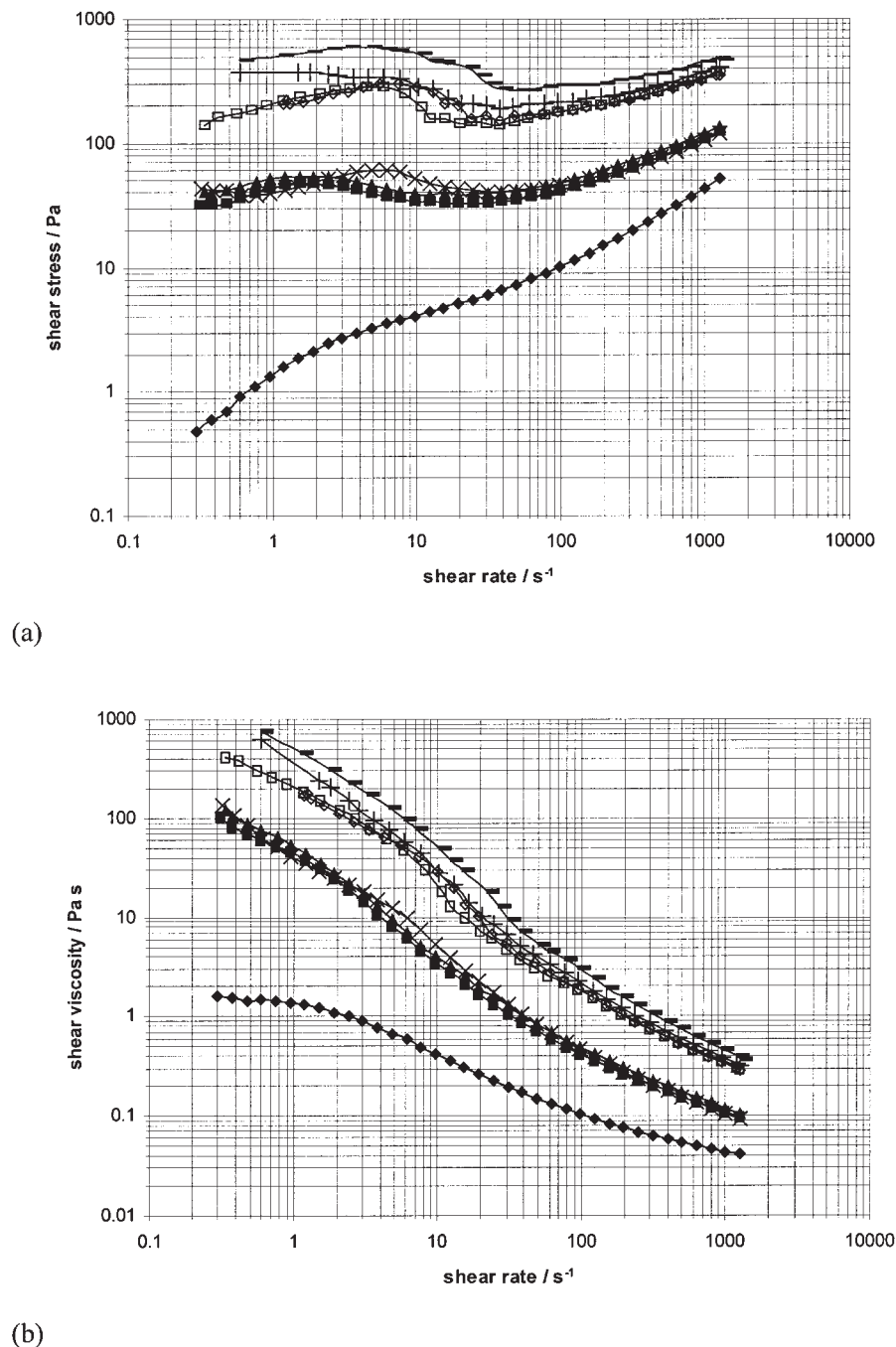
Figure 1 Shear stress (a) and shear viscosity (b) versus shear rate for 10% PMMA/MMA solutions with different Cloisite 30B contents. Key: ◆, 3% (w/w); ■, 4% (w/w); ▲, 5% (w/w); ×, 6% (w/w); □, 7% (w/w); ◇, 8% (w/w); [+], 9% (w/w); [—], 10% (w/w).

associated with the high viscosity at low shear rate and shear thinning behavior. However, the observed dramatic increase in the viscosity is indicative of the creation of a three-dimensional structure, which represents a more interacting phase structure than predicted by theory.[23] The observed similarity of the viscosities for the 4, 5, and 6% (w/w) samples implies that a structure has been created that corresponds to the theoretical predictions of a nematic phase. The

increased viscosities observed for the 7–10% (w/w) samples would then correspond to a smectic A or columnar phase that represents a more ordered structure.

The viscosity versus shear rate curves in Figure 1(b) exhibit a distinctive "kink" for concentrations greater than 4% (w/w) and this can be associated with the dynamic break-up of the house of cards structure. As the percentage Cloisite increases, the shear rate at
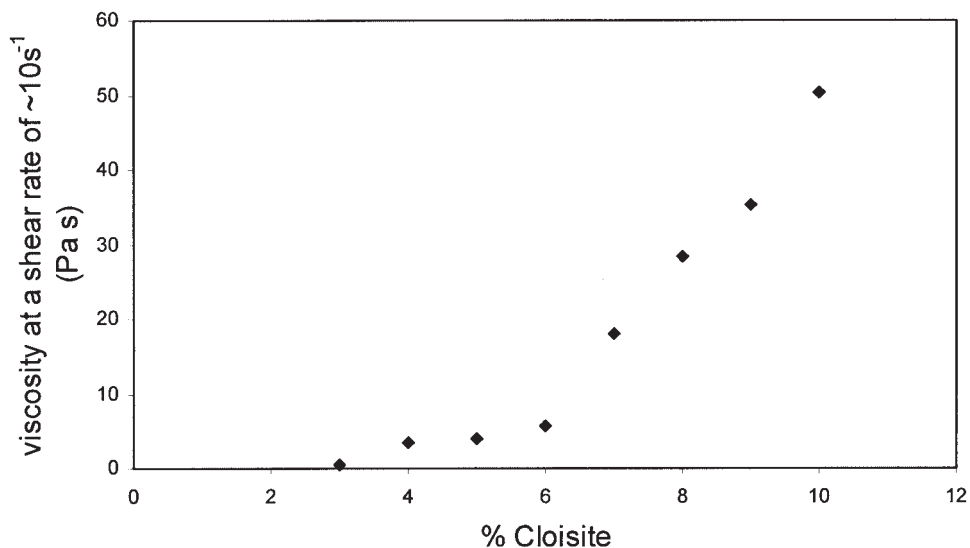
Figure 2   Viscosity at 10 s^{-1} of 10% PMMA/MMA solutions containing Cloisite 30B as a function of Cloisite content (mass %).

which this kink appears increases. This would be consistent with an increased number of interactions and the influence of the phase structure on the possible relative alignment of the platelets. The 4, 5, and 6% (w/w) Cloisite samples show the kink at a shear rate of ~4 s^{-1}. By 10% (w/w) Cloisite, the kink has shifted to a shear rate of ~16 s^{-1}. Also, the kink appears to be less pronounced in the 10% (w/w) Cloisite sample. The kink can be attributed to a dynamic yield process, consistent with the breaking of platelet–platelet contacts and the creation of a more perfectly aligned structure in the fluid. The value of the viscosity will, however, reflect the creation of the longer range order,

consistent with the phase diagrams that have been proposed by Balazs and coworkers.[20–23]

The yield stress associated with the break-up of the initial structure has been determined as follows. For each concentration of interest, the suspension was sheared at a fixed shear stress for 5 min (or sometimes 10 min), to give a typical deformation curve as seen in Figure 4(a). Initial viscosity values are high, but after a certain period of time (dependent upon the shear stress set), the viscosity falls dramatically as the initial structure collapses. The time at which this occurs can be found from the point of inflection in the given curve. This was determined as the critical time for that
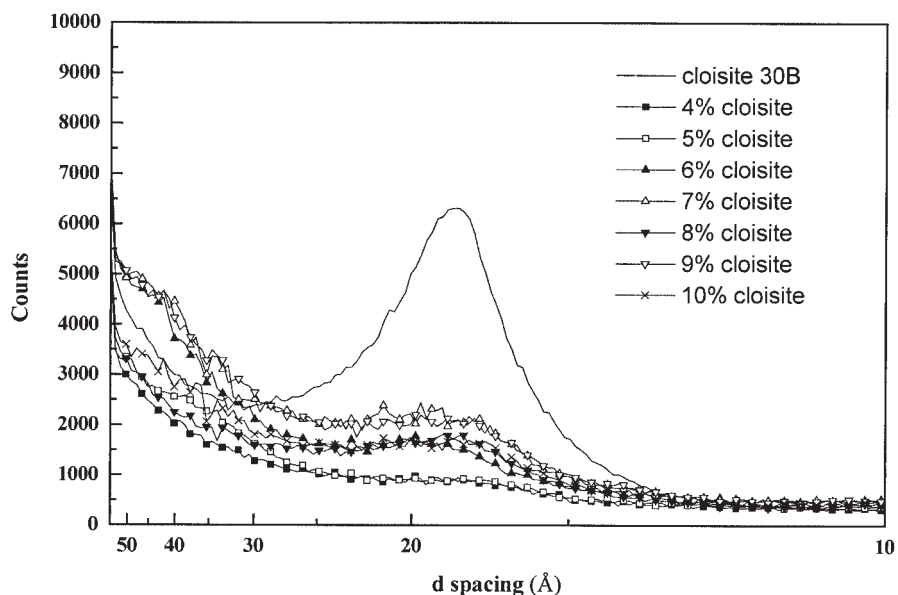

Figure 3   Wide-angle X-ray diffractograms for sonicated dispersions of Cloisite 30B in MMA. The diffractogram for Cloisite 30B is shown for comparison.
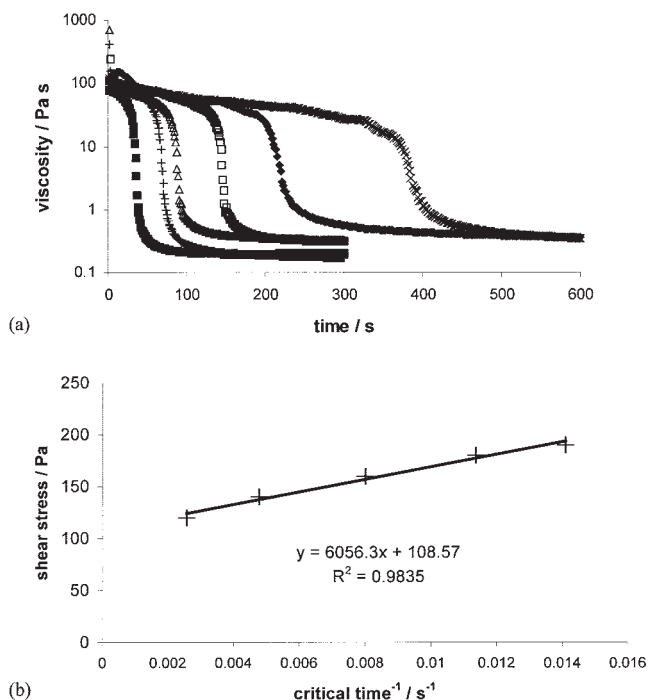
Figure 4 10% PMMA/MMA solution with 6% Cloisite 30B. (a) Viscosity versus time of shearing. Key: ✕, 120 Pa; ◆, 140 Pa; □, 160 Pa; △, 180 Pa; [+], 190 Pa; ●, 200 Pa. (b) Set shear stress versus the reciprocal of the critical time at that stress. The trend line is indicated, and the value of the stress at $x = 0$ is designated as the yield stress for that concentration.

stress. The stress was then plotted as a function of the reciprocal of this critical time in Figure 4(b). By extrapolating back to the y-axis ($x = 0$), we can determine the stress at which the critical time is infinite. This is designated as the yield stress. The value of the yield stress for the range of concentrations is shown in Figure 5. Once again, we see distinct regions.
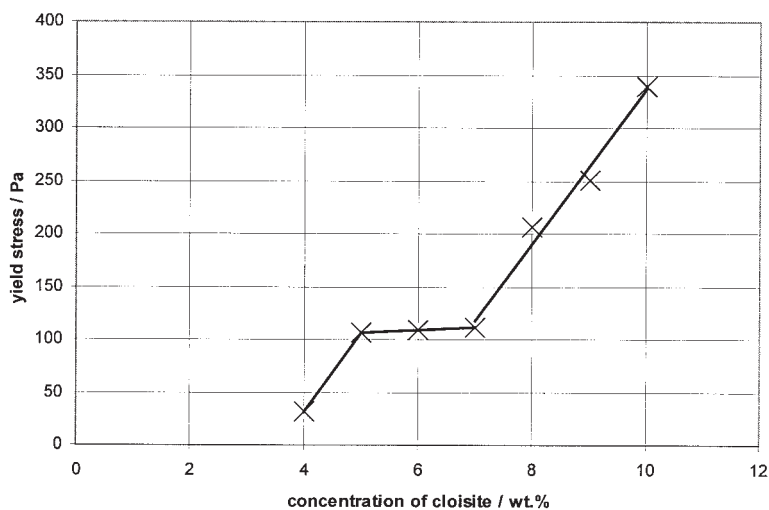
A study was undertaken on the reproducibility of the shear rate measurements and the data are shown in Figure 6. The repeat measurement after obtaining the initial trace indicates that the interactions destroyed by the initial shear of the suspension are not immediately recovered, and lower values of the viscosities are observed in both cases. For the 4% (w/w) Cloisite suspension, the loss is very dramatic and indicates that the interaction between the platelets in the high shear aligned state is significantly less than in the presheared suspension. A similar situation is observed for the 9% (w/w) mixture. Leaving the mixture to stand for a period of 10 min allows randomization of the platelets to occur and for the 4% (w/w) Cloisite mixture it is clear that there is a regrowth of the initial random structure, evidenced by the increase in the viscosity at low shear rate. For the 9% (w/w) dispersion, the change after 10 min is significantly smaller than for the 4% (w/w) dispersion and this is consistent with the concept of the process being that of a relaxation in induced order. The higher the viscosity, the slower the relaxation process, and hence the 4% (w/w) would be expected to be more effective at rebuilding structure than the more viscous 9% (w/w) mixture.

A study was undertaken on the effect of holding the shear rate constant on the structure generated under shear and the results are shown in Figure 7. The suspension was first sheared from 0.3 s^{-1} to 1260 s^{-1} and then held at a constant shear rate of 1260 s^{-1} for 5 min while the shear stress was monitored. The shear stress remains fairly constant, but it is noticeable that the value for the 10% (w/w) mixture is significantly lower than that for the lower concentrations. In terms of the phase diagram it would be expected that the platelet structure would be approaching the nematic to smectic or columnar boundary[21–23] and the latter would allow some reagglomeration of the platelets, resulting in a decrease in stress.
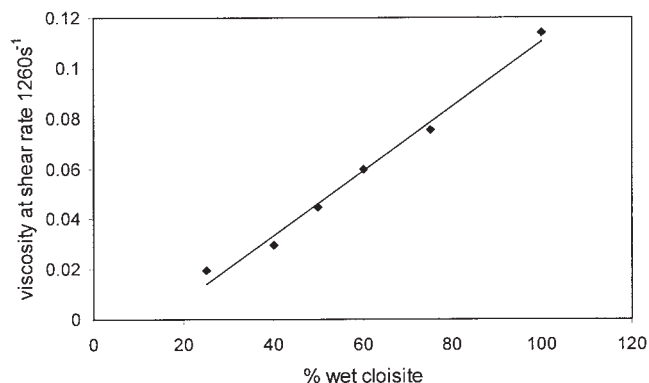

**Figure 5** The calculated yield stress as a function of Cloisite concentration.

(a)
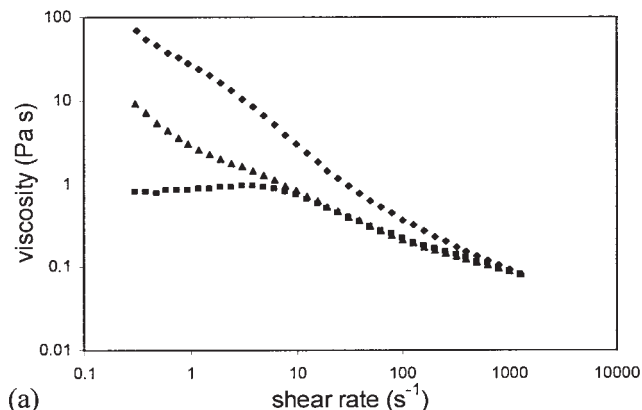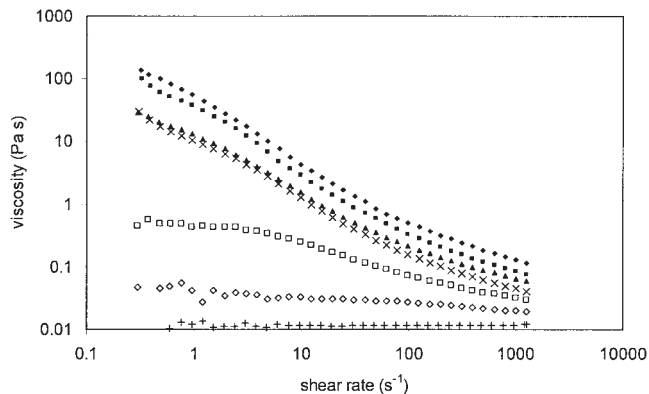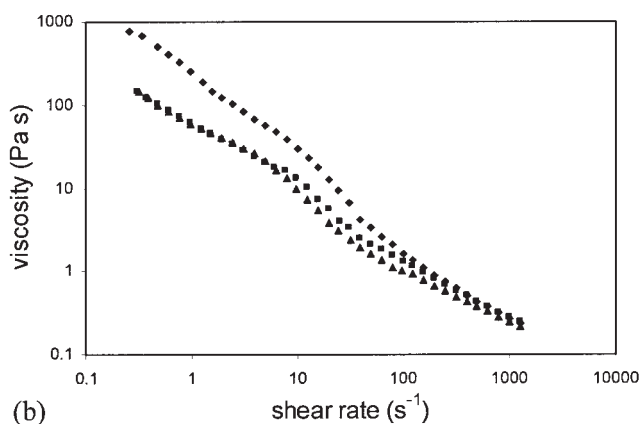
(b)

Figure 6 Viscosity versus shear rate for 10% (w/w) PMMA/MMA solution with (a) 4% (w/w) Cloisite 30B, and (b) 9% (w/w) Cloisite 30B. Key: ♦, fresh sample; ■, immediate repeat experiment after shear measurement; ▲, measurement after waiting for 10 min.

Effect of moisture content on the exfoliation process

The role of the moisture content of the Cloisite on the exfoliation process was investigated. A sample of
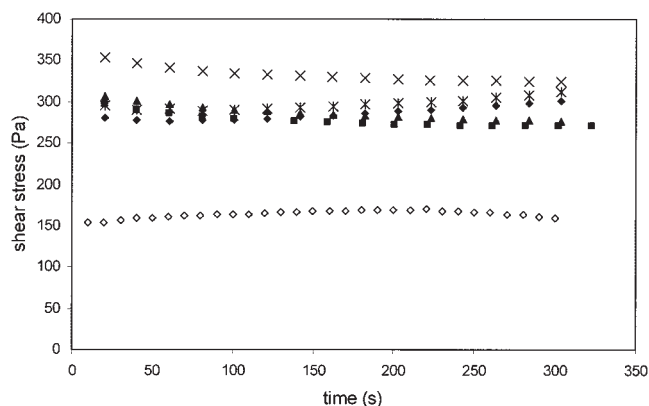
Figure 7 Shear stress (at 1260 s^{-1}) versus time for samples of 10% (w/w) PMMA/MMA solutions with different Cloisite 30B contents. Key: ♦, 5% (w/w); ■, 6% (w/w); ▲, 7% (w/w); ×, 8% (w/w); *, 9% (w/w); ◇, 10% (w/w).

(a)

(b)

Figure 8 (a) Viscosity versus shear rate for 10% (w/w) PMMA/MMA solutions containing 5% (w/w) of Cloisite 30B with varying mixtures of wet and dry clay. Key: ♦, 100% wet; ■, 75% wet, 25% dry; ▲, 60% wet, 40% dry; ×, 50% wet, 50% dry; □, 40% wet, 60% dry; ◇, 25% wet, 75% dry; [+] 100% dry. (b) Viscosity at a shear rate of 1260 s^{-1} versus percentage wet Cloisite 30B.

Cloisite 30B was dried in an open crucible at 105°C for 24 h and the mass was observed to decrease by 2.0%, in agreement with previous reports.[24] Figure 8(a) shows the shear thinning behavior for samples containing various percentages of wet and dry clay. There appears to be a threshold moisture content of the clay that is necessary for exfoliation and, for Cloisite 30B in the mixtures used in this study, it appears to be 50% of wet clay. At a shear rate of 1260 s^{-1}, the viscosity increases linearly with increase in moisture content [Fig. 8(b)]. This observation implies that the ultrasonic waves are able to couple with the water hydrating sites on the surface of the clay platelets, thus aiding the exfoliation process. The ability of ultrasound to strip the water of hydration from cations is well documented[25,26] and provides a mechanism whereby energy can be specifically absorbed to create desorbed water molecules, which will be able to assist in the exfoliation process.
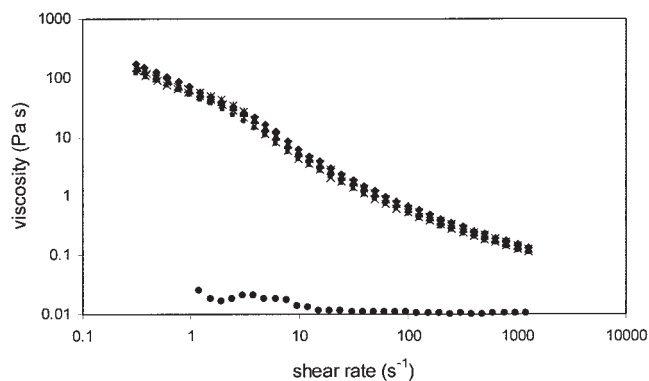
Figure 9 Viscosity versus shear rate for 10% (w/w) PMMA/MMA solution containing 5% (w/w) Cloisite 30B and various LMA contents. Key: ♦, 0% (w/w) LMA; ■, 2.5% (w/w) LMA; ▲, 3% (w/w) LMA; ×, 4% (w/w) LMA; *, 5% (w/w) LMA; ●, no LMA and no Cloisite.

### Laurylmethacrylate as an aid to exfoliation and effects of sonication power

LMA has been used to aid exfoliation of clay platelets within a polymer matrix.[27] It is thought that the LMA can penetrate the intergallery spacing, pushing the clay platelets apart, thus aiding exfoliation. Dietsche et al.[27] attribute the ability of LMA to penetrate the intergallery spacing to its greater compatibility with the organic modifier on the clay. The effect of LMA on exfoliation with 5% (w/w) Cloisite 30B and 26.06 W sonication power is shown in Figure 9. It is clear that LMA is not required to achieve exfoliation, as all the samples demonstrated high viscosity at low shear rate and significant shear thinning, indicative of successful exfoliation. There was little difference between the dispersion that contained the LMA and those that did not. In a previous paper,[9] it had been noted that the sonication power level appeared to have an effect on the degree of exfoliation. Using different sonication power levels, mixtures containing 5% (w/w) of Cloisite 30B were investigated (Fig. 10). The high initial viscosities of the samples prepared using 14.24, 17.66, and 26.06 W show that these samples are extensively exfoliated, whereas the sample prepared using 7.16 W has a much lower viscosity and less pronounced shear thinning. The latter sample is clearly only partially exfoliated, implying that there is a threshold value of sonication power for optimum dispersion. The data in Figure 9 suggest that LMA is not necessary for exfoliation; however, these observations were made at the maximum sonication power. It was, however, thought that LMA might allow exfoliation at lower sonication powers, that is, below the power threshold observed in Figure 10. Figure 11 shows the rheological behavior of samples produced with and without LMA and at different sonication power levels. Surprisingly, and in contrast to the previous reports,[27] the presence of LMA appeared to hinder exfoliation.

Only at the highest sonication power did the mixtures with LMA demonstrate exfoliation. It is possible that the lower viscosity of the LMA samples is due to the LMA acting as a viscosity modifier.[27] However, viscosity measurements on MMA solutions containing PMMA and LMA but no Cloisite discounted this theory. It is more likely that LMA is penetrating the platelet gallery and is actually stabilizing the intercalated form and thereby hindering full exfoliation.

Coupling agents

Ginzburg and Balazs[21] have proposed that, to achieve a locally uniform structure, effective long-range interactions between the clay particles should be made as neutral as possible. The creation of the house of cards long range interactions are probably a consequence of short range electrostatic interactions between positive charges, which are located on the edges of the platelets, and the negative charged sites, which are distributed across the surface of the platelets, and are decorated by the organic long chain length quaternary ammonium ions.[28] In an attempt to mask the edge charges, it was proposed to add titanate coupling agents to the mixtures. These molecules can be selectively adsorbed to specific sites on the clay platelets. The proposition was that these might selectively bind to the edge sites and hence inhibit the electrostatic interactions that create the long-range interactions. A consequence of this blocking effect would be a reduction in the viscosity of the mixture by inhibiting the creation of the house of cards structure.

Titanate coupling agents are known to influence the physical properties of conventional composite materials,[29–32] and have been used in the formation of polymer–clay nanocomposites,[33] but they have not been used with polymer–clay nanocomposites in the man-
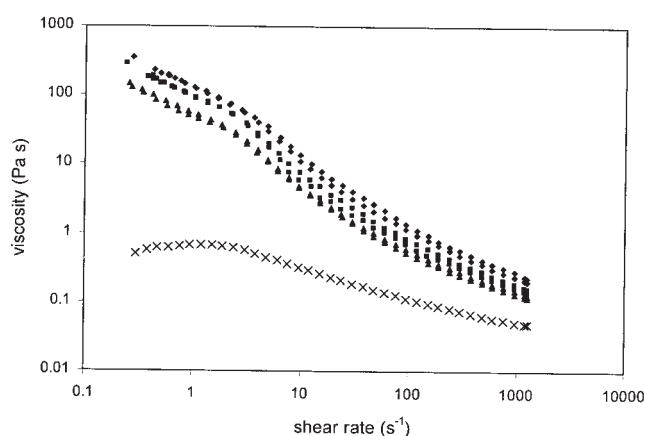
Figure 10 Viscosity versus shear rate for 10% (w/w) PMMA/MMA solution containing 5% (w/w) Cloisite 30B sonicated at different power levels. Key: ♦, 26.06 W; ■, 17.66 W; ▲, 14.24 W; ×, 7.16 W.
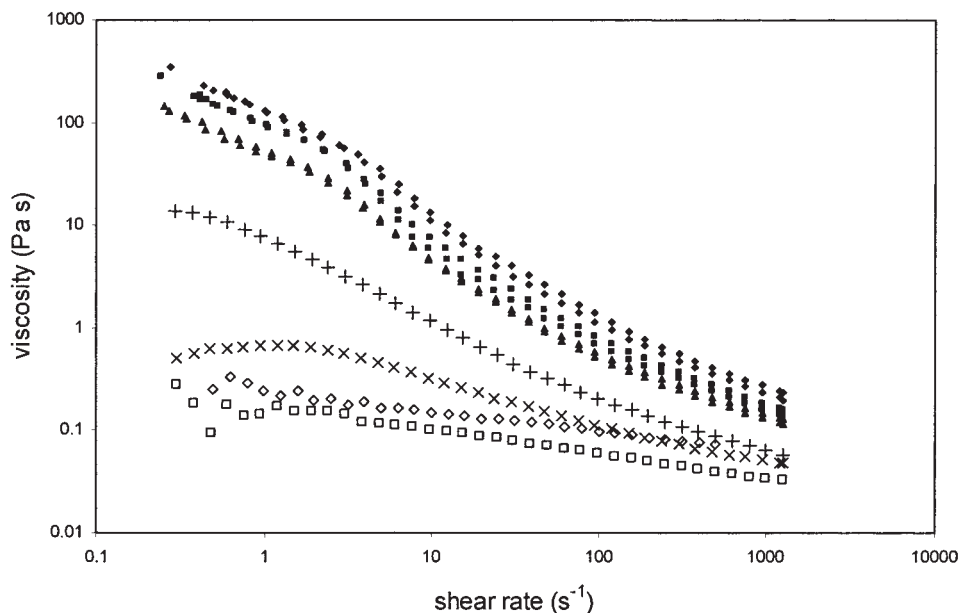
Figure 11 Viscosity versus shear rate for 10% (w/w) PMMA/MMA solution containing 5% (w/w) Cloisite 30B sonicated at different power levels [S] and LMA additions [LMA]. Key: ♦, 26.06 W [S], 0% (w/w) LMA; ■, 17.66 W [S], 0% (w/w) LMA; ▲, 14.24 W [S], 0% (w/w) LMA; ×, 7.16 W [S], 0% (w/w) –LMA; ◇, 7.16 W [S], 10% (w/w) LMA; □, 17.66 W [S], 10% (w/w) LMA; [+], 26.06 W [S], 10% (w/w) LMA.

ner suggested here. Silane coupling agents have been used to improve properties in polymer–clay nano-composites[34,35] but are assumed to modify the surface of the Cloisite rather than undergoing specific interactions with the charged sites. A series of titanate compounds were obtained, the structures of which are shown in Figure 12, and the effect on the rheological properties of these suspensions were investigated. About 1–2% (w/w) of the LICAs in relation to the total added Cloisite 30B was added to the PMMA/MMA solution. Addition after sonication was to demonstrate that any lowering in the viscosity was not due to the coupling agents interfering with exfoliation, which would result in spurious low viscosity data. Figure 13 demonstrates that only LICA-44 appears to be working as a coupling agent, reducing the initial viscosity from over 200 Pa s to below 20 Pa s. The lack of effect of LICA-97 may be due to a lack of solubility of this LICA in the mixture.

During the preparation of some of the LICA samples, strong color formation was observed upon addition of MMA. Colors of the LICA/MMA solutions ranged from a light yellow for LICA-44, to orange/red for LICA-38. A slight yellow color is obtained for all the LICAs upon dissolution in other solvents such as xylene and represents the intrinsic color of the LICAs. However, upon addition to MMA, LICA-01, 12, and 38 displayed a distinct bathochromic shift. This observation would suggest that a colored complex could be formed between the LICAs and MMA that would reduce their ability to interact with the clay platelets

and in part explains the lack of viscosity modification effect observed in the rheological data.

UV–vis spectrometry

To investigate the possibility of complex formation between the LICA and MMA, the UV–vis spectra of solutions of the LICA in MMA were measured (Fig. 14). No additional features were observed in the visible region for the MMA; however, a peak was observed between 390 and 490 nm for the LICA-38/MMA solution. The intensity and wavelength of the peaks alter slightly depending on the coupling agent, but it is clear that LICA-01, 12, and 38 solutions demonstrate the extra peak not present in the neat solutions. The appearance of this extra peak in the UV–vis spectra of the LICA/MMA solutions supports the theory that some form of complex is forming. The LICA-44/MMA solution did not show this extra peak.

FTIR

If a complex is being formed between the titanate coupling agents and MMA, it is likely to involve interactions with the carbonyl group of the MMA. FTIR spectra were measured for solutions of the LICA in MMA. There were no shifts in the carbonyl peak for any of the LICA-01 mixtures. The LICA-12 and LICA-38 solutions display a small shift in the carbonyl peak, for the samples containing Cloisite 30B. However, these cannot be attributed to the presence of
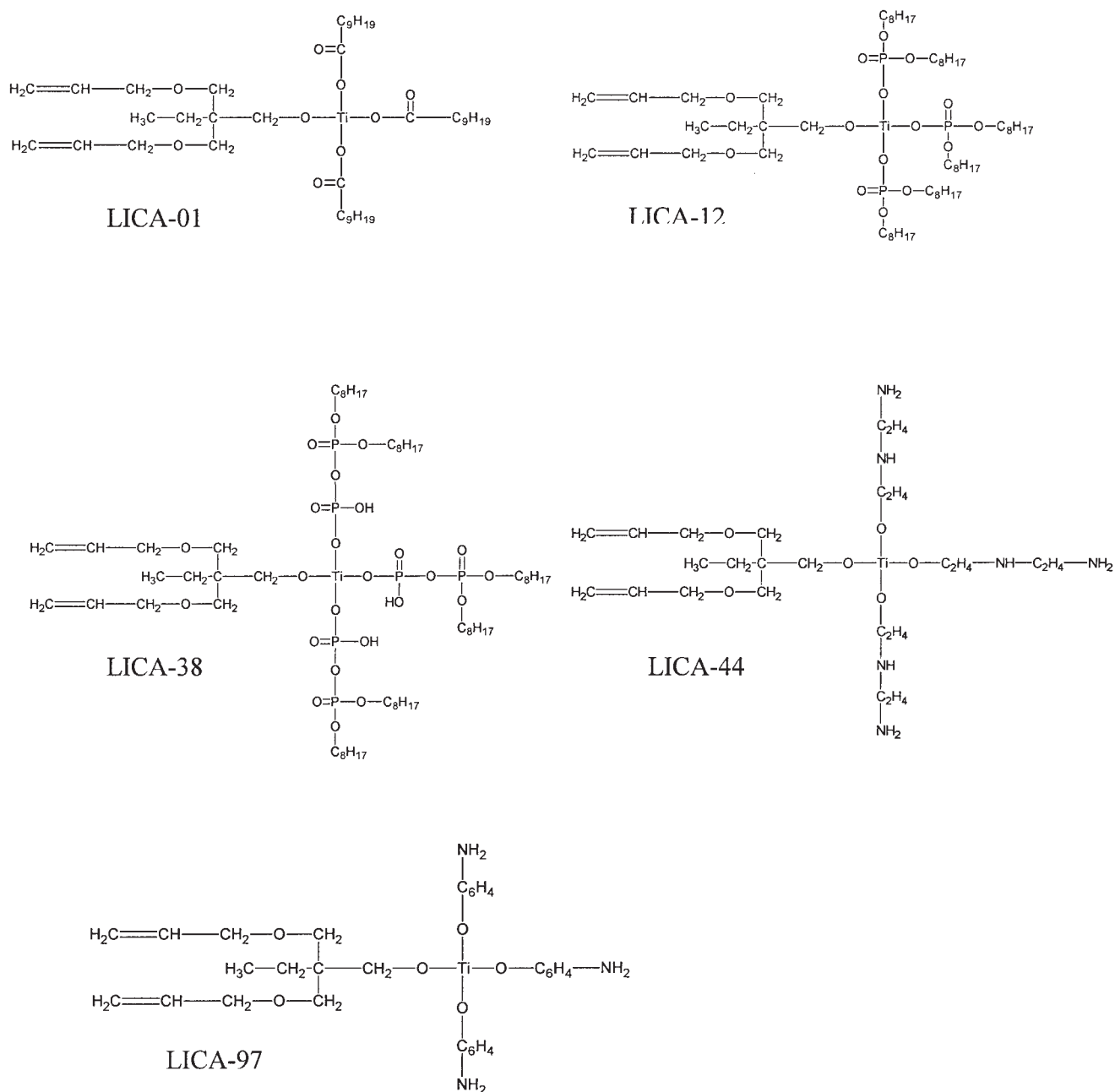
Figure 12 Structures of the LICA compounds used in this study.

LICA, as they also occur when LICA is absent. The LICA-44 and LICA-97 samples do, however, exhibit shifts in the carbonyl peak in the absence of Cloisite. The LICA-01, LICA-12, and LICA-38 solutions had shown the extra peaks in the UV–vis spectra, implying the formation of a colored complex, which had been assumed to also involve carbonyl interactions.

Molecular modeling

In an attempt to understand the spectroscopic and rheological data, molecular modeling was carried out

on the LICA compounds, and the charge densities are displayed in Figure 15. It is assumed that the complexation with the Cloisite 30B involves the ligands attached to the titanium atom coordinating with the edges of the clay platelets. The precise structure of the end sites is unknown but is known to have the ability to become charged and is usually assumed to be a positive site. Inspection of the cross-sectional structure of the clay platelet indicates that it is a layered structure of silica–alumina–silica. If the central alumina layer were missing at certain sites, this would leave a cavity with the ability to bond positively charged spe-
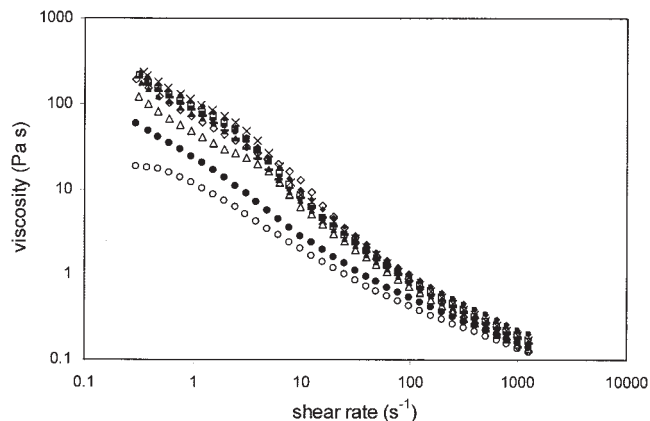
Figure 13 Viscosity versus shear rate for 10% PMMA/MMA mixtures containing 5% (w/w) Cloisite 30B and 1–2% (w/w) LICA. Key: ■, 1% LICA-01; □, 2% LICA-01; ♦, 1% LICA-12; ◇, 2% LICA-12; ▲, 1% LICA 38; △, 2% LICA-38; ●, 1% LICA-44; ○, 2% LICA-44; [–], 2% LICA-97; ×, no LICA.

cies such as the sodium ions that are present naturally in clay. Alternatively, an extra aluminum atom would also leave the edge with a positive charge. In the former case, displacement of the sodium and replacement by a coordinated cation can effectively block the site. In the latter case, addition of a species that can balance the positive charge would reduce its effect. Titanate compounds have this potential. The charges on the titanium atom and the surrounding oxygen atoms are very similar for LICA-01, LICA-44, and LICA-97. The LICA-12 and LICA-38 structures have titanium atoms that are slightly more positive and the surrounding oxygen atoms are more negative than those in the corresponding LICA-01, LICA-44, and LICA-97. The higher charge density on the atoms of LICA-12 and LICA-38 would imply that stronger interactions would be possible with the sites on the clay particles; however, this does not agree with the observed viscosity data. It is possible that the higher charges result in stronger complex formation with MMA, leaving these LICAs unable to interact with the sites on the platelets. However, if this were the case, only LICA-12 and LICA-38 would be expected to form strong complexes, whereas the UV–vis spectrometry data suggested that LICA-01 also forms a complex.

The coupling agents are proposed to work by interacting with and hence shielding the end charges of the clay platelets. Montmorillonite clay platelets are alumina sheets sandwiched between two silica sheets. The end charge could be the result of an end aluminum not being fully co-ordinated (i.e., having an empty co-ordination site) and the charge on the end of the platelet will be positive. Hence, a negative charge is desired to co-ordinate with the edge sites. LICA-97 has $\delta+$ terminal nitrogen atoms, and would not be expected to work as a coupling agent. This agrees with the viscosity data, as LICA-97 did not lower the vis-

cosity of the mixtures with Cloisite 30B. LICA-01, LICA-12, LICA-38, and LICA-44 all contain atoms with $\delta-$ charge densities (Fig. 15). However, they do not all work as coupling agents and there must be another factor influencing whether or not they can act as coupling agents. For these titanium compounds, the ability to bring the charged sites into close contact with the receptor sites may be a controlling factor and reflect a steric contribution to the complex formation. LICA-01, LICA-12, and LICA-38 have $\delta-$ oxygen atoms, but they also contain large bulky alkyl groups, which will render the $\delta-$ oxygen atoms sterically unavailable. LICA-44 has two $\delta-$ nitrogen atoms on each flexible branch, each probably available for co-ordination. The LICA-44 also has the smallest positive charge, which will, if isomorphous substitution is a factor, lead to a net reduction of the overall positive charge on the edge sites. There is probably more than one type of co-ordinating site on the platelet, and it is possible that the coupling agent may be more effective if it can co-ordinate with more than one site. Of the molecules studied, it would appear that LICA-44 best fits the criteria for blocking the edge sites and is the only compound to reduce the viscosity of the mixtures.

CONCLUSIONS

The rheological measurements indicate that a number of factors influence the exfoliation of Cloisite 30B within the PMMA/MMA mixtures. There appears to be a threshold sonication power, moisture content, and clay loading below which exfoliation was not achieved. LMA was used as a swelling agent to aid exfoliation but was found to have the reverse effect. The titanate coupling agents were found to be relatively ineffective at altering the viscosity of the mix-
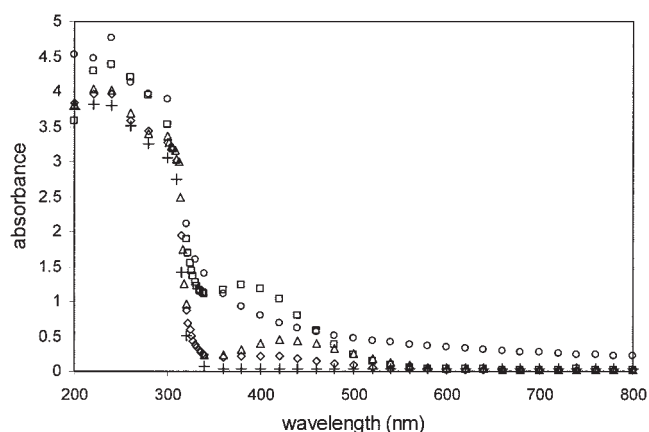
Figure 14 Absorbance versus wavelength for different LICAs in MMA. Key: [+], MMA; □, LICA-01 + MMA; ◇, LICA-12 + MMA; △, LICA-38 + MMA; ○, LICA-44 + MMA.
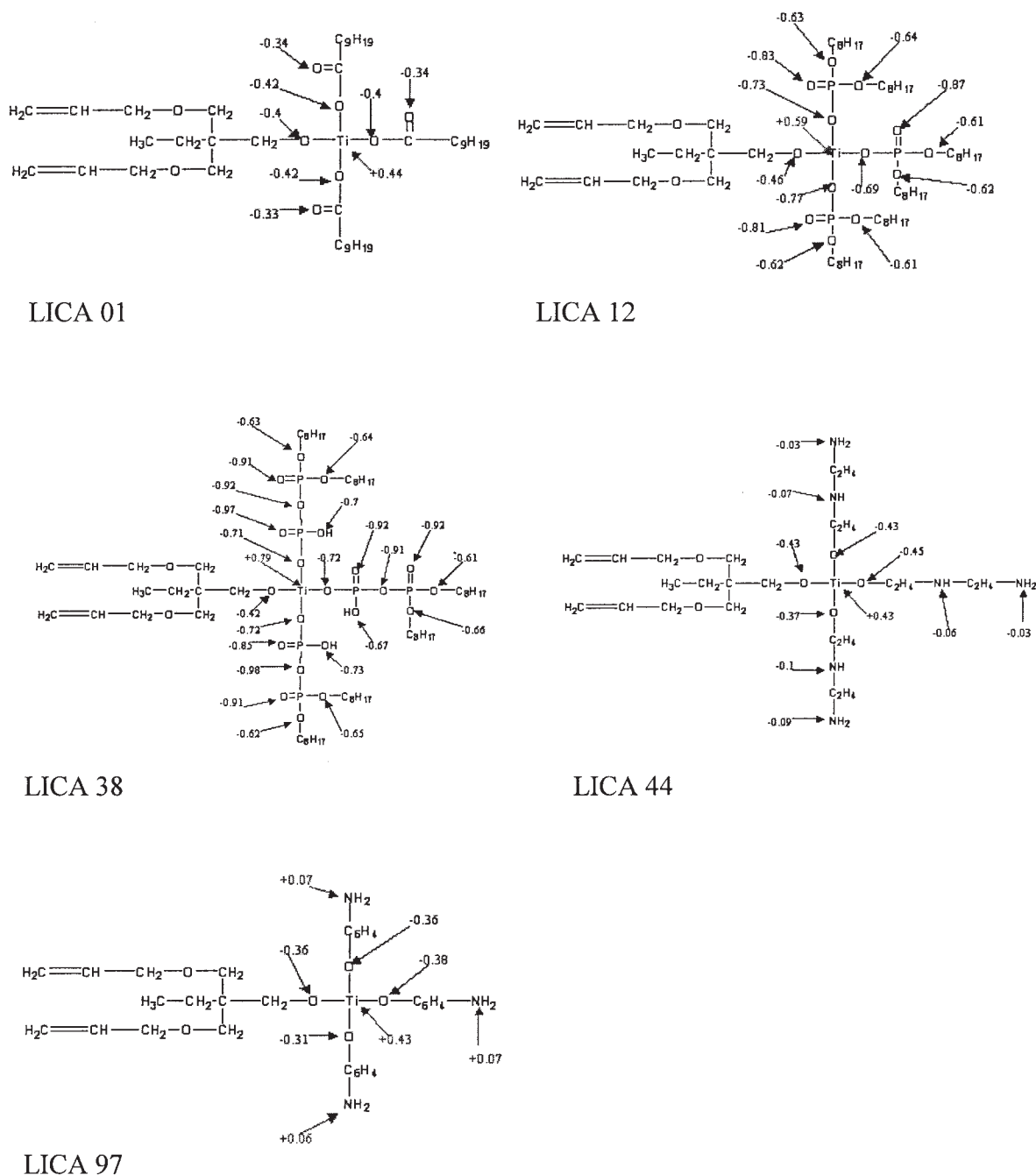
Figure 15 Calculated charge densities for the LICA coupling agents.

tures with the exception of LICA-44. Molecular modeling suggests that charge density and steric availability appear to have the greatest influence as to whether a titanate coupling agent is effective in blocking the edge sites on the clay particles. Blocking the edge sites reduces the possibility of the creation of the house of cards structure in solution and the effects of the associated yield stress behavior. This article indicates the importance of understanding how these factors influence exfoliation if a nanocomposite is to be produced with the desired topography.

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