Temperature Dependent Intercalation and Self-Exfoliation of Clay/Polymer Nanocomposite

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Abstract

The temperature dependence of structural development in a self-exfoliating nanocomposite system has been studied utilizing time resolved small angle x-ray scattering (SAXS) and time resolved mechanical spectroscopy (TRMS) employing small amplitude oscillatory shear (SAOS). This system consists of a montmorillonite organoclay and end-functionalized polybutadiene. Self-exfoliation refers to a system where a layered component, in this case clay, breaks into individual sheets randomly distributed throughout the matrix without any shear, sonication, or other external input. With SAOS, a maximum rate of modulus growth was found at intermediate temperatures. With SAXS complete exfoliation was found to occur fastest at intermediate temperatures. A comparison between SAXS and SAOS showed that the early rapid change in rheological properties corresponds to the expansion of the clay stacks and intercalation. Alternative exfoliation mechanisms are hypothesized to fully explain the new SAOS and SAXS findings along with several other inconsistencies with this system's previously proposed mechanism.

Keywords: physical gel; clay-polymer composite; exfoliation

Introduction

For nanocomposites of clay in polymer, longstanding problems include the lack of exfoliation of the clay particles into individual sheets, the distribution of clay sheets throughout the polymer, and the randomization of the clay orientation. Such exfoliation is desirable since property enhancements are generally most pronounced when exfoliation is complete. A single clay sheet, also called a leaf, is composed of a predominantly aluminum core with a layer composed of silicon, hydrogen, and oxygen on both faces. This study concerns self-exfoliation, which does not require any external energy input, i.e., exfoliation occurs without intense shearing or sonication. Random orientation of clay sheets is beneficial to mechanical and transport properties for certain applications. Nanocomposites can achieve advantageous properties such as increased heat resistance, low gas permeability, favorable mechanical properties over pure polymer components, increased electrical conductivity, and reduced mass compared to conventionally filled polymers [1-11].

This study focuses on nanocomposites with exfoliated silicates, in this case montmorillonite, as the reinforcing component of a polymer. The clay is not commonly incorporated as found in nature, where sodium counterions, Na^+ , neutralize external and internal surface charges and make the clay hydrophilic and immiscible to most polymers [8,12]. Instead, compatibility with polar polymers is achieved by modifying the clay surfaces with polymeric counterions such as aliphatic amines or alkyl phosphonium. Such “organo-clay” potentially can disperse in a polar polymer matrix to form a nanocomposite. Several exfoliation techniques have been developed to separate the organo-clay particles into individual clay leaves. These techniques include: in situ intercalative polymerization [13-15], emulsion polymerization [16,17], sol-gel template synthesis [18,19], and melt compounding [20-23].

The breakup of clay stacks into individual sheets has often been augmented by shearing the clay/polymer mixture, for instance in a twin-screw extruder [8,24-27]. The stress aids the breaking of clay aggregates into particles, the breaking of particles into thin tactoids, and finally the separation of individual sheets from the tactoids. The flexibility of clay sheets and the extra spacing that the diffused polymer chains create facilitate the separation of individual clay sheets from their clay stack. Organic

counter ions are used to increase the gallery spacing and lower the energy required to further separate the stacks into clay sheets [28].

In an alternative approach, which is the focus of this study, Sun and co-workers discovered that suitably end-functionalized (“sticky”) macromolecules exfoliate organo-clay without shearing or sonication and thus can create a nanocomposite with randomly oriented clay sheets [29]. The final exfoliated nanocomposite was reported to be a soft physical gel of polymer-decorated clay sheets and bridge molecules between neighboring clay sheets. Sun achieved this self-exfoliation using carboxyl-terminated polybutadiene (CTPB) or hydroxyl-terminated polybutadiene (HTPB). Such end-functionalization makes the macromolecules “sticky” (capable of bonding) to the clay surface. The attraction between the chain ends and the clay is most likely the result of hydrogen bonding between the carboxylic acid or hydroxyl end groups and the clay surface. Montmorillonite sheet surfaces are known to have hydrogen-bonding sites [30]. The organo-clay was synthesized by substituting the naturally occurring Na^+ counterions on the clay surface with macro-counterions that have either one or two alkane tails, octadecyltrimethyl ammonium or (di)octadecyldimethyl-ammonium (commercial names are DK1 and DK4, respectively). The degree of exfoliation in these nanocomposites depends on clay concentration and sample temperature, but also on the number of alkyl tails on the clay modifier [31,32].

Unclear is the underlying mechanism that causes the rapid self-exfoliation. The initial and final states are known but the path between them is not definitively known. The graphical abstract shows a decrease in internal energy from the initial state, which is clay stacks in polymer, to the final state, which is fully exfoliated clay in a polymer matrix. The details of the stages of exfoliation and their associated energy barriers are covered in more detail in the discussion section where the results of this study are used to formulate a mechanism consistent with all observations.

Variations in experimental conditions have been used to gain further insight. Surprising is that the self-exfoliation happens so fast. At suitable temperatures a nearly complete exfoliation was found to occur within minutes while full exfoliation required about two hours [33]. In a range of experiments it became clear that, without the sticky end groups on the polymer, no exfoliation occurs despite the

compatibility of the polybutadiene with the macro-counterions on the clay surface [29,31-34]. Even intensive shear would not lead to exfoliation of the non-sticky system [35]. Surprisingly, a blend of functionalized and non-functionalized polybutadiene was found to exfoliate the fastest [34]. Larger counterions (two alkane tails instead of one) on the clay surface accelerate the exfoliation process but weaken the network connectivity (lower modulus) [32]. These observations need to be explained by a meaningful model for the exfoliation process.

Classical, purely diffusive exfoliation models assume that the polymer molecules diffuse into galleries between the clay sheets (“intercalate”) and eventually separate the clay sheets so that the clay sheets loose alignment, randomly orient, and distribute throughout the polymer matrix. The diffusion model attributes the exfoliation process primarily to the intercalation and swelling of stacks by internal pushing [29,33,36]. However, there appear to be some inconsistencies with this model when applied to the exfoliation process of Sun. Unmodified polybutadiene is compatible with the organic counterion yet, when used alone, no exfoliation occurs. This suggests that compatibility with the clay surface is also needed. However, pure diffusion should only require compatibility with the alkyl tails of the organic counterions inside the galleries, unless it is also governed by surface diffusion. Also inconsistent with the diffusion model is the observation that unmodified polybutadiene does not exfoliate while a blend of modified and unmodified polybutadiene exfoliated the clay at the highest rate [34]. The two diffusion coefficients should not interact in a way that would result in an effective diffusion coefficient that exceeds each of the individual diffusion coefficients. These inconsistencies and the search for a more plausible exfoliation mechanism motivate the experiments of this study as they suggest the mechanism may involve more than simple diffusion.

Previously proposed alternative mechanisms are also problematic. The model of Balazs et al. predicts an intercalated final state with telechelic polymers gluing the sheets together due to the high affinity of the end groups for the clay surface [36]. Yet the final observed state was fully exfoliated and no longer intercalated. The model of Sinsawat et al. results in similar difficulty with the end result being glued sheets [9].

Rheologically, clay/polymer nanocomposites can be viewed as physical gels during exfoliation [36]. It has been hypothesized that end-functionalized bridge molecules tie randomly oriented clay sheets into a sample-spanning network of increasing connectivity, which would explain the sharply increased modulus and yield stress. In this way, rheology is a sensitive indicator of the evolving exfoliation and the increasing accessible internal surface area of the clay [31].

The structural ripening of DK1 in CTPB can best be observed through time-resolved rheology [37]. Dynamic mechanical experiments showed that, after mixing, the sample passes through the gel point very quickly [38]. Most of the structural development occurs in the solid state as shown schematically in Figure 1. As a consequence, the characteristic modulus $G_c(t_r)$ and relaxation time $\tau_{max}(t_r)$, respectively, grow or decay by orders of magnitude in the solid state, while their product $G_c(t_r) \tau_{max}(t_r)$ was found to remain approximately constant during most of the ripening process [38]. The ripening time t_r is defined as the time since mixing clay and polymer together if both mixing and ripening are done at the same temperature. For ripening experiments at elevated temperature, the components were mixed at low temperature and $t_r=0$ is chosen as the time when the temperature was raised for the ripening experiment. The growing connectivity in the ripening network structure expresses itself in a growing mechanical strength and in requiring larger and larger shear stress to induce flow. In this way modulus growth and increasing yield stress are expected to correlate with each other.

Figure 1: Characteristic modulus, G_c , and characteristic relaxation time, τ_{max} , with respect to ripening time, t_r , during physical gelation [38]. The physical gel point is reached early in the self-exfoliation (small t_c). Most of the structure develops beyond the gel point ($t_r > t_c$). As a universal property of solid states beyond the gel point τ_{max} is decaying while G_c is growing with increasing ripening time [39].

Small Angle X-Ray Scattering (SAXS) is a powerful method of probing systems on a nanometer scale. Using SAXS, the exfoliation process can be observed as it progresses from clay aggregates dispersed in a polymer, to an intercalated clay polymer nanocomposite, and finally to full exfoliation where the layer-to-layer alignment is lost and the peak in the scattering pattern disappears.

In this study, the temperature dependence of the exfoliation process was examined over a temperature range that was larger than in earlier studies. The experiments are designed to further the understanding of the mechanism of self-exfoliation. This became necessary since a purely diffusional model is called into question by some previous observations. Studying the temperature dependence of the kinetics of the exfoliation process allows comparison with expected behavior for each potential mechanism. The rate of exfoliation in a purely diffusional mechanism should approximately follow Arrhenius form with respect to temperature dependence. For a mechanism with an adsorption/desorption process as the rate-limiting step, a maximum rate is expected at intermediate temperatures.

Experiment

Materials The nanocomposite of this study combines two components, carboxyl-terminated polybutadiene (CTPB) from Sigma-Aldrich, with M_n of 4200 g/mole, and a modified organo-clay, DK1, from Fenghong Clay Corp. (China). DK1 is a montmorillonite clay neutralized with counterions of octadecyltrimethyl ammonium (C18A) chloride, which has a single alkyl tail of 18 carbons. The initial interlamellar spacing is about 2.3 nm for DK1 organoclay. An individual clay sheet is about 1 nm thick and 100 nm wide. Its width is difficult to quantify because the sheets are irregularly shaped and broadly distributed in size. A concentration of 8 wt% clay was chosen for the experiments throughout this study because nanocomposites with 8 wt% clay still allow full exfoliation (being below 10 wt%).

[40]whilecontaining enough clay to show strong growth of mechanical properties (compared to pure CTPB). The antioxidant (BASF Irganox B225) was added in small quantities, 0.2wt%, to prevent the polybutadiene from oxidizing and thermally cross-linking at elevated temperatures. A control was run with CTPB mixed with 0.2wt% B225, but without clay, kept at 100°C for 4 hours and no significant change in G' was observed. However, a second control with unmodified polybutadiene (M_n of 5000 g/mole, Sigma-Aldrich), 8wt% DK1, and 0.2wt% B225, showed some, relatively small compared to what would be expected from exfoliation, increase in modulus after 4 hours at 100°C. This could be the result of clay-catalyzed thermal cross-linking or some other clay catalyzed reaction. A dedicated study of possible organo-clay catalysis of polybutadiene cross-linking is outside the scope of this study but may be done as a follow on.

Rheometers A strain-controlled rheometer (ARES-TA Instruments Corp.), with 50mm diameter parallel plates, was equipped with a torque transducer, which autoranges between a sensitive mode with range 0.0002-2 $g \cdot m$ and a durable mode that extended the range to 20 $g \cdot m$. Its 0.0002 $g \cdot m$ lower resolution limit allows for high accuracy in the small amplitude oscillation shear (SAOS) measurement, while its 20 $g \cdot m$ upper limit allows for large strains to detect the onset of yielding in strain sweeps. Data collected for the developing rheology was all within the limit of the sensitive mode. The strain amplitude used in the SAOS measurements was adjusted in the range of 0.1-4.0% depending on the degree of exfoliation. The strain was confirmed to be in the linear viscoelasticity region by strain sweep experiments. A frequency range between 0.1 and 100rad/s allowed for many repeated SAOS sweeps (between 20 and 80 sweeps) during the ripening of the structure. The instrument was equilibrated at the desired run temperature for 20 minutes prior to each run. Then the gap was zeroed to account for thermal expansion. All experiments were carried out with a sample thickness of about 0.8mm.

SAXS Beamline In-situ SAXS measurements were performed at the Advanced Polymers Beamline (X27C) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength of the synchrotron radiation was 1.371 Å. The 2D scattering patterns were collected with a charged coupled device (CCD, MAR-USA) detector (resolution 1024 X 1024 and each

pixel size is 158.44 μm). The sample-to-detector distance was 1830.1 mm calibrated by AgBe. The sample temperature was controlled with an INSTEC HCS600V single-cell heating stage with aSTC200 temperature controller, which was equipped with a LN2-SYS liquid nitrogen cooling system. The hot stage was capable of controlling the temperature to ± 0.1 K, and had a maximum temperature of 400 $^{\circ}\text{C}$.

Sample Preparation and Experimental Protocol for Rheology Precaution was taken to keep early exfoliation to a minimum. This involved a special temperature protocol for the ARES time resolved SAOS experiments: Once the plates had been zeroed at the desired temperature, the rheometer was opened, the top plate was removed, and the rheometer was closed again. The top plate was then placed in the freezer ($\approx -18^{\circ}\text{C}$) and allowed to cool for 20 minutes. A metered sample of CTPB ($\sim 3.5\text{g}$) was placed in a 3 dram glass vial and also placed in the freezer for 20 minutes. Meanwhile, corresponding amounts of DK1 and B225 were massed on pieces a weighing paper. At the end of the 20-minute cooling period both the CTPB and plate were removed from the freezer and the B225 and DK1 were added to the CTPB and mixed gently, in order to minimize shear induced orientation, with a small spatula by hand until no large clay aggregates were visible. Mixing took ~ 45 seconds. The homogenized clay/polymer mixture was then placed on the top plate and subjected to $\sim 95\text{kPa}$ of vacuum for 5 minutes to remove air bubbles in a room temperature vacuum oven. Then the top plate was loaded into the preheated rheometer and the temperature was allowed to equilibrate for 3 minutes. Removing and replacing the top plate of the rheometer introduces some error into the gap setting but repeated trial showed this introduced error to be negligible for the instrument used.

In this study, the isothermal structural ripening of DK1 in CTPB nanocomposites was monitored rheologically, through SAOS, at temperatures from 20°C to 100°C . Rheological changes are expressions of changes in the nanostructure of the material. Therefore, rheology can give insight into the exfoliation dynamics despite the fact that exfoliation is a nanoscale process and rheology is a macroscale probe. Samples, with changing structure, can be characterized with Fourier transform mechanical spectroscopy [41,42] and time-resolved rheometry [37] as long as the structural changes are slow enough. Data points are deemed acceptable as long as both mutation numbers

$$N'_{mu} = \frac{2\pi}{\omega} \frac{\partial G'}{\partial t} \quad ; \quad N''_{mu} = \frac{2\pi}{\omega} \frac{\partial G''}{\partial t} \quad (1)$$

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201 maintain values below a tolerable limit (typically $N'_{mu} < 0.1$ while $N''_{mu} \ll N'_{mu}$) . $2\pi/\omega$ is chosen as the
 202 reference time in the definition of the mutation numbers because SAOS is a spectroscopic technique,
 203 which reaches quasi-stable condition in about one sampling period [37].

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Sample Preparation and Experimental Protocol for SAXS

The sample was prepared by

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massing two grams of CTPB in a 20ml glass vial. The polymer was then cooled to $\sim 0^\circ\text{C}$ in a walk-in

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refrigerator. 8 wt% DK1 organoclay and 0.2 wt% Irganox B225 antioxidant were then massed and added

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to the vial. The sample was gently mixed by hand using a small stainless steel spatula. A folding motion

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was used to thoroughly mix the sample. Once the sample was deemed homogenous by visual inspection

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after an average time of 50s, it was divided and mounted in a series of copper sample holders and then

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one subsample was mounted on the pre-cooled (0°C) instrument hot stage. The rest were stored in a

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Dewar flask of liquid nitrogen so that each successive run starts with an identical sample, as the

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temperature of liquid nitrogen is far below the glass transition of the polymer (-78°C), effectively locking

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the structure in place. The temperature was rapidly raised to the experimental temperature and, once

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thermal equilibrium was established, the experiment began. The data acquisition time was 83s and the

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data storage time was 7s for each image collection.

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Experimental Results

Rheological Results The ripening process ends in a stable clay dispersion (SCD) in the polymer as previously demonstrated [29,31-34]. The rheology of this stable state serves as the reference for this study. The dynamic moduli from repeated frequency sweeps were replotted as time functions for each frequency as shown in Figure 2 and as a function of frequency with time as a parameter in Figure 3. Next they were collapsed onto the data of the final structure (longest time), Figure 4. Shifting the frequency sweep data of figure 3 to the final time data requires multiplication of G' and G'' by the horizontal and vertical shift factors a_t and b_t , respectively, shown in Figure 9. The values of a_t and b_t are a measure of the distance (rheologically) from the final structure.

Figure 2: Dynamic moduli from repeated frequency sweeps at 60°C, replotted as a function of time. Only selected frequencies are shown here while 5 frequencies per decade were used. Open symbols represent G' and filled symbols represent G'' .

The dynamic moduli of Figure 3 can be shifted to collapse onto the moduli of the longest time to form a master curve as a function of frequency, Figure 4. This is different than the standard method of generating a master curve through time-temperature superposition, as the temperature is constant and the structure is developing with time. It can be called a time-time superposition master curve. Figure 5 shows the shift factors needed to shift $G'(\omega, t_r)$ and $G''(\omega, t_r)$ at various times to the moduli of the longest time. For DK1 in CTPB dispersions, the horizontal, a_r , and vertical, b_r , were found to be identical for all times during the ripening process. This agrees with the previous observation that the product of relaxation time and characteristic modulus is constant throughout the ripening process [38]. The slope of the changing shift factors remains constant for most of the ripening process but declines significantly at the end of the process.

Figure 3: Storage modulus G' (open symbols) and loss modulus G'' (closed symbols) as a function of frequency ω from a series of frequency sweeps at 60°C. Successive frequency sweeps occur later and later in the exfoliation process. This was repeated at temperatures of 20, 25, 35, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100°C. Data for 60°C is given as an example.

Figure 4: SAOS Master Curve shifted to the longest time at 60°C. Storage modulus G' is shown as open circles, loss modulus G'' as closed circles, and the solid line is $\tan \delta$, which is shown to demonstrate the limits of the shifting below 1 rad/s.

Figure 5: Horizontal, a_r , and vertical, b_r , shift factors for SAOS at 60°C. Crosses represent a_r and closed circles represent b_r . The two shift factors have approximately the same value. This is true for every temperature tested.

The maximum normalized rate of change in storage modulus was found by fitting a sum of two exponential decays and shifting back to $t_r=0$ (the time the sample was placed in the temperature controlled instrument). An example of this fitting, using the scaled slopes of the single frequency modulus growth curves from Figure 2 is shown in Figure 6.

A sum of two exponential decays was chosen because it is reasonable to expect reaction rates to decrease exponentially and a single exponential decay did not provide a reasonable fit while a sum of three or four exponential decays did not improve the fit. The definition of $t_r=0$ here is reasonable because exfoliation is suppressed at low temperatures and the temperature of the sample quickly increases as soon as it is mounted in the pre-heated rheometer. This was done for temperatures from 20°C to 100°C in small increments. The frequency and time sweeps, for the temperatures besides the 60°C example, are included in the supporting information.

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269 Figure 6: Percent change in storage modulus per second. At the y-intercept, $t_i=0$, the rate that is used for
 270 comparison between temperatures is found. The 60°C fitting is shown.

271 *Temperature Effects from SAOS* For every temperature there are two distinct regimes; a fast
 272 increase in the beginning of the experiment followed by a very slow increase leading to the final fully
 273 exfoliated state. The maximum, scaled rate of change in storage modulus is strongly temperature
 274 dependent as shown in Figure 7. A sharp decrease in rate is observed above 80°C and below 40°C.
 275 The horizontal error bars (for temperature) in Figure 7 are based on observed temperature drift in the
 276 rheometer temperature controller that increases with increasing temperature. The vertical error bars (for
 277 scaled rate of change of modulus) are found from max min variance including both sample to
 278 sampledifferences and instrument noise interpolated back to time zero for 60°C. This temperature was
 279 chosen because four experiments were performed at 60°C, which was enough to estimate sample-to-
 280 sample variation. Other temperatures did not have enough repeated runs to find sample-to-sample
 281 variance. The error in rate is assumed to be similar for all temperatures. The high temperatures, 95°C and
 282 100°C, were found to have a higher storage modulus throughout than any of the other temperatures.

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Figure 7: Percent change in storage modulus per second at $t_r=0$ as a function of temperature. The value was determined by extrapolation to $t_r=0$. Note the clear decrease in rate at low and high temperatures.

SAXS Results

Representative SAXS patterns, during the exfoliation process, at 83°C are shown in Figure 8. From the figure we can see that the SAXS profiles roughly give rise to q^{-2} power law behavior at the high q region ($q > 1 \text{ nm}^{-1}$) at the early stage. This asymptotic power law behavior is attributed to the form factor of randomly oriented thin disks, as reported previously [43,44,45]. On the other hand, at the late stage of the process, a deviation in the high- q region of $I(q)$ from q^{-2} to q^{-1} is evidenced. Similar asymptotic behavior of q^{-1} was seen in clay/PEO solutions [46,47] but the origin may be different: the polymer used in this study is a telechelic molecule so that microphase separation between the monomers and end-functional groups takes place in the melts [48,49] giving rise to scattering associated with the domain structures. While further SAXS experiments for the pure telechelic PB are currently in progress to clarify the origin of the deviation, we here focus on the exfoliation process of the clay disks based on the time dependence of

multiple peaks that originate from the interclay spacing in the polymer matrix.

Figure 8: Time resolved SAXS results for the clay-PB film at 83°C.

In order to determine the domain spacing accurately, we here used an approach proposed by Kroon and co-workers [50] for disk-shaped clay nanoparticles in a solution. They decomposed the observed SAXS scattering intensity $I(q)$ into a static structure factor of the clay disks, $S(q)$, and a form factor of randomly oriented clay disks, $F(q)^2$ ($F(q)$ is the scattering amplitude of the object) [51] via

$$I(q) \sim S(q)F(q)^2. \quad (2)$$

Figure 9: Time dependence of $S(q)$ of the clay/PB film at 105°C. The peak at around $q \sim 0.6 \text{ nm}^{-1}$ corresponds to the nearest-neighbor clay-clay correlation.

We calculated $F(q)^2$ for a rectangular solid based on a program developed by Kline [52]. We assumed the width of 100 nm, the length of 200 nm, and the thickness of 1 nm for the individual clay disk. The detailed formula for the calculation of the form factor is available at http://www.ncnr.nist.gov/programs/sans/data/red_anal.html. $S(q)$ can be then obtained from Eq. (2) by dividing $I(q)$ by the form factor. It should be noted that the effect of polydispersity on the form factor [50] was not considered here since the effect is not significant in the observed q -range. Fig. 9 shows representative $S(q)$ for the clay-PB film at 105°C. From the figure we can see the peak corresponding to the clay interspacing followed by a plateau that indicates that the scattering intensity follows $I(q) \sim q^{-2}$ at $q > 0.1 \text{ nm}^{-1}$. At least two peaks are seen in $S(q)$ at the early stage, indicating that the clay-clay correlation becomes weaker as time goes by. In the present study, we defined the exfoliation time as the time when the correlation peak in $S(q)$ is completely gone.

The interdomain spacing obtained from $S(q)$ is summarized in Fig. 10. At 42°C, which is close to the lower temperature limit in the effective exfoliated process (Fig. 7), we can see a very rapid increase in the spacing of the clay sheets over 3 times the initial spacing within 90 sec and the spacing then remains unchanged up to 600 min, which is the longest annealing time used for the SAXS measurements. The data

hence suggests that the sample is not fully exfoliated at this temperature. Around 80°C where we can see the maximum rate of change in storage modulus, the time until $S(q)$ disappearance is also minimized. While the spacing remained nearly constant, the broad peak finally disappeared at $t \geq 420$ min (Fig. 8), indicating the complete exfoliation of the clay disks. At 105°C, where the rate of change in storage modulus is much slower than that at 42°C or 83°C, we can clearly see a gradual increase in the spacing at $t < 20$ min until the spacing reached the saturated value of 9.7 ± 0.2 nm. This indicates that the exfoliation process at 105 °C is much slower than those at 42 and 83°C. Hence, we can see the correlation between the microscopic structural changes and the macroscopic changes in the rheological property during the exfoliation process.

Figure 10: Time dependence of the clay spacing at the three temperatures. Note that the correlation peak in $S(q)$ is gone at $t > 420$ min in the isothermal process of 83°C and the annealing time at 105° C was limited to 300 min.

Discussion

In this study, an unexpected temperature dependence was found when experiments were conducted at temperatures that were higher than in previous publications. Where pure diffusion is expected to increase exfoliation rates with increasing temperature, a maximum rate was found at intermediate temperatures with a strong decrease in rate at high temperatures. There are multiple ways to

hypothesize a mechanism consistent with this observation, as it could result from temperature dependent phase behavior, thermal degradation, sheet alignment, or an adsorption dependent process.

One possible mechanism is diffusion with temperature dependent phase behavior. The decline in rate at high temperatures might be explained by the clay and polymer becoming incompatible, although no bulk phase separation and no change in opacity due to smaller scale phase separation was observed. There are no studies on the phase behavior of this system to support this hypothesis, however. Neutron scattering experiments could be conducted to rule out micro-phase separation, but that is beyond the scope of this study.

The high temperature control runs, shown in the supporting material, show that clay-catalyzed polybutadiene thermal cross-linking is a possibility. The observation of higher modulus at the highest temperatures also supports the possibility of a thermal cross-linking. This could conceivably interfere with exfoliation by immobilizing the system prematurely. No literature is available on DK1 organoclay's catalytic activity, with respect to polybutadiene, but it is known to catalyze reactions in other systems. IR (Infrared Spectroscopy), NMR (Nuclear Magnetic Resonance), and TGA (Thermal Gravimetric Analysis), could be utilized to characterize any catalytic reactions, but this is outside the scope of this study.

The rate could decrease if the SAOS was inducing clay sheet alignment at high temperature, but the SAXS experiments were unsheared and displayed the same behavior so an alignment explanation is not plausible.

Still needed is a mechanism that is consistent with all experimental observations. Figure 11 schematically outlines such a mechanism, which is assumed to rely on entropic pushing of attached PB macromolecules. We hypothesize that sticky PB molecules quickly attach to the outer edges of the clay sheets and entropically push against each other. In this way, the enthalpically favorable hydrogen bond adsorbed polymer brush causes the clay stack to expand and, thus, facilitates macromolecules to enter the stacks by diffusion and pressure driven flow. Based on this model, unmodified PB (no sticky ends) does not promote exfoliation since the outer entropic force is missing along with the favorable enthalpic

contribution of the hydrogen bonds. The model is also consistent with the short time that is required for intercalation of clay when exposed to the sticky PB. Intercalation is fast since little time is required for the expansion of the clay stacks and the establishment of a force balance. The external edge brush will form quickly and its entropic force gets instantaneously balanced by swelling the stack against the internal cohesion forces. The rapid expansion of the clay stacks into an intercalated state is followed by a slow approach of the final exfoliated state by molecular diffusion. Adsorbed polymer brushes on all faces of the clay sheets stabilize the final fully exfoliated state. It is a three-step process. The adsorption step explains the temperature dependence as increasing temperature increases the thermal motion of the polymers leading to an increased entropic pushing at first but then causing desorption when the temperature is raised further. The high temperature desorption is a well-known characteristic of adsorption mechanisms represented in a simple case by Langmuir adsorption.

The hypothesized energy diagram is presented in the graphical abstract where the clay before adsorption of polymer is represented by energy level 1, adsorbed polymer on clay by level 2, an intercalated composite by level 3, and the final fully exfoliated state by level 4. The energy barriers, which are the activation energies for these processes, between the first three levels are thought to be small because they still proceed even at fairly low temperature. The energy barrier between intercalated and exfoliated states is thought to be significant because of the apparent lack of full exfoliation at low temperature seen in the SAXS experiment. This diagram is strictly qualitative, as no values have yet been estimated for the energy levels and activation energies.

Figure 11: Exfoliation by edge adsorption is shown in several steps. Step 1 shows a clay stack in its initial state with no polymer adsorbed or in the galleries. Step 2 shows polymer chain ends hydrogen bonding to the edges of the clay sheets and expansion. Step 3 shows further expansion by diffusion of polymer into the galleries and some loss of sheet alignment along with a growing distribution of sheet-to-sheet distances. Finally, step 4 shows the fully exfoliated state along with four possible polymer arrangements: loop (both ends of a polymer are bonded to the same sheet), bridge (two sheets are linked by a polymer bonded on one end to each), free chain, and single end tethered. The c18 counterions are omitted. It is possible that the stacks break into smaller stacks as they expand but the SAXS analysis used in this study cannot determine this.

The model is also consistent with the observation of Wang et al. [34] of effective exfoliation in a PB blend of sticky with non-sticky molecules. While the edge coverage with sticky macromolecules is not affected by the presence of non-sticky macromolecules, molecular diffusion into the opened galleries is expected to be easier for the non-sticky macromolecules. The diffusion of sticky macromolecules is slowed down by the ‘gluing effect’ as described by Sinsawat et al.[9].

Another unexpected observation in this study was that SAXS showed that much of the growth in rheological properties occurred while the system was intercalated rather than exfoliated. This was unexpected because this system was thought to derive most of its reinforcement from the sample-spanning network formed by polymer bridges between clay sheets in the fully exfoliated state.

Conclusions

During self-exfoliation the clay gallery spacing initially expands very rapidly, tripling within five minutes at a suitable temperature. Self-exfoliation of the clay polymer nanocomposite is fastest at an intermediate temperature. This temperature dependence required the search for a new explanation of the self-exfoliation. A multistep mechanism was hypothesized to account for the previously unexplained exfoliation behavior of organo-clay in a sticky polymer. The mechanism is consistent with a diverse set of

experimental observations, not just the unexpected temperature dependence. At this point the hypothesized mechanism is strictly qualitative and much work still needs to be done. Work is actively being pursued on further understanding this system in a quantitative way. Full characterization of the DK1 organoclay is being pursued so that its size dispersity can be known and a diffusional mechanism fully ruled out. The possibility of organo-clay being a catalyst for polybutadiene thermal cross-linking is also being actively pursued.

Intercalation was found to contribute more strongly to reinforcement in the system than expected. With the majority of the moduli growth coming at the beginning of the process while the polymer is intercalated in the clay sheets.

The gel point was found to occur early in the self-exfoliation process when the system was intercalated. Rheological experiments showed that the majority of the structural development occurred in the solid state, past the physical gel point.

With understanding of the mechanism, optimization and extension to other materials should be more achievable. Currently, we know no comparable self-exfoliating systems. Self-exfoliation has the potential to be a valuable technique in creating industrial applicable and affordable nanocomposites.

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559 TOC: Graphical Abstract