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Unusual Rheological Behavior of Liquid Polybutadiene Rubber/Clay Nanocomposite Gels: The Role of Polymer−Clay Interaction, Clay Exfoliation, and Clay Orientation and Disorientation

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ABSTRACT: The rheological properties of liquid polybutadiene rubber/organo-clay nanocomposite gels were investigated by rheological experiments, focusing on the effects of clay exfoliation and orientation−disorientation as well as polymer−clay interaction and temperature. Both irreversible and reversible viscosity transitions were observed in the temperature range from 26 to 136 °C in steady shear experiments on as-prepared and exfoliated samples. These transitions depend strongly on the end groups, molecular weight of the liquid rubber, and the shear field. The irreversible transition is attributed to the exfoliation of the clay, and the reversible transition can be understood as a shear-induced orientation−disorientation transition of the clay sheets. Polymer−clay interaction is confirmed to be a key controlling factor of the orientation−disorientation transition, whereas the shear field plays a critical role to induce such a transition. To our knowledge, this is the first rheological observation of the in-situ exfoliation process and the shear-induced orientation−disorientation transition of layered silicate in polymer/organo-clay nanocomposites. A tentative model was suggested on the basis of the clay exfoliation and orientation−disorientation transition, and the model is used to explain the observed unique rheological behavior.

Introduction

Because of their unique physical and chemical properties such as high modulus, high thermal stability, decreased flammability, and barrier properties, polymer/clay nanocomposites have been intensively studied in the past few years.[1] The dispersion state of the clays and the polymer−clay interaction are of great significance for the design of tailored polymer systems with enhanced properties. It has been shown that these factors play a crucial role in controlling the final physical and chemical properties of the nanocomposites. In addition, it is well-known that the clay nanostructure and the polymer−clay interaction can strongly influence the linear and nonlinear rheological responses of polymer/clay nanocomposites. Because of the widespread use of fillers in polymeric products, the influence of the filler particles on the viscoelastic properties of polymer-based composite materials has been of significant technological interest. Understanding the rheological properties of nanocomposites is important to gain a fundamental knowledge of the processability of these materials. At the same time, rheological properties are essential to determine the structure−property relationships of these materials.[1] Furthermore, rheological studies of these systems might also lead to a better understanding of the dynamics of nanoscopically confined polymers.[2−4]

It has been shown that rheology is a unique technique for the study of polymer/clay nanocomposites. Krisnamoorti and Giannelis[5] reported the rheological properties of in-situ polymerized nanocomposites with end-tethered polymer chains. They observed that the flow behavior of poly(ϵ-caprolactone) (PCL) and nylon-6-based nanocomposites differed significantly from that of the corresponding neat matrices. The linear dynamic mechanical properties of polymer/clay nanocomposites have been intensively studied for a wide range of polymer matrices including nylon-6 with various matrix molecular weights,[6] (low-density polyethylene)/(ethylene vinyl acetate copolymer) blend,[7] polystyrene−polyisoprene (PS−PI) block copolymers,[8,9] poly(butylene succinate),[10a] and other systems.[1,2] On the other hand, although liquid rubber has been widely used in industrial applications, few works were reported on liquid rubber/clay nanocomposite gels except some recent studies.[11−13]

Clay sheets are highly anisotropic inorganic nanoparticles, which can be oriented under shear field. Shear-induced orientation of the polymer/clay nanocomposites has attracted considerable interest recently. Krishnamoorti et al.[14] reported shear-induced orientation−disorientation of clays in PS−PI/intercalated-clay nanocomposites. Schmidt et al.[15] reported shear-induced structural change in PEO/intercalated-clay solutions using the small-angle neutron scattering (SANS) technique. They concluded that a strong flow field could enhance and maintain a continuous increase in the clay orientation of the polymer−clay system. The response of the intercalated and exfoliated nanocomposites to external flow is vital to their processing. In addition, rheology measurements of polymer/clay systems will also provide a systematic study of the response of highly anisotropic layers suspended in a viscoelastic medium. It is also noted that the origin of the disorientation process and the factors controlling this process have attracted substantial recent atten-

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tion. The disorientation process under quiescent conditions immediately after alignment of the layers, achieved by large-amplitude oscillatory or long-time steady shear, has been studied by several groups.[15,16] However, many questions on the origin of clay disorientation in nanocomposites have not been answered. It was suggested that by carefully controlling the thermodynamic interactions the origins of the disorientation processes in these systems could be determined.[16]

We have recently reported a new class of gel-like telechelic rubber/exfoliated-clay nanocomposites using liquid polybutadiene and highly anisotropic, organically modified silicates. These nanocomposites have been characterized by a variety of techniques including transmission electron microscopy (TEM), X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS).[11,12] It was also observed that the end groups of HTPB have a significant effect on the exfoliation of the clays. However, a good understanding of the effects of the polymer−clay interaction and temperature on the clay exfoliation in these nanocomposite gels is still lacking. In this article, we focus our attention on the steady and dynamic shear properties of these rubber/organo-clay nanocomposites. In particular, the influence of a variety of factors, such as the processing temperature, molecular weight of the polymers, polymer−clay interaction, and the highly anisotropic nature of the layered silicates, on the rheological properties of these nanocomposites is investigated. Unusual rheological behavior, including irreversible and reversible transitions of clay microstructures, is observed in the temperature range of 26−136 °C for the liquid rubber/organo-clay nanocomposites. The origins of the irreversible and reversible transitions were elucidated. On the basis of the rheological experiments, a tentative model for the unusual rheological behavior and shear-induced microstructural change of the clays in the HTPB/organo-clay nanocomposites is postulated. We believe that the current study provides a better understanding of the rheological behavior as well as the influence of polymer−clay interaction, shear, and temperature on the clay exfoliation and orientation−disorientation in polymer/organo-clay nanocomposites.

Experimental Section

The hydroxyl-terminated 1,4-polybutadiene oligomers (HTPB) were purchased from Qilu Ethylene Chemical and Engineering Co. Ltd. (China). The samples have average molecular weights (M_n) of 2200 and 4200 (HTPB2200, HTPB4200), respectively, with a polydispersity index of 2.6. The liquid 1,2-polybutadiene oligomer (12PB with M_n of 3300) without hydroxyl end groups was purchased from Aldrich Chemical Co. The microstructures of these liquid rubbers have been determined by ^{1}H NMR (Varian UNITYplus-400 MHz NMR spectrometer) previously.[11,12] The organo-clay (C18-clay) was prepared as follows: 10.0 g of industrially purified pristine montmorillonites (Tianjin Organic Clay Corp. China, cation exchange capacity is 1 mequiv/g) was dispersed into 1000 mL of distilled water at 87 °C for cation exchange with 3.5 g (equal to 1 mequiv/g) of octadecyltrimethylammonium chloride (denote as C18A) for 12 h. The processed clay was washed with distilled water and checked with a 0.1 N $AgNO_3$ solution for residue Cl^-. After the washing, the organo-clay was dried at 87 °C for 12 h before use. Rubber/clay nanocomposite gels were prepared by simply compounding the desired amount of organo-clays with liquid rubbers at room temperature (about 26 °C) with slight stirring, as described previously.[11,12]

X-ray diffraction (XRD) experiments were performed in reflection mode on a Rigaku D/max-2500 X-ray powder diffractometer with Cu Kα ($\lambda = 0.154$ nm) radiation at a generator voltage of 40 kV and a current of 100 mA.

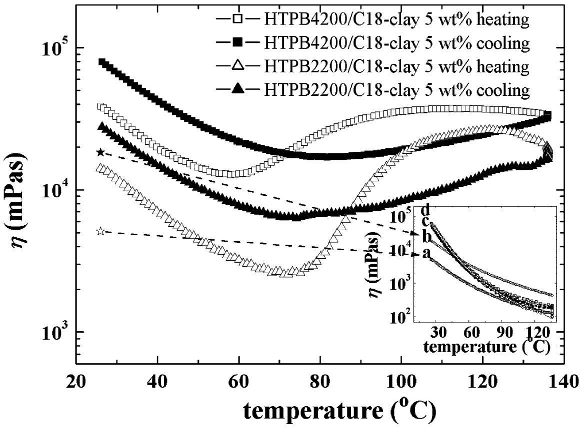

Figure 1. Temperature dependence of the steady shear viscosity for HTPB4200/C18-clay (5 wt %) and HTPB2200/C18-clay (5 wt %). ★ and ☆ are the steady shear viscosity of pure HTPB4200 and -2200 at 26 °C, respectively. Temperature dependence of steady shear viscosity for (a) pure HTPB2200, (b) HTPB4200, (c) 12PB, and (d) 12PB/C18-clay (5 wt %) are shown in the inset. All the curves shown in the inset behave like a common liquid. The heating began immediately after a shearing of 1 s^{-1} for 15 min at 26 °C. After heating, the sample was kept at 136 °C for 2 min and then cooled.

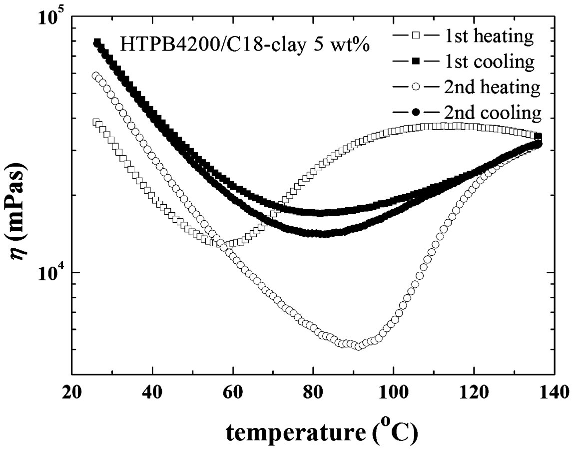

Figure 2. Temperature dependence of the steady shear viscosity for HTPB4200/C18-clay (5 wt %). The first and the second heating scans began immediately after a shear of 1 s^{-1} for 15 min at 26 °C. After heating, the sample was kept at 136 °C for 2 min and then cooled.

Rheology experiments were conducted on a HAAKE RheoStress 600 instrument. Steady and dynamic oscillatory shear measurements were conducted by using a set of 35 mm diameter parallel plates with a sample thickness of ca. 0.8 mm. In all the dynamic oscillatory shear measurements, the strain deformation was fixed at 0.05, which is large enough to obtain a reasonable intensity signal even at elevated temperature, while it is small enough to avoid nonlinear response. The temperature dependence of the dynamic storage modulus (G') and loss modulus (G'') was measured at frequencies (ω) of 6.28 and 31.4 rad/s and in the temperature range 26−136 °C with a heating rate of 2 °C/min. The temperature dependence of the steady shear viscosity was obtained in the same temperature range with typical shear rates of 0.05, 1, and 5 s^{-1}. To start with an oriented state, a shear of 1 s^{-1} for 15 min was imposed to the as-prepared samples before heating. To prevent the degradation of the samples, all the rheological experiments at elevated temperatures were performed under the protection of nitrogen gas.

Results and Discussion

1. Unique Rheological Behavior Observed in Steady Shear Experiment: The Effect of End Group, Molecular Weight, and Shear Field. In the temperature range from 26 to 136 °C, it is observed that the HTPB/organo-clay nanocomposites exhibit novel rheological properties, as shown in Figures 1 and 2. To obtain a better understanding of these unique rheological results,

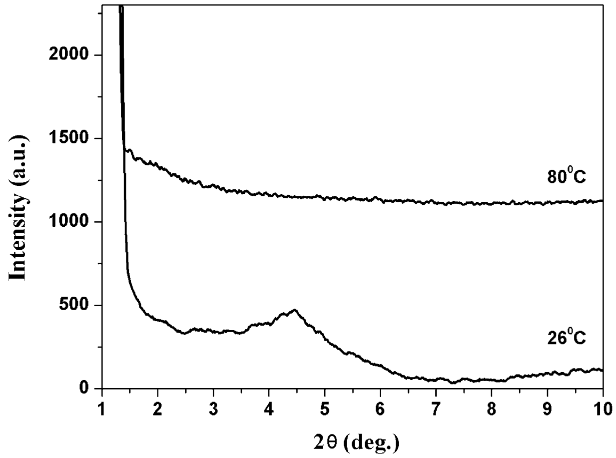

Figure 3. WAXS patterns of HTPB4200/C18-clay (5 wt %) nanocomposite: (a) as-prepared sample mixed at room temperature; (b) sample after heating to 80 °C.

we consider three important factors that significantly affect the rheological behavior in the steady shear measurement. The first factor is the end group effect of the polymer−clay interaction, which is temperature-sensitive and has been shown to be a crucial factor controlling the exfoliation of clay in our previous paper.[11] The second factor is the shear-induced orientation effect. Shear-induced orientation can led to a considerable decrease in the sample viscosity. Krishnamoorti reported that even at the lowest shear rates accessed in the steady shear measurements for the PS−PI/clay nanocomposites, significant orientation of the layered silicate occurs.[14] It should be mentioned that the polymer chains themselves do not orient significantly at shear rates less than 30−40 s^{-1}. Therefore, at a shear rate less than 5 s^{-1}, orientation effects are due to the anisotropic component in the nanocomposite gels, i.e., the clay sheets.[15] The third factor is the temperature. A decrease of the viscosity with increasing temperature for the polymer matrix is expected because of thermal motion. These three factors compete with each other or override one another to determine the final rheological properties of the rubber/clay nanocomposite gels.

First, attention should be paid to the steady shear viscosity at 26 °C before and after heating (Figure 1). The steady shear viscosity of HTPB2200/C18-clay (5 wt %) was about 2 and 5 times the viscosity of pure HTPB2200 before and after heating, respectively. The HTPB4200/C18-clay (5 wt %) was about 2 and 4.5 times the viscosity of pure HTPB4200 before and after heating, respectively. On the contrary, heating does not lead to obvious differences between the viscosity of 12PB/C18-clay (5 wt %) and pure 12PB. A larger increase of viscosity indicates the presence of a stronger polymer−clay interaction. The measured characteristics of the viscosity provide important information about the degree of exfoliation and agree with our previous work.[11]

In Figure 1, for the first heating scan of the as-prepared HTPB4200/C18-clay samples, we found that the steady shear viscosity gradually decreased with increasing temperature from 26 to 60 °C. This behavior is similar to that of common liquids. What surprising is that a dramatic increase of the viscosity occurred after a transition temperature (about 60 °C), indicating the presence of strong polymer−clay interaction leading a structure transition of HTPB4200/C18-clay from an intercalation state to an exfoliation state.[11,12] This conclusion is further confirmed by the WAXS results shown in Figure 3. The XRD pattern of the as-prepared HTPB4200/C18-clay at 26 °C shows a weak and broad hump at around 4.5° (2θ), indicating the existence of intercalated/exfoliated clay mixture. After heating to 80 °C, which is greater than the transition temperature, the absence of the (001) basal reflection peak of this sample implies the complete exfoliation of clay. Detailed microstructure characterization of HTPB2200/exfoliated clay gel can be found in our previous paper.[11] The continuous increase of the viscosity with further increases in temperature from 60 to 110 °C implies that the polymer−clay interaction-induced clay exfoliation dominates the shear orientation and temperature effect. On the other hand, from 110 to 136 °C, the exfoliation process was completed, and the shear-induced orientation and temperature effects can overcome the polymer−clay interaction effect, resulting in slight decrease in the viscosity. The rheological behavior for the HTPB2200/C18-clay (5 wt %) nanocomposites was similar to that of the HTPB4200/C18-clay (5 wt %), except that the former sample shows a relative higher transition temperature. The critical transition temperature of the HTPB2200/C18-clay (5 wt %) sample corresponds well to the optimal pretreating temperature in our previous work.[11] Since the as-prepared samples are intercalated nanocomposites, the rheological experiment is a direct observation of the in-situ exfoliation of clay in the nanocomposites, and the critical temperature for clay exfoliation can be accurately determined.

Two important factors affect the clay exfoliation in our system: the polymer−clay interaction and the special conformation of the polymers under confinement. It is well-known that the polymer−clay interaction is a key factor in controlling the clay exfoliation. In the HTPB/clay nanocomposites, there exist interactions between PB chains, end hydroxyl groups, polar head and alkyl chain of C18A, and the pristine surface of the silicate. Temperature may significantly enhance the polymer−clay interaction. In our previous work, we observed that C18A was readily dissolved in HTPB by simple mixing at about 56 °C and then cooling to room temperature. This implies that the interaction between HTPB and the organic modifier is temperature-sensitive, and a strong polymer−clay interaction can be achieved above 56 °C. The mixture of 14PB/C18A was turbid, and C18A gradually precipitated later.[11] The result of the mixing experiment of 12PB without the hydroxyl end group is the same as 14PB. In the current study we use 12PB instead of 14PB used in our previous work because the viscosity of the 14PB is out of the measurement limit of the rheometer at elevated temperatures. The miscibility experiments indicate that HTPB has a stronger interaction with the C18A modifier, which leads to a strong interaction with the silicate layers in the HTPB/C18-clay nanocomposites at temperatures above the transition temperature (ca. 60 °C for HTPB4200/C18-clay (5 wt %) and ca. 75 °C for HTPB2200/C18-clay (5 wt %), as shown in Figure 1). These results from the mixing experiments are in good agreement with the rheological results presented above. It was reported that hydrogen bonding to the oxygen basal plane of the silicate sheet is an important intermolecular interaction enabling melt exfoliation of clays in polymer/clay nanocomposites.[10] On the basis of this earlier work, it is reasonable to suggest that the hydrogen bonding between the telechelic rubber and silicate layers is also a critical factor in the clay exfoliation in our system. Furthermore, Malvaldi[4] recently reported that confinement has an important effect on the melt properties of the polymer with terminal groups. In particular, strongly attractive walls can produce a radical change in chain conformations, such as the cluster-like structure of HTPB.[17] Balaze et al.[18] predicted that star-shaped polymers would improve clay exfoliation. Therefore, it is reasonable that the cluster-like structure of HTPB could also improve the clay dispersion. In addition, it should be noted that shear processing might also help to improve the clay exfoliation. Okamoto et al.[1a] reported that the mechanical properties of PA6/clay nanocomposites are significantly improved after shear processing of the material in the molten state, indicating that the shear processing may help to enhance clay exfoliation and change the rheological properties.

When the sample was kept under shear at 136 °C for 2 min, the viscosity decreased due to the shear-induced orientation of the exfoliated clays. This shear thinning effect is similar to what was reported in previous work.[14] In the cooling scan from 136 to 26 °C, a similar viscosity transition can also be found. However, the transition temperature (around 85 °C) is slightly higher than the transition temperature (60 °C) in the heating process. This unusual rheological behavior can be attributed to a different mechanism, in contrast to the transition which occurred in the first heating scan. The unique rheological behavior in the first heating scan is irreversible. The irreversibility of this transition can be confirmed by the fact that the final viscosity at the end of cooling is much higher than that in the first heating scan at the same temperature below the transition point. This irreversible transition can be attributed to the complete exfoliation of the clays in the polymer matrix with a strong polymer−clay interaction. This process started from the intercalated state in the as-prepared samples with a weak polymer−clay interaction. The clay exfoliation is unchanged after the cooling scan. One may wonder why the exfoliated clay does not recover to the intercalated structure. We suggest that two factors prevent the exfoliated clay sheets from aggregating to re-form the intercalated clay. The first factor is the formation of the interfacial polymer−clay interaction, typically hydrogen bonding as suggested in previous work,[10] can be achieved in the exfoliation process of clay. As reported in our previous work, the second factor is the good miscibility of HTPB with C18A when cooling the mixture of HTPB and C18A from high temperature to room temperature.[11]

In contrast with the HTPB/C18-clay (5 wt %), the steady shear viscosity of the 12PB/C18-clay (5 wt %) sample, which lacks the hydroxyl end groups of the polymers, keeps decreasing with increasing temperature. No viscosity transition was found for this sample, as shown in the inset of Figure 1. This behavior is similar to that observed in the bulk HTPB2200 and HTPB4200 samples, as shown in the same figure (inset). We have suggested in our previous work that the functional end group is a crucial factor controlling the clay dispersion in the rubber/organo-clay nanocomposites. Compared with the HTPB2200/C18-clay which contains exfoliated clay, the 14PB/C18-clay sample only shows intercalated structure.[11] The above unique rheological results for the rubber/C18-clay nanocomposites with and without hydroxyl end groups are in good agreement with our previous conclusions. On the other hand, with decreasing HTPB molecular weight, the critical transition temperature of HTPB2200/C18-clay (5 wt %) increased to about 75 °C, indicating a weaker polymer−clay interaction and hardness of the clay exfoliation in the polymer matrix. Results for the nylon-6/clay nanocomposites with various matrix molecular weights led to similar conclusions.[6] This result is important for designing tailored structures of the rubber/clay nanocomposites with improved physical and chemical properties.

In the second heating and cooling scans of the HTPB4200/exfoliated-C18-clay samples, a reversible transition in the viscosity is clearly observed at a temperature (ca. 90 °C for heating and 85 °C for cooling) which is higher than the transition temperature observed in the first scan (Figure 2). The initial viscosity decrease with increasing the temperature from room temperature can be attributed to shear-induced orientation and the temperature effect. What surprising is that a viscosity increase can still be observed above the reversible transition temperature, whereas clay exfoliation is not possible in this case. This observation implies that the shear-induced orientation of the clays at a temperature lower than the transition point is destroyed above the transition temperature, resulting in a viscosity increase corresponding to the disorientation of the clays. Since the polymer−clay interaction between HTPB and the organic modifier is temperature-sensitive as mentioned above and a reversible transition cannot be observed in 12PB/C18-clay (5 wt %) sample, this experiment clearly demonstrates that the temperature-sensitive polymer−clay interaction in HTPB/clay nanocomposites is a key factor for the reversible orientation−disorientation transition under a shear field.

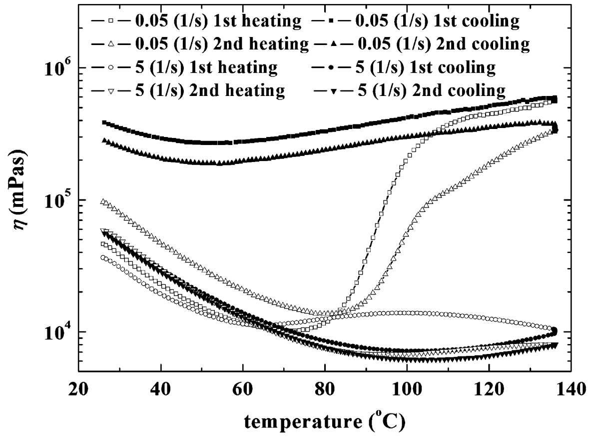

Figure 4. Temperature dependence of the steady shear viscosity at shear rates of 0.05 and 5 s^{-1} for HTPB4200/C18-clay (5 wt %). The first and the second heating began immediately after a shearing of 1 s^{-1} for 15 min at 26 °C. After heating, the sample was kept at 136 °C for 2 min and then cooled.

2. Effect of the Steady Shear Rate on the Rheological Behavior. To study the influence of the shear stress on the rheological behavior and to obtain a better understanding of the reversible transition, we further performed steady shear experiments at different shear rates. Figure 4 shows the temperature dependence of the steady shear viscosity at shear rates of 0.05 and 5 s^{-1} for the HTPB4200/C18-clay (5 wt %) sample.

For the first heating scan of the as-prepared sample, the irreversible transition temperature shows a moderate decrease from 72 to 60 °C when the shear rate is increased from 0.05 to 5 s^{-1}. As discussed above, this irreversible transition arises from the clay exfoliation due to the strong polymer−clay interaction above the transition temperature. The current observation implies that shear stress can improve the clay exfoliation. Stronger shear stress leads to a lower transition temperature. This conclusion is in good agreement with previous work on polymer/clay nanocomposites.[1a,2] The viscosity of the as-prepared sample at 26 °C changes slightly with different shear rates. However, the viscosity at 136 °C decreases remarkably with the increasing shear rates after the first heating scan. This indicates that a strong shear stress can led to partial orientation of the exfoliated clay sheets above the transition temperature and weakens the irreversible transition in the first heating scan. The most obvious irreversible transition corresponding to clay exfoliation in the first heating scan can be observed under a relatively low shear rate. This observation is very important when using rheological measurements to determine the critical temperature of the clay exfoliation when preparing polymer/exfoliated-clay nanocomposites.

For the first cooling scan and the second heating and cooling scans shown in Figure 4, the reversible transition under shear rates of 0.05 and 5 s^{-1} can also be observed. The existence of the reversible transition under different shear rates indicates that the origin of this transition is independent of the shear field. The second heating scan began immediately after a shear of 1 s^{-1} for 15 min at 26 °C. A dramatic orientation−disorientation transition can be observed under a shear rate of 0.05 s^{-1}, and the final viscosity at 136 °C is much higher than the initial value. On the contrary, because of the strong shear orientation effect under high shear rate of 5 s^{-1}, this transition is weakened and the transition temperature is increased. The final viscosity at 136 °C is considerably lower than that at a shear rate of 0.05 s^{-1}. Since the effect of the shear field on the reversible transition is less important under very low shear rate, the origin of the reversible transition could be well elucidated. It is interesting to note that the remarkable reversible transition in the second heating scan is very similar to the irreversible transition in the first heating scan at a low shear rate of 0.05 s^{-1}. This provides more evidence that the temperature-sensitive polymer−clay interaction should be a key factor for the reversible and irreversible transitions under shear field. This result provides further support to our earlier conclusion about the origin of the reversible transition at shear rate of 1 s^{-1}.

In the second cooling scan, the reversible transition is very weak due to the weak shear orientation effect on the disordered exfoliated clay at a shear rate of 0.05 s^{-1}. As a result, the final viscosity at 26 °C is much higher than the initial viscosity at the beginning of second heating scan. On the other hand, the reversible transition is also very weak due to a strong shear orientation effect at a shear rate of 5 s^{-1}. The final viscosity at 26 °C is much lower than that at shear rate of 0.05 s^{-1}, and it reaches the initial value at the beginning of second heating scan. This result also indicates that the disorientation state of clay cannot be fully destroyed by the shear rate of 0.05 s^{-1}, as 5 s^{-1} does. It is direct evidence for the maintenance of the shear-induced disorientation. We also observed in Figure 4 that shear-induced orientation under stronger shear field will result in the increase of the transition temperature. The above results indicate that an obvious reversible transition in the second cooling scan can only be observed at a moderate shear rate, e.g. 1 s^{-1}, as shown in Figure 2.

In the previous work by Schmidt et al.,[15] it was concluded that the recovery from the SANS anisotropy is much faster than expected from simple Brownian motion of only the clay particles, which is indicative of the dynamic coupling of the polymer chains to the clay. This conclusion is consistent with our conclusions. Although there have been several rheological studies of shear-induced orientation of the intercalate polymer−clay nanocomposites and solutions,[15] most of these studies were performed at a fixed temperature. Few studies were reported on reversible orientation−disorientation transition near certain critical temperature for the exfoliated-clay polymer nanocomposites. To our knowledge, our work is the first rheological observation of the in-situ exfoliation process and reversible orientation−disorientation transition of layered silicate in polymer/organo-clay nanocomposites under steady shear field.

3. Observation of the Unusual Rheological Behavior by Dynamic Oscillatory Shear. In the linear dynamic oscillatory shear experiments, we focus on the storage modulus (G') instead of the loss modulus (G''), as G' is much more sensitive to the mesoscopic structural changes of the samples in dynamic oscillatory shear experiments than G'' is.[1a] On the other hand, because of the small-amplitude oscillation in the linear region, shear-induced orientation is unlikely to take place. Therefore, we can study the effect of a shear field on the unusual rheological behavior in steady shear experiments by comparing to the corresponding results in the dynamic shear experiments.

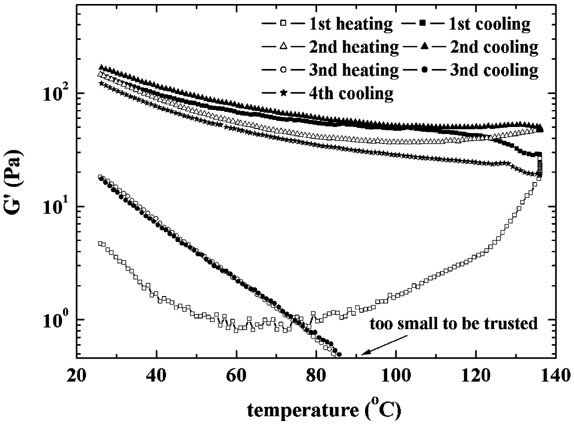

Figure 5. Temperature dependence of the storage modulus (G') of HTPB4200/C18-clay (5 wt %) nanocomposites at constant $\omega = 6.28$ rad/s. The first and the third heating scans began immediately after a shearing of 1 s^{-1} for 15 min at 26 °C and began with the as-prepared sample and exfoliated sample, respectively. The second heating scan began without shearing immediately after first scan. The fourth cooling scan began immediately after a shearing of 1 s^{-1} for 30 min at 136 °C, and the heating process is displayed in Figure 6. In the third heating and cooling scans, the value of G' was too small to be trusted from 85 to 136 °C because of the limitations of the rheometer.

Figure 5 shows the temperature dependence of storage modulus G' for the HTPB4200/C18-clay (5 wt %) nanocomposite at different scan times. It is interesting to note that an obvious transition temperature (ca. 65 °C) close to that obtained in the steady shear experiment can be observed in the first heating scan of the as-prepared sample. Because shear-induced orientation is negligible during small-amplitude oscillation in the linear region, the above result unambiguously confirms again that a strong polymer−clay interaction is the determining factor for the irreversible structure transition of the clays from an intercalation state to an exfoliation state. In subsequent cooling and second heating and cooling scans, because the exfoliated clays cannot be orientated under small-amplitude oscillation in the linear region, no obvious G' transition can be observed. The decrease/increase of G' in the cooling/heating scan should be attributed to the temperature effect. Comparing this result with that obtained in the cooling scan at a shear rate of 0.05 s^{-1} shown in Figure 4, it is interesting to note that only a steady shear field can induce the observable orientation−disorientation transition.

The third heating scan began with the exfoliated sample after the same pretreatment condition in the second heating scan shown in Figure 2. We found that G' is much smaller than that in the second scan due to the strong shear-induced orientation, and no obvious G' transition was observed. The large decrease of G' in the third heating scan can be ascribed to the temperature effect. The perfect match of the heating and cooling curves means no irreversible chemical changes took place during the scans, and the orientation state of the clays was kept unchanged during the heating and cooling scans. These results indicate that thermal motion alone cannot overcome the energy barriers between the orientation and disorientation state.[19] The above dynamic oscillatory experiments were also carried out with a frequency of 31.4 rad/s, and similar rheological behavior was obtained. On the basis of the above experiments, we conclude

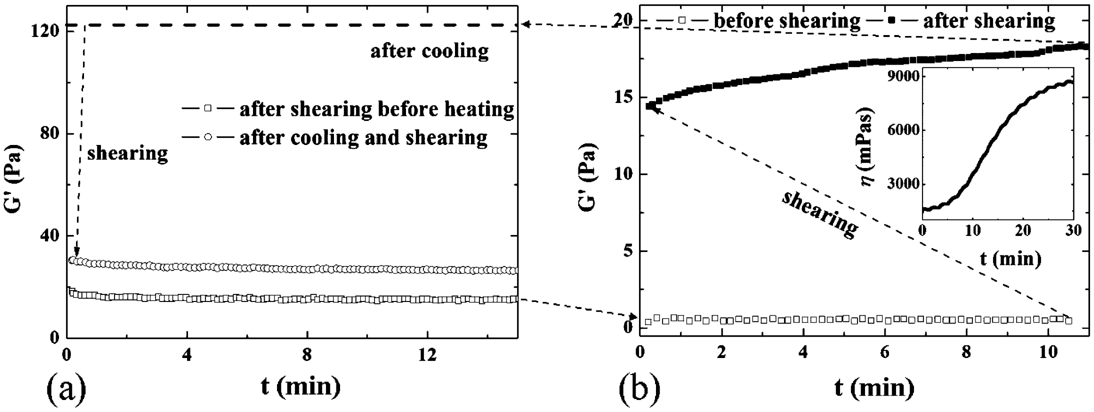

Figure 6. Time dependence of the storage modulus (G') of HTPB4200/C18-clay (5 wt %) nanocomposites at (a) 26 and (b) 136 °C, respectively. The cooling process from 136 to 26 °C is shown in Figure 5. The experiments in (a) began immediately after a shear of 1 s^{-1} for 15 min at 26 °C. The lower line in (b) began without shear. The inset in (b) is the time dependence of the steady shear viscosity of the sample (squares) under a shear of 1 s^{-1} for 30 min at 136 °C, indicating "shear-induced disorientation", and the upper line of the filled squares in (b) began immediately after shearing is shown in an inset.

that the temperature-sensitive polymer−clay interaction alone is not enough to account for the observable orientation−disorientation transition. A shear field with strong enough strength is needed to induce such a reversible transition. This phenomenon can be termed a "shear-induced orientation−disorientation" transition.

4. Shear-Induced Disorientation and Disorientation Kinetics. Both the oriented and disoriented states of the fillers have significant effects on the final physical and chemical properties of nanocomposites. These effects are of great importance to specific applications. Disorientation relaxation of different oriented nanocomposites immediately after orientation−disorientation has been studied by several groups, and different mechanisms related to the origins of the disorientation process and the factors controlling it have been proposed.[15,16] It was suggested that the recovery of the microstructure following flow-induced alignment is far from resolved for the case of polymer/clay nanocomposites. In the above sections, shear-induced orientation−disorientation transition of clays under different shear fields has been investigated. To obtain a better understanding of the shear-induced disorientation and explore the disorientation process of clay without a shear field, we performed disorientation relaxation experiments in the linear viscoelastic region for the HTPB/exfoliated-clay gels.

The time dependence of the storage modulus of the HTPB4200/C18-clay (5 wt %) nanocomposites immediately after a shear of 1 s^{-1} for 15 min at 26 °C is shown in Figure 6a (squares). We found that G' is roughly a constant, which is contrary to the results of Ren and co-workers.[16] After the sample was heated to 136 °C without shear, no relaxation of G' can be observed, as shown in Figure 6b (squares). However, when this oriented sample was sheared at 136 °C (a temperature greater than the transition temperature) at a shear rate of 1 s^{-1} for 30 min, the steady shear viscosity increased dramatically and nearly reached its maximum after 30 min (inset in Figure 6b). The viscosity was 6 times that before shearing. On the basis of our previous discussion of the origin of the orientation−disorientation transition of the clays under different shear fields, this result is not surprising and provides additional direct experimental evidence of what is termed "shear-induced disorientation". After shear-induced disorientation, we began immediately to observe the time dependence of G'. It is very interesting to note that the same G' relaxation was observed as that reported by Ren et al.[16] The sample was then cooled in a dynamic oscillatory shear experiment, as shown in Figure 5 (fourth cooling scan). A remarkable decrease of G' after a shear at 1 s^{-1} for 15 min at 26 °C indicates that only physical processes took place during the many heating and cooling scans. The above different behavior of the disorientation relaxation at different temperature observed in the HTPB/exfoliated-clay nanocomposites clearly indicates that the origin of the disorientation process under quiescent conditions should be attributed to the temperature-sensitive polymer−clay interaction instead of Brownian motion.

It should be noted that "shear-induced disorientation" does not mean that shear is the only way to induce disorientation in these nanocomposites. For the 12PB sample without hydroxyl end groups, "shear-induced disorientation" cannot be observed. As mentioned above, the polymer−clay interaction is the key factor controlling the disorientation process. In the previous rheological study on PS/clay nanocomposites by Ren et al.,[16] it was found that the viscosity changes by about 2 orders of magnitude from 140 to 170 °C under large-amplitude oscillatory experiments. This result is similar to the observed "shear-induced disorientation" in our system (HTPB/C18-clay) above the transition temperature. They suggested that the disorientation process is non-Brownian and that Brownian forces alone are unable to overcome the energy barriers created by such structures.[19] Application of shear is considered to change the energy landscape and allow for the system to access new metastable states.[20] They also proposed that the weak attraction between the polymer and the layered silicate and the geometric restrictions resulting from the network structure and collective motions possibly provide the driving force for the recovery. Ren et al. also suggested that the precise origin of the disorientation process in polymer/clay systems can be determined and should be pursued by carefully controlling the thermodynamic interactions (i.e., making them extremely weak and extremely strong). The HTPB/C18-clay and 12PB/C18-clay nanocomposites used in our present work are almost ideal systems with strong and weak interactions between polymer and clay, respectively.

Based on the above conclusions, our experimental results are consistent with those reported by Ren et al., which demonstrated that the disorientation process observed in the PS/clay nanocomposites could be attributed to the improved polymer−clay interaction between PS and the clay. Compared with previous work on the disorientation process, the importance of our present work is that the origin of the disorientation transition and relaxation under shear field and quiescent conditions are well elucidated. Our experimental results clearly indicate that both the polymer−clay interaction and the shear field are critical to

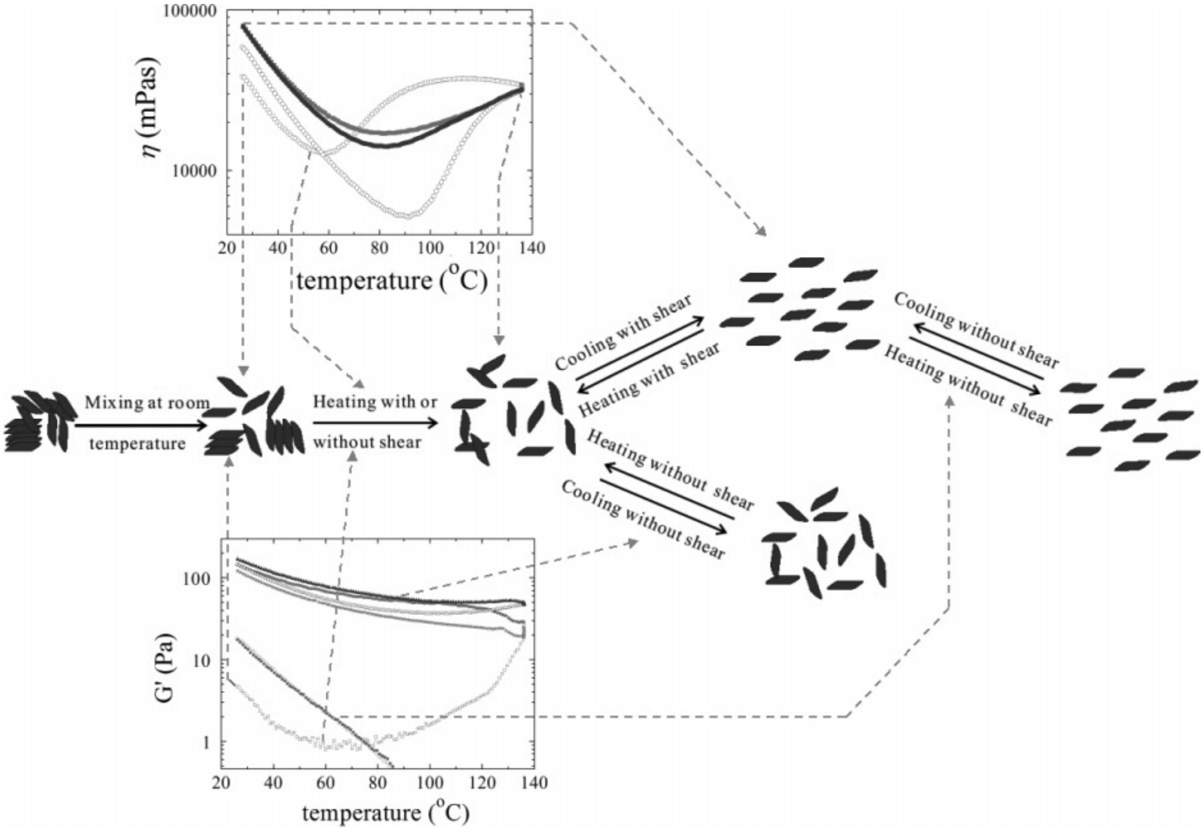

Figure 7. Schematic diagram related to the unique rheological behavior and evolution of clay structures.

control the disorientation process of oriented clay layers. It should be pointed out that the alignment of the silicate layers in rubber/clay gels is easily achieved at low shear rates, whereas large-amplitude oscillation shear can led to the alignment in many polymer/clay nanocomposites with higher T_g for the polymers. The merit of our sample is that both the orientation and disorientation process can be observed within a wide range of temperature. As a result, the origin of the orientation−disorientation process can be clearly elucidated.

5. Suggested Model Related to Clay Exfoliation, Clay Orientation, and Disorientation as Well as Polymer−Clay Interaction. On the basis of the foregoing rheological results, a tentative model could be suggested to describe the clay exfoliation, clay orientation, and disorientation behavior as well as polymer−clay interaction related to the observed unique rheological behavior at different temperature in rubber/clay nanocomposite gels. A schematic diagram is shown in Figure 7. For the as-prepared HTPB/C18-clay sample mixing at room temperature, the clay is partially exfoliated; when heating with or without shear, complete exfoliation can be achieved at temperatures greater than the transition temperature. The exfoliated silicate layers can be oriented by cooling with shear. Shear-induced disorientation can be observed at temperatures greater than the transition temperature. The orientation of silicate layers can be maintained at wide range of temperatures without shear. Both the temperature-sensitive polymer−clay interaction and the shear field are critical factors controlling the disorientation process of oriented clay layers. This model can be used to explain our observations, and it is consistent with all previous experiments from other groups.

Conclusions

We have presented steady and dynamic oscillatory shear experiments to investigate the exfoliation and orientation−disorientation transition of clays, focusing on the influence of the polymer−clay interaction and the shear field on the rheological properties in liquid polybutadiene rubber/organoclay nanocomposite gels. Both irreversible and reversible viscosity transitions were observed in the temperature range from 26 to 136 °C in steady shear experiments on as-prepared and exfoliated samples, respectively. We attribute the irreversible transition to the clay exfoliation process and the reversible transition to orientation−disorientation of the exfoliated clays. These transitions depend strongly on the end groups, molecular weight of the liquid rubber, and the shear field. These results confirm our previous conclusions.[11] Determination of the transition temperature can be very useful for the preparation of liquid rubber/exfoliated-clay nanocomposites. Combined with the results from steady and dynamic shear experiments, our experiments clearly demonstrated that the temperature-sensitive polymer−clay interaction is key to the nature of the reversible orientation−disorientation transition, while the shear field is a crucial factor inducing this reversible transition. We regard this disorientation process as “shear-induced disorientation”. We suggest that the application of shear could change the energy landscape and allow for the system to access new metastable states.[16,20]

To the best of our knowledge, this is the first rheological observation of the in-situ exfoliation process and orientation−disorientation transition of clays arising from the polymer−clay interaction, the shear field, and temperature in polymer/clay nanocomposites. Finally, a tentative model was suggested to describe the exfoliation and orientation−disorientation transition of the clays as well as the polymer−clay interaction related to the observed unique rheological behavior in these nanocomposite gels. We also suggested that the HTPB/clay nanocomposite gels could be an ideal model system because it can provide detailed information about the effect of the polymer−clay interaction on the exfoliation of the clays and unique rheological behavior in polymer/nanocomposites over a wide range of temperatures. Further investigations may provide new insight into the mechanism of clay exfoliation for the development of novel polymer nanocomposites with unique rheological behaviors.

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