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Room temperature spontaneous exfoliation of organo-clay in liquid polybutadiene: Effect of polymer end-groups and the alkyl tail number of organic modifier

Jianjun Zhu [a], Xiaoliang Wang [b], Fangfang Tao [b], Gi Xue [b,*], Tiehong Chen [a,*], Pingchuan Sun [a,*], Qinghua Jin [a], Datong Ding [a]

[a] *Key Laboratory of Functional Polymer Materials, Ministry of Education, Department of Materials Chemistry, College of Chemistry and College of Physics, Nankai University, Tianjin 300071, China*
[b] *Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, China*

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Abstract

Disorderly exfoliated telechelic liquid polybutadiene/organo-clay nanocomposite gel was, for the first time, successfully prepared at room temperature of 26 °C by simply compounding of carboxyl-terminated polybutadiene (CTPB) with organo-clay containing surfactant modifier with two alkyl tails. The dispersion behavior of organo-clay in liquid polybutadiene/organo-clay nanocomposite gels were systematically investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM), rheology and compatibility experiments, focusing on the influence of the functional end-groups of the liquid rubber and the alkyl tails number of the organic modifier on the clay exfoliation. A unique liquid-like reversible rheological behavior was observed for CTPB/exfoliated clay nanocomposite gels with organic modifier having two alkyl tails, which is totally different with that of other samples (HTPB/C18-clay, HTPB/D18-clay and CTPB/C18-clay). And it is noteworthy that CTPB exhibits a higher level of dispersion with an organo-clay with two alkyl tailed surfactant than that with one alkyl tail.

Keywords: Carboxyl-terminated polybutadiene; Organo-clay; Nanocomposite gels

1. Introduction

Because of the nanoscale effect, high interface areas and strong interfacial interaction between dispersed phase and polymer matrix, polymer/clay nanocomposites exhibit unique physical and chemical properties typically not shared by their conventional macro- or micro-composite and have attracted much attention over the past decades [1–7]. The final properties of nanocomposites are determined by the quality of the clay dispersion in the polymer matrix, and therefore, the control of clay dispersion morphology is currently an attractive research field. On the basis of the dispersion state of the clay sheets in polymer matrix, two types of morphology can be achieved in the composites: intercalated or exfoliated. The exfoliated nanocomposites are more desirable than intercalated ones because strong synergistic effects between polymer and silicate layers can be obtained and the properties of the nanocomposite materials are optimized. Usually, complete exfoliation of clay in polymer matrix requires special conditions, such as matching of the proper reactive temperature and polymerization rate, curing agent or suitable shearing stressing [8–14]. Till now, a simple and mild condition to prepare the polymer/exfoliated clay nanocomposites is still a significant challenge, and which is of great importance to industrial field.

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* Corresponding authors. Tel./fax: +86 22 23507975.
E-mail addresses: spclbh@nankai.edu.cn (P. Sun), chenth@nankai.edu.cn (T. Chen), xuegi@nju.edu.cn (G. Xue).

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To facilitate the efficient industrial production of exfoliated polymer/clay nanocomposites, proper conditions have to be selected to promote the penetration of polymer into the gallery between the clay sheets. The key approaches for improving the degree of clay exfoliation is to adjust polymer/clay interaction, and then minimizes energy barrier for the clay dispersion [15–20]. Generally, organic modifiers, such as proper cationic surfactants, are employed to modify the clay surface and the surfactants may contain reactive functional groups and/or molecular units similar to those of the polymer matrix [21–24]. When cationic surfactants were used as organic modifiers, the number of alkyl tails played different roles in the preparation of polymer/clay composites. Paul and co-workers reported that a polar polymer such as nylon-6, exhibits a higher level of exfoliation with organo-clay containing surfactant with one alkyl tail than that with two alkyl tails, while nanocomposites prepared from non-polar polymers, such as polyethylene, show completely opposite trends [25–28].

The effects of end-functionalized polymers on the preparation and the morphologies of polymer/clay nanocomposites have been studied both theoretically and experimentally in recent years. In the systematic theoretical works by Balazs et al. using self-consistent field (SCF) theory, it has been concluded that the addition of functionalized chains can promote the separation of the clay sheets within the polymer matrix [17–20]. In our previous work, we have reported a new class of telechelic rubber/exfoliated clay nanocomposite gels using hydroxyl-terminated polybutadiene (HTPB) and organically modified clay [29,30]. This result is believed to stem from the favorable interaction of the end-functional hydroxyls with the polar head of the organic modifier promotes the formation of hydrogen bonding between the hydroxyl end-groups and the oxygen and/or hydroxyls of the clay sheet. However, to achieve exfoliation of the clay, heating the mixture at about 80 °C is indispensable. This indicates that there exists an energy barrier for the clay to be intercalated and exfoliated in the polymer matrix and spontaneous exfoliation of the clay remains still a challenge.

The rheological behavior of polymer/clay has also attracted significant attention in recent years [31–38]. It is well known that both the nanostructure of clay and the polymer/clay interaction can strongly influence the rheological behaviors of polymer/clay nanocomposites. Understanding the rheological properties of nanocomposite is not only important to obtain fundamental knowledge of polymer process, but also is helpful to understand the structure-property relationship in these composite materials. Studies on these systems might also lead to a better understanding of the dynamics of nanoscopically confined polymers. In our previous work, rheology has been proved to be a powerful technique to elucidate the effect of polymer/clay interaction on the clay exfoliation, clay orientation and disorientation [38].

In this work, by adjusting the interaction between polymers with functional end-groups and the organic modifiers, we report, for the first time, a room temperature spontaneous exfoliation of the organo-clay in carboxyl-terminated polybutadiene (CTPB) with the clay concentration as high as 10 wt%. This simple and mild condition to prepare the polymer/exfoliated clay nanocomposites is of great importance to industrial applications. The cooperation of the functional end-groups of polymer and alkyl tail number of organic modifier is proved to govern the degree of clay exfoliation by rheology and compatibility experiment.

2. Experimental section

2.1. Materials

Liquid polybutadiene oligomer (PB with average molecule weight (M_n) of 3300) without functional end-groups was purchased from Aldrich Chemical Co. The commercial products, hydroxyl-terminated polybutadiene (HTPB) and carboxyl-terminated polybutadiene (CTPB), were purchased from Zibo Qilong Chemical and Engineering Co. Ltd. (China), with M_n of 4200 and 4100, respectively. Organo-clays (C18-clay (commercial name DK1) and D18-clay (commercial name DK4)), were purchased from Fenghong Clay Corp. (China), which contain octadecyltrimethylammonium chloride (C18A) and dioctadecyldimethylammonium chloride (D18A), respectively. The main difference of these two organo-clays is the number of alkyl tails in organic modifier which is attached to the surface of clay sheets.

2.2. Preparation of liquid polybutadiene/organo-clay nanocomposite gels

Liquid polybutadiene/organo-clay nanocomposite gels can be easily prepared by simply compounding organo-clay (10 wt%) with liquid rubber at room temperature (26 °C) with a slight stir.

2.3. Compatibility experiments of liquid polybutadiene with organic modifier

The mixtures of liquid polybutadiene and organic modifier were placed at room temperature (26 °C) for several hours. The weight ratio of organic modifier and liquid polybutadiene was 1:49, which is the same as the weight ratio of organic modifier and liquid polybutadiene in nanocomposite gels. The corresponding mixtures were denoted as HTPB/C18A, HTPB/D18A, CTPB/C18A and CTPB/D18A.

2.4. Characterization

2.4.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) experiments were performed in reflection 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.

2.4.2. Transmission electron microscopy (TEM)

The microstructure of clay in nanocomposite gels was observed on a HITACHI-800 transmission electron microscope. Samples for TEM were cut into ultra-thin sections with a diamond knife at a temperature of −90 °C using a LKB2008 microtome. Microtomed thin sections were mounted on copper grids without staining.

2.4.3. Rheology experiments

Rheology experiments were conducted on a HAAKE RheoStress 600 instrument. Steady shear measurement was conducted by using a set of 35 mm diameter parallel plates with a sample thickness of ca. 0.8 mm. The viscosities of three liquid rubbers and their clay composites at 26 °C were measured with the shear rate of 0.05 s^{-1} for 10 min. The viscosity value was the mean value of the equilibrium viscosity. The temperature dependence of the steady shear viscosity was obtained in the temperature range 26–116 °C with a heating rate of 2 °C/min and the shear rate of 0.05 s^{-1}. It is reported that polymer chain 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 clay sheets in the nanocomposite gels [39,40]. To start with an oriented state, a shear of 0.05 s^{-1} for 10 min was imposed on the as-prepared samples before heating. To prevent the degradation of the samples, all the rheological experiments at elevated temperatures were performed under protection of nitrogen gas.

3. Results and discussion

3.1. Dispersion and morphology of organo-clay in liquid polybutadiene/organo-clay nanocomposite gels

Liquid polybutadiene/organo-clay nanocomposite gels can be easily prepared by compounding organo-clay with liquid polybutadiene at room temperature of 26 °C with slight stir. Fig. 1 illustrates the transparent property of CTPB/D18-clay nanocomposite gels after mixing the D18-clay and CTPB for 2 min and 2 h at room temperature. It can be observed that the intercalating process was fast, and it looked as if the D18-clay was "dissolved" in CTPB, and a transparent gel-like homogenous composite could be obtained from the starting turbid mixture after several hours. The same phenomenon for HTPB/C18-clay, HTPB/D18-clay and CTPB/C18-clay was also observed.

The degree of clay dispersion is usually characterized by XRD. Generally intense reflection in the range of 3–9° (2θ) indicates an ordered intercalated nanocomposites. In exfoliated nanocomposites, on the other hand, where single silicate layers (1 nm thick) are homogeneously dispersed in the polymer matrix, and XRD patterns with no distinct diffraction peak in the range of 3–9° (2θ) could be observed. The XRD patterns of the two organo-clays (C18-clay and D18-clay) and the series of polymer/clay composites (with 10 wt% of clay) are displayed in Fig. 2. From Fig. 2, the d_{001}-spacing of D18-clay containing two alkyl tails surfactant is 3.6 nm, which is greater than that of C18-clay (2.3 nm). This indicates that organic modifier containing two alkyl tails can separate the platelets farther apart than that containing one alkyl tail, thereby greatly reducing the attraction between platelets. From the XRD patterns of the C18-clay, the PB/C18-clay, it is obvious that at room temperature PB (without functional end-groups) chains failed to intercalate the C18-clay. The XRD patterns of HTPB/C18-clay and CTPB/C18-clay prepared at room temperature display weak and broad humps, indicating the existence of intercalated/exfoliated clay. From the XRD patterns of the D18-clay, the PB/D18-clay and the HTPB/D18-clay, it is obvious that at room temperature both PB and HTPB chains failed to intercalate the D18-clay, giving rise to immiscible structures of clay tactoids. However, the XRD pattern of CTPB/D18-clay prepared at room temperature displays no obvious (001) basal reflection peak, indicating possible exfoliation of the clay. The absence of the (001) peak is not due to the low quantity of clay in the nanocomposite gels, as the (060) in-plane reflection peak of the single-clay sheet could still be detected (the inset of Fig. 2b) [41]. Therefore, these experiments clearly indicate again that the

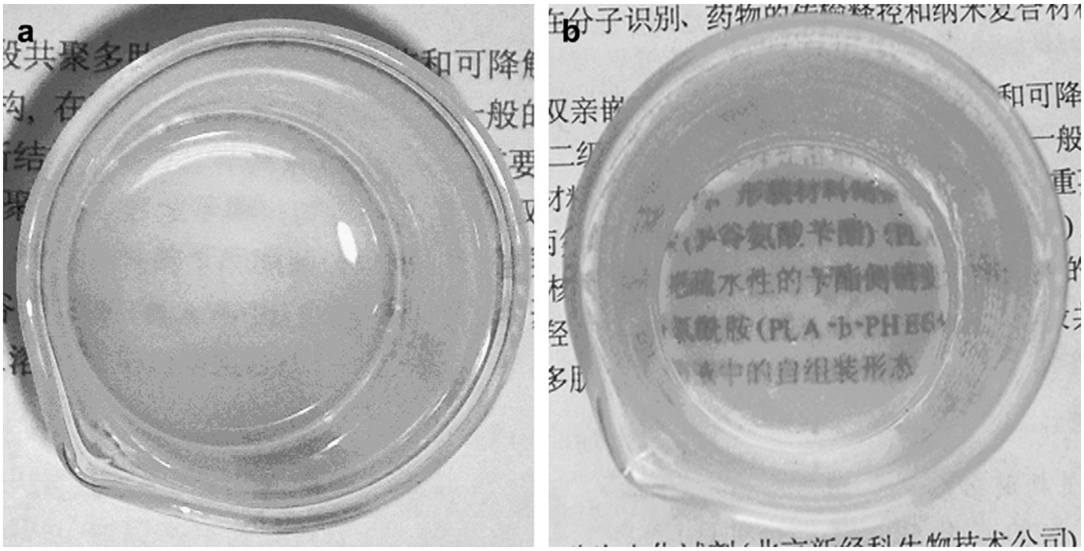

Fig. 1. The transparent property of CTPB/D18-clay after mixing the D18-clay and CTPB for (a) 2 min and (b) 2 h at room temperature. The thickness of the gel is about 5 mm, and the letters are on the other side of the gel.

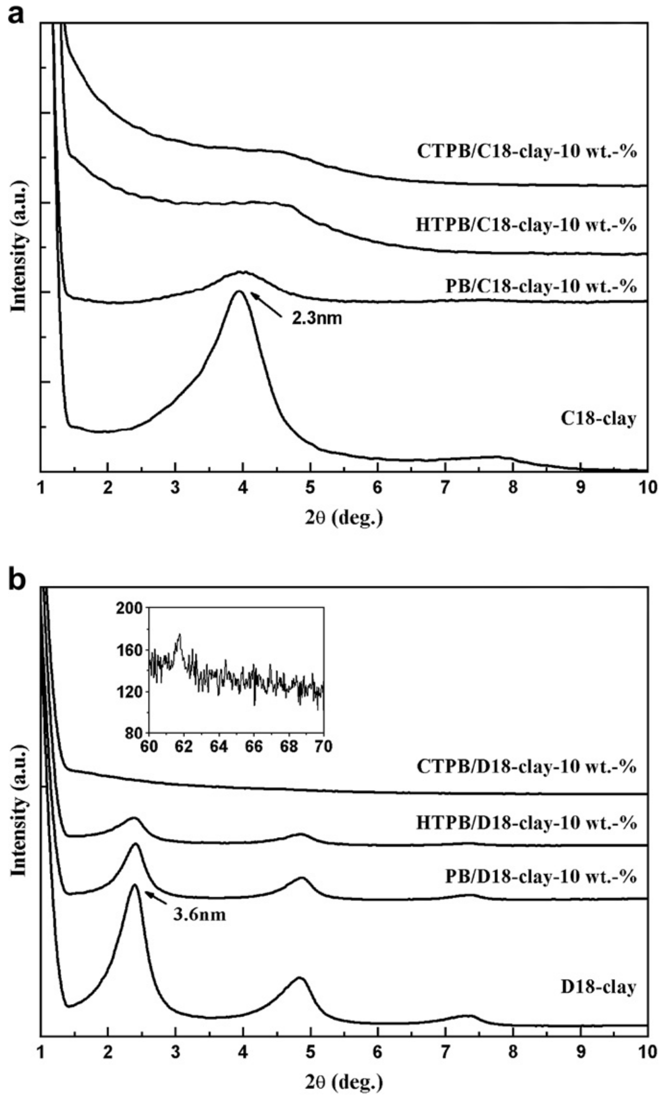

Fig. 2. XRD patterns of organo-clays and corresponding liquid polybutadiene/organo-clay nanocomposite gels for organic modifier having (a) one and (b) two alkyl tails. These samples are prepared by simple compounding at room temperature. The inset of Fig. 2b displays the in-plane 060 clay reflection of CTPB/D18-clay (10 wt%).

end-groups of liquid rubber have a significant effect on the exfoliation of the clays, which is consistent with the results of our previous work [29,30]. The most important finding from these XRD experiment is that disorderly exfoliated rubber/clay nanocomposite gel is possibly obtained by one-step compounding of CTPB with organo-clay having two alkyl tails surfactant rather than one alkyl tail organo-clay at room temperature (26 °C).

In general, the absence of diffraction peaks can be attributed to two possible reasons: (a) exfoliated structure and (b) disordered intercalated structure with an average *d*-spacing higher than 7 nm. Because XRD generally fails to distinguish the disordered intercalated and exfoliated morphology (absence of diffraction peaks in XRD patterns), TEM measurements have been further performed to observe the dispersion morphologies of clay directly. Fig. 3 shows the TEM micrographs of the CTPB/D18-clay (10 wt%) and CTPB/C18-clay (10 wt%) nanocomposite gels. The nanoscale structure of the completely exfoliated clay sheets in CTPB/D18-clay (10 wt%) nanocomposite gel is clearly observed (the dark lines is the silicate layers). Fig. 3a is a low magnification version, in which the disorderly exfoliated nanolayers of the clays were observed. Moreover, individually dispersed clay platelets were clearly observed at a high magnification version in Fig. 3b, which further confirms the disorderly exfoliated clay structure. The partial exfoliated clay sheets in CTPB/C18-clay (10 wt%) is observed in Fig. 3c. These TEM observations are consistent with the above XRD results. Therefore, one can incontestably identify that in the CTPB/D18-clay nanocomposite gels, which is with a clay loading up to 10 wt% and prepared at room temperature, the clays are spontaneously and completely exfoliated.

One may wonder why clay with organic modifier having two alkyl tails can be exfoliated easily in CTPB at room temperature with the clay loading up to 10 wt%. In the following section, rheological measurements and compatibility experiments are performed to elucidate polymer/clay interaction and the process of clay exfoliation, which should be crucial to understanding the above results.

3.2. Discussion of polymer/clay interaction

It is well-known that the polymer/clay interaction is a key factor in controlling the clay exfoliation. In the following section, polymer/clay interaction is studied by rheological measurements and compatibility experiments. The viscosities of three liquid rubbers and their clay composites (with 10 wt% of clay) were measured and the results are listed in Table 1. The viscosities of PB/C18-clay and PB/D18-clay increased only 1.42 and 1.65 times, respectively, if compared with that of the pure PB, indicating the absence of strong polymer/clay interaction in these two composites [38]. It is noteworthy that the viscosities of CTPB/D18-clay, CTPB/C18-clay and HTPB/C18-clay were increased by 464, 325 and 260 times, respectively, if compared with the pure liquid rubbers, indicating the presence of strong polymer/clay interaction [38]. On the contrary, the relative viscosity of HTPB/D18-clay increased only 5.5 times than HTPB. It is not surprising that both types of the organo-clays can not be intercalated or exfoliated by PB because no strong attractive interaction can be expected between PB and the surfactant residing at the clay surface due to the lack of functional end-groups. Organo-clay with one alky tail rather than that with two alky tails can be partly exfoliated in HTPB matrix at room temperature, while for the case of CTPB/D18-clay, spontaneous exfoliation of organo-clay at room temperature can be achieved.

The above phenomena would be ascribed to the different polymer/clay interactions, which can be tuned by adjustment of the interaction between the end-functionalized polymer and the surfactant modifiers in organo-clay. Compatibility between the liquid polybutadiene and organic modifiers are shown in Fig. 4. It is interesting to note that at room temperature well compatibility only exists between CTPB and D18A (transparent mixture), while others show poor compatibility (turbid mixture).

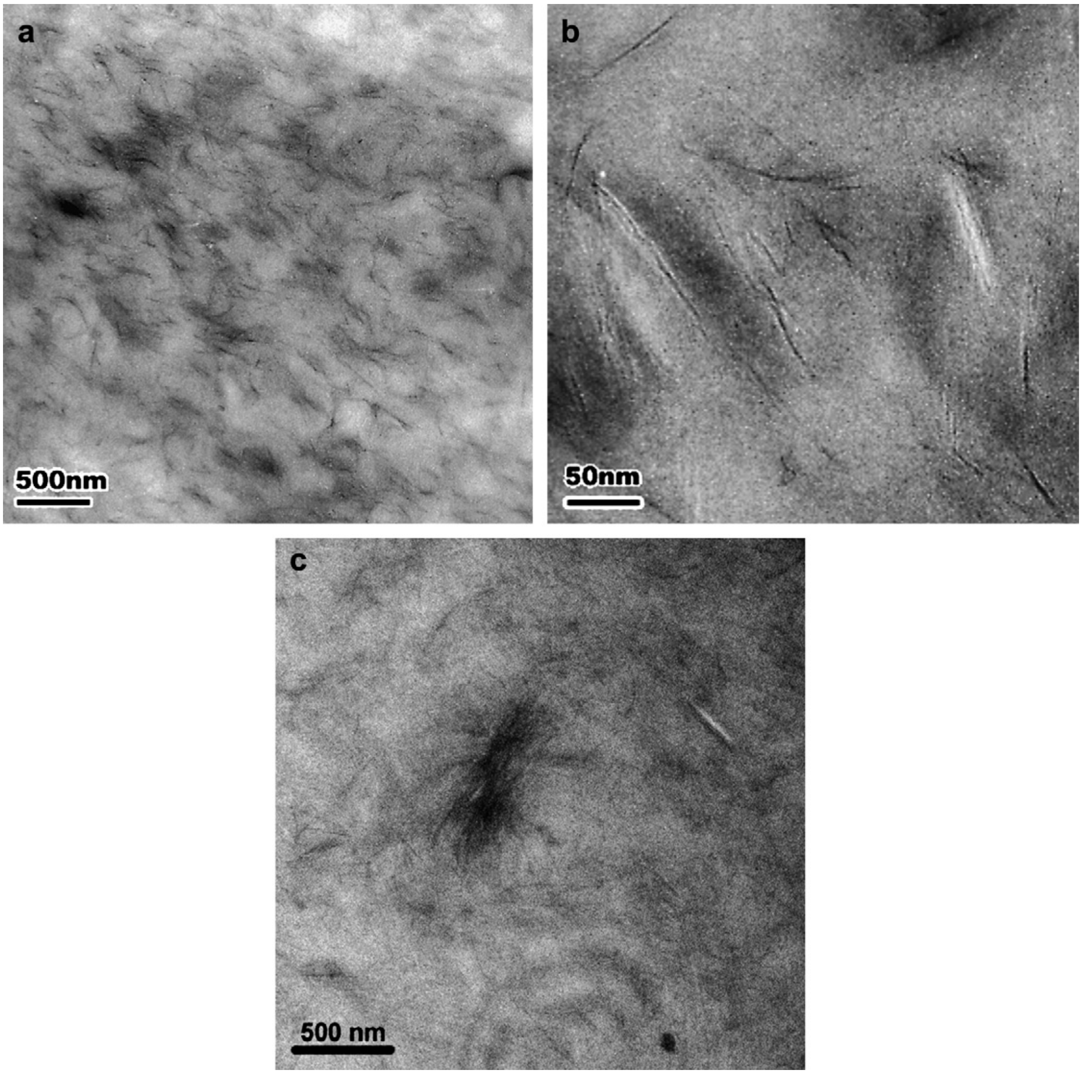

Fig. 3. TEM micrographs of the CTPB/D18-clay (10 wt%) nanocomposite gel with (a) low and (b) high magnifications. (c) TEM micrographs of the CTPB/C18-clay (10 wt%) nanocomposite gel with low magnification.

3.3. Unique rheological behavior of liquid polybutadiene/organo-clay nanocomposite gel

It is well known that the nanostructure of clay and the polymer/clay interaction can strongly influence the linear and nonlinear rheological responses of polymer/clay nanocomposites. Clay sheets are highly anisotropic inorganic nanoparticles, which can be oriented under shear field. Shear-induced orientation can led to a considerable decrease of the sample viscosity. The origin of the clay disorientation process and the factors controlling this process has been discussed [42]. In our previous work on HTPB/organo-clay nanocomposite gels, unusual irreversible and reversible rheological behaviors were observed under steady shear, and rheological experiments have been proved to be a powerful tool to investigate the polymer/clay interaction and their temperature dependence, the

Table 1
Steady shear viscosity at shear rate of 0.05 s^{-1} and room temperature (26 °C) of different liquid polybutadiene/organo-clay nanocomposite gels

	$\eta_{\text{pure rubber}}$ (mPas)	C18-clay (10 wt%)	D18-clay (10 wt%)
		η (mPas)	η (mPas)
PB	5.47×10^4	7.77×10^4	9.03×10^4
HTPB	2.06×10^4	5.36×10^6	1.04×10^5
CTPB	2.67×10^4	8.69×10^6	1.24×10^7

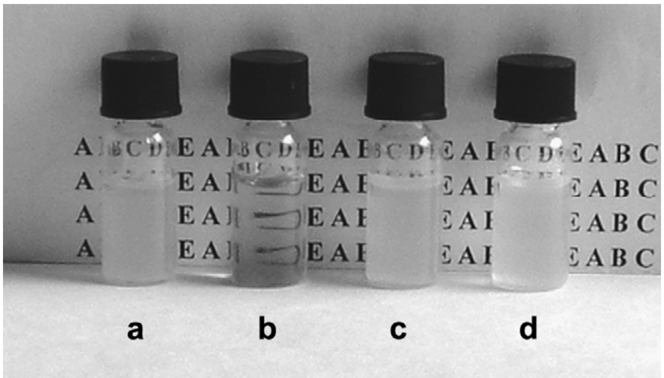

Fig. 4. Images of the compatibility of (a) CTPB/C18A, (b) CTPB/D18A, (c) HTPB/C18A and (d) HTPB/D18A mixtures at room temperature.

process of in situ clay exfoliation, and clay orientation and disorientation. Three factors, including temperature-sensitive polymer/clay interaction, shear-induced orientation effect and temperature effect should be considered. These three factors compete with each other or override one another to determine the final rheological properties of HTPB/organo-clay nanocomposite gels [38].

To elucidate the origin of clay exfoliation behavior in liquid polybutadiene/organo-clay with different polymer end-groups and alkyl tail number of organic modifier, and to get a better understanding of the influence of polymer/clay interaction and their temperature dependence on the process of clay exfoliation, rheological experiments were further carried out on these liquid polybutadiene/organo-clay nanocomposite gels.

In Fig. 5, it is observed that rheological behaviors of as-prepared samples with different polymer end-groups and alkyl tail number of organic modifier are obviously different for the heating and cooling scan. Firstly, attention should be paid to the steady shear viscosity at 26 °C before and after heating. In Fig. 5a, the steady shear viscosity of HTPB/C18-clay and CTPB/C18-clay at 26 °C after heating and cooling was about 7 and 3 times higher than that of samples at 26 °C before heating, while the steady shear viscosity of PB/C18-clay at 26 °C before and after heating and cooling are almost unchanged. In Fig. 5b, the steady shear viscosity of HTPB/D18-clay at 26 °C after heating and cooling was about 123 times higher than that of HTPB/D18-clay at 26 °C before heating, while the steady shear viscosities of PB/D18-clay and CTPB/D18-clay at 26 °C before and after heating and cooling are almost unchanged. The above rheological results provide another evidence of the exfoliation of clay in these gels, that is, the obviously different viscosity of samples (such as HTPB/C18-clay, CTPB/C18-clay and HTPB/D18-clay) at 26 °C before and after heating and cooling implies that further clay exfoliation happens at higher temperature, while the viscosity of samples (such as PB/C18-clay, PB/D18-clay and CTPB/D18-clay) at 26 °C before and after heating and cooling are almost unchanged, which implies that no further clay exfoliation occurred. Here, it is noticed that at 26 °C before heating PB chains failed to intercalate the organo-clay (according to the results of XRD), and PB chains still can not to intercalate the organo-clay at higher temperature. We can also infer that most of the clay sheets in the as-prepared CTPB/D18-clay nanocomposite gel have been exfoliated at 26 °C before heating. This assumption is supported by the above results of XRD and TEM. The steady shear viscosity provides important information about the degree of exfoliation, and agrees with our previous work on HTPB/organo-clay nanocomposite gels [29].

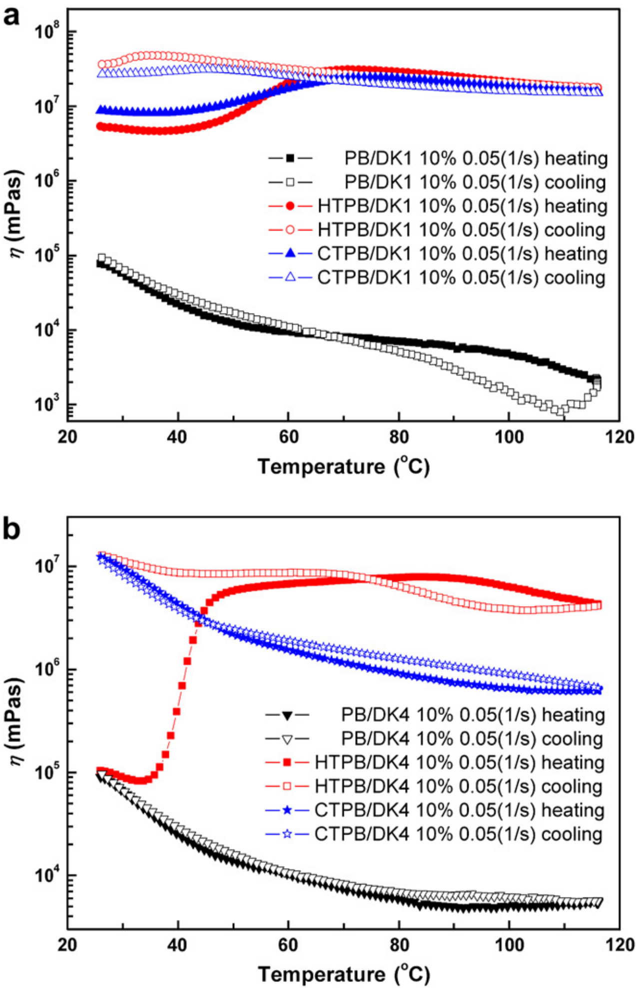

Fig. 5. Temperature dependence of the steady shear viscosity for liquid polybutadiene/organo-clay nanocomposite gels for organic modifier having (a) one and (b) two alkyl tails. The heating scans began immediately after a shear of 0.05 s^{-1} for 10 min at 26 °C. After heating, the sample was kept at 116 °C for 2 min and then cooled.

Again in Fig. 5a, for the first heating scan of the as-prepared CTPB/C18-clay samples, we found that the steady shear viscosity gradually decreased with increasing temperature from 26 °C to 48 °C, which can be attributed to the shear-induced orientation and temperature effect [38]. A dramatic increase of the viscosity occurred after a transition temperature (about 48 °C) indicates the presence of strong polymer/clay interaction leading a structure transition of CTPB/C18-clay from an intercalation state to an exfoliation state. This conclusion is further confirmed by the XRD results shown in Fig. 6. The XRD pattern of the as-prepared CTPB/C18-clay at 26 °C shows a weak and broad hump at around 4.5°(2θ), indicating the mixture of intercalated/exfoliated clay. After heating to 60 °C, which is greater than the transition temperature, the absence of the (001) basal reflection peak implies the complete exfoliation of clay. It is worthy to note that rheological behavior of HTPB/C18-clay, CTPB/C18-clay and HTPB/D18-clay are similar through the whole scan. The only difference among these samples is the transition temperature from intercalated to exfoliated state. In Fig. 5b, to our surprise, unique reversible rheological behavior of CTPB/D18-clay nanocomposite gels with organic modifier having two alkyl tails is observed, which is obviously different from that of those samples discussed in the above section. The steady shear viscosity of CTPB/D18-clay continuously decreases with increasing temperature in the range of 26−116 °C, and vice versa. The reversible transition can be confirmed by the fact that the final viscosity after the heating and cooling scans is close to that before the first heating, and the curve of rheology is almost completely

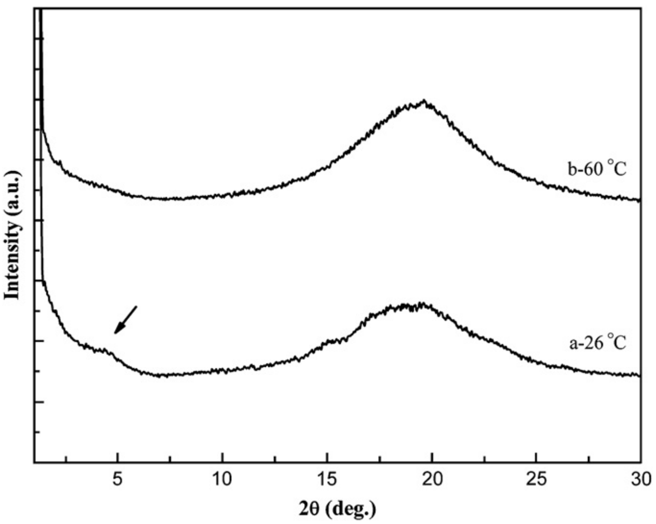

Fig. 6. XRD patterns of (a) as-prepared CTPB/C18-clay mixed at 26 °C and (b) as-prepared CTPB/C18-clay after heating to 60 °C.

overlapped for the heating and cooling scans. The absence of the irreversible transition corresponding to the exfoliation of clay in the first heating scan and high initial viscosity of CTPB/D18-clay implies that clay should be completely exfoliated in the as-prepared sample before the first heating scan. This completely exfoliated structure was confirmed by the XRD and TEM experiments (Figs. 1 and 2). The above rheological experiment for the as-prepared sample is a direct observation of the in situ exfoliation of clay in polymer/clay nanocomposites, and the critical temperature for clay exfoliation can be accurately determined, and this temperature is very important for preparing polymer/exfoliated clay nanocomposites.

3.4. Comparison with related work on polymer/organo-clay nanocomposite gels with different alkyl tail number of organic modifier

It is interesting to compare the present results with recent studies of polymer/clay nanocomposites with organic modifier having different alkyl tail numbers. Fornes et al. reported that a high level of exfoliation was achieved by using one alkyl tail organo-clay rather than zero/two alkyl tail organo-clay in nylon-6 nanocomposite systems [25]. They believed that the higher level of clay exfoliation was largely governed by the balance between the amount of platelet−platelet separation, the level of exposed silicate surface that the organic modifier permits, and the number of unfavorable interactions that can occur between the aliphatic modifier and the polar polyamide. The main reason is that the polyamide chains have no affinity for the aliphatic tails of the organic modifier. On the contrary, in CTPB/organo-clay system, a better exfoliation is achieved by using two tails organo-clay than using one tail organo-clay. We believe that the formation of exfoliated CTPB/D18-clay nanocomposite gels is predominantly governed by polymer/clay interaction of CTPB with D18-clay. On the basis of the above compatibility and rheology experimental results, polymer/clay interaction of CTPB with D18-clay is higher than that of CTPB with C18-clay. So a higher degree of exfoliation of D18-clay in CTPB is achieved because of the higher polymer/clay interaction. Therefore, as for the role of alkyl tails number of organic modifier on the exfoliation of clay, it is reasonable to be analyzed discriminatingly according to the different systems.

3.5. A suggested mechanism of the polymer/clay interaction and temperature effect on the clay dispersion in liquid polybutadiene matrix

On the basis of the above experimental results, a tentative mechanism was suggested to describe the dispersion of organo-clay in CTPB matrix. As enlightened by the pervious theoretical work of Balazs et al. [17−20], from a thermodynamic viewpoint, a strong interaction between end-functional groups of polymer and the oxygen and/or hydroxyls of the clay sheet can be formed, once polymer chains access the clay surface. Therefore, polymer end-groups have a significant effect on the exfoliation of the clays. Compared with organic modifier having one alkyl tail, the organic modifier having two alkyl tails can enlarge the distance between clay sheets, and then lower the large entropic barrier associated with the molten polymers penetrating the gallery [18]. This makes the polymer easier to access the gallery of the clays. However, Paul et al. [25−28] found that the role of the number of the alkyl tail in clay exfoliation differs from different polymer matrix. In our present work, the difference was also found between CTPB/D18-clay and HTPB/D18-clay. To understand this difference, polymer/clay interaction should be taken into account. The proper interaction between the end-functionalized polymer and the organo-clay could make the system reach its global free energy minima at exfoliated state, while the weak polymer/clay interaction would prevent the exfoliation of clay in polymer matrix [17−20,29−30,43,44]. Rheological experiments clearly indicates that the polymer/clay interaction between CTPB and D18-clay is remarkably stronger than that between HTPB and D18-clay, therefore, the CTPB/D18-clay nanocomposite gel offers the best degree of clay exfoliation. Based on the above discussion, we suggest that the polymer/clay interaction between end-functionalized liquid polybutadiene and the organo-clay, and the number of alkyl chain of organic modifier all play important roles in the exfoliation of organo-clay in these nanocomposite gels. We can conclude that the cooperation of the end-groups of polymer and alkyl tail number of organic modifier governs the degree of clay exfoliation.

4. Conclusion

Disorderly exfoliated liquid rubber/organo-clay nanocomposite can be easily prepared at room temperature by one-step compounding of CTPB with organo-clay that contains surfactant modifier with two alkyl tails. To our knowledge, this is the first example of spontaneous exfoliating organo-clay spontaneously at room temperature in polymer matrix. It was observed that the presence of functional end-groups can promote the exfoliation of clay. Moreover, the number of alkyl tails of the organic modifier plays a crucial role in the spontaneous and disordered exfoliation of the clay sheets. Organo-clay having two alkyl tails (D18-clay) in the modifier can be spontaneously exfoliated in CTPB at room temperature, while organo-clay with one alkyl tail (C18-clay) in the modifier can only be exfoliated in CTPB at temperature higher than 48 °C. The effect of polymer/clay interaction on the clay exfoliation was investigated by rheological and compatibility experiment. The cooperation of the end-functional groups of the polymer and the alkyl tails number of the organic modifier was proved to govern the exfoliation of the organo-clay. We believe that the ease of clay exfoliation using the commercial product CTPB could pave a new way to prepare rubber/exfoliated clay nanocomposites and may lead to potential industrial application, and the present work may also provide a new insight into the mechanism of clay exfoliation for the development of novel polymer/clay nanocomposites.

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