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# Exfoliation of Organo-Clay in Telechelic Liquid Polybutadiene Rubber

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## Introduction

Because of their unique physical and chemical properties, polymer/clay nanocomposites have been intensively studied in the past few years since the pioneering work by Toyota scientists.[1] Generally, the properties of polymer/clay 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 actively researched subject.[2] The exfoliated nanocomposites are more desirable than intercalated ones because strong synergistic effects between polymer and silicate layers could be obtained, and the properties of the composite materials are optimized in exfoliated systems. However, complete exfoliation of clays is a challenging task, and sometimes it requires special conditions, such as the matching of the proper reactive temperature and polymerization rate, curing agent, and/or suitable shearing stressing.[3] Therefore, understanding the mechanism of clay exfoliation in polymer/clay nanocomposites is of fundamental and practical significance.[4,5]

Many methods have been used in the recent past to produce intercalated and exfoliated structures in polymer−nanoclay composites, e.g., in situ polymerization of monomers, melt blending, and solution blending using polar organic solvents.[1,6] It has been proposed that increasing polar interaction between polymer and modifier and maximizing the favorable polymer−surface interactions would lead to favorable conditions for melt intercalation and exfoliation.[7] Hydrogen bonding formed either between polymer and organic modifier or between polymer and the oxygen basal plan of the clay sheet has been proven to be an important intermolecular interaction favoring melt exfoliation of clay in polymers, such as polyamide,[8] polyurethanes,[9] maleated polypropylene,[10] rubber,[11] and poly(ethyl-*ran*-vinyl alcohol).[12] One of the recent trends is to explore reactive-group-containing ammonium surfactants to modify clays, by which the interaction among the monomer, the surfactant, and the clay surface is tailored for the exfoliated morphology.[13]

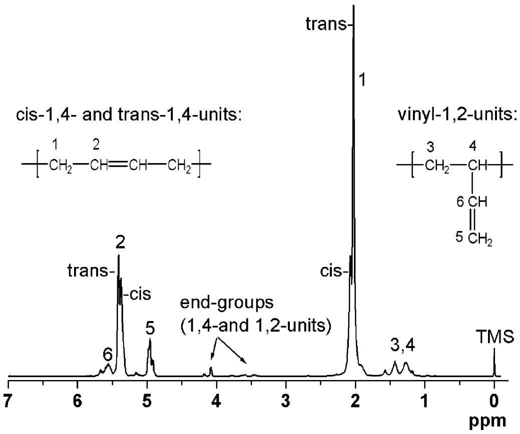

**Figure 1.** $^1$H NMR spectrum of HTPB in $CDCl_3$.

The effects of end-functionalized polymers and telechelic polymers on the preparation of polymer/clay composites have been studied theoretically. It has been proposed that the addition of functionalized chains can promote the separation of the clay sheets within the polymer matrix.[14] It has also been proposed that the presence of telechelic polymers could prohibit the formation of exfoliated structures; however, this prediction was based on the presupposition that the end groups do not react with themselves and with other monomers.[15] Another recent progress is that, based on the theoretical prediction of Balazs et al.,[16] Robello et al. have prepared an exfoliated PS/clay nanocomposite with a carefully designed 5-armed starlike structure of polystyrene,[17] and the exfoliation process became so simple that a significant advance in polymer/clay nanocomposites field may be expected.

Recently, we unexpectedly found that by compounding with a commercially available telechelic liquid polybutadiene rubber (hydroxyl-terminated polybutadiene, HTPB), the organo-clay can be easily exfoliated.[18] The ease of clay exfoliation in this cheap industrial product could open another way for the preparation of rubber/exfoliated-clay nanocomposites, and this process may lead to potential industrial applications. In the present work, we focus on elucidating the mechanism of clay exfoliation in this rubber/exfoliated-clay system. The presence of functional end hydroxyl groups in HTPB was confirmed to be an important factor in controlling the exfoliation of clay in the nanocomposite gel.

## Experimental Section

The commercial product hydroxyl-terminated 1,4-polybutadiene oligomer (HTPB) was purchased from Qilu Ethylene Chemical and Engineering Co. Ltd. (China), with average molecular weight ($M_n$) of 2200 and polydispersion of 2.6. Liquid 1,4-polybutadiene oligomer (14PB) without hydroxyl end groups, a standard polybutadiene sample for GPC, was purchased from Aldrich Chemical Co., with $M_n$ of 2010 and polydispersion of 1.04. The microstructures of these liquid rubbers were determined by $^1$H NMR (Varian UNITYplus 400 MHz NMR spectrometer). Figure 1 shows the $^1$H NMR spectrum of HTPB; the functional end groups can be clearly assigned at 3.8−4.5 ppm. The 1,4-polybutadiene/vinyl ratios for HTPB and 14PB samples are 78.5/21.5 and 89.8/10.2, respectively.

The organo-clay was prepared as follows: 10.0 g of industrially purified pristine montmorillonite (Tianjin Organic Clay Corp. China, cation exchange capacity is 1 mequiv/g) was

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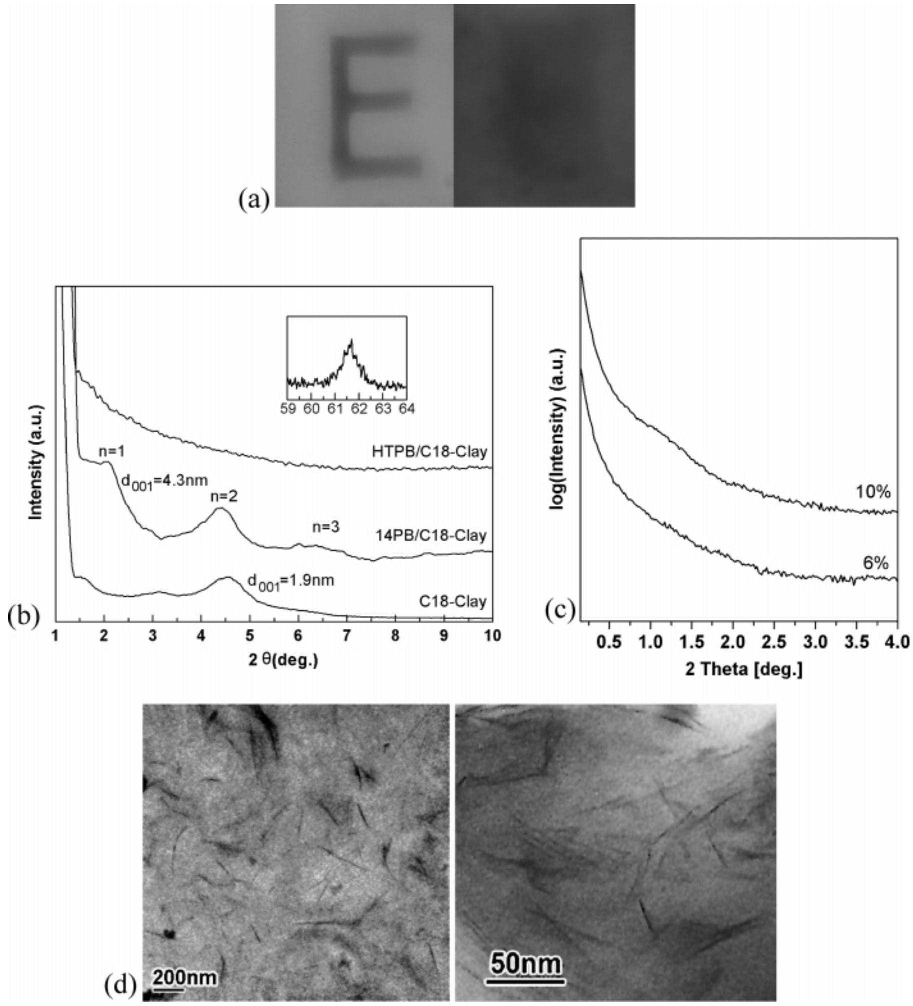

**Figure 2.** (a) Transparent property of the nanocomposite, HTPB/C18-clay (10 wt %, left) and 14PB/C18-clay (10 wt %, right), with the gel thickness of 5 mm; the letter "E" was on the other side of the gel. (b) XRD patterns of the organo-clay, 14PB/C18-clay (10 wt %) and HTPB/C18-clay (10 wt %) composite. The inset displays the in-plane 060 clay reflection of HTPB/C18-clay (10 wt %). (c) SAXS patterns of HTPB/C18-clay (6 and 10 wt %). (d) TEM micrographs of the HTPB/C18-clay (10 wt %) with low and high magnifications.

dispersed into 1000 mL of distilled water at 360 K for cation exchange with 3.5 g (equal to 1 mequiv/g) of octadecyltrimethylammonium chloride (denote as C18A) for 12 h. The exchanged clay was washed with distilled water and checked with 0.1 N $AgNO_3$ solution for residue $Cl^-$. The organo-clay obtained was dried at 360 K for 12 h before use. Rubber/clay nanocomposite gels could be easily prepared by simply compounding the organo-clay (10 wt %) with liquid rubbers at room temperature (preferentially at 310−353 K) with a slight stirring as described previously.[18]

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. Transmission electron microscopy (TEM) was carried out on a Philips EM 400ST microscope operating at 80 kV. The specimens for TEM observation were prepared by epoxy resin imbedded microsectioning (around 150 nm thickness) and were mounted on a copper grid. Small-angle X-ray scattering (SAXS) experiments were performed on a Bruker NanoStar SAXS system (Cu Kα radiation source at a voltage of 40 kV and a current of 35 mA).

## Results and Discussion

Typically, the HTPB/C18clay nanocomposite gel could be easily prepared with compounding the organo-MMT (less than 15 wt %) with HTPB at room temperature (preferentially at 310−353 K) with a slight stir for mixing. The liquid rubber intercalating process was fast, and it looked as if the organo-clay was "dissolved" in the liquid rubber, and a transparent gel-like homogeneous composite (Figure 2a, left) could be obtained from the starting turbid mixture. In the XRD pattern of the samples (Figure 2b), the absence of the (001) basal reflection peak of HTPB/C18-clay implies that the clay may be exfoliated. This lacking of the (001) peak is not due to the low quantity of clay in the composite as the (060) in-plane reflection peak of the single-clay sheet could still be detected.[3b] To further investigate the clay dispersion morphology, SAXS measurements were performed, and the results are displayed in Figure 2c. It can be seen that for the HTPB/C18-clay (10 wt %) there is still a weak and broad hump at around 1.2° $2\theta$, indicating the existence of some swelling tactoids. This result is reasonable because when the clay content reaches as high as 10 wt %, absolute and complete exfoliation is very difficult. The TEM image (Figure 2d) further reveals that most of the clay layers are disorderly dispersed in the rubber matrix, together with some swelling tactoids. For comparison, the SAXS pattern of the composite with 6 wt % clay indicates complete exfoliation.

For comparison, if 14PB (without end groups) was used in the same compounding procedure, only a turbid suspension mixture was obtained (Figure 2a, right), and

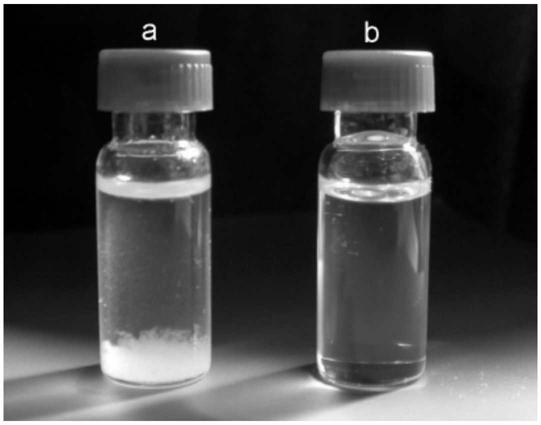

**Figure 3.** Mixtures of (a) 14 PB and (b) HTPB with 2 wt % C18A organic modifier.

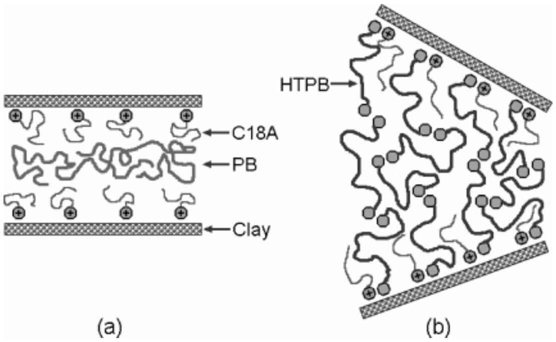

**Figure 4.** Schematic illustration of the mechanism of (a) clay intercalation with 14PB and (b) clay exfoliation and tuning the basal spacing with HTPB.

after some time, the organo-clay gradually precipitated. The XRD pattern showed that the 14PB/clay was intercalated composite with the basal spacing of around 4.3 nm (Figure 2b). These results indicate that the functional end groups of HTPB must play an important role in the clay exfoliation process.

In the HTPB/clay nanocomposite, there exist pairwise interactions between PB chain, end hydroxyl groups, polar head and alkyl chain of C18A, and the pristine surface of the silicate. The interaction between polymer and the clay surface could be strongly influenced by the presence of the modifiers. To check the affinity between the liquid rubber and the C18A, we prepared mixtures of the liquid rubber and C18A by simple mixing them at 333 K and then cooled to room temperature (Figure 3). It is interesting to note that C18A was readily dissolved in HTPB as the mixture of HTPB/C18A was clear, while the mixture of 14PB/C18A was turbid and C18A gradually precipitated later. This may be explained by the presence of the hydroxyl group in HTPB and its interaction to the polar head of the surfactant.

From the above discussions, we propose a possible mechanism of clay intercalation or exfoliation in the liquid rubber, as depicted in Figure 4. Without the end-functional groups, the 14PB rubber chains could be difficult to access the clay surface so only intercalated structure of clay was formed (Figure 4a). For HTPB, the favorable interaction of the end-functional hydroxyls with the polar head of the C18A modifier promotes the formation of hydrogen bonding between the hydroxyl end groups and the oxygen and/or hydroxyls of the clay sheet. Furthermore, the end hydroxyl groups could also form hydrogen bonding between the polymers, thus resulting in clusterlike structures of HTPB chains.[19] According to the prediction of Singh and Balazs,[16] star-shaped ploymers could improve clay exfoliation. Therefore, it is reasonable to believe that the clusterlike structure of HTPB could also improve the clay dispersion. All these factors would favor the exfoliation process to occur (Figure 4b). Improvement of the physical properties, such as the gas barrier, flame retardancy, and the mechanical strength of the rubber/exfoliated-clay nanocomposite, could be expected, and our research on these related topics is in progress.

## Conclusion

It was discovered that disordered exfoliation of clay could be easily formed in HTPB/clay nanocomposite. It is suggested that functional end groups of HTPB interact with both the organo-modifier and the clay surface and thus promote the exfoliation of clay layers. The ease of clay exfoliation using the commercial product HTPB may provide useful information to elucidate the exfoliate mechanism of clay and potential development of rubber/clay nanocomposites.

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