New Method for Preparing Polybutadiene Rubber/Clay Composites

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ABSTRACT: Polybutadiene rubber (BR)/clay/dimethyl dihydrogenatetallow ammonium chloride (DDAC) composites were prepared by a new preparation method named *in situ* organic modification. That is, BR, pristine clay, and quaternary ammonium salt were directly melt-mixed without the usual pretreatment of the pristine clay with an intercalatant. BR/pristine clay, BR/organoclay DK4 (modified with DDAC), and BR/clay/DDAC composites were analyzed with X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis. The vulcanization characteristics and mechanical properties of the BR/pristine clay, BR/DK4, and BR/clay/DDAC composites were investigated. Finally, the effects of the processing conditions, clay/DDAC ratio, and clay content on the structure and properties of the BR/clay/DDAC composites were investigated. The results showed that intercalated BR/clay/DDAC composites were prepared. Organoclay DK4 and clay/DDAC effectively accelerated the vulcanization reaction of BR, which was attributed to the existence of the intercalatant used to modify the clay. The tensile strength, elongation at break, and tear strength of the BR/clay/DDAC vulcanizates were greatly improved in comparison with those of gum BR and BR/pristine clay vulcanizates but were somewhat lower than those of BR/DK4 vulcanizates. The dispersion of clay particles in the BR/clay/DDAC and BR/DK4 composites was much better than that in the BR/pristine clay composite. The temperature at the thermal degradation peak of the BR/clay/DDAC composite obviously increased in comparison with those of the gum BR, BR/clay and BR/DK4 composites. The mixing temperature and rotor speed had remarkable effects on the structure and properties of the BR/clay/DDAC composite. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 227–237, 2005

Key words: clay; composites; modification; polybutadiene; rubber

INTRODUCTION

Clay is a cheap natural resource that has been used for many years as a filler for rubber to save rubber consumption and to reduce the composite cost.[1] However, the application of clay in the rubber industry is restricted because of its weak reinforcing capability.[2] The weak reinforcing effect can be attributed to the agglomeration of clay particles and their low surface activity.[3] Much research has been carried out to improve the properties of rubber/clay composites by acid activation[4,5] and surface modification of the clay with coupling agents.[6–8]

Since the Toyota group initially introduced an *in situ* intercalative polymerization method to prepare polyamide/organoclay nanocomposites,[9,10] polymer/clay nanocomposites have attracted more and more attention of researchers because of their superior mechanical properties, thermal stability, gas-barrier properties, and flame retardancy. Until now, polymer/clay nanocomposites have been prepared by various routes, including exfoliation adsorption,[11–14] *in situ* intercalative polymerization,[15,16] melt intercalation,[17–19] and template synthesis.[20] The clay is less compatible with organic polymers because of its hydrophilicity. To prepare polymer/clay nanocomposites by melt intercalation, it is generally necessary to modify the clay with an intercalatant such as alkylammonium or alkylphosphonium, except for a few polar polymer systems such as poly(ethylene oxide)[21,22] and epoxidized natural rubber.[23] Organophilic modification makes the clay more compatible with polymers. Thus, it is possible for the clay layers to disperse into polymer matrices at a nanoscale level in the form of an intercalated or exfoliated microstructure. However, the modification of clay results in high costs and long manufacture cycles.

In this study, a new potential preparation method named *in situ* organic modification was used to prepare polybutadiene rubber (BR)/clay composites with good mechanical properties. That is, BR, pristine clay, and an intercalatant were directly mixed in a Haake rheometer at a given temperature without the pretreatment of the pristine clay with the intercalatant. Dubois et al.[24] used a similar method to prepare EVA/clay nanocomposites with good thermal stability. The main differences between their investigation and our investigation lie in the addition order of the clay and

intercalatant and the processing conditions, besides the different polymer matrices. In our previous work, we found that the organoclay modified with dimethyl dihydrogenatetallow ammonium chloride (DDAC) endows the BR vulcanizate with better mechanical properties. Therefore, DDAC was chosen as the intercalatant in this study. The DDAC content was the same as that in organoclay DK4 analyzed by thermogravimetric analysis (TGA) if not specified. The morphology of the BR/clay composites was investigated by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). TGA was used to investigate the thermal degradation properties of BR vulcanizates filled with clay. The effects of the processing conditions, clay/DDAC ratio, and clay content on the structure and properties of the BR/clay/DDAC composite were also investigated.

EXPERIMENTAL

Materials

BR (BR9000) was produced by Yanshan Petrochemical Co., Ltd. (Beijing, China). Pristine clay (sodium montmorillonite, 80%) with a cation-exchange capacity of 90 mmol/100 g, DDAC (75%), and organoclay DK4 modified with about 40% DDAC were provided by Zhejiang Fenghong Clay Chemicals Co., Ltd. (Anji, China). The chemical formula for DDAC is as follows.

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle HT}{|}}{N^+}}-HT \quad Cl^-$$
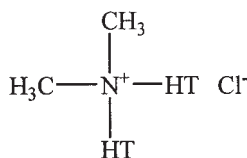
where HT is hydrogenated tallow ($\sim$65% C18, $\sim$30% C16, and $\sim$5% C14). All the other additives were industrial-grade products.

Compounding and sample preparation

BR, pristine clay, DDAC, or organoclay DK4 was melt-mixed in a Rheocord90 rheometer (Haake Co., Vreden, Germany) at 90°C and a rotor speed of 90 rpm for 6 min. Then, 2 phr stearic acid, 4 phr zinc oxide, 2.5 phr accelerator N-cyclohexylbenzothiazole-2-sulfenamide, and 1.5 phr sulfur were added to the mixture at 30°C and 60 rpm, and the mixture was mixed for another 5 min. When discussing the effects of the processing conditions on the structure and properties of the BR/clay/DDAC composite, we changed the processing parameters in the first mixing stage. The mixing temperature was referred to the set temperature when the mixing began. The resultant compounds were mixed further on a two-roll mill at the ambient temperature for about 10 min. Finally, the compounds were compression-molded at 150°C under 10 MPa for the optimum cure time (t_{90}) to yield vulcanizates.
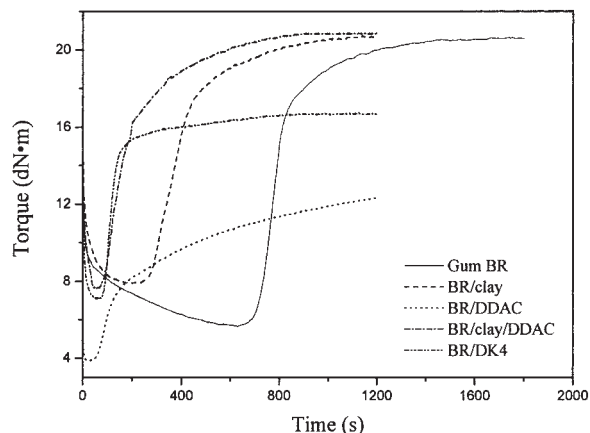

Figure 1 Effects of clay, DDAC, clay/DDAC, and DK4 on the vulcanization curves of BR.

Measurement and characterization

Wide-angle XRD was used to study the expansion of the clay interlayer distance. The XRD patterns were obtained with a diffractometer (Dmax-rc, Rigaku, Tokyo, Japan) at the Cu Kα wavelength of 1.5406 Å with a generator voltage of 40 kV and a generator current of 100 mA. The diffractogram was scanned in the 2θ range from 1 to 20° at a rate of 4°/min.

The fracture morphologies of tensile specimens were observed by SEM (model S-2150, Hitachi, Tokyo, Japan) after the fractural surfaces were sputter-coated with gold.

TGA was carried out on a PerkinElmer TGA7 TG analyzer (Perkin Elmer, Wellesley, MA) from room temperature to 800°C in a nitrogen flow at a heating rate of 20°C/min. The measurement precision of the instrument for the temperature and weight was ±2°C and 10 ppm, respectively.

The vulcanization characteristics were determined with an oscillating disk rheometer (UN 2030, Nantou, Taiwan). The tensile properties were measured with dumbbell specimens (6 mm wide in the cross section) according to ASTM D 412-98a. The tear strength was tested according to ASTM D 624-00 with an unnotched 90° angle test piece. Both tensile and tear tests were performed on an Instron series IX 4465 material tester (Instron Co., Norwood, MA) at a crosshead speed of 500 mm/min.

RESULTS AND DISCUSSION

Vulcanization characteristics

The effects of pristine clay, DDAC, and organoclay DK4 on the vulcanization characteristics of BR are shown in Figure 1 and Table I. The scorch time (T_2) of the BR compound was sharply reduced by the addition of DDAC to the compound, and the optimum

TABLE I
Effect of pristine clay, DDAC, and organoclay DK4 on the vulcanization characteristics of BR compounds (150°C)

| Filler	Content (phr)	Scorch time (min) T_2	Vulcanization time (min)		ML (dNm)	MH (dNm)	ΔM (dNm)
			T_{10}	T_{90}			
None	0	12.1	12.0	17.0	5.7	20.6	14.9
Pristine clay	18	5.1	4.9	11.2	7.9	20.7	12.8
DDAC*	12	1.6	1.2	14.0	3.8	12.3	8.5
Pristine clay/DDAC	18/12	1.8	1.7	8.2	7.6	20.8	13.2
DK4	30	1.7	1.5	4.8	7.1	16.7	9.6

* The DDAC content was determined by the practical content of DDAC in 30 phr DK4 analyzed via TGA.

vulcanization time (T_{90}) decreased a little. The scorch time and optimum vulcanization time of the BR compound greatly decreased with the addition of pristine clay, clay/DDAC, or organoclay DK4. The facts indicate that organoclay and clay/DDAC are effective accelerators for the BR vulcanization reaction. Other researchers have found the same phenomenon in organoclay (modified with octadecyltrimethylamine or octadecylamine) filled styrene-butadiene rubber (SBR)[25] and natural rubber (NR).[26–28] In addition, the scorch time of the BR compound filled with DK4 or clay/DDAC was the same as that of the compound filled with DDAC. This indicates that the vulcanization acceleration effect of organoclay and clay/DDAC should mainly be attributed to DDAC.

The fact that the organoclay and clay/DDAC obviously increased the reaction rate in the induction period could be explained by the following facts. The following key accelerator species form during the induction period for the sulfur/sulfenamide vulcanization system:[29,30]
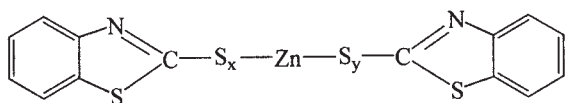
This activated intermediate can react with an amine to form the following chelate:
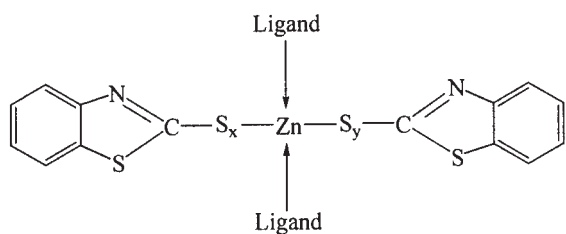
where the ligand denotes amines. This chelate is more active than the sulfenamide accelerator.[30]

The minimum torque (ML) of the BR compound greatly decreased when DDAC was added to it. This means that DDAC acted as a lubricant for the BR compound. However, this phenomenon was not observed for the BR compound filled with DK4 or clay/DDAC. This indicates that most of DDAC in DK4 and clay/DDAC intercalated into the gallery of clay. This coincides with the results of XRD analysis. The maximum torque (MH) of the BR compound greatly decreased with the addition DK4 or DDAC. MH slightly increased for the BR compound filled with clay or clay/DDAC. In general, there is a direct relation between the calculated shearing modulus and the crosslinking density.[31] That is, the change in the torque ($\Delta M = MH - ML$) is proportional to the crosslinking density.

Table II shows the effects of the processing conditions on the vulcanization characteristics of BR/clay/DDAC compounds. The scorch time slowly increased, whereas the optimum vulcanization time slightly decreased, with increasing temperature. The scorch time and optimum vulcanization time changed a little with an increase in the mixing time, except when the mixing time exceeded 20 min. The scorch time and optimum vulcanization time were greatly reduced at a long mixing time. The optimum vulcanization time slowly decreased with increasing rotor speed, whereas the scorch time changed a little. In all cases, no obvious change could be observed in MH and ML.

Mechanical properties

The influences of clay, DDAC, clay/DDAC, and DK4 on the mechanical properties of the BR vulcanizates are shown in Figure 2. The reinforcing effects of clay and DDAC were very poor. However, there was a synergistic effect on the mechanical properties when clay and DDAC were simultaneously added to the BR vulcanizate. The tensile strength, elongation at break, and tear strength of the BR/clay/DDAC vulcanizate increased 679, 667, and 573%, respectively, with respect to those of the gum BR vulcanizate. However, the mechanical properties of the BR/DK4 vulcanizate were superior to those of the BR/clay/DDAC vulcanizate. This synergistic effect could be attributed to the *in situ* organic modification of clay with DDAC. The DDAC molecules could intercalate into the gallery of

TABLE II
Effect of processing conditions on vulcanization characteristics of BR/clay/DDAC composites (150°C)

Processing condition	Scorch time (min) T_2	Vulcanization time (min)		ML (dNm)	MH (dNm)	ΔM (dNm)
		T_{10}	T_{90}			
Temperature (°C)	rotor speed = 90 rpm, mixing time = 10 min.					
30	1.4	1.3	10.8	6.9	21.0	14.1
50	1.4	1.3	11.4	7.6	21.1	13.5
70	1.5	1.4	8.3	6.7	20.7	14.0
90	1.8	1.7	8.2	7.6	20.8	13.2
110	1.9	1.8	8.1	8.1	21.2	13.1
Time (min)	mixing temperature = 80°C, rotor speed = 90 rpm					
5	1.5	1.4	9.2	5.7	18.5	12.8
10	1.8	1.7	8.2	7.6	20.8	13.2
15	1.5	1.4	6.9	7.0	20.4	13.4
20	1.5	1.4	7.8	7.5	20.1	12.6
30	1.1	1.0	5.2	6.5	21.1	14.6
Rotor speed (rpm)	mixing temperature = 80°C, mixing time = 10 min.					
30	1.6	1.3	11.3	8.7	22.4	13.7
60	1.4	1.4	10.3	9.5	24.1	14.6
90	1.6	1.5	8.7	9.0	22.8	13.8
120	1.6	1.5	8.0	8.9	21.9	13.0
150	1.4	1.4	8.5	9.6	22.3	12.7

pristine clay by cation-exchange reactions with the aid of a shearing force. In general, this cation-exchange reaction is carried out in a hot water suspension under vigorous stirring. However, this cation-exchange reaction can also proceed in the solid state when the host (clay) and guest (organoammonium salts) are mixed in the solid state.[32]

Effects of the processing conditions on the mechanical properties

The effects of the processing conditions on the mechanical properties of the BR/clay/DDAC vulcanizates are shown in Figures 3–5. The mixing time and rotor speed were 10 min and 90 rpm, respectively, when the mixing temperature was a variable. The tensile strength and elongation at break of the BR/clay/DDAC vulcanizate greatly increased with increasing mixing temperature. Then, the tensile strength and elongation at break decreased when the mixing temperature exceeded 80°C. A similar trend could be observed for the dependence of the permanent set and tear strength on the mixing temperature. However, the maximum tear strength was obtained at about 100°C.

The mixing temperature and rotor speed were 80°C and 90 rpm, respectively, when the mixing time was a variable. The tensile strength of BR/clay/DDAC showed an obvious increase when the mixing time was 5–10 min, and then this trend leveled off. The elongation at break slightly increased with increasing mixing time. The permanent set and tear strength of the BR/clay/DDAC vulcanizate were influenced a little by the mixing time.
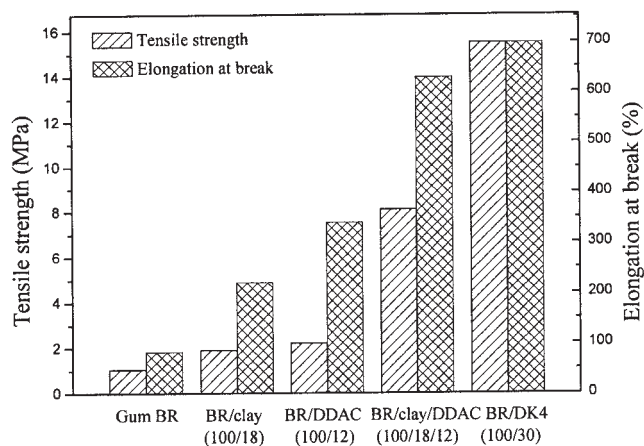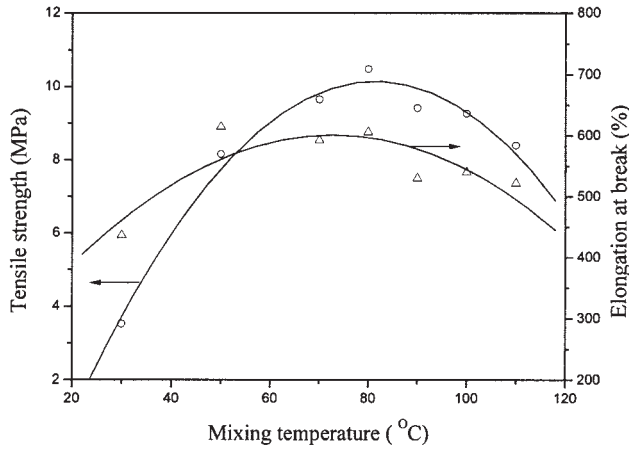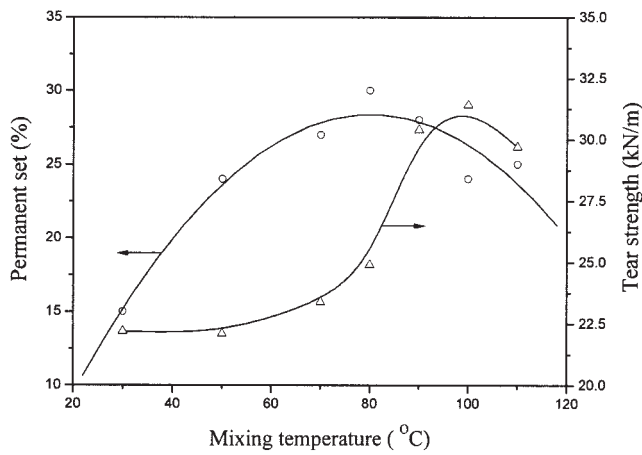

(a)
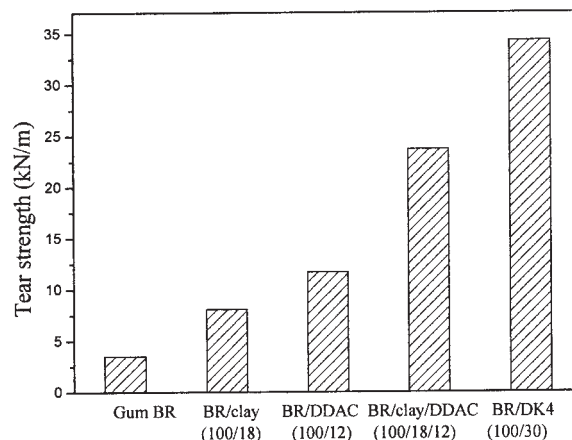
(b)

Figure 2 Effects of clay, DDAC, clay/DDAC, and DK4 on the mechanical properties of BR composites.

(a)

(b)

Figure 3 Effect of the mixing temperature on the mechanical properties of BR/clay/DDAC vulcanizates.

The mixing temperature and time were 80°C and 10 min, respectively, when the rotor speed was a variable. The tensile strength and elongation at break of the BR/clay/DK4 vulcanizate greatly increased with increasing rotor speed. The tear strength reached a maximum under 90 rpm before decreasing with increasing rotor speed. In general, increasing the rotor speed will increase the possibility of filler particles breaking into smaller aggregates. The mechanical properties of rubber composites will benefit from the improved dispersion of the filler.

As previously mentioned, the mixing temperature and rotor speed had profound influences on the mechanical properties of the BR/clay/DDAC vulcanizate. The effect of the mixing time on the mechanical properties was not obvious when the mixing time exceeded 10 min. Therefore, we chose 80°C, 10 min, and 150 rpm as the optimum processing conditions to prepare BR/clay/DDAC composites.

Effects of the clay/DDAC ratio and clay content on the mechanical properties

The dependence of the mechanical properties on the clay/DDAC ratio (represented by the molar ratio of Na^+ to DDAC) is shown in Figure 6. The clay content was 20 phr when we investigated the influence of the Na^+/DDAC ratio on the mechanical properties. The optimum tensile strength was obtained when the Na^+/DDAC ratio was 1/0.85. Therefore, this ratio was used to investigate the effect of the clay content on the mechanical properties. The results are shown in Figure 7. The mechanical properties of the clay-filled BR vulcanizates (without DDAC) are also included in this figure. Obviously, the tensile strength and elongation at break of the BR/clay/DDAC vulcanizates were much higher than those of the BR/clay vulcanizates at all clay contents. The optimum tensile strength was obtained at about 40 phr clay.
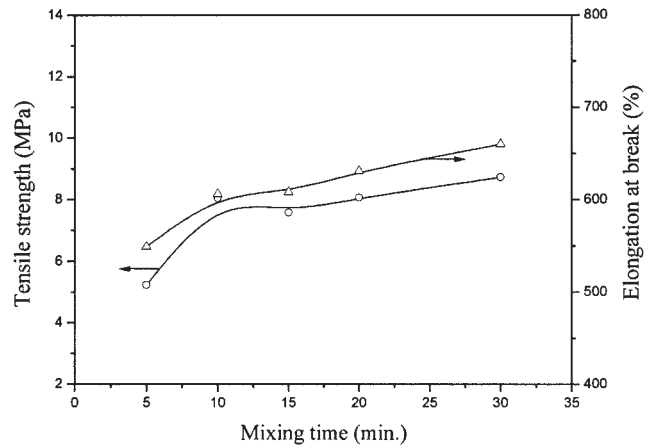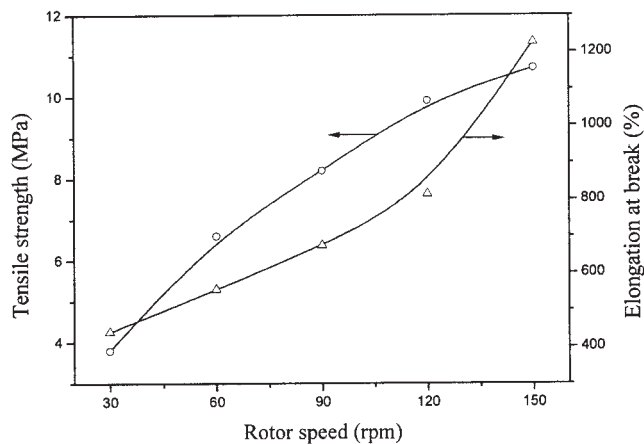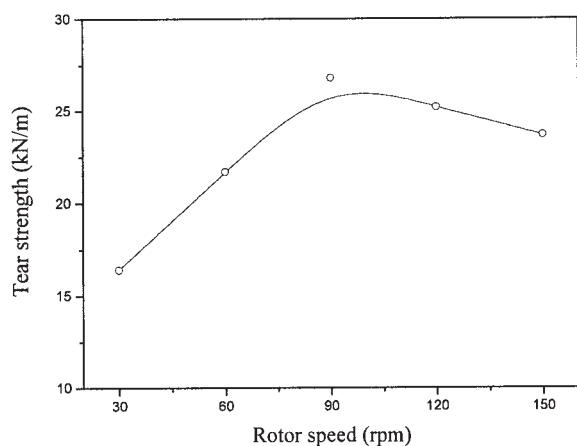

(a)
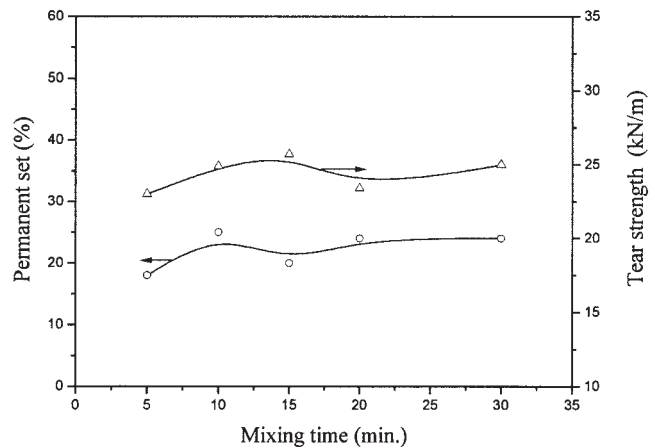
(b)

Figure 4 Effect of the mixing time on the mechanical properties of BR/clay/DDAC vulcanizates.

(a)

(b)

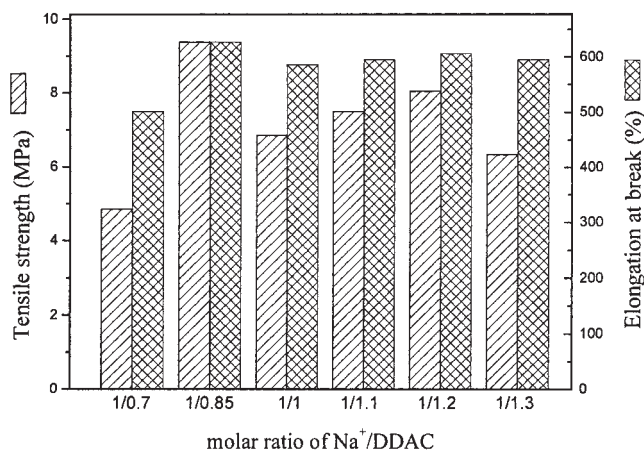**Figure 5** Effect of the rotor speed on the mechanical properties of BR/clay/DDAC vulcanizates.

Figure 6 Dependence of the mechanical properties of BR/clay/DDAC vulcanizates on the molar ratio of Na^+ to DDAC.
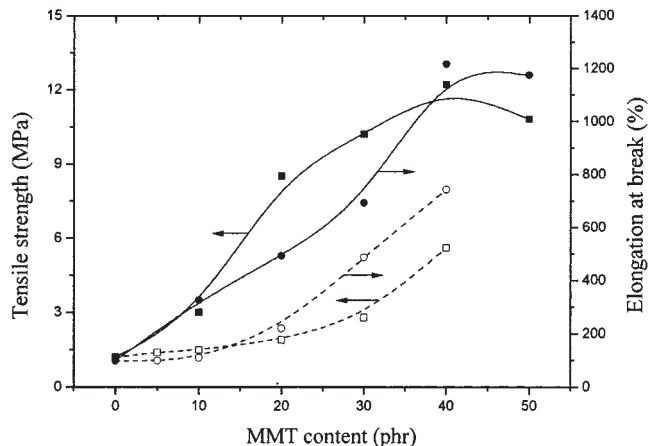

Figure 7 Dependence of the mechanical properties on the clay content for BR/clay and BR/clay/DDAC vulcanizates (the open symbols and dashed lines denote the BR/clay vulcanizates, and the filled symbols and solid lines denote the BR/clay/DDAC vulcanizates; MMT = montmorillonite).

Characterization

XRD

The XRD spectra for pristine clay, DDAC, and organoclay DK4 are shown in Figure 8. The pristine clay showed a single (001) diffraction peak at $2\theta = 5.84°$, corresponding to an interlayer distance of 1.51 nm. The (001) diffraction peaks of DK4 obviously shifted toward a low-angle direction; this indicated the effective expansion of the interlayer distance of the clay. That is, the interlayer distance of the clay expanded about 2 nm from the original 1.51 nm. This expansion of the gallery height was attributed to the intercalation of intercalatant chains by a cation-exchange reaction. This intercalation of alkylammonium increased the hydrophobicity of the clay and the affinity of the clay to the BR matrix. The main diffraction peaks of DDAC
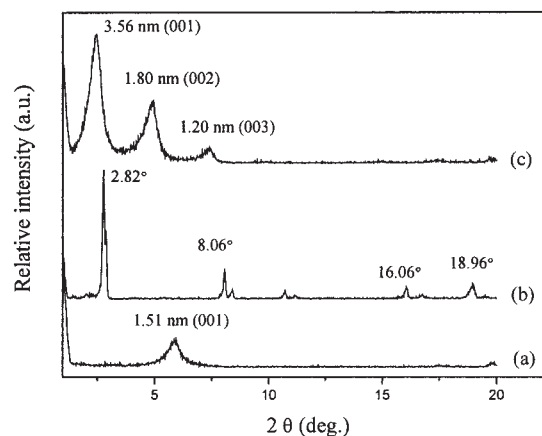

Figure 8 XRD spectra for (a) pristine clay, (b) DDAC, and (c) organoclay DK4.
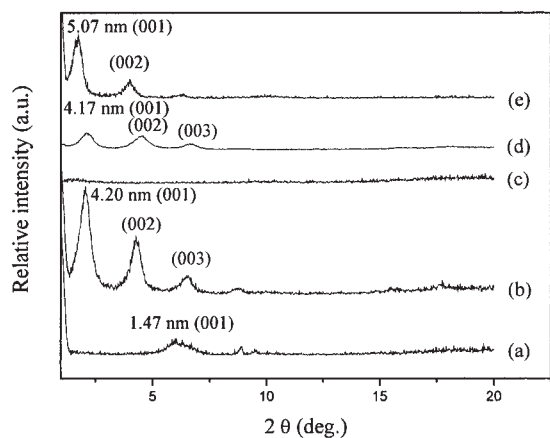
Figure 9 XRD spectra for (a) BR/pristine clay (100/18), (b) BR/DK4 (100/30), (c) BR/DDAC (100/12), and (d) BR/clay/DDAC (100/18/12) compounds and (e) BR/clay/DDAC (100/18/12) vulcanizate.

were located at about 2.82, 8.06, 16.06, and 18.96°. It is important to demonstrate here that the very strong diffraction peak of DDAC at about 2.82° was in the vicinity of the (001) diffraction peak of DK4. Thus, the characterization of intercalation of BR molecules became difficult because of the interference of DDAC. Fortunately, no diffraction peak could be observed in the XRD spectrum of the BR/DDAC vulcanizate [Fig. 9(c)]. That is, the displacement of the (001) diffraction peak toward a low-angle direction with respect to the pristine clay still indicated the intercalation of BR molecules into the interlayer of the clay.

As shown in Figure 9, the (001) diffraction peak of the clay in the BR/pristine clay vulcanizate was located at $2\theta = 6.02°$, corresponding to an interlayer distance of 1.47 nm, which was just the same as that of the pristine clay. This indicates that BR chains could not intercalate the gallery of the pristine clay. The (001) diffraction peaks of the clay in the BR/DK4 and BR/clay/DDAC vulcanizates obviously shifted toward a low-angle direction with respect to the corresponding organoclay DK4 and pristine clay, respectively. This means the expansion of the interlayer distance of the clay. The expansion of the interlayer distance is associated with the intercalation of BR molecules into the gallery of the clay. Therefore, intercalated BR/DK4 and BR/clay/DDAC composites were prepared. BR chains could intercalate into the gallery of the pristine clay by simple melt mixing in the presence of DDAC. As can be seen in Figure 9(d), the interlayer distance of the BR/clay/DDAC compound before vulcanization was 4.17 nm. This interlayer distance expanded to 5.07 nm [Fig. 9(e)] after the compound was vulcanized. These facts indicate that intercalation occurred during mixing and this intercalation degree could be enhanced further by vulcanization. In the mixing stage, DDAC intercalated into the

gallery of the clay by a cation-exchange reaction even if no hot water acted as a medium. That is, the clay was *in situ* organically modified. Obviously, the modified clay became organophilic. Its interlayer distance was expanded, and its surface energy was lowered. Therefore, the modified clay was more compatible with BR. This facilitated the intercalation of BR chains.

In addition, (002) and (003) diffraction peaks appeared in the XRD patterns of the BR/DK4 and BR/clay/DDAC vulcanizates. Joly et al.[33] observed the same phenomenon when they investigated an NR/montmorillonite [modified with dimethyl hydrogenated tallow (2-ethylhexyl) ammonium] nanocomposite. They explained that these harmonics were a strong indication of a very homogeneous swelling of the organomodified montmorillonite, without exfoliation of the lamellae.

Figure 10 shows the effect of the mixing temperature on the XRD spectra of the BR/clay/DDAC vulcanizate. The interlayer distance of the BR/clay/DDAC vulcanizate slightly increased with increasing mixing temperature. Then, it decreased if the mixing temperature was increased further. This means that the exorbitant mixing temperature did not benefit the intercalation of BR molecules. This is consistent with the change trend of the mechanical properties with increasing mixing temperature.

As shown in Figure 11, the interlayer distance of the BR/clay/DDAC vulcanizates increased with increasing rotor speed, especially for the vulcanizate prepared at 150 rpm. Another phenomenon was that the intensity of the diffraction peak decreased with increasing rotor speed. Under higher shearing stress, the clay aggregations broke into smaller aggregates more easily. This process may have accelerated the mass transport of BR molecules into the primary particles of the clay. Vaia et al.[34] believed that the mass transport into the primary particles of host silicate is the key
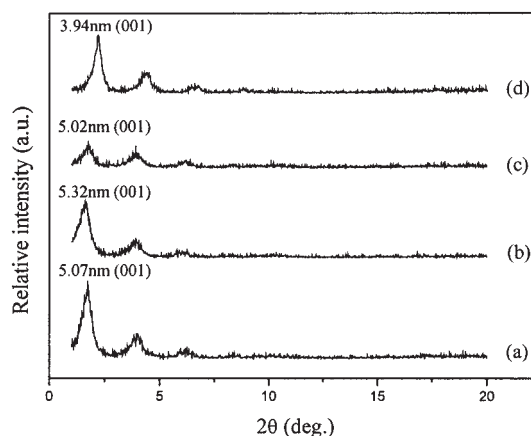

Figure 10 Effect of mixing temperature on XRD spectra of BR/clay/DDAC vulcanizate (a) 30°C, (b) 50°C, (c) 80°C and (d) 110°C.
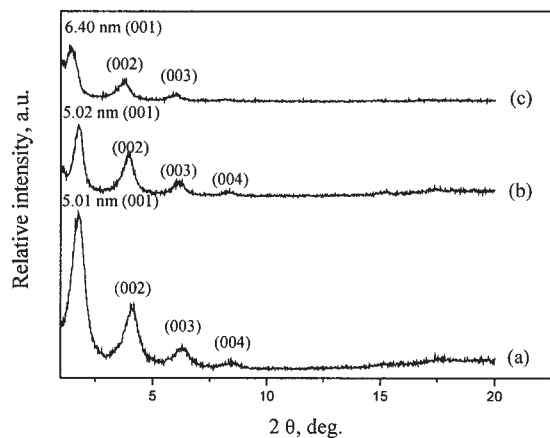
Figure 11 Effect of the rotor speed on the XRD spectra of BR/clay/DDAC vulcanizates: (a) 30, (b) 90, and (c) 150 rpm.

factor in preparing hybrids. Therefore, increasing the rotor speed is advantageous to intercalation.

Fracture morphologies of the tensile specimens

The tensile fracture morphologies of the BR/clay, BR/DK4, and BR/clay/DDAC vulcanizates are shown in Figure 12. To compare the sizes of the clay particles before and after mixing with BR, SEM photographs of the pristine clay and organoclay DK4 are shown in Figure 12(a,b). The size of the pristine clay particles ranged from about 10 to 100 μm. This indicates that the clay particles aggregated into agglomerates.[34] The size of organoclay DK4 was a little smaller than that of the pristine clay. Moreover, the particle size distribution was more uniform than that of the pristine clay. However, the organoclay DK4 particles also belonged to agglomerates.

There were many larger clay particles on the fracture surface of the BR/clay vulcanizate [Fig. 12(c)]. The size of the clay particles was still in the range between clay agglomerates and primary particles (whose size ranges from 1 to 10 μm[34]), even though the size of the clay particles was smaller than that of the pristine clay itself because of the shearing effect during the mixing process. The interface between the clay particles and the rubber matrix was distinct. Moreover, many cave structures that were attributed to the falling off of the clay particles from the rubber matrix under stress were observed. These phenomena indicated that the compatibility and the interaction between the clay phase and rubber phase were weak. Therefore, the BR vulcanizate was not effectively reinforced by the pristine clay.

The fracture morphologies of the BR/DK4 and BR/clay/DDAC vulcanizates [Fig. 12(d,e), respectively] were quite different from that of the aforementioned vulcanizate. Many parallel strips were distributed on

these fracture surfaces. In addition, the size of the clay particles on the fracture surfaces of the BR/DK4 and BR/clay/DDAC vulcanizates was much smaller than that in the BR/clay vulcanizate. Moreover, the interface between the clay and rubber was very blurry, and this indicated a stronger interface interaction. The high reinforcing capacity of DK4 and clay/DDAC is related to this morphology.

The effect of the mixing temperature on the tensile fracture morphologies of the BR/clay/DDAC vulcanizates is shown in Figure 13. Many larger clay particles and cave structures were distributed on the fracture surfaces of the BR/clay/DDAC vulcanizates prepared at lower mixing temperatures. The size of the clay particles became small, and the interface between the clay and rubber became blurry, with increasing mixing temperature. Furthermore, the size and number of the cave structures decreased with an increase in the mixing temperature. However, an exorbitant mixing temperature did not benefit the dispersion of clay particles in the BR matrix. These results are consistent with the results of the XRD analysis and mechanical property measurement.

TGA

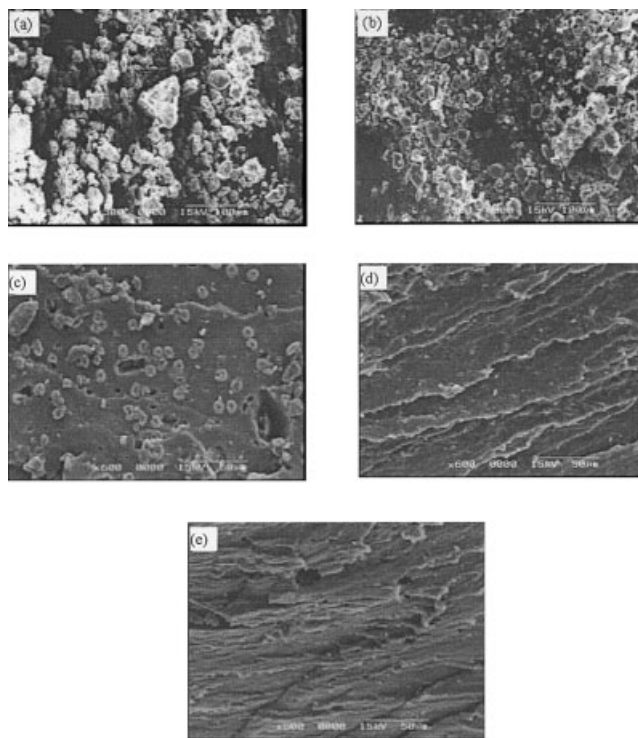The thermal decomposition behavior of the gum BR, BR/pristine clay, BR/DK4, and BR/clay/DDAC vul-

Figure 12 SEM photographs of (a) pristine clay, (b) organoclay DK4, and the tensile fracture surfaces of (c) BR/clay (100/18), (d) BR/DK4 (100/30), and (e) BR/clay/DDAC (100/18/12) vulcanizates.
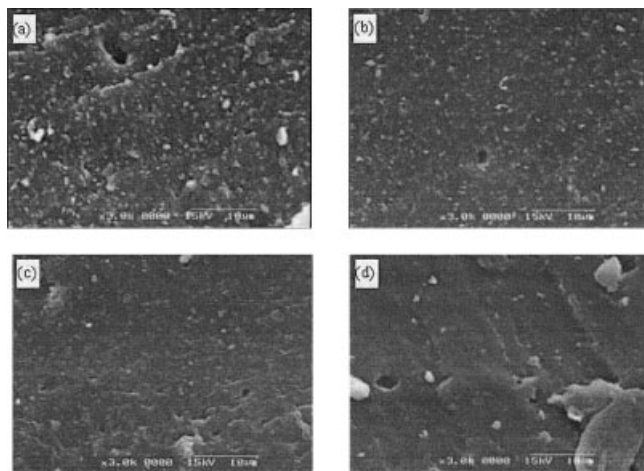
Figure 13 Influence of the mixing temperature on the morphology of BR/clay/DDAC vulcanizates: (a) 30, (b) 50, (c) 70, and (d) 110°C.

Figure 15 DTG curves of (a) gum BR vulcanizate, (b) BR/clay (100/30) vulcanizate, (c) BR/DK4 (100/30) vulcanizate, and (d) BR/clay/DDAC (100/18/12) vulcanizate.

canizates was assessed by TGA. The results are shown in Figure 14. A slight increase in the thermal decomposition temperature was observed for the BR/DK4 and BR/pristine clay vulcanizates with respect to the gum BR vulcanizate. However, the decomposition temperature greatly increased for the BR/clay/DDAC vulcanizate. The derivative thermogravimetry (DTG) curves of these vulcanizates are shown in Figure 15. The temperature at the degradation peak in the DTG curve is the temperature at which the weight-loss rate is the fastest.[35] The temperature at the degradation peak increased 5°C when pristine clay was added to BR. For DK4 and clay/DDAC, the temperature increased 16 and 77°C, respectively. Obviously, clay/DDAC was much more effective in improving the thermal decomposition temperature of BR, and this
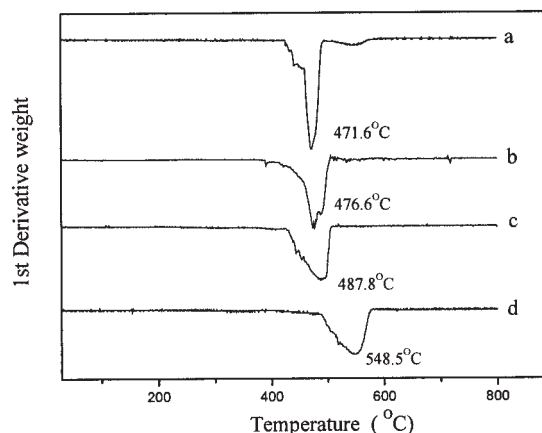
could be explained by the better dispersion of clay particles in the rubber matrix. This could be proved by the previous morphology observation from SEM. This better dispersion enhanced the effective volume fraction of the clay in the rubber matrix. The good thermal stability of the BR/clay/DDAC composite can be attributed to hindered out-diffusion of the volatile decomposition products.[21] The dispersion of DK4 in the rubber matrix was very good, but the thermal decomposition temperature of this vulcanizate was only slightly improved with respect to the gum BR vulcanizate. The change in the crosslinking density may be the reason for this phenomenon. In general, the thermal stability of a vulcanizate increases with increasing crosslinking density when the decomposition energy of the crosslink is high.[30] The vulcanization degree of the BR composite greatly decreased when DK4 was
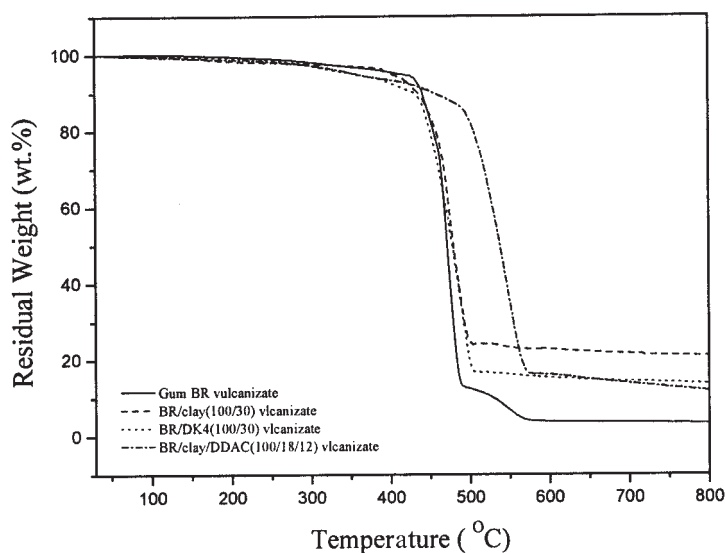

Figure 14 TGA thermograms of gum BR, BR/pristine clay, BR/DK4, and BR/clay/DDAC vulcanizates.

added to BR, as shown in Table I. The effect of the crosslinking degree partially counteracted the effect of the better dispersion of clay particles on the thermal decomposition behavior of BR.

The effects of the mixing temperature on the TGA thermograms and DTG curves of the BR/clay/DDAC vulcanizates are shown in Figures 16 and 17, respectively. The TGA thermograms changed slightly with increasing mixing temperature. The temperature at the degradation peak in the DTG curves of the BR/clay/DDAC vulcanizate slightly increased with increasing mixing temperature. The temperature at the degradation peak decreased when the mixing temperature exceeded a given value. This phenomenon was consistent with the results of XRD and morphology analysis.

Figure 17 Effect of the mixing temperature on the DTG curves of BR/clay/DDAC vulcanizates.

CONCLUSIONS

BR/clay/DDAC composites with intercalated structures were prepared by a new preparation method named *in situ* organic modification. That is, BR, pristine clay, and quaternary ammonium salt were directly melt-mixed without the usual pretreatment of the pristine clay with an intercalatant. The results showed that organoclay DK4 and clay/DDAC effectively accelerated the vulcanization reaction of BR, and this was attributed to the intercalatant used to modify the clay. The tensile strength, elongation at break, and tear strength of the BR/clay/DDAC vulcanizate were greatly increased with respect to those of the gum BR and BR/clay vulcanizates. The mixing temperature and rotor speed in melt mixing had profound effects on the structure and properties of the BR/clay/DDAC composite, whereas the mixing time had little influence on the properties of the BR/clay/DDAC composite. The mechanical properties of the BR/clay/DDAC composites were greatly influenced
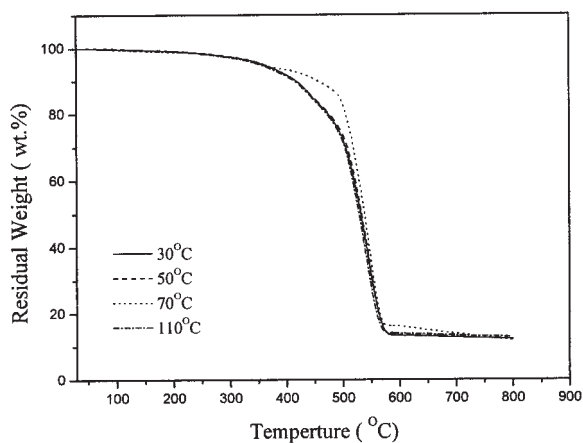
by the clay/DDAC ratio, which was represented by the molar ratio of Na^+ to DDAC. The optimum tensile strength was obtained when Na^+/DDAC was 1/0.85. The temperature of the thermal degradation for the BR/clay/DDAC composite was about 77, 72, and 61°C higher than those of the gum BR, BR/clay, and BR/DK4 composites, respectively. The (001) diffraction peak of the BR/clay/DDAC composite obviously shifted to a low-angle direction with respect to the pristine clay and organoclay DK4, and this that indicated intercalated BR/clay composites were prepared. The morphology of the fracture surface of the BR/clay/DDAC composite was quite different from that of the BR/clay composite and similar to that of the BR/organoclay DK4 composite. The dispersion of clay particles in the BR/clay/DDAC and BR/DK4 composites was much better than that in the BR/clay composite.

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Figure 16 Effect of the mixing temperature on the TGA thermograms of BR/clay/DDAC vulcanizates.

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