

Preparation and Properties of Natural Rubber Nanocomposites with Solid-State Organomodified Montmorillonite

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Received 9 July 2006; accepted 12 March 2007

DOI 10.1002/app.26539

Published online 15 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel organomodified montmorillonite prepared by solid-state method and its nanocomposites with natural rubber were studied. The nanocomposites were prepared by traditional rubber mixing and vulcanizing process. The properties of solid-state organomodified montmorillonite were investigated by Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The dispersion of the layered silicate in rubber matrix was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results showed that the nanocomposites consisting of solid-state organomodified montmorillonite and natural rubber are obtained. The solid-state organomodified montmorillonite can not only accelerate the curing process, but also improve

the mechanical and aging resistance properties of NR. The properties improvement caused by the fillers are attributed to partial intercalation of the organophilic clay by NR macromolecules. In addition, the dynamic mechanical analysis (DMA) results showed a decrease of $\tan\delta_{\max}$ and increase of T_g when the organoclay is added to the rubber matrix, which is due to the confinement of the macromolecular segments into the organoclay nanolayers and the strong interaction between the filler and rubber matrix. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2786–2792, 2008

Key words: natural rubber; organoclay; nanocomposites; modification; preparation

INTRODUCTION

Polymer–clay nanocomposites are a rapidly developing class of composites, which is defined as molecular composites of polymer and organophilic silicate layers of clay mineral. Since Toyota group showed a considerable enhancement of properties of nylon by incorporating layered silicates, these polymer–clay nanocomposites have recently aroused a significant amount of interests from polymer scientists because of the mutual interaction between the polymer and clay, which afford interesting physical properties.¹ The dispersion of small amount of clay in the polymer matrix can impart radical improvement in mechanical properties, solvent resistance, ionic conductivity, flammability resistance, gas barrier properties, and biodegradability of polymers. Numerous researchers have already worked on polymer–clay nanocomposites based on a variety of polymers, namely nylon,^{2,3} polypropylene,^{4,5} polyethylene,^{6,7} polystyrene,^{8,9} epoxy resin,^{10,11} polymethylmethacrylate,^{12,13} polyurethane,^{14,15} natural rubber,^{16,17} styrene butadiene rubber,^{18,19} epoxidized rubber,²⁰ ethylene–propylene–diene rubber,²¹ etc.

Montmorillonite, hectorite, and saponite are the most commonly used layered silicates. These kinds of clay are characterized by a moderate negative surface charge, which is known as the cation exchange capacity (CEC). To confer these hydrophilic clay more organophilic, the hydrated cations of the interlayers can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium. When the exchangeable cations are ion-exchanged with organic cations, which usually results in a larger interlayer spacing and the organophilic modified clay, the surface energy of the clay is lowered and become more compatible with organic polymers. Therefore, the key to prepare polymer–clay nanocomposites is the organic modification of clay. Unfortunately, the literature survey showed that most clay is organically modified with long chain cation surfactant in solution state. The modification process is complex and organophilic clay is expensive, so it is difficult to apply in industry, which forced researchers to have a look at alternative methods. If a novel and cheap modifier is used to modify the layered silicate in solid state, it will be advantageous to the industrialization of polymer–clay nanocomposites. Accordingly, in this article the modification of montmorillonite with tetraethylene pentamine as a cheaper modifying agent in solid state was studied, which process is simple and can lower the cost

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of organoclay. Furthermore, the preparation and characterization of natural rubber/solid-state organo-modified montmorillonite nanocomposites were investigated.

EXPERIMENTAL

Materials

Natural rubber ISNR-3 was used, [volatile matter, 1% (max.) by mass; ash, 1% (max.) by mass; dirt content 0.03% (max.) by mass; nitrogen content 0.6% (max.) by mass; initial plasticity 30 (min.) and plasticity retention index 60 (min.)]. Na-montmorillonite (MMT), with a cationic exchange capacity of 90 meq/100 g, is supplied by Nanhai Inorganic Factory (China, Guangdong). The tetraethylene pentamine (TEPA) is purchased from Shanghai Reagent Factory (China), CP grade.

Preparation of solid-state organo-modified montmorillonite

In a 0.5 L flask, 60 g of sodium montmorillonite was blended with 7 g of tetraethylene pentamine, followed by vigorously stirring at 100°C for 4 h. After cooling, the product was sieved by a 200-mesh-sized sieve (0.076 mm). The solid-state organo-modified montmorillonite is abbreviated as SOM. No solvent was used during the whole process.

Preparation of NR/SOM nanocomposites

NR (100 g) and 2 ~ 8 g solid-state organo-modified montmorillonite were mixed for 10 min at room temperature with 1.5 g sulfur, 5 g ZnO, 2 g stearic acid, 1.5 g accelerator CBS(*N*-cyclohexylbenzothiazole-2-sulfenamide), and 0.5 g accelerator DM (Dibenzothiazole disulfide) in an $\phi 160 \times 330$ mm open mill. The rotors operated at a speed ratio of 1 (front): 1.22 (back). The compounds were vulcanized in an electrically heated press at 143°C for the optimum cure time (t_{90}), which is previously determined with rubber process analyzer (RPA 2000, Alpha Technologies), to obtain the sheets of natural rubber vulcanizates with 2 ~ 8 wt % SOM. The samples were termed as NR/SOM (2 ~ 8 phr). To use as reference, corresponding NR vulcanizate was prepared in a same process described above by using 5 wt % sodium montmorillonite (Na-MMT) as filler, which termed as NR/MMT (5 phr). Compounds containing the TEPA with MMT and containing TEPA only in the absence of MMT were also prepared to determine the effect of the TEPA on the properties of NR, which termed as NR/TEPA/MMT (5 phr) and NR/TEPA. In these cases, the amount of neat TEPA added to the recipe corresponds with that incorporated in the 5 g SOM.

Characterization

Wide-angle X-ray diffraction (XRD) was used to characterize the montmorillonite and to study the nature and extent of the dispersions of the montmorillonite in the filled sample. X-ray diffraction patterns of the samples were recorded on a D/MAX-III-diffractometer (30 kV, 10 mA) by using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) with a scanning rate 2°/min at room temperature. Bragg's law, defined as $\lambda = 2d\sin\theta$, was used to compute the crystallographic spacing (d) for montmorillonite, solid-state modified montmorillonite and their rubber composites.

Fourier-transform infrared spectroscopy (FTIR) was recorded on a Nicolet Fourier-transform infrared spectrophotometer. Clay powder was pressed with KBr powder for FTIR measurement in transmission mode at a resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA) was carried out in a TA2890 (TA Instrument, USA) thermogravimetric analyzer over a temperature range from room temperature to 900°C at a heating rate of 20°C/min. Nitrogen flow (80 mL min⁻¹) was utilized to remove all corrosive gases involved in the degradation and to avoid thermoxidative degradation.

Rubber process analyzer (RPA 2000, Alpha Technologies) was used to determine the curing characteristics of rubber compound and measure the mechanical loss factor of vulcanized rubber under the frequency from 0.5 to 25 Hz with 0.5° strain at 60°C.

The dynamic mechanical spectra of the samples were obtained by using TA 2890 (TA Instrument, USA) dynamic mechanical analyzer (DMA). The specimens were analyzed in tensile mode at a constant frequency of 1 Hz, a strain of 0.1%, and a temperature range from -80 to 20°C at a heating rate of 2°C min⁻¹. Mechanical loss factor ($\tan\delta$) and storage modulus (E') were measured as a function of temperature for the samples under identical conditions.

Transmission electron microscopy (TEM) images were taken with a JEM-100CXII at an accelerator voltage of 120 kV. Thin sections (ca.100 nm) of the samples were cut out with a diamond knife at ca. -120°C and used without staining.

Tensile stress-strain properties were measured according to ISO 37-1997 specifications, on an U-can dynamometer, at 25°C with crosshead speed of 500 mm min⁻¹. Tensile strength, elongation at break, tear strength, and modulus at 100 and 300% elongation were determined.

RESULTS AND DISCUSSION

Characterization of solid-state organo-modified montmorillonite

Figure 1 shows the X-ray diffraction pattern of (a) MMT and (b) SOM. MMT shows a characteristic dif-

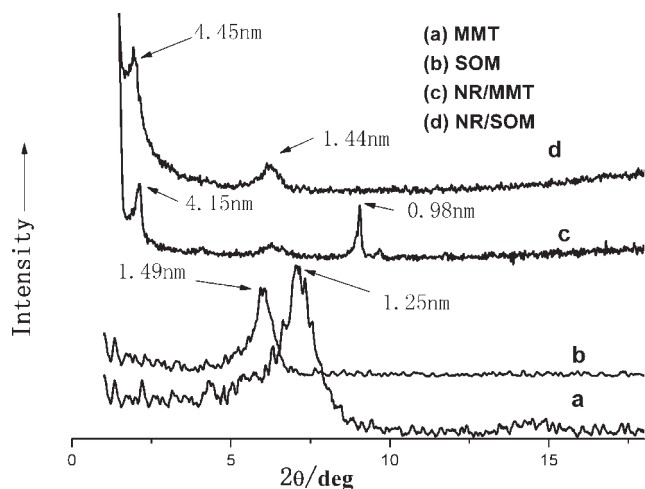


Figure 1 X-ray diffraction patterns of (a) MMT; (b) SOM; (c) NR/MMT and (d) NR/SOM.

fraction peak at $2\theta = 6.90^\circ$, which is assigned to the interlayer platelet spacing (001 diffraction peak) of montmorillonite, with a spacing of 1.25 nm. When intercalating agent is added, the peak moves to lower angles. The organoclay presents a peak at $2\theta = 5.94^\circ$, which as deduced by the Bragg equation corresponds to an interlayer distance of 1.49 nm. According to those results, it is assumed that the tetraethylene pentamine behaves as an effective intercalating agent, enlarging the interlayer spacing of montmorillonite. When MMT was incorporated with NR [(c) in Figure 1], a peak presents at $2\theta = 2.12^\circ$, which corresponds to an interlayer distance of 4.15 nm. This result means that the NR can intercalate partial MMT to some extent under the force of mixing. It is interesting that a distinct peak appears at $2\theta = 9.04^\circ$, which corresponds to an interlayer distance of 0.98 nm. This maybe is caused by the extraction of water in the interlayer of MMT during the mixing and thermal setting process. After the SOM incorporated with NR, the NR/SOM nanocomposite [(d) in Figure 1] shows the interlayer spacing of SOM in NR increases to 4.45 nm because the long chains of macromolecules are intercalated into the interlayers of organic clay. It is worth noting that there is a weak diffraction peak of NR/SOM nanocomposites presents at $2\theta = 5.94^\circ$, which means that there are still a small amount of organic clays have not been intercalated by NR, so the intercalated and unintercalated clay species coexist in the nanocomposites. Further more the peak corresponding to the interlayer distance of 0.98 nm in the NR/MMT disappears. From those results it can be deduced that the modification of clay could lead more intercalation of NR into interlayers of clay.

Figure 2 shows the FTIR spectra of montmorillonite and solid-state organomodified montmorillonite. Montmorillonite presents two typical peaks. A strong

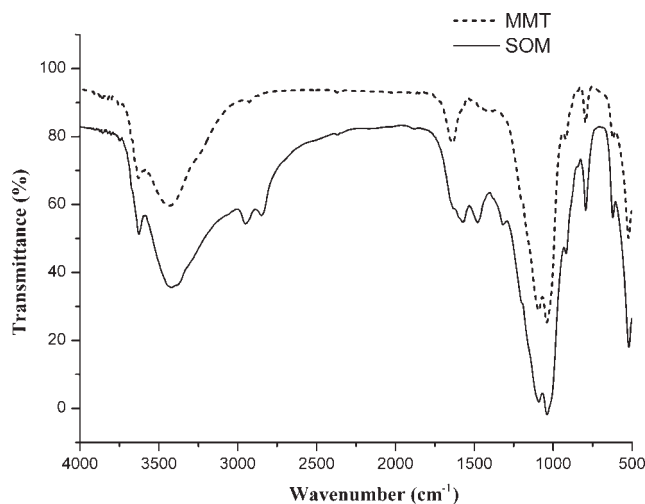


Figure 2 FTIR spectra of pristine montmorillonite (MMT) and solid-state organomodified montmorillonite (SOM).

absorption band at 1063 cm^{-1} is observed, corresponding to the Si—O stretching vibration of the silicate. The band observed at 1638 cm^{-1} is assigned to the deformation vibrations of the interlayer water of the montmorillonite. Note that in the case of the SOM, three new peaks appear in the FTIR spectrum. Bands at 2928 and 2851 cm^{-1} are attributed to the C—H asymmetric and symmetric stretching vibrations of tetraethylene pentamine, respectively. The band at 1474 cm^{-1} corresponds to the ammonium salt. Furthermore, the deformation vibration of the interlayer water of the montmorillonite is shift to 1568 cm^{-1} , which is assumed that the intercalating agent has reacted with the water in the interlayer. These results further indicate that the tetraethylene pentamine has been incorporated within the silicate layers.

The thermal decomposition expressed in terms of weight loss as a function of the temperature for

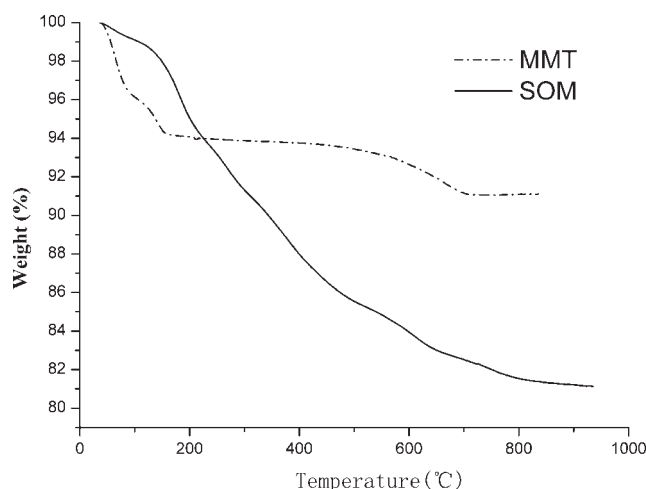


Figure 3 TGA thermograms of MMT and SOM.

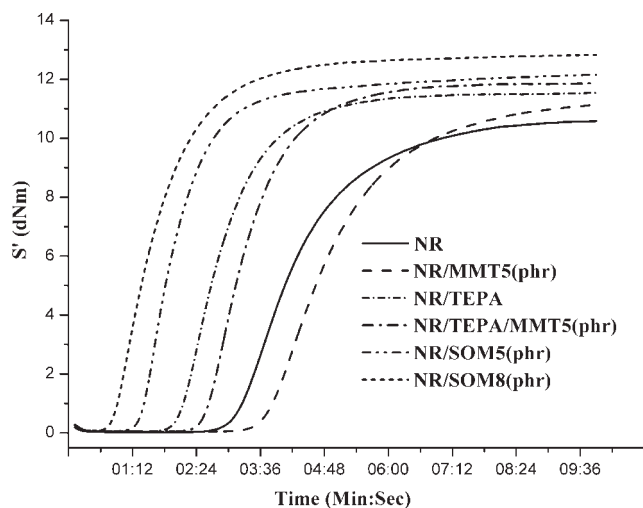


Figure 4 Vulcanization curves of the compounds at 143°C.

the montmorillonite and solid-state organomodified montmorillonite is represented in Figure 3. When the temperature is up to 200°C, the weight loss of the montmorillonite is about 6%, which corresponds to the escape of surface and interlayer adsorbed water. Heating above 600°C begins to remove the water resulting from the structural OH groups of clay. At 800°C, the total weight loss of the clay is about 8%. When an intercalating agent is added, the decomposition of the organoclay is characterized by two steps. The first one, which is the decomposition of the surface and interlayer adsorbed water, decreases to 2% loss weight below 150°C. The second one has a total weight loss of ~ 18%, which is due to the decomposition of intercalating agent. In the second step, it is interesting to notice that the intercalating agent decomposes slowly and lasts to a very high temperature, which is different to the normal thermal decomposition. These results show that the decomposition of TEPA requires a higher temperature, which confirm that the TEPA has been incorporated into the galleries of the MMT.

Vulcanization characteristics

The vulcanization curves of NR and its composites with MMT, SOM, TEPA, and TEPA + MMT are

graphically represented, as obtained from the RPA 2000 measurements, in Figure 4. The curing characteristics, expressed in terms of the vulcanization times, ts_2 (scorch time) and t_{90} (optimum cure time), as well as the maximum and minimum values of the torque, S_{max} and S_{min} , respectively, and delta torque ΔS ($\Delta S = S_{max} - S_{min}$), are deduced from the curves. These parameters, along with the cure rate index, CRI expressed as $CRI = 100/(t_{90} - ts_2)$, are compiled in Table I.

Note that vulcanization time, ts_2 and t_{90} , were sharply reduced by the incorporating of TEPA and TEPA + MMT, showing accelerated vulcanization with respect that of pure NR. It is deduced that the TEPA behaves as an effective vulcanizing agent for natural rubber. These results are confirmed by the cure rate index values, CRI, which shows a significant increase with addition of TEPA and TEPA + MMT. It can be attributed to the amine functionalities. It is well known that amine groups facilitate the curing reaction of natural rubber compound. Nevertheless, it is important to note that a further prominent effect on NR curing is observed in the presence of the organoclay. In fact, the intercalation of TEPA within the silicate galleries facilitates the vulcanization reaction, showing a marked decrease of the necessary time for vulcanizing NR as compared to the blend with only TEPA and TEPA + MMT.

On the other hand, the maximum torque and delta torque increase by addition of SOM, showing the strong reinforcing effect of this filler. These results suggest that the natural rubber become more cross-linked in the presence of the organoclay.

Morphology of the nanocomposites

The TEM images of NR/MMT and NR/SOM composites are shown in Figure 5. The light regions represent rubber and the dark regions are the silicate layers. The image of NR/MMT (a) displays a clay tactoid structure. This indicates that the clay cannot be intercalated by NR macromolecular and not be well dispersed in the matrix. Interestingly, large clay tactoid are not observed in the TEM images of the NR/SOM nanocomposites and the SOM layers

TABLE I
Curing Characteristics of Various Systems at 143°C

	ts_2 (min)	T_{90} (min)	S_{min} (dNm)	S_{max} (dNm)	ΔS (dNm)	CRI (min^{-1})
NR	3.47	5.97	0.02	10.58	10.56	40.00
NR/MMT (5 phr)	4.70	7.63	0.04	11.13	11.09	34.13
NR/TEPA	1.87	3.30	0.05	10.95	10.90	69.93
NR/TEPA/MMT(5 phr)	2.45	3.91	0.04	11.86	11.82	68.49
NR/SOM (5 phr)	1.51	2.95	0.05	12.16	12.11	69.44
NR/SOM (8 phr)	1.17	2.66	0.07	12.83	12.76	67.11

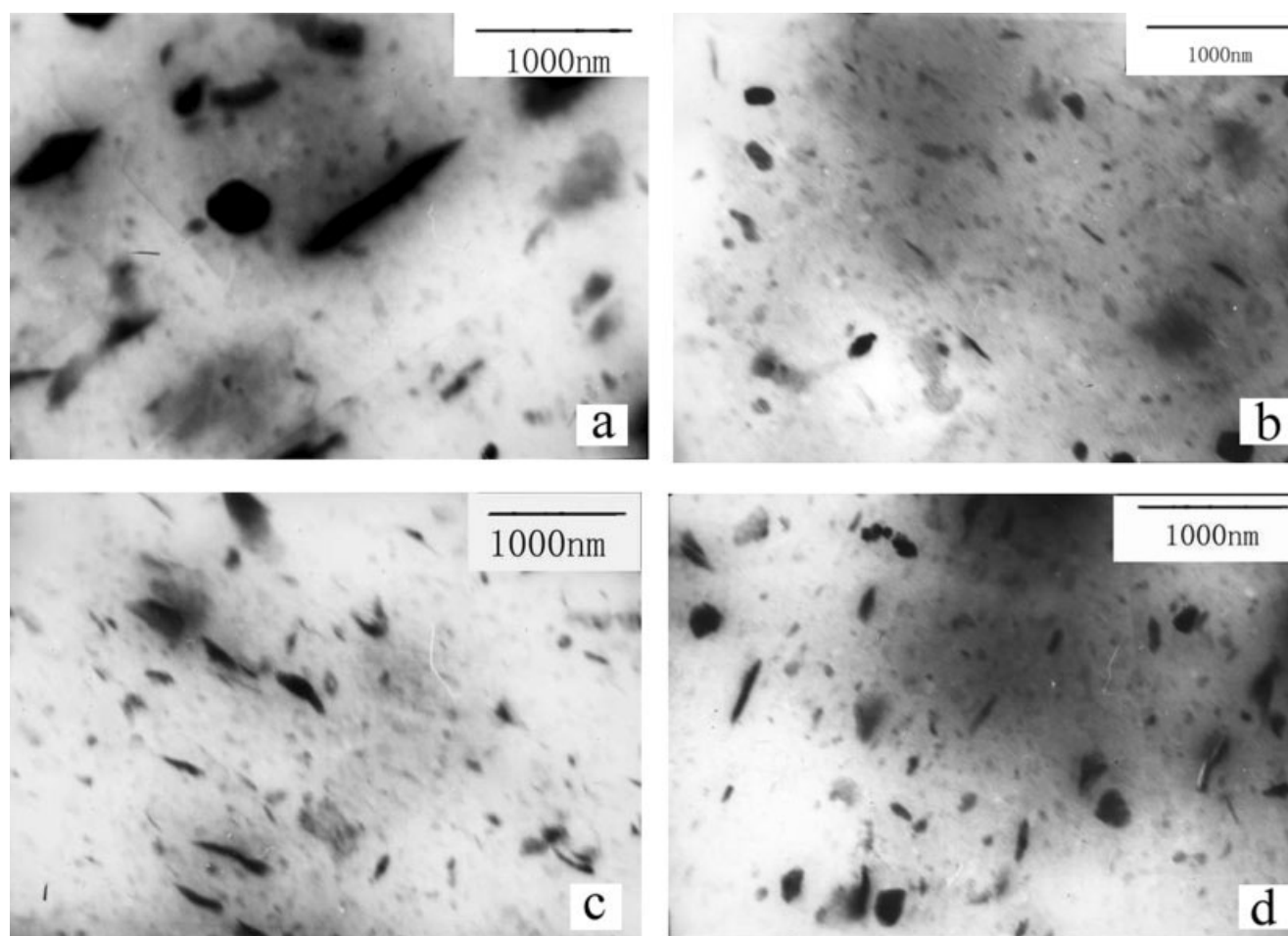


Figure 5 TEM images of the NR composites. (a) NR/MMT (5phr); (b) NR/SOM (2phr); (c) NR/SOM (5phr) and (d) NR/SOM (8phr).

are well dispersed in polymer matrix. As seen in Figure 5, silicate layers are homogeneously dispersed in the NR matrix with some orientation, and the thickness of most silicate layers is below 100 nm and the width about 200–400 nm. Moreover, there are some exfoliated individual silicate layers. The orientation deteriorates and stacks become bigger with the increasing of SOM content because the dispersion becomes worsen when more SOM is added.

According to the results of TEM micrographs and XRD patterns in Figure 1 [(d), NR/SOM nanocomposites], it is believed that highly intercalated natural rubber nanocomposites based on solid-state organo-modified montmorillonite can be obtained by the mechanical mixture method.

Dynamic mechanical properties

Dynamic mechanical analysis (DMA) measures the responses of a given material to a cyclic deformation as a function of the temperature. The dynamic mechanical properties of pristine natural rubber and its composites with clay were investigated over a

wide temperature range. The variations of mechanical loss factor as a function of temperature for the studied materials are showed in Figure 6.

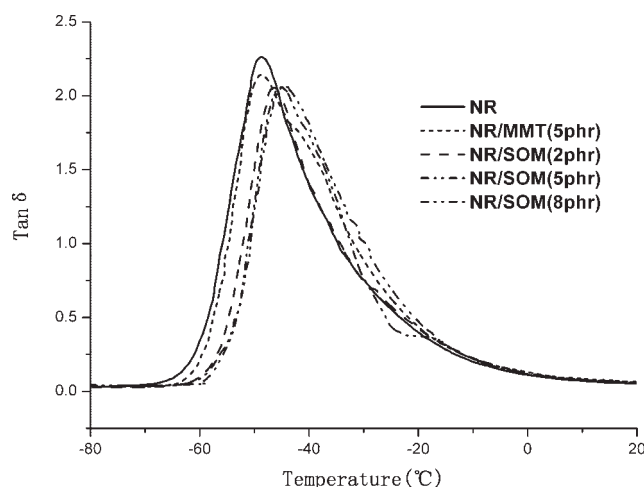


Figure 6 $\text{Tan } \delta$ as a function of temperature for the various systems.

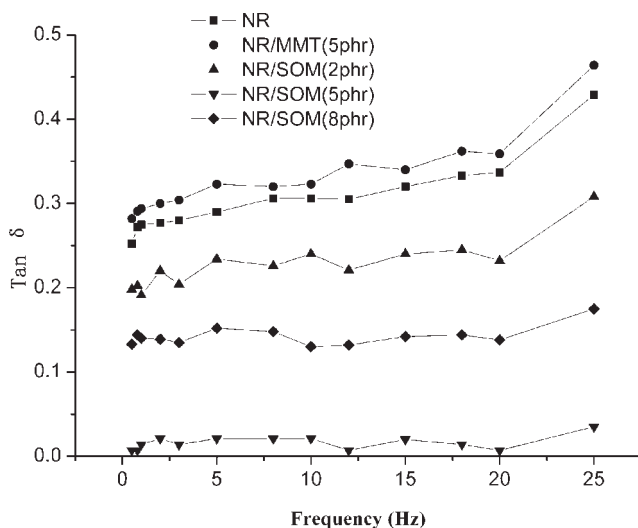


Figure 7 Frequency sweep of NR and NR/clay composite at 60°C.

The glass transition temperature (T_g) shift slightly towards higher temperature when SOM is incorporated, but MMT has no effect on it. T_g goes from -47.6°C for natural rubber to -44.9°C for the composite with 5 phr SOM. These results suggest that there exists a strong adhesion between the filler and polymer. In general, the interaction between the filler and the rubber is strong enough, T_g will shift to a higher temperature. In this study, the obtained results are in concordance with the general tendency reported in the literatures.^{22,23}

Furthermore, after the adding of clay, the $\tan\delta_{\text{max}}$ becomes smaller. It is known that the height of the dynamic transition of a composite apparently reflects the relative quantity of the component itself. The decrease of $\tan\delta_{\text{max}}$ is the result of a reduction of the amount of polymer being deformed during strain oscillation and thus reduces the amount of dissipated energy in the dynamic transition because

the greater amount of polymer includes in intercalated stacks.

It is often believed that the mechanical loss factor at 60°C has apparently relation with rolling resistance when the rubber is used for tire. The lower value of mechanical loss factor at 60°C indicates lower rolling resistant. The frequency sweep of the NR and NR/clay composite at 60°C under 0.5° strain is reported in Figure 7. The results show that pristine MMT slightly increase the mechanical loss factor under experiment conditions because the weak interaction between the clay and matrix. On the contrary, SOM decrease the mechanical loss factor. It is interesting to point out that the decrement is much more in the case of 5 phr SOM and with more SOM is incorporated the storage modulus increases again, but still lower than pristine nature rubber vulcanizate. From these results, it can be deduced that NR reinforced with 5 phr SOM has the lowest rolling resistant. It is assumed that at the experiment conditions the SOM gets the best dispersion and morphology in the rubber matrix, which lead to best dynamic mechanical properties. When adding more inorganic fillers in the matrix, the dynamic mechanical properties become worse because the superabundant filler cannot deform and absorb energy during strain oscillation.

Mechanical properties

Table II lists the mechanical properties of NR and their composites before and after heat aging in air. From the obtained results, it can be deduced that MMT can reinforce the NR in a limited degree at the cost of decreasing the tensile strength and elongation at break. The TEPA and TEPA + MMT can also improve the mechanical properties of NR in a limited degree, because TEPA can behave as vulcanizing agent for natural rubber. But the incorporation of organic silicate gives rise to a noticeable increase

TABLE II
Mechanical Properties of NR and Its Composites

Properties	NR	NR/MMT (5 phr)	NR/TEPA	NR/TEPA/ MMT (5 phr)	NR/SOM (5 phr)	NR/SOM (8 phr)
Modulus, 100% (Mpa)	0.80	0.90	0.95	0.99	1.12	1.13
Modulus, 300% (Mpa)	1.98	2.31	2.28	2.41	3.54	3.76
Tensile strength (Mpa)	22.05	20.88	22.58	22.76	25.47	26.26
Elongation at break (%)	612	582	633	631	646	589
Tear strength (kN/m)	21.17	22.81	22.75	23.08	24.22	25.87
Hardness, Shore A	33	34	34	34	36	38
After heat aging in air ($100 \pm 1^\circ\text{C}$, 48 h)						
Modulus, 100% (Mpa)	1.12	1.13	1.15	1.18	1.27	1.29
Modulus, 300% (Mpa)	4.19	4.31	3.95	4.04	5.28	5.7
Tensile strength (Mpa)	12.00	10.58	14.88	14.99	19.39	20.85
Elongation at break (%)	405	382	452	450	468	481
Properties descend ratio (%) ^a	63.99	66.74	52.94	53.68	44.85	35.16

^a $\{[(\text{tensile strength} \times \text{elongation at break})_{\text{before aging}} - (\text{tensile strength} \times \text{elongation at break})_{\text{after aging}}] / (\text{tensile strength} - \text{elongation at break})_{\text{before aging}}\} \times 100\%$.

in tensile strength, elongation at break and modulus, which shows the strong reinforcing effect of the inorganic fillers. The improvements of tensile strength and tensile modulus in case of polymer-clay nanocomposites were given by some researchers.^{22,24,25} Their studies suggested that the increase of strength and modulus is related to the degree of dispersion of clay layers into the polymer matrix. Some explanations were presented on the basis of interfacial properties and restricted mobility of the polymer chain. From those references, it is deduced that the main reason for the reinforcement in this case is the perfect dispersion of SOM into polymer matrix and the strong interface bonding between rubber chains and silicate layers, which is provided by tetraethylene pentamine through ionic or Van der Waals type interaction. The reinforcement is also associated with the anisotropy and high aspect ratio of organoclay nanofillers, which act as short reinforcing fibers with nanoscale architecture. Clay with high aspect ratio is more efficient in restricting the rubber chains and in resisting the development of cracks than spherical fillers.²⁶

Furthermore, SOM can improve the aging resistance properties of NR. After aging the tensile strength and elongation at break of NR pure gum vulcanizate decrease sharply while the tensile modulus increase because of the oxidation and degradation of natural rubber. The SOM can reduce the decrease of tensile strength and elongation at break and enhance the modulus at the same time. The studies on the improvement of aging resistance and thermal stability by polymer-clay nanocomposites have been extensively reported.²⁷⁻²⁹ Generally, the incorporation of clay into the polymer matrix is found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition.

CONCLUSIONS

A novel preparation method of organoclay, which modify the MMT with TEPA in solid state, is proposed. The results showed that in solid state the TEPA could intercalate into the interlayers of montmorillonite and hence lead to the increase of interlayer spacing and the improvement of the compatibility between the filler and the rubber. On the other hand, NR/SOM nanocomposites can be prepared in mechanical mixing and vulcanizing process. The structure and properties of NR/SOM

nanocomposites were investigated. In these nanocomposites, the silicate layers are homogeneously dispersed in NR matrix at a nanometer scale with some orientation. The SOM can not only accelerate the curing process, but also improve the mechanical and aging resistance properties of NR.

References

1. Usuki A.; Kawasumi M.; Kojima Y.; Okada A. *J Mater Res* 1993, 8, 1174.
2. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1993, 49, 1259.
3. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O.; Kaji, K. *J Polym Sci Part B: Polym Phys* 1995, 33, 1039.
4. Kato, M.; Usuki, A.; Okada, A. *J Appl Polym Sci* 1997, 66, 1781.
5. Hasegawan, N.; Okamoto, H.; Kato, M.; Usuki, A. *J Appl Polym Sci* 2000, 78, 1918.
6. Heinemann, P.; Reichert, R.; Thomann, R. *Macromol Rapid Commun* 1999, 20, 423.
7. Rong, J.; Jing, Z.; Li, H.; Sheng, M. *Macromol Rapid Commun* 2001, 22, 329.
8. Fu, X.; Qutubuddin, S. *Polymer* 2001, 42, 807.
9. Chen, G.; Liu, S.; Zhang, S.; Qi, Z. *Macromol Rapid Commun* 2000, 21, 746.
10. Wang, M. S.; Pinnavaia, T. *J Chem Mater* 1998, 10, 1820.
11. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. *J Chem Mater* 1995, 7, 2144.
12. Huang, X.; Brittain, W. *J Macromol* 2001, 34, 3255.
13. Zeng, C.; Lee, L. *J Macromol* 2001, 34, 4098.
14. Wang, W.; Pinnavaia, T. *J Chem Mater* 1998, 10, 3769.
15. Tien, Y. I.; Wei, K. H. *Polymer* 2001, 42, 3213.
16. Varhese, S.; Karger-Kocsis. *Polymer* 2003, 44, 4921.
17. Lopez-Manchado, M. A.; Herrero, B.; Arroyo, M. *Polym Int* 2003, 52, 1071.
18. Sadhu, S.; Bhowmick, A. K. *Rubber Chem Technol* 2003, 76, 860.
19. Sadhu, S.; Bhowmick, A. K. *J Appl Polym Sci* 2004, 92, 698.
20. Vu, Y. T.; Mark, J. E.; Pham, L. H.; Engelhardt, M. *J Appl Polym Sci* 2001, 82, 1391.
21. Chang, Y. C.; Yang, Y.; Ryu, S.; Nah, C. *Polym Int* 2002, 51, 319.
22. Lopez-Manchado, M. A.; Herrero, B.; Arroyo, M. *Polym Int* 2004, 53, 1766.
23. Maiti, M.; Bhowmick, A. K. *J Polym Sci* 2006, 44, 162.
24. Bala, P.; Samantaray, B. K.; Srivastava, S. K. *J Appl Polym Sci* 2004, 92, 3853.
25. Varghese, S.; Gatos, K. G.; Apostolov, A. A. *J Appl Polym Sci* 2004, 92, 543.
26. Wang, Y.; Zhang, H.-Z.; Wu, Y.-P. *J Appl Polym Sci* 2005, 96, 318.
27. Blumstein, A. *J Polym Sci Part A: Gen Pap* 3 1965, 3, 2665.
28. Burnside, S. D.; Giannelis, E. P. *Chem Mater* 1995, 7, 1597.
29. Wang, S. J.; Long, C. F.; Wang, X. Y. *J Appl Polym Sci* 1998, 69, 1557.