Flame Retardance of Montmorillonite/Rubber Composites

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ABSTRACT: The effect of dispersion of clay in rubber on the mechanical properties and flame retardance of rubber/montmorillonite (MMT) nanocomposites and rubber/MMT microcomposites were investigated in the present article, and the results were compared with the performance of silica reinforced rubber composites. Cone calorimeter test and limiting oxygen index test were employed to evaluate the flame retardance. From the results, it could be seen that the rubber/MMT nanocomposites always possessed the best flame retardance, such as lower peak heat release rate and higher fire performance index value. In addition, the rubber/MMT nanocomposites also showed better mechanical properties than the pure rubber and the other composites, especially in tear strength. With the rubber/silica composites, as expected, the silica could appropriately endow the rubber with flame retardance. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3318–3324, 2008

Key words: clay; cone calorimeter; dispersion; flame retardance; rubber/MMT composites

INTRODUCTION

Because of the nanometer effect and stronger interaction between nanoparticle and matrix, nanocomposites can exhibit excellent performance, compared with polymer matrix or microcomposites.[1–3] As a special kind of nanocomposites, polymer–clay composites have attracted a great deal of interest owing to their improved mechanical, thermal, gas barrier and reduced flammability properties at low cost.[4–5] Polymer–clay nanocomposites are hybrids composed of layered silicates dispersed in a polymer matrix in the form of reticular layer of crystals about 1 nm thick and with a lamellar aspect ratio between 100 and 1000. In general, the methods of preparing polymer–clay nanocomposites to achieve molecular-level incorporation of the layered silicate into the polymer are: *in situ* polymerization, polymer melt intercalation, and polymer solution intercalation.[6–7] In this article, the method of polymer latex compounding was employed to prepare the rubber/clay nanocomposites.

Polymer–clay nanocomposites have been developed as a new kind of halogen-free flame retarding composites, and the flame retardance of many plastics–clay nanocomposites have been studied.[8–10] It was found that low filling level (< 5 wt % mostly) could make the nanocomposites possess good flame retardance and mechanical properties. The flame retarding mechanism of polymer/clay nanocomposites was also investigated, and the improved flame retardance of nanocomposites results from the flame retardant element (Si) and the MMT-rich surface of the char, which is caused by the gradual degradation and gasification of the polymers or the migration of the MMT to the surface driven mainly by the lower surface free energy of the MMT.[11–12]

In this article, several kinds of rubber/clay composites were investigated to find an effective way to enhance the flame retardance and mechanical properties simultaneously, including styrene-butadiene rubber (SBR), natural rubber (NR), and nitrile-butadiene rubber (NBR).

EXPERIMENTAL

Material

Na-montmorilonite with a cationic exchange capacity (CEC) of 93 mequiv/100 g was provided by Siping Montmorillonite Co., Jilin Province, China. Three kinds of rubber latex were used in the present work: SBR1502 latex, from Qilu Rubber Co., Shandong Province, China; NR latex, from Beijing Rubber Latex Factory; NBR latex with 26% AN, from Synthetic Rubber Factory of Lanzhou Petroleum and Chemical Corp. SiO_2 with an average particle size of ~ 20–40 nm was bought from Nanji Chemical Technology Company (Jiangsu Province, China).
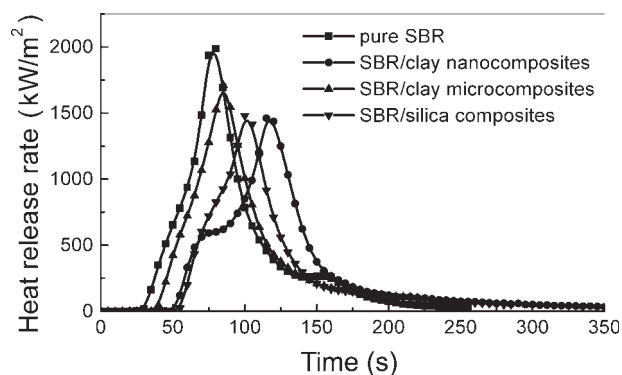
Figure 1 Comparison of the heat release rate plots for pure SBR and its composites.

Basic formulas (phr)

SBR or NR systems: SBR, 100; clay or silica, 20; zinc oxide, 5.0; stearic acid, 2.0; dibenzothiazole disulfide (DM), 0.5; diphenyl guanidine (D), 0.5; tetramethyl thiuram disulfide (TMTD), 0.2; sulfur, 2.0; *n*-isopropyl-*N'*-phenyl-*p*-phenylene dianime, 1.0.

NBR system: NBR, 100; clay or silica, 20; zinc oxide, 5.0; stearic acid, 1.0; dibenzothiazole disulfide (DM) 1; sulfur 1.5; *n*-isopropyl-*N'*-phenyl-*p*-phenylene dianime, 2.0.

Preparation of composites

Na-MMT was dispersed in water with vigorous stirring at a concentration of 5%, and the aqueous suspension of silicate was achieved. To purify Na-MMT, the aqueous suspension was kept at room temperature for 24 h and the deposition was removed. The concentration of the resulting suspension was calculated. The suspension and rubber latex, were added into a vessel, stirred for 20 min, coagulated by adding dilute sulfuric acid (2%), washed with water several times until its pH was about 7, and dried at 70°C for 24 h to obtain the MMT/rubber nanocomposites.

To obtain the vulcanizates, the MMT/rubber nanocomposites were mixed with ingredients according to the recipe of the basic formulas in an open two-roll mill for 10 min and then vulcanized at 150°C in a hot press for an optimum cure time (t_{90}). Viscosity was determined by a rheometer (Beijing Huan Feng Mechanical Factory) and the rubber/MMT nanocomposites were obtained. The above-mentioned method could also be used to prepare silica/rubber nanocomposites.

The MMT/rubber microcomposites and rubber/silica composites were prepared for comparison. Na-MMT was directly blended with SBR, NR, or NBR in a two-roll mill for 10 min respectively, and then the ingredients according to the basic formulas were added and mixed for 5 min. The resulting blends were vulcanized at 150°C for t_{90} to yield vulcanizates of microcomposites.

Measurements

### Mechanical properties measurement

Measurement of mechanical properties of all the samples was carried out based on corresponding ASTM standards at a strain rate of 500 mm/min and at 25°C ± 2°C by an Instron 3211 tensile tester.

TEM analysis

TEM observations were carried out with an H-800 TEM (Hifachi, Japan) by using an acceleration voltage of 200 kV.

Flame retardance testing

Limiting oxygen index (LOI) is an indicator of the minimum oxygen concentration that is needed to cause the material fired in an oxygen–nitrogen atmosphere through downward burning of a vertically mounted specimen. Test specimen is required to be 70–150 mm in length, 6.5 mm in width, and 3 mm in thickness, according to Chinese state standard GB/T2406-93, using a Jiangning Analyzer Plant instrument JF-3, China. Cone calorimeter is a kind of novel instrument to comprehensively evaluate the flame retardance of composites.[13] The cone calorimeter produced by FTT Company of UK uses a truncated conical heater element to irradiate test specimen at heat fluxes from 10 to 100 kW/m² to simulate a range of fire intensities. In the present work, cone calorimeter tests were carried out according to ISO5600-93, using the incident heat flux of 50 kW/m². The bottom and edges of each specimen with a dimension of (100 × 100 × 3) mm³ are wrapped with an aluminum foil. Heat release rate (HRR), ignition time (IT), residual mass of the composite, and fire performance index (FPI), defined as the ratio of IT to peak RHR (FPI = IT/Peak RHR), can be obtained through the test at one time. It has been suggested that FPI value relates to the time to flashover (or the time available for escape) in a full-scale fire situation.
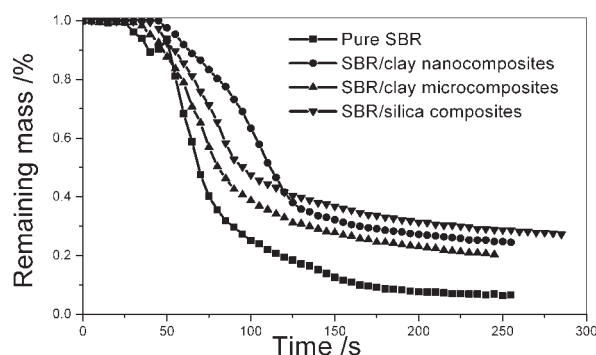
Figure 2 Comparison of the remaining mass plots for pure SBR and its composites.

TABLE I
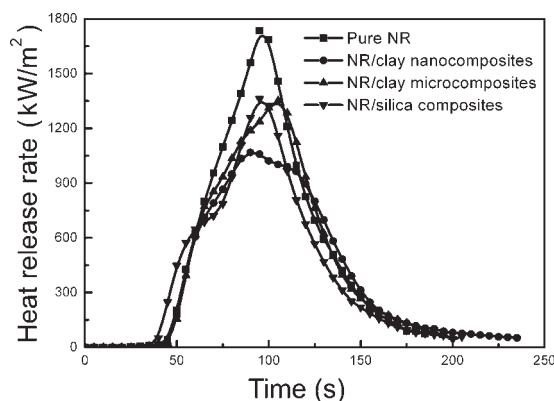**Important Parameters of Pure SBR and Its Composites**

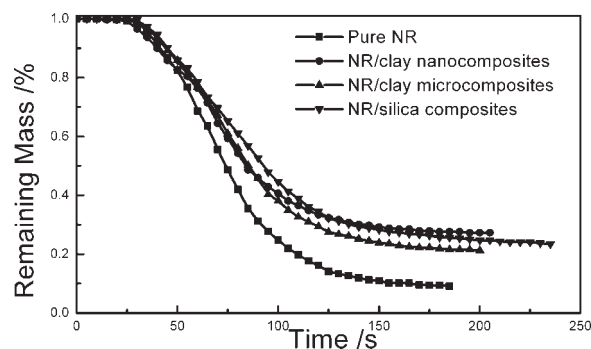| Sample	IT (s)	PHRR (kW/m^2)	t_{PHRR} (s)	FPI
Pure SBR	18	1984.73	76	0.009
SBR/clay nanocomposites	44	1461.29	117	0.03
SBR/clay microcomposites	31	1710.79	85	0.018
SBR/silica composites	45	1478.72	100	0.03

RESULTS AND DISCUSSION

Flame retardance of SBR composites

Cone calorimetry, which is based on the oxygen-consumption principle, can provide important information on the flame retardance of polymer composites, such as HRR, peak heat release rate (PHRR), mass loss rate (MLR), the remaining mass, FPI, etc.

The cone calorimeter results of SBR/filler systems are presented in Figures 1 and 2, and the related important parameters can be found in Table I. Compared with the other three systems, an important result obtained from curves of HRR to time (Fig. 1) is that the SBR/clay nanocomposites exhibit the lowest peak HRR, and the longest time getting to the maximum RHR. It has been suggested that FPI of composites relates to the time to flashover (or the time available for escape) in a full-scale fire situation. This index can well reflect the potential danger of composites in fire. The higher the FPI value, the longer the time to flashover is, which means there is more time for people to escape in fire situation. In Table I, the SBR/clay nanocomposite also presents a higher FPI value. Figure 2 shows the relationship between the remaining mass and heat radicalization time under the heat flux of 50 kW/m^2. It can be seen that the SBR/clay nanocomposites keep the highest remaining mass among four SBR systems before 120 s; however, the SBR/silica composites hold more remaining mass than do the nanocomposites after 120 s. Generally
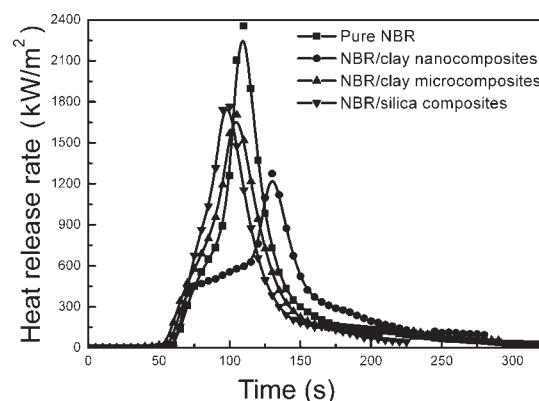
Figure 4 Comparison of the remaining mass plots for pure NR and its composites.

speaking, the more the remaining mass in fire, the better the flame retardance of composites. Hereby, these results strongly confirm that the SBR/clay nanocomposite possesses excellent flame retardance.

From the above-mentioned data, it can also be seen that the composites filled with nanosilica show certain flame retardance properties, such as longer IT and the time corresponding to PHRR, lower PHRR, and higher FPI value. This is ascribed not only to the dilution mechanism of silica, but to its flame retardance and the strong interaction between SBR and nanoparticles. In the opinion of authors, the strong interaction between inorganic flame retardant and polymer matrix benefits the enhancement of flame retardance of composites.[14]

Flame retardance of NR/clay and NBR/clay systems

To get an exact and overall conclusion, i.e., to find the difference of flame retardance between rubber/clay nanocomposites and rubber/clay microcomposites, the cone calorimeter measurement of NR, NBR, and their compounds was carried out. HRR and remaining mass of these composites are presented in Figures 3 and 5 (HRR curves) and Figures 4 and 6 (remaining mass). Related parameters are also shown in Tables II and III.

Figure 3 Comparison of the heat release rate plots for pure NR and its composites.

Figure 5 Comparison of the heat release rate plots for pure NBR and its composites.
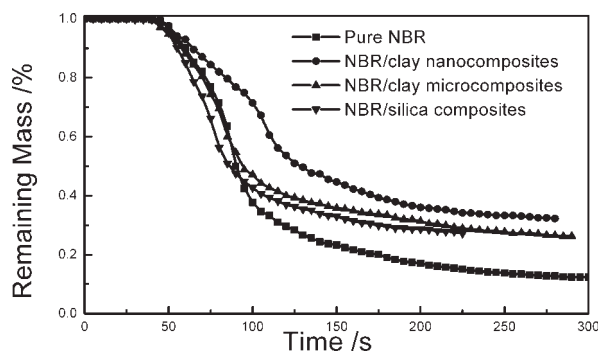
Figure 6 Comparison of the remaining mass plots for pure NBR and its composites.

In natural rubber systems, shown in Figure 3 and Table II, it can be seen that there is little difference in IT and the time corresponding to the PHRR among pure NR and its composites; however, the NR/clay nanocomposites also exhibit the lowest PHRR and highest FPI values as do the SBR/clay nanocomposites. From the curves of remaining mass to heat radiation time, shown in Figure 4, it can be seen that the incorporation of filler can enhance the remaining mass of NR compound, but the NR/silica composites seemly hold the higher remaining mass than do NR/clay nanocomposites before 125 s.

As shown in Figure 5 and Table III, it can be seen that the NBR/clay nanocomposites also possess the best flame retardance among four NBR systems, exhibiting the lowest PHRR, the longest time corresponding to PHRR, and the highest FPI values. In Figure 6, the curves of remaining mass to time of NBR composites are little different from the curves shown in Figures 4 and 2, and NBR/clay nanocomposites always hold the highest remaining mass value among pure NBR and NBR composites.

From the above-mentioned results, the similar conclusion that the NR/clay nanocomposites and NBR/clay nanocomposites possess the best flame retardance can be reached. They show the lowest PHRR values, the highest FPI values, and the highest final residue mass.

Although LOI test cannot reflect the actual combustion situation of material in fire, the data can be well repeated and give a primary and relative com-

TABLE III
Important Parameters of Pure NBR and Its Composites

Sample	IT (s)	PHRR (kW/m^2)	t_{PHRR} (s)	FPI
Pure NBR	46	2355.45	110	0.02
NBR/clay nanocomposites	43	1273.63	130	0.034
NBR/clay microcomposites	40	1702.71	105	0.023
NBR/Silica composites	43	1764	100	0.024

parison of the flammability of materials. So it is still employed to evaluate flame retardance of rubber-based composites in this work. Comparing the LOI values of pure rubber and related composites in each of SBR, NR, and NBR systems in Figure 7, it can be seen that all the rubber/MMT nanocomposites prepared by polymer latex compounding present the highest LOI values.

Morphology analysis

TEM images of SBR/MMT, NR/MMT, and NBR/MMT composites are shown in Figure 8. The dark lines or areas are the intersections of the silicate layer bundles dispersed in rubber. As seen in Figures 8(a), (c), and (e) of microcomposites, some large aggregates of the clay layer exist in the rubber matrix, and the stacked structure should be the same as that of clay powder. Apparently, layers of pristine clay cannot be separated from each other by common rubber mechanical mixing. However, in Figures 8(b), (d), and (f) of nanocomposites, it can be clearly seen that silicate layers are dispersed homogeneously in the rubber matrix at the nanometer level (i.e., thickness of layer bundles <100 nm), and the thickness of most silicate layer bundles is about 10 nm and the width is about 200–300 nm. No larger-scale stack is observed. The macroscopical performance of rubber/clay composites is usually controlled by the microcosmic structure of composites. In the

TABLE II
Important Parameters of Pure NR and Its Composites

| Sample	IT (s)	PHRR (kW/m^2)	t_{PHRR} (s)	FPI
Pure NR	29	1733.65	95	0.017
NR/clay nanocomposites	32	1067.73	90	0.03
NR/clay microcomposites	31	1350.44	105	0.023
NR/silica composites	24	1361.33	95	0.018
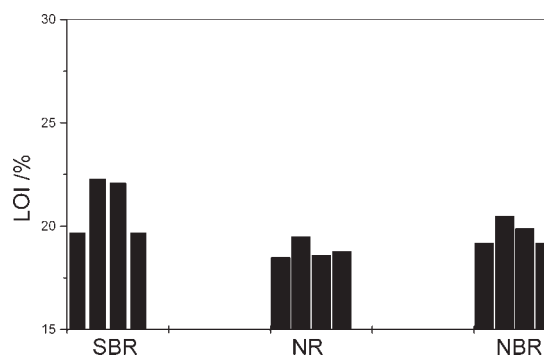
Figure 7 LOI values of pure rubber and rubber composites (from left to right: pure rubber; rubber/clay nanocomposites; rubber/clay microcomposites; rubber/silica composites).

a) SBR/clay microcomposites

b) SBR/clay nanocomposites

c) NR/clay microcomposites

d) NR/clay nanocomposites

e) NBR/clay microcomposites

f) NBR/clay nanocomposites
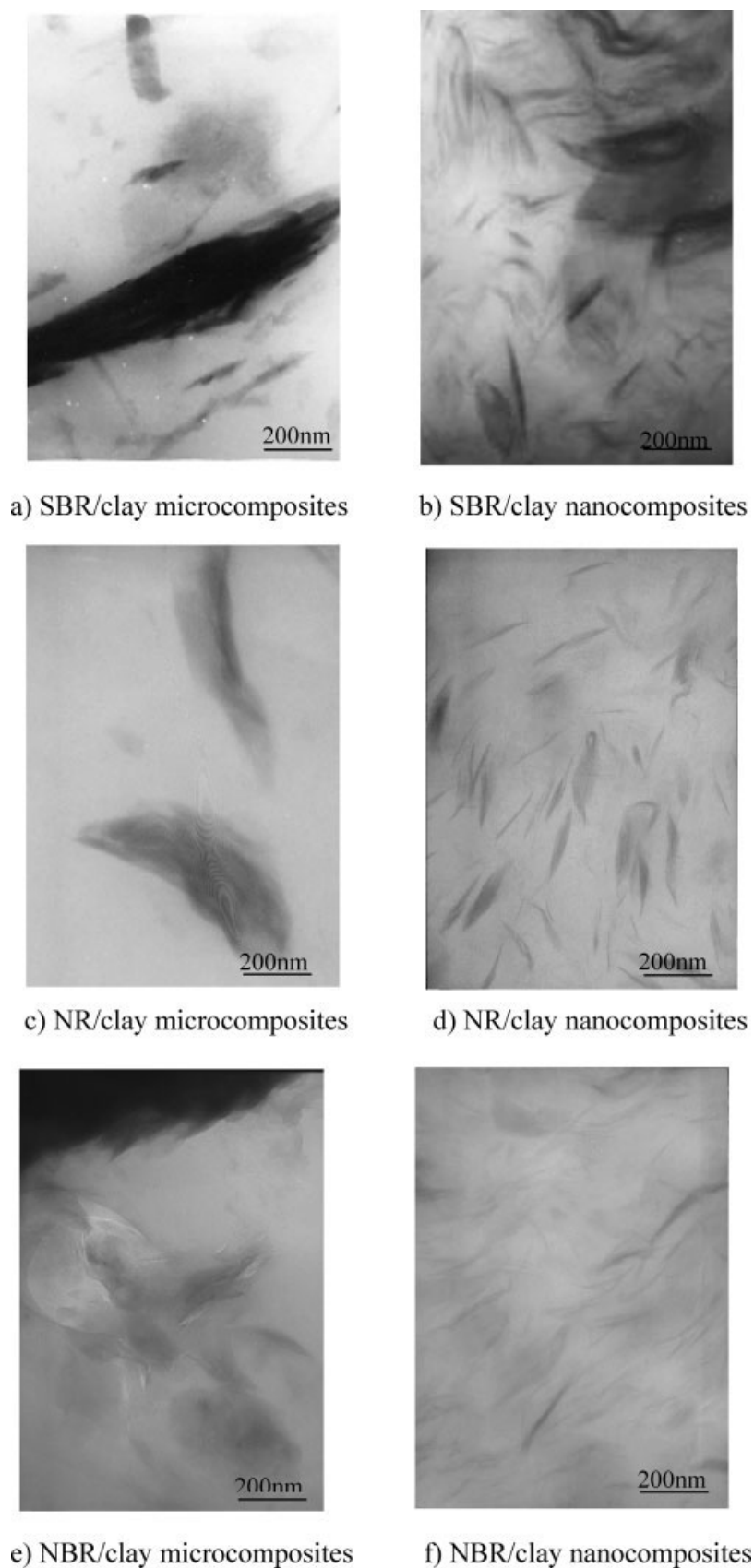
Figure 8   TEM images of rubber/clay composites (rubber/clay = 100/20): (a) SBR/clay microcomposites, (b) SBR/clay nanocomposites, (c) NR/clay microcomposites, (d) NR/clay nanocomposites; e) NBR/clay microcomposites, and (f) NBR/clay nanocomposites.

TABLE IV
Mechanical Properties of SBR and Its Composites

Sample	Stress at 300% (MPa)	Tensile strength (MPa)	Shore A hardness	Tear strength (kN/m)
Pure SBR	1.8	1.9	46	14.1
SBR/clay nanocomposites	8.1	14.5	60	47.4
SBR/clay microcomposites	1.9	2.5	51	15.3
SBR/silica composites	7.2	16.9	64	30.3

present article, the most difference of structure between nanocomposite and microcomposites is the dispersion of clay in rubber matrix.

Therefore, the different flame retardance of microcomposites and nanocomposites should be ascribed to the dispersion of silicate layer. According to the flame retardance mechanism of polymer/clay composites, on the one hand, the layers of clay are separated from each other, and so it is easy for nanoscale silicate layer to migrate from the inside to surface in fire; on the other side, the nanometer dispersion of clay increases the surface specific area of silicate layer, and this benefits the ability of gas barrier[15] and increase of single MMT layer content in burned composites surface. Therefore, the nanodispersion of clay in rubber endows the nanocomposites with the best flame retardance. However, the rubber/silica nanocomposites do not exhibit such good flame retardance as do rubber/clay nanocomposites because of the absence of nanolayer structure.

Effect of dispersion of clay on mechanical properties of composites

The mechanical properties of SBR/MMT nanocomposites, in comparison with the pure SBR, SBR filled with microclay, and SBR/silica nanocomposites, are listed in Table IV.

As shown in Table IV, the SBR/clay nanocomposites exhibit better mechanical properties, compared with pure SBR and SBR/clay microcomposites. Contrasting the SBR/clay nanocomposites with SBR/silica nanocomposites, it can be seen that SBR/clay

nanocomposites possess as good a performance as the silica-reinforced SBR material; however, the tear strength of SBR/clay nanocomposites is far higher than that of silica-reinforced SBR because of the special layer structure of nanoclay. The sheet-like filler with large aspect ratio strongly limits the deformation of macromolecules due to a highly efficient stress transfer. As a result, the nanocomposite possesses high modulus, stiffness, and strength.

From Tables V and VI, it can also be seen that the rubber/clay nanocomposites show the best mechanical properties, such as the highest stress at 300%, very high tensile strength, and the highest tear strength.

Therefore, from the above-mentioned results and analyses, the conclusion can be reached that the rubber/MMT nanocomposites exhibit better mechanical properties and flame retardance at low cost, owing to nanodispersion of silicate layer and stronger interaction between nanoclay and rubber, compared with pure rubber, rubber/clay microcomposites and the silica-reinforced rubber composites.

CONCLUSIONS

In this article, the effect of dispersion of silicate layer on flame retardance and mechanical properties of pure rubber and rubber/clay composites were investigated when compared with those of silica-reinforced rubber composites in SBR, NR, and NBR systems. It could be seen that the rubber/clay nanocomposites prepared by polymer latex compounding always possessed the best flame retardance such as

TABLE V
Mechanical Properties of NR and Its Composites

Sample	Stress at 300% (MPa)	Tensile strength (MPa)	Shore A hardness	Tear strength (kN/m)
Pure SBR	1.8	1.9	46	14.1
SBR/clay nanocomposites	8.1	14.5	60	47.4
SBR/clay microcomposites	1.9	2.5	51	15.3
SBR/silica composites	7.2	16.9	64	30.3

TABLE VI
Mechanical Properties of NBR and Its Composites

Sample	Stress at 300% (MPa)	Tensile strength (MPa)	Shore A hardness	Tear strength (kN/m)
Pure NBR	1.1	2.6	58	12.9
NBR/clay nanocomposites	11.6	14.1	84	40.5
NBR/clay microcomposites	1.4	3.8	62	15.3
NBR/Silica composites	1.6	19.6	65	31.8

the lowest PHRR values and the highest FPI values obtained from cone calorimeter test. With the LOI values of pure rubber and its composites in the SBR, NR, and NBR, the rubber/MMT nanocomposites always showed the highest LOI values and exhibited the best flame retardance. The good flame retardance of rubber/clay nanocomposites was ascribed to the nanodispersion of silicate layer in rubber matrix and strong interaction between nanoclay and rubber. In addition, the rubber/clay nanocomposites also exhibited good mechanical properties because of the nanodispersion of silicate layer in rubber matrix and strong interaction.

References

1. Hua, Y.; Zhang, Z.; Huang, Y. Polym Mater Sci Eng 2002, 18(2), 1.
2. Tang, Y.; Hu, Y.; Wang, S. Polym Degrad Stab 2002, 78, 555.
3. Fukushima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. Clay Mater 1988, 23, 27.
4. Jeffrey, W. Gilman; Morgan, A. In Tenth Annual BCC Conference on Flame Retardancy; Stanford University Press: Stanford, CA, 1999; p 56.
5. Giamellis, E. Adv Mater 1996, 8, 29.
6. Wang, S.; Long, C.; Wang, X.; Li, Q.; Qi, Z. J Appl Polym Sci 1998, 69, 1557.
7. Burnside, S.; Giamellis, E. Chem Mater 1995, 7, 1597.
8. Bourbigot, S.; Le Bras, M.; Dabrowski, F. In Tenth Annual BCC Conference on Flame Retardancy; Stanford University Press: Stanford, CA, 1999; p 100.
9. Zhang, J.; Charles, A. Wilkie. Polym Degrad Stab 2003, 80, 163.
10. Richard Hull, T.; Price, D.; Liu, Y.; Wills, C.; Brady, J. Polym Degrad Stab 2003, 82, 365.
11. Lewin, M. In Thirteenth Annual BCC Conference on Flame Retardancy; Stanford University Press: Stanford, CA, 2002; p 160.
12. Kashiwangi, T.; Shields, J.; Harris, R.; Awad, W.; Zhang, X.; Briber, R. In Fourteenth Annual BCC Conference on Flame Retardancy; Stanford University Press: Stanford, CA, 2003; p 14.
13. Gallia, G.; Bravin, E.; Badalucco, C.; Audisio, G.; Armanini, M.; Chirice, A.; Provasoli, F. Fire Mater 1998, 22, 15.
14. Huang, H.; Zhang, L.; Tian, M.; Chen, Z.; He, Z. China Plast Ind 2003, 31(12), 8.
15. Zhang, H.; Wang, Y.; Zhang, L.; Wu, Y.; Yang J. J Appl Poly Sci 2005, 97, 844.