Study on Flammability of Montmorillonite/Styrene-Butadiene Rubber (SBR) Nanocomposites

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ABSTRACT: The flammability of montmorillonite (MMT)/SBR nanocomposites, prepared by the technique of cocoagulating rubber latex and clay aqueous suspension, was investigated. Flammability studies, performed on the cone calorimeter, showed that the maximum heat release rate (HRR) of SBR decreased from 1987 to 1442 kw/m^2 with the introduction of nanoclay (20 phr). This nanocomposite had the lowest mass loss rate and the largest amount of char upon combustion compared with conventional SBR composites with the same clay loading and pure SBR. The permeability properties of MMT/SBR composites were also measured. It was deduced that the lowered permeability was responsible for the reduced mass loss rate and hence the lower HRR. Unfortunately, the oxygen index (OI) of the nanocomposites was not as high as expected. Combination of $Mg(OH)_2$ and clay was effective for the improvement of both mechanical properties and OI. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 844–849, 2005

Key words: flame retardance; clay; rubber; nanocomposites

INTRODUCTION

Styrene-butadiene rubber (SBR) is widely employed in the tire industry and for other rubber items. Great attention has been attached to modifying the combustion characteristics of SBR to reduce any potential hazard the material may present.[1–5] Some approaches have been used to prepare rubber compositions with decreased tendency to burn, comprising:[6–9] 1) compounding with flame-retardant additives, such as metal hydroxide, phosphorus-containing additives, and chlorinated compounds; 2) postreaction of the elastomer with specific reagents; 3) preparing modified rubber by copolymerization with a small amount of special comonomers; and 4) modifying the cure system. In practice, it is very important that the flame-retardant compounding formula doesn't severely impair the mechanical properties of the rubber. However, it is difficult to optimize among performance, burning behavior, and cost when the flame-retardant rubber is prepared using the above-mentioned method. A technique that is low cost, halogen free, and has no negative effect on mechanical properties is required.

Polymer layered silicate nanocomposites present unique properties compared with their pure polymers or conventional filled polymers[10–15] in aspects such as improved mechanical properties, decreased gas permeability, and increased solvent resistance. Moreover, this kind of nanocomposite usually exhibits increased thermal stability and improved flame retardancy, which are important characteristics for high-temperature applications.[15–20] Blumstein[21] first reported the improved thermal stability of a polymer–clay nanocomposite prepared by free radical polymerization of methyl methacrylate (MMA) intercalated with montmorillonite clay. The polymethylmethacrylate (PMMA) nanocomposite resisted thermal degradation under conditions that would otherwise completely degrade pure PMMA.

Fujiwara and Sakamato[22] first mentioned the potential flame-retardant properties of these types of materials in a patent application on nylon-6 clay nanocomposites. They found that the nylon-6 clay nanocomposites exhibited reduced flammability and form retention after burn compared with pure nylon-6. In 1997, Lee and Giannelis[23] reported on polyimide–clay nanocomposites with improved thermal stability and reduced flammability. Subsequently, more reports about the flammability of polymer layered silicate nanocomposites have appeared.[24–28]

For many polymers, preparing polymer–clay nanocomposites is a good way to, not only reduce the flammability of a polymer, but also to improve its mechanical properties. This is a promising advantage over many flame retardant materials that improve fire retardancy but reduce mechanical properties of polymers. The aims of this work were to investigate the

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TABLE I
Recipe of the SBR Compounds

Ingredients	Contents (phr)
SBR	100
Clay	Variable
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

flammability of MMT/SBR nanocomposites and to find an effective way to improve both flame retardancy performance and mechanical properties of SBR.

EXPERIMENTAL

Materials

Na–montmorillonite (Na–MMT), with a cationic exchange capacity (CEC) of 93 mEq/100 g (from Siping Montmorillonite Co. Ltd., Zhejiang Province, China), and SBR1502 latex(from Qilu Rubber Co. Ltd., Shandong Province, China) were used in this study. The ratio of the styrene unit to butadiene unit in SBR is 23.5%, and the *trans* 1,4-structure and the *cis* 1,4-structure contents of butadiene are 55 and 9.5%, respectively. The 1,2-structure content of butadiene is 12%. The number average molecular weight (M_n) is about 100,000 and the molecular weight distribution is about $4 \approx 6$.

Preparation of nanocomposites

Na–MMT was dispersed in water with vigorous stirring at a concentration of 5% and an 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 rejected. The concentration of the resulting suspension was calculated. The suspension, a stoichiometric amount of interfacial agent ($C_4H_9N^+(CH_2CH_2OH)_3Br^-$, 0.1 mol/100 g clay) and SBR latex, was 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/SBR nanocompounds.

To obtain the vulcanizates, the MMT/SBR nanocompounds were mixed with ingredients according to the recipe listed in Table I in an open two-roll mill for 10 min and then vulcanized at 150°C in a hot press for the optimum cure time (t_{90}). Viscosity was determined by a rheometer(Beijing Huan Feng Mechanical Factory) and the MMT/SBR nanocomposites were obtained.

The preparation of the nanocomposites containing $Mg(OH)_2$ was the same as the above-mentioned process except for the addition of $Mg(OH)_2$ before mixing with the additives.

Preparation of microcomposites

The MMT/SBR microcomposites were prepared to compare with the MMT/SBR nanocomposites. Na–MMT was directly blended with SBR in a two-roll mill for 10 min and then the ingredients according to Table I were added and mixed for 5 min. The resultant blend was vulcanized at 150°C for the t_{90} to yield microcomposite vulcanizates.

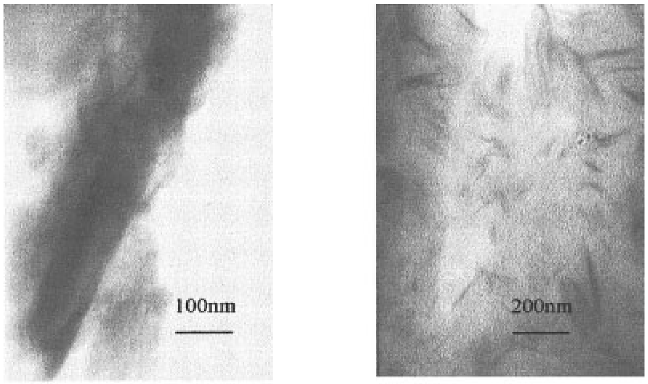
Characterization

TEM observations were carried out with an H-800 TEM by using an acceleration voltage of 200 kV. TG analyses were performed using a TGS-2 type at 10°C/min from room temperature to 500°C under nitrogen gas flow. A cone calorimeter was used to evaluate the flammability of these composites under a heat flux of 50 kW/m^2 according to ASTM 1356-90. The oxygen index(OI) was measured using a JF-3-type instrument-(made in China) on strips of $120 \times 6 \times 3$ mm^3 according to the GB (Chinese Standard) 10707–89. The permeation experiment of nitrogen was carried out with a gas permeability–measuring apparatus. The pressure on one face of the sheet (about 1 mm thickness and 8 cm diameter) was maintained at 0.57 MPa with the other face at zero pressure initially, and the nitrogen permeated through the sheet. The rate of transmission of nitrogen at 40°C was obtained by gas chromatography and with which the nitrogen permeability was calculated. Measurement of mechanical properties of all the samples was carried out based on relative ASTM standards at a strain rate of 500 mm/min and at 25 ± 2°C by an Instron 3211 tensile tester.

RESULTS AND DISCUSSION

Morphology of MMT/SBR nanocomposites

TEM micrographs of the MMT/SBR microcomposite and the MMT/SBR nanocomposite are shown in Figure 1(a and b), respectively. The dark lines or areas are the intersections of the silicate layer bundles dispersed in SBR. As seen in Figure 1(a), some large aggregates of the clay layer exist in the rubber matrix, whose stacked structure should be the same as that of clay powder. Apparently, layers of pristine clay cannot be separated from each other through general rubber processing. However, Figure 1(b) clearly shows that silicate layers are dispersed homogeneously in the



(a)microcomposite (b)nanocomposite

Figure 1 TEM micrographs of MMT/SBR composites (SBR/clay: 100/20).

SBR matrix at the nano level (i.e., thickness of layer bundles < 100 nm), and the thickness of most silicate layers bundles is about 10 nm and the width is about 200–300 nm. No larger-scale stacks are observed. The clay/rubber nanocomposites with this structure prepared by our research group have some advantages over the rubber composites filled with carbon black and silica because of the presence of nanoscale clay.[29–35]

Thermal stability

Thermal gravimetric analysis provides information on the course of the thermal degradation of the polymer. The thermal behaviors of the SBR and MMT/SBR nanocomposite are shown in Figure 2. The two curves are similar up to 310°C. Owing to the presence of the nanodispersed clay, the temperature at which 50% degradation of materials occurs for the nanocomposite is 470°C and is 10°C higher than that of pure SBR. The amount of residual material of pure SBR at 500°C is 5.52%, which is the residue of ingredients of the SBR compound, such as ZnO, while that of the nanocomposite is 18.59%, corresponding to the amount of clay that has been added. The residual material for the MMT/SBR nanocomposites would be 24.5% compared to the 5.5% for SBR alone in view of the addition of 20 phr clay. The smaller residual of the nanocomposite may be attributed to the loss of aqueous layers in the gallery of the clay on combustion, which are formed by 6 ion exchange during the preparation process of the nanocomposites. It can be concluded that the nanocomposite has better thermal stability than that of SBR, but the incorporation of nanoclay doesn't remarkably improve the thermal stability of SBR.

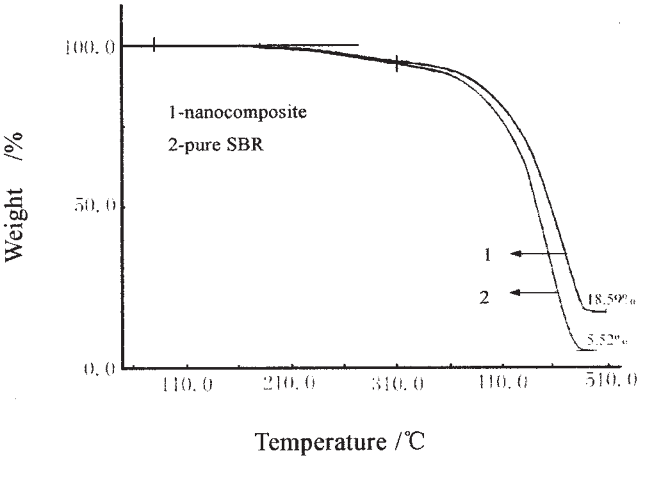


Figure 2 TG curves of SBR and MMT/SBR nanocomposite(SBR/clay: 100/20).

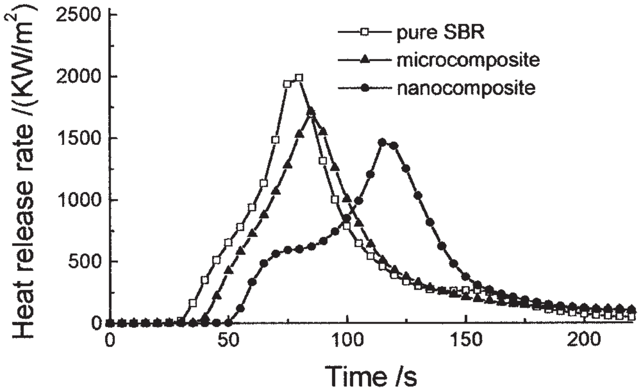


Figure 3 Comparison of the heat release rate (HRR) plot for pure SBR and its composites (SBR/clay: 100/20) at 50 kW/m^2 heat flux.

Flammability properties

Characterization of the flammability properties of a variety of polymer–clay nanocomposites, using the cone calorimeter under fire-like conditions, have revealed that the flammability properties of many polymers have been improved by compounding with nano-layered silicate.[36] The measuring principle is the oxygen-consumption principle. The principle states that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released.[37] In many case, the ignition of a material can be expected to occur due to thermal radiation from nearby flames, not from the direct impingement of a small flame onto the material. The cone calorimeter has the capability of radiant ignition of materials in laboratory. The heat flux of ignition is selected from 25, 50, and 100 kW/m^2. Therefore, the cone calorimeter is one of the most effective bench scale methods for studying the flammability properties of materials.

TABLE II
Cone Calorimeter Data for Pure SBR and Its Composites

	t_{ignition} (s)	PHRR (kw/m^2)^a	t_{PHRR} (s)	Mean HRR (kw/m^2)
Pure SBR	18	1987	76	393
Nanocomposite	44	1442(27)	117	234
Microcomposite	31	1693(13)	85	371

[a] Values in parentheses are % difference.

Heat release rate (HRR), in particular peak value of HRR, has been found to be the most important parameter to evaluate fire safety.[36]

The heat release rate plots for pure SBR, SBR/20 phr nanocomposite, and SBR/20 phr microcomposite at 50 kW/m^2 heat flux are shown in Figure 3 and the cone calorimetry data are found in Table II. The cone calorimetry data show that the peak HRR of MMT/SBR nanocomposite decreases 27% compared with that of pure SBR. However, the peak HRR of a microcomposite, which contains the same amount of clay as that of the nanocomposite, is very similar to that of pure SBR and is slightly lower because of the dilution effect. The heat release, and the peak of HRR for the nanocomposite, begin later than that for virgin SBR and conventional composite, which means a significant reduction of the flammability of the MMT/SBR nanocomposite. As shown in Table I, the time to ignite the nanocomposite occurs at 44 s and, for the pure SBR, at 18 s. The nanocomposite exhibits the longest time to ignite and time to burn out among others. This result is not consistent with the results of other polymer–clay nanocomposites prepared from organic modified clay, such as PA6/clay,[17] PS/clay,[27] PE/clay,[26] and ABS/clay[28] nanocomposites, and the times to ignite these nanocomposites are relatively short in comparison with those of their pure polymers. The main reason is that partial degradation of the organic modified clay used in these polymer–clay nanocomposites took place, whereas inorganic clay in the MMT/SBR nanocomposite can endure a higher temperature than the modified clay. The effect of the clay amount on the HRR is illustrated in Figure 4. The HRR drops with the increasing amount of clay.

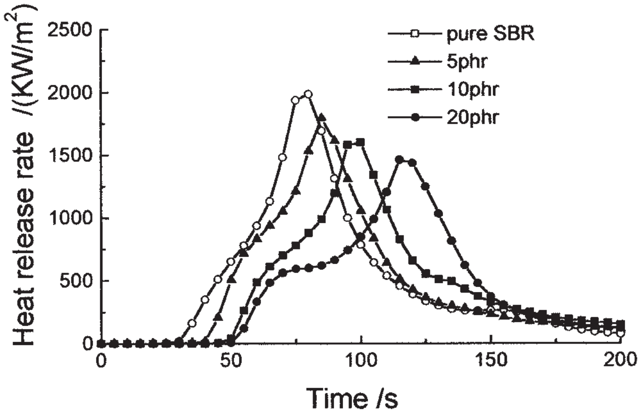


Figure 4 Comparison of the heat release rate (HRR) plot for MMT/SBR nanocomposites with different loading amount at 50kW/m^2 heat flux.

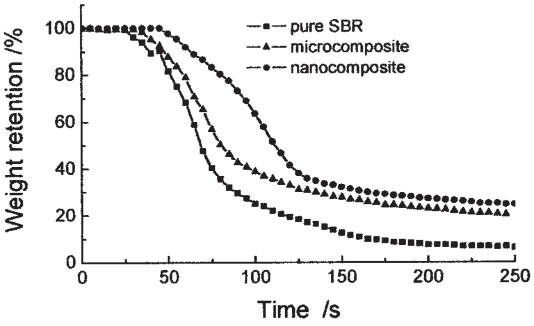


Figure 5 Residual mass versus time of pure SBR and its microcomposite and nanocomposite (SBR/clay: 100/20).

The residual mass upon combustion, with regard to the above-mentioned three systems, is illustrated in Figure 5. The residue amount from the nanocomposite is largest during combustion compared with a conventional composite with the same clay loading. This may be attributed to the structure of nanoscale clay lamella, whose effects will be discussed later. The mass loss rate versus combustion time is plotted in Figure 6. The lowest mass loss rate is also found with the nanocomposite. This suggests that the nanocomposite is critical to improved thermal property and fire resistance. However, Figure 6 shows an increased initial mass loss rate for microcomposite compared to SBR. This may be caused by the unsteadiness of the combustion process for the microcomposite, which has almost no improved flammability resistance.

The well- accepted mechanisms of flame retardancy of the clay–polymer composites described in the literature suggest that the source of the improved flammability properties of these materials is due to differences in condensed phase decomposition processes

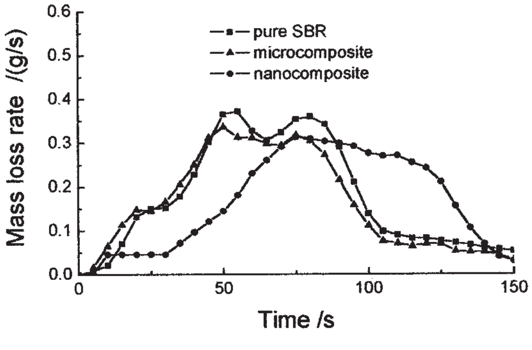


Figure 6 Mass loss rate of pure SBR and its microcomposite and nanocomposite (SBR/clay: 100/20).

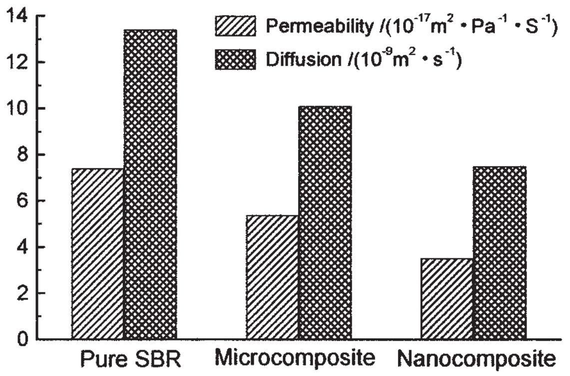


Figure 7 Permeability of pure SBR and its microcomposite and nanocomposite (SBR/clay: 100/20).

and not to a gas phase effect.[36] It is thought that the crucial parameter responsible for the lower HRR of the nanocomposites is the mass loss rate (MLR) during combustion, which is significantly reduced for nanocomposites compared with the pure polymers. To study the condensed phase decomposition process of the nanocomposites, Gilman[36] conducted pyrolysis experiments. The pyrolysis experiments for nylon-6 and nylon-6 nanocomposite showed that it is the formed char covering the surface of the nanocomposite that controls the MLR and therefore the flammability. It is deduced that the nanoscale clay filler in the nanocomposite promotes formation of the char layer, which acts as an excellent insulator and mass transfer barrier. The insulating effect of the char layer slowed down the escape of the volatile products generated while nylon-6 was decomposing.

In this study, lower MLR and a higher amount of residue for nanocomposites are observed. In the opinion of these authors, the presence of layered silicate first hinders diffusion of volatile decomposition products from the nanocomposite and acts as a barrier to diffusion of oxygen into the nanocomposite at the same time. These subsequently result in the partial reduction of MLR and HRR and are helpful for the char forming during combustion due to prevention of complete decomposition. Together with the layered silicate, the formed char layers provide a stronger barrier property. This deduction is supported by the reduced permeability and the decreased diffusion of the MMT/SBR nanocomposite as illustrated in Figure 7. The permeability of the nanocomposite decreases by 50% compared with pure SBR while the permeability of the conventional composites declines by just 28%.

Mechanical properties

The mechanical properties of the MMT/SBR nanocomposite, in comparison with the pure SBR and a classical SBR filled with microclay, are listed in Table III. Among these three systems, all of the properties shown here are highest with respect to the nanocomposite. This demonstrates that the introduction of nanoclay in the SBR provides improved mechanical properties of SBR and reduced flammability, which is significant for flammability–retardancy of rubber.

TABLE III
Mechanical Properties of Pure SBR and Its Composites (Clay 20 phr)

	Stress at 300% (MPa)	Tensile strength (MPa)	Tear strength (KN m^{-1})	Shore A hardness
Pure SBR	1.8	1.9	14.1	46
Microcomposites	1.9	2.5	15.3	51
Nanocomposites	8.1	14.5	47.4	60

Combination of nanocomposites and conventional flame retardants

The OI test, because of its simplicity and good reproducibility, is often used to characterize materials with respect to their relative flammability. The OI values of these MMT/SBR nanocomposites are shown in Figure 8. Although the HRR of the nanocomposite decreased, its OI unfortunately changed little compared with that of pure SBR.

Magnesium hydroxide ($Mg(OH)_2$), long used as a filler for rubber articles, has been shown to be both an effective smoke inhibitor and a flame retardant for polymer. Heat removal, through endothermic dehydration, dilution of combustion fuels by water vapor, and participation by water in flame processes or pyrolysis reaction of the polymer, have been cited as mechanisms through which flame retardation is effected. However, to obtain flame retardant polymer, generally a large amount(over 60 wt %) of $Mg(OH)_2$ must be added into the polymer. This is inefficient in the enhancement of physical properties for rubbers, due to serious aggregation of particles, thus it cannot

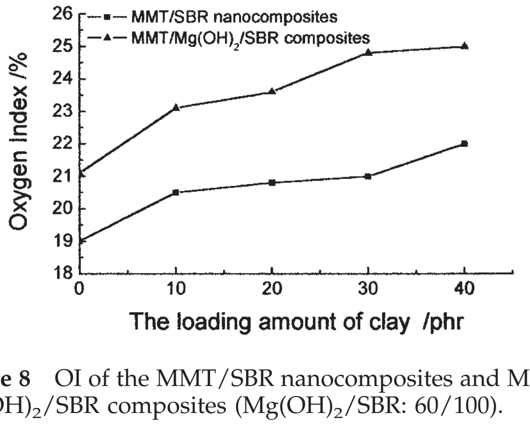


Figure 8 OI of the MMT/SBR nanocomposites and MMT/$Mg(OH)_2$/SBR composites ($Mg(OH)_2$/SBR: 60/100).

TABLE IV
Effect of Nanoclay on Mechanical Properties of $SBR/Mg(OH)_2$ (100/60)Flame Retardant Formulation

Clay loading amount(phr)	0	10	20	30	40
Stress at 300% (MPa)	2.3	4.3	6.1	9.4	11.5
Tensile strength (MPa)	5.4	17.4	17.5	17.1	15.8
Tear strength (KN m^{-1})	18.0	28.9	40	40.8	40.4
Shore A hardness	60	68	72	76	80

satisfy applications for which high tensile strength is required. Therefore, introducing $Mg(OH)_2$ into the MMT/SBR nanocomposite is probably a good way to obtain MMT/SBR nanocomposites with excellent mechanical properties and high OI. The mechanical properties of the nanocomposites containing $Mg(OH)_2$ are listed in Table IV and the OI is illustrated in Figure 8. The stress at 300% and hardness of the MMT/$Mg(OH)_2$/SBR are increased almost linearly with increased loading amounts of nanoclay, and its tensile strength and tear strength are also improved greatly by addition of the nanoclay. In Figure 8, the OI of MMT/$Mg(OH)_2$/SBR rises with the increase of the amount of the clay, and the OI of the system is higher than that of $Mg(OH)_2$/SBR without MMT and MMT/SBR without $Mg(OH)_2$. It appears that the effect of nanoscale clay on OI is intensified by the presence of $Mg(OH)_2$. It is observed that the combination of $Mg(OH)_2$ and clay is also effective in reducing visible smoke. Consequently, the small amount of the nanoclay present in $Mg(OH)_2$/SBR allows for improvement in mechanical properties and OI over the $Mg(OH)_2$/SBR formulation containing no clay. It is a feasible and practical method to prepare SBR with reduced flammability and improved mechanical properties.

CONCLUSIONS

A cone calorimeter was used to evaluate the flammability of SBR. The maximum heat release rate of MMT/SBR nanocomposite decreased by 27% below that of pure SBR. The nanocomposite has the lower mass loss rate and forms a larger amount of char upon combustion compared with conventional SBR composite with the same clay loading and pure SBR. The excellent gas barrier property of the nanocomposite is responsible for the changes in mass and heat transfer and therefore reduction in flame propagation.

Although the HRR of the nanocomposite decreases, its OI unfortunately is little changed compared with pure SBR. Combinations of $Mg(OH)_2$ and clay are effective for the improvement of both mechanical properties and OI. In light of these results, MMT/SBR nanocomposites exhibit reduced flammability and improved mechanical properties.

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