

Preparation and Characterization of Flame Retardant and Low Smoke Releasing Oil-resistant EVA/NBR Blends^{*}

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Abstract Nano-SiO₂ and/or MoO₃ were introduced to ethylene-vinyl acetate/nitrile butadiene rubber (EVA/NBR) blends containing magnesium hydroxide (MH) and red phosphorus (RP) to further improve the mechanical properties, oil resistance, smoke suppression and flame retardancy. The results indicated that the tensile strength and oil resistance were significantly improved by incorporating nano-SiO₂. Smoke suppression tests for EVA/NBR blend samples showed that both nano-SiO₂ and MoO₃ can significantly reduce smoke release amount. The flammability characterization indicated that the blended sample with an LOI value of 33.0 could achieve V-0 level in the UL-94 test. Cone calorimetry test data showed the peak heat release rate was 67% lower than that for pure EVA/NBR. Thermal analysis showed that the presence of both nano-SiO₂ and MoO₃ was beneficial to promoting char formation of the EVA/NBR blends. Char residual analysis suggested that MoO₃ aggregated in solid phase during combustion.

Keywords: Ethylene-vinyl acetate/nitrile butadiene rubber; Tensile properties; Oil resistance; Smoke suppression; Flame retardancy.

INTRODUCTION

Ethylene-vinyl acetate (EVA) has been widely used because of its outstanding ozone resistance and high machinability, however, its poor oil resistance, relatively low tensile strength and unsatisfactory fire performance cannot meet industrial requirements in many cases^[1, 2]. Nitrile butadiene rubber (NBR) shows excellent oil resistance because of the strong polarity of molecules^[3, 4]; however, its price is high. So it might be expected that blending EVA with NBR may increase the oil resistance of EVA. This could make oil resistance with reasonable cost available, which is significant in the fast increasing offshore oil industry.

Carbon black, nano-clay and zinc methacrylate (ZDMA) are common reinforcing agent for rubber processing^[5–8]. It has been reported that N550, SiO₂ and ZDMA may be used to improve the tensile properties of HNBR and that nano-SiO₂ is the most effective among the three additives^[9]. Nano-SiO₂ can significantly improve the mechanical properties of matrix; however, the effect of nano-SiO₂ on the flame retardancy and smoke suppression of EVA/NBR has never been investigated before.

The fire performance of EVA/NBR blends is usually below commercial flame retardant product standard. Conventional flame retardants (FRs) used in EVA are organic halogen compounds, which have been challenged and restricted by RoHS and WEEE legislations in EU because of the release of toxic agents and high levels of smoke density generated with combustion of polymeric material containing these compounds^[10]. Halogen-free

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flame retardants, especially metal hydroxide flame retardants have attracted increasing attention in recent years^[11–12]. Magnesium hydroxide (MH) is a typical metal hydroxide flame retardant, which has been widely used due to its high decomposition temperature and environmental friendliness. Unfortunately, large loadings are usually required to obtain an apparent increase of LOI value for combustion of the polymer. And high loadings are damaged to the mechanical properties of the material^[13–15]. MH in association with montmorillonite (layered silicate) has also been used to enhance the fire performance of EVA^[16]. However, a loading of 50 wt% MH and 5 wt% OMMT was required to achieve an LOI of 29 for the combustion of the polymer. Red phosphorus (RP) can be used to decrease the required loading of MH. Combustion EVA/NBR blends may produce large amount of smoke and tiny soot particles, which may be harmful to people. Molybdenum compounds, ferrocene and some metallic oxides as well as zinc stannate are common smoke suppressants^[17]. The smoke suppressants and their smoke suppression action have been summarized^[18]. The smoke suppression function of MoO₃ is not affected by oxidation during combustion. However, the effect of MoO₃ on smoke suppression and char formation of EVA/NBR blends has not been found so far.

In this work, nano-SiO₂ and/or MoO₃ have been introduced into EVA/NBR to prepare oil-resistant and flame retardant blends. The effects of nano-SiO₂ and/or MoO₃ on the mechanical and oil resistance properties of the blends have been investigated. The effect of both nano-SiO₂ and/or MoO₃ on smoke suppression of the blends was first analyzed and a mode of smoke suppression has also been proposed. The flammability of the blends was characterized using LOI, UL-94 and cone calorimetry. The thermal behavior of the blends was investigated using TGA and DTG. Morphology of both the blends and residual char from combustion was observed and analyzed by using SEM. The composition of residual char was determined using EDS.

EXPERIMENTAL

Materials

Nitrile butadiene rubber with 41% acrylonitrile content was purchased from JSR, Japan. Ethylene-vinyl acetate copolymer with 18% vinyl acetate content was obtained from Beijing Organic Chemical Plant, China. Maleic anhydride grafted ethylene-vinyl acetate copolymer (EVA-g-MAH) with a trademark of EVA-G-1 was provided by Nanjing Deba polymer materials Co., Ltd, China. Magnesium hydrate (MAGNIFIN H 5 IV) with a bulk density of 0.45–0.60 g/cm³ and a particle size between 0.40–0.70 μm was obtained from Martinswerk Co., Ltd, Germany. Red phosphorus (RP) with a trade name of CPS-X50 was purchased from Rongtai Industry & Trade Co., Ltd, China. Nano-SiO₂ (VN-3) with a bulk density of 120 g/L and an average particle size of 7 nm was provided by Evonik Wellink Silica (Nanping) Co., Ltd. Molybdenum trioxide (MoO₃) was purchased from Jinke Chemical Research Institute, Tianjin, China. Other additives such as calcium stearate, bis-(γ-triethoxysilylpropyl)-tetrasulfide (Si69), poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (antioxidant RD), dicumyl peroxide (DCP), triallyl isocyanurate (TAIC) were obtained from local chemical suppliers.

Sample Preparation

Formulations of blend samples are listed in Table 1. Each formulation includes 1 phr calcium stearate, 1 phr antioxidant RD, 1.5 phr Si69, 1.5 phr DCP and 1.2 phr TAIC. All the components were mixed by using a two-roll mill at 80 °C for 10–15 min and vulcanized afterwards on a press molding machine for 25 min at a pressure of 45 MPa (160 °C), then cold pressed at 40 MPa for 3–5 min at ambient temperature.

Characterization

Tensile properties of blends (dumbbell-shaped specimens, thickness = 2 mm) were characterized using a computerized universal testing machine (WDW-50E, Jinan Shijin Group Co., Ltd, China) at a speed of 200 mm/min according to ISO 527-2. All samples were tested five times, and the average value was used with a variance of ± 5%.

Table 1. Formulation of EVA/NBR blends

Sample	EVA (phr)	NBR (phr)	EVA-g-MAH (phr)	FR (phr)	Nano-SiO ₂ (phr)	MoO ₃ (phr)
1	40	60	0	0	0	0
2	40	60	20	65	0	0
3	40	60	20	65	20	0
4	40	60	20	65	40	0
5	40	60	20	65	60	0
6	40	60	20	65	80	0
7	40	60	20	65	0	0.5
8	40	60	20	65	40	0.5
9	40	60	20	65	40	1.0
10	40	60	20	65	40	1.5
11	40	60	20	65	40	2.0

Oil resistance of the blends was measured according to ISO 14001. Specimens were immersed in ASTM#2 oil at 40 °C for 72 h and 75 °C for 48 h, respectively. Thereafter, the test specimen was removed from the oil, and wiped lightly with filter paper to remove excess oil from the surface. Finally, tensile strength and mass of the samples were measured.

The morphology of the blends and residual combustion char was examined using a SEM instrument (S-4700, Hitachi, Japan) with an acceleration voltage of 20 kV at ambient temperature. Samples of the blends were obtained by cryogenically fracturing in liquid nitrogen, and char samples were obtained from the smoke density test.

The smoke releasing behavior was investigated using a JCY-2 smoke density tester (Jiangning, China) with a sample dimension of 25 mm × 25 mm × 3 mm according to the procedure described in ISO 5659-2. All samples were tested three times, and the average value was used as final.

The limiting oxygen index (LOI) test was carried out using a JF-3 oxygen index apparatus (Jiangning, China) with a sample dimension of 120 mm × 6.5 mm × 3 mm according to ISO 4589-2.

The UL-94 vertical flammability was measured using a CZF-3 apparatus (Jiangning, China) with a sample dimension of 125 mm × 13 mm × 3 mm according to ISO 10351.

FTT0007 cone calorimeter (Fire Testing Technology Co., United Kingdom) tests were carried out according to ISO 5660. Square specimens (100 mm × 100 mm × 2 mm) were irradiated at a heat flux of 50 kW/m².

Thermogravimetric analysis (TGA) was undertaken using a HENVEN HCT-1 TG-DSC analyzer with a heating rate of 10 K/min over a temperature range of 25–800 °C under dynamic air conditions. The mass of each sample was around 5 mg.

RESULTS AND DISCUSSION

Mechanical Properties

Tensile properties of the EVA/NBR blends containing different amounts of nano-SiO₂ are presented in Fig. 1. It can be seen that tensile strength increases significantly with initial nano-SiO₂ loading, reaches the highest value of 12.8 MPa which is 288% higher than that of the sample containing no nano-SiO₂, and then decreases slightly. The sample would stick to the roll and it is very difficult to achieve uniform distribution of the additives in the polymer matrix when the nano-SiO₂ loading is more than 60 phr. The elongation at break decreases significantly as nano-SiO₂ loading increases. It is well known that nano-SiO₂ is a conventional reinforcing agent for rubbers^[19], from Fig. 1 it can be proposed that nano-SiO₂ is also efficient for improving the tensile strength of EVA/NBR blends. However, the tensile strength of the blends decreases when the nano-SiO₂ loading exceeds the critical value of 40 phr. This may be related to the self-aggregation of nano-SiO₂ particles and nano-SiO₂ cannot disperse homogeneously due to their large surface activity^[20]. Tensile properties of the blends containing 40 phr nano-SiO₂ and different amounts of MoO₃ are presented in Fig. 2. It can be seen that the tensile strength and elongation at break do not change clearly, this may because that there are only a few MoO₃ in the blends.

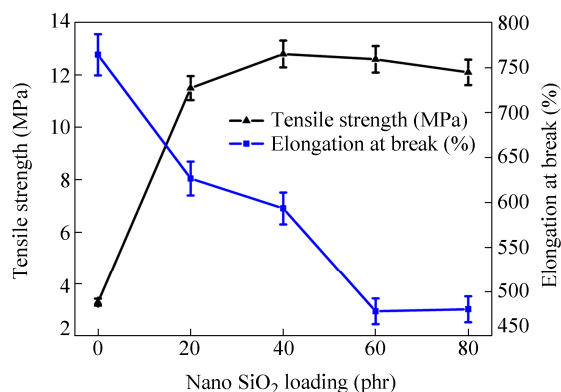


Fig. 1 The effect of nano-SiO₂ loading on tensile strength and elongation at break for EVA/NBR blends

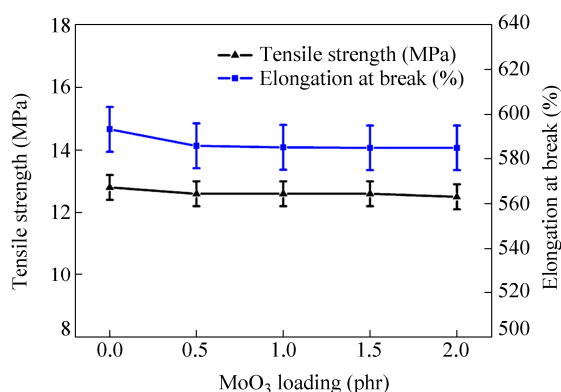


Fig. 2 The effect of MoO₃ loading on tensile strength and elongation at break for EVA/NBR blends containing 40 phr nano-SiO₂

Phase morphology of the blends was studied using SEM. Figure 3 contains the SEM photographs of cryogenically fractured surfaces of the blends containing 0 phr and 40 phr nano-SiO₂, respectively. It can be seen clearly that the filler in the blends containing nano-SiO₂ (Fig. 3b) is more evenly dispersed and the fractured surface is much more compact than that in the sample without nano-SiO₂ (Fig. 3a), demonstrating that good dispersion of additive is mainly responsible for the improvement of tensile strength presented in Fig. 1.

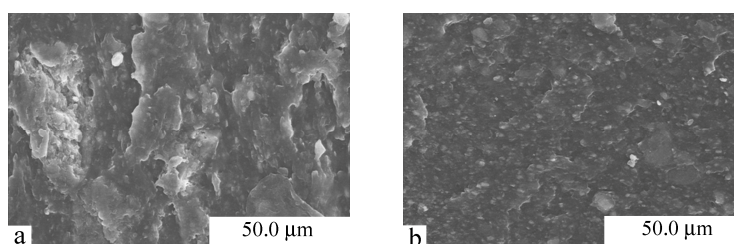


Fig. 3 SEM images of cryogenically fractured surfaces of (a) EVA/NBR blend without nano-SiO₂ and (b) EVA/NBR blend containing 40 phr nano-SiO₂

Oil Resistant Properties

The tensile strength before and after oil immersion was measured and compared to characterize the oil resistance of the EVA/NBR blends. The change in the tensile strength (R_{ts}) of blends containing different amounts of nano-SiO₂ as a function of time immersed in oil is shown in Fig. 4. This change may be calculated according to the following formula:

$$R_{ts} = (S_b - S_a) / S_b \times 100\%$$

where R_{ts} is the rate of change in tensile strength, S_b is tensile strength of the sample before oil immersion and S_a is the tensile strength of the sample after oil immersion.

As expected, R_{ts} decreases with the loading of nano-SiO₂. The values for immersion at 40 °C (72 h) are much smaller than those for immersion at 75 °C (48 h). This demonstrates that oil molecules cannot fully penetrate the blends and most of the blend structure remains intact at a temperature of 40 °C. NBR contains highly polar groups and the nano-SiO₂ also has polar Si—OH groups on its surface. Therefore, strong dipolar attractions between the filler and the polymer are possible. As a result, the oil resistance of the blend is improved in the presence of nano-SiO₂. The change of tensile strength of all samples is significant after oil immersion at 75 °C for 48 h. However, the rate of change in tensile strength for the samples containing nano-SiO₂ is much smaller than that for the sample without nano-SiO₂. The tensile strength of the latter could not be determined because of high swelling. Molecular movement becomes more vigorous at 75 °C. As a result, inorganic fillers

can migrate from the blends and oil can penetrate easily, which can lead to a significant decrease in tensile strength. The R_{ts} of blends containing 40 phr nano-SiO₂ and different amounts of MoO₃ as a function of time immersed in oil is shown in Fig. 5, and the change of R_{ts} is also not clear.

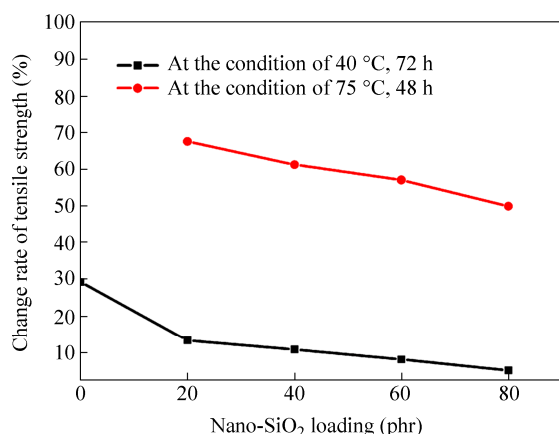


Fig. 4 Change of tensile strength of EVA/NBR blends as a function of immersion time in oil under different nano-SiO₂ loadings

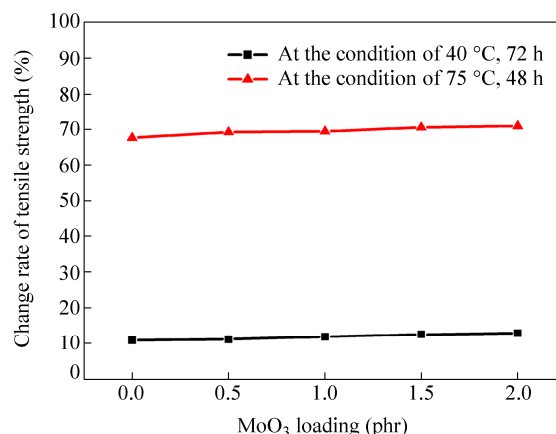


Fig. 5 Change of tensile strength of EVA/NBR blends containing 40 phr nano-SiO₂ as a function of immersion time in oil under different MoO₃ loadings

Smoke Density Analysis

The maximum smoke density (MSD) and smoke density rating (SDR) were measured to evaluate the effect of nano-SiO₂ and/or MoO₃ on smoke suppression during combustion of EVA/NBR blends. MSD and SDR values for combustion of samples containing nano-SiO₂ and MoO₃ are presented in Table 2. It can be seen that pure EVA/NBR (sample 1) has a MSD value of 99.1% and EVA/NBR loaded with FR (sample 2) has a MSD value of 93.7%, indicating the emission of large amount smoke during the combustion. The MSD decreases to its minimal value of 75.5% at the presence of 80 phr nano-SiO₂ in the blends. This may be attributed to the filling and covering effects of nano-SiO₂^[21]. The introduction of MoO₃ to the blends containing nano-SiO₂ can further suppress the smoke generation during combustion, and the smoke density result shows that MoO₃ in association with nano-SiO₂ has synergistic effect on reducing the smoke release of the blends. The MSD value for sample 8 is 33.0% lower than that of sample 2. The presence of only 40 phr nano-SiO₂ (sample 4) can decrease the MSD value from 93.7% to 81.8%, while the presence of only 0.5 phr MoO₃ (sample 7) can increase the MSD value from 93.7% to 97.3%, therefore, the sum of the decrease in MSD value for both samples 4 and 7 is (93.7%–81.8%) + (93.7%–97.3%) = 11.9% + (–3.6%) = 8.3%, which is much lower than 93.7%–60.7% = 33.0% (sample 8), indicating that nano-SiO₂ and MoO₃ have synergistic effect on smoke suppression in EVA/NBR blends. However, the decrease of MSD and SDR caused by a further increase of MoO₃ loading is minimal. It is proposed that large amount of acidity MoO₃ may accelerate the decomposition of MH during the combustion, which can lead to a negative effect on char formation and the smoke suppression.

Smoke density curves for the EVA/NBR blends are shown in Fig. 6. The presence of 40 phr nano-SiO₂ can delay the initial smoke release time to 27 s which is 8 s longer than that of the sample without nano-SiO₂. The smoke production rate is decreased significantly and the time to reach MSD is considerably prolonged, the sample containing 0.5 phr MoO₃ displays a much longer smoke release time of 42 s, and time to reach MSD is longer, which indicates that MoO₃ may reduce the amount of the volatiles released from EVA/NBR blends.

Table 2. MSD and SDR values for the EVA/NBR blends

Sample	1*	2	3	4	5	6	7	8	9	10	11
MSD (%)	99.1	93.7	89.4	81.8	78.6	75.5	97.3	60.7	62.1	62.5	62.8
SDR	88.9	63.7	62.9	53.1	57.2	51.6	79.8	43.3	44.6	45.2	43.1

* Pure EVA/NBR

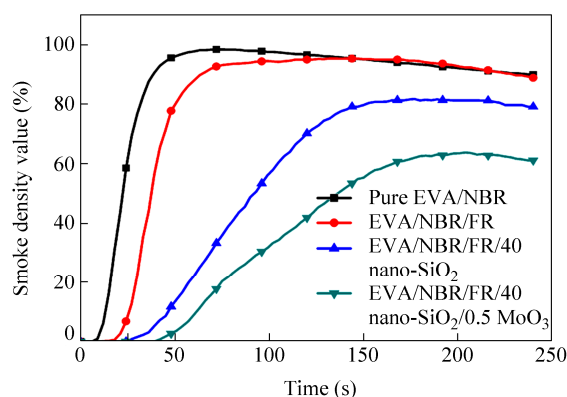


Fig. 6 Smoke density curves for combustion of EVA/NBR blends

Digital photographs of residual char from smoke density tests are shown in Fig. 7. During the combustion, nano-SiO₂ can promote the residual char formation of the polymer surface. The char may absorb heat and insulate the polymer so that pyrolytic generation of combustible fuel fragments is diminished. The formation of a well-structured char layer (see Fig. 7b) may be responsible for a decrease in burning rate and a reduction in smoke release as the polymer is undergoing combustion. However, it is difficult to observe any difference between Figs. 7(b) and 7(c) (sample containing MoO₃), therefore, SEM has been used to further characterize these two samples.

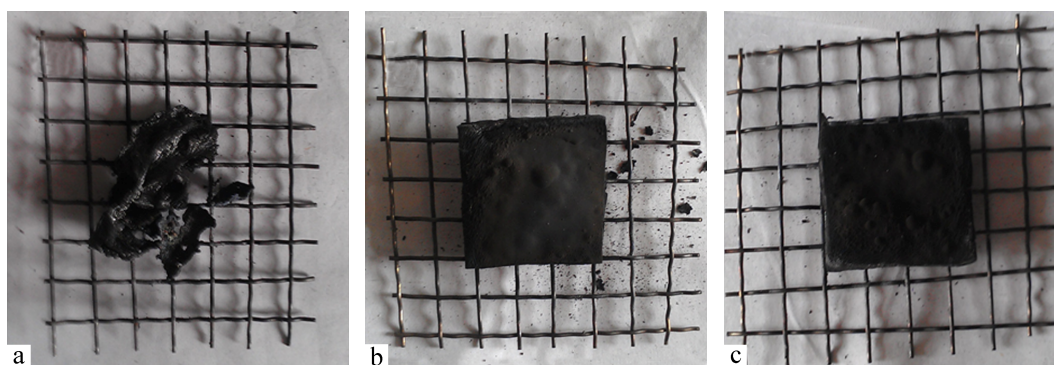


Fig. 7 Photographs of residual char: (a) EVA/NBR, (b) EVA/NBR/40 phr nano-SiO₂ and (c) EVA/NBR/40 phr nano-SiO₂/0.5 phr MoO₃

SEM images displayed in Fig. 8 show the microstructures of residual char from the combustions the EVA/NBR/nano-SiO₂ blends with and without MoO₃, respectively. Small white particles can be observed on the surface of both residue samples (Figs. 8a and 8b). The particles in the sample containing MoO₃ are more evenly dispersed (Fig. 8b) than those in the sample without MoO₃ (Fig. 8a). It can be obviously seen that the particle size in Fig. 8(d) is bigger than that in Fig. 8(c), suggesting that MoO₃ can improve the adsorption capacity of nano-SiO₂ in the blends and hence improve the smoke suppression effect.

Generally, gaseous organic volatiles consist of alkanes, alkenes, aromatics and so on, which are the major components of smoke^[22]. With an increase in the loading of nano-SiO₂, the amount of released combustible volatiles is reduced, which may be related to the fact that nano-SiO₂ can promote char formation and be capable of adsorbing small particles in volatiles. The char layer could not only hinder heat from spreading into the non-combusted EVA/NBR matrix, but also prevent flammable volatiles produced by the substrate from being transmitted to the flame zone. The adsorption ability of nano-SiO₂ can significantly reduce the formation of small particles during burning and hence hinder soot nucleation and aggregation, which results in a decrease in smoke density.

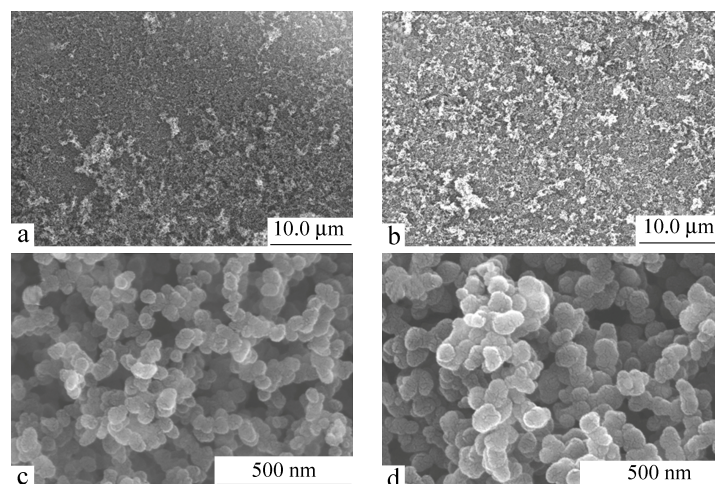


Fig. 8 SEM images of residual char of (a, c) EVA/NBR/40 phr nano-SiO₂ and (b, d) EVA/NBR/40 phr nano-SiO₂/0.5 phr MoO₃

It is proposed that MoO₃ acts as smoke suppressant mainly in the solid phase and reduces smoke release through Lewis acid or coupling reduction^[22]. During combustion, MoO₃ can promote the formation of some polycyclic products and increase intermolecular cross-linking reaction within the blend. Therefore, the evolution of volatile aromatic compounds, such as benzene and toluene, is suppressed and the generation of smoke is diminished. Results of element analysis of residual char remaining after combustion are contained in Table 3. It can be seen that major elements in the residual char are Mg, Si, C and O, indicating that MgO, SiO₂ and residual carbon are the main compounds of the residual char. The concentration of Mo in the residual char from combustion of a sample containing 0.5 phr MoO₃ is 4.97%, which is 21.6 times more than that in the sample before combustion. This demonstrates the solid phase is enriched in MoO₃ after combustion and indicates that MoO₃ mainly acts in the condensed phase during the smoke suppression process.

Table 3. Energy dispersive spectrometer (EDS) data for residual char remaining after combustion				
Element	EVA/NBR/FR/nano-SiO ₂		EVA/NBR/FR/nano-SiO ₂ /MoO ₃	
	wt% [*]	at% ^{**}	wt% [*]	at% ^{**}
C	26.71	37.14	23.62	35.31
O	35.94	38.79	32.35	36.31
Mg	23.72	16.23	24.97	18.44
Si	13.63	7.84	14.09	9.01
Mo	—	—	4.97	0.93

^{*} wt%: weight percent; ^{**} at%: atomic percent

Flammability

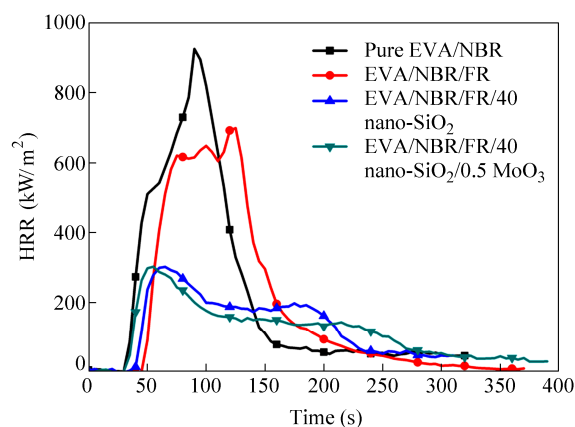
LOI and UL-94 tests results for the EVA/NBR blends are shown in Table 4. The LOI value for blend combustion is increased from 30.8 to 33.0 in the presence of nano-SiO₂. The improvement in LOI is mainly due to the fact that nano-SiO₂ has good thermal stability and remains in the char layer during combustion. The formation of a stable char suppresses heat feed back to the polymer and consequent formation and volatilization of combustible gases to feed the flame. There is no rating in UL-94 test for the sample containing nano-SiO₂ and MoO₃ respectively. The addition of MoO₃ has minimal effect on the LOI value; however, it can improve the UL-94 rating of EVA/NBR/FR/SiO₂ blends to a V-0 level. This suggests that nano-SiO₂ and MoO₃ can enhance the flame retardancy of the blends. Data presented in Table 4 also show that compared with sample 2, the sum of the changes of LOI value in the presence of 40 phr nano-SiO₂ and 0.5 phr MoO₃ respectively is (32.1–30.8) + (30.0–30.8) = 0.5 that is much lower than 2.2 (the increased LOI of sample 8 compared with sample 2), and the sample 8 is the only sample that can reach V-0. This provides further evidence of synergism between nano-SiO₂ and MoO₃ on improving the flame retardancy of EVA/NBR blends.

Table 4. Flammability of EVA/NBR blends

Sample	FR (phr)	nano-SiO ₂ (phr)	MoO ₃ (phr)	LOI (%)	UL-94 (3mm)	Dripping
1*	0	0	0	18.9	No rating	Yes
2	65	0	0	30.8	No rating	No
4	65	40	0	32.1	No rating	No
7	65	0	0.5	30.0	No rating	No
8	65	40	0.5	33.0	V-0	No

*Pure EVA/NBR

Heat release rate (HRR) curves for combustion of the EVA/NBR blends are shown in Fig. 9 and the key data are summarized in Table 5. The PHRR for the sample containing 40 phr nano-SiO₂ is reduced to 302 kW/m². Concurrently, it was found that further addition of MoO₃ does not decrease the PHRR value for combustion of the blend. However, the presence of MoO₃ can decrease the average mass loss rate (AMLR) and total smoke production (TSP). This suggests that both nano-SiO₂ and MoO₃ play an important role in improving the fire performance of EVA/NBR blends during the cone test.

**Fig. 9** HRR curves for combustion of EVA/NBR blends**Table 5.** Cone calorimeter data for combustion of EVA/NBR blends

Sample	1*	2	4	8
FR (phr)	0	65	65	65
nano-SiO ₂ (phr)	0	0	40	40
MoO ₃ (phr)	0	0	0	0.5
PHRR (kW/m ²)**	924 ± 19	698 ± 17	302 ± 14	302 ± 13
THR (MJ/m ²)**	69.6 ± 0.9	67.4 ± 0.6	40.6 ± 0.8	43 ± 0.7
Ti (s)**	31 ± 1	47 ± 2	41 ± 2	31 ± 2
AMLR (g/s)**	11.24 ± 0.24	16.07 ± 0.18	7.86 ± 0.19	5.95 ± 0.21
TSP (m ²)**	15.2 ± 0.4	20.2 ± 0.6	16.6 ± 0.5	13.5 ± 0.4

* Pure EVA/NBR

** PHRR: peak heat release rate; THR: total heat release; Ti: time to ignition; AMLR: average mass loss rate; TSP: total smoke production

Thermal Analysis

Thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves for pure EVA/NBR and EVA/NBR blends are presented in Figs. 10 and 11, respectively. It can be observed from Fig. 10 that the decomposition process of all samples has three steps. For the first decomposition step, the degradation onset temperature for the blends is at 340 °C, which is 50 K higher than that for pure EVA/NBR. During this stage, VA groups in the side chain of EVA decompose. Decomposition of the EVA/NBR matrix is hindered by the presence of thermally stable MH and nano-SiO₂^[23]. The second step of decomposition occurs between 390–490 °C, where the matrix decomposes rapidly and a maximum mass loss rate is reached. During this stage,

the main chain of EVA and the side chain of NBR begin to break down. The addition of MH and nano-SiO₂ increases the maximal decomposition temperature from 452 °C to about 460 °C and reduces the maximal mass loss rate significantly as demonstrated in Fig. 11. MH and nano-SiO₂ begin to degrade and absorb heat which may inhibit the thermo-oxidation of the EVA/NBR matrix during degradation^[24, 25]. The final step of decomposition happens above 490 °C. In this stage, the main chain of NBR begins to decompose, and the degradation of unmodified EVA/NBR is complete at about 650 °C. However, decomposition of samples containing inorganic fillers is complete at about 550 °C. This may be due to the decomposition of MH and the formation of moisture, which can accelerate the hydrolysis of NBR. As a result, the sample containing MH completes decomposition earlier than the unmodified EVA/NBR. Degradation of a sample containing nano-SiO₂ generates a char residue corresponding to 41% of the initial sample mass. Further addition of MoO₃ leads to an increase in degradation char residue to 46% of the initial sample mass. This suggests that MoO₃ can promote the char formation during combustion of the blend.

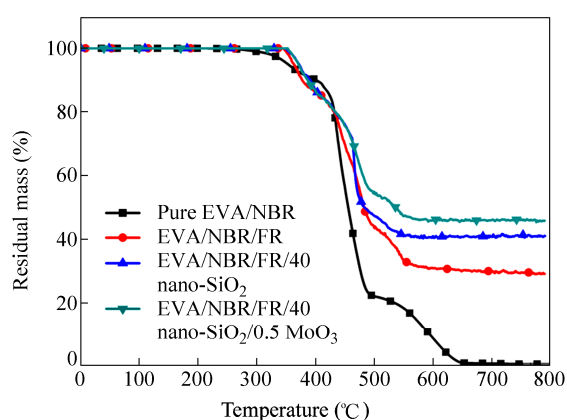


Fig. 10 TGA curves for decomposition of EVA/NBR blends in an air atmosphere

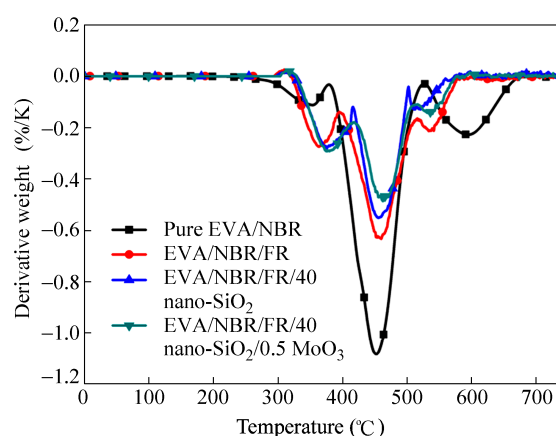


Fig. 11 DTG curves for decomposition of EVA/NBR blends in an air atmosphere

CONCLUSIONS

Halogen-free flame retardant and oil-resistant blends were prepared by blending EVA/NBR with nano-SiO₂ and MoO₃. The tensile properties and oil resistance were significantly enhanced by the presence of nano-SiO₂. The presence of 40 phr nano-SiO₂ can improve the tensile strength of the blend from 3.3 to 12.8 MPa, and it can enhance the oil-resistance significantly.

The addition of both nano-SiO₂ and MoO₃ significantly reduces smoke release and enhances the char formation during combustion of EVA/NBR blends. The corresponding MSD value can be reduced by 40% and char amount increases from 41% to 46% in the presence of these additives.

It is suggested there exist synergistic effects between nano-SiO₂ and MoO₃ on reducing smoke release and enhancing flame retardancy of EVA/NBR blend.

REFERENCES

- 1 Lee, E.J., Yoon, J.S. and Park, E.S., *J. Appl. Polym. Sci.*, 2012, 125(S1): E691
- 2 Thavamani, P. and Khastgir, D., *Adv. Polym. Technol.*, 2004, 23(1): 5
- 3 Zhang, Z.X., Chen, C.H., Gao, X.W., Kim, J.K. and Xin, Z.X., *J. Appl. Polym. Sci.*, 2011, 120(2): 1180
- 4 Ramesan, M.T., *React. Funct. Polym.*, 2004, 59(3): 267
- 5 Hwang, S.S., Liu, S.P., Hsu, P.P., Yeh, J.M. and Yang, J.P., *Int. Commun. Heat Mass*, 2012, 39(3): 383
- 6 Kim, K.J., *J. Appl. Polym. Sci.*, 2012, 124(4): 2937

- 7 Zhang, S., Hull, T.R., Horrocks, A.R., Smart, G. and Kandola, B.K., *Polym. Degrad. Stab.*, 2007, 92(4): 727
- 8 Chen, X.S., Zhang, S., Xu, G.Z., Zhu, X.J. and Liu, W., *J. Appl. Polym. Sci.*, 2012, 125(2): 1166
- 9 Li, Q., Zhao, S.H. and Pan, Y., *J. Appl. Polym. Sci.*, 2010, 117(1): 421
- 10 Yuan, D.D. and Cai, X.F., *Chinese J. Polym. Sci.*, 2013, 31(10): 1352
- 11 Xiao, S.S., Chen, M.J., Dong, L.P., Deng, C., Chen, L. and Wang, Y.Z., *Chinese J. Polym. Sci.*, 2014, 32(1): 98
- 12 Zhang, S., Horrocks, A.R., Hull, R. and Kandola, B.K., *Polym. Degrad. Stab.*, 2006, 91(4): 719
- 13 Bonnet, J., Bounor-Legaré, V., Melis, F., Camino, G. and Cassagnau, P., *Polym. Degrad. Stab.*, 2012, 97(4): 513
- 14 Du, L.C., Qu, B.J. and Xu, Z.J., *Polym. Degrad. Stab.*, 2006, 91(5): 995
- 15 Andrea, S., András, S., Nikolett, T., Péter, A. and György, M., *Polym. Degrad. Stab.*, 2006, 91(3): 593
- 16 Kiliaris, P. and Papaspyrides, C.D., *Prog. Polym. Sci.*, 2010, 35(7): 902
- 17 Shi, L.S., *React. Funct. Polym.*, 2000, 45(2): 85
- 18 Ou, Y.X., Chen, Y., Han, T.J. and Xu, D.M., *China Plastic (in Chinese)*, 2006, 20(2): 6
- 19 Qian, K., Luo, L.F., Chen, C.B., Yang, S.F. and Huang, W.X., *Chem. Cat. Chem.*, 2011, 3(1): 161
- 20 Soares, B., Almeida, M. and Guimarães, P., *Eur. Polym. J.*, 2004, 40(9): 2185
- 21 Laoutid, F., Ferry, L., Leroy, E. and Lopez, C., *Polym. Degrad. Stab.*, 2006, 91(9): 2140
- 22 Li, B., *Polym. Degrad. Stab.*, 2002, 78(2): 349
- 23 Balachandran, M. and Bhagawan, S.S., *J. Appl. Polym. Sci.*, 2012, 126(6): 1983
- 24 Alongi, J. and Malucelli, G., *Carbohydr. Polym.*, 2012, 90(1): 251
- 25 Xu, T. and Huang, X.M., *J. Anal. Appl. Pyrolysis*, 2010, 87(2): 217