Properties and Thermal Decomposition of SBS Flame Retarded with Phosphorus- and Nitrogen- Containing Flame Retardants

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Abstract. Flame retardant and mechanical properties of ammonium polyphosphate (APP), melamine phosphate (MP) and their combination with dipentaerythritol (DPER) in styrene-butadiene-styrene rubber (SBS) were studied. The results indicate that MP is more effective in raising limiting oxygen index **(**LOI) in SBS than APP. When DPER is incorporated into the SBS/APP and SBS/MP composites, a great improvement in flame retardancy of the composites is observed. Moreover, thermal decomposition and mechanical properties of the SBS composites were investigated.

Introduction

Styrene-butadiene-styrene rubber (SBS) is an important rubber, which is widely used as wires and cables, conveying belts, and tires, and so on. However, SBS is very flammable, and flame retardation is needed in some applications. Nowadays, it is usually flame retarded with halogen-containing compounds or their combination with antimony oxide. Nevertheless, these halogen-containing compounds on heating or in fires can produce a lot of smoke and toxic gases. Therefore, halogen-free flame retardation of SBS products has aroused a great attention.

Halogen-free flame retardants used in rubbers include metal hydroxides [1,2], phosphorus and nitrogen compounds [3,4], etc. Nowadays, phosphorus- and nitrogen-containing compounds such as ammonium polyphosphate (APP) and melamine phosphate (MP) are promising flame retardants. However, incorporation of the above compounds alone is usually difficult to meet strict flame retardancy requirement of the rubber products (e.g. conveying belts). In recent years, intumescent flame retardants (IFR) have been the focus of flame retardancy of polymers. The IFR system is composed of three components, i.e. an acid source (e.g. APP, MP), a carbon source, such as pentaerythritol (PER) and starch, and a blowing agent, e.g. melamine (MEL) [5,6]. There are also some publications on the application of IFRs in rubbers. For example, the effect of metallic oxides on flame retardancy and thermal stability of styrene butadiene rubber (SBR) composites based on ammonium polyphosphate (APP) and pentaerythritol (PER) were studied [7]. Wang, et al. investigated flame retardation of natural rubber using APP, microencapsulated APP and some synergists (i.e. 4A zeolite) [8,9].

The aim of this paper was to study flammability, mechanical properties and thermal decomposition of intumescent flame retarded SBS.

Experimental

Materials. SBS was provided by Shanghai Lingen Plastic Rubber Co., Ltd., APP, MP and DPER were all commercial products.

Preparation of SBS composites. All samples were prepared on a two-roll mill at a temperature about 170 C for 15 min. After mixing, the samples were hot-pressed at about 170 C into sheets of suitable thickness and size for analysis. The formulations are given in Table 1.

Table 1 Formulations of flame retarded SBS composites

Sample Code	SBS (%)	APP (%)	MP (%)	DPER (%)
SBS	100	0	0	0
SAPP	60	40	0	0
SMP	60	0	40	0
SAPPDP	60	30	0	10
SMPDP	60	0	30	10

Measurements

Limiting oxygen index (LOI) test was measured using a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) on sheets 120×6.5×3 mm3 according to ASTM D2863/77.

UL-94 test: The UL-94 test was carried out on sheets (3mm thick) using CFZ-2-type instrument (Jiangning Analysis Instrument Company, China), according to the UL-94 test procedure.

Mechanical properties: The tensile strength and elongation at break were measured using a Universal Testing Machine DCS-5000 (Shimadzu, Japan) at the cross head speed of 50 mm/min according to ASTM D 638 method.

Thermogravimetry (TG): Samples were examined under an air flow rate of 50 ml/min on a DTG-60H apparatus (Shimadzu Company, Japan) at a heating rate of 10 C /min.

Results and Discussion

LOI values and UL94 ratings

Table 2 presents the LOI and UL 94 testing results of the flame retarded SBS composites. The LOI value of the SBS resin itself is only 19.3%. When 40% APP was added into SBS, the LOI value of the SBS/APP composite (sample SAPP) is 21% The LOI value of sample SMP containing 40% MP increases to 24%. Nevertheless, there is no rating for both sample SAPP and sample SMP during the UL 94 test. The results indicate that the use of APP or MP alone does not play a good flame retarding role in SBS.

In order to improve the flame retardancy of the SBS/APP and SBS/MP composites, a carbon source, dipentaerythritol (DPER) was applied. It is observed from Table 2 that the LOI value of the samples SAPPDP and SMPDP with DPER increases to 27%, which is higher than their corresponding binary composites without DPER. Moreover, both sample SAPPDP and sample SMPDP pass the UL 94 V-0 rating test. The reason for the improvement in the flame retardant properties of the SBS composites containing DPER may be because the presence of DPER in the SBS composites is helpful to the formation of the good and compact char, which can prevent the heat and mass transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning and retard the pyrolysis of polymers and exert excellent flame retarding effect.

Table 2 LOI values UL 94 results of the FR SBS composites

Sample Code	LOI (%)	UL 94 testing
SBS	19.3	No rating, with dripping
SAPP	21	No rating, with dripping
SMP	24	No rating, without dripping
SAPPDP	27	V-0
SMPDP	27	V-0

Mechanical properties

Table 3 shows mechanical properties of the SBS composites. The tensile strength, elongation at break and impact strength of the SBS resin are 25.6 MPa, 1106% and 130.9 kJ/m2, respectively. When 40% APP or MP is added into the SBS resin, the values decrease greatly. When DPER is incorporated into the SBS binary composites, the mechanical properties of the SBS ternary composites change slightly.

Table 3 Mechanical properties of SBS and the FR SBS composites

Sample Code	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
SBS	1106	25.59	130.9
SAPP	419	11.98	70.5
SMP	458	11.25	68.7
SAPPDP	414	11.10	65.7
SMPDP	418	11.27	62.6

Thermal decomposition

Fig. 1 shows TG curves of SBS and the SBS composites. There are two steps in the thermal decomposition of the SBS resin. The initial decomposition of the resin is at about 200 C, and the temperature at 5% weight loss (T-5%) is 255 C. The first step is in the range 200 C to 400 C with a mass loss of about 20%. The second step happens from about 400 C to 500 C, and nearly all of the resin degrades at 500 C. The initial decomposition of SBS/APP and SBS/MP composites is slightly improved compared with the one of the SBS resin. The T-5% values for sample SAPP and sample SMP are 411 C and 468 C, respectively. The temperature at 50% weight loss (T-50%) for sample SAPP and sample SMP are 281 C and 273 C, respectively, while the temperature for SBS is 445 °C. The residue left at 800 C sample SAPP is 7.7%, which is much lower than that for sample SMP (12.3%). As shown in Fig. 1, the initial decomposition temperatures of the ternary composites with DPER (samples SAPPDP and SMPDP) are lower than their corresponding binary composites. The T-5% values for samples SAPPDP and sample SMPDP are 238 C and 246 C, respectively. The T-50% value for sample SAPPDP is higher than the one for sample SAPP, whereas he T-50% value for sample SMPDP is lower than the one for sample SMP. The residue left at 800 C for samples SAPPDP and sample SMPDP is 13.5% and 14.6%, respectively, which is all higher than that of the binary composites.

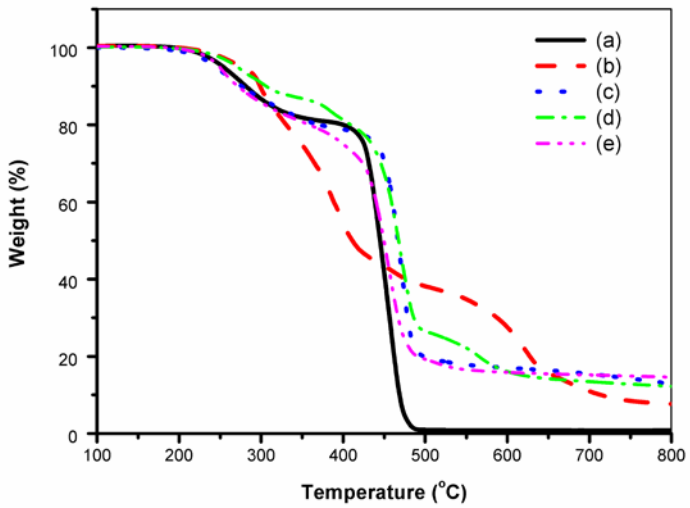

Fig. 2 TG Curves, (a) SBS; (b) SAPP; (c) SAPPDP; (d) SMP; (e) SMPDP

Conclusions

Use of APP or MP in SBS alone does not have good flame retardancy even at 40 % loading, and MP is more effective in raising LOI in SBS than APP. When dipentaerythritol is incorporated into the SBS/APP and SBS/MP composites, a great improvement in flame retardancy of the composites is observed. The addition of the flame retardants leads to a great decrease in mechanical properties of the SBS composites. The incorporation of APP or MP improves the initial thermal stability of SBS, and dipentaerythritol decreases the stability of the SBS/APP and SBS/MP composites slightly.

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