Comparison of Aluminium Hydroxide and Magnesium Hydroxide as Flame Retardants in SEBS-Based Composites

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Received: 22 November 2007, Accepted: 8 April 2008

SUMMARY

The flame retardancy and mechanical properties of styrene-ethylene/butylene-styrene block copolymer (SEBS) based composites, containing paraffinic hydrocarbon extender oil filled SEBS (O-SEBS), blended with copolymer polypropylene (PP), and flame-retardant filler aluminium hydroxide (ATH) or magnesium hydroxide (MH) were investigated. Limiting Oxygen Index (LOI) values of both ATH and MH filled composites increased substantially as the amount of ATH and MH increased, respectively. Furthermore, the LOI values of the ATH system are higher than those of MH for the same addition level. When MH is introduced, progressively, into ATH-filled composites, and for a constant combined filler loading of 65 wt.%, LOI only decreases, when the ratio of MH to ATH exceeds 40%. Combining the two retardants, in the composites, may have a synergistic effect with respect to fire retardance. Tensile strength, up to 50 wt.% filler, and elongation at break of the composites decrease as the amount of filler increases. However, the elongation at break of the composites filled with MH is a little higher than that with ATH, but for tensile strength there is little difference between them. At filler loading greater than 50 wt.%, the tensile strength levels off but the% elongation is dramatically reduced. Introduction of MH in ATH filled composites leads to some variation in the mechanical properties of the composites. For a combined filler loading of 65 wt.%, the elongation at break increases from around 180 to 200% for a progressive increase in the ratio of MH to ATH up to 40% and there is a large increase in% elongation to around 300% when MH ratio reaches 55-60%, thereafter the% elongation falls. This effect may be linked to particle size distribution of the respective MH and ATH fillers. In contrast, there is little effect on the tensile strength. The thermogravimetric analysis (TGA) and differential TG (DTG) data show that ATH and MH increase the thermal stability of the SEBS-based composites.

1. INTRODUCTION

Styrene-ethylene/butylene-styrene (SEBS) block copolymers are new styrenic-based thermoplastic elastomers (TPE), synthesized by hydrogenating the rubber midblock of the styrene-butylene-styrene (SBS) copolymers, with the elimination of the C=C bonds in the butadiene component[1].

SEBS TPEs have excellent mechanical properties, good tear and abrasion resistance, good electrical properties, excellent resistance to chemicals and weathering, resistance to low and high temperatures from –30 °C to +140 °C, and good processing stability, and they are recyclable[1,2]. SEBS TPEs are commonly used compounding solutions[3,4], adhesives and sealants[5], coatings[6], plastics modification[7,8], bitumen modification[9,10], packaging[11] and medical applications[12,13].

Among these applications, the compounding composites[3,4], which use SEBS as a basic resin, and are modified with rubber extender oils, polyolefin plastics and mineral fillers, drawing more and more attention. They are increasingly replacing thermosetting rubber, soft PVC, olefin TPE or thermoplastic polyurethane (TPU) in a variety of applications including the automotive sector[14,15] (acoustic barriers, window encapsulation, airbag covers, etc.), wire and cables[16], domestic applications, sports and leisure, personal care and toys[17].

However, SEBS-based TPE is easily ignitable, and will give out heavy smoke when burned. Moreover, both rubber extender oil and polyolefin resin, used in SEBS-based composites, can easily catch fire as well. Consequently this results in easy burning of SEBS-based composites[18]. Up to now, there has been little information available on the relationship between the flammability and flame-retardancy of these systems, including the introduction of flame-retardants for SEBS-based composites.

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No systematic study about the effect of halogen-free flame-retardants on SEBS composites has been carried out.

Aluminium hydroxide (ATH) and magnesium hydroxide (MH) are both well-known flame-retardants for elastomers, thermosetting resins and thermoplastics free from halogens[19-22]. In comparision, aluminium hydroxide has a lower decomposition temperature than magnesium hydroxide, and therefore the latter is more stable at higher temperature[23]. Normally, either aluminium hydroxide or magnesium hydroxide can be incorporated in the same polymer as a flame-retardant if the processing temperature of the polymer is appropriate[24]; but sometimes both of them are simultaneously incorporated into the same polymer[25].

This work presents a comparative study of the effect between ATH and MH on the flame-retardancy and mechanical properties of SEBS-based composites. Furthermore, we simultaneously incorporated MH and ATH into SEBS-based composites, so as to explore if there is any synergism effect on the flame-retardancy and mechanical properties of the composites.

2. EXPERIMENTAL

2.1 Materials

The SEBS materials were a commercial thermoplastic elastomer, a styrene-ethylene-butylene-styrene block copolymer (Shell Kraton® G 1660, with a styrene to rubber ratio of 30/70 wt.%, abbreviated as SEBS), produced by Kraton™ Polymers, USA.

Commercial polypropylene copolymer (PP, grade 3015), with melt flow index (MFI) 2.0 g/10 min (230 °C, 2.16 kg), and density 0.90 g/cm^3, was produced by Taiwan Yung Chia Chemical Industries Corporation, China.

The rubber extender oil (KP-6020), containing primarily paraffinic hydrocarbons, with a kinematic viscosity of 22.8 mm^2/s (100 °C), and density 0.881 g/cm^3, was produced by Petrochina Karamay Petrochemical Company, China.

Aluminium hydroxide (ATH), with a mean particle size of 2.0 μm and density 2.40 g/cm^3, was produced by Shandong Aluminium Co., Ltd, China.

Magnesium hydroxide (MH), with a mean particle size of 1.5 μm and density 2.39 g/cm^3, was produced by YiYang HuaRi Advanced Materials Co., Ltd, China.

Antioxidants Irganox 1010 and Irgafos 168 were produced by Ciba Specialty Chemicals, Switzerland.

2.2 Preparation of SEBS-Based Composites

Composites were prepared from SEBS, polypropylene, extender oil and filler ATH or MH. The extender oil was first soaked up in the SEBS (the ratio of SEBS: oil is 50/50). Then the oil-containing SEBS powder (abbreviated as O-SEBS) was dry-mixed with polypropylene and filler. The ratio of O-SEBS: PP was kept constant at 85/15, while the filler loading increased from zero to 75 wt.%. 0.2 wt.% of Irganox 1010/Irgafos 168 (2/1 wt.%) was added as stabilizer during melt processing.

The dry-mixtures were prepared by mixing in an open two-roll mill at 170 °C for 10 min. Then the mixtures were compression molded into plates of suitable thickness using a heated hydraulic press at 175 °C. Test bars for mechanical and flammability tests were either punched or cut from the plates.

2.3 Limiting Oxygen Index and Vertical Burning Test

The percentage of oxygen in an oxygen/nitrogen mixture just sufficient to sustain burning is the limit oxygen index (LOI). The LOI values were measured on specimens of size 120 mm x 6.5 mm x 3 mm in a LOI instrument (HC-2 Analytical Instrument Factory, China), according to ASTM D2836, and the results used to evaluate the flammability of SEBS-based composites.

A vertical flammability test was also conducted according to Underwriter's Laboratory test 94 (UL-94), which was used to determine the flammability of 125 mm x 13 mm x 3 mm specimens. Classification was determined as a function of flaming combustion time (t_1 and t_2) after two 10 s applications of the burner flame, by the glowing combustion time (t_3) after the second burner flame application, and by noting whether the samples burned up to the holding clamp, as well as whether the burning drops were able to ignite cotton wool.

2.4 Mechanical Properties

Tensile stress-strain tests were performed following the ASTM D-638 Standard Test Method at room temperature using a Zwick-Roell Z020 tensile tester, at a crosshead speed of 500 mm/min. The ultimate tensile strength and the failure strain values reported are the averages determined from between 5 and 8 specimen tests.

2.5 Scanning Electron Microscope (SEM) Observation

Scanning Electron Microscopy (ZEISS EVO 50 Series SEM) was used for the morphological observation. The specimens were immersed in liquid nitrogen and fractured by using an impact tester. (Ray-Ran Test Equipment Ltd, UK). The fractured surfaces were coated with a thin layer of gold, and examined in the SEM.

2.6 Thermogravimetric Analysis (TGA)

TGA was performed in a Mettler Toledo TG50 Thermal Analyzer, at a heating rate of 20 °C/min

from room temperature to 800 °C in an air atmosphere. The sample size was controlled between 5 and 10 mg. The common degradation parameters for the thermal stability of polymer composites are the initial decomposition temperature (IDT) and the temperature of the maximum rate of weight loss (T_{max})[26]. IDT is defined as the temperature at which the weight loss reaches 5 wt.%. T_{max} is obtained from the peak value in the differential thermogravimetric thermograms.

3. RESULTS AND DISCUSSION

3.1 Flame-Retardancy

Limit oxygen index determinations and vertical flame tests were performed with both kinds of composites. As can be seen from **Figure 1**, the minimum oxygen concentration necessary to ignite the materials increased as the ATH or MH concentration increased. At the same loading level, ATH gave a higher LOI value than MH, and this suggests that ATH is more suitable for flame-retardancy of SEBS-based composites than MH. **Table 1** shows that only the composite containing 70 wt.% ATH could be classified as a V0 material, according to the UL-94 test, while for MH, the content is 75% to get a satisfactory flame-retardant result. The other compositions did not achieve these good classifications because they showed a longer after-flaming time, or their drips ignited the cotton, or some of them burned to the clamp.

When MH is introduced, progressively, into ATH-filled composites, and for a constant combined filler loading of 65%, LOI only decreases, when the ratio of MH to ATH exceeds 40%. There may be a synergistic effect between ATH and MH for flame-retardancy of SEBS-based composites. However, from **Figures 1** and **2**, as the difference is small between LOI of ATH and MH at 65% filler loading, then the effect of increasing MH at the expense of ATH may not be so significant at lower levels of MH.

3.2 Mechanical Properties

Figure 3 shows the results of tensile strength and elongation at break of the composites filled with ATH or MH. Tensile strength, up to 50 wt.% filler, and elongation at break of the composites decreased as the amount of filler increased. However, the elongation at break of the composites filled with MH was a little higher than that with ATH, but for tensile strength, there was little difference between them. At filler loadings greater than 50 wt.%, the tensile strength levelled off around 5 MPa but the % elongation was dramatically reduced.

Introduction of MH in ATH filled composites, for a constant combined filler loading of 65 wt.%, led to some variation in the mechanical properties of the composites (**Figure 4**). The elongation at break increased from

Figure 1. LOI of o-SEBS/PP/filler composites vs. filler content. O-SEBS/PP=85/15

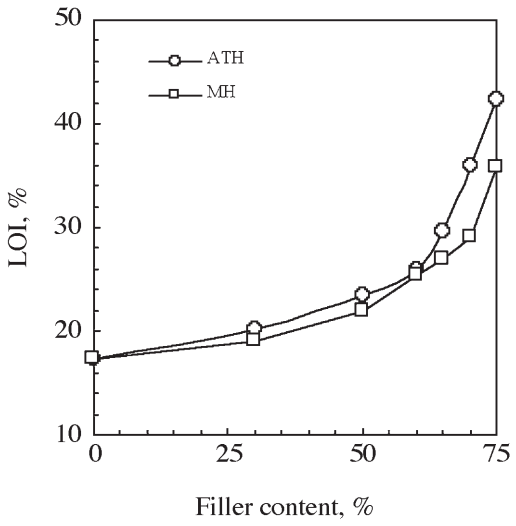


Table 1. Vertical flammability properties of the O-SEBS/PP/filler composites vs. filler weight content

Filler (wt.%)	t_1 (s)		t_2 (s)		t_3 (s)		Burned to clamp		Cotton ignition by dripping		UL94 classification	
	ATH	MH	ATH	MH	ATH	MH	ATH	MH	ATH	MH	ATH	MH
0	lasting	lasting	-*	-	-	-	Yes	Yes	Yes	Yes	Flame	Flame
30	lasting	lasting	-	-	-	-	Yes	Yes	Yes	Yes	Flame	Flame
50	≤ 25	lasting	lasting	-	-	-	Yes	Yes	Yes	Yes	Flame	Flame
60	≤ 3	lasting	≤ 56	-	≤ 45	-	No	Yes	Yes	Yes	Flame	Flame
65	≤ 1	≤ 1	≤ 20	lasting	≤ 9	-	No	No	No	Yes	V1	V1
70	0	0	≤ 1	lasting	≤ 3	-	No	No	No	No	V0	V1
75	0	0	0	≤ 1.5	≤ 1	≤ 9	No	No	No	No	V0	V0
*: not performed												

Figure 2. LOI of o-SEBS/PP/filler composites vs. mh content in filler. O-SEBS/PP/filler=29.75/5.25/65

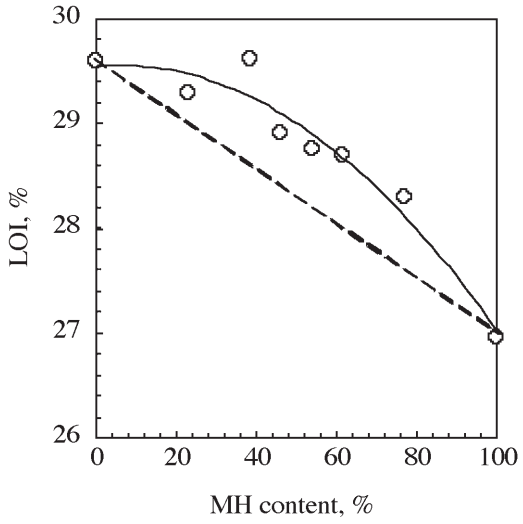
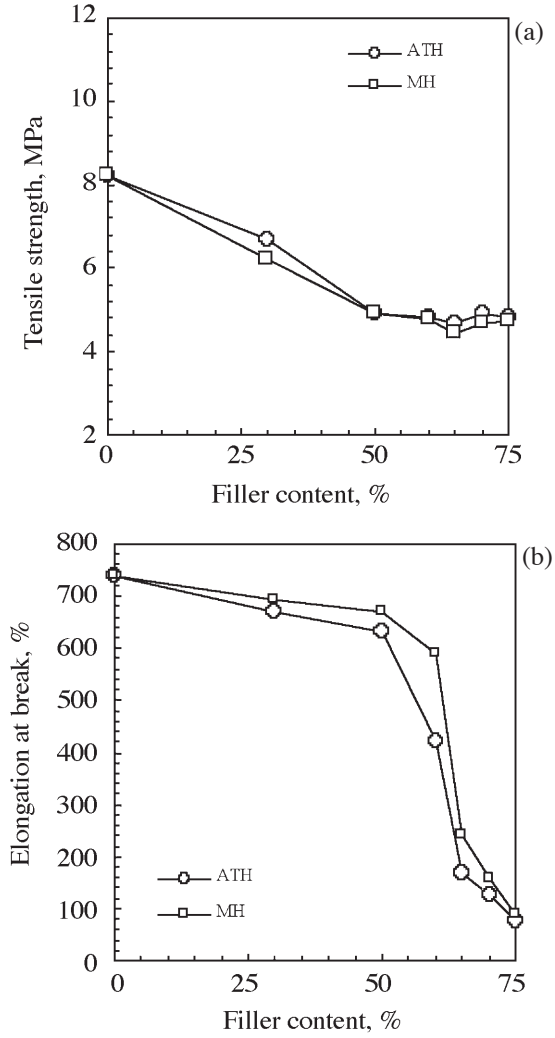


Figure 3. Tensile strength (a) and elongation at break (b) of O-SEBS/PP/filler composites vs. filler content. O-SEBS/PP=85/15

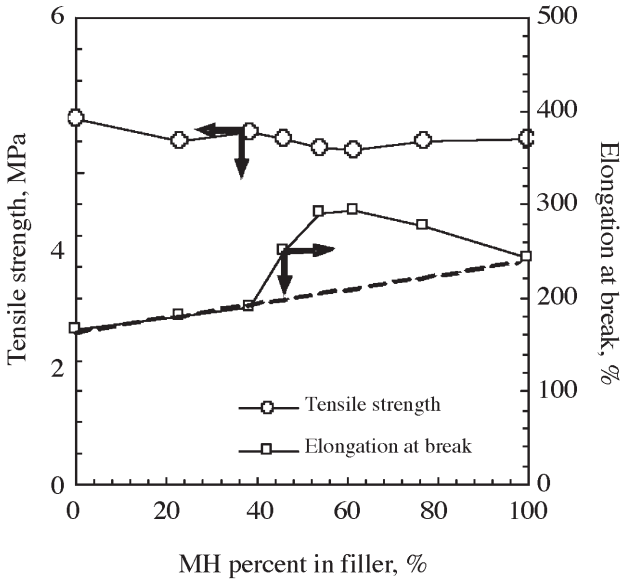


around 180 to 200% for a progressive increase in the ratio of MH to ATH up to 40% and there was a large increase in % elongation to around 300% when MH ratio reached 55-60%, thereafter the % elongation fell. This effect may be linked to particle size distribution of the respective MH and the ATH fillers. In contrast, there was little effect on the tensile strength.

3.3 Morphological Observation

In **Figure 5** a series of fractographs are shown, for composites with a 65 wt.% filler loading, and with varying ratios of MH to ATH. Examination of **Figures 5a** (100% ATH) and **5f** (100% MH) show that for both fillers there is a wide particle size distribution. In each case the particles are also seen to be distributed unevenly in the composite matrix with large particles clustering together and similarly small particle cluster groups. Particle size comparisons show that the largest particles in ATH (**Figure 5a**) are greater in size than the largest MH particles (**Figure 5f**) and similarly the smallest ATH particles are greater in size that the smallest MH particles. When the composites containing a MH loading

Figure 4. Tensile strength and elongation at break of O-SEBS/PP/filler composites vs. MH percent in filler. O-SEBS/PP/filler=29.75/5.25/65



of 50-60% to ATH are compared, see **Figures 5c** and **5d**, it can be seen that the particles are more evenly distributed in the matrix and a large variation in particle size distribution is not evident. The mixing of the two fillers ATH and MH at a ratio of around 50:50 appears to have produced a composite that is more favorable with respect to% elongation at failure, see **Figure 4**. Tensile strength, however, is unaffected and appears to be dependent on total filler loading.

3.4 TGA Analysis

Figures 6 and **7** show the TGA thermograms and differential thermogravimetric curves of the flame-retardants ATH and MH in air, and their thermal parameters are summarized in **Table 2**. ATH and MH decomposed endothermically, in a single step between 201-353 °C for ATH and 321-451 °C for MH, and with a mass loss of 35.17% and 31.27%, respectively. The initial decomposition temperature (IDT)[26], where the weight loss reached 5 wt.%, occurred at 249.3 °C for ATH and 364.9 °C for MH, and the T_{1max} values, where the maximum rate of weight loss took place, were 289 °C and 417 °C, respectively. This suggests that MH is more stable than ATH.

As can be seen from **Figures 8** and **9**, the thermo-oxidative degradation of unfilled O-SEBS/PP took place in two steps, the first one occurred mainly between 249-465 °C, and the second step occurred in the 473-537 °C range, and the IDT, where the weight loss reached 5 wt.%, was 265.1 °C.

The decomposition of the ATH filled O-SEBS/PP composite was relatively complicated, especially in the initial degradation stage, which started at lower temperatures. There were three decomposition steps occurring mainly between 217-329 °C, 337-409 °C and 441-521 °C and with the temperatures of the maximum rates of weight loss at 297 °C, 361 °C and 489 °C, respectively, the early

Figure 5. SEM fractographs of SEBS-based composites with different MH content in ATH/MH mixture filler: (a) 0%; (b) 38.15%; (c) 53.85% (d) 61.54%; (e) 76.92% (f) 100% O-SEBS/PP/filler=29.75/5.25/65

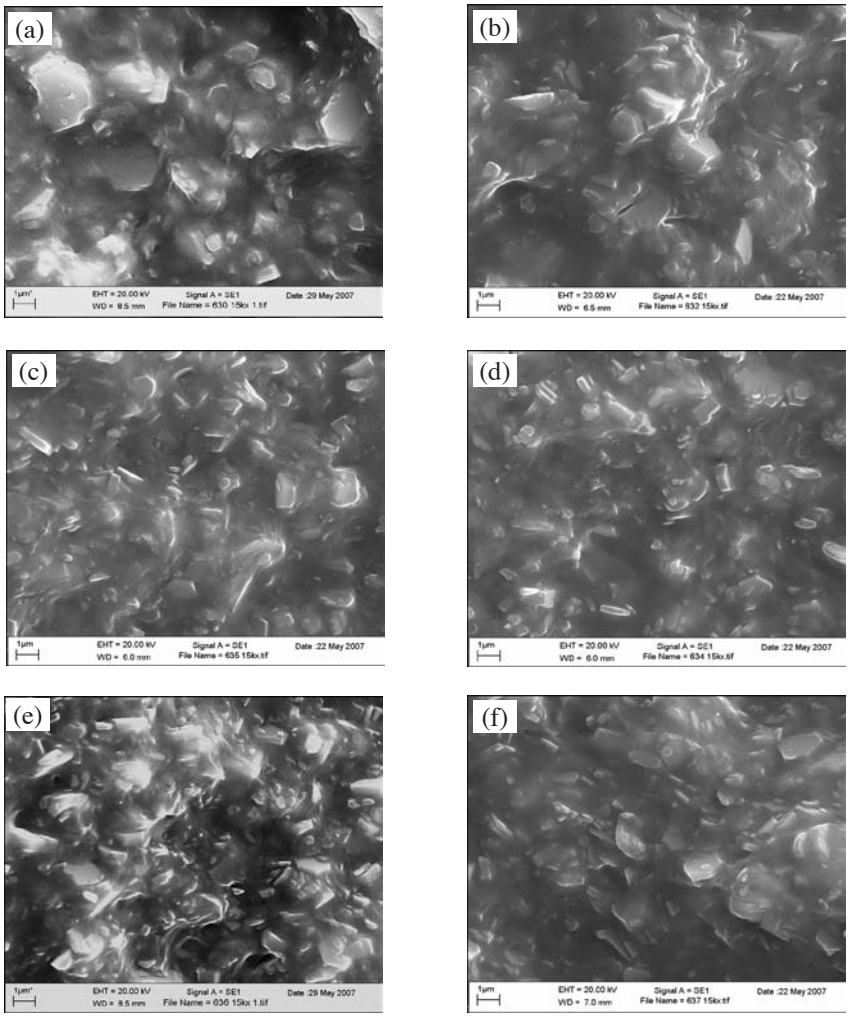


Figure 6. The TGA thermograms curves of ATH and MH in air atmosphere

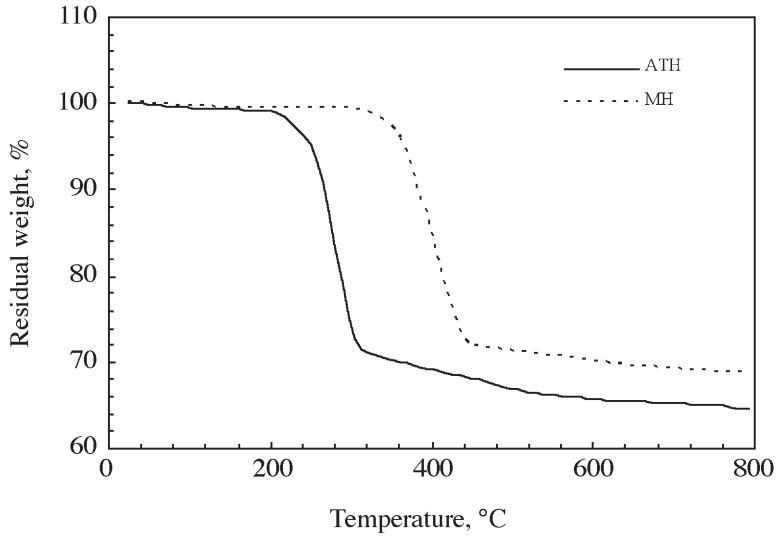


Figure 7. The differential thermogravimetric curves of ATH and MH in air atmosphere

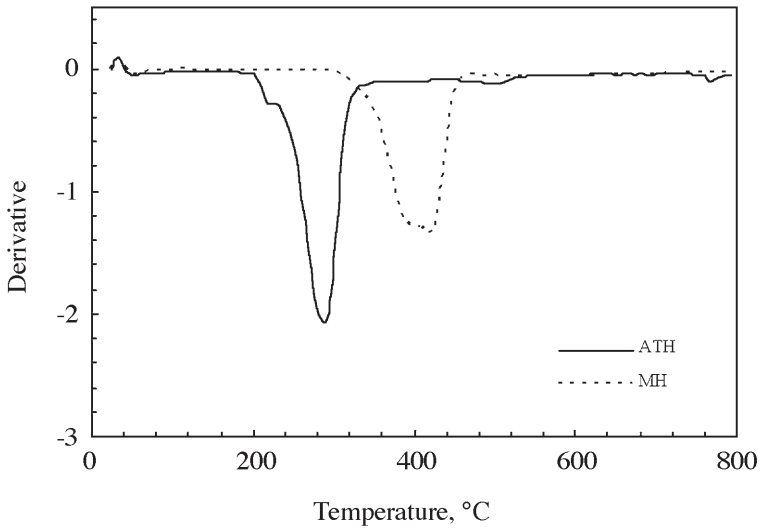


Figure 8. The TGA thermograms curves of SEBS-based composites in air atmosphere

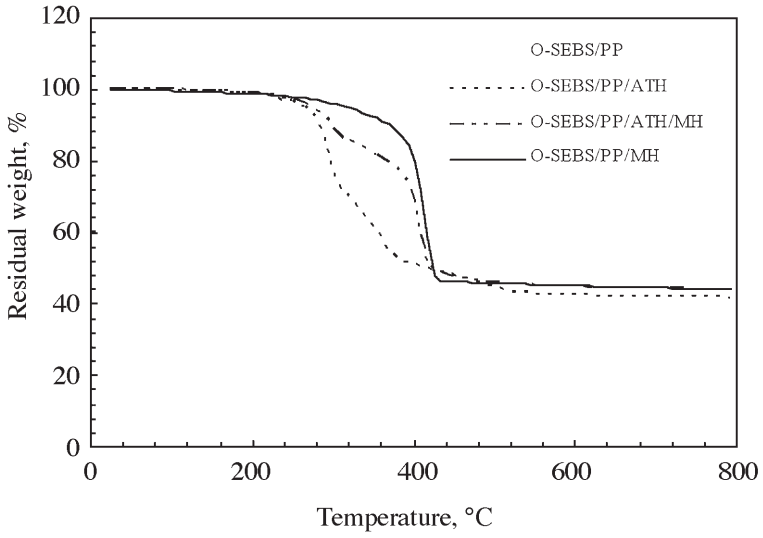


Table 2. Thermal decomposition features of ATH and MH in air atmosphere

Sample	Decomposition range (°C)	Bound water content (%)	IDT (°C)	T_{1max} (°C)
ATH	201-353	35.17	249.3	289
MH	321-451	31.27	364.9	417

Table 3. Thermal stability of the SEBS-based composites in air atmosphere

Composition	IDT (°C)	T_{1max} (°C)	T_{2max} (°C)	T_{3max} (°C)
O-SEBS/PP (85/15)	265.1	313	497	—
O-SEBS/PP/ATH (29.75/5.25/65)	262.2	297	361	489
O-SEBS/PP/MH (29.75/5.25/65)	314.8	417	—	—
O-SEBS/PP/ATH/MH (29.75/5.25/25/40)	272.8	297	417	—

decomposition step was mainly due to the decomposition of ATH itself, and the IDT was 262.2 °C.

In the case of MH filled composites, the decomposition curve moved to a higher temperature compared to the unfilled O-SEBS/PP composite and the O-SEBS/PP/ATH composite. The decomposition mainly occurred between 281-441 °C, with the maximum rate of weight loss at 417 °C, and the IDT was 314.8 °C.

The stability of the O-SEBS/PP/ATH/MH composite was better than that of O-SEBS/PP and O-SEBS/PP/ATH composites, but less than the O-SEBS/PP/MH composite. Its two degradation stages took place between 233-321 °C and 337-457 °C, respectively, with the temperatures of maximum rates of weight loss at 297 °C and 417 °C, respectively, and the IDT was 272.8 °C.

These results showed that ATH and MH increased the thermal stability of the SEBS-based composites, and MH increased the thermal stability more than ATH.

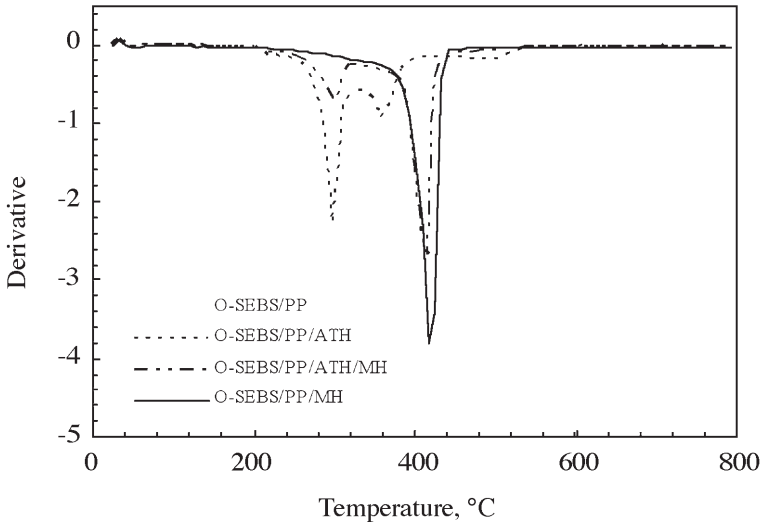
4. CONCLUSIONS

Limiting Oxygen Index (LOI) values of both ATH and MH filled O-SEBS/PP composites increased substantially as the amount of ATH and MH increased. Furthermore, the LOI value of the ATH system was higher than that of MH at the same addition level.

When MH was introduced, progressively, into ATH-filled composites, and for a constant combined filler loading of 65 wt.%, the LOI only deceased when the ratio of MH to ATH exceeded 40%.

Tensile strength, up to 50 wt.% filler, and elongation at break of the composites decreased as the amount of filler increased. However, the elongation at break of the composites filled with

Figure 9. The differential thermogravimetric curves of SEBS-based composites in air atmosphere



MH was a little higher than that with ATH, but for tensile strength there was little difference between them. At filler loading greater than 50 wt.%, the tensile strength levelled off but the% elongation was dramatically reduced.

Introduction of MH in ATH filled composites, for a total filler loading of 65 wt.%, led to some variation in the mechanical properties of the composites. The elongation at break increased from around 180 to 200% for a progressive increase in the ratio of MH to ATH up to 40% and there was a large increase in% elongation to around 300% when MH ratio reached 55-60%, thereafter the% elongation fell. This effect may be linked to particle size distribution of the respective MH and ATH fillers. In contrast, there was little effect on the tensile strength.

The thermogravimetric analysis (TGA) and differential TG (DTG) data showed that ATH and MH increased the thermal stability of the SEBS-based composites.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support from Shenzhen Sungallon Rubber & Plastics Co. Ltd., People's Republic of China.

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