Flammability Performance of Ethylene-propylene-diene-terpolymer/ Polypropylene-Based Thermoplastic Elastomers†

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The synergistic effect of organically modified montmorillonite on flammability properties and thermal stability of magnesium hydroxide and red phosphorous flame retardant ethylene-propylene-diene-terpolymer/polypropylene thermoplastic elastomers was investigated. The results revealed that organically modified montmorillonite could improve fire safety of thermoplastic elastomer/magnesium hydroxide/red phosphorus [TPE/MH/RP] materials by promoting the formation of compact and integrated chars.

Key Words: Ethylene-propylene-diene-terpolymer, Polypropylene, Thermoplastic elastomers, Flame retardant.

INTRODUCTION

Thermoplastic elastomers (TPEs) have attracted considerable technological interest because they combine the physical properties of elastomers with the process ability of thermoplastic polymers¹. Because thermoplastic elastomers are inherent flammable, it is important to improve their flame retardancy. Incorporation of magnesium hydroxide (MH) and phosphorous-containing compounds into polymeric materials is the common way to protect them from fire and heat². However, the effective flame retardancy has to be achieved at the expense of deterioration of the material mechanical properties due to the high global loading of magnesium hydroxide. The partial replacement of magnesium hydroxide by red phosphorus (RP) has led this flame retardant system exhibit good synergy and imparted the materials with improved flame retardancy³. For the past decades, combination of montmorillonite (MMT) with traditional flame retardants to improve the material properties concurrently, such as reduced flammability and permeability, improved mechanical properties and thermal stability has been studied intensively⁴. The complicated chemical and/or physical mechanisms are responsible for the improvements. In this paper, MH/RP/MMT flame retardant thermoplastic elastomers were prepared by melt blending. The effect of the combined flame retardants on improving flame retardancy of the materials was also reported.

EXPERIMENTAL

Flame retardant ethylene-propylene-diene-terpolymer/polypropylene [EPDM/PP]-based thermoplastic elastomers

were melt compounded of EPDM/PP (60/40 by weight) with desired amount of flame retardants, magnesium hydroxide and red phosphorous microencapsulated with melamine-formaldehyde resins (MRP) in a Brabender mixer at 180 °C for 10 min, using 5 phr (part of reagent per hundred of EPDM) SP-1045 (Phenol-formaldehyde resin) in combination with 1 phr SnCl₂ and 1.5 phr ZnO as curing agent systems. To obtain organically modified montmorillonite (OMT) containing thermoplastic elastomers (NTPEs), PP/MAPP (maleated polypropylene)/OMT (85/15/10 by weight) masterbatch was firstly extruded using a twin-screw extruder at 160-180 °C. The strands were then pelletized and mixed with EPDM and flame retardant additives in the mixer for 10 min. The formulations are shown in Table-1.

RESULTS AND DISCUSSION

Thermal stability: Thermal stability of thermoplastic elastomers was carried out by TGA (Fig. 1). TPE0 displays a one-step degradation process, starting at 493 °C ($T_{10\%}$, the temperature point at which 10 wt% thermal degradation occurs) with T_{max} (the maximum weight loss temperature) at 459 °C and completing at 500 °C with 2.5 % residual char. An apparent two-step degradation process is observed for the selected samples, TPE1 and TPE4. The first degradation in the temperature 320-450 °C is attributed to the endothermic decomposition of magnesium hydroxide, while the second is assigned to the degradation of polymers and the degradation of TPE0 over 450 °C is effectively retarded by the presence of magnesium

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TABLE-1
COMPOSITION AND FLAMMABILITY PERFORMANCE
OF FLAME RETARDANT TPEs^a

Sample code	Composition (g)					LOI	UL-94 Testing
	EPDM	PP	PP/MAPP/OMT Master batch (85/15/10)	MH	MRP		
TPE0	60	40				19	Fail
TPE1	60	40		100		32	Fail
TPE2	60	40		130		35	Fail
TPE3	60	40		140		36	Fail
TPE4	60	40		160		39.5	V-0
TPE5	60	40		90	10	34.5	Fail
TPE6	60	40		86	14	33.5	Fail
TPE7	60	40		82	18	32.5	V-0
TPE8	60	40		78	22	32	V-0
NTPE0	60		40			20	Fail
NTPE1	60		40	130		36	Fail
NTPE2	60		40	140		37	Fail
NTPE3	60		40	150		38.5	Fail
NTPE4	60		40	155		40.5	V-0
NTPE5	60		40	90	10	34.5	Fail
NTPE6	60		40	86	14	33	V-0
NTPE7	60		40	82	18	32.5	V-0

Fig. 1. TGA curves of flame retardant TPEs

hydroxide. Organically modified montmorillonite (OMT) has a positive effect with magnesium hydroxide in the improvement of thermal stability; NTPE0 and NTPE4 samples exhibit increased T_{1max} , T_{2max} and char yields compared to TPE0 and TPE4, respectively. The similar results have been found in MH/RP/OMT flame retardant NTPE6 sample.

Flammability studies: A set of fire related parameters obtained from the MCC including heat release capacity, peak heat release rate (PHRR), total heat release, the temperature at peak heat release rate (T_p) and the reduction in peak heat release rate (Reduct-MCC, $100 \times [\text{PHRR}_{(N)/\text{TPEs}} - \text{PHRR}_{\text{TPE0}}] / \text{PHRR}_{\text{TPE0}}$) are listed in Table-2 and the heat release rate curves of flame retarded TPEs are shown in Fig. 2. All the parameters of thermoplastic elastomers with magnesium hydroxide alone, heat release capacity, peak heat release rate and total heat release decrease gradually with increasing magnesium hydroxide loadings, while T_p -MCC shifts to a higher temperature slightly (Fig. 2a). As expected, the limited oxygen index value is increased from 19 of TPE0 to 39.5 of TPE4 and UL 94 V-0

TABLE-2
MCC DATA OF FLAME RETARDANT TPEs

Sample	HRC (J/g·k)	PHRR (W/g)	THR (kJ/g)	T_p (°C)	Reduct-MCC (%)
TPE0	1171	1165	44	494	NA
TPE1	678	673	23	495	42
TPE3	545	541	19	493	53
TPE4	477	475	17	497	59
TPE5	643	639	22	498	45
TPE6	670	666	23	498	43
TPE7	662	658	23	496	43
NTPE2	562	559	18	494	52
NTPE4	478	475	17	499	59
NTPE5	591	586	22	496	50
NTPE6	609	605	22	497	48
NTPE7	621	616	23	498	47

classification is achieved at TPE4. NTPE4 exhibits the similar MCC feature to that of TPE4, but the replacement of polypropylene with PP/MAPP/OMT masterbatch imparts the material with increased flame retardancy in terms of limited oxygen index. Fig. 2B shows the heat release rate curves of MH/MRP and MH/RP/OMT flame retarded TPEs. The heat release rate curves are much the same for all the samples, but NTPE6 and 7 shows higher Reduct-MCC compared to TPE 6 and 7. Meanwhile, the limited oxygen index values decrease with increasing RP/MH ratios for TPE and NTPE samples and the V-0 classification is achieved at TPE7 with MH/RP ratio of 82/18 while NTPE6 with a higher ratio of 86/14. The results indicate that too much MRP will deteriorate the improvement of material flammability properties due to its own inherent combustibility and there is an optimum amount of MRP should be present in different flame retardant systems.

Fig. 2. HRR curves of flame retardant TPEs

SEM studies: The physical properties of the char have an important role in the material fire performance. TPE1 leaves a loose char with poor mechanical properties (Fig. 3A₁ and A₂), while a more compact and rigid char bestrewn with holes and cracks is observed in TPE7 (Fig. 3B₁ and B₂). For sample NTPE6, an integrated and tight char is left (Fig. 3C₁ and C₂), which provides the underlying materials better thermal protection than other TPE1 or TPE7. Two things, the segregation and Hofmann degradation of organically modified montmorillonite, are mainly taken into consideration for the difference. The first is that acidic sites in the aluminosilicate (LS⁺H) generated from the Hofmann degradation of organically modified montmorillonite accelerate the endothermic decomposition of magnesium hydroxide. On the other hand, immigration of clay within polymeric matrix to resemble on the sample surface will be promoted by the water vapour in addition to the degradation polymer products and thus the well-known carbonaceous-silicate barrier will generate. As a result, both the transfer of water vapour and phosphorus vapour from melamine-formaldehyde resins will be impeded by the segregation, which is beneficial to ensure the completing oxidation to form the glassy phosphoric acid coating on the substrate.

Fig. 3. SEM micrographs of the residual chars

Conclusion

Melamine-formaldehyde resins is a good synergist in improving flame retardancy of TPE/MH composites; organically modified montmorillonite has crucial importance on the interaction with MH/MRP by increasing the integration and mechanical strength of the char, which is favourable to improve flammability performance of the materials.

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