

Novel PBT Blends with Magnesium Hydroxide Flame Retardant

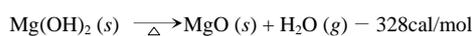
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Introduction

Polyester resins are widely applied to industrial, architectural and electronic fields nowadays with their superior properties and competitive prices. Polybutylene terephthalate (PBT) is a representative polyester and its excellent features including mechanical, electrical, chemically stable and thermally robust characteristics make the resin's usage extending. Notwithstanding the merits, PBT is regarded as a vulnerable resin to hydrolysis, especially in the presence of metal hydroxide [1]. The mechanism of hydrolysis is well known and metal moiety in the blend accelerates the reaction as a kind of catalyst [2].

Recently it arouses public concern about endowing plastics parts with flame retardant properties. Use of traditional brominated flame retardants is now partly banned because of their toxicity [3]. Also, some substitutable nitrogen- or phosphorus-containing products show less fire suppressing capability [4]. Metal (normally magnesium) hydroxide flame retardants that follow the mechanism (**Figure 1**) are non-toxic and efficient for wide range of polymers. Hydroxides of magnesium hydroxide ($Mg(OH)_2$) decompose endothermically when heated according to the reactions:



Generated water and char as well as the heat absorption suppress the flame effectively. The gaseous water phase is believed to envelop the flame, thereby excluding oxygen and diluting flammable gases. Char, a heat insulating material is formed on the surface of the plastic in contact with the flame, reducing the flow of potentially flammable decomposition products to the gas phase where combustion occurs. In the reaction, the decomposition products are non-toxic and the mineral phases, especially MgO, are alkaline, reducing the likelihood of acidic, corrosive gases exiting the plastics.

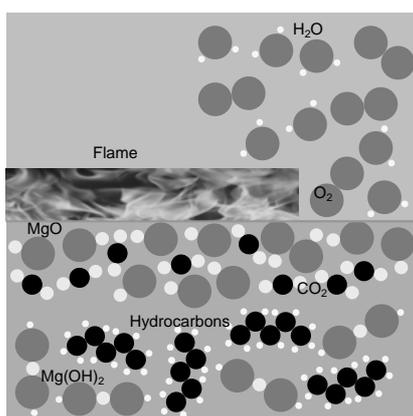


Figure 1. The mechanism of combustion and decomposition of magnesium hydroxide

Magnesium moiety in the flame retardant, nevertheless, can promote the decomposition reaction of polyester and it is known that addition of $Mg(OH)_2$ is not appropriate for PBT. The objective of this study is to investigate PBT blends having practically applicable mechanical and flame retardant properties. Several kinds of additional resins were introduced to hold flame retardant and reduce the possibility of interactions with PBT. Modified resins were adopted also to improve compatibility with PBT. Mechanical testing, scanning electron microscopy and maximum smoke density evaluation were performed to characterize the blends.

Experimental

Materials. The materials used in this study were as shown (**Table 1**). PBT, polyolefin copolymers and elastomers were used as base resins and magnesium hydroxide and stabilizers were added to enhance properties. A PBT resin was a general product ($IV=1.31$) that was not added any additive and an ethylene-butyl acrylate copolymer (EBA) resin contained 17 wt% of butyl acrylate. The basic chemical structure of a maleic anhydride (MAH) grafted ethylene-octene copolymer was similar to a polyolefin elastomer and the anhydride moiety was introduced for the intention of good adhesion to other polymers. An ethylene-vinyl acetate copolymer (EVA) resin contained 18 wt% of vinyl acrylate was used for high compatibility with many additives. Polyester thermoplastic elastomers have structural differences – TPEE 1 was classified as a polyether-ester type while TPEE 2 was a kind of polyester-ester. Adopted additives were a flame retardant and a stabilizer. H5MV is a special surface-treated $Mg(OH)_2$ grade for effective mixing. A phenolic antioxidant, pentaerythritol tetrakis(3-3,5-di-tert-butyl-4-hydroxyphenyl) propionate, was used for thermal and hydrolytic stabilization.

Table 1. Materials

Category	Composition	Trade name	Maker
Resins	PBT	Lupox [®] SV-1120	LG Chem.
	EBA	Elvaloy [®] AC 3117	DuPont
	Ethylene-octene copolymer-(g)-MAH	Fusabond [®] MN 493D	DuPont
	Polyolefin elastomer	Engage [®] 8440	DuPont
	EVA	Elvax [®] 460	DuPont
	TPEE 1	Hytre [®] 3078	DuPont
	TPEE 2	Arnitel [®] UM551	DSM
Additives	$Mg(OH)_2$	Magnifin [®] H5MV	Albemarle
	Phenolic stabilizer	Irganox [®] 1010	Ciba

Preparation. The PBT resin was dried in an oven for 4 hours at 110°C and mixed with other components using an internal mixer (Thermohaake[®] Rheomix 3000P) at 250°C. Mixing speed and time were controlled as 50 rpm and 15 minutes respectively for sufficient blending. Compositions of recipes in this study are as given (**Table 2**). Obtained blend was then crushed into fine granules and specimens were made using Babyplast[®] injection molding machine. Dimensions of the specimens in this study are specified in ASTM D 638.

Table 2. Recipes

	1	2	3	4	5	6	7	8
PBT	100	80	80	80	80	80	80	80
EBA		10	10					
Ethylene-(co)-octene-(g)-MAH				10	10	10		
Polyolefin elastomer		10		10				
EVA			10		10	10		
TPEE 1							20	
TPEE 2								20
$Mg(OH)_2$	15	15	15	15	15	25	15	15
Stabilizer	2	2	2	2	2	2	2	2
Total	117	117	117	117	117	127	117	117

Evaluation. Mechanical properties of blends were tested at room temperature and after aging at 180°C for a week. The properties were evaluated using an Instron[®] 5566 universal testing machine in accordance with ASTM D 638 and the crosshead speed was 50mm/min. Morphological analyses using scanning electron microscopy (Hitachi[®] S-2500C) were carried out on liquid nitrogen frozen and fractured samples. The smoke densities were tested using Fire Testing Technology[®] smoke density chamber and the radiant energy was set to 2.5W/cm² as specified in ASTM E 662.

Results and discussion

Mechanical properties. Mechanical properties of all blends were estimated at room temperature and after aging as shown (**Table 3**).

Even though the condition for aging was very severe for common polymer blends, it is suitable to test properties at practical extreme environment. In blend 1, the flame retardant was added alone to the neat PBT without any other resin to estimate the effect of metal hydroxide. Worse than expected, the shape of the mixture was crumbly sand-like powder after blending in the machine and it showed severe decrease in properties as a result of hydrolysis. The excessively inferior condition interrupted further estimation for the blend.

As given above (Table 2), some additional resins were included in blend 2-8 to prevent falloff of the properties by means of promoting adhesion, holding additives and restraining the possibility of contacts between PBT and $Mg(OH)_2$, and. In blend 2 and 3, an EBA resin was adopted and a polyolefin elastomer or an EVA resin was used additionally but poor tensile elongation values were shown in both trials in contrast to sufficient tensile strength. An ethylene-octene copolymer grafted with maleic anhydride moiety was applied in blend 4 and 5 with same additional resins and elongation values were greatly improved at R.T. and after aging. This trend was sustained with larger amount of flame retardant, in blend 6, and the decreases of properties were not severe as expected.

As another trial, TPEE resins were mixed with PBT, a kind of polyester, but the results were not sufficient as shown in blend 7 and 8. Though intimate phases between PBT and additional resins could be achieved, as the 'like dissolves like' rule, lack of holding capability of polyester resins might cause the inferior properties.

Table 3. Mechanical properties

		1	2	3	4	5	6	7	8
at R.T.	Strength (kgf/mm ²)	-	4.00	1.36	3.33	3.39	3.30	1.75	4.33
	Elongation (%)	-	26	15	140	127	111	21	82
aged	Strength	-	4.04	1.52	3.73	3.64	3.44	1.08	5.85
	Elongation	-	19	14	125	102	99	14	41

Scanning electron microscopy. The micrographs of the fractured surfaces of the blends were shown (Figure 2). Due to the intrinsic incompatibility between PBT and $Mg(OH)_2$, in blend 1, two ingredients are merely together, not mixed thoroughly (2a). Incorporating additional resins with the intention of adhesion promotion, two blends showed quite different morphological appearances in blend 3 (2b) and 5 (2c). The results were originated probably from the differences in the affinity of additional resins. That is, the performance of the ethylene-(co)-octene-(g)-MAH resin was more efficient than that of EBA. In case of blend 7 (2d), the mixed states of resins seemed to be fair but agglomerated particles of additives not fully mingled with resins were observed. The holding efficiency of additional polyester resins was not sufficient and it might relate to poor mechanical properties. In this study, blends that had good mechanical properties showed overall indefinite domain boundaries and indistinctive particles. It means that compatibility between PBT and additional resins is essential to enhance mechanical properties, as well as the additives-holding capability.

Smoke densities. It is known that most fire casualties come from inhalation of smoke and toxic gases, not from burning by flame or heat. Hence a smoke density of a specific blend indicates the degree of danger arising from the real fire situation. As depicted (Figure 3), the smoke density dropped drastically via addition of flame retardant, compared a reference blend (same composition as blend 4 except flame retardant) with others. There was a rough tendency between the composition of resins and smoke densities, that is, the more polyethylene moiety in additional resins was, the amount of generated smoke slightly increased. Since the ethylene-(co)-octene-(g)-MAH and the polyolefin elastomer have similar basic structures like polyethylene, the smoke density of blend 4 rose a little in contrast with blend 3. The lowest smoke density was observed in blend 6 and it might be resulted from the extended fire suppressing effect of extra $Mg(OH)_2$. Relatively low smoke densities of blend 7 and 8 were due to inherent characteristics of TPEE resins.

Conclusion

PBT-based blends containing additional polyolefin and EVA resins with $Mg(OH)_2$ flame retardant were obtained and shown practically improved properties. Concerned deterioration of properties

was overcome via the adoption of other resins that played roles of holding the flame retardant and promoting the adhesion to PBT. In this study, PBT / Ethylene-(co)-octene-(g)-MAH / EVA or polyolefin elastomer blend showed notable mechanical properties even after aging at harsh condition. The states of mixtures were observed using SEM. Blends with dim phase boundaries might indicate fair compatibility between resins and good properties as well. The results of smoke evolution test gave simulative information at real fire and the effect of resin composition.

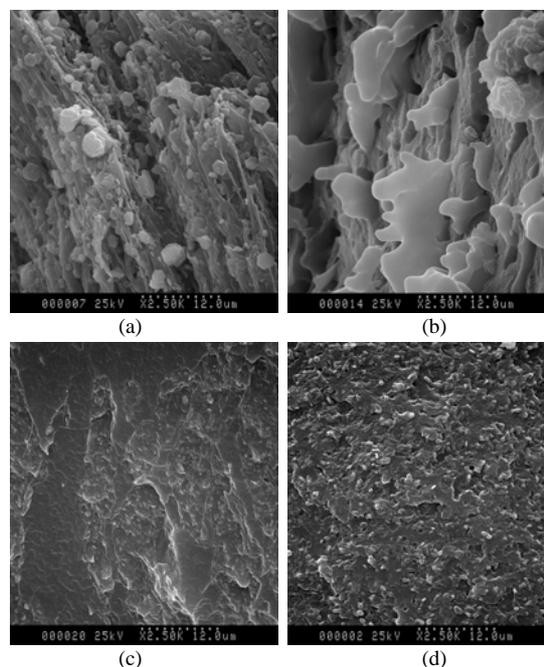


Figure 2. Micrographs of scanning electron microscopy; (a) blend 1, (b) blend 3, (c) blend 5, (d) blend 7

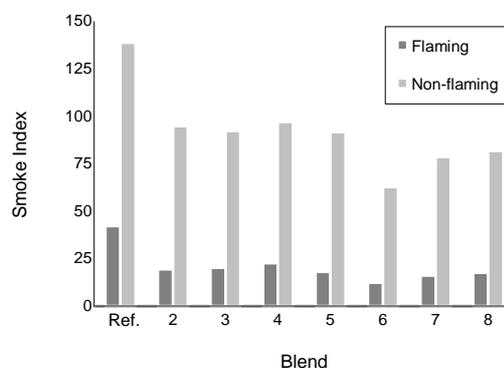


Figure 3. Smoke densities

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