

Synergistic Effect of Metal Oxides on the Flame Retardancy and Thermal Degradation of Novel Intumescent Flame-Retardant Thermoplastic Polyurethanes

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ABSTRACT: The synergistic effects of some metal oxides on novel intumescent flame retardant (IFR)–thermoplastic polyurethane (TPU) composites were evaluated by limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis (TGA), cone calorimetry, and scanning electron microscopy. The experimental data indicated that the metal oxides enhanced the LOI value and restricted the dropping of the composites. The IFR–TPU composites passed the UL-94 V-0 rating test (1.6 mm) in the presence of magnesium oxide (MgO) and ferric oxide (Fe_2O_3) at 35 wt % IFR loading, whereas only the MgO-containing IFR–TPU composite reached a UL-94 V-0 rating at 30 wt % IFR loading. The TGA results show that the metal oxides had different effects on the process of

thermal degradation of the IFR–TPU compositions. MgO easily reacted with polyphosphoric acid generated by the decomposition of ammonium polyphosphate (APP) to produce magnesium phosphate. MgO and Fe_2O_3 showed low flammability and smoke emission due to peak heat release rate, peak smoke production rate, total heat release, and total smoke production (TSP). However, zinc oxide brought an increase in the smoke production rate and TSP values. Among the metal oxides, MgO provided an impressive promotion on the LOI value. The alkaline metal oxide MgO more easily reacted with APP in IFRs. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1951–1960, 2011

Key words: degradation; flame retardance; polyurethanes

INTRODUCTION

Thermoplastic polyurethane (TPU) is an engineering thermoplastic elastomer,¹ which is a linear alternating copolymer consisting of hard and soft segments.² TPU has been widely used in many industrial area, such as wires and cables, conveyor belts, and protective coatings,³ because of its high performance, including excellent abrasion resistance, high tensile strength, high compressive and tear strengths, good flexibility, and good hydrolytic stability.^{4–7} Like many other thermoplastics, it also is a flammable polymeric material,⁸ therefore, its applications are restricted in most aspects. To achieve the good flame

retardancy of TPU composites, several kinds of flame-retardant additives can be used in TPUs.

Halogen-containing flame retardants are effective and show a good ratio of property to price for flame-retardant TPUs, but their uses have been limited because of life safety and environmental problems. Therefore, the demands for halogen-free flame retardants have become more and more important.⁹ Inorganic flame retardants, such as metal hydroxides, are a kind of halogen-free flame retardants used in TPUs.^{10–13} It has been reported that aluminum hydroxide (ATH) and mica can be incorporated into TPU composites as inorganic fire retardants,^{11,12} but their high loading seriously destroys the mechanical properties of the composites. Organophosphorus compounds, whether additive or reactive, are important flame retardants in TPUs and have been reported in the literature.^{14–17} Schmelzer et al.¹⁴ disclosed that a combination of an aromatic polyphosphonate and bisphenol A polycarbonate makes TPUs achieve a vertical burning test (UL-94) V-0 rating. Richardson and Dellar^{15,16} reported that the Al salt of *O*-methyl methylphosphonic acid enhanced the limiting oxygen index (LOI) value of TPU composites.^{10,17}

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Intumescent flame retardants (IFRs) are well known as a new generation of flame retardants because of their merits, such as low smoke emission and toxic gases produced during burning and antidripping properties. Several new IFR systems have been investigated, such as the pentaerythritol-based phosphate system¹⁸ and the triazine-range-based macromolecular charring agent system.^{19–23} Many studies have shown that some inorganic materials,^{24–31} such as metal oxide zeolite and montmorillonite, can be used as synergistic agents in IFR systems. Over the last 10 years, many researchers have paid attention to investigations on the synergistic effect of metal oxides or other inorganic compounds in IFR systems. Yang and coworkers^{32,33} reported that transition-metal oxides present synergistic effects in the IFR polypropylene system. A lot of facts have proven that most metal oxides are efficient additives for improving the thermal stability and morphological structure of char residues and the flame retardancy of polyolefines.^{25,28,30} However, there has rarely been a report on the effect of metal oxides in IFR–TPU systems.

In this study, three metal oxides, magnesium oxide (MgO), zinc oxide (ZnO), and ferric oxide (Fe₂O₃), were selected to investigate their synergistic effects in new IFR–TPU composites with LOI, UL-94, thermogravimetric analysis (TGA), cone calorimetry (CONE), and scanning electron microscopy (SEM). A new effective IFR was used in TPU, consisting of ammonium polyphosphate (APP) and a charring–foaming agent (CFA; a triazine polymer), which was reported in our previous articles.^{19–23}

EXPERIMENTAL

Materials

TPU was a polyether polyurethane supplied by BASF (1185A, Ludwigshafen am Rhein, Germany). APP (GD-101, Crystalline form II, Polymerization degree (n) > 1500), having a soluble fraction in water below 0.2 g/100 mLH₂O and an average particle size of 15 μ m, was supplied by Zhejiang Longyou GD Chemical Industry Co, Ltd. (Longyou, China) CFA (a triazine polymer) was synthesized in our laboratory and had an average particle size of 10 μ m.

MgO, Fe₂O₃, and ZnO were produced by Tianjin Shuangchuan Chemical Co, Ltd. (Tianjin, China). The average diameter of all of the metal oxides was about 45 μ m.

Compounding

The IFR–TPU composites consisted of TPU and IFR, and the loadings of IFR were kept at 30 or 35 wt %

on the basis of the composite weight. The fixed components of the IFR were 13.6 wt % CFA, 81.4 wt % APP, and 5.0 wt % metal oxide according to our primary investigation. The TPU and IFRs were melt-mixed on a two-roll mill (Harbin Plastic Co., Harbin, China) in the temperature range 180–185°C for 10 min and then compressed into sheets on a curing machine at 110°C for 2 min.

Flame-retardancy tests

The flame retardancy of all of the samples was characterized by the LOI and UL-94 methods. LOI data were obtained at room temperature on an oxygen index instrument (JF-3, produced by Jiangning Analysis Instrument Factory, Jiangning, China) according to the GB/T-2406-1993 standard. The dimensions of all samples were 130 \times 6.5 \times 3.2 mm³. The UL-94 ratings of all of the samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, with sample dimensions of 125 \times 12.5 \times 1.6 mm³.

TGA

All TGA tests were carried out on a PerkinElmer Pyris 1 thermal analyzer (Massachusetts, USA) at a linear heating rate of 10°C/min under pure nitrogen or air within the temperature range 50–800°C. The weight of every sample was kept within 2–4 mg.

CONE testing

All CONE data were taken from a cone calorimeter (manufactured by Fire Testing Technology (East Grinstead, UK)) at an incident heat flux of 50 kW/m² according to the ISO 5660-1 standard. The samples (100 \times 100 \times 4 mm³) were laid on a horizontal sample holder.

Mechanical properties testing

Determinations of the tensile strength and elongation at break of all specimens were performed by a Regeer computer-controlled mechanical instrument (Shenzhen, China) according to GB/T 1040-1992. The average value from five specimens is reported.

SEM

SEM was used to examine the morphology of the char residue obtained on CONE tests with an FEI QuanTa200 scanning electron microscope (Oregon, USA). The accelerating voltage was 15 kV. The surface of the char residues was sputter-coated with a gold layer before examination.

TABLE I
LOI and UL-94 Data of the IFR-TPU Composites

Sample	Composition of IFR	Loading (wt %)	LOI (%)	UL-94 test		
				t_1 (s)/ t_2 (s)	Flaming dripping	Rating
TPU	No IFR	0	Flammable	—/—	Yes	No rating
A	APP-CFA	35	29.6 ± 0.1	1.2/—	Yes	No rating
B	APP-CFA-MgO	35	48.6 ± 0.1	0.8/1.7	No	V-0
C	APP-CFA-MgO	30	33.0 ± 0.1	0.9/7.5	No	V-0
D	APP-CFA-Fe ₂ O ₃	35	44.8 ± 0.1	0.8/1.0	No	V-0
E	APP-CFA-Fe ₂ O ₃	30	32.1 ± 0.1	0.9/—	Yes	No rating
F	APP-CFA-ZnO	35	35.3 ± 0.1	0.8/—	Yes	No rating
G	APP-CFA-ZnO	30	24.9 ± 0.1	1.0/—	Yes	No rating

RESULTS AND DISCUSSION

LOI and UL-94 rating

The LOI values of the IFR-TPU composites containing metal oxides are listed in Table I. The determination of LOI for pure TPU was difficult because it melted very quickly and caused the flame to be extinguished because of material absence.³⁴ The LOI value of the metal oxide-free IFR-TPU composite reached 29.6% when the IFR content was 35 wt %. The LOI values had a substantial increase with 5 wt % loading of metal oxides in the IFRs, and the LOI value of the MgO-containing IFR-TPU composite could reach 48.6%. Such a large increase in the LOI value showed that the metal oxides provided a clearly synergistic effect on the LOI values of the IFR-TPU composites. However, when the addition of the IFR was 30 wt %, the LOI values of the IFR-TPU composites showed a substantial decline. When we compared the LOI values of these composites carefully, we found that the order in which the metal oxides increased the LOI values was as follows: MgO > Fe₂O₃ > ZnO.

The UL-94 test results of the IFR-TPU composites containing the metal oxides are given in Table I. The

burning time after first ignition (t_1) and the burning time after second ignition (t_2) were recorded from the UL-94 tests on the basis of the average burning time of five specimens. MgO and Fe₂O₃ effectively solved the dripping problem during the burning of the IFR-TPU composites at 35 wt % IFR loading, and they passed the V-0 rating, whereas the IFR-TPU composites with ZnO failed to pass the UL-94 test. However, when the IFR addition was 30 wt %, only the MgO-containing IFR-TPU composite passed the V-0 rating.

The results of the LOI and UL-94 tests indicated that the metal oxides showed obviously synergistic effects on the flame retardancy of the IFR-TPU composites, and their synergistic effects were different. MgO played a good role in inhibiting the flaming dripping.

Thermal degradation behavior under nitrogen and air

Tables II and III show the TGA data of the IFR (CFA+APP), metal oxides containing IFRs, and the IFR-TPU composites with 35 wt % IFR loading under pure nitrogen and air, respectively. Figure 1

TABLE II
Thermal Degradation and Char Residue Data of the IFRs and IFR-TPU Composites Under Pure Nitrogen by TGA

Sample	$R_{1\text{peak}}/T_{1\text{peak}}$ (% min ⁻¹ /°C)	$R_{2\text{peak}}/T_{2\text{peak}}$ (% min ⁻¹ /°C)	$R_{3\text{peak}}/T_{3\text{peak}}$ (% min ⁻¹ /°C)	$R_{4\text{peak}}/T_{4\text{peak}}$ (% min ⁻¹ /°C)	Char residue at 700°C (%)		
					Experimental	Calculated	Difference
IFR (APP+CFA)	2/315	1.8/367	1.8/436	3.9/601	19	—	—
IFR-MgO	2.8/316	1.1/380	1.6/444	1.3/572	48	23	25
IFR-Fe ₂ O ₃	2.1/310	1.2/386	1.7/440	2.7/593	33	23	10
IFR-ZnO	1.8/304	1.6/366	1.7/442	2.6/589	35	23	12
TPU	10.5/350	9.9/411	—	—	2	—	—
TPU-IFR	8.1/306	9.9/356	—	—	26	7	19
TPU-IFR-MgO	9.0/312	8.6/358	—	—	30	18	12
TPU-IFR-Fe ₂ O ₃	8.4/315	9.4/363	—	—	28	13	15
TPU-IFR-ZnO	8.6/319	8.5/350	—	—	27	13	14

$R_{1\text{peak}}$, $R_{2\text{peak}}$, $R_{3\text{peak}}$ and $R_{4\text{peak}}$ stand for the thermal degradation rate of first peak, second peak, third peak and fourth peak, respectively.

$T_{1\text{peak}}$, $T_{2\text{peak}}$, $T_{3\text{peak}}$ and $T_{4\text{peak}}$ stand for the thermal degradation temperature of first peak, second peak, third peak and fourth peak, respectively.

TABLE III
Thermal Degradation and Char Residue Data of the IFRs and IFR-TPU Composites Under Air by TGA

Sample	$R_{1\text{peak}}/T_{1\text{peak}}$ (% min ⁻¹ /°C)	$R_{2\text{peak}}/T_{2\text{peak}}$ (% min ⁻¹ /°C)	$R_{3\text{peak}}/T_{3\text{peak}}$ (% min ⁻¹ /°C)	$R_{4\text{peak}}/T_{4\text{peak}}$ (% min ⁻¹ /°C)	Char residue at 700°C (%)		
					Experimental	Calculated	Difference
IFR (APP+CFA)	1.6/309	1.7/373	1.5/428	3.4/623	21	—	—
IFR-MgO	2.1/310	1.4/386	1.5/430	1.8/694	47	25	22
IFR-Fe ₂ O ₃	1.8/306	1.7/379	1.7/435	2.4/631	31	25	6
IFR-ZnO	1.4/307	1.8/388	1.5/434	2.3/651	34	25	9
TPU	9.4/358	7.2/401	—	—	0	—	—
TPU-IFR	8.1/311	4.7/350	—	—	29	7	22
TPU-IFR-MgO	9.1/317	4.6/356	—	—	33	16	17
TPU-IFR-Fe ₂ O ₃	8.8/317	4.0/354	—	—	33	11	22
TPU-IFR-ZnO	8.0/321	6.0/353	—	—	32	11	21

$R_{1\text{peak}}$, $R_{2\text{peak}}$, $R_{3\text{peak}}$ and $R_{4\text{peak}}$ stand for the thermal degradation rate of first peak, second peak, third peak and fourth peak, respectively.

$T_{1\text{peak}}$, $T_{2\text{peak}}$, $T_{3\text{peak}}$ and $T_{4\text{peak}}$ stand for the thermal degradation temperature of first peak, second peak, third peak and fourth peak, respectively.

shows the thermogravimetric curves of the IFRs. The thermal degradation behavior of metal oxides containing IFRs presented a clear phenomenon: all of the curves showed four thermal degradation steps at about 310, 380, 440, and 590°C. The four thermal degradation steps were assigned to be dehydration, ammonia release, catalysis of the charring process, and decomposition of the polyphosphoric acid chain, respectively. With the addition of MgO, the first thermal degradation peak ($T_{1\text{peak}}$) increased obviously. As shown in Table II, the metal oxides evidently promoted the char residue formation of the CFA-APP system. For instance, the char residue of the IFR without metal oxides was only 19 wt % at 700°C, whereas that of the IFR system with 5 wt % MgO was 47 wt %. According to the calculated result [with the influence of metal oxide loading and IFR (CFA + APP) charring removed], the metal

oxides clearly enhanced the char residue of the IFR (see the char residue in Table II). MgO was the most effective synergistic agent and increased the char residue of the IFR by 25%, whereas other metal oxides only increased the char residue of the IFR by 10–12%. Figure 2 shows the thermogravimetric curves of the IFRs under air. When we compared Figures 1 and 2, we could see that the trend of the curves was almost consistent. This indicated that the oxygen in air had little effect on the thermal degradation behavior of the IFRs.

Figures 3 and 4 show the thermogravimetric curves of pure TPU, IFR-TPU, MgO-IFR-TPU, Fe₂O₃-IFR-TPU, and ZnO-IFR-TPU under pure nitrogen and air, respectively. The neat TPU [Fig. 3(a)] showed two thermal degradation peaks at 350 and 410°C, respectively, and nearly no char residue remained at over 500°C. The first stage took place

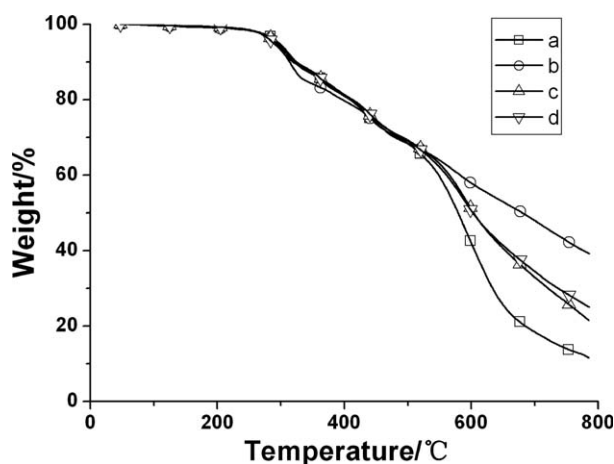


Figure 1 TGA curves of IFRs with and without metal oxides under pure nitrogen: (a) IFR (CFA-APP), (b) IFR-MgO-5 wt %, (c) IFR-Fe₂O₃-5 wt %, and (d) IFR-ZnO-5 wt %.

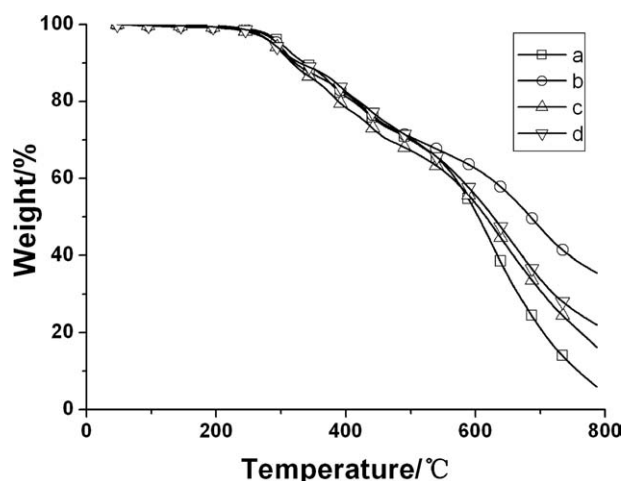


Figure 2 TGA curves of IFRs with and without metal oxides under air: (a) IFR (CFA-APP), (b) IFR-MgO-5 wt %, (c) IFR-Fe₂O₃-5 wt %, and (d) IFR-ZnO-5 wt %.

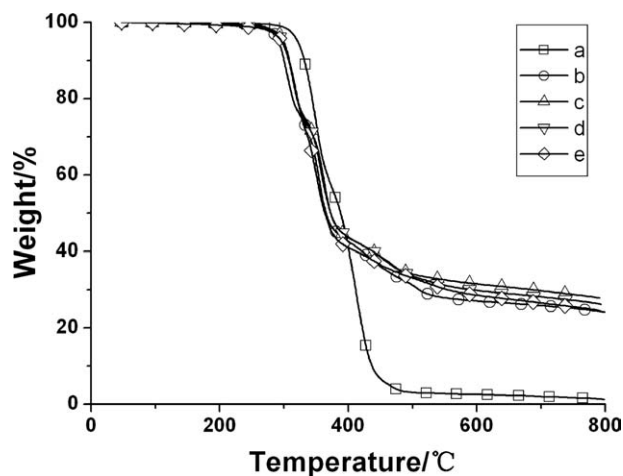


Figure 3 TGA curves of the IFR-TPU composites with and without metal oxides under pure nitrogen: (a) TPU, (b) IFR-TPU, (b) IFR-TPU-MgO-5 wt %, (c) IFR-TPU-Fe₂O₃-5 wt %, and (d) IFR-TPU-ZnO-5 wt %.

between 300 and 380°C; this was responsible for the scission of the TPU main chains; whereas the second stage occurred between 380 and 500°C and was attributed to the further destruction of the C—C and C—O bonds on the main chain. This result was in agreement with the literature.^{5–40} The first step was due to thermal degradation of the hard segment; it was because of the formation of isocyanate, alcohol, primary or secondary amine and olefin, and carbon dioxide. The second step was due to the thermal decomposition of the soft segment. As shown in Figure 3, however, the IFRs obviously reduced $T_{1\text{peak}}$ and the second thermal degradation peak ($T_{2\text{peak}}$) of TPU. That is, $T_{1\text{peak}}$ decreased from 350°C for TPU to about 310°C for the IFR-TPU composites, and $T_{2\text{peak}}$ decreased from 410°C for TPU to about 360°C for the IFR-TPU composites. These facts were attributed to the catalyzing effect of polyphosphoric acid

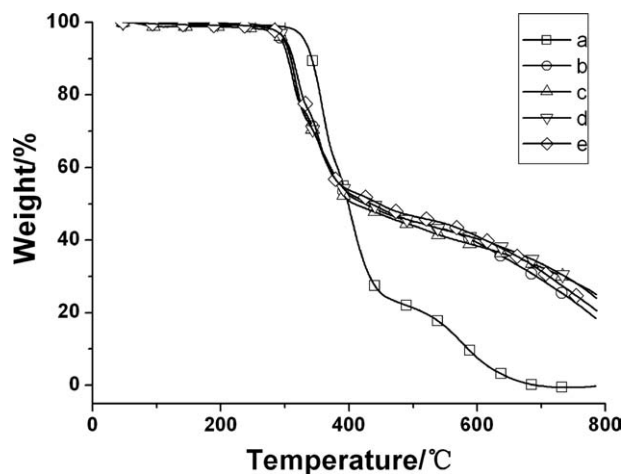
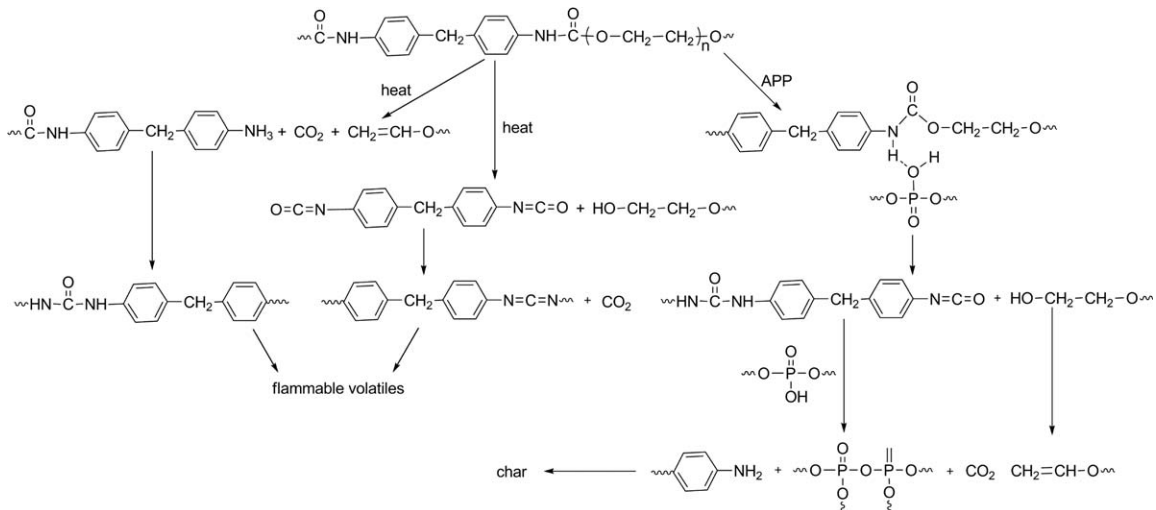


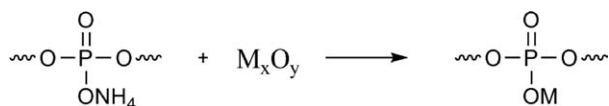
Figure 4 TGA curves of the IFR-TPU composites with and without metal oxides under air: (a) TPU, (b) IFR-TPU, (b) IFR-TPU-MgO-5 wt %, (c) IFR-TPU-Fe₂O₃-5 wt %, and (d) IFR-TPU-ZnO-5 wt %.

produced from the decomposition of APP on the thermal degradation of the [bond]CONH[bond] bonds. For a more intuitive interpretation, the schemes give the main thermal degradation of TPU, the thermal degradation of TPU with APP (Scheme 1), and the reaction of APP with the metal oxides (Scheme 2).¹⁰ With the same trend in Figure 1, $T_{1\text{peak}}$ of the IFRs increased with the addition of MgO, as shown in Figure 3. This illustrated that MgO reacted more easily with APP than did Fe₂O₃ and ZnO.

To further investigate the effect of the metal oxides on the IFR-TPU composites, the calculated result of IFR-TPU was based on 65 wt % TPU and 35 wt % IFR. According to the experimental data and calculated values of the char residues formed from the IFR-TPU composites given in Table II, their difference is used to present the charring ability of the IFR and IFRs containing metal oxides. It is



Scheme 1 Main thermal degradation of TPU and TPU with APP.



Scheme 2 Reaction of APP with the metal oxides.

clearly shown that IFR (APP + CFA) was a very effective charring catalyst for TPU, in which the char residue increased from 2 to 19%, and metal oxides presented different effects on the char formation of TPU. Compared with the metal-oxide-free IFR-TPU, MgO obviously reduced the char formation of TPU on the basis of difference given in Table II. This was because MgO is the strongest alkaline metal oxide in the metal oxides; it reacted easily with polyphosphoric acid generated by the decomposition of APP to produce stable ion bonds of magnesium phosphate. This resulted in a decrease in the catalysis of the char-formation ability of polyphosphoric acid. The rapid formation of magnesium phosphate in the char residue effectively restricted the dripping of the composites during burning.

According to Tables II and III and the comparison of Figures 3 and 4, $T_{2\text{peak}}$ decreased significantly. At the end of the second thermal degradation step, the remaining residue of TPU was 3% under pure nitrogen and 22% under the air, respectively. The remaining residues of the IFR-TPU and the IFR-TPU with metal oxide were about 41–44%, as shown in Figure 3. However, as shown in Figure 4, their remaining residue was about 50–54%. These results indicate that the oxygen in air enhanced the char formation of TPU and IFR-TPU. At high temperatures, however, the char residue was further oxidized because of the downtrend of thermal degradation.

Flammability of the IFR-TPU composites by the CONE study

Table IV shows the data of TPU and TPU with 35 wt % IFR composites obtained from the CONE tests at an incident heat flux of 50 kW/m², and Figures 5–10 show the plots of the samples. Figure 5 gives the heat release rate (HRR) curves: the neat TPU

burned very fast after ignition, and the sharp HRR peak appeared with a heat release rate peak (PHRR) of 1047 kW/m². The largest total heat release (THR), 134.3 MJ/m², was measured (see in Fig. 6). In contrast, the curves of the IFR-TPU composites showed much lower HRR peaks and THR values than those of the neat TPU, and the time to ignition (TTI) also decreased. That is, the APP-CFA system was very effective in reducing the peaks of HRR, smoke production rate (SPR), THR, total smoke production (TSP), and mass loss rate (MLR) of TPU. When MgO and Fe₂O₃ were added to the IFR-TPU composites, the PHRR showed a little decline. The synergistic effect between these metal oxides and the IFR-TPU composites was not obvious under these conditions.

The SPR and TSP curves of the samples are shown in Figures 7–8. Similar to the HRR and THR, the smoke release of the IFR-TPU composites was significantly reduced compared with that of pure TPU. MgO and Fe₂O₃ showed effective smoke suppression in the IFR-TPU composites, whereas ZnO brought increases in the SPR and TSP values.

Figures 9 and 10 give the MLR and mass loss curves versus time for the samples. MLR was recognized to be the primary parameter responsible for decreasing HRR and SPR during combustion. The mass loss behavior was in agreement with the behavior of heat release and smoke suppression. The decrease in MLR was attributed to char formation and its morphological structure on the surface of the composites, which is given in following section.

From the char residue data from CONE and TGA, the flame retardancy (LOI value and UL-94 rating) of the composites showed no good correlation with the char residue content. This was probably due to different experiment conditions and complicated combustion.

Mechanical properties

Table V shows the effect of metal oxides on the tensile strength and elongation at break of the pure TPU and IFR-TPU composites. With the addition of 35 wt % APP-CFA in TPU, the mechanical

TABLE IV
CONE Data of the Pure TPU and TPU-IFR Composites

Sample	Parameter						
	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	PSPR (m ² s ⁻¹)	TSP (m ² kg ⁻¹)	MLR (%min ⁻¹)	Char residue (%)
TPU	43	1047	134	0.235	30	0.434	3
TPU-IFR	30	109	87	0.020	18	0.056	34
TPU-IFR-MgO	30	99	75	0.019	15	0.051	33
TPU-IFR-Fe ₂ O ₃	31	95	87	0.019	17	0.045	39
TPU-IFR-ZnO	32	110	92	0.024	19	0.051	35

PSPR = smoke production rate peak.

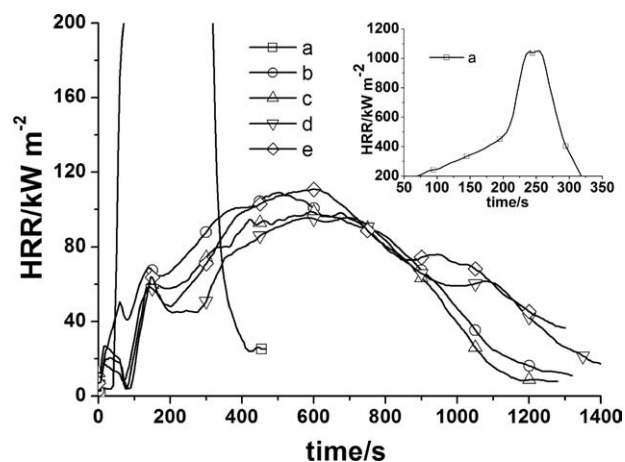


Figure 5 HRR curves of the TPU and IFR-TPU composites: (a) TPU, (b) IFR-TPU, (c) IFR-TPU-MgO, (d) IFR-TPU-Fe₂O₃, and (e) IFR-TPU-ZnO.

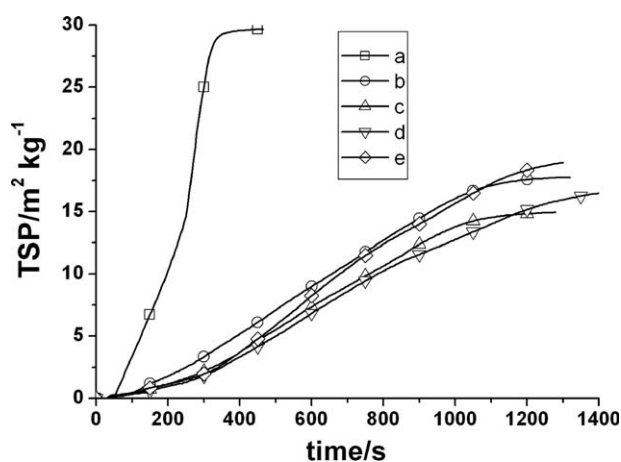


Figure 8 TSP curves of the TPU and IFR-TPU composites: (a) TPU, (b) IFR-TPU, (c) IFR-TPU-MgO, (d) IFR-TPU-Fe₂O₃, and (e) IFR-TPU-ZnO.

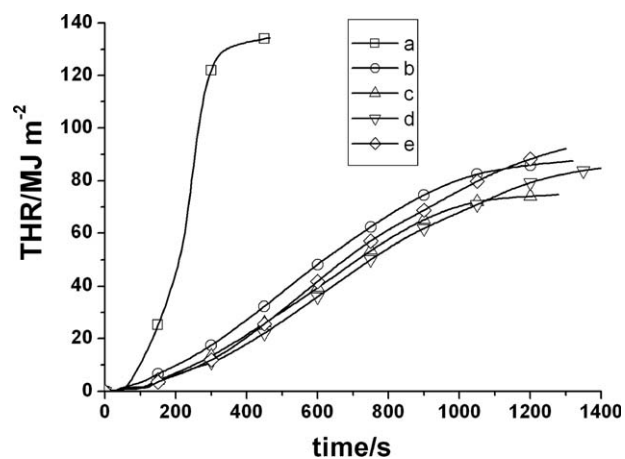


Figure 6 THR curves of the TPU and IFR-TPU composites: (a) TPU, (b) IFR-TPU, (c) IFR-TPU-MgO, (d) IFR-TPU-Fe₂O₃, and (e) IFR-TPU-ZnO.

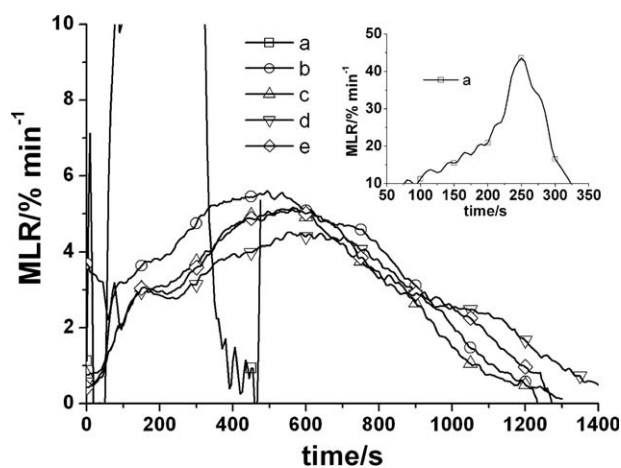


Figure 9 MLR curves of the TPU and IFR-TPU composites: (a) TPU, (b) IFR-TPU, (c) IFR-TPU-MgO, (d) IFR-TPU-Fe₂O₃, and (e) IFR-TPU-ZnO.

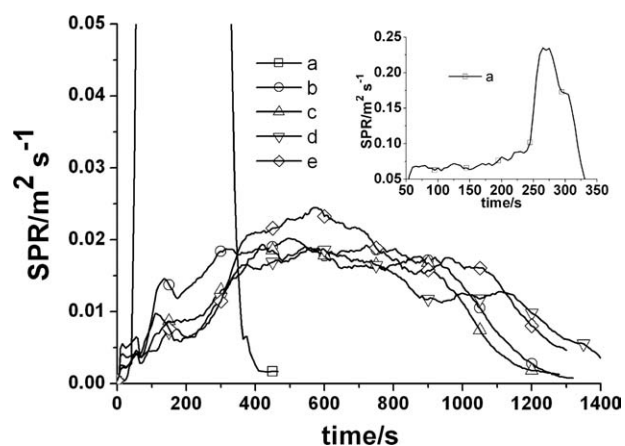


Figure 7 SPR curves of the TPU and IFR-TPU composites: (a) TPU, (b) IFR-TPU, (c) IFR-TPU-MgO, (d) IFR-TPU-Fe₂O₃, and (e) IFR-TPU-ZnO.

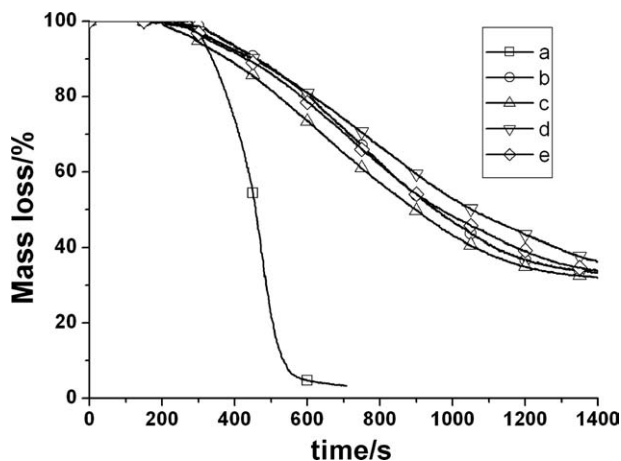


Figure 10 Total mass loss curves of the TPU and IFR-TPU composites: (a) TPU, (b) IFR-TPU, (c) IFR-TPU-MgO, (d) IFR-TPU-Fe₂O₃, and (e) IFR-TPU-ZnO.

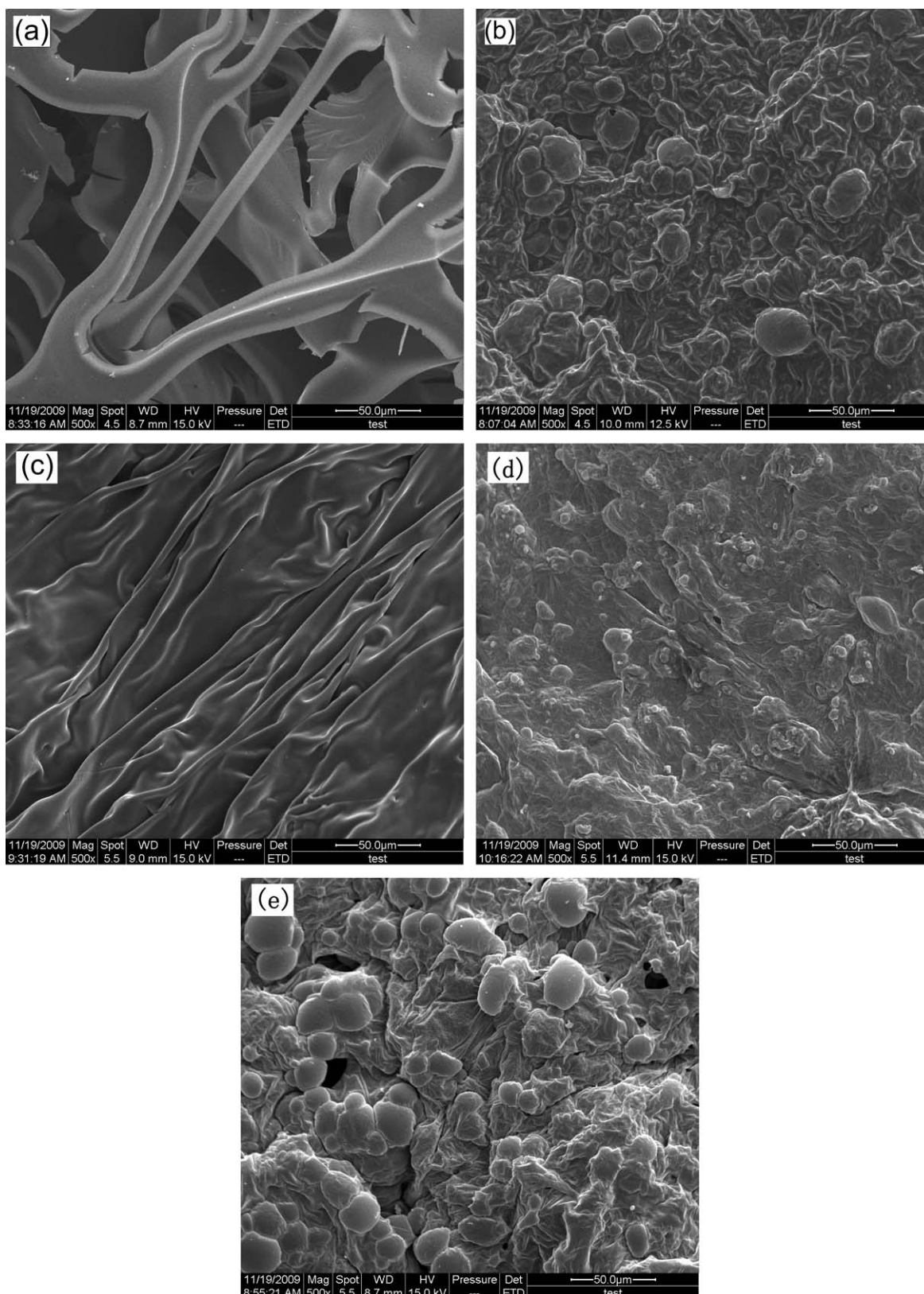


Figure 11 SEM photos of the char residues of the IFR-TPU composites: (a) pure TPU, 500×; (b) IFR-TPU, 500×; (c) IFR-TPU-MgO, 500×; (d) IFR-TPU-Fe₂O₃, 500×; and (e) IFR-TPU-ZnO, 500×.

properties of the IFR-TPU composites declined significantly. However, when the metal oxides were filled in the composites, the tensile strength and

elongation at break were improved. For instance, when no metal oxides existed in the IFR-TPU composites, the tensile strength and elongation at break

TABLE V
Mechanical Properties of the Pure TPU and IFR-TPU Composites

Sample	Tensile strength (MPa)	Elongation at break (%)
TPU	38.7 ± 0.3	550 ± 15
TPU-IFR	9.2 ± 0.2	69 ± 9
TPU-IFR-MgO	14.8 ± 0.3	201 ± 10
TPU-IFR-Fe ₂ O ₃	12.8 ± 0.5	104 ± 10
TPU-IFR-ZnO	13.0 ± 0.2	61 ± 7

of the IFR-TPU composites were 9.2 MPa and 69%, respectively; however, when MgO was added to the IFR-TPU systems, the tensile strength and elongation at break of the IFR-TPU composites increased to 14.8 MPa and 201%, respectively. The alkaline metal oxide was more beneficial to the mechanical properties. This result was probably due to the effect of APP on the thermal degradation of TPU. APP, as an acidic compound, catalyzed the thermal degradation of —CONH— bonds in TPU and resulted in a clear decline of the mechanical properties of TPU during processing. Metal oxides, especially MgO, reduced the influence of APP through surface interaction between the metal oxides and APP. However, ZnO obviously decreased the elongation at break. This was probably due to the catalyzing degradation effect of ZnO on TPU, which will be further investigated. In general, according to the data in Table V, these IFR systems clearly decreased the mechanical properties. This problem could be solved through the surface modification of IFRs, which is being investigated further.

Morphology of the burnt composites

Figure 11 shows SEM micrographs of the char residue of TPU with 35 wt % IFR composites to elucidate the relationship between the microstructure of protective char and the flame retardancy. The char residues were collected from the CONE experiments. The microstructures of the char residue of the IFR-TPU composites [Fig. 11(b)] displayed a more homogeneous and compact structure than the pure TPU [Fig. 11(a)]. Compared with the metal oxide systems, there were more crevasses and holes on the surface of the char residue with ZnO [Fig. 11(e)]; therefore, during burning, heat and flammable volatiles could easily penetrate the char layer into the flame zone. This indicated that the char layer formed from ZnO-IFR-TPU was unstable. This result was almost similar to that of the Fe₂O₃ system. On the contrary, MgO enhanced the intensity of the char residue; because of the easy reaction of MgO and APP, the char residue surface containing MgO [Fig. 11(c)] almost had no flaws, and the char layer was the same as the mountain ridge formed by the shrinkage

after the char layer expanded. The SEM micrographs of the char residue further confirmed that the addition of ZnO was not beneficial to improving the flame retardancy of TPU.

CONCLUSIONS

Three metal oxides were used as synergistic agents in a novel IFR-TPU system. The flame retardancy, thermal degradation, flammability, and mechanical properties of the IFR-TPU composites were investigated carefully. Some conclusions were drawn, as follows:

All three metal oxides, especially MgO, remarkably enhanced the LOI values of the IFR-TPU composites. The composites containing MgO passed the UL-94 V-0 rating (1.6 mm) in the case of the IFR (30 wt %).

The metal oxides clearly enhanced the char residue of the IFR. MgO was the most effective synergistic agent and increased the char residue of the IFR by 25%. MgO was the most effective inhibitor for the dripping of TPU because of the easy reaction of MgO and APP.

MgO and Fe₂O₃ showed efficiency in reducing the peaks of HRR, SPR, THR, TSP, and MLR obtained from the CONE test. The fire degradation behavior and char residue morphology gave a better understanding of the reduction of the peaks of HRR, SPR, THR, and TSP.

On the basis of the data of LOI, UL-94, HRR, THR, and mechanical properties, the alkaline metal oxide, MgO, was the most effectively synergistic agent for the novel IFR-TPU composites.

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