

## A Commercial Phosphorous–Nitrogen Containing Intumescent Flame Retardant for Thermoplastic Polyurethane

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**ABSTRACT:** The aim of this work is to develop a halogen-free thermoplastic polyurethane (TPU) composite with significantly improved fire performance by using a highly commercial phosphorous–nitrogen containing intumescent flame retardant (P–N IFR). Based on the characterizations of thermogravimetric analysis and *in situ* Fourier transform infrared spectra, P–N IFR powder was proved a desired flame retardant for TPU in theory and the thermal degradation property of PU/PNIFR composites at elevated temperatures was investigated as well. Fire performance was evaluated by limiting oxygen index, underwriters laboratories 94 testing and char residue morphologies. Results showed that the addition of P–N IFR promotes the formation of char residues which were covered on the surface of polymer composites resulting in the improvement of thermal stability and flame retardancy. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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### INTRODUCTION

Thermoplastic polyurethane (TPU) is an important commercial polymer material that exhibits excellent physical characteristics, such as high elasticity, high mechanical strength, abrasion resistance, and ageing resistance. These properties of TPU have led to its utilities in both industrial areas and daily life.<sup>1,2</sup> However, the flammability and poor heat-resistance of TPU have limited its further applications in last few years. In order to expand its service life in kinds of severe environments, the fire resistance and thermal stability of TPU should be enhanced, such as by filling suitable flame retardant.<sup>3,4</sup>

Recently, many attentions have been paid to the chemical intumescent flame retardant (IFR) additives.<sup>5–7</sup> A typical IFR system usually contains three main substances: acid source, carbon source, and gas source.<sup>8</sup> In an event of fire, these three substances will form a porous char layer with heat insulation function, which can prevent flame propagation, retard polymer matrix degradation, and reduce smoke generation.<sup>9</sup> Generally, IFRs are considered as desirable halogen-free flame retardant materials due to their advantages, such as high efficiency, no melt drip, low smoke, nontoxic, and no corrosive gas release, which meet the requirement of the environmental friendly flame retardant system. Therefore, they are considered as desirable halogen-free flame retardant materials. At present there are some successful commercial IFRs in the world, for example, the Exolit<sup>®</sup> series of

Clariant and the Melapur<sup>®</sup> series of Ciba.<sup>10–12</sup> Toldy et al.<sup>10</sup> used various IFRs to measure the flame retardancy of TPU, containing Exolit AP422, OP550, OP1230, Melapur MC, and so on. However, to achieve a higher fire retarded classification using traditional phosphorus-based or nitrogen-based IFR additives, more than 20 wt % loadings are needed, and the relatively lower flame retardant efficiency restricts its further application.<sup>13–15</sup>

The purpose of this study is to prepare a PU composite with enhanced flame retardancy by using a novel commercial phosphorous–nitrogen containing intumescent flame retardant (P–N IFR). Very low loading of this new compound is enough to achieve high flame retardancy, and it has relatively cheap price (60 ¥/kg). The fire performances of the composites were evaluated by thermal gravimetric analysis (TGA), limiting oxygen index (LOI), and underwriters laboratories (UL) 94 testing. In addition, results for char residue morphologies and *in situ* Fourier transform infrared (FT-IR) spectra were also discussed.

### EXPERIMENTAL

#### Materials

In this work, TPU (SW-5060RH) was kindly supplied by Anli Artificial Leather. The polyether polyurethane was synthesized by polymerization of 4,4'-diphenyl methylene diisocyanate with poly(tetramethylene glycol) and poly( $\epsilon$ -caprolactone). The P–N IFR master batch (XR-50A) (phosphorus content 24 wt %,

nitrogen content 22 wt %, density 1.8 g/cm<sup>3</sup>, and moisture < 0.5%) was supplied by Shandong Moris Technology. Ammonium polyphosphate (APP-II,  $n > 1000$ ) was purchased from Shandong Shian Chemical. All materials were commercially available and dried to remove the residue water or solvent.

### Preparation of PU Composites

The flame retardant powders were gridded with a 180 mesh sieve and blended with PU by using a Torque Rheometer (XSS-300, Shanghai Kechuang Rubber & Plastic Machinery) at 180°C for 12 min. The roller speed was 60 rpm for the preparation of all samples. Then the blends were molded by hot press at 200°C for 5 min in order to obtain 3 mm thick plaques. PU composites containing 5, 10, and 15 phr P-N IFR were successfully prepared and labeled as PU/PNIFR5, PU/PNIFR10, and PU/PNIFR15, respectively. Meanwhile, another PU composite with 15 phr APP-II was prepared as a reference in the same way and named as PU/APP15.

### Characterization

TGA was carried out with an analyzer (Pyris 1 TGA, PerkinElmer) by heating from 50 to 700°C at a heating rate of 10°C/min in both nitrogen and air with a flow rate of 40 mL/min. LOI test was performed using a JF-3 instrument (Jiangning Analytical Instrument Factory, China), according to ASTM D2863 with sample dimensions of 100 × 6.5 × 3 mm<sup>3</sup>. Based on the UL-94 test ASTM D3801-1996 standard, the vertical burning test was carried out on an AG5100A-type instrument (Zhuhai Angui Testing Instruments, China) with specimen dimensions of 130 × 13 × 3 mm<sup>3</sup>.

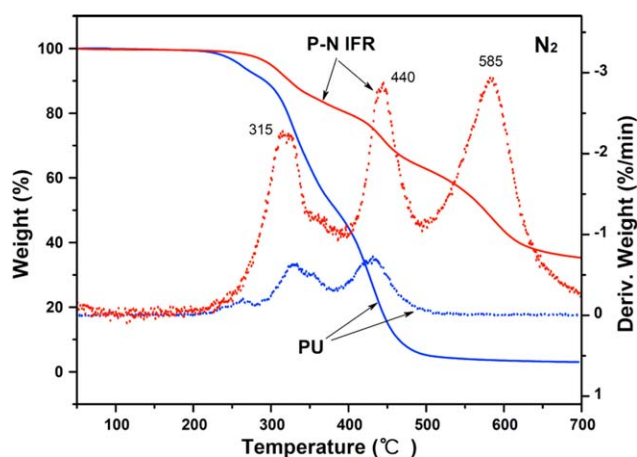
The morphologies of PU composites and their residual chars were analyzed by a field emission scanning electron microscope (SEM) (Sirion 200, FEI). The former composites were cryogenically fractured in liquid nitrogen, and the latter chars were collected after LOI tests. The SEM morphologies were obtained at an accelerating voltage of 10 kV, with specimens gold-coated. The appearance of residues after UL-94 testing for PU/PNIFR composites was taken by digital camera.

*In situ* FT-IR spectra were recorded on a Nicolet MAGNA-IR 750 spectrometer (Nexus, Nicolet Instrument) over the range of 400–4000 cm<sup>-1</sup>. P-N IFR powders were ground with KBr, pressed into tablets, and tested at various temperatures by heating the sample from 20 to 500°C at a heating rate of 10°C/min in air.

## RESULTS AND DISCUSSION

### Thermal Degradation Behavior

The TGA curves of pure PU and P-N IFR powders in nitrogen atmosphere are shown in Figure 1. Solid lines represent the thermogravimetry (TG) curves and dotted lines represent the differential TG (DTG) curves. According to the figure, the initial decomposition temperature of P-N IFR is about 250°C, slightly higher than that of pure PU. And there is about 37% residue at 700°C, which will enhance the thermal stability of polymers. Based on the DTG data, the thermal decomposition of P-N IFR is characterized by three steps with three maximal mass loss rates at 315, 440, and 585°C. These three decomposition proc-



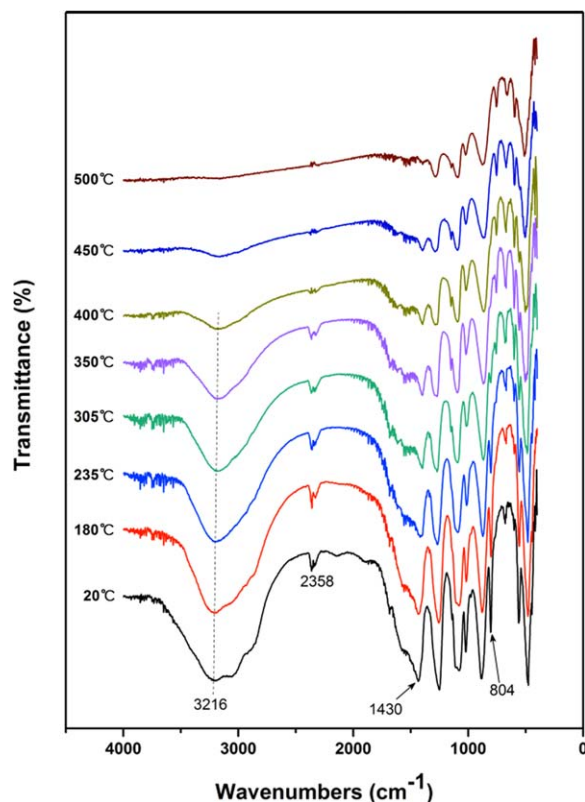
**Figure 1.** TGA curves of PU and P-N IFR under nitrogen condition. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

esses may consist essentially of elimination of PH<sub>3</sub>, NH<sub>3</sub>, and H<sub>2</sub>O gases,<sup>16</sup> which will dilute the flammable gas in a fire of PU. Moreover, for the DTG curve of PU, there are two main thermal decomposition peaks that are coincide with the previous two steps of P-N IFR roughly. Therefore, the flame retardant effect of P-N IFR will be quite fit for this kind of TPU.

For further studies of P-N IFR structural changes at elevated temperatures, the P-N IFR powders were analyzed by means of *in situ* FT-IR as shown in Figure 2. First of all, it can be seen that there are no obvious variations for the spectra from 20 to 235°C, but the intensity of all the absorption bands weaken a little. Compared with the curves above, the spectrum at 305°C shows the P—O—P bending vibration at 804 cm<sup>-1</sup> disappeared gradually, which indicates that the thermal decomposition of P-N IFR generates a phosphorous gas, like PH<sub>3</sub>. The spectrum at 400°C changes observably: N—H stretching vibration at 3216 cm<sup>-1</sup> vanished, which indicates an escape process of NH<sub>3</sub>. The decrease of the absorption band of C—C (1430 cm<sup>-1</sup>) stretching vibration above 500°C reveals the complete degradation of P-N IFR, and the peak of CO<sub>2</sub> (2358 cm<sup>-1</sup>) belonging to that in atmosphere under ambient temperature also disappeared. Meanwhile, the peaks in the fingerprint region transfer to the low-frequency direction, attributing to the loss of hydroxyl groups at a high temperature. These results mainly agree with the facts obtained in the TGA.

Furthermore, the fracture surfaces of pure PU and PU/PNIFR composites were analyzed by SEM, as shown in Figure 3. Pure PU shows a smooth and dense surface without any holes, but there are a few holes among the PU/PNIFR composites, which indicate that the mechanical properties decrease with the increase of flame retardant.

Thermal stability is an important property for the polymer composites containing flame retardant. The TGA results of pure PU and PU/PNIFR composites in air atmosphere are shown in Figure 4 and summarized in Table I. The thermo-oxidative degradation of pure PU is characterized by two main decomposition steps, 250–515°C and 515–670°C, of which are related to



**Figure 2.** FT-IR spectra of heated P-N IFR powder at different temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

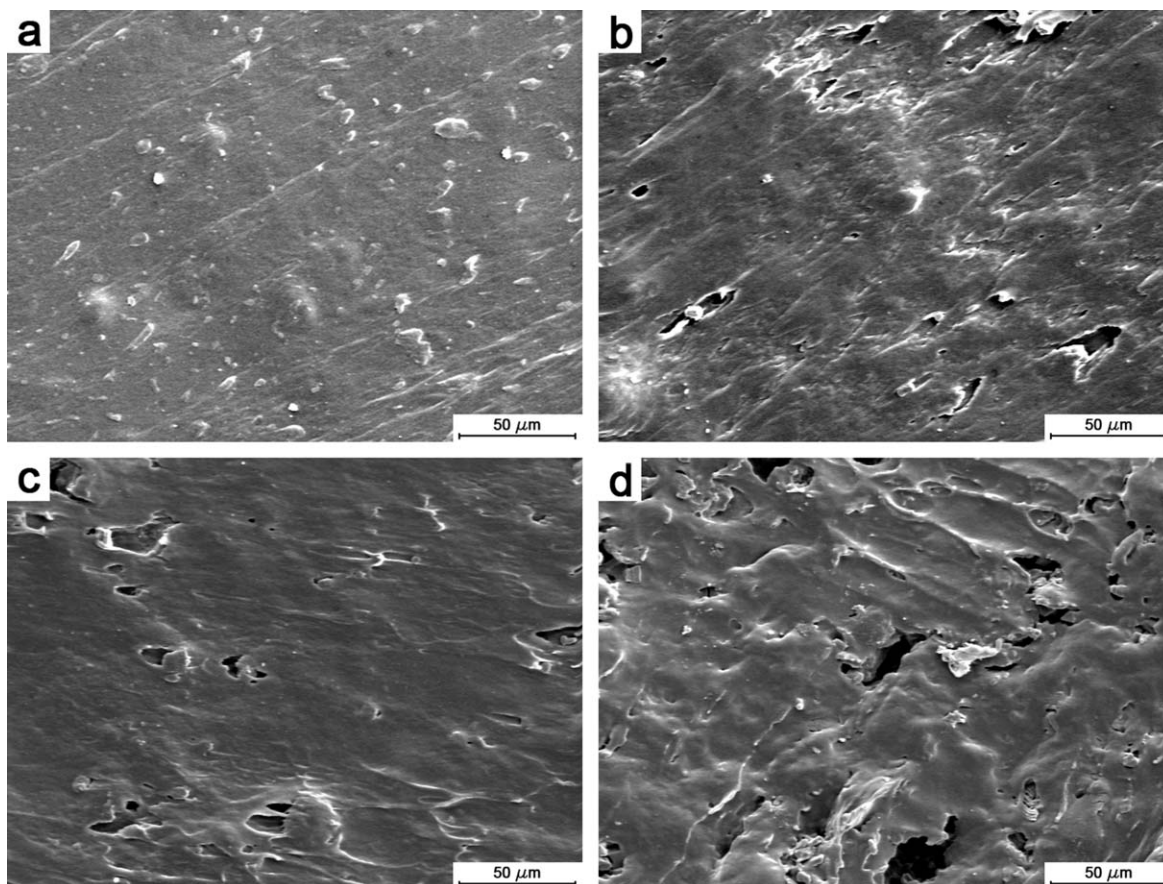
the main chain scission of polyether and the release of small molecular gas-phase products.<sup>17,18</sup> The decomposition process begins at 284°C ( $T_{-3\%}$ ) with the maximum mass loss rate at 422°C and a few residues (0.20 wt %) at 700°C. It is known that the pyrolytic process is a reversal of the polymerization, accompanied by the generation of olefinic group, carbon dioxide, and trace of water.<sup>13</sup> When P-N IFR is added, the thermal-oxidized decomposition curves show two stages, with a dividing temperature around 440°C. In the first stage (below 440°C), the decomposition temperature of PU/PNIFR composites shifts to a lower temperature compared to pure PU, which proves that the decomposition of P-N IFR promotes the thermal degradation of PU/PNIFR composites. However, in the second stage (higher than 440°C) the decomposition temperature of PU/PNIFR composites shifts to a higher temperature and delays the decomposition with the increase of P-N IFR. The residue also increases from 2.46 wt % for PU/PNIFR5 to 9.18 wt % for PU/PNIFR15. The possible reason for results above may be that the rapid thermal degradation of P-N IFR at a low temperature promotes the formation of a physical protective barrier on the surfaces of the materials at the initial stage, which could limit the oxygen and heat diffusion.<sup>16</sup> Therefore, a higher decomposition temperature is required to break through this barrier at the latter stage, and the presence of P-N IFR could make the thermal stability of PU composites further enhanced. A similar result was reported by Fang et al.<sup>5</sup> on preparation of Poly(butylene terephthalate)/PNIFR composite using P-N IFR as flame retardant.

### Fire Performance

UL-94 and LOI tests were performed to determine the flame class and study the combustion behavior of composites. The results are summarized in Table II. Pure PU is a flammable polymeric material with a LOI of 22.2%. In the UL-94 test, pure PU does not self-extinguish and has a serious dripping in the combustion process. When 5 phr P-N IFR is added, the composite still appears dripping during combustion, but the burning specimen can extinguish after the removal of flame, so it obtains V-2 classification. When the addition level is up to 10 phr, the formulation reaches V-1 ranking and does not drip at all. Besides, the burning time for the PU composites decreases and the LOI values increase with the increase of P-N IFR contents. The LOI of PU/PNIFR15 increases to 26.4%, and its twice combustion time are very short, which meets the demand of V-0 level, the highest flame retarded grade. These results show that the novel P-N IFR is an effective flame retardant for PU. As a reference, PU composite with 15 phr APP only reaches V-2 classification, of which the flame retardant effect of APP is more inferior to that of P-N IFR. Similar results were provided by Hu et al.<sup>6</sup> on preparing PU composite with 20 wt % APP by melt blending method and the samples reached V-2 ranking. Besides, the result of using P-N IFR is also better than some other IFRs. For example, Toldy et al. added 25 wt % Exolit OP1230 in the PU composite but only gets V-2 ranking.<sup>10</sup>

In order to reveal the fire retardant mechanism, it is necessary to study further about the char layers after combustion. The digital photographs of optimized PU/PNIFR composites after UL-94 tests are shown in Figure 5. It is clearly seen that the specimen's combustion degree is regularly reduced with the increase of P-N IFR. The fore-ends of all the specimens become expansion and bend due to the role played by the IFR. The obvious dripping trace of PU/PNIFR5 bar indicates that the char layer is not thick enough to prevent molten drops when the content of P-N IFR is not high. Furthermore, the larger combustion area and thicker char layer of PU/PNIFR10 bar may prevent dripping effectively. Then the combustion area of PU/PNIFR15 bar is not larger than the former with a longest remaining specimen, which demonstrates that its burning time is very short when the content of P-N IFR is high enough. According to the TGA results, the addition of P-N IFR significantly improves the formation of char, which enhances the self-extinguishment of PU composites. In addition, the thermally stable residues not only prevent the flame spreading upward but also possess certain mechanical strength, making the dripping restrained.<sup>19</sup>

The LOI residues of all PU/PNIFR composites were also analyzed by SEM (Figure 6). First, the pure PU burned completely and left in a negligible scale, so it is not discussed in this article. With the introduction of P-N IFR to PU matrix, the charring property has been improved. And with the increase of P-N IFR, the chars undergo a process from loose to compact and cover on the surface of polymer. For instance, the char residue of PU/PNIFR5 is arranged by lots of tiny solid granule, both in low and high magnification images, as shown in Figure 6(a,b). Its microscopic structure is quite loose, and the

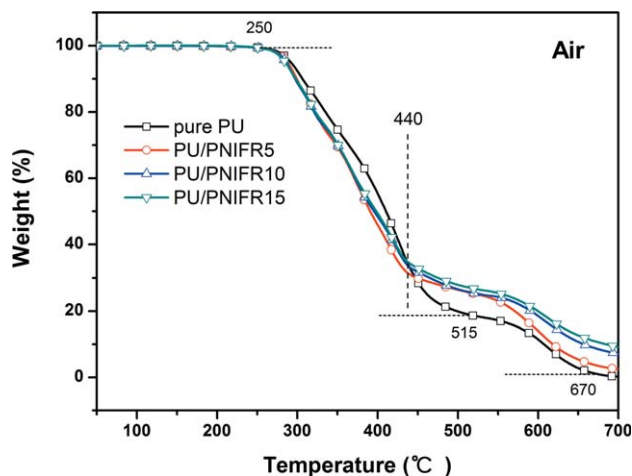


**Figure 3.** SEM images of fracture surface: (a) pure PU, (b) PU/PNIFR5, (c) PU/PNIFR10, (d) PU/PNIFR15

char is fragile in macroscopic condition, so it only provides weaker protection on the internal polymer matrix. When the content of P-N IFR is 10 phr, a kind of “bubble-like” or “island-like” char is formed, and these bubbles are shaped by the impact of the gas emission produced by the pyrolysis of the internal material.<sup>20</sup> In the experiment, the mechanical

strength of this structure is also weak and the bubbles are easy to crack, thereby the flammable gas, oxygen, and heat will be released, which is unfavorable for the flame retardancy. However, the appearance of PU/PNIFR15 char residue shows a bulk structure as a whole. This char layer is so tough and dense that it can withstand the impact of the rising gas. Therefore, it not only reduces the transportation rate of heat or oxygen, but also inhibits the release of flammable or toxic volatiles, resulting in an enhancement of flame retardancy.

It is favorable to understand the flame retardant mechanism by combining the results of thermal behavior and fire



**Figure 4.** TGA curves of pure PU and PU/PNIFR composites under air condition. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** TG and DTG Data for Pure PU and PU/PNIFR Composites under Air Condition

Sample	$T_{-3\%}^a$ (°C)	$T_{-50\%}^b$ (°C)	$T_{max}^c$ (°C)	Residue <sup>d</sup> (wt %)
pure PU	284	410	422	0.20
PU/PNIFR5	281	391	372	2.46
PU/PNIFR10	279	396	369	7.11
PU/PNIFR15	277	398	420	9.18

<sup>a</sup> Temperature at weight loss 3 wt %.

<sup>b</sup> Temperature at weight loss 50 wt %.

<sup>c</sup> Temperature at weight loss peak.

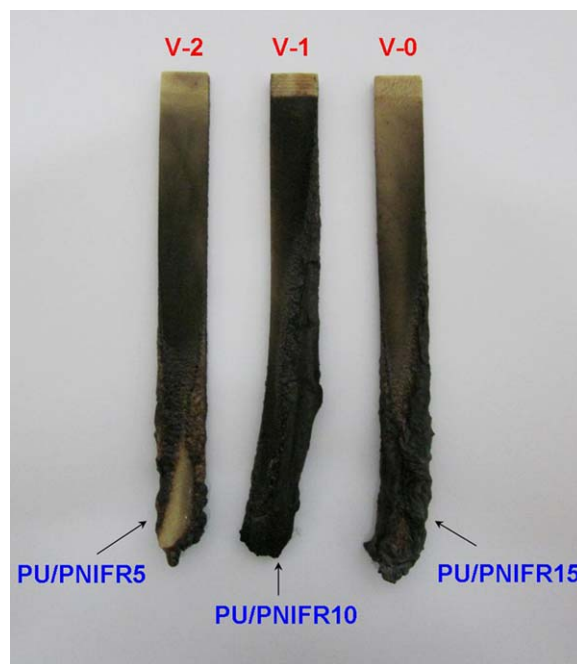
<sup>d</sup> at 700°C.

**Table II.** Results of LOI and UL-94 Tests for Pure PU and PU/PNIFR, PU/APP Composites

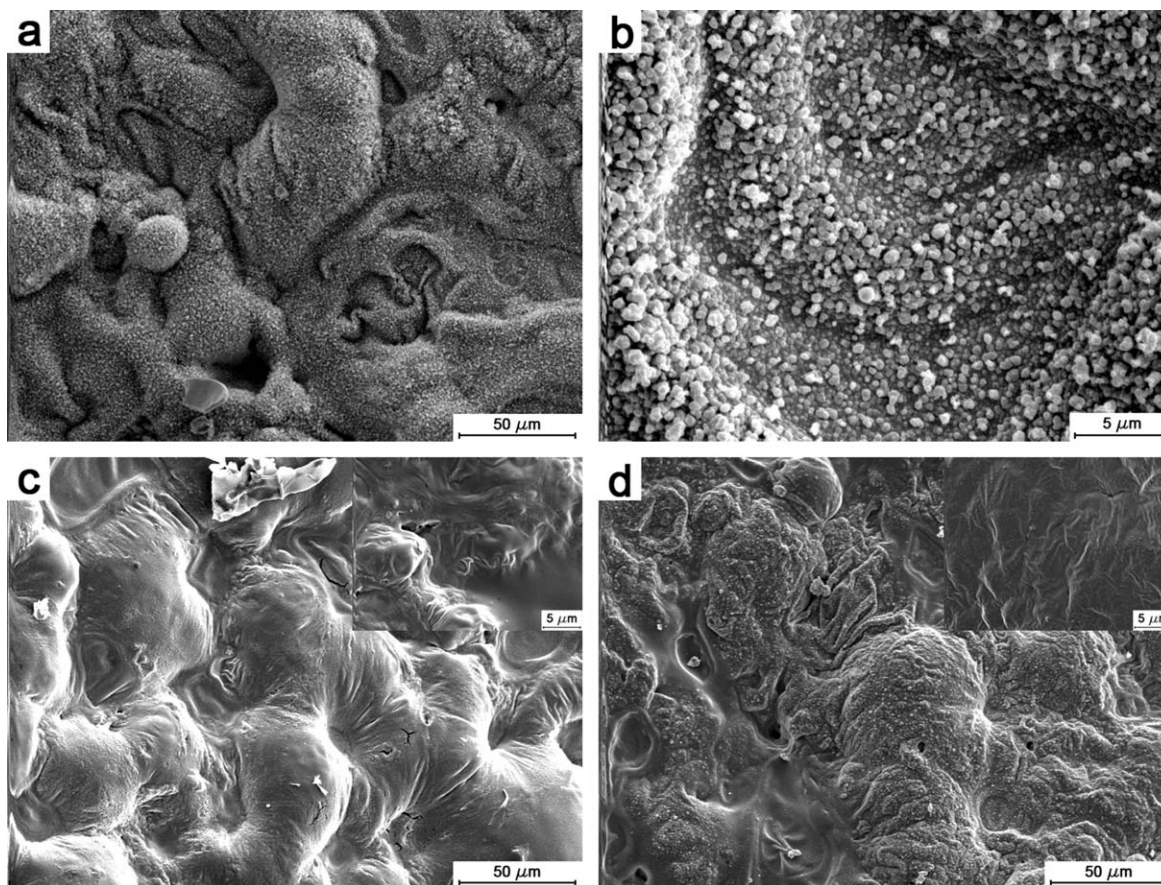
Sample	LOI (%)	$t_1$ (s)	$t_2$ (s)	Dripping	Rating
pure PU	22.2	—	—	Yes	NR
PU/PNIFR5	24.0	18.7	2.5	Yes	V-2
PU/PNIFR10	25.5	12.5	6.8	No	V-1
PU/PNIFR15	26.4	1.5	9.0	No	V-0
PU/APP15	24.4	18.9	10.1	Yes	V-2

$t_1$  and  $t_2$ , average combustion time after the first and second applications of the flame. NR, not rated.

performance. At low temperatures, P-N IFR can promote the thermal degradation of PU, which is in favor of allegro forming protective layer. With the increase of its content, the layer will be more compact, which will improve the LOI value and slow down the burning rate. At high temperatures, the formed layer with compact and stable structure can restrain the thermal degradation of PU; the slow overall decomposition process is in favor of decreasing the burning rate, as well as lessening the melt drip gradually till to none. Therefore, the incorporation of P-N IFR significantly improves the flame retardancy of PU composites.



**Figure 5.** Digital photographs of residues after UL-94 testing for PU/PNIFR composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** SEM images of residues after LOI tests: (a) PU/PNIFR5, (b) local enlargement of figure a, (c) PU/PNIFR10, (d) PU/PNIFR15

## CONCLUSIONS

In this work, halogen-free TPU composites were fabricated using a commercial ecofriendly flame retardant, P–N IFR, through melt blending process. Either the loading or the cost of this kind of flame retardant can be controlled as a commercially acceptable range. First of all, it can be concluded that the flame retardant effect of P–N IFR will be excellent for the TPU according to the results of TG and FT-IR. Then the thermal stability of PU/PNIFR composites was studied by TGA. The pyrolytic temperatures of these composites are delayed in a section of temperature higher than 440°C. Moreover, the flammability properties were tested by LOI and UL-94. The PU composite with 15 phr P–N IFR could achieve a V-0 classification with LOI of 26.4%. Finally, the residue characterization revealed that the compact char layer is an excellent barrier to protect the underlying material from the action of the heat flux or flame based on a condensed-phase fire resistant mechanism.

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