Synthesis and evaluation of a novel N–P-containing oil-based fire-retardant plasticizer for poly(vinyl chloride)

Pu-you JIA1, Guo-dong FENG1,2, Yun HU1, Yong-hong ZHOU1,3,*
1Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Nanjing, P.R. China
2Jiangsu Qianglin Bio-Energy and Bio-Materials Limited Company, Liyang, Jiangsu, P.R. China
3Institute of New Technology of Forestry, Chinese Academy of Forestry, Beijing, P.R. China

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Abstract: A novel N–P-containing soybean-oil-based fire-retardant plasticizer was synthesized using soybean oil methyl ester, 9,10-dihydro-9-oxa-phosphaphenanthrene-10-oxide (DOPO), and tris(2-hydroxyethyl) isocyanurate (THEIC). The structure was verified by Fourier transform infrared (FTIR) spectrometry and nuclear magnetic resonance (NMR) spectroscopy. The blends were characterized by thermogravimetric analysis (TGA), FTIR spectrometry, scanning electron microscopy (SEM), and dynamic mechanical analysis (DMA). TGA showed that the thermal stability of the blends were acceptable. DMA indicated that the plasticizer had good plasticity for PVC. The limiting oxygen index (LOI) of the blends ranged from 21.3 to 29.6. The flammability and thermal stability of PVC/THEIC-DOPO-ESOME was better than that of PVC/TCPP.

Key words: Soybean oil, flame retardant, plasticizer, PVC, SEM

1. Introduction
Plasticizers are organic substances added to polymers to improve their flexibility and process ability, and can increase the softness, elongation, and low temperature flexibility and decrease the concentration of intermolecular forces and the glass transition temperature (Tg) of polymers.1 Poly(vinyl chloride) (PVC) is widely used in construction, toys, medical devices, and food packaging materials.2 The most commonly used plasticizers in PVC formulations are the phthalates, with production rates of about 5 million tons per year, which accounts for more than 75% of the current global plasticizer production.3 Recent studies have reported that phthalate plasticizers, such as di(ethylhexyl) phthalate (DEHP), are thought to be endocrine disruptors and carcinogenic agents.4 As a result, many countries have introduced strict bans regarding the use of phthalates in many specific applications such as children’s toys.5 Recently, there has been growing interest in the use of plasticizers obtained from renewable resources because of their advantages of being nontoxic, environmentally friendly, biodegradable, and renewable raw materials.6 Fenollar et al. prepared epoxidized linseed oil and epoxidized fatty acid ester plasticizer, and evaluated the plasticized effect on PVC.7–9 The thermal stability of PVC plasticized with epoxidized soybean oil was characterized by Karmalm et al.10 Nihul et al. synthesized a natural-based plasticizer by epoxidation of nontoxic rice bran oil (RBO) with peroxo acid generated in situ that was added to PVC.11 Silva et al. prepared a natural polymeric plasticizer through polyesterification of

*Correspondence: yhzhou777@sina.com
Mehta et al. prepared a bio-based plasticizer by two-step esterification reaction of castor oil fatty acid with benzyl and octanoic acid. Sunflower can be epoxidized and the epoxidized sunflower oil has potential use as a plasticizer for PVC. Benaniba and Lardjane et al. studied the synthesis and characterization of epoxidized sunflower oil; they found that the di-(2-ethyl hexyl) phthalate could be replaced by epoxidized sunflower oil as a bio-based plasticizer for flexible PVC. The other bio-based plasticizers such as low molecular-weight glycerol ester, epoxidized safflower oil, and oleic acid polyester were studied.

The advantages of using renewable feedstocks in the synthesis of plasticizers such as vegetable oils include their low cost, availability, and sustainability, as well as possible enhanced compostability and biodegradability of the resultant polymer materials at the end of their life. Vegetable oils containing unsaturated fatty acids can be used in the production of bio-based plasticizers. However, in common with other aliphatic polymer materials they are highly combustible. Most synthetic materials cause unwanted fires, major environmental damage, and a waste of resources; thus, it is essential that sustainable strategies for fire retardant materials are developed.

Phosphorus- and nitrogen-containing polymers are well recognized for their flame-retardant properties, and they are increasing in popularity compared with their halogen counterparts, as they generally give off nontoxic combustion products. Therefore, the incorporation of phosphorus- and nitrogen-containing polymers in the plasticizer structure is recognized as an efficient way of obtaining an environmentally friendly flame-retardant plasticizer. To further extend the application of renewable resources and to obtain flame-retardant plasticizers, we chose to study industrially promising plasticizers from soybean oil, DOPO, and THEIC. The aim of the present work was to explore soybean oil-based flame-retardant plasticizers with phosphorus and nitrogen elements, and investigate the mechanical and flame-retardant properties of PVC with different contents of plasticizer.

2. Results and discussion
2.1. FT-IR studies of THEIC-ESOME-DOPO
Figures 1A–1C show the FT-IR spectra of THEIC-SOME, THEIC-ESOME, and THEIC-ESOME-DOPO, respectively. In Figure 1A, the absorption peak at 1747 cm$^{-1}$ can be ascribed to the carbonyl group on the aliphatic chain, that at 3017 cm$^{-1}$ to the $=\text{C}–\text{H}$ stretching vibration of the unsaturated bond, those at 2918 and 2832 cm$^{-1}$ to the $\text{C}–\text{H}$ stretching vibration of the saturated hydrocarbon chain, those at 1462 and 1377 cm$^{-1}$ to the methyl bending vibration, and that at 1689 cm$^{-1}$ to the C=O absorption of THEIC. This spectrum is consistent with successful transesterification between THEIC and soybean oil methyl ester.

Comparing Figures 1A and 1B, it is evident that the absorption at 3017 cm$^{-1}$ seen for THEIC-soybean oil ester is no longer seen in the spectrum of THEIC-SBOE, whereas a new absorption peak appears at 833 cm$^{-1}$. That is to say, the characteristic absorption peak of $=\text{C}–\text{H}$ in the ester is no longer seen in the spectrum of THEIC-SBOE, and an epoxy bond absorption peak appears in the spectrum of this product. The results are consistent with conversion of C=C to an epoxy bond in the reaction.

As shown in Figure 1C, a new absorption peak appears at 908 cm$^{-1}$ related to aromatic bond stretching and the stretching of P–O–Ar. This denotes the presence of DOPO in the molecule. When the epoxide group was present in a compound structure, characteristic absorption occurred at 1270–1230 cm$^{-1}$ and at 880–805 cm$^{-1}$. The absorption peak at 3500 cm$^{-1}$ is related to the hydroxy groups –OH. These results confirm the successful synthesis of THEIC-ESOME-DOPO.
2.2. NMR studies of THEIC-ESOME-DOPO

The structure of the THEIC-ESOME-DOPO compound was also characterized by $^1$H NMR and $^{31}$P NMR as shown in Figure 2. As shown in Figure 2A, the chemical shifts at 8.93 ppm represent the hydroxy groups –OH. The peaks between 6.94 and 8.90 ppm were assigned to the benzene ring. The absorption peaks at 4.62 and 4.22 ppm were assigned to the peaks P–C–H and N–C–H, respectively. The signal at 2.18 ppm was assigned to the methylene protons adjacent to the carbonyl groups. The peaks observed at 0.79, 1.50, and 1.17 ppm were attributed to CH$_3$CH$_2$, which belonged to the aliphatic groups. Furthermore, P–Ph exhibited a single peak at 36.18 ppm in the $^{31}$P NMR spectra in Figure 2B. These findings indicated the structures of DOPO and THEIC in the obtained compound.
2.3. Elemental composition analysis

The elemental composition can provide information about the different chemical structures and functional groups. The elemental compositions of THEIC, THEIC-SOME, THEIC-ESOME, and THEIC-ESOME-DOPO are shown in Table 1. On going from THEIC to THEIC-SOME, the composition changed from 41.22% C, 6.10% H, 16.03% N, and 36.64% O to 69.79% C, 10.15% H, 4.20% N, and 15.85% O. After the introduction of oxygen atoms by epoxidation, the C, H, and N contents were slightly decreased, and the O content increased from 15.85% to 19.35%. Similarly, when DOPO was introduced to THEIC-ESOME, the C, H, N, and O contents of the THEIC-ESOME-DOPO were 67.67%, 8.98%, 2.54%, and 18.58%, respectively. These results further confirmed that THEIC-ESOME-DOPO had been successfully synthesized.

Table 1. Elemental analysis of THEIC, THEIC-SOME, THEIC-ESOME, and THEIC-ESOME-DOPO.

<table>
<thead>
<tr>
<th>Item</th>
<th>C/%</th>
<th>H/%</th>
<th>N/%</th>
<th>O/%</th>
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<tr>
<td>THEIC</td>
<td>41.22</td>
<td>6.10</td>
<td>16.03</td>
<td>36.64</td>
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<tr>
<td>THEIC-SOME</td>
<td>69.79</td>
<td>10.15</td>
<td>4.20</td>
<td>15.85</td>
</tr>
<tr>
<td>THEIC-ESOME</td>
<td>67.67</td>
<td>9.92</td>
<td>3.04</td>
<td>19.35</td>
</tr>
<tr>
<td>THEIC-ESOME-DOPO</td>
<td>67.49</td>
<td>8.98</td>
<td>2.54</td>
<td>18.58</td>
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</table>

2.4. TGA of PVC sheets

The thermal stability of PVC samples plasticized from 0 w/w to 30 w/w plasticizer was analyzed by TG and DTG, and the results are shown in Figure 3.

Figure 3A and Table 2 show the TG results for PVC sheets. The PVC sheets’ degradation stages are indicated by the three steps in Table 2 and their corresponding peaks in Figure 3B. The dehydrochlorination of PVC was initiated at approximately 225 °C. The subsequent autocatalytic effect of HCl led to intensive dehydrochlorination, indicated by a sharp peak at 292 °C. The thermal cracking of polyene chains resulting from the dehydrochlorination process contributed to the first weight loss. The cross-linking of other polyenes caused the second major weight loss at approximately 450 °C. The third major weight loss was due to oxidation of the char residue. The incorporation of 30 phr flame retardant plasticizer into PVC resulted in lower weight
losses in the first stage. The lower weight loss in the second stage was due to the presence of less PVC. The third peak was over a narrower temperature range.

Table 2. Thermogravimetric analysis data for PVC/THEIC-ESOME-DOPO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature for specific % weight loss 1 wt%</th>
<th>Temperature for specific % weight loss 10 wt%</th>
<th>Temperature at rapid mass loss rate First stage</th>
<th>Temperature at rapid mass loss rate Second stage</th>
<th>Temperature at rapid mass loss rate Third stage</th>
<th>Residual mass (wt%)</th>
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<td>a</td>
<td>169</td>
<td>252</td>
<td>295</td>
<td>475</td>
<td>512</td>
<td>10.06</td>
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<tr>
<td>b</td>
<td>172</td>
<td>254</td>
<td>289</td>
<td>474</td>
<td>581</td>
<td>10.88</td>
</tr>
<tr>
<td>c</td>
<td>174</td>
<td>253</td>
<td>288</td>
<td>473</td>
<td>594</td>
<td>11.40</td>
</tr>
<tr>
<td>d</td>
<td>177</td>
<td>254</td>
<td>285</td>
<td>470</td>
<td>529</td>
<td>11.96</td>
</tr>
<tr>
<td>e</td>
<td>182</td>
<td>255</td>
<td>283</td>
<td>467</td>
<td>579</td>
<td>12.18</td>
</tr>
<tr>
<td>f</td>
<td>194</td>
<td>255</td>
<td>280</td>
<td>462</td>
<td>584</td>
<td>14.98</td>
</tr>
</tbody>
</table>

2.5. DMA of PVC sheets

The variation in Tg is a very important factor in the evaluation of the plasticizer effects. The Tg value of the PVC composites without plasticizer was about 85 °C. Figure 4 shows the dynamic thermomechanical analysis of samples (a–f) as the tan δ plots from −50 to 150 °C. The main peak of the tan δ plots is related to the glass transition temperature. The storage modulus, loss modulus, and tan δ values of various PVC/THEIC-ESOME-DOPO ratios are shown in Figures 4a–c, respectively. The Tg values are shown in Figure 4a.

It has been reported that both loss modulus curves and tan δ curves can indicate the glass transition temperature. In our study, both the loss modulus curve and tan δ showed the same trend as Tg; however, the tan δ curves were more distinct and it was easier to obtain accurate Tg values. Figure 4a shows the relationship between tan δ values and the amount of plasticizer in the blends. It can be seen that the glass transition temperature decreases with increased plasticizer. Figure 4b shows that the storage modulus decreases with increasing THEIC-ESOME-DOPO, because the increase in plasticizer improved the mobility of PVC molecules. This phenomenon corresponds to the softening effect of the plasticizer on PVC. The loss modulus is smaller, showing that the tan δ (damping loss factor) of the material is small; the material is close to the ideal elastic material. Figure 4c shows that the loss modulus decreased with increased plasticizer and the elasticity of PVC sheets increased; the peaks appeared at lower temperature when the amount of plasticizer increased, which indicated that the plasticizer had good plasticity for PVC.

2.6. SEM of PVC sheets and residual char

The SEM micrographs of each sample and residues are shown in Figure 5. In Figure 5A a miscible fractured surface of PVC sheets is shown that exhibited the phase separation of plasticizer, especially Figure 5A(a) and Figure 5A(b); the separated phase appears in the form of a fibrous structure. With an increase in the percentage of THEIC-ESOME-DOPO, the two phase interface of sample f in the Figure 5A(f) was fuzzy, and the particles of the dispersion phase were smaller. It indicated that THEIC-ESOME-DOPO could disperse in the PVC matrix uniformly and surrounded intimately by PVC continuous phase, and there is no clear boundary between them to be observed. Therefore, this indicated that THEIC-ESOME-DOPO had good plasticity for PVC too. Figure 5B shows that the residue char surfaces of the PVC were very different from the char of each sample. Figures 5B(a) and 5B(b) show a small pore structure. The latter contained a honeycomb structure; the cellular structure is clearly visible and the structure is loose. This is due to a large amount of gas released due to the combustion
process of decomposition, which indicated that the flame retardant plasticizer had excellent inflation foaming function. The bubble charcoal layer can effectively prevent heat and combustible gas contacting with the fire retardant system. The carbon residue surface of samples (j) in the Figure 5B(j) material was relatively smooth after burning, while the carbon residue of samples (j) appears looser than that of samples (g) in Figure 5B(g), which was due to THEIC-ESOME-DOPO/PVC that formed some volatile substances released by decomposing on the surface. The expansion carbon layer may prevent the heat from transferring and play the role of isolated oxygen source, which can effectively prevent the flames spreading. THEIC-ESOME-DOPO decomposed to produce phosphate and polyphosphate acid, which supplied an acid source and charring agent for PVC and produced a phosphorous-rich layer. The phosphorus-rich layer could promote polymer carbonization and form a consolidated and thick flame-retardant coating quickly. The phosphorus-rich layer promotes PVC carbonization and forms a consolidated and thick flame-retardant coating quickly, which prevented oxygen and heat, making the PVC blends thermal stable. The phosphorus compounds functioned as a source of acid, which can promote cross linking of the PVC compound, leading to rapid charring. These findings proved that the fire retardant plasticizer greatly increased the LOI and the char yield.

2.7. Mechanical properties, LOI, and TG test of PVC sheets.

The important mechanical properties measured were the elasticity modulus, elongation at break, tensile yield stress, and stress at break of PVC sheets. These measurements and LOI are shown in Table 3.

![Figure 4. The tan δ values (a), storage modulus (b), and loss modulus (c) of the samples.](image-url)
Table 3 shows that when THEIC-ESOME-DOPO instead of 10 phr DOP was added to the blend, the elasticity modulus increased to 6.8 MPa from 5.1 MPa for a content of 10 phr THEIC-ESOME-DOPO and 40 phr DOTP, with a reduction of 1.6 MPa in tensile yield stress, 2.4 MPa of stress at break, and strain at break decreased to 223.8%. A further increase in THEIC-ESOME-DOPO content caused a similar trend. As the amount of THEIC-ESOME-DOPO increased, the mechanical properties of PVC sheets decreased, but the decline was not great. Even if the dosage was increased to 30%, its mechanical performance was good. Comparing data (h, j, k, and l) in Table 3, when the same amount of TCPP and THEIC-ESOME-DOPO was added, the mechanical properties did not appear to be much different. However, flammability and thermal stability of PVC/THEIC-DOPO-ESOME were better than those of PVC/TCPP. On the other hand, Figure 6 shows that the thermal stability of PVC sheet (j) was much better than that of g and k, which was mainly due to the thermal stability of DOTP, and small molecules of flame retardant plasticizer TCPP were worse than THEIC-DOPO-ESOME. The LOI value of PVC sheets was increased significantly when the THEIC-ESOME-DOPO was added. That may be mainly caused by synergy between nitrogen and phosphorus in the plasticizer.

An oil-based flame-retardant plasticizer was successfully synthesized using soybean oil methyl ester, which was confirmed by FTIR spectrometry, $^{31}$P NMR, and $^1$H NMR. The product was then used as a plasticizing agent for PVC. TGA was used to determine the thermal stability of the blends with PVC and the results showed that the blends were heat stable. DMA characterization showed that when the concentration was above 20 wt%, the plasticizer was compatible with PVC and efficiently lowered the glass transition temperature of
the blend. In addition, the product not only functioned as a plasticizer, but also had good flame retardant properties. The LOI value of the plasticized PVC reached 29.6. In addition, SEM of the PVC sheets and the char indicated that the fire retardant plasticizer had good plasticity and flammability. The thermal stability and flammability of THEIC-ESOME-DOPO was better than that of TCPP and DOTP. This work suggested that the THEIC-ESOME-DOPO was an excellent agent for PVC with plant oil-based plasticizer and flame-retardant properties.

![Figure 6. TG curves for PVC sheets (g, j, and k).](image)

3. Experimental

3.1. Materials

Soybean oil methyl ester, 9,10-dihydro-9-oxa-phosphaphenanthrene-10-oxide (DOPO), tris (2-hydroxyethyl) isocyanurate (THEIC), and dioctyl terephthalate (DOTP) were supplied by Jiangsu Qianglin Bio-Energy & Bio-Materials Co., Ltd. (Changzhou, China, industrial grade, purity ≥ 99%); formic acid, methanol, and sodium hydroxide were purchased from Shanghai Lingfeng Chemical-Reagent Co., Ltd. (Shanghai, China, AR). PVC resin powder was kindly donated by South Korea Hanwha Group (South Korea, KM-31, DP = 1300 ± 100, K value = 71). Tris (chlorisopropyl) phosphate (TCPP), hydrogen peroxide (30%), sulfuric acid, tetrabutyl titanate, calcium stearate, and zinc stearate were provided by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China, AR).

3.2. Synthesis of THEIC-soybean oil ester (THEIC-SOME).

THEIC (52.4 g), soybean oil methyl ester (177.6 g), and tetrabutyl titanate (2.3 g) as a catalyst were added to a three-necked flask equipped with a stirring device and a Thorn fractionating column. The transesterification reaction was maintained at around 220 °C under stirring until no more methanol was distilled off. The excess soybean oil methyl ester was removed by vacuum distillation. The product was then dried to obtain THEIC-soybean oil ester (THEIC-SOME).

\[^1\text{H NMR (CDCl}_3\), \delta: 0.87 (m, C–CH}_3\), 1.24 (m, C–CH}_2–C); 4.20 (m, N–CH}_2–C), 4.14 (m, C–CH–O), 5.14 (s, C–CH=C).\]
### 3.3. Synthesis of THEIC-epoxy soybean oil ester (THEIC-ESOME)

THEIC-soybean oil ester (100 g) and formic acid (2 g) were placed in a three-necked flask equipped with a stirrer, a thermometer, and a pressure-equalizing dropping funnel. p-Toluenesulfonic acid (3 g) was added as a catalyst and the mixture was stirred at 70 °C. Hydrogen peroxide (30%, v/v; 30 g) was then slowly dropped into the reaction mixture at such a rate as to maintain the temperature at 70 °C until the epoxy value of the product showed no further change (usually for 6 h). The mixture was then slowly poured into a separatory funnel, the layers were allowed to separate, and the lower aqueous phase was drained. The upper organic layer was then washed sequentially with 2% sodium hydroxide solution and distilled water, and then the water was distilled off under reduced pressure to afford the epoxidation product (THEIC-ESOME).

**^1H NMR (CDCl$_3$, δ):**

- 0.87 (m, C−CH$_3$)
- 1.23 (m, C−CH$_2$−C)
- 4.21 (s, N−CH$_2$−C)
- 4.14 (s, C−CH{O})
- 5.36 (s, C−CH−O)

### 3.4. Synthesis of THEIC-DOPO-ESOME

According to the procedure found in the literature, DOPO (21.6 g) and THEIC-ESOME (110 g) were added to a three-necked flask equipped with a stirring device and then stirred at 140 °C for 9 h under nitrogen protection. Finally the yellow viscous product of oil-based fire-retardant plasticizer (THEIC-DOPO-ESOME) with a triazine ring and DOPO structure was obtained. The reaction is shown in the Scheme.

### 3.5. Preparation of PVC sheets

The PVC sheets were prepared by torque rheometer (Haake Company, Germany) at 165 °C for 3 min using the recipes given in Table 4. A Mini Jet II micro-injection molding machine (cylinder: 170 °C; mould: 60 °C;
pressure: 540 bar; time: 3 min) (Haake Company, Germany) gave dumbbell-shaped and bar samples of PVC sheets for subsequent testing.

Table 4. Formulations of PVC sheets with flame-retardant plasticizer.

<table>
<thead>
<tr>
<th>S. no</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
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<th>j</th>
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<tbody>
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<td>40</td>
<td>30</td>
<td>20</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
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<td>0</td>
<td>10</td>
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</tbody>
</table>

3.6. Detection method

The FTIR spectra were recorded on a Nicolet Magna-IR550 spectrometer (USA), with a resolution setting of 4 cm$^{-1}$ and a scanning range of 400–4000 cm$^{-1}$. $^1$H and $^{31}$P NMR spectroscopy of the product was carried out using a Bruker Avance AV II-400 NMR spectrometer (Germany), using CDCl$_3$ or DMSO as a solvent and tetramethylsilane as a reference. The chemical shifts of the $^{31}$P NMR spectra are relative to the external standard of 85% H$_3$PO$_4$. Elemental analysis was performed with a PE-2400 elemental analyzer (PE Co., USA). Epoxy value was measured according to ASTM standard method D1652-04. The dynamic mechanical analysis (DMA) and thermal analysis measurement were carried out on a dynamic mechanical thermal analyzer (Q800, TA Company, USA). Each specimen of PVC sheets ($7.7 \times 1.1 \times 0.5$ cm$^3$) was tested. A testing temperature was scanned from −50 and 120 °C with a heating rate of 3 °C/min and a fixed frequency of 1 Hz. Thermogravimetric studies were used to investigate the behavior in a nonoxidative environment using a Micromeritics TGA (Netzsch 409PC, Germany). For a nitrogen atmosphere, a flow rate of 10 mL/min was used. Samples were placed in platinum pans and heated from ambient temperature to 600 °C at a constant heating rate of 10 °C/min. The LOI test (GB/T2406-2008) was carried out on bar specimens of dimensions 80 × 10 × 4 mm$^3$ using the JF-3 oxygen index apparatus (Nanjing Lei instrument Co. Ltd., Nanjing, China). Scanning electron microscopy (Hitachi 3400-I, Japan) was used to monitor the surface morphology and residual char of PVC sheets. The surface of PVC sheets was sputtered with 2-nm-thick gold after molding on a MiniJetII micro-injection molding machine for SEM observation. The residual char of PVC blends was sputtered with gold after LOI tests for SEM observation. Elasticity modulus, strain at break, tensile yield stress, and stress at break were determined according GB/T 1040.1-2006 (China) under ambient conditions, using a Universal Testing Machine (MTS Instrument Crop., China). The reported values were the average of 5 samples.

Acknowledgments

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References