Synthesis and Application of UV-curable Phosphorous-containing Acrylated Epoxidized Soybean Oil-based Resins

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Abstract: A novel phosphorous-containing acrylated epoxidized soybean oil-based (P-AESO) resin was developed via the ring-opening reaction of epoxidized soybean oil (ESO) with diphenylphosphinic chloride (DPPC), followed by acrylation of the resulting groups. The chemical structure was characterized by Fourier transform infrared spectroscopy (FT-IR), and 1H nuclear magnetic resonance (1H NMR). Subsequently, the viscosity and volumetric shrinkage of the obtained P-AESO resins were studied. Then the oligomer was formulated into UV-curable coatings, and the mechanical, thermal, and coating properties of the resulting UV-cured bioresins were studied by tensile testing, dynamic mechanical thermal analysis (DMA), thermogravimetric analysis (TGA) coupled with FT-IR spectroscopy (TGA-FT-IR), hardness, adhesion, pencil hardness and chemical resistance. Furthermore, the UV-curing behavior of the P-AESO resin was determined by real-time real-time infrared (RT-IR). Meanwhile, compared with coating from acrylated epoxidized soybean oil (AESO), the P-AESO system coatings showed better volumetric shrinkage, excellent adhesion, and enhanced thermal and glass transition temperature ($T_g$) while maintaining reasonably final C=C conversions and cross-link density. For instance, the obtained P-AESO/trimethylolpropanetriacrylate (TMPTA) 20 material possessed a volumetric shrinkage of 4.1%, $T_g$ of 115.6℃, char yield of 9.47%, and final C=C conversions of 81.4% respectively, which exhibited superior values than that of the AESO/TMPTA20 material. The improvement of the P-AESO coating performances could contribute to the architectures that combined the structural features of phosphorous-containing rigid benzene. The developed P-AESO resin is promising for applications in the UV-curable coatings.

Keywords: biobased; UV-curable coatings; acrylated epoxidized soybean oil; diphenylphosphinic chloride

1 Introduction
Due to the dramatic price fluctuation of petroleum reserve and environmental problems, renewable materials have been receiving increased attention for environmental and economic values, such as proteins, lignins, carbohydrates, natural oils (Dai et al., 2016; Li et al., 2017). The UV-curing is one of the most promising material-fabrication technologies featured by its fast curing rate at ambient temperature, low energy consumption, low capital investment and extremely low volatile organic chemical (VOC) emissions (Liu et al., 2016a; Liu et al., 2017). Therefore, the utilization of biorenewable resources in the UV-curable coatings method will provide a promising “green+green” strategy to prepare the bio-based coatings (Liu et al., 2015).

As one source of biobased chemicals, vegetable oils are prominent candidates to replace fossil feedstock due to biodegradability, abundant and relatively low cost, which have been widely applied in various fields such as inks, elastomers, coatings, and adhesives (Sharmin et al., 2015; Zhou et al., 2015; Auclair et al., 2016; Liu et al., 2016b; Wang et al., 2017; Zhang C Q et al., 2017). Numerous plant oil-based oligomers and monomers have been developed for the UV-curable materials (Dai et al., 2015a; Dai et al., 2016b). Li et al. (2015) developed a biobased waterborne polyurethane acrylate from castor oil and the properties of mechanic and thermal were increased for the cross-linked network and enhanced intermolecular forces. Dai et al. (2015b) reported the synthesis of itaconic acid unsaturated polyesters and then used them to co-photopolymerize with acrylated epoxidized soybean oil (AESO). The obtained UV-cured coatings exhibited excellent properties of high adhesion, outstanding flexibility and high hardness as well as excellent solvent resistance. In our previous work, castor oil-based polyfunctional polyurethane acrylate (COPUA) and acrylate monomers as well as reactive diluents synthesized from cardanol have been synthesized to

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strengthen the COPUA (Hu et al., 2018a; Hu et al., 2018b; Hu et al., 2018c). Despite the good performance of the UV-curing systems, the volumetric shrinkage is commonly observed and eager to be overcome diphenylphosphinic chloride (DPPC). Soybean oil, as the most readily available and inexpensive vegetable oil, has been used as an attractive alternative to petroleum-based resources to prepare polymers (Li et al., 2017). Especially, its derivative AESO has been widely applied in the UV-curable coatings due to the easily polymerizable groups. In order to achieve the necessary rigidity and strength required for some applications, several comonomers were used together, such as styrene, eugenol-based substance (Dai et al., 2016a; Dai et al., 2017; Zhang Y H et al., 2017), benzoxazines (Dai et al., 2018) and other crosslink agent (Ma et al., 2014; Auclair et al., 2015; Dai et al., 2015b; Dai et al., 2016b). Furthermore, novel oligomers were synthesized by chemically introducing special construction to epoxidized soybean oil (ESO) to produce coatings with satisfying properties (Liu et al., 2017; Liu H J et al., 2018). Hence, the raw material can be modified according to particular application. The structure of the AESO can be modified with rigid structure to reduce the volume shrinkage of the cured resins. The DPPC is a phosphorus-containing chemical reagent with a benzene ring structure, which not only reduces the shrinkage of the UV-curable AESO resin, but also improves the thermal stability of the resin.

In this work, a new synthetic method of phosphorous-containing acrylated epoxidized soybean oil-based (P-AESO) UV-curable coating was presented to overcome the disadvantages of mentioned above. The phosphorous-containing epoxidized soybean oil (P-ESO) was synthesized by the reaction of the ESO with the DPPC. Then the P-ESO was reacted with acrylic acid (AA) to obtain the P-AESO (Fig. 1). The structural characteristics of the P-ESO and P-AESO were analyzed by Fourier transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR). The thermal stability, viscosity, shrinkage, and ultimate properties of the UV-cured P-AESO and AESO were compared and discussed. Furthermore, the UV-curing kinetics of the obtained bioresins were investigated via realtime infrared (IR).

2 Materials and Methods

2.1 Materials
The AESO (Fig. 2) was obtained from Shouguang Luke Chemical Engineering Co., Ltd. (China) with a viscosity of 37 500 mPa·s. Ethyl acetate (EA, ≥99.5%) and triethanolamine (TEA, analytically pure) were purchased from Shanghai Titan Scientific Co., Ltd. (China). The trimethylolpropanetriacrylate (TMPTA) (99%) (Fig. 2), acrylic acid (98%), diphenylphosphinic chloride (98%), tetrabutylammonium bromide (TBAB, 99%), and Darocur 1173 (98%) were provided by Sahn Chemical Technology Co., Ltd. (China). Anhydrous magnesium sulfate (MgSO4, ≥98%) was obtained from Xilong Chemical Engineering Co., Ltd. (China). Toluene (≥99.5%) and styrene (St, ≥99%) were supplied by Nanjing Chemical Reagent Co., Ltd. (China). The ESO (3.99 epoxy groups per triglyceride, molar mass 950 g/mol) was purchased from Shanghai Aladdin Chemistry Co., Ltd. Potassium carbonate (K2CO3, ≥98%) was obtained from Tianjin Chemical Reagent Institute Co., Ltd. (China).

2.2 Synthesis of P-ESO compounds
About 52.63 g (0.055 mol) of the ESO, 47.78 g (0.202 mol) of DPPC, 6.44 g (0.02 mol) of TBAB and 80 mL of toluene were placed together in a 250 mL four-neck round-bottom flask equipped with a thermometer, mechanical stirrer, and a refluxing condenser. The mixture
was heated at 80°C for 0.5 h, then heated to 110°C for 9 h by an oil bath and agitated. Then 30 mL of the TEA was added, stirred and filtered. After that, 120 mL of the EA were added to the mixture and washed with deionized water for 3 times. At the end of the reaction, the mixture was dried by anhydrous magnesium sulfate for overnight and then filtered off. Finally, the EA was removed by rotary evaporation and the intermediate P-ESO product was obtained. The synthetic route is shown in Fig. 1.

### 2.3 Synthesis of P-AESO compounds

There were 13.80 g (0.168 mol) of acrylic acid, 71.2 g (0.03 mol) of intermediate P-ESO, 25.14 g (0.078 mol) of the TBAB, and 11.60 g (0.084 mol) of K2CO3 placing in a 250 mL four-neck round-bottom flask equipped with a thermometer, mechanical stirrer, and a refluxing condenser, heated to 70°C for 0.5 h, then heated to 110°C for 9 h by an oil bath and agitated. Then 80 mL of toluene was added, washed with saturated salt solution and deionized water, respectively. At last, the mixture was dried by anhydrous magnesium sulfate for overnight and then filtered off. Finally, the toluene was removed by rotary evaporation and the P-AESO product was obtained.

### 2.4 Preparation of UV-curable crosslinked polymers

The compositions of the cross-linked networks are listed in Table 1. The UV-curable samples were prepared by blending the P-AESO or AESO, with the TMPTA diluents (20% of total weight), styrene (10% of total weight) and the Darocur 1173 photoinitiator (3% of the total weight) at room temperature for about 20 min. For the P-AESO/TMPTA20 and AESO/TMPTA20 samples, no styrene was added. All the mixtures were centrifuged to remove air bubbles, and then poured into homemade polytetrafluoroethylene (PTFE) molds or coated on polished tinplate sheets with a coating apparatus. Finally, the resins were cured by an Intelliray UV-light-curing microprocessor (Uvitron International Corporation, USA) with an exposure intensity of 100 mW/cm². The exposure time is 20 min for all the samples and kept in a glass desiccator at room temperature for seven days before tests.

### Table 1 Formulation, viscosity and volumetric shrinkage of different UV-curable systems

<table>
<thead>
<tr>
<th>Sample</th>
<th>P-AESO (g)</th>
<th>AESO (g)</th>
<th>TMPTA (g)</th>
<th>St (g)</th>
<th>Viscosity (mPa·s)</th>
<th>Volumetric shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-AESO/TMPTA20</td>
<td>20</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>8968±11</td>
<td>4.1±0.2</td>
</tr>
<tr>
<td>AESO/TMPTA20</td>
<td>0</td>
<td>20</td>
<td>6</td>
<td>0</td>
<td>9339±4</td>
<td>5.3±0.2</td>
</tr>
<tr>
<td>P-AESO/TMPTA20/ST10</td>
<td>20</td>
<td>0</td>
<td>6</td>
<td>3</td>
<td>708±7</td>
<td>3.7±0.2</td>
</tr>
<tr>
<td>AESO/TMPTA20/ST10</td>
<td>0</td>
<td>20</td>
<td>6</td>
<td>3</td>
<td>737±17</td>
<td>4.2±0.1</td>
</tr>
</tbody>
</table>

Notes: P-AESO, phosphorous-containing acrylated epoxidized soybean oil-based; AESO, acrylated epoxidized soybean oil; TMPTA, trimethylolpropanetriacrylate; St, styrene.

### 2.5 Characterization

The FT-IR spectroscopy of samples were performed with a Nicolet iS10 IR spectrometer (Thermo-Fisher Corporation) in the scanning range of 4000–500 cm⁻¹ with a resolution of 4 cm⁻¹. The ¹H Nuclear Magnetic Resonance (¹H NMR) spectra of samples were performed on a DRX-300 Advance NMR spectrometer (Bruker, Germany) with CDCl₃ as the solvent.

The viscosities (Vₛ) of all the liquid samples were measured by the DVS+ digital-display viscometer (Brookfield Corporation, USA) coupled with a small sample adapter at 25°C.

The gel content (C₉) of the UV-cured samples was extracted with refluxing acetone via Soxhlet extraction. The cured resins of around 0.5 g were cut and put into acetone for 24 h. Then dried in vacuum oven at 60°C for 24 h to give a constant weight and weighed again. The C₉ values were determined from the weight of the dry samples before and after extraction.

The measurement of volumetric shrinkage (ΔV) was conducted on a ZMD-2 electronic automatic density meter (Shanghai Fangrui Instrument Corporation, China). The ΔV value was calculated by determining the density of the resins before and after UV-curing at room temperature according to the following equation:

\[
\Delta V = \frac{\rho_s - \rho_l}{\rho_s} \times 100\% 
\]

where \(\rho_s\) was the density of the solid materials after the UV-curing, and \(\rho_l\) was the density of the liquid resins before the UV-curing.

The Dynamic Mechanical Analysis (DMA) tests were performed on a Q800 solids analyzer (TA Corporation) in stretching mode. The cured samples with a size of 40 mm × 6 mm × 1 mm were examined from −80°C to 200°C at a heating rate of 3°C/min with a frequency of 1 Hz.

The thermogravimetric analysis (TGA) coupled with FT-IR spectroscopy (TGA-FT-IR) measurements were conducted on an STA 409PC thermogravimetry instrument (Netzsch Corporation) coupled with a FT-IR spectrometer.
Approximately 10 mg of UV-cured samples was heated from 40°C to 800°C at a rate of 10°C/min under N₂ atmosphere. The temperature of the transfer line between the TGA and FT-IR instruments was 250°C. The spectra were acquired in the range of 4000–500 cm⁻¹ at a resolution of 4 cm⁻¹.

Tensile properties of the UV-cured polymer materials were detected by a SANS7 CMT-4304 universal tester (Shenzhen Xinsansi Jiliang Instrument Corporation) at a cross-head speed of 5.0 mm/min. Dumbbell specimens within a size of 62 mm × 10 mm × 3 mm were evaluated. Five specimens were tested for each sample to calculate the average values.

Adhesion tests of the UV-cured samples were carried out using an adhesion test machine (Tianjin Shiboweiye Glass Instrument Corporation) on the basis of the procedures specified in GB 1720-79(89). Typically, a prepared tinplate sheet with a film thickness of about 100 μm was placed on the substrate of the test machine, circled clockwise by a needle in a distance of 7–8 cm, and graded with a magnifying glass. The grade of adhesion ranged from 1 (best) to 7 (worst). Tests of pencil hardness were performed on a QHQ-A pencil hardness tester (Tianjin Litengda Instrument Corporation) according to the procedures specified in GB/T 6739-2006. Pencil hardness tester of the sample was measured according to GB/T 6739-1996. By fixing the coated tinplate sheets horizontally, the pencil hardness tester was set with a pencil of known hardness and then pushed along the coating surface at a speed of about 1 mm/s. The hardness involved the grades of 6H, 5H, 4H, 3H, 2H, H, HB, B, 2B, 3B, 4B, 5B, and 6B (from hardest to softest). The coating’s flexibility was performed on a QTY-32 paint film cylindrical bending machine (Tianjin Litengda Instrument Corporation) using GB/T 1731-93. Upon testing, the tinplate sheets were fixed tightly under the cylindrical shafts of the machine and bent. The classes of flexibility was determined on the basis of the diameter of the shaft used, including 2 mm, 3 mm, 4 mm, 6 mm, 8 mm, 10 mm, 12 mm, etc. (the diameter is lower, the rate of flexibility is better).

Swelling measurements of the cured samples were carried out with water. Typically, the samples were weighed and immersed to solvents for 48 h at room temperature, then dried with filter papers and weighed. The swelling of water was calculated by Equation (2):

\[ S = \left( \frac{W_1 - W_0}{W_0} \right) \times 100\% \]  

where \( W_0 \) and \( W_1 \) are the weights of materials before and after being immersed into solvent, respectively.

The UV photocuring kinetics of the liquid resins was studied on a modified Nicolet 5700 spectrometer (Thermo-Nicolet Instrument Corporation). The C=C conversion was determined by monitoring the intensity of C=C peak at about 810 cm⁻¹.

### 3 Results and Discussion

#### 3.1 Synthesis and characterization of P-AESO

The chemical structures of the P-ESO and P-AESO were confirmed by the FT-IR and ¹H NMR analysis. Figure 3 demonstrates the FT-IR spectra of the ESO, intermediate of the P-ESO and P-AESO. In the spectrum of the ESO, the characteristic peaks at 1738 cm⁻¹ and 823 cm⁻¹ were shown, which represented ester carbonyl and epoxy groups, respectively (Wu et al., 2018). In the spectrum of P-ESO, several typical peaks were shown: Ph-H stretching (3052 cm⁻¹), ester carbonyl (1730 cm⁻¹), benzenoid ring (1449–1600 cm⁻¹). The peak for the epoxy group at about 823 cm⁻¹ disappeared. Moreover, a new but small peak occurred at 3397 cm⁻¹, which corresponded to the hydroxyl groups generated because of the opening reaction of epoxy groups. All of these demonstrated the occurrence of ring-opening between the ESO and DPPC. Compared the spectrum of the P-AESO with that of the P-ESO, the peak of hydroxyl at 3397 cm⁻¹ disappeared, the peak of ester carbonyl shifted from 1736 cm⁻¹ to 1730 cm⁻¹, and new peaks of C=C groups occurred at 1633 cm⁻¹ and 808 cm⁻¹. These changes indicated that the P-ESO was successfully acrylated.

![Fig. 3 The FT-IR spectra of ESO, P-ESO and P-AESO](http://jbb.xml-journal.net)
consumed completely. Compared the spectrum of the P-AESO with that of the P-ESO, new peaks at $\delta 5.7-6.4$ and $\delta 5.0$ were observed, which are corresponding to the protons on acrylate C=C groups and the protons on the methine group connecting to the functionalized acrylate, respectively. The results also suggested the successful synthesis of the P-AESO product.

3.2 Viscosity comparison between P-AESO and AESO based samples
The viscosity of precursor is one of the key factors to determine the end use of thermosetting resin (Dai et al., 2016a). Table 1 shows the variation of viscosity of the obtained P-AESO and AESO based samples with the content of diluent. The viscosity values decreased to 8968 mPa·s and 9339 mPa·s for the P-AESO and AESO based samples with the increase of the TMPTA content to 20%. The styrene acted as not only a comonomer for mechanical properties enhancement, but also a diluent agent for easy process (Dai et al., 2016a). Besides, when the 10% content of the St was added, the viscosity value dropped to 708 mPa·s and 737 mPa·s, respectively. Obviously, the viscosity of the P-AESO resin was lower than that of the AESO resin.

### 3.3 Volumetric shrinkage comparison between P-AESO and AESO based samples
Volumetric shrinkage of acrylic resins after curing may influence the molding accuracy of finished products and even lead to the deformation of them (Liu C G et al., 2018). As shown in Table 1, when the content of the TMPTA was 20%, the $\Delta V$ of the P-AESO systems was 4.1%, which was obviously lower than that of the AESO systems. Notably, with the St content increased to 10%, the $\Delta V$ decreased to 3.7% and 4.2%, respectively. Therefore, the P-AESO resin was clearly superior to the AESO in inhibiting volumetric shrinkage, which may attributed to the fact that the P-AESO contained the groups of phosphorus benzene ring structure.

3.4 Gel content of UV-Cured samples
Gel content is a crucial indicator and has a direct relationship with the properties of the resins (Li et al., 2017). In this work, the $C_{gel}$ values of the UV-cured resins were determined by Soxhlet extraction, and the corresponding data are summarized in Table 2. Although the P-AESO owned a similar amount of reactive groups relative to the AESO, the P-AESO systems showed slightly lower gel content (89.6%–86.3%) than the AESO systems (96.3%–95.1%). This might be due to the fact that the P-AESO contained two benzene rings increasing the space resistance. As a result, a relatively higher amount of unreacted P-AESO remained in the P-AESO networks than that of unreacted AESO that remained in the AESO networks. Meanwhile, for both the P-AESO systems and AESO systems, the gel content was decreased with the introduction of the St. The St is a monofunctional monomer; during the free radical polymerization, the chain propagation proceeded linearly. As a result, introducing styrene would increase the length of chain segment and lower the cross-link density of the systems, which would decrease the $C_{gel}$ (Li et al., 2017).

### Table 2 Gel content and thermal property of UV-cured resins

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{gel}$ (%)</th>
<th>$E'_{25}$ (MPa)</th>
<th>$T_g$ (℃)</th>
<th>$V_c$ (10^2 mol/m^3)</th>
<th>$T_5$ (℃)</th>
<th>$T_p$ (℃)</th>
<th>W_char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-AESO/TMPTA20</td>
<td>89.6</td>
<td>175.3</td>
<td>115.6</td>
<td>3.61</td>
<td>205.3</td>
<td>413.0</td>
<td>9.47</td>
</tr>
<tr>
<td>AESO/TMPTA20</td>
<td>96.3</td>
<td>454.4</td>
<td>98.9</td>
<td>3.64</td>
<td>310.5</td>
<td>467.0</td>
<td>3.01</td>
</tr>
<tr>
<td>P-AESO/TMPTA20/St10</td>
<td>86.3</td>
<td>139.1</td>
<td>101.1</td>
<td>3.73</td>
<td>212.8</td>
<td>425.5</td>
<td>9.77</td>
</tr>
<tr>
<td>AESO/TMPTA20/St10</td>
<td>95.1</td>
<td>530.1</td>
<td>96.9</td>
<td>3.25</td>
<td>322.5</td>
<td>426.9</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Notes: $C_{gel}$ gel content; $E'_{25}$, storage modulus at 25 ℃; $T_g$, glass transition temperature were determined by the average values of two peak temperatures of the tan delta curves; $V_c$, crosslink density; $T_5$, 5% weight loss temperature; $T_p$, peak temperature at the curves of weight loss rate; W_char, char yield.

3.5 Properties of UV-Cured P-AESO resins
3.5.1 Dynamic mechanical analysis
The DMA was used to determine the glass transition temperature ($T_g$), modulus, and cross-link density of the cured samples. The curves of storage modulus and tan $\delta$ of the cured samples as a function of temperature are
shown in Fig. 5, and the data are summarized in Table 2. The peaks of the tan $\delta$ curves were used to determine the $T_g$ of the cured samples. The tan $\delta$ peaks of the P-AESO systems are much broader than those of the AESO systems, suggesting that phase separation of the P-AESO system occurred more easily. The modulus values at $T_g + 60^\circ$C were utilized to calculate the cross-link density of the cured samples according to Equation (3):

$$V_c = \frac{E'}{3RT}$$

where $V_c$ is crosslink density, $E'$ is the storage modulus in the rubbery plateau region ($E'$ was determined at $T_g + 60^\circ$C for the calculation of $V_c$), $R$ is the universal gas constant, and $T$ is the absolute temperature.

As can be seen in Table 2, all the P-AESO and AESO systems showed similar crosslink density, while the $T_g$ of the P-AESO were higher than that of the AESO/TMPTA20, which was attributed to the higher rigidity of the P-AESO than that of the AESO. The $T_g$ and the modulus of the crosslinked polymers were closely related to the cross-link density and the rigidity of the chain segment structure. The higher rigidities of the chain segment are, the higher $T_g$ are, which suggests that the P-AESO is more rigid than the AESO. The St has only one reactive group, resulting in the decreased $T_g$ of the St modified P-AESO and AESO systems.

### 3.5.2 The TGA and TGA-FTIR analysis

The TGA thermograms curves of the cured P-AESO and AESO systems are shown in Fig. 6. The corresponding results of the obtained resins, including 5% weight-loss temperature ($T_5$), peak temperature at the curves of weight-loss rate ($T_p$), and char yield ($W_{\text{char}}$), are listed in Table 2. Compared with the AESO systems, the P-AESO systems showed a comparable $T_5$ but higher $W_{\text{char}}$ and lower $T_p$ values. The $W_{\text{char}}$ values of the P-AESO were three times than those of the P-AESO systems, but $T_p$ values were around $210^\circ$C while the AESO systems reached $310^\circ$C. The reason can be attributed to phosphonate of the P-AESO. The phosphonate of the P-AESO degraded firstly and formed phosphoric acid, which acted as an acid catalyst to accelerate the chain scission of methylene linkages and the breaking of ester groups in the P-AESO and diluents. However phosphoric acid could further react with the decomposition products, resulting in the formation of complex phosphorus-rich char. The char could protect the residues from oxygen and heat, indicating that the flame retardancy of the P-AESO was superior to that of the AESO resin (Jia et al., 2018).

![Fig. 5](image_url) Storage modulus versus temperature (a) and loss factor versus temperature (b) of UV-cured materials

As can be seen in Table 2, all the P-AESO and AESO systems showed similar crosslink density, while the $T_g$ of the P-AESO were higher than that of the AESO/TMPTA20, which was attributed to the higher rigidity of the P-AESO than that of the AESO. The $T_g$ and the modulus of the crosslinked polymers were closely related to the cross-link density and the rigidity of the chain segment structure. The higher rigidities of the chain segment are, the higher $T_g$ are, which suggests that the P-AESO is more rigid than the AESO. The St has only one reactive group, resulting in the decreased $T_g$ of the St modified P-AESO and AESO systems.

To further investigate the thermal degradation process, the thermal degradation of samples P-AESO/TMPTA20/St10 and AESO/TMPTA20/St10 were investigated at different temperatures by the TGA-FT-IR. The 3D TGA-FTIR spectra of the pyrolysis gases are shown in Fig. 7, and the detailed FT-IR spectra obtained at the maximum evolution rates are exhibited in Fig. 8. The evolved gaseous products for the P-AESO/TMPTA20/St10 at $425^\circ$C exhibit characteristic absorbance of CO$_2$ (2351 cm$^{-1}$ and 2310 cm$^{-1}$), CO (2176 cm$^{-1}$), H$_2$O (3500–3600 cm$^{-1}$), alkane (3000–2800 cm$^{-1}$), aromatic ring (1450–1600 cm$^{-1}$), carbony (1725 cm$^{-1}$), which was similar to that of the AESO/TMPTA20/St10 at $426^\circ$C (Chen et al., 2013; Feng et al., 2018). In fact, the new
unobvious absorption band at around 1298 cm\(^{-1}\) appeared in the P-AESO system at 210\(^{\circ}\)C, which is due to the structures of P=O (Jia et al., 2016). Therefore, it can be concluded that the P-AESO/TMPTA20/St10 decomposed to form polyphosphate, which can react with other pyrolysis products. In addition, the P-AESO/TMPTA20/St10 resins decompose faster as compared with the EA at lower temperature. This result is in accordance with the TGA analysis above. Those indicate that the incorporation of the P-AESO can catalyze the degradation of the resins at low temperature and promote the formation of char at high temperature (Qian et al., 2011).

### 3.5.3 Mechanical property

The mechanical properties of the cured samples were examined by tensile test, and the results are shown in Fig. 9. The tensile strength of the P-AESO systems (4.3 MPa and 6.1 MPa) was lower than those of the AESO systems (9.2 MPa and 12.1 MPa), which might be from the effects of both cross-link density and steric hindrance (Wu et al., 2018). Furthermore, the elongation at break of the P-AESO systems was close to even higher than that of the AESO systems. After copolymerization with the St, the stiffness of the obtained P-AESO and AESO materials can be heightened and the molecular mobility reduced; as a result, the elongation at break declined (Li et al., 2017).

### 3.5.4 Coating property

The coating properties of the UV-cured P-AESO materials, including adhesion, pencil hardness, and flexibility, water resistance were analyzed, and the results are summarized in Table 3. All the cured samples of P-AESO materials demonstrated inferior resistance to water than to the AESO, which were in agreement with the results of gel content. Both the P-AESO and AESO based coatings showed outstanding flexibility of 2 mm and the same pencil hardness of the HB. Flexibility was closely related to cross-link density (Li et al., 2017). The P-AESO and AESO have long nonpolar aliphatic chains, and part of their polar groups such as ester bonds and hydroxyl groups might be buried in the matrix resins and had a low chance to connect with the polar groups on the surface of the substrate; as a result, almost all of the samples showed poor adhesion toward tinplate sheets (Li et al., 2017).
Although the P-AESO systems showed weak water resistance, they showed better adhesion of 2 than that of the AESO. The P-AESO has more groups containing phosphorus than the AESO, corresponding to the better adhesion property. From the above results, it can be concluded that the P-AESO coatings possessed comparable even higher properties than AESO-based coatings.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>(A_d)</th>
<th>(P_h)</th>
<th>(F_l) (mm)</th>
<th>Swelling (%)</th>
<th>Final C=C conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-AESO/TMPTA20</td>
<td>2</td>
<td>HB</td>
<td>2</td>
<td>4.2</td>
<td>81.4</td>
</tr>
<tr>
<td>AESO/TMPTA20</td>
<td>3</td>
<td>HB</td>
<td>2</td>
<td>0.2</td>
<td>79.6</td>
</tr>
<tr>
<td>P-AESO/TMPTA20/St10</td>
<td>2</td>
<td>HB</td>
<td>2</td>
<td>3.2</td>
<td>74.5</td>
</tr>
<tr>
<td>AESO/TMPTA20/St10</td>
<td>3</td>
<td>HB</td>
<td>2</td>
<td>0.3</td>
<td>76.2</td>
</tr>
</tbody>
</table>

Notes: \(A_d\), adhesion of coatings; \(P_h\), pencil hardness of coatings; \(F_l\), flexibility of coatings.

#### 3.6 Photopolymerization kinetics of P-AESO resins

The RT-IR technique was used to study the photopolymerization kinetics of the P-AESO resins. Figure 10 shows the C=C conversions of the P-AESO resins by monitoring the intensity of the absorption peak at about 810 cm\(^{-1}\), and the related results are listed in Table 3. Compared with the AESO/TMPTA20 resin, the P-AESO/TMPTA20 resin showed slightly better lower C=C conversions throughout the UV curing, which may be attributed to functional group from the DPPC on P-AESO. However, as 10% content of the St was added, the final C=C conversion of the P-AESO system decreased from 81.4% to 74.5%, and that of the AESO decreased from 79.6% to 76.2%, indicating that the steric structure of the St would also have a negative effect on the final C=C conversion (Wu et al., 2018). Moreover, it can be seen from the inserted figures that the C=C conversions for the P-AESO resins reached relatively stable values only within about 15 s, indicating the initial curing rates were not only rapid but also as excellent as those of the AESO resins.

### 4 Conclusions

Through the synthesis and employment of the DPPC and AA, a soybean oil-based acrylate oligomer P-AESO was prepared via a two-step procedure by using the ESO as raw materials. Compared with the AESO system, the properties of the P-AESO resins showed superior effects on the volumetric shrinkage, adhesion, \(T_g\) of the resulting materials. Meanwhile, the ultimate properties of the viscosity, cross-link density, flexibility, the initial curing rates and final C=C conversions were comparable or superior to those of the AESO resins. The properties such as gel content, tensile strength and swelling of the P-AESO resins were inferior to those of the AESO resins in some extents. Therefore, the P-AESO showed great potential as alternative to the AESO in the development of the UV-curable materials.

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