Modification of Unsaturated Polyester Resin by Eleostearic Acid

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ABSTRACT: General type unsaturated polyester resin (UPR) is largely used in coating industry as a film-forming resin. However, the general type UPR has some disadvantages which limit its applications such as poor water resistance, heat resistance and mechanical properties. Modifications, especially structural modifications are needed to improve UPR’s comprehensive performance. Here, eleostearic acid (EA), a derivative from a Chinese renewable vegetable oil, Tung oil, has been employed to modify UPR’s structure. Influences of EA’s dosage in EA-modified-UPR on water absorption and tensile strength, scanning electron microscope morphology and thermal stability were investigated. Experimental results show that the water resistance and tensile strength of UPR have been improved a lot and the heat resistance of UPR also has a certain degree of improvement after EA-modification. When the mass dosage of EA is 9% of UPR, the water absorption of UPR are decreased by 12.3% while the tensile strength is increased by 35.5% after modification and the final thermal decomposition temperature are increased from 440 °C to 458.7 °C.

1 INTRODUCTION

General type unsaturated polyester resin (UPR) is largely used in coating industry as a film-forming resin. However, the general type UPR has some disadvantages which limit its applications such as poor water resistance, heat resistance and mechanical properties. Modifications, especially structural modifications are needed to improve UPR’s comprehensive performance (Li, 2011). At present, polyurethane or pre-polyurethane, acrylic resin, epoxy resin, organic silicone, nanometer material, vegetable oil, etc., have been adopted to modify UPR (Li, et al., 2012; Zhao et al., 2012; Worzakowska, 2009; Sharma, et al., 2012; Baskaran, et al., 2011; Zhao, 2007; Das, et al., 2011; Qin, et al., 2008). Among them, more and more importance is attached to the modification of UPR with vegetable oil’s renewability, reactivity and other good features (Zhao, 2007; Das, et al., 2011; Qin, et al., 2008). However, because of vege-
table oil’s self-polymerization (Zhao, 2007) and bad compatibility with UPR (Das, et al., 2011), the modifications of UPR by directly introducing of vegetable oil through chemical reaction or blending to UPR system would not give the expected effects. Therefore, vegetable oil is derivatized first to improve its compatibility with UPR and then is introduced into UPR system has been an important approach for the modification of UPR by vegetable oil (Qin, et al., 2008).

Eleostearic acid, EA, is one of the derivatives of Tung oil through saponification reaction in mixed solvent of methanol and water. EA’s structure is shown in Figure 1 (Li, et al., 2014). Since EA’s structure features relative long molecular chain and unsaturated double bonds, which is similar to that of UPR, they would have better compatibility. Thus, the modification of UPR by EA was studied and the specific results are reported as follows.

\[ \text{CH}_3 - (\text{CH}_2)_3 - \text{C} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOH} \]

Figure 1. Structural formula of eleostearic acid (EA).

2 EXPERIMENTAL SECTION

2.1 General information

General unsaturated polyester resin (UPR), Type Y-196, industrial grade, was purchased from Tianjin Yabang Chemical Co., Ltd., China. EA was prepared according to literature (Li, et al., 2014) and its raw material, Tung oil, was purchased from Xiangxi Autonomous Prefecture of Hunnan Province of China. Benzoyl peroxide (BPO) and N, N-dimethyl aniline were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd., China.

Pyris-6 Thermogravimetric Analyzer (PerkinElmer Inc. US); JSM-6380LV Scanning Electron Microscope (JEOL Co., Ltd., Japan); Computer control electronic universal testing machine (Jinan Assaying Group Co., Ltd., China).

2.2 Preparation of EA modified UPR film sample

A certain amount of EA (wt% = 0%, 3%, 6%, 9%, 12%, calculated by the mass of UPR) was mixed with low viscosity UPR at room temperature by stirring and then, the initiator, BPO, and the solvent, N,N-dimethyl aniline (wt% = 1%), calculated by the mass of UPR) were added in successively. After being stirred uniformly and defoamed, the mixture system was flow-casted on a plain tinplate to form film. Subsequently, the film was put into a vacuum dryer for 12 hrs at 50 °C after the film was gelificated. At last, EA modified UPR (M-UPR) film with smooth appearance and no bubble was obtained. Good M-UPR film samples were selected out and put into the desiccator for following test.
2.3 Performance test

The tensile tests were performed according to GB/T 1040-2006 with stretching rate 50 mm/min at 25 ºC on Computer control electronic universal tensile testing machine. The water resistance tests were performed according to GB/T 1733-1993. Morphology investigations were performed by JSM-6380LV on impact fracture surfaces of film samples. Thermal stability was studied by Thermogravimetric Analyzer, programmed temperature rising method was used in a dynamic nitrogen flow of 40 mL/min from room temperature to 800 ºC at rate of 10 ºC /min (Peng, 2010).

3 RESULTS AND DISCUSSION

3.1 Effects of EA dosage on the tensile strength of UPR film

As shown in Figure 2 and Figure 3, along with the increase of the EA dosage, the tensile strength of UPR film increases. The main reason lies in that EA’s molecular structure contains conjugated double bonds which can take place oxidization crosslinking reactions with UPR’s unsaturated bonds under the given condition. The increase of crosslinking density results in the improvement on the tensile strength of sample film. When the EA dosage increases from 0% to 9%, the tensile strength increases from 12.1 MPa for normal unmodified UPR to 16.4 MPa for EA-modified UPR, with an increase degree of 35.5%. At the same time, it is worth pointing out that there is no significant change of the tensile strength film when the EA dosage increases from 9% to 12%. Thus, the appropriate EA dosage would be 9% of UPR’s mass in the EA-modified UPR system.

![Figure 2. Effect of EA dosage on the tensile strength of UPR film.](image1)

![Figure 3. The Tensile strength increase degree of UPR film after EA-modification.](image2)
3.2 Effects of EA dosage on the water absorption of UPR film

UPR’s water resistance has been improved after UPR’s being modified by EA. As shown in Figure 4 and Figure 5, along with the increase of the EA dosage in EA/UPR modification system, the water absorption of UPR film decreases remarkably. There are two reasons to explain the improvement. On the one hand, it is probably that the hydrophobic long aliphatic carbon chain of EA could concentrate and distribute on the surface of the EA-modified UPR during the modified film forming. Therefore, the modified UPR film would stay in a state of low surface energy and the binding energy of Modified UPR film’s surface to water molecules is reduced and lead to the decrease of the water absorbing rate and correspondingly, the increase of the water resistance (Zhang, et al., 2011). On the other hand, because of the increase of crosslinking density of the system due to the oxidation crosslinking reactions among unsaturated bonds of EA and UPR and other chemical reactions among the carboxyl groups of EA and carboxyl, hydroxyl groups of UPR, the space in the modified polymer system, both intermolecular and intramolecular, is reduced. Therefore, water molecules are not so easily and largely to be absorbed into modified UPR system. As a result, the water resistance is improved.

![Figure 4](image1.png)  ![Figure 5](image2.png)

Figure 4. Effects of EA dosage on the water absorption of UPR film.  
Figure 5. The absorption decline degree of UPR film after EA-modification.

When the EA dosage increases from 0% to 9%, the water absorption decreases from 19.5% for normal unmodified UPR to 17.1% for EA-modified UPR, with water absorption decrease degree of 12.3%. Further, when the EA dosage increases from 9% to 12%, there is no significant decline of the water absorption.

3.3 Thermal stability

Table 1 lists the characteristic thermo-decomposition temperatures of normal UPR and EA modified UPR with different EA dosage which were obtained from thermogravimetric analysis.
and differential thermogravimetric analysis. $T_{d5\%}$, $T_{d15\%}$, $T_{d30\%}$, $T_{d50\%}$ and $T$ have got some increase after modification means the improvement of thermal stability. Particularly, the final decomposition temperature has increased $18.7 ^\circ$C. The main reason may also lie in that the introduction of EA has increased the crosslinking density of UPR.

<table>
<thead>
<tr>
<th>Thermo-decomposition temperature</th>
<th>$T_{d5%}/^\circ$C</th>
<th>$T_{d15%}/^\circ$C</th>
<th>$T_{d30%}/^\circ$C</th>
<th>$T_{d50%}/^\circ$C</th>
<th>$T/^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal UPR</td>
<td>225.3</td>
<td>332.4</td>
<td>375.2</td>
<td>401.5</td>
<td>440.0</td>
</tr>
<tr>
<td>EA modified UPR*</td>
<td>227.2</td>
<td>333.9</td>
<td>378.7</td>
<td>405.6</td>
<td>458.7</td>
</tr>
</tbody>
</table>

Table 1. The thermo-decomposition temperatures of normal UPR and EA-modified UPR.

Note: $T$ is final decomposition temperature, and $T_{d5\%}$, $T_{d15\%}$, $T_{d30\%}$ and $T_{d50\%}$ are the temperatures for thermal weight loss 5%, 15%, 30% and 50% respectively; EA dosage is 9% of UPR’s mass.

3.4 SEM morphology analysis of the impact fracture surface of UPR film

Figure 6 is the SEM photos of the impact fracture surface of normal UPR film (A) and EA modified UPR film (B). For the impact fracture surface photo of normal UPR film, the surface is relatively smooth and the characteristic microporous structure appears and the stripes arrange disorderly. As for EA modified UPR (B), the fracture surface is very rough and the SEM photo (B) takes on a clear look of ductile fracture. The SEM morphology also echoes with the relation between tensile strength and EA dosage. Along with the increase of EA dosage in EA/UPR modification system, the tensile strength increases and the impact fracture develops into typical ductile fracture.

![Figure 6](image)

Figure 6. SEM photos of the impact fracture surface of normal UPR film (A) and EA modified UPR film (B).

4 SUMMARY

By the introduction of EA to normal UPR, EA modified UPR material was prepared. After modification, UPR’s tensile strength, water resistance and thermal resistance are improved.
When EA’s dosage is 9% of UPR mass in the modified UPR system, the tensile strength would increase by 35.5% and the water absorption would decline by 12.3% and the final thermal decomposition temperature would increase by 18.7 °C compared with those of normal UPR. SEM morphology shows that the modified UPR has a ductile fracture mechanism.

REFERENCES


