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Unsaturated polyester resins with low-viscosity: preparation and mechanical properties enhancement by isophorone diisocyanate (IPDI) modification

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Abstract

Durable unsaturated polyester resins (UPRs) with low-viscosity are essential for scaling up the production of down-streamed industrial products. Yet, lower viscosity usually means the compromise of some basic properties of cured materials such as reduced toughness and decreased heat tolerance. In this study, a series of UPRs with viscosities suitable for the vacuum infusion molding process (VIMP), a novel but promising technique for material molding at industry-scales, were successfully synthesized by simply controlling the amount of alcohol used in reactants. Isophorone diisocyanate (IPDI), for the first time, was applied during the curing of the unsaturated polyester to enhance the physical performances of thus-generated UPRs. Characterizations were performed to study the changes in resin structure after modification, and the effects of the addition amount (mass fraction) of IPDI on the properties of UPRs castings were also discussed. Results showed that IPDI could enhance the mechanical properties of UPR castings by more than 30%, with the optimal performances (tensile strength, 55.95 MPa; bending strength, 120.11 MPa; tensile modulus, 3.34 GPa; flexural modulus, 2.97 GPa and Barcol hardness, 43 HBa) obtained when 9 wt% of IPDI was used. The thermal stability of the castings could also be enhanced in the presence of IPDI. Therefore, the proposed strategy may provide a simple avenue for preparing performance enhanced low-viscosity UPRs to meet industrial requirements.

1. Introduction

As a novel molding technique for composite materials, the vacuum infusion molding process (VIMP), where vacuum pressure is applied to drive resins into a laminate, has been witnessed a expanding circle of applications in different industries [1, 2]. Mainly because it can provide a number of advantages including higher economic benefits [3–5] (better fiber-to-resin ratio and less wasted resins), consistent resin usage, unlimited set-up time and cleaner production (significantly reducing the volatility of styrene). Due to its excellent properties such as low cost, easy curing, superior corrosion resistance and mechanical features when compared to other analogues (epoxy resin and phenolic resin), unsaturated polyester resin (UPR), a blend of unsaturated polyester (UP) and a diluent like styrene or active solvents [6–8], is one of the most commonly used thermosetting resins in different industrial applications (construction, marine, chemical and others) [9–12].

Yet, for being an ideal resin in the VIMP, one should at least meet some basic requirements such as good flowability or low-viscosity (<300 mPa·s) to provide sufficient time for mold filling, and excellent toughness to ensure product quality and stability [13]. However, the commonly-used UPRs usually misfit the VIMP especially in industry-associated applications, because of their larger viscosity; and thus seeking for VIMP-applicable UPRs...
Table 1. The proportion of raw materials for the synthesis of UPRs.

| No. | MAH (mol) | PAH (mol) | 2-Methyl-1,3-propanediol (mol) | EG (mol) | ED (mol) | ST (wt%) | Excess alcohol* (mol%) |
|-----|-----------|-----------|--------------------------------|----------|----------|----------|------------------------|
| A   | 8         | 4         | 7.2                            | 2.4      | 4.8      | 35       | 20                     |
| B   | 8         | 4         | 7.5                            | 2.5      | 5.0      | 35       | 25                     |
| C   | 8         | 4         | 7.8                            | 2.6      | 5.2      | 35       | 30                     |
| D   | 8         | 4         | 8.1                            | 2.7      | 5.4      | 35       | 35                     |

* The excess of the total alcohol over the total acid.

is important [14]. Currently, there are two main methods applied to synthesize low-viscosity UPRs: one is by adding excess diluents to reduce viscosity; and the other is by introducing small-component linear molecular chains to reduce the chain entanglement [13, 14]. The first method usually leads to excessive crosslinking during the curing process, affecting the performances of the obtained resins and/or causing unforeseen environmental problems [13]. Therefore, the second method is now being widely considered for the production of low-viscosity UPRs. Unfortunately, UPRs with low-viscosity usually suffer from poor mechanical and thermal properties, and thus require further modification to improve such properties. Currently, the most discussed methods for the modification of low-viscosity of UPRs mainly include (1) adding a second phase materials such as inorganic nanoparticles [15–17], cellulose nanocrystal [18, 19] and rubber particles [20]; (2) physically blending UPR with other polymers like polyurethane, epoxy resin to form interpenetrating polymer networks [21–23], and (3) grafting a flexible molecular segments into the UPR chains [24]. The method of adding a second phase material usually fails in toughening the UPRs, making further reinforcement necessary. Although the addition of other polymers to form interpenetrating networks could considerably increase the crosslinking density and dose well in strength enhancement, this way would then enlarge the viscosity of UPRs. Duan et al., used toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HDI) trimers respectively to modify UPRs [25, 26]. Some polyurethane soft segments would compose interpenetrating polymer networks after curing in UPRs. Hence, the tensile strength and thermal stability of the resin were enhanced to a great extent while the viscosity of the resin kept almost steady. However, some problems are still found with these methods. For example, TDI contains benzene structures, which might darken the color of the system and the color of the cured UPRs would be dark brown; while HDI is volatile and highly toxic.

In this study, low-viscosity UPRs were synthesized by using the method of excess alcohol in reactants. To make the obtained UPRs qualified candidates in the VIMP, and to satisfy the requirements for a cleaner and greener production in industrial applications, low toxicity isophorone diisocyanate (IPDI), containing no benzene in the structure, was for the first time applied for the chain extension modification during the curing process. The use of IPDI might result in the introduction of polyurethane flexible structures to the UPR castings, and thus enhancing the mechanical and thermal performances of the UPRs.

2. Experimental

2.1. Materials

The main raw materials for UPR preparation were all at industrial grade. Among them, maleic anhydride (MAH), phthalic anhydride (PAH), 2-Methyl-1,3-propanediol and ethylene glycol (EG) were purchased from Jinan Aochen Chemical Co., Ltd, China. Ethylene diglycol (ED) and styrene (ST) were purchased from Jinan Century Tongda Chemical Co., Ltd, China. Both curing agent (ethyl ketone peroxide) and the accelerant were produced from Changzhou Tianma Chemical Co., Ltd, China. Hydroquinone and triphenyl phosphite used as polymerization inhibitors were bought from Shanghai Reagent I Factory, China. Isophorone diisocyanate (IPDI) was offered by Jining Baichuan Chemical Co., Ltd, China. Dibutyltin dilaurate, which was utilized to catalyze the reaction between IPDI and UPRs, was provided by Jining Baichuan Chemical Co., Ltd, China.

2.2. Synthesis of UPR

According to the ratio shown in Table 1, 2-Methyl-1,3-propanediol, EG, MAH, PAH and a small amount of antioxidants were put into a four-necked flask with a mechanical stirrer, cooler, thermometer and fixed nitrogen inlet, and then reacted in a program temperature controlled manner. When the temperature of the system was heated to 190 °C, the heating voltage was kept constant until the acid value of the system did not change evidently. Meanwhile, a certain amount of EG was added to esterify with carboxyl groups in the flask before the temperature was further increased to 210 °C and maintained at such temperature for hours. Afterwards, the reaction system was kept under vacuum condition until the acid value of the resultant lower than 5 mg
KOH g$^{-1}$. Finally, 35 wt% of styrene was put into the flask with frequent stirring when the temperature of the system had been cooled down to about 80$^\circ$C to obtain a series of UPRs with low-viscosity.

### 2.3. Preparation of IPDI modified UPR

IPDI with mass fraction of 0 wt% and 5–10 wt% were blended with 100 g generated UPR, respectively. Then a certain amount of dibutyltin dilaurate, cobalt isooctanoate and methyl ethyl ketone peroxide were added with continuously stirring for 2 min at room temperature. The reaction of IPDI with unmodified UPR was shown in figure 1. The mixture was poured into a silicone rubber model and cured at room temperature for 24 h before it was post cured at 40$^\circ$C and 80$^\circ$C for 2 h, respectively. Lastly, the cured bodies were cooled to room temperature and left for 12 h. The modified UPRs with different dosage of IPDI (wt%) were prepared and the internal cross-linked network structure was displayed in figure 2.

![Figure 1. The reaction formula of IPDI with unmodified UPR.](image1)

![Figure 2. The formation of cross-linked network structure of IPDI/UPRs.](image2)

### 2.4. Characterization

The molecular structure of UPRs before and after modification were analyzed on a Fourier-transform infrared (FTIR) spectrometer (Nicolet Avatar 330, Thermo Electron Co., USA). The scanning wave number ranged from 4000 to 500 cm$^{-1}$. The viscosity of the resins was tested according to the GB/T 7193–2008 (China national standard) using a rotary viscometer (NDJ-1, Shanghai Precision Scientific Instrument Co., China). The hydroxyl value was measured according to the GB/T 7193–2008 (China national standard). The mechanical properties including tensile and flexural performances were measured by using a universal tensile testing machine (HZ-2009, Shanghai Hengzhun Technology Co., China) based on the GB/T 2567–2008 (China national standard). The Barcol hardness was obtained by a Barcol hardness tester (934-1, Shanghai Precision Instrument Co., China) according to the GB/T 3854–2017 (China national standard). Each sample was tested up to 5 times, and the results were shown as the average ± standard deviation. The thermal stability of the resins was tested by a thermogravimetric analyzer (STD-Q600, TA Co., USA). The heating rate was 10$^\circ$C min$^{-1}$ from room temperature to 800$^\circ$C under a nitrogen atmosphere. Seeing that the fracture surface morphologies of specimens could further confirm the mechanical properties (toughness in particular) of UPRs, scanning electron microscope (S-4800, Hitachi, Japan) was then performed.
3. Results and discussion

3.1. FTIR spectroscopy of unmodified and modified UPR

Figure 3 detailed the FTIR spectra of UPRs before and after modification with IPDI. For pure UPR, the broadest and the intense –OH peak, assigned to the –OH groups on the terminal part of UPR chains, was found at about 3543 cm⁻¹, and the telescopic vibration peak at 2964 cm⁻¹ was responded to –CH. The typical absorption peak of ester carbonyl and –CH₂–O–CO– stretching of the ester appeared at 1732 and 1269 cm⁻¹, respectively. However, the peak at 1788 cm⁻¹ for the absorption peak of anhydride did not appear evidently, indicating that the esterification reaction was achieved. Compared with that of unmodified UPR, the –OH peak of IPDI/UPR was significantly weakened. In the meantime, the stretching vibration and bending vibration peak due to –NH was observed at 3396 and 1522 cm⁻¹, respectively. And the characteristic peak of –NCO group at 2255 cm⁻¹ was hardly found in the FTIR spectrum. Besides, the intensity of C=O absorption peak at 1732 cm⁻¹ was significantly increased when adding an extra carbonyl from carbamate group into UPRs. These peaks demonstrated that the IPDI was almost consumed via the reaction with –OH groups on the terminal UPR chains to bring the carbamate group.

3.2. Effects of the amount of glycol on the properties of UPR

The proportion of the raw materials for synthesizing UPRs, especially the amount of dihydric alcohol, could usually determine the final molecular weight of the resins. Also it would in turn affect viscosity and mechanical properties of UPRs. In this consideration, a series of studies to reveal the changes were conducted with results detailed in Table 2. It was found that both the average molecular weight and the viscosity value of UPRs gradually decreased along with the increasing proportion of dihydric alcohol. This could be attributed to the phenomenon that a part of dihydric alcohol was consumed as the blocking agent, which would prevent the chains from growing constantly during the polymerization reaction. And the greater the percentage of the surplus resin chains is, the easier the chain growth would stop. In the meantime, the length of the resin chain would also be shortened. As a consequence, the strong entanglements among short resin chains would hardly take place.

| No. | Acid value (mg g⁻¹) | Hydroxyl value (mg KOH g⁻¹) | Average molecular weight | Viscosity (mPa·s) | Tensile strength (MPa) | Flexural Strength (MPa) |
|-----|---------------------|-----------------------------|--------------------------|------------------|-----------------------|------------------------|
| A   | 10.94 ± 0.16        | 51.80 ± 0.08                | 1807.0 ± 0.7             | 250.0 ± 0.7      | 48.10 ± 0.53          | 112.58 ± 0.20          |
| B   | 7.80 ± 0.14         | 69.40 ± 0.06                | 1428.0 ± 0.5             | 170.0 ± 0.6      | 45.60 ± 0.58          | 97.32 ± 0.24           |
| C   | 5.20 ± 0.14         | 96.70 ± 0.06                | 1103.0 ± 0.4             | 125.0 ± 0.7      | 40.68 ± 0.50          | 83.26 ± 0.19           |
| D   | 4.00 ± 0.13         | 128.60 ± 0.07               | 886.0 ± 0.4              | 95.0 ± 0.6       | 35.20 ± 0.48          | 70.13 ± 0.22           |

* General UPRs for analyzing were commercial products offered by Yongyue Science & Technology Co., Ltd, Fujian, China.
making the viscosity of reins staying at low values. In addition, Table 2 also revealed that the tensile and flexural properties of UPR castings became worse when the addition of dihydric alcohol was gradually increased. The reason was that the UPRs were incompletely cured, due to the lower crosslinking density than the general UPRs. Taking these properties into consideration, the experiment C with the excessive part of 30 mol% of dihydric alcohol was chosen as the better proportion for ensuring the low-viscosity of the resin with good mechanical properties.

### 3.3. Effects of IPDI components on the properties of UPR with low-viscosity

#### 3.3.1. Mechanical properties

The results of the mechanical properties of the cured UPR samples along with different IPDI contents are shown in figures 4, 5 and 6. With the increasing addition of IPDI, all the curves presented a up first and then down tendency. And when 9 wt% IPDI was put into to pure UPRs, the highest point where the best mechanical properties of UPRs were witnessed, including the tensile strength of 55.95 MPa, the bending strength of 120.11 MPa, the tensile modulus of 3.34 GPa, the flexural modulus of 2.97 GPa, and the Barcol hardness of 43 HBa. Compared with the unmodified UPRs possessing the tensile strength of 40.68 MPa, the bending strength of 83.26 MPa, the tensile modulus of 2.03 GPa, the flexural modulus of 2.27 GPa, and the Barcol hardness of 28 HBa, the mechanical properties were enhanced by 37.5%, 44.3%, 64.5%, 30.8% and 53.6%, respectively.

Conspicuously, the grafting of IPDI was able to effectively improve the mechanical properties of UPRs, because of the internal structure of IPDI/UPRs. When a certain amount of IPDI reacted to the hydroxyl groups on the end of UPR chains, the generated structure of urethane groups would also assist the linkage of UPR chains.
with other molecules. In such manner, the length of UPR chains was expanded and the interpenetrating networks were also produced. Meanwhile, the increase of the crosslinking density of the cured UPRs, a prerequisite to obtain a resin with good mechanical performances, was then obtained \[27\]. Therefore, such performances of UPRs was expected to be well enhanced continually with the developed crosslinking density of low-viscosity UPRs. It was also worth noting that there were some soft structures of polyurethane derived from the reaction, which would also benefit the toughness of the UPRs. However, when the added amount of IPDI exceeded 9 wt%, the properties of the resins went down. These changes were due to the side reactions between superfluous IPDI and the imine bond in the new networks \[27\]. IPDI reacting with the imine group and to generate new allophanate groups, would promote the crosslink density to an excessive level leading to the implosion of the curing system. Consequently, the behaviour of further crosslinking would produce cracks inside the cured UPR samples and then weaken the properties of the resins.

3.3.2. Thermal properties

Figure 7 illustrated the TG curves of the UPRs before and after modification with 5–10 wt% IPDI, with the degradation data concluded in Table 3. Clearly, all modified UPRs shown a more outstanding thermal stability. The temperature for 5%, 10%, 50% weight loss and maximum mass loss rate of the unmodified UPR was 240.3 °C, 296.8 °C, 375.0 °C, and 382.0 °C, while that for modified UPRs maximally increased to 275.5 °C, 320.1 °C, 384.6 °C, and 396.6 °C, respectively. This confirmed that the thermal stability of UPR could be improved...
by introducing IPDI, since the flexible structures of polyurethane would do thermal motion inside UPRs when they were heated. And a part of thermal energy would then be expended for the movement of molecular chains. As a result, the casting bodies of modified UPR possessed a better thermal stability.

3.3.3. Morphologies of fracture surface
The excellent modification effect introduced by IPDI modification was further confirmed via SEM images of the fracture surface. A large number of linear gullies and warped edges (Figure 8(a)) appeared on the fracture surface of the unmodified UPR samples, which revealed the low crosslinking density when UPR was cured. In this case, the lost of the linkage between UPR chains with other structures or molecules would make the resins distinctly brittle. Conversely, as for the modified UPR with 6 wt% of IPDI, less amount of slim river lines emerged, while closed loops were formed by parts of those lines (Figure 8(b)). Most specially, when the proportion of IPDI was increased to 8 wt% and/or 9 wt%, less crackles but many dimple structures emerged and some ‘sea-island’ structures were also witnessed on the fracture surfaces. These phenomena shown in Figures 8(b)–(d) was well consistent with the increasing trend of the crosslinking density and of the content of soft segments in UPRs.

| Content of IPDI (wt%) | T for 5% weight loss (°C) | T for 10% weight loss (°C) | T for 50% weight loss (°C) | T for max. Degrad. Rate (°C) |
|-----------------------|--------------------------|---------------------------|---------------------------|-----------------------------|
| 0                     | 240.3                    | 296.8                     | 375.0                     | 382.0                       |
| 5                     | 267.8                    | 309.4                     | 380.7                     | 394.8                       |
| 6                     | 274.3                    | 316.4                     | 382.6                     | 395.6                       |
| 7                     | 275.4                    | 320.1                     | 383.2                     | 396.6                       |
| 8                     | 273.6                    | 317.9                     | 384.1                     | 393.1                       |
| 9                     | 272.7                    | 317.5                     | 384.6                     | 392.3                       |
| 10                    | 271.3                    | 319.8                     | 382.3                     | 387.0                       |

Figure 8. SEM images of the fracture surfaces from UPRs with or without modification. (a) the pristine UPR, (b) 6 wt% IPDI, (c) 8 wt% IPDI and (d) 9 wt% IPDI.
modified by an increasing amount of IPDI. Furthermore, these ripples and small 'islands' were able to disperse the energy generated from the impact behaviours, which would easily make the cracks from the unmodified UPRs developed in one direction and leading to poor toughness. The rougher the fracture surface was, the greater amount of energy from shear deformation would be dissipated, and thus the better toughness and mechanical property enhancement would be obtained [28].

4. Conclusions

In this study, unsaturated polyester resins (UPRs) with low-viscosity, was prepared for meeting the resins requirements in the vacuum infusion molding process (VIMP) technique. The resins were containing excess alcohol of 30% in order to receive the hydroxyl ending resin chains. Isophorone diisocyanate (IPDI) was blended into the curing system to toughen the obtained UPRs. IPDI could creat the soft segments of polyurethane and expand the length of UPR chains with grafting reaction confirmed by the FTIR spectra. Casted samples of IPDI modified and unmodified UPRs were prepared for mechanical properties tests. Results proved that the UPR samples exhibited the best properties when 9 wt% IPDI was grafted on UPR chains, which also contributed to a better thermal stability. Since the addition of the low toxic IPDI would not compromise the viscosity of UPRs, the method discussed in this study might provide a simple and effective strategy to get ideal UPRs with low-viscosity but enhanced toughness suitable for practical applications even at industry-scales.

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