Styrene-free unsaturated polyesters for hemp fibre composites

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ABSTRACT

N-vinyl-2-pyrrolidone (NVP) and tri(ethylene glycol) divinyl ether (TDE) are utilized as reactive diluents to replace carcinogenic styrene (St) during the formulation of unsaturated polyester (UPE) resins. The processability and thermomechanical properties of the UPE resin-containing hemp fibre composites are evaluated. Both NVP-UPE and TDE-UPE resins exhibit better miscibility than the St-UPE resin. Rheological and curing measurements reveal that the St-free resins have much lower viscosity and curing temperatures than the St-UPE resin, indicating their superior processability. Furthermore, hemp fibre composites with NVP-UPE resin show comparable mechanical properties to the St-UPE composites. Composites of TDE-UPE have comparable tensile and impact strengths to the St-UPE composites. However, the flexural strength and modulus, storage modulus, and glass transition temperature of TDE-UPE composites are all lower than those of the St-UPE composites.

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1. Introduction

Unsaturated polyester (UPE) has widely been used in fibre-reinforced composites because of its advantages of low cost, good processability, and superior mechanical properties [1]. In industry, styrene (St) is often adopted as a reactive diluent (RD) to dissolve UPE. The St-UPE mixture exhibits low viscosity and wets the reinforcing fibres well. Meanwhile, St is capable of crosslinking the C=C bonds in different UPE chains effectively, further improving the mechanical strength of the composite. However, St is a volatile organic compound (VOC) and a hazardous air pollutant (HAP). It is also carcinogenic [2]. Therefore, developing an environmentally friendly RD to replace all or part of St is highly desired in the UPE based composite industry.

Vinyl monomers, (meth)acrylate monomers, and St analogues, such as vinyl toluene, divinylbenzene, and α-methylstyrene, have been investigated as alternative UPE solvents [3–5]. However, the main drawbacks of these solvents are their high cost and toxicity. Cheap bio-based RDs have been developed from vegetable oils [6–8], carbohydrates [9,10], and lignin [11–13] to replace St. The utilization of (meth)acrylated fatty acids as RDs for UPE, vinyl ester (VE), and triglyceride-based thermosets has been evaluated due to their availability, degradability, low cost, and low HAP or VOC emission [6–8]. However, resins with vegetable oil-based RDs exhibit poor mechanical and thermal properties because of their limited reactive sites and long, soft aliphatic chains. Lignin-derived monomers were used to generate several aromatic bio-based methacrylates that could serve as alternatives for St in VE resins [11–13]. The lignin-based VE resins show comparable thermomechanical properties to the St-VE resins because the aromatic character of lignin provides structural rigidity and thermal stability. Nevertheless, the major obstacle to using these bio-based RDs is the high viscosity of the resulting resins, which reduces their processability significantly, especially for liquid moulding techniques.

Conversely, natural fibres from hemp, jute, flax, bamboo, and many others have been widely used in traditional St-based UPE composites because of their availability, low cost, high specific strength and modulus, and low carbon footprint [14–17]. The reinforcing capability of natural fibres in the composites strongly depends on the fibre properties and the interfacial bonding between the fibres and UPE matrix. Different raw materials and processing techniques lead to different fibre properties, which greatly affect the performance of the final composites [18,19]. However, the major scientific challenge for natural fibre reinforced St-UPE composites is the weak interaction between the hydrophilic fibre and the hydrophobic matrix. The hydrophilicity of natural fibres is ascribed to the hydroxyl groups of cellulose, while the nonpolar St is responsible for the hydrophobicity of the UPE matrix.

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Researchers have adopted various strategies, either physical or chemical, to modify the fibre surface [20], but little effort has been given to the development of novel St-free UPE resins for wetting fibres more effectively.

In this work, two St-free UPE resins are prepared using *N*-vinyl-2-pyrrolidone (NVP) and tri(ethylene glycol) divinyl ether (TDE) as RDs. The solubility mechanism and processability (both rheological and curing behaviour) of the resins as well as the mechanical properties of the resulting hemp/UPE composites are investigated. Both NVP and TDE are reactive vinyl monomers without HAP or VOC emissions. They can undergo a fast polymerization to form homopolymers and copolymers under suitable conditions, and thus have been widely used as RDs in UV curing inks, adhesives, and coatings [21,22]. Additionally, NVP is a good hydrogen bonding acceptor and has a high binding affinity with several molecules [23]. The novel St-free UPE resins are expected to provide improved interfacial adhesion with hemp fibres through possible hydrogen bonding or other polar–polar interactions.

2. Experimental techniques

2.1. Materials

Propylene glycol (98%), isophthalic acid (≥99%) and fumaric acid (99.5%) were obtained from Sigma–Aldrich. Tetra-n-butyl titanate (98%, Fluka, China) was the catalyst for esterification, and 4-methoxyphenol (97%, Sigma–Aldrich) was the inhibitor during the UPE preparation. St (99%, Sinopharm Chemical Reagent, China), NVP (99%, stabled with NaOH, Aladdin, China), and TDE (97%, Sigma–Aldrich) were the RDs for the UPE. The free-radical initiator, *tert*-butyl peroxybenzoate (TBPB, 98%, Sigma–Aldrich), was used for curing UPE resins. As reinforcements, hemp fibres with an average length of 3.86 cm and an average fibre fineness of 7.69 dtex were obtained from Sanxing Hemp Industry, China.

2.2. Preparation of UPE resins

A 250-mL three-neck flask was charged with propylene glycol (87.610 g, 1.15 mol), isophthalic acid (83.174 g, 0.5 mol) and tetra-n-butyl titanate (0.106 g, 0.3 mmol). The mixture was mechanically stirred and reacted under N$_2$ protection at 230 °C for 20 min and then at 210 °C for 370 min. After being reheated to 230 °C, fumaric acid (58.098 g, 0.5 mol) and 4-methoxyphenol (0.024 g, 0.2 mmol) were added and the reaction was continued at 230 °C for 260 min and then at 240 °C for 100 min. Finally, the mixture was pumped under vacuum for 60 min and then cooled to room temperature (r.t.) to generate the solid UPE.

The solid UPE (48 g) was powdered and then dissolved gradually in RD (32 g) in a beaker at 70 °C using a magnetic stirrer at 500 rpm. The weight ratio of UPE/RD was 60/40. After cooling to r.t., TBPB (1.6 g, 2 wt% of the total mixture) was added to the mixture, which was further stirred for 2 min to form the final resins. The resulting resins containing 40 wt% St, 40 wt% NVP, and 40 wt% TDE, respectively, were designated as 40St-UPE, 40NVP-UPE, and 40TDE-UPE. Similarly, the resins with 50 wt% NVP or TDE were prepared and denoted as 50NVP-UPE or 50TDE-UPE.

2.3. Characterization of UPE resins

Differential scanning calorimetry (DSC) analysis was conducted on an STA 449 F3 Jupiter Simultaneous Thermal Analyser (NETZSCH, Germany). The sample (5–10 mg) was placed in a standard porcelain crucible with a lid. The scans were carried out at a heating rate of 10 °C/min from 25 to 250 °C under N$_2$ (flow rate: 30 mL/min). The total heat (Δ*H*) of the curing reaction was obtained

from the integrated area of the exothermic peak. Rheological measurements were performed on a HAAKE MARS III rotational rheometer (Thermo Electron, USA) using a PP35Ti parallel plate (gap: 0.105 mm) with a shear rate of 10 γ/s and a heating rate of 10 °C/min from 25 to 100 °C.

2.4. Preparation of hemp/UPE composites

Randomly orientated hemp fibre mats with dimensions of 20 × 20 × 0.5 cm^3 were manually prepared by a carder and then oven-dried at 103 °C for 24 h. For the fabrication of hemp/UPE composites with 50 wt% fibre content, five fibre mats (75 g) were separately coated with the prepared UPE resins (75 g) by hand. The fibre mats were stacked and pressed in a mould (20 × 20 × 3 cm^3) under a pressure of 6-MPa. While maintaining the pressure, the mould was sequentially kept at r.t. for 5 min, 70 °C for 5 min, and 160 °C for 30 min. The formed composite board was removed from the mould after it was cooled to r.t..

2.5. Evaluation of hemp/UPE composites

Dumbbell specimens of 50-mm gauge length and 10-mm section width were prepared for the tensile test according to ASTM D 638-10. Rectangular composite specimens (80 × 10 mm^2) were used for the flexural property and impact strength tests based on ASTM D 790-10 and ISO 179-10, respectively. The tensile and flexural tests were conducted on a CMT6104 universal testing machine (MTS Systems, USA) with a crosshead motion rate of 10 mm/min. The unnotched impact strength test was carried out on a ZBC-25B Charpy impact tester (MTS Systems, USA). Five replicates were measured for each type of composite. Dynamic mechanical analysis (DMA) was performed with a DMA 242 (NETZSCH, Germany) using the single cantilever bending mode at a frequency of 1 Hz; samples with a dimension of 55 × 10 mm^2 were tested at a heating rate of 5 °C/min from 30 to 200 °C. To evaluate the interfacial adhesion between hemp fibres and different UPE resins, the tensile-fractured surfaces of different composites were analysed with a JOEL JSM-7500F scanning electron microscope (SEM) (JOEL, Japan). The specimens were gold-coated and imaged with a 5.0 kV electron beam.

3. Theoretical background

3.1. Prediction of the miscibility of UPE with RD

Based on Hansen's theory, three types of molecular forces contribute to the solubility parameter (δ) of a substance, i.e., dispersion forces (δ_d), polar forces (δ_p) and hydrogen bonding (δ_h). This relationship can be expressed as Eq. (1) [24]:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

Using the group contribution method, Hoftyzer and Van Krevelen proposed that the solubility parameter components could be predicted using Eqs. (2)–(4) [24]:

$$\delta_d = \sum \mathbf{F}_{di} / \mathbf{V} \tag{2}$$

$$\delta_p = \left(\sum \mathbf{F}_{pi}^2 \right)^{1/2} \Big/ \mathbf{V} \tag{3}$$

$$\delta_h = \left(\sum \mathbf{E}_{hi} / \mathbf{V} \right)^{1/2} \tag{4}$$

where $\mathbf{F}_{di}$ and $\mathbf{F}_{pi}$ are the molar attraction constants given by