



# Synthesis, characterization and curing optimization of a biobased thermosetting resin from xylitol and lactic acid

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## ABSTRACT

A biobased thermoset resin was synthesized by direct condensation reaction of lactic acid with xylitol followed by the end-functionalization of the hydroxyl groups of branches by methacrylic anhydride. Chemical structures of resins were evaluated and confirmed by  $^{13}\text{C}$  NMR and Fourier-transform infrared spectroscopy (FT-IR). Different techniques were employed for the optimization of the curing process. Techniques including Microscopy, Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) were employed for characterization of the cured resins. Thermogravimetric analyses (TGA) were also carried out to check the thermal stability of the cured resins. The viscosity of the neat resin was measured at different temperatures and different stress levels. Water adsorption tests were also carried out to check the water absorption properties of cured resins. The glass temperature ( $T_g$ ) of the resin was 98 °C, and the viscosity of the resin was 2.97 Pa s at room temperature which drops to 0.07 Pa s upon increasing the temperature to 85 °C. The biobased content of the resin was calculated as 77%. Cheap raw materials, high biobased content, biodegradability, good thermomechanical and rheological properties, good processability and good thermal stability are of advantages of the synthesized resin which makes the resin comparable with commercial unsaturated polyester resins.

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## 1. Introduction

Due to a shortage of petroleum resources, ecological and economic concerns associated to petroleum based resins, different biobased raw materials have been suggested for production of biobased resins including vegetable oils [1–3], polyols and polyphenols [4,5] and lactic and itaconic acid [6]. Poly lactic acid (PLA) is a biodegradable aliphatic polyester which is derived from lactic acid [7]. Versatile and economical renewable sources of lactic acid (LA), and biodegradability of the products makes LA a suitable source for production of bioplastics [8,9].

Thermoplasts are a class of polymers with high molecular weight where the chains are associated through intermolecular forces and their structure is weakened rapidly upon temperature increase. In contrast, thermosets form chemical bonds during the curing process and the structure cannot be reformed upon further heating-cooling processes [9,10]. Thermosets can be tailored for a desired property by changing cross-linking density or structure which makes them capable of being engineered for a certain functionality.

Limitations in impregnation of viscous matrix to fibers is a major problem in composites. Poor impregnation makes the production process to be slow and also reduces the mechanical strength of the composites [11,12]. Low viscosity of

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thermosets results in better processability and better impregnation of fibers making thermosets desirable as a matrix for reinforced composite applications [13]. In addition, PLA's hydrophobic nature makes it incompatible with natural fibers [14–16]. Hydrophilic fibers cannot be efficiently employed for reinforcing the PLA matrix as the adhesion of the fiber to the hydrophobic resin is poor which contributes to poor mechanical properties of the produced composites [17]. Several studies carried out to enhance the compatibility of the natural fibers in the matrix include treating the fibers with hydrophobic functional groups such as maleic anhydride [18,19], ultrasonic and plasma treatment [20,21] and co-polymerization of PLA with a more hydrophilic monomer like glycolic acid monomers [22].

Different studies have been performed on synthesis of LA based thermosetting resins suitable for different applications including structural composites, biomedical applications, drug-delivery applications, tissue engineering, coating applications or smart packaging [22–28]. Recently, thermoset resins prepared by direct condensation of LA with glycerol [5], allyl alcohol terminated LA oligomers [25], and pentaerythritol [24] have been introduced for biocomposite productions. Star-shaped molecules resulted after direct condensation of the core molecule with LA were further functionalized with an end-capping agent [28]. It is presumed that more hydroxyl groups of the core molecule provide a better extended network of the final thermosets [29]. In addition, unsaturated hydroxyl groups of the core molecule may ultimately increase the hydrophilicity of the produced resin and make the resin more compatible with natural fibers which ultimately increases the mechanical properties of biocomposites produced from natural fibers and PLA thermoset.

In this study, the possibility of producing resins from LA and xylitol have been investigated. Thermoset resin was synthesized in a two-step synthesis procedure: a direct condensation-polymerization followed by an end-functionalization reaction. The structure of the resin was confirmed using  $^{13}\text{C}$  NMR and FTIR. The curing process was optimized and the thermomechanical properties of cured resins was investigated using Dynamic Mechanical Thermal Analysis (DMTA), Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA). The advantages of using xylitol as the core molecule are that (1) it is biobased and relatively inexpensive, (2) it lowers the viscosity of the final resin enhancing its processability, (3) xylitol has more hydroxyl groups providing a better extended network which results in better thermomechanical properties of the cured resin and (4) unsaturated branches of xylitol molecule, increase the hydrophilicity of the produced resin leading to a resin which is more compatible with natural fibers.

## 2. Materials and methods

### 2.1. Materials

L (+)-lactic acid ( $\geq 90\%$ ; Acros Organics) and xylitol ( $\geq 99\%$ ; Sigma-Aldrich) were used as the main reactants. Toluene ( $\geq 99.8\%$ ; Sigma-Aldrich) as the solvent, Methanesulfonic acid ( $\geq 99.0\%$ ; Sigma-Aldrich) as the catalysts, Hydroquinone ( $\geq 99.5\%$ ; Sigma-Aldrich) as the inhibitor, Methacrylic anhydride ( $\geq 94\%$ ; Sigma-Aldrich) as the end-functionalization agent were also used in synthesis. Benzoyl peroxide ( $\geq 98\%$ ; Sigma-Aldrich) was used as the free radical initiator for crosslinking phase. Xylenes ( $\geq 98.5\%$ ; Sigma-Aldrich) and Isopropyl alcohol (99.5%; Sigma-Aldrich) were employed for the titration. Potassium hydroxide ( $\geq 85\%$ ; Sigma-Aldrich) solution in absolute ethanol was used as the titrant with phenolphthalein (1% in ethanol, Fluka) as the indicator.

### 2.2. Synthesis

The resin was synthesized by direct condensation reaction of LA with xylitol and further end-functionalizing of the hydroxyl groups of branches by methacrylic anhydride. Xylitol molecules played the role of a clustering agent in the final polymer structure. Eventually, a star-shaped oligomer of xylitol and LA was prepared in the step-one reaction. In the step-two reactions, branches were end-functionalized with methacrylic anhydride. The chemical reactions and idealized structures are presented in Fig. 1.

#### 2.2.1. Step-one reactions: poly-condensation of LA with xylitol

The first synthesis step was carried out employing a direct condensation polymerization technique in the presence of toluene as an auxiliary solvent for water removal. LA (1.5 mol) was added to 0.1 mol of xylitol diluted in 75 g of toluene containing 0.1wt% of the catalyst methanesulfonic acid (see Fig. 1). The components were transferred to a three-neck, round-bottom flask, equipped with a magnetic stirrer in which one neck was connected to a nitrogen flow and toluene reflux from and the azeotropic distillation apparatus. The other two necks were used for toluene reflux from an azeotropic distillation unit and connecting a thermometer. In the third neck, an azeotropic distillation unit was connected to a condenser for toluene recovery. The flow of the nitrogen in the system was ensured by employing a mini gas bubbler in the outlet of the condenser. The temperature inside the flask was set to 145 °C for two hours and then increased to 165 °C for seven hours.

#### 2.2.2. Step-two reactions: End functionalization of the oligomers

The oligomers resulted from condensation reactions would have reactive groups but yet, the groups are not reactive enough for a satisfactory cross-linking. The branches were further functionalized with methacrylic anhydride to improve their reactivity by adding carbon double bonds. The resulted resin was cooled to 90 °C and 1 wt% hydroquinone was added

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