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Lignin valorization by forming toughened lignin-co-polymers: Development of hyperbranched prepolymers for cross-linking

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ABSTRACT

The preparation of hyperbranched polymers from a unique combination of commercially available A_2, B_3 and CB^1_3-type monomers is presented. Direct melt condensation of aliphatic dicarboxylic acid (A_2) to compounds having trihydroxy groups ((B_3), triethanolamine) and trihydroxy-monoamino groups ((CB^1_3), tris(hydroxymethyl)aminomethane) led to a series of hyperbranched polyesters with amine cores and amide linkages. Because of the monomers availability and simplicity of the synthetic process, hyperbranched poly(ester-amine-amide) (HBPEAA) materials can be readily scaled up. This approach was used to synthesize series of prepolymers with varying degree of branching (DB) and distance between branching points. Taking the advantage of reactivity differences of COOH with the NH_2 and OH groups, the hyperbranched polymer with different arrangement of amide linkage along the network was synthesized. The influence of reaction conditions such as monomer compositions, temperature and mode of mixing on the polymerization was examined. The DB of the HBPEAA (0.46–0.63) was dependant on the synthetic route. The HBPEAA exhibited moderate molecular weights as determined by NMR and ESI-MS. Thermogravimetric analysis revealed that the prepolymers exhibit reasonable thermal stability. The synthesized prepolymer was successfully utilized to copolymerize with 40% lignin to form toughened elastomeric materials with tensile strength of 12 MPa, Young's modulus of 33 MPa and 149% elongation.

1. Introduction

Hyperbranched polymers (HBPs) are an attractive type of polymer due to its structure and functionality and have been much explored in recent years [1–4]. Owing to their highly branched polar structure and tailorable properties, HBPs are promising for future applications in many areas, for instance as biodegradable additives [5], tougheners [6], commercial coatings and resin application [7], biomedical applications [8].

Polyesters are a dominating this class of materials in the field of HBP [9] because of commercial availability of its monomers and, the relative ease of synthesis. In addition, polyesters have in general a high level of commercial importance, and a variety of well known processing technologies are available. Thus, aliphatic, lower molar mass polyesters can be used very effectively in coatings and resins, and the combination of the property profile of polyesters with high functionality, low viscosity, and improved miscibility make the hyperbranched products in these fields very attractive. Branched polyesters have been extensively reviewed recently and have been proved that its application for making useful material properties by our own recent work [10]. Some of the

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very early work is related to hyperbranched copolyesters [11,12] and considerable research in the early 1990s addressed aliphatic [13,14], aliphatic–aromatic [15] and aromatic [16–20] hyperbranched polyesters.

Polycondensation is the classical way to prepare HBPs by using various monomers with and without core moieties. There are several studies reported on the synthesis of different types of HBPs via polymerization of functionally symmetric diacid (A_2) and trihydroxy (B_3) monomer pairs but a few studies report $A_2 + B_3$ polymerization in the melt phase [21–24]. Melt polymerization has been demonstrated to be a cost effective methodology for the synthesis of highly branched polyesters.

The above-described hyperbranched structures cover most of the general synthetic methodologies. However, in order to further increase the structural variety and complexity of the designed macromolecular structures, combinations of various highly branched structures need to be developed. As such, a unique combination of commercially available A_2, B_3 and trihydroxy-monoamino (CB_3^1) type monomers were selected for the synthesis of HBP. The condensation reaction between the monomers at various combinations will yield highly branched polymers with different branching. The highly branched polymers from various dicarboxylic acids will have a well-defined distance between the branch points. The HBP with a different distance between the branch points are expected to exhibit interesting thermal and mechanical properties. Thus, mainly two series of highly branched polyester prepolymers, one with varying distance between branch points, and the other with varying degree of branching show promise to tailor polymer properties.

In this study, HBPs were prepared by making use of the reactivity difference between hydroxyl and amine with carboxylic functional group in hyperbranched prepolymer components. The hyperbranched poly(ester-amine-amide) (HBPEAA) were synthesized without solvent and catalyst in a one-pot step. The synthetic conditions for HBP were chosen for developing suitable mixing phase with medium range molecular weight for thermoplastics or thermoset polymeric smart materials. High conversion will result in the gelation of the polymer which would not be suitable for further steps (cross-linking). Therefore, step one was monitored/controlled to form prepolymer structures by maintaining a low reaction temperature, of 100 °C. The structural variations and its thermal properties were measured and compared with the other two set of polyesters. Finally, the synthesized HBP were used to demonstrate it as a toughening aid with bio-based lignin to form elastomers.

2. Experimental part

2.1. *Materials*

The syntheses of HBPEAA prepolymers were carried out with commercially available 1,1,1-triethanolamine (TEA, B_3, CAS # 102-71-6), tris(hydroxymethyl)aminomethane (THAM, CB_3^1, CAS # 77-86-1), adipic acid (AA, A_2, CAS # 124-04-9), succinic acid (SA, A_2, CAS # 110-15-6), pimelic acid (PA, A_2, CAS # 111-16-0), and dodecanedioic acid (DDDA, A_2, CAS # 693-23-2). All monomers were obtained from Acros Organics and used as received. Methanol soluble fraction of a commercial soda pulp lignin from agricultural residues (Protobind 1000 by ALM India Pvt. Ltd., Chandigarh 160009, India; $M_n = 65{,}000\ \mathrm{g\ mol^{-1}}$, $T_g = 102\ ^\circ\mathrm{C}$) was used for the synthesis of copolymers and previously characterized [10].

2.2. *Synthesis of hyper branched (HBPEAA) prepolymers (1a–1h);* monomer composition

All the reactions were performed in bulk by adding all the three monomers; adipic acid (AA, 0.740 g, 5.02 mmol), triethanolamine (TEA, 0.375 g, 2.51 mmol) and tris(hydroxymethyl)aminomethane (THAM, 0.305 g, 2.51 mmol) at 1:1:2 ratio (prepolymer **1a**) correspond to AA:TEA:THAM, in a flat glass crystallizing-dish (50 mm dia). The crystallizing-dish was then placed inside a preheated vacuum oven (100 °C) and a vacuum of 16 kPa was applied to avoid the monomers loss. As the reaction mixture temperature was raised, the acid started to melt first followed by THAM. At the initial stage of the reaction (0–3 h), bubbling occurred until the reactants melted completely. Then the pressure reduced to 66 kPa to accelerate the condensation reaction. The reaction was continued at 100 °C for several hours (Table 1; **1a**–**1d**). The reaction was repeated for the preparation of HBPEAAs at different monomer ratio of 1:1:2.5, 1:1.5:2 and 1.5:1:2 (Table 1, **1b**–**1d**). Another batch of HBPEAAs was also prepared with different dicarboxylic acids (AA, SA, PA, and DDDA) by following the monomer ratio of prepolymer **1a** (Table 1; **1e**–**1g**). In addition, two other syntheses of; (a) poly(ester-amine) between TEA and AA; (b) poly(ester-amide) between THAM and AA were conducted (Table 1; **1h**–**1i**). Dimethylformamide (DMF) was used sparingly as solvent to mix THAM with AA for prepolymer, **1i**.

2.2.1. *Prepolymer **1a***

FTIR ($\mathrm{cm^{-1}}$): 3500–3200 (OH); 1718 (C=O); 1557 (COO–); 1655, 1560, 1459 (NHCO); ^{1}**HNMR**, (DMSO-*d6*): 7.44, 7.24, 7.11 (NHCOO); 4.70–5.08 (OH, broad); 3.4 ($\mathrm{N{-}CH_2{-}CH_2{-}OH}$); 2.73–2.76 ($\mathrm{N{-}CH_2{-}CH_2{-}O{-}}$); 4.02–4.05 ($\mathrm{N{-}CH_2{-}CH_2{-}O{-}}$); 2.27–2.3 ($\mathrm{{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COO{-}}$); 4.00–4.30($\mathrm{C(}CH_2\mathrm{O)}n\mathrm{(CH_2OH)_{3-n}}$); 3.30–3.52 ($\mathrm{C(CH_2O)}n(CH_2\mathrm{OH})_{3-n}$); 2.25–2.32 ($\mathrm{OCO}CH_2\ \mathrm{(CH_2)_3{-}CONH}$); 2.02–2.25 ($\mathrm{OCO(CH_2)_3}CH_2\mathrm{CONH}$); 1.30–1.50 ($\mathrm{OCOCH_2{-}}\ (CH_2)\ _2\mathrm{CH_2CONH}$). ^{13}**CNMR**, (DMSO-*d6*): 59.28, ($\mathrm{N{-}CH_2{-}CH_2{-}OH}$); 52.64–53 ($\mathrm{N{-}CH_2{-}CH_2{-}O{-}}$); 62.1–62.14 ($\mathrm{N{-}CH_2{-}CH_2{-}O{-}}$); 33 ($\mathrm{{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}{-}COO{-}}$); 172.54–172.63 (ester carbonyl carbons). 174.58 (COOH); 173.53, 173.10, 172.58 (NHCO); 168.25, 167.38, 166.37 (CH2OCO); 76.18, 74.10, 72.10, 58.47 ($\mathrm{C(CH_2OCO)}n\mathrm{(CH_2OH)_{3-n}}$); 65.91, 65.47, 64.05, 61.14–62.65, 60.77, 60.08, 59.84, 56.31 ($\mathrm{C(CH_2OCO)}n\mathrm{{-}(CH_2OH)_{3-n}}$); 35.56, 35.38 ($\mathrm{OCOCH_2\ (CH_2)_3CONH}$); 33.66, 33.05 (broad, OCO $\mathrm{(CH_2)_3CH_2CONH}$); 27.05, 26.95, 24.87, 24.66, 23.74 ($\mathrm{OCOCH_2(CH_2)_2CH_2CONH}$).

2.3. *Synthesis of 2a (two step temperature)*

AA (0.740 g, 5.02 mmol), THAM (0.305 g, 2.51 mmol) and TEA (0.375 g, 2.51 mmol) were melt condensed in a crystallizing-dish for 10 h under reduced pressure (66 kPa) at 45 °C in a vacuum oven, then the temperature was increased to 100 °C and kept for another 10 h. The final product was analysed.