



Highly biobased thermally-stimulated shape memory copolymeric elastomers derived from lignin and glycerol-adipic acid based hyperbranched prepolymer



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ABSTRACT

Copolymers containing as high levels of bio-derived components were obtained mainly from two industrial byproducts, glycerol and lignin. A series of hyper branched prepolymers (HyBP) were prepared from in the first step by melt condensation of glycerol (Gly, B²B₃²) and adipic acid (AA, A₂) and the prepolymer structure was also modified by the addition of commercially available diisopropanolamine (DIPA, DB⁴₂) and tris(hydroxymethyl) aminomethane (THAM, CB₃¹) units. The HyBP were reacted with lignin to form thermally-stimulated shape memory copolymeric elastomers in the second step in the same pot by melt polycondensation. The prepolymers were characterized chemically by FTIR, NMR, and ESI-MS. Thermal and rheological behaviors were analyzed by DSC, DMA, TGA and dynamic rheometry. The higher branching crosslinkers, DIPA and THAM, were shown to influence the chemical and thermal properties of the prepolymers. The hyperbranched biobased lignin-copolymers demonstrated good shape memory and elastic properties. The shape transition temperature (T_{trans}) could be tuned by variations of Gly, DIPA and THAM proportions for applications under different temperature circumstances. This study demonstrates that renewable Gly and AA based prepolymers could be incorporated into lignin based copolymeric systems with high biobased contents acting as soft segment to perform shape memory effect behavior.

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1. Introduction

Lignin, an underutilized biopolymeric byproduct from both the pulping (about 5×10^{10} kg produced in 2004) and cellulosic ethanol industries, shows potential as a substrate for producing bioplastic materials because being abundant in supply and hydroxyl functional groups present for substitution (Zakzeski et al., 2010). Lignin's utilization is impaired by its high glass transition temperature (T_g) and brittleness due to its rigid aromatic backbone, high intra/inter hydrogen bonding, and heterogeneity (Yoshida et al., 1987). Applications for lignin has been to incorporate it as a filler (Mousavioun et al., 2013), extender or as a reinforcing pigment in rubber (Wang et al., 1992) and in thermoset resins (Feldman, 2002). Another alternative to endow thermoplasticity properties to lignin has been conducted by various chemical modifications, such as alkylation (Li and Sarkanen, 2002), benzoylation (McDonald and Ma, 2012), and oxypropylation (Cui et al., 2013; Li and Ragauskas, 2012; Sadeghifar et al., 2012; Wu and Glasser, 1984), which inhibits

hydrogen bonding and thus lower's its T_g and more processable. More recent work has been using lignin as a hard segment in the preparation of highly and hyper branched smart elastomeric copolymers with tunable shape memory properties (Li et al., 2015; Sivasankarapillai and McDonald, 2011; Sivasankarapillai et al., 2012). The properties were easily tailored by changing the prepolymer branching structure and lignin content.

Highly branched, or hyperbranched, polymers (HyBP) are attractive types of dendritic polymers due to their high branching structures, less tedious preparations, as well as affordable up-scale pathways (Gao and Yan 2004; Hult et al., 1999; Muscat and van Benthem, 2001; Sivasankarapillai et al., 2012; Voit and Lederer, 2009). The term "hyperbranched polymers" was first introduced in 1988 to describe the structure of an imperfect dendrimer by preparation of polyphenylenes with AB_x type monomers (Kim and Webster, 1988). HyBP based on polyesters were then become increasingly attractive due to incorporating commercial availability of monomers with more diverse functionalities (e.g., symmetric diacid (A₂) and trihydroxy (B₃)) and ease of preparation by standard melt polycondensation methodology (Muscat and van Benthem, 2001). Combinations of various branched structures were involved such as A₂, B₃ and trihydroxy-monoamino

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(CB₃¹) monomer units to increase the structural diversity from branched to HyBP (Sivasankarapillai et al., 2012). The key of this approach is the employment of multifunctional monomers with suitable unequal reactivity, where both B and C can react with an A group, as a result, hyperbranched poly(ester-amide)s with amine cores and amide linkages can be formed (Li et al., 2004, 2005, 2006; Sivasankarapillai et al., 2012). Furthermore, a series of lignin HyBP-copolymers have been produced by melt condensation with lignin using the monomers: adipic acid (AA, A₂), triethanolamine (TEA, B₃) and tris(hydroxymethyl) aminomethane (THAM, CB₃¹). The advantage of this system was that TEA acted as the reaction solvent and catalyst, and THAM introduced the amide linkage and increased the complexity of the structure. In addition, these lignin HyBP copolymers showed interesting thermal properties and elasticity (Sivasankarapillai and McDonald, 2011; Sivasankarapillai et al., 2012).

The global biodiesel production by 2016 is estimated as 1.4×10^{11} L according to the report, which leads to approximately 1.5×10^{10} L of crude glycerol (Gly) available as a byproduct for utilization into biobased products (Anand and Saxena, 2012; Yang et al., 2012). Gly with trihydroxy functionality, consequently, makes it a sustainable alternative crosslinker for synthesis of HyBPs. Other benefits of Gly are that it can act as a solvent and has a high boiling point. Gly based HyBPs have been synthesized as early as 1929 (Kienle and Hovey, 1929). Stumbe and Bruchmann first synthesized HBP with Gly and AA using a tin catalyst at 150 °C (Stumbe and Bruchmann, 2004). An alternative to tin based catalysts, Kulshrestha et al. (2005) produced glycerol copolyesters using a lipase catalyst to control branching and molar mass. Wyatt et al. (2006) synthesized a series of Gly based highly branched oligomers for use in coatings (Wyatt et al., 2006a,b, 2011). More complex polymers based on poly(oleic diacid-co-glycerol) have been synthesized by Yang et al. (2011). In polyurethanes, Gly is also utilized as a polyol cross-linker (Chun et al., 2007).

AA is a high volume (2.6×10^9 kg) commodity chemical traditionally produced from petrochemicals, primarily used in nylon 66, is now being produced via several bio-based routes (De Guzman, 2010). One commercial approach by Verdezyne has been to convert vegetable or coconut oil to AA (Beardslee and Picataggio, 2012). An alternate process by Rennova has been to oxidize glucose to gluconic acid, which is then hydrogenated to AA. These new technologies clearly show a need for biobased building blocks.

Therefore, the aim of this study was to develop a new series of hyper branched prepolymers based on bio-derived Gly and AA by a simple approach with addition of different crosslinkers such as diisopropanolamine (DIPA, DB₂) or THAM (CB₃¹) to evaluate their effect on properties. Corresponding high biobased-content lignin copolymers were synthesized based on these prepolymers. The effect of prepolymer composition on thermal, mechanical, and shape memory effect (SME) properties of the prepolymers and lignin copolymers were investigated.

2. Materials and methods

2.1. Materials

Protobind 1000 soda lignin was supplied by ALM India Pvt., Ltd. The methanol soluble fraction of the soda lignin was used for copolymer synthesis because of its low T_g and good dispersability in the prepolymer (lignin content = 93.3%, M_w = 958 g/mol (ESI-MS), aromatic/aliphatic hydroxyl group ratio = 0.93, T_g = 132 °C (DSC)) (Li and McDonald, 2014; Li et al., 2015). Glycerol (Gly), tris(hydroxymethyl) aminomethane (THAM), diisopropanolamine (DIPA), adipic acid (AA), methanol and tetrahydrofuran (THF) were obtained from Acros Organics and used as received.

2.2. Methods

2.2.1. Synthesis of hyperbranched prepolyesters G1 and G2

A mixture of Gly (2.30 g, 24.98 mmol) and AA (6.00 g, 41.06 mmol) with mole ratio of total OH to COOH 1:1.1 was prepared in a beaker (50 mm dia), then the beaker was placed in a preheated vacuum oven (100 °C), and a vacuum of 495 mm Hg was applied to avoid monomer loss for 30 min. Then the temperature and vacuum were raised to 150 °C and 120 mm Hg, respectively, for 3.5 h to afford the prepolymer G1. The prepolymer G2 was prepared as described above with Gly (1.68 g, 18.24 mmol) and AA (6.00 g, 41.06 mmol) with mole ratio of total OH to COOH of 1:1.5. The final G1 and G2 prepolymers were white highly viscous liquids at room temperature and soluble in common organic solvent such as methanol, acetone, and THF.

Yield: G1 = 86.6% and G2 = 86.5%; IR (ATR, cm^{-1}): ν = 3500–3100 (vb; $\nu(\text{OH stretching})$), 2923 (s; $\nu_{\text{as}}(\text{CH}_2)$), 2853 (s; $\nu_{\text{s}}(\text{CH}_2)$), 2500 (vb; (OH of COOH)), 1730 (vs; (C=O from ester)), 1712 and 1696 (C=O of COOH), 1455 (w, (CH₂)), 1393 (w; (OH)), 1169 and 1140 cm^{-1} (vs; (COO in ester)); ¹H NMR (500 MHz, DMSO-*d*₆, δ): 11.97 (s, COOH), 5.18 (m, CH(OCO)(CH₂OCO)₂), 4.94 (m, CH(OCO)(CH₂OCO)(CH₂OH)), 4.24 and 4.14 (dd, CH(OCO)(CH₂OCO)₂), 4.24 and 4.12 (dd, CH(OCO)(CH₂OCO)(CH₂OH)), 3.98 (t, CH(OH)(CH₂OCO)₂), 4.10 and 3.92 (dd, CH(OH)(CH₂OCO)(CH₂OH)), 3.86 (t, CH(OH)(CH₂OCO)₂), 3.63 (m, CH(OH)(CH₂OCO)(CH₂OH)), 3.49 (dd, CH(OCO)(CH₂OCO)(CH₂OH)), 3.33 (m, CH(OH)(CH₂OCO)(CH₂OH)), 2.50 (p, DMSO-*d*₆), 2.31 (m, OOCCH₂CH₂), 2.20 (m, HOOCCH₂CH₂), 1.50–1.53 (m, OOCCH₂(CH₂)₂CH₂COO); ¹³C NMR (125.76 MHz, DMSO-*d*₆, δ): 174.19–174.27 (COOH), 172.03–172.60 (COO), 71.94 (CH(OCO)(CH₂OCO)(CH₂OH)), 69.29 (CH(OH)(CH₂OCO)(CH₂OH)), 68.76 (CH(OCO)(CH₂OCO)₂), 66.16 (CH(OH)(CH₂OCO)₂), 65.54 (CH(OH)(CH₂OCO)(CH₂OH)), 64.81 (CH(OH)(CH₂OCO)₂), 62.64 (CH(OH)(CH₂OCO)(CH₂OH)), 62.30 (CH(OCO)(CH₂OCO)(CH₂OH)), 61.81 (CH(OCO)(CH₂OCO)₂), 59.51 (CH(OCO)(CH₂OCO)(CH₂OH)), 32.84–33.37 (OOCCH₂CH₂ and HOOCCH₂CH₂), 23.65–24.02 (OOCCH₂(CH₂)₂CH₂COO).

2.2.2. Synthesis of hyperbranched prepoly(ester-amide)s D1–D4

The prepolymer D1 was prepared from a mixture of Gly (3.00 g, 32.58 mmol), DIPA (1.08 g, 8.11 mmol) and AA (9.57 g, 65.49 mmol) with mole ratio of total OH and NH to COOH 1:1.1 in a beaker (50 mm dia), then the beaker was placed in a preheated vacuum oven (100 °C), and a vacuum of 495 mm Hg was applied to avoid monomers loss for 30 min. Then the temperature and vacuum were raised to 150 °C and 120 mm Hg, respectively, for 3.5 h. The prepolymers D2–D4 were prepared as described above with: D2 (Gly (2.00 g, 21.72 mmol), DIPA (1.45 g, 10.89 mmol) and AA (7.86 g, 53.78 mmol); D3 (Gly (2.00 g, 21.72 mmol), DIPA (2.17 g, 16.29 mmol) and AA (9.16 g, 62.68 mmol)); and D4 (Gly (2.00 g, 21.72 mmol), DIPA (2.89 g, 21.72 mmol) and AA (9.16 g, 71.64 mmol)), with mole ratio of total OH to COOH of 1:1.1. The final D1–D4 prepolymers were yellowish highly viscous liquid at room temperature and soluble in methanol, acetone, and THF.

Yield: D1–D4 = 91.4, 88.6, 89.6, and 90.5%, respectively; IR (ATR, cm^{-1}): ν = 3500–3200 (vb; $\nu(\text{OH stretching})$), 2923 (vs; $\nu_{\text{as}}(\text{CH}_2)$), 2853 (vs; $\nu_{\text{s}}(\text{CH}_2)$), 2500 (vb; (OH of COOH)), 1730 (vs; (C=O from ester)), 1712 and 1696 (C=O of COOH), 1620 (vs; (C=O from tertiary amide)), 1455 (w, (CH₂)), 1391 (w; (OH)), 1169 and 1140 cm^{-1} (vs; (COO in ester)); ¹H NMR (500 MHz, DMSO-*d*₆, δ): 5.18 (m, CH(OCO)(CH₂OCO)₂), 5.05, 3.76–3.92 (m, NCH₂CH(O)(CH₃)), 4.94 (m, CH(OCO)(CH₂OCO)(CH₂OH)), 4.73 (m, CH(OCO)(CH₂OH)₂), 4.24 and 4.14 (dd, CH(OCO)(CH₂OCO)₂), 4.24 and 4.12 (dd, CH(OCO)(CH₂OCO)(CH₂OH)), 3.98 (t, CH(OH)(CH₂OCO)₂), 4.10 and 3.92 (dd, CH(OH)(CH₂OCO)(CH₂OH)), 3.86 (t, CH(OH)(CH₂OCO)₂), 3.63 (m, CH(OH)(CH₂OCO)(CH₂OH)), 3.49 (dd,

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