

Lignin Valorization by Forming Thermally Stimulated Shape Memory Copolymeric Elastomers—Partially Crystalline Hyperbranched Polymer as Crosslinks

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ABSTRACT: Lignin based thermal-responsive elastomers were produced by a melt polycondensation reaction with a long alkyl chain hyperbranched poly(ester-amine-amide) ($B_3-A_2-CB_3^1$). The effect of lignin content on elastomers properties was investigated. The thermal and mechanical properties of the copolymers were characterized by DMA, DSC, and TGA. The morphology of the copolymer was examined by SEM. Tensile properties were dominated by HBP <25% lignin content while lignin dominated >25% content. The copolymers glass transition temperature (T_g) increased with lignin content. The elastomer with 30% lignin content demonstrated optimal mechanical properties (tensile strength 5.3 MPa, Young's modulus 8.9 MPa, strain at break 301%, and toughness 1.03 GPa). Thermally stimulated dual shape memory effects (SME) of the copolymers were quantified by cyclic thermomechanical tests. The transition temperature (T_{trans}) of the polymer was able to be controlled (room to body temperature) by varying the amount of lignin added which broadens the range to medical applications. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41103.

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INTRODUCTION

Lignin is an underutilized biopolymer byproduct from both the pulping (about 5×10^{10} kg produced in 2004) and cellulosic ethanol industries and shows potential as a substrate for producing bioplastic materials.¹ Lignin's utilization is hampered by its high glass transition temperature (T_g) and brittleness due to its high intra/inter H-bonding. Applications for lignin has been to incorporate it as a filler, extender or as a reinforcing pigment in rubber² and in thermoset resins.³ Another approach to alter lignin brittleness has been to chemically modify lignin, by either alkylation,⁴ benzylation,⁵ or oxypropylation,⁶⁻⁹ which inhibits intramolecular H-bonding and thus lowers its T_g . More recent work has been using lignin as a hard segment in the preparation of highly and hyper branched elastomeric copolymers with tunable properties.¹⁰⁻¹² The properties were easily tuned by changing the copolymer structure and lignin content.

Hyperbranched polymers (HBP) are an attractive type of dendritic polymer due to its high branching density and structure.¹³ HBP based on polyesters are attractive due to the availability of monomers (e.g., symmetric diacid (A_2) and trihydroxy (B_3)) and ease of preparation by polycondensation. To

increase the structural diversity of the HBP combinations of various branched structures are required such as A_2 , B_3 and trihydroxy-monoamino (CB_3^1) monomer units. 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 polyesters with amine cores and amide linkages can be formed.^{12,14-16} A series of lignin HBP-copolymer have been formed by melt condensation using the monomers: adipic acid (A_2), triethanolamine (TEA, B_3) and tris(hydroxymethyl)aminomethane (THAM, CB_3^1). 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. Furthermore, these lignin HBP copolymers showed interesting thermal properties and elasticity.^{11,12}

Dodecanedioic acid (DDDA) is a C_{12} diacid which has been extensively applied to polymer synthesis with superior thermal and mechanical properties. Furthermore, DDDA was also involved medical polymer synthesis because of its solubility in water, low acidity and being biocompatible.^{17,18} Barbiroli et al. synthesized a series polyethylene-like polymers with DDDA and different alkyl chain diols and were shown to have melting and

crystalline behavior.¹⁹ Nagata produced polyesteramines based on TEA and different alkyl-chain length diacids including DDDA.²⁰ The polyesteramines made with DDDA showed a T_g at -34°C and melting temperature (T_m) at 13°C . Melting peaks were also found in HBP based on diacid-TEA which demonstrated a crystalline surface and amorphous interior.^{11,12}

Based on previous research,¹² we hypothesize that the hyperbranched prepolymer, based on using the diacid DDDA (as a soft segment), when copolymerized with lignin (as the rigid netpoint segment) will have a good elasticity and shape memory properties. This current study, will investigate the elastomers from copolymerization of DDDA-based hyperbranched prepolymer with lignin. The effect of lignin content on thermal, mechanical, and shape memory effect (SME) properties of elastomers were studied.

MATERIALS AND METHODS

Materials

Protobind 1000 soda lignin was supplied by ALM India. The methanol soluble fraction of the soda lignin was used for copolymer synthesis (lignin content = 93.3%, $M_w = 958 \text{ g mol}^{-1}$ (ESI-MS), aromatic/aliphatic hydroxyl group ratio = 0.93, $T_g = 138^\circ\text{C}$ (MTDSC)).¹⁰ TEA, THAM, DDDA, methanol, and tetrahydrofuran (THF) were obtained from Acros Organics and used as received.

Methods

Synthesis of Hyperbranched Prepoly(ester-amine-amide) (D1).

The synthetic method was described in our previous work.¹⁰ The mixture of TEA (2.98 g, 0.02 mol), THAM (2.42 g, 0.02 mol), and DDDA (9.21g, 0.04 mol) with mole ratio 1 : 1 : 2 was prepared in a beaker (50 mm dia), then the beaker was placed in a preheated vacuum oven. The polycondensation reaction was controlled to below 650 mmHg at 100°C for 13 h. The D1 prepolymer was a yellow-pale solid at room temperature.

Yield: 95%; IR (ATR, cm^{-1}): $\nu = 3500\text{--}3200$ (vb; $\nu(\text{OH stretching})$), 2923 (vs; $\nu_{\text{as}}(\text{CH}_2)$), 2853 (vs; $\nu_s(\text{CH}_2)$), 2500 (vb; (OH of COOH)), 1730 (vs; (C=O from ester)), 1651 (vs; (C=O from amide)), 1555 (b; (N—H and COO⁻)), 1455 (w, (CH₂)), 1391 (w; (OH)), 1169 and 1140 cm^{-1} (vs; (COO in ester)); ¹H NMR (500 MHz, DMSO-*d*₆, δ): 7.44, 7.24, and 7.11 (s, NHCOO), 4.00–4.06 (m, NCH₂CH₂O), 3.49–3.62 (m, C(CH₂)₃O), 3.39–3.46 (m, NCH₂CH₂OH), 2.72–2.79 (m, NCH₂CH₂O), 2.56–2.63 (m, NCH₂CH₂OH), 2.50 (p, DMSO-*d*₆), 2.25–2.31 (m, OOCCH₂CH₂), 2.17–2.23 (m, HOOCCH₂CH₂), 1.45–1.57 (m, OOCCH₂(CH₂)₈CH₂COO); ¹³C NMR (125.76 MHz, DMSO-*d*₆, δ): 174.79 (COOH), 173.86, 173.38 (NHCOO), 172.83, 172.61, 166.44 (CH₂OCO), 76.09, 74.19, 71.87, 62.19, 60.28 (C(CH₂OCO)_{*n*}(CH₂OH)_{*3-n*}), 70.40, 70.18, 65.86, 64.08, 61.91, 61.69, 60.88, 60.47, 59.85(C(CH₂OCO)_{*n*}(CH₂OH)_{*3-n*}), 62.16 (NCH₂CH₂O), 59.38, 59.33, and 59.17 (NCH₂CH₂OH), 57.14, 56.96, and 56.74 (NCH₂CH₂OH), 53.04, 52.96 and 52.78 (N-CH₂-CH₂-O), 35.86 (OCOCH₂(CH₂)₈CONH), 34.07 (HOOC-CH₂-CH₂-), 33.51 (OOCCH₂CH₂), 28.84, 28.71, 28.59, 28.44, 24.66, 24.39, (OCOCH₂(CH₂)₈CH₂COO).

Synthesis of Lignin-Copoly(Ester-Amine-Amide) (Lignin-D1-Copolymer). Lignin was dispersed in the minimum amount of THF and mixed with prepolymer D1 proportionally to synthe-

size the lignin-copoly(ester-amineamide) (lignin-D1-copolymer). THF was then removed under a stream of N₂ at 80°C . The highly viscous mixture was then transferred to a prepared aluminum pan ($15 \times 15 \text{ cm}^2$) and was placed into vacuum oven at 80°C and 750 mmHg to remove residual solvent and moisture (about 30 min). Then the reaction temperature was increased to 120°C at 650 mmHg, and the reaction proceeded for 40 h. The final lignin-D1-copolymer displayed a highly bright and glossy surface and was insoluble in organic solvents. The D1 prepolymer was fully polymerized as described above as a control sample (D1 polymer).

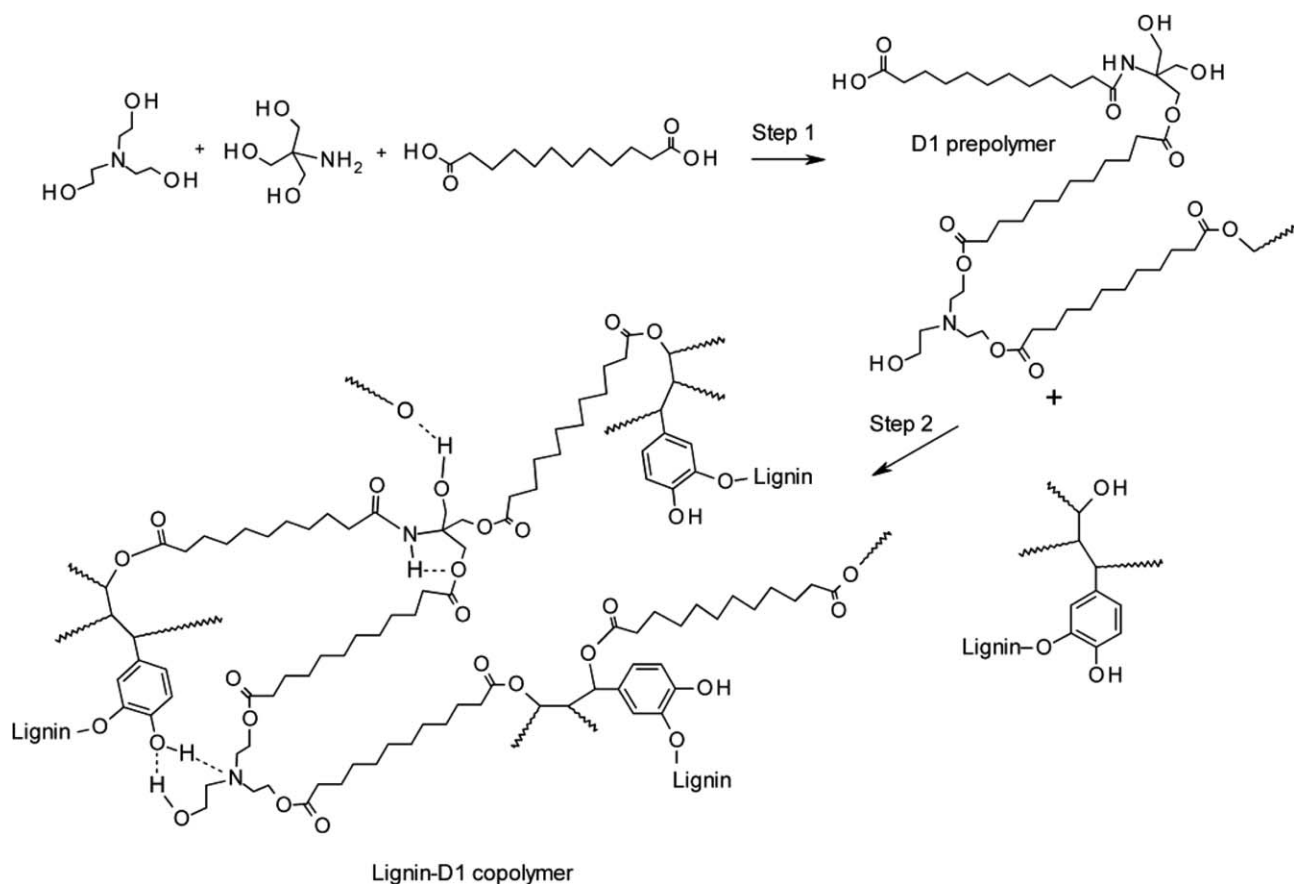
IR (ATR, cm^{-1}): $\nu = 3500\text{--}3200$ (vb; $\nu(\text{OH stretching})$), 2945 (vs; $\nu_{\text{as}}(\text{CH}_2)$), 2870 (vs; $\nu_s(\text{CH}_2)$), 1729 (vs; (C=O from ester)), 1651 (s; (C=O from amide), 1600 (m; aromatic skeletal vibration), 1549 (w; N—H bending), 1511 (m; aromatic skeletal vibration), 1457 (w, (CH₂)), 1419 (w, CH in-plane deformation), 1378 (w, CH₃), 1169 and 1140 cm^{-1} (vs; (COO in ester)).

Characterization Techniques

FTIR and NMR. All Fourier transform infrared (FTIR) spectra were carried out with a Thermo Nicolet Avatar 370 spectrometer operating in the attenuated total reflection (ATR) mode (Smart performance, ZnSe crystal). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on prepolymer D1 and acetylated lignin²¹ on a Bruker Avance 500 spectrometer. Chemical shifts were referenced to DMSO-*d*₆ at 39.5 for ¹³C and 2.50 for ¹H spectra at 30°C .

Electrospray Ionization—MS. Molar mass of the lignin and D1 prepolymer samples were determined by positive ion ESI-MS on a LCQ-Deca instrument (Thermo Quest). Samples were dissolved in methanol (1 mg mL^{-1}) containing 1% acetic acid and introduced into the ESI source at a flow rate of $10 \mu\text{L min}^{-1}$.²² The ion source and capillary voltages were 4.48 kV and 47 V, respectively, at a temperature of 275°C . The MS were scanned between *m/z* (mass to charge ratio) 100 and 2000. The number average molar mass (M_n) was calculated as $M_n = \sum M_i N_i / \sum N_i$ and weight average molar mass (M_w) as $M_w = \sum M_i^2 N_i / \sum M_i N_i$, where M_i and N_i are the *m/z* and intensity of the ions, respectively.²³

Thermal and Mechanical Analysis. Differential scanning calorimetry (DSC) was performed on a TA instruments model Q200 DSC equipped with a refrigeration cooling unit to monitor the thermal behavior of materials. Modulated temperature DSC (MTDSC) mode was applied. The lignin and polymers (5–7 mg) were equilibrated at -50°C for 5 min, then heated by modulated heating $\pm 0.66^\circ\text{C}$ every 50 s, and then ramped from -50 to 180°C at 5°C min^{-1} . The inflection point of heat flow change from reversible heat flow curve was assigned as T_g . Thermogravimetric analysis (TGA) was performed on a TGA-7 (Perkin Elmer) instrument from 50 to 900°C at a heating rate of $20^\circ\text{C min}^{-1}$ in N₂. Dynamic mechanical analysis (DMA) experiments were performed using a TA Instruments model Q800 DMA, both under isothermal and non-isothermal conditions in N₂ atmosphere in the tensile mode ($12 \text{ mm} \times 4 \text{ mm} \times 0.2 \text{ mm}$). The heating scans were carried out at 1 Hz and at a heating rate of 3°C min^{-1} . The tensile properties of the lignin



Scheme 1. Synthesis approach for producing the lignin-D1-copolymer and proposed H-bonding interaction between lignin and prepolymer as well as prepolymer–prepolymer shown in dashed lines.

based elastomers (in triplicate) were measured using DMA at room temperature with ramp 3 N min^{-1} .

The SME of lignin based copolymers were determined in the tensile mode using a DMA. A stress-controlled cycle thermomechanical test was applied. Four programming steps were proceeded, in which the copolymers were: (1) heated to a temperature of $T_g + 20^\circ\text{C}$ (designated as T_{high}) with ramp of 5°C min^{-1} , then set load to 2 N static force with ramp of 0.2 N min^{-1} , the copolymers were stretched to temporary shapes; (2) in the next step, cooled to $T_g - 20^\circ\text{C}$ (ramp 5°C min^{-1}) (designated as T_{low}); and (3) release the static force while keeping at T_{low} , the copolymers kept the temporary shapes; (4) heated up to T_{high} again and kept isothermal for 15 min, the permanent shape recovered again. The same procedure was repeated for three times (cycle 1 to 3). The recovery elasticity of lignin based elastomers also applied the stress-controlled cycle mechanical test at 30°C . In detail, elastomers were stretched to $\sim 100\%$ strain then release the load for 15 min recovery and repeated for four times.

The crosslink density (η) and molar mass between crosslinks (M_c) was determined by eq. (1) referring to the theory of rubber elasticity²⁴:

$$\eta = \frac{E_0}{3RT} = \frac{\rho}{M_c} \quad (1)$$

where η is the number of active network chain segments per unit volume (mol m^{-3}); M_c is the molar mass between cross-

links (g mol^{-1}); E_0 is Young's modulus from tensile strength (Pa); R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the absolute temperature (K); and ρ is polymer density (g m^{-3}) as measured from punched disc samples (3 mm diameter and 2 mm thickness) ($n = 5$).

Morphological Analysis. Field emission scanning electron microscopy (SEM) was performed on a FEI Quanta 200F instrument at 10 kV. The cut cross-sections were dried and sputter coated with gold prior to examination.

RESULTS AND DISCUSSION

Preparation of D1 Prepolymer and Lignin-D1-Copolymers

The prepolymer D1 ($B_3 + A_2 + CB_3$)¹ was prepared according to our previous procedure (Scheme 1).^{10,12}

The diacid, DDDA, was used because of its long alkyl chain length and this can partially crystallize with other DDDA units in the HBP. This will provide additional structural features to the lignin-D1-copolymer and possessed a T_g above room temperature.^{12,20} The amine core with amide linkage endowed a complex structure and strengthened properties. The resulting polymers were slightly yellowish in color and were highly viscous at elevated temperature and solid at room temperature. Ester and secondary amide formation were confirmed by FTIR (1730 , 1651 , and 1555 cm^{-1}) and ^{13}C NMR (173.86 , 173.38 , 172.83 , 172.61 , 166.44 ppm). The carboxylic acid group (174

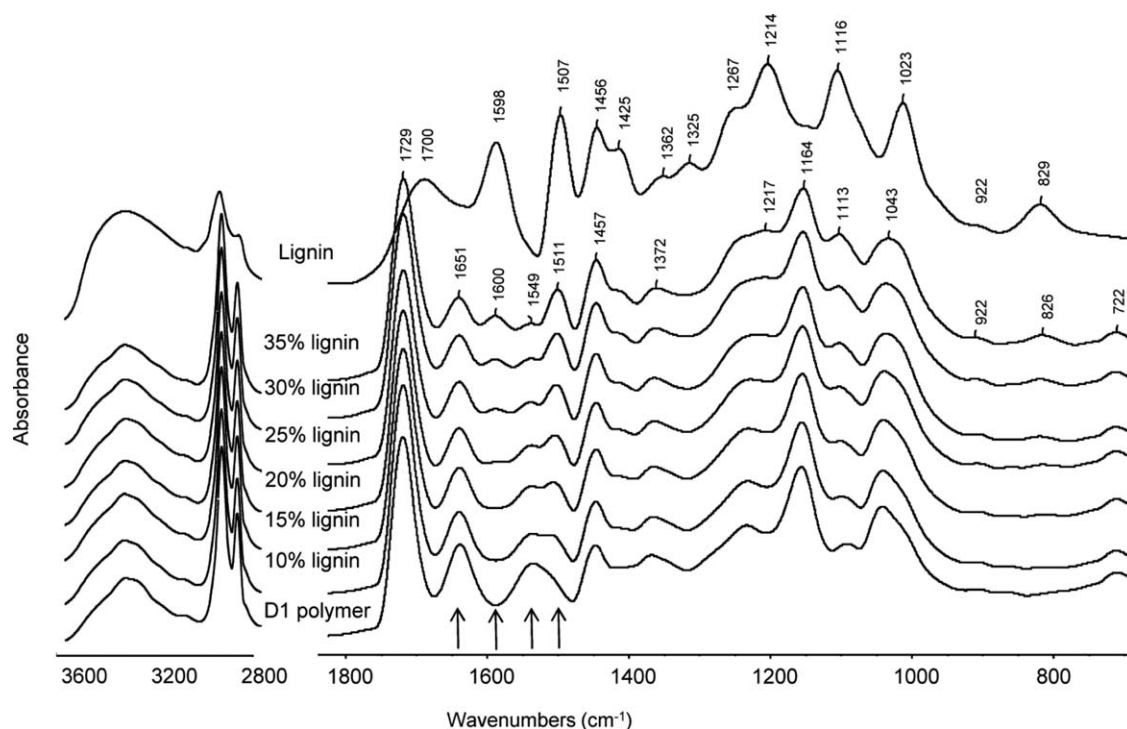


Figure 1. FTIR spectra of lignin, D1 polymer and lignin-D1-copolymers.

ppm) in the D1 prepolymer and the hydroxyl group (3500 cm^{-1}) in lignin were monitored for their depletion during esterification. Furthermore, acid (CH_2COOH 2.20 ppm) conversion to ester ($\text{CH}_2\text{COO-ester}$ 2.30 ppm and $\text{CH}_2\text{CONH-amide}$ 2.17 ppm) could be determined by ^1H NMR and 61% acid groups were available for the subsequent polycondensation, where acid group remaining = $I_{2.20}/(I_{2.20} + I_{2.30} + I_{2.17})$.²⁵ The degree of branching (DB) for the D1 prepolymer was determined by ^1H NMR and chemical shifts at 7.44, 7.24, and 7.11 ppm were assigned to semi-dendritic (sD), linear (L) and terminal (T) structures without dendritic structure, respectively.¹² From these assignments and peak intensity the DB was calculated at 0.256, where $\text{DB} = 2\text{D}/(\text{L} + 2\text{D})$.²⁶ The calculated value revealed a low crosslink occurrence during prepolymerization. The M_w (831 g mol^{-1}) and polydispersity index (1.74) of D1 were determined by ESI-MS. The low M_w obtained was consistent with a low DB.

The synthesis route for the lignin-D1-copolymer was carried out with a two-step one-pot bulk polymerization (melt polycondensation) process (Scheme 1).²⁷ The lignin based elastomer formulation was adjusted by varying lignin content in order to tune properties. In some preliminary work, lignin content $>35\%$ in the copolymer was shown to be brittle and tensile properties could not be determined successfully. Therefore, lignin-D1-copolymers with lignin contents from 0 to 35% were chosen for full evaluation.

The lignin-D1-copolymers, D1 polymer and original lignin were analyzed by FTIR spectroscopy (Figure 1). Ester formation between lignin and D1 prepolymer was supported by the reduction of the OH band ($3600\text{--}3100\text{ cm}^{-1}$) and an increase in the

ester carbonyl band (1729 cm^{-1}). The ester band at 1729 cm^{-1} (normally at 1740 cm^{-1}) was affected by H-bonding between lignin and prepolymer as proposed in Scheme 1.²⁸ As lignin content increased, four functional groups changed dramatically, which involved a reduction of the amide I (1651 cm^{-1}) and amide II (1549 cm^{-1}) bands, as well as an increase of lignin aromatic skeletal vibration bands at 1600 and 1511 cm^{-1} . The reduction of amide bands with an increase in lignin content supports that amide formation was essentially complete during prepolymerization and did not participate with linkage to lignin.²⁹ Furthermore, no band at 1762 cm^{-1} (characteristic of an aromatic carbonyl ester) was observed suggesting that the prepolymer was ester linked with aliphatic hydroxyl groups of lignin (Figure 1).

Mechanical Properties

The tensile properties of lignin copolymers are shown in Figure 2. Generally, the tensile strength and Young's moduli of the lignin copolymers were shown to increase with lignin content. For example, the tensile strength increased from 0.7 to 2.7 MPa when lignin content increased from 0 to 25% then dramatically increased to 7.0 MPa at 35% lignin content. A similar trend was observed for the Young's modulus. The observed phenomena might be explained since lignin is acting as a reinforcing agent thus improving the mechanical properties of the copolymer due to high levels of crosslinking between the rigid lignin structure and prepolymer. The strain at break and toughness (as assessed by the energy at break (EAB)) of the copolymers are shown in Figure 2(b). All the lignin copolymers showed excellent strain at break values due to the presence of the long chains of DDDA in the prepolymer. The copolymer strain at break and EAB reached

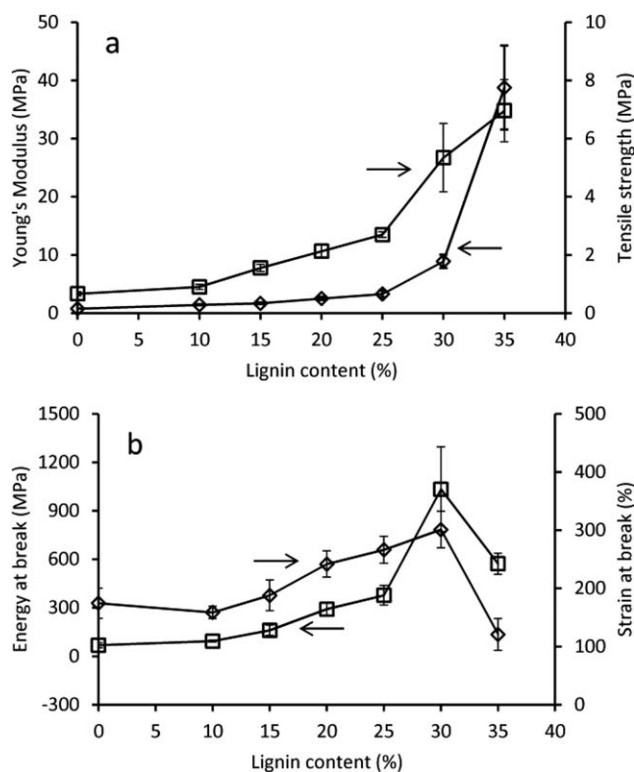


Figure 2. Tensile properties of lignin-D1-copolymers.

values of 301% and 1.03 GPa, respectively, at a lignin content of 30%. However, at 35% lignin content both the strain at break and EAB decreased indicating that the lignin was contributing to its brittleness. Therefore, the optimal lignin content in the copolymers for good elastomeric properties was 30%.

Thermal Properties

Thermal properties of the lignin copolymers were characterized by MTDSC and DMA (Figure 3). The D1 polymer has a T_g of 4.4°C and a sharp melting peak at 18.5°C which had been observed in previous reports.^{11,12,20} A sharp endothermic melting peak was due to the crystallization of the methylene units in long diacid chains.²⁰ The melting peak decreased considerably as lignin content increased and disappeared above 20% lignin content. This result can be explained since the amorphous nature of lignin is intertwined with the D1 matrix and interrupted the long chain crystalline state. The T_g is a second-order phase transition of an amorphous polymer which not only confines its threshold in engineering applications and determine the shape memory effect of smart polymers.^{30,31} The determination of T_g of the lignin copolymers was quantified by reversible heat flow of MTDSC and DMA from the maxima of the E'' peak [Figure 3(b)]. All the lignin copolymers demonstrated an appreciably low and single T_g although lignin itself has a high T_g (138°C). These results indicate the dominating effect of the D1 structure and the excellent miscibility between lignin and D1 over the lignin content range studied. Little T_g variations were found (5.3 to 7.7°C) below 30% lignin content by DMA. However, above 30% lignin the T_g increased to a maximum of 16.8°C at 35%. The MTDSC results of the lignin copolymers also showed similar trend but displayed relative lower T_g values than those from DMA.^{32,33}

Crosslink Properties

The condensation reaction between the HBP D1 and lignin at different ratios will influence crosslink density (η , active network chain segments per unit volume) and therefore polymer properties. Thus varying degree of cross-linking shows promise to tailor polymer properties. The T_g of polymers can be increased by increasing cross-link density.³⁴ Density (ρ), η , and molar mass between crosslinks (M_c) were determined according to eq. (1) and results are shown in Figure 2. The ρ of lignin copolymers was shown to range from 1.13 to 1.25 g cm⁻³ which are in the region of commercial elastomers.³⁵ The η for the lignin copolymers showed a dramatic increase from 104 mol m⁻³ for the control D1 polymer to 5182 mol m⁻³ for the lignin-D1-copolymer at 35% lignin content. In contrast, the polymer M_c was shown to decrease from 10,800 g mol⁻¹ for the D1 polymer to 226 g mol⁻¹ for the lignin-D1-copolymer at 35% lignin. The results indicate that reacting lignin with the D1 prepolymer matrix led to crosslinked copolymers. High correlation between η and T_g from E'' were achieved as shown in Figure 4(c) indicating positive relations between the two parameters. Furthermore, reacting lignin with the D1 prepolymer matrix forms a tightly packed network structure and improved tensile and thermal properties as discussed above.

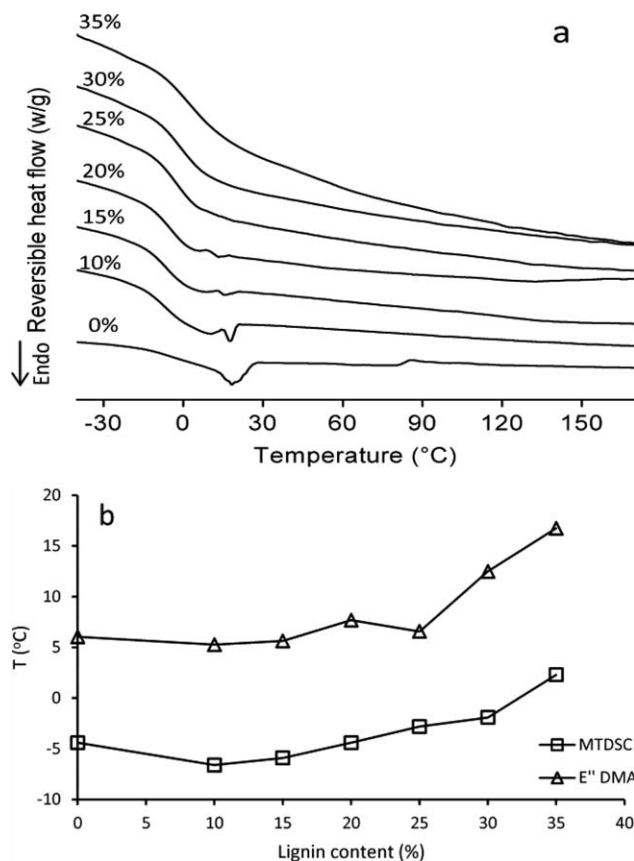


Figure 3. (a) MTDSC thermograms of lignin-D1 copolymers showing the reversible heat flow, and (b) T_g values of lignin-D1-copolymers from E'' of DMA and MTDSC.

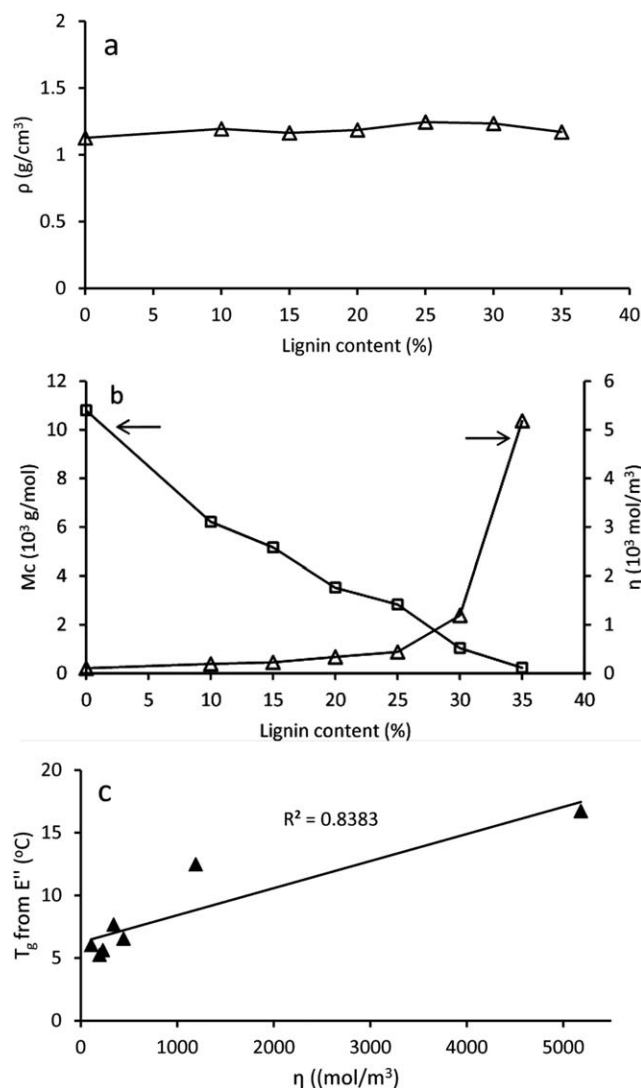


Figure 4. Bulk density (ρ) (a), crosslink density (η) and molecular weight between crosslinks (M_c) (b), and correlation between η and T_g (c) of lignin-D1-copolymers.

Thermal Stability

The thermal stability of the lignin copolymers was studied by TGA. Three stages of decomposition were observed by TGA for all lignin copolymers (Table I and Figure 5). To observe decomposition transitions differential TGA (DTG) was also performed (Figure 5). The first stage was between 170 and 380°C. The second stage was between 380 and 500°C. The third stage was between 500 and 650°C. The first and second stages are most likely assigned to the D1 component of the copolymer since these are constituted with highly branched aliphatic chains with labile ester linkages,^{36,37} although side chain of lignin also participated the decomposition (Figure 5). The long DDDA chains in D1 likely forms crystalline zones in the copolymer and will decompose at temperature range from 420 to 480°C (2nd stage herein).³⁸ The 3rd stage of decomposition is most likely due to the lignin component of the copolymer because of its highly crosslinked aromatic structure to form appreciable amount of char.³⁹ Lignin content affected the 3rd stage decomposition residual mass such as 23.5%

mass remaining at 580°C with a copolymer lignin content of 35%. Two DTG peaks (490 and 615°C) were observed in copolymers and assigned to D1 and lignin components, respectively.

Thermal-Stimulated Shape Memory Effect (T_s -SME)

Thermally stimulated shape memory effect (T_s -SME) can be obtained in a polymer system which contains two kinds of segments, i.e., soft segment controlling temporary shape and net-point segment determining permanent shape.³⁵ Our previous research has shown the development of a series of lignin-copolymers with T_s -SME properties, where a short chain diacid highly branched polyesteramine prepolymer functioned as the soft segment and lignin as the netpoints segment.¹⁰ Following this concept, we further modified the soft segment to be semi-crystalline by using a long chain diacid (DDDA) in the hyper-branched prepolymer. The shape memory properties of the lignin-D1-copolymers (with 15, 25 and 35% lignin contents) were quantified by stress-controlled cyclic thermomechanical testing. Figure 7(a) shows the result of cyclic thermomechanical testing of lignin-D1-copolymer with 15% lignin content. The shape memory recovery ratio (R_r) and fixity ratio (R_f) were calculated from the test data according to the following equations³²:

$$R_r(N) = \frac{\varepsilon_l(N) - \varepsilon_p(N)}{\varepsilon_l(N) - \varepsilon_p(N-1)} \times 100\% \quad (2)$$

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_l(N)} \times 100\% \quad (3)$$

where $R_r(N)$ is the shape recovery ratio at N th cycle, $R_f(N)$ is the shape fixity ratio at N th cycle, N is cycle number from 1 to 3, $\varepsilon_l(N)$ is the maximum strain with load, $\varepsilon_u(N)$ is the tensile strain after unloading at T_{low} , $\varepsilon_p(N-1)$ and $\varepsilon_p(N)$ are the recovered strain in two successive cycles in the stress-free state before exertion of yield stress at T_{high} . The results were an average of three cycles. The same training effect was observed and attributed to the occurrence of some chain relaxation during the first mechanical cycle, leading to a deviation in the later cycles.^{10,40,41} R_f describes the ability to fix the mechanical deformation under T_{low} , while R_r quantifies how well the shape recovers in the N th cycle (for $N > 1$) in terms of the recovered shape of the previous ($N-1$)th cycle.⁴² The results of R_r and R_f of lignin-D1 copolymers are shown in Figure 6(a). All measured copolymers demonstrated relative low R_f from 81 to 88%. Decreasing R_r values were observed from 98 to 83% as lignin content increased. R_f and R_r values for the lignin copolymer (at a lignin content of 35%) were >95% and was comparable to other lignin based elastomers.¹⁰ T_{trans} is another important parameter of T_s -SME polymers and was determined since this is the temperature at which the polymer can be switched back to its original shape upon removal of external stimuli and measured as first derivative peak of the strain versus temperature plot. The T_{trans} of lignin copolymers as a function of lignin content is shown in Figure 6(a). T_{trans} was shown to increase from 24 to 36°C by increasing lignin content from 15 to 35%. These results show that T_{trans} can be tuned by varying lignin content. An interesting point to mention is that T_{trans} of 36°C is close to mammalian body temperature and these polymers have the potential to be used in medical applications

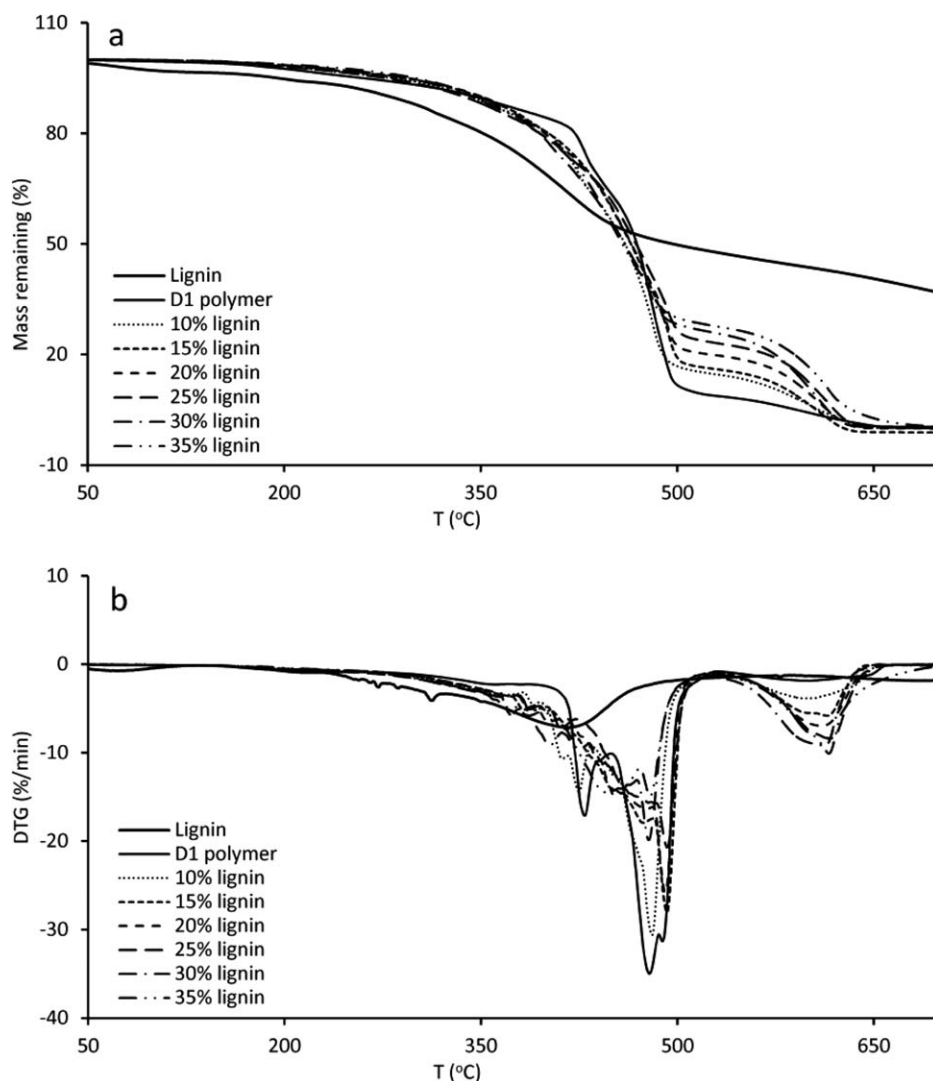


Figure 5. TGA (a) and DTG (b) thermograms of lignin, D1 polymer and lignin-D1 copolymers.

and/or consumer products.⁴³ Furthermore, shape recovery time (R_t), the time that takes for a SMP to reach its recoverable strain under free strain recovery at T_{high} ,⁴⁴ was measured by the time between two onsets for each cycle as shown in Figure 7(b). R_t increases from 7.4 min to 16.1 min as lignin content increases from 15 to 35% [Figure 6(b)].

To further measure the elasticity of the lignin copolymers, cyclic tests ($n = 4$) were carried out to determine the recovery rate $R_{r,e}$ [Figure 7(b)] using eq. (2). The lignin copolymers all demonstrated excellent $R_{r,e}$ (>90%) values [Figure 6(c)]. Furthermore, the more lignin added in the copolymer system, the lower the $R_{r,e}$ will be achieved (from 100 to 92%).

Table I. Thermal Decomposition of Lignin Based Long Chain Elastomers

Lignin content (%)	1st stage		2nd stage		3rd stage		Max peaks (°C)
	T (°C)	Remaining mass (%)	T (°C)	Remaining mass (%)	T (°C)	Remaining mass (%)	
0	422	82.0	496	11.2	565	7.2	480
10	408	81.2	489	16.8	575	11.1	480, 600
15	409	80.9	499	17.5	576	12.8	491, 613
20	366	90.0	498	21.2	580	16.2	490, 612
25	360	88.5	500	25.0	583	19.1	492, 616
30	379	87.5	487	29.3	572	21.8	477, 615
35	359	90.1	491	30.3	581	23.5	479, 616

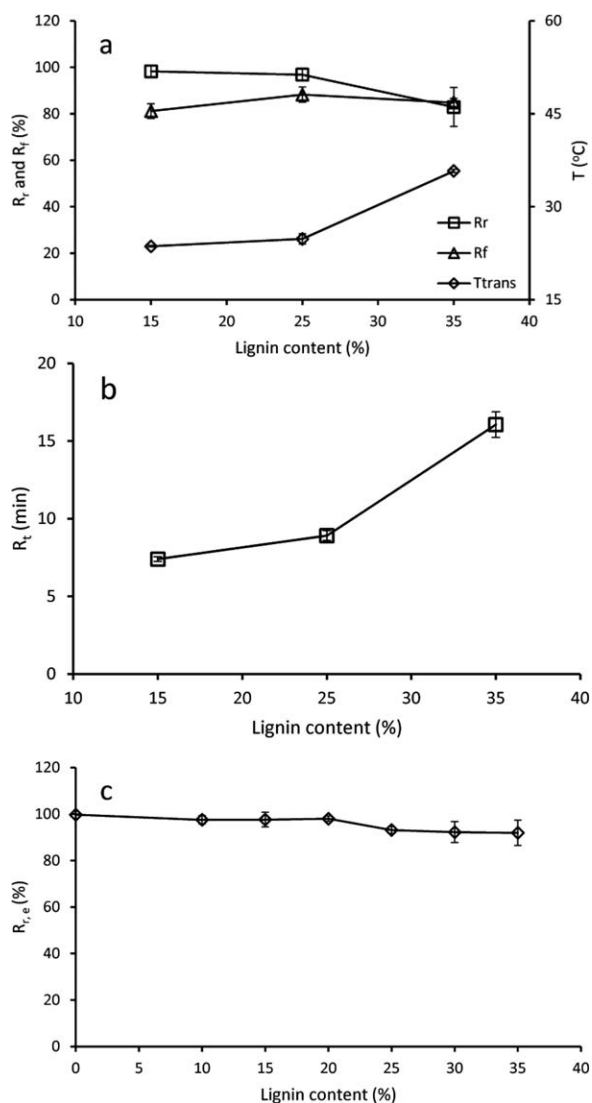


Figure 6. (a) Shape recovery (R_r), shape fixity (R_f) and T_{trans} of T_s -SME lignin-D1-copolymers determined by cyclic thermomechanical testing, (b) Recovery time (R_t) under free strain recovery at T_{high} , and (c) Elasticity recovery ($R_{r,e}$) determined at 30°C.

Morphological Properties

The lignin-D1-copolymer morphology of cross-cut sections was examined by SEM (Figure 8). Good miscibility between lignin and D1 polymer was observed for all copolymers which was consistent with the results of single T_g from DSC and single peak of E' from DMA. At lignin contents between 0 and 30% a smooth cut surface was observed in the lignin-copolymers. As the lignin content increased (>35%) in the lignin-D1-copolymers the level of surface crazing increased. These observations could explain that as lignin content increased, the copolymers became more rigid, therefore, more fracture crazing was observed in the samples. An extreme example can be observed in the copolymer with 45% lignin content, which was very brittle, where high amounts of fracture were found.

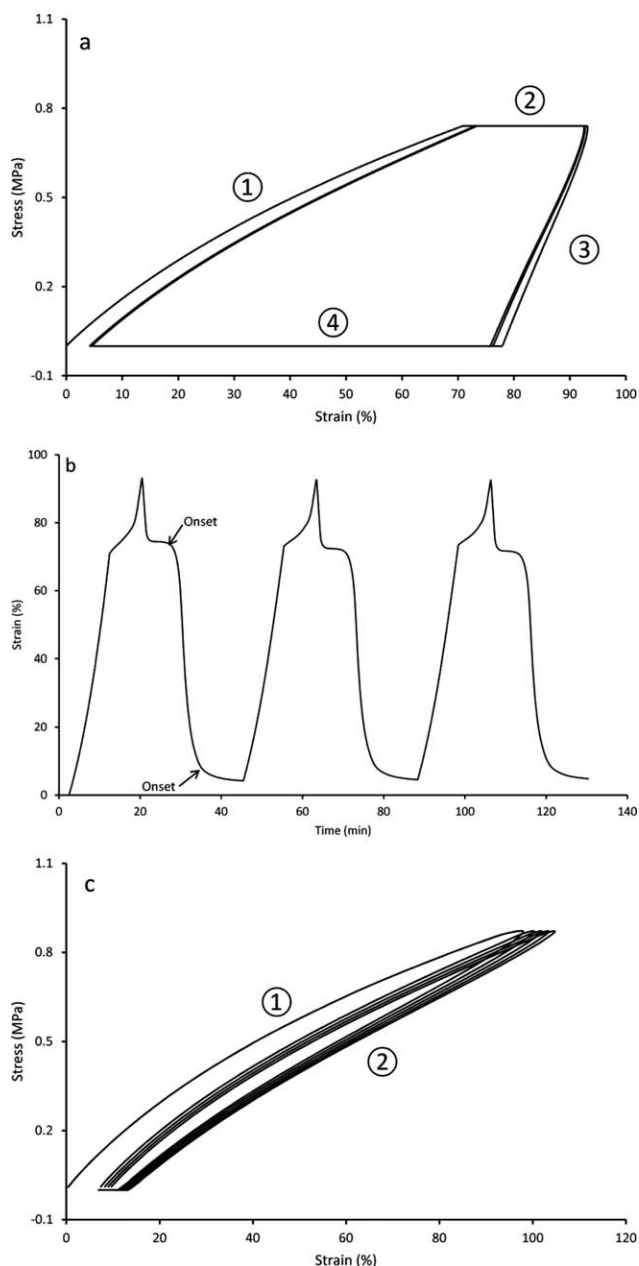


Figure 7. Cyclic thermomechanical testing of lignin-D1-copolymer (15% lignin content) showing (a) T_s -SME behavior (Four steps: 1, Stretching at T_{high} , 2, keep load at T_{low} , 3, unload at T_{low} , and 4, recovery at T_{high}), (b) T_s -SME behavior of strain versus time, where R_t was determined as time between two onsets in each cycle by TA Universal Analysis 2000 software, and (c) elasticity recovery behavior at 30°C (Two steps: 1, stretching at 30°C, and 2, unload and recovery at 30°C).

CONCLUSIONS

Lignin-copolymers with elastomeric properties were successfully developed using a long alkyl chain (C_{12}) hyperbranched prepoly(ester-amine-amide) in a one-pot two-step bulk polycondensation reaction. Lignin-copolymer properties (tensile, thermal, and thermomechanical) were able to be tuned by variation of lignin content. The introduction of C_{12} diacid units in the hyperbranched prepolymer improved the polymer elasticity

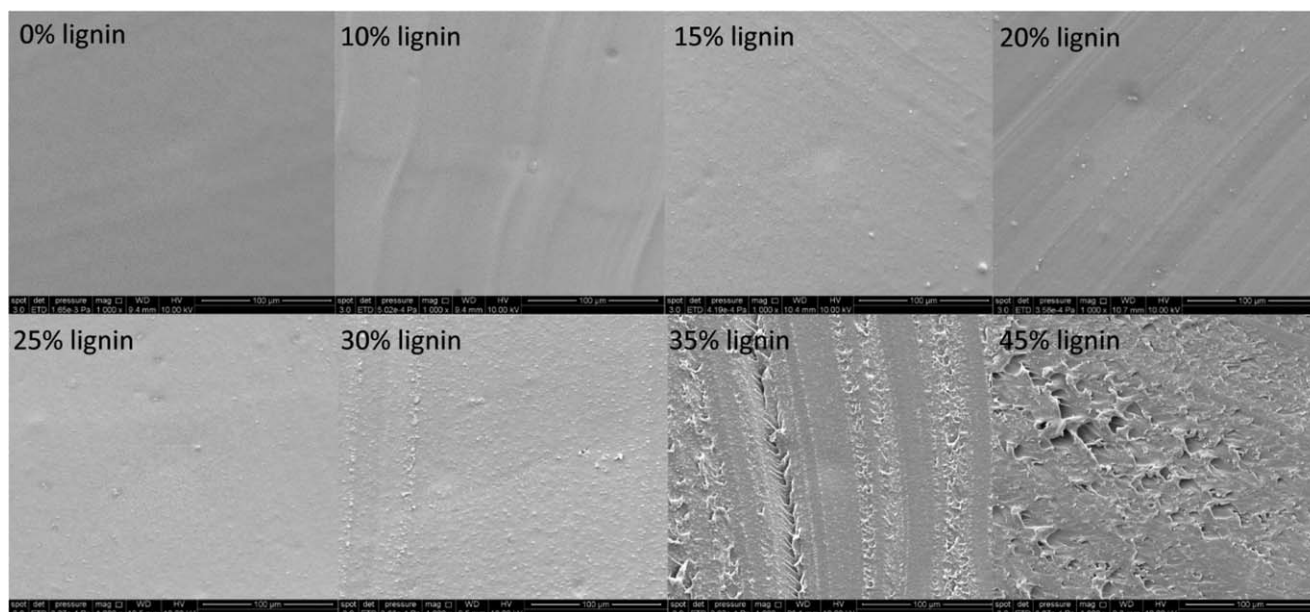


Figure 8. SEM micrographs of cut cross-sections of the lignin-D1-copolymers with increasing lignin content ($\times 1000$).

behavior by increasing the bond length between branch points. At high lignin levels ($>25\%$) the copolymer mechanical properties were dominated by the lignin segment while $<25\%$ lignin the properties were dominated by hyperbranched prepolymer segment. The lignin copolymer elastomers with 30% lignin content showed optimal mechanical properties and good SME behaviors. The T_{trans} of the lignin copolymers was tunable by lignin content to give a range of temperatures between room and body temperature. These developed polymer systems could be used in medical applications and consumer products where body temperature actuation of the material is required. Furthermore, this study clearly demonstrates that lignin, a renewable resource and industrial byproduct, can be used as a netpoint segment in polymer systems with SME behavior.

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