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Plant Oil and Lignin-Derived Elastomers via Thermal Azide−Alkyne Cycloaddition Click Chemistry

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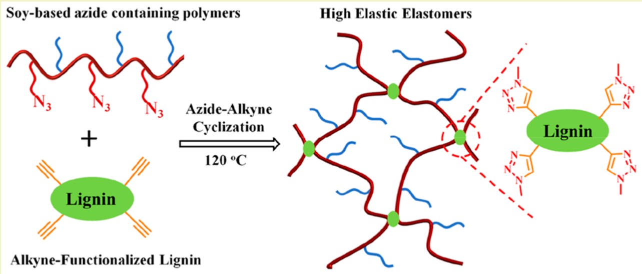
Supporting Information

ABSTRACT: The developments of sustainable elastomers from natural biomass to compete fossil fuel-derived elastomers are gaining increasing attention during recent years. In this work, elastomer derived from soybean oil and lignin was developed via a metal-free thermal azide−alkyne cycloaddition reaction (TAAC). Azide-containing polymers derived from soybean oil and alkyne-functionalized lignin were first prepared and confirmed via FT-IR, NMR, and GPC. A mixture of azide-containing polymers/lignin-alkyne was then thermal cured via TAAC, which afforded thermoset elastomers. The mechanical properties as well as elasticity were calculated via tensile tests. Moreover, mechanical properties of these elastomers could be facilely tuned via controlling the azide content in the soy-based polymers and the ratio of lignin-alkyne cross-linkers.



KEYWORDS: *Natural biomass, Soybean oil, Thermoset elastomers, Click chemistry, Lignin*

INTRODUCTION

In view of sustainable development of our human society, the development of polymeric materials from renewable biomass is gaining more and more attention in both industry and academia.[1] Elastomers are one of the most important polymeric materials that have been widely used in various fields, such as electronics, clothing, coatings, tires, and adhesives.[2] Compared with the commercial success of biomass-based plastics, the development of biomass-based elastomers is still in the initial stage.[3] Besides natural rubbers, petroleum-based synthetic rubbers, such as styrene butadiene rubber (SBR), butadiene rubber (BR), and nitrile rubber (NBR), dominate the world market of rubbers.[4−6] For a sustainable development, efforts are being made to replace or complement petrochemical-based elastomers with biobased counterparts derived from renewable natural resources.[2,7−12] Small molecular biomasses, such as plant oils, terpenes, menthol, lactones, etc., have been explored in the design of polymers with elastomeric properties.[13−19]

Thermoplastic elastomer (TPE) is an important type of elastomers. One general approach is to incorporate biomass polymers with low glass transition temperature (T_g) as an elastic component into TPEs.[3,20−23] For example, poly(menthide) (T_g = −22 °C), poly(*β*-methyl-*δ*-valerolactone) (T_g = −51 °C), and poly(*δ*-decalactone) (T_g = −51 °C) have been used as the soft middle block for constructing ABA triblock copolymer TPEs.[24−26] On the other hand, biomass-derived hard polymers, such as poly(*α*-methyl-*p*-methylstyrene) and polylactide, were use as hard segments in TPEs.[12] Thermoset elastomers from bioderived reactive precursors are receiving increasing attention due to scalable and economical processing.[27−30] These precursors could be small molecules or polymers. For example, Zhang et al. reported bioelastomers through cross-linking of soybean oil-based polymeric precursors with T_gs between −30 and −17 °C.[27] Sarkar and coworkers prepared poly(*β*-myrcene) via emulsion polymerization, which exhibited very low T_g (−70 °C). A series of poly(*β*-myrcene-*co*-styrene) copolymers were then prepared and vulcanized to obtain sustainable thermoset elastomers.[31]

Plant oil is one of the most abundant natural biomasses. Due to the existence of multiple reactive groups, direct polymerization of plant oil usually leads to highly cross-linked thermoset materials, such as polyester, polyurethane, and epoxy resin.[32] However, to the best of our knowledge, the elasticity of these plant oil-derived thermosets are not high enough, due to the poor network structure as well as high cross-linking density.[13] During recent years, monofunctional monomers, such as (meth)acrylates, vinyl ethers, norbornenes, and oxazolines, derived from plant oils and their side chain polymers with low T_g values were developed.[33] In our previous work, we developed a novel approach toward a series of soybean oil-derived polymers with T_g values in the range of

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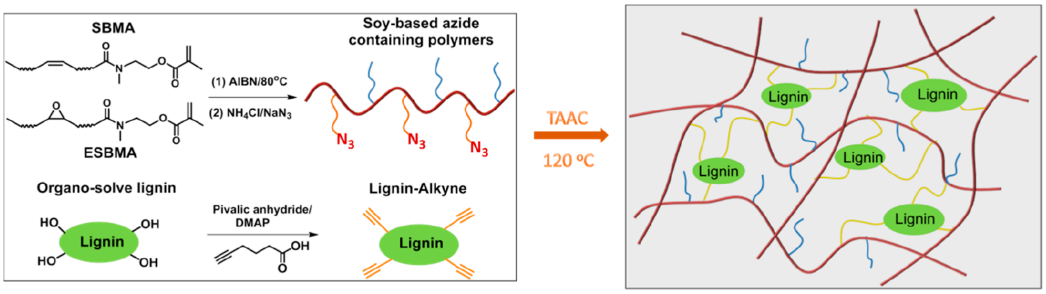
Scheme 1. Biobased Elastomers Prepared by TAAC of Soy-Based Azide Containing Polymers and Lignin-Alkyne



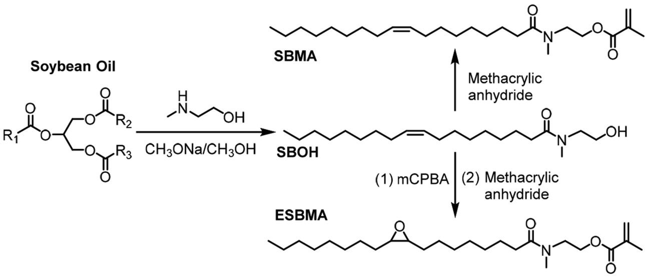
−60 to 60 °C.[34] Plant oil-derived polymers with T_g values lower than room temperature were then used in the development of sustainable TPEs. Moreover, the fatty side chains of plant oil-derived polymers usually contain reactive double bonds, which are a good candidate in the design of chemically cross-linked elastomers.[18] There are three principals in the design of elastic elastomers, (1) three-dimensional cross-linking network structures, (2) long and flexible polymer chains in between the cross-linking points, and (3) low intermolecular friction. Plant oil-derived polymers with low T_g values are extremely flexible. Moreover, the existence of fatty side chains in plant oil-based polymers may act as a plasticizer, which can decrease the interchain friction greatly. Thus, we predict that if a well-defined chemical network can be created, thermoset elastomer-derived plant oil polymers with good elasticity may be obtained.

Cross-linking could undergo either a nonselective or selective chemical process. Cross-linking through controlled covalent bonding offers versatility over the cross-linking density and network structures.[35−39] Strategies for controlled cross-linking include in situ ketene generation and coupling,[40−42] Diels−Alder coupling,[43−45] triazolinedione-ene coupling,[46,47] azide−alkyne Huisgen cycloaddition,[48−52] etc. In contrast, a nonselective process is usually uncontrolled with the formation of ill-defined networks. For example, cross-linking by autooxidation of soybean oil-derived polymers usually results in undesirable brittle materials.[53] Herein we report controlled thermal azide−alkyne cycloaddition (TAAC) on the cross-linking of plant oil-based polymers toward sustainable elastomers. As shown in Scheme 1, high oleic soybean oil-derived monomers, methacrylate monomer (SBMA) and epoxidized methacrylate monomer (ESBMA), were prepared according to our previous reported work.[23,34] By copolymerizing SBMA with ESBMA followed with an azidation reaction, soy-based azide containing polymers were obtained. Organosolve lignin was reacted with pivalic acid to afford alkyne-functionalized lignin (lignin-alkyne). Soy-based azide containing polymers were then mixed with lignin-alkyne and subjected to TAAC reactions to yield elastic thermoset elastomers. The cross-linking density and therefore mechanical properties can be facilely controlled via tuning the contents of azide and/or alkyne.

■ RESULTS AND DISCUSSION

Preparation of Azide Containing Soybean Oil Polymers. A soybean oil methacrylate polymer (PSBMA) with a T_g of −6 °C was prepared according to our early reports,[23,34] which was selected as an elastomeric matrix. In order to design soybean oil-based elastomers, well-defined networks are required, which could be achieved via controlled cross-linking chemistry. As shown in Scheme 2, to create reactive polymers, we first prepared a monomer (ESBMA) from soybean oil with an epoxy group. Figure 1A shows the ^1H NMR spectra of an epoxy fatty hydroxyl amide precursor from soybean oil and ESBMA. Protons of $-CH_2OH$ shifted completely from 3.75 to 4.28 ppm after methacrylation. New peaks at 6.09, 5.56, and 1.93 ppm are attributed to the methacrylate group. The ^{13}C NMR of ESBMA and its epoxide precursor also confirmed the transformation of plant oils to the monomer ESBMA (Figure S1). In our previous report, ESBMA was grafted onto lignin and cross-linked by maleic anhydride to form rigid epoxy resins.[54]

Scheme 2. Soybean Oil-Based Methacrylate Monomers SBMA and ESBMA



Two copolymers of SBMA and ESBMA containing 30 and 10 mol % ESBMA were prepared via free radical polymerization and labeled as **P30** and **P10**, respectively. Then, nucleophilic ring-opening of the oxirane group by sodium azide was carried out to afford azide-functionalized polymers, labeled as **PA30** and **PA10**, respectively. The ^1H NMR spectra of **P30** and **PA30** were given in Figure 1B. Protons on the oxirane ring were observed at 2.88 ppm for **P30**. In the spectrum of **PA30**, new peaks at 3.08 ($-CHN_3-$) and 1.48 ppm ($-CH_2$-CHOH−) were observed after the complete disappearance of the peak at 2.88 ppm. The Fourier transform infrared spectrometry (FT-IR) spectrum of **PA30** shows a sharp absorption peak at ~2104 cm^{-1} (Figure 2A), indicating the presence of azide moieties in **PA30**. The azide concentration was calculated to be 0.24 mmol/g in **PA10** and 0.71 mmol/g in **PA30** based on the molecular weight of the monomers.

Gel permeation chromatography (GPC) curves of soybean oil-based copolymers are shown in Figure S2. As listed in Table 1, the molecular weight of these polymers is in the range of 17.4−27.8 kg/mol. Figure 2B shows differential scanning calorimetry (DSC) curves of **P10**, **P30**, **PA10**, and **PA30**. Compared to **P10** with **P30**, the introduction of more ESBMA into copolymers led to an increasement of T_g. By converting

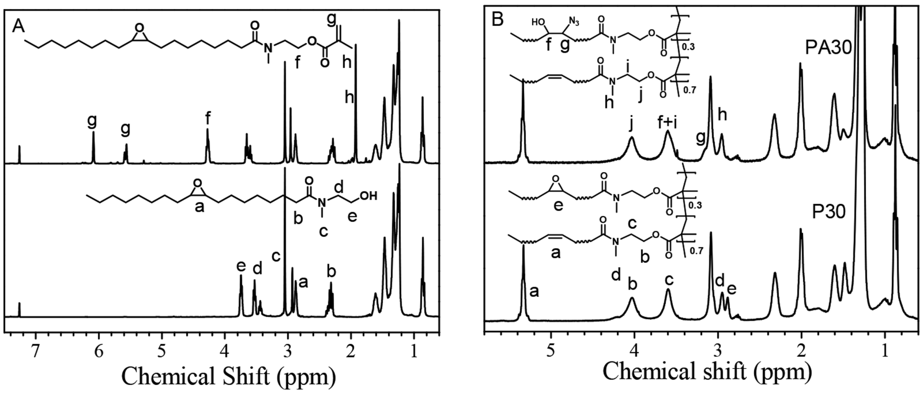


Figure 1. ^{1}H NMR spectra of (A) ESBMA and its epoxy fatty hydroxyl amide precursor. (B) Soybean oil-derived polymers **P30** and **PA30**.

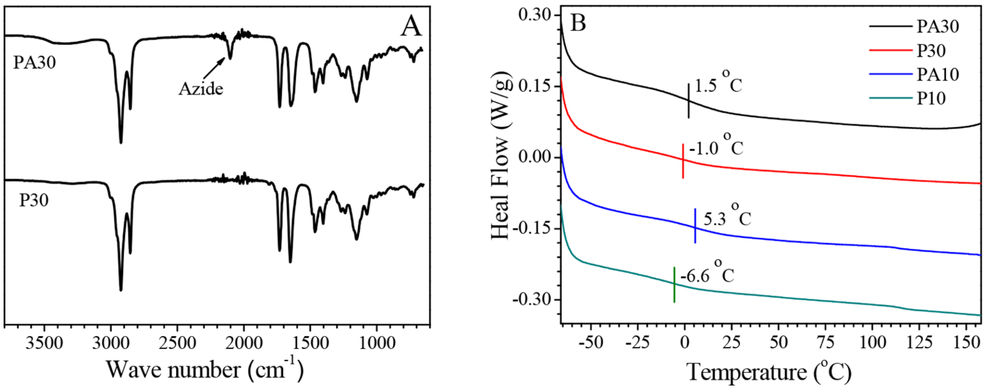


Figure 2. (A) FT-IR spectra of soybean oil-derived polymers **P30** and **PA30**. (B) DSC curves of soybean oil-derived copolymers.

Table 1. Characteristics of Soybean Oil-Derived Copolymers

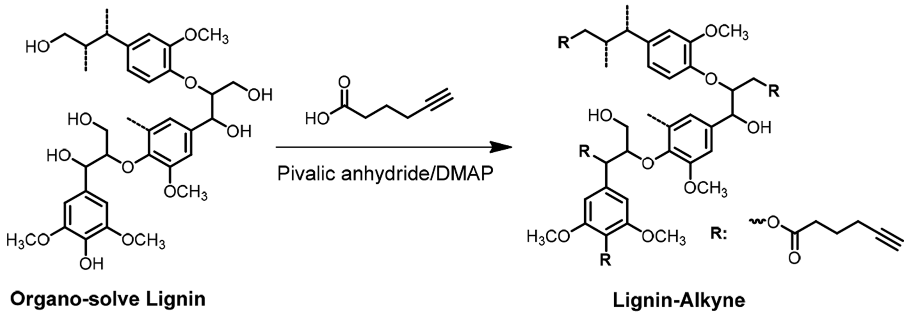
entry[a]	M_n[b] (g/mol)	$Đ$[b]	T_g[c] (°C)
P30	27 800	1.8	−1.0
PA30	23 000	1.6	1.5
P10	23 500	1.6	−6.6
PA10	17 400	1.6	5.3

[a] Entries are defined as follows: the numbers 30 and 10 represent the content of ESBMA. [b] Molecular weight (M_n) and polydispersity ($Đ$) were obtained according to GPC results. [c] Glass transition temperatures (T_gs) were calculated via DSC experiments.

oxirane to azide, the copolymers also showed slightly increased T_gs. Overall, all of these reactive copolymers showed T_gs below room temperature, which are potential candidates for biobased elastomers design.

Synthesis of Alkyne-Modified Lignin as Multifunctional Cross-Linker. Lignin is one of the most abundant biomasses and has been widely used as a filler/cross-linker in many materials, such as epoxy resins, polylactide, silicone elastomers and polyurethanes.[55−59] Recently, we reported functionalization of lignin with azide or alkyne groups for making thermoset polymers via the TAAC click chemistry.[60] We hypothesized that alkyne-functionalized lignin could also serve as a cross-linker to make soy-based elastomers via TAAC. As shown in Scheme 3, lignin-alkyne was prepared by direct esterification coupling between hydroxyl groups on lignin and 5-hexynoic acid. ^{1}H NMR spectra of lignin and lignin-alkyne demonstrated the presence of the 5-hexynoic group in the modified lignin (Figure 3A). Solid state ^{13}C NMR also confirmed the attachment of 5-hexynoic acid onto lignin (Figure S3). FT-IR spectra show a strong ester group (1749 cm^{-1}), terminal alkyne group (3289 cm^{-1}), and an apparent

Scheme 3. Preparation of Alkyne-Functionalized Lignin (Lignin-Alkyne) in THF



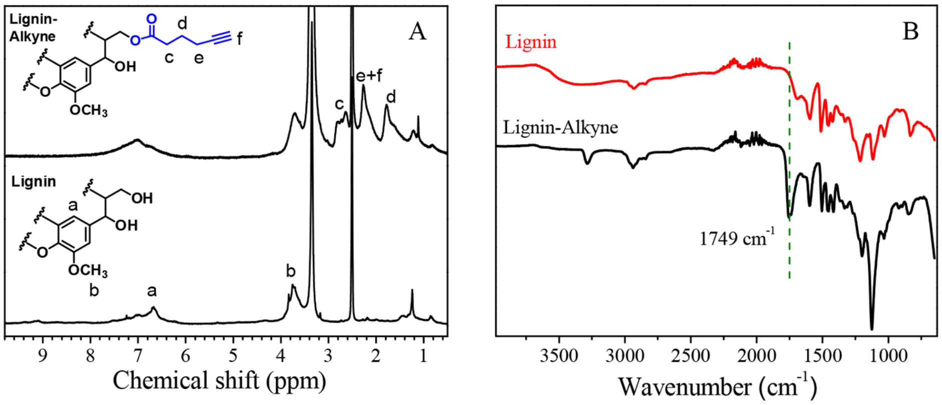
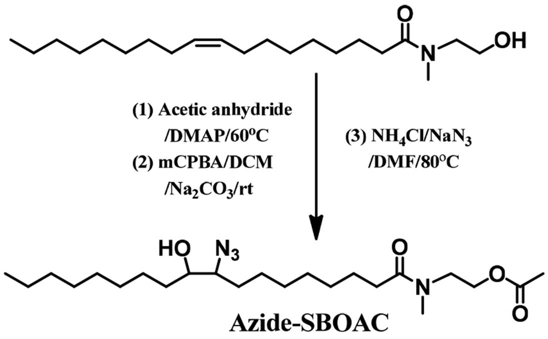


Figure 3. (A) ^{1}H NMR spectra of organosolv lignin and lignin-alkyne in DMSO-d_6. (B) FT-IR spectra of unmodified lignin and lignin-alkyne.

decrease of the broad peak (3200−3500 cm^{-1}) from the hydroxyl groups after the modification (Figure 3B). The alkyne content was 3.81 mmol/g, determined by ^{1}H NMR using 1,3,5-trioxane as a reference (Figure S4). The molecular weight of lignin-alkyne is 5.5 kg/mol with $Đ$ = 2.1, as characterized by GPC (Figure S5). The DSC curve of lignin-alkyne shows that the T_g of lignin-alkyne is ∼89.0 °C (Figure S6).

Model Study of Thermal Azide−Alkyne Cycloaddition. After succeeding in the preparation of azide-functionalized polymers and lignin-alkyne, we aimed at making thermoset elastomers via TAAC. A model study was first performed to demonstrate the reactivity between soybean oil polymer-azide and lignin-alkyne. Azide-soybean oil acetate (azide-SBOAC), structurally similar to the azide-containing side chains in **PA-30**, was prepared from soybean oil (Schemes 4 and S1 and Figure S7). Azide-SBOAC and lignin-alkyne were mixed together and heated under vacuum at 120 °C for 16 h. Figure 4 presents the ^{1}H NMR spectrum of the purified product. The proton on the triazole ring at ∼7.5 ppm and the proton from the −C*H*− at 4.4 ppm were clearly confirmed. The model study directly indicated the good reactivity between the azide group on the soy-based fatty chains and the alkyne group from the modified lignin.

Scheme 4. Preparation of Soy-Derived Azide Containing Compound Azide-SBOAC



Preparation of Elastomers from Soybean Oil and Lignin via TAAC Reaction. The TAAC curing between soybean oil polymer-azide (**PA30** and **PA10**) and lignin-alkyne was then carried out at 120 °C, which was far above the T_gs of **PA30** and **PA10**. The actual weight and moles of functional groups relating to each sample code are included in Table S1. FT-IR spectra of the uncured and the cured mixture of **PA30-L10** are shown in Figure 5A, normalized with the peak at 2925 cm^{-1} from the C−H symmetric stretching vibration. The intensity of the azide peak at 2104 cm^{-1} was dramatically decreased after curing, demonstrating the occurrence of the TAAC reaction during heating. The residual peak from the unreacted azide group was observed, which was also reported from other TAAC-cured systems.[60]

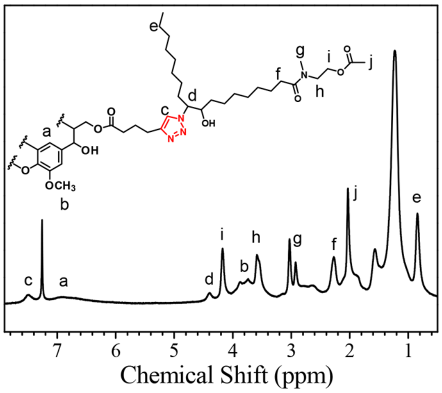


Figure 4. ^{1}H NMR spectrum of products after TAAC reaction between lignin-alkyne and azide-SBOAC in $CDCl_3$.

Soxhlet extraction of the cured elastomers was performed. The extracted soluble part ranged from 5.2 to 12.0 wt %, as shown in Table 2. Films from **PA30** had higher insoluble content than films from **PA10**, due to the higher level of cross-linking in **PA30** films. Thermogravimetric analysis (TGA) was performed for the cured samples from **PA30**. Similar decomposition behavior was observed for films with various contents of lignin-alkyne (Figure 5B). The onset temperature of decomposition (5% weight loss) was around 280 °C.

Lignin-alkyne was mixed with **PA30** (30% azide unit) and thermally cured at 120 °C. Cured films with high lignin-alkyne content (12, 15, and 20 wt %) had rough surfaces, possibly due to inferior compatibility. Films with lower lignin-alkyne content (1, 2, 5, 8, and 10 wt %) produced uniform films with a smooth surface after TAAC curing (Figure 6A). Colors from light yellow to dark were observed due to the presence of lignin. All cured films from **PA30** exhibited a monotonic increase in stress with strain without yields before failure (Figure 6B), a typical property of elastomers. Moreover, the elongation-at-break and stress-at-break displayed an apparent dependence on the cross-linker content (Table 2). The stress-at-break increased gradually from 0.84 to 2.12 MPa when the cross-linker content increased from 1 to 10 wt %, while the

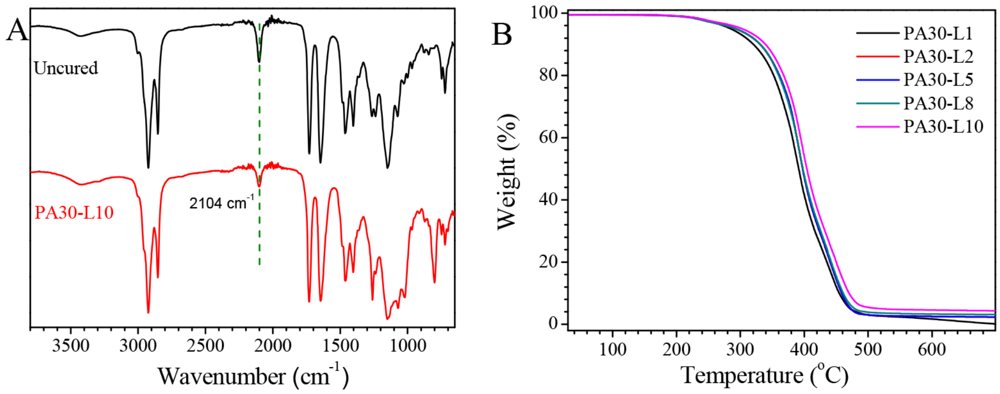


Figure 5. (A) FT-IR spectra of a mixture of **PA30** and **L10** before and after thermal curing. (B) TGA curves of thermally cured films from **PA30**.

Table 2. Tensile Tests and Solvent Extraction Results of Elastomers from TAAC

sample code[a]	tensile strain (%)[b]	tensile stress (MPa)[b]	solid content (%)[c]
PA30-L1	127	0.84	94.5
PA30-L2	124	0.92	92.7
PA30-L5	114	1.09	92.4
PA30-L8	115	1.66	93.0
PA30-L10	112	2.12	94.4
PA10-L2	134	0.69	88.0
PA10-L5	132	0.86	88.6
PA10-L10	133	1.06	88.5

[a] Sample codes are defined as follows: numbers 30 and 10 represent the content of ESBMA, and the numbers behind L represent lignin-alkyne weight content. [b] Stress and strain were obtained according to tensile results. [c] Solid contents were calculated via Soxhlet extraction.

strain-at-break decreased slightly from 127 to 112%. The elongations from these elastomers were higher than cross-linked resins using plant oil-based precursors.[45] The influence of the azide content was elucidated using **PA10**, which had a lower content of azide groups than **PA30**. Three films with 2, 5, and 10 wt % of lignin-alkyne were prepared and exhibited similar mechanical properties to those from **PA30**. However, the films from **PA10** were more elastic than films from **PA30**, as their strain-at-break was above 130%. Their stress-at-break was lower than cured **PA30** films, given that the cross-linker content was the same (Figure 6C). With lower azide content, lignin-alkyne would be less reactive with azide, leading to lower cross-linking points in the film.

Since our chemically cross-linked elastomers contain well-defined networks, flexible soybean oil polymer chains, and low intermolecular frictions, they should exhibit good elasticity. To investigate the elasticity of our designed soybean oil and lignin-derived elastomers, step-cycle tensile deformation was performed. Cyclic tensile curves of **PA30-L10** are shown in Figure 7. For clarity, the curves of each cycle are shifted on the strain axis. About 35% residual strain with a large hysteresis loop was observed in the first cycle, while nearly complete

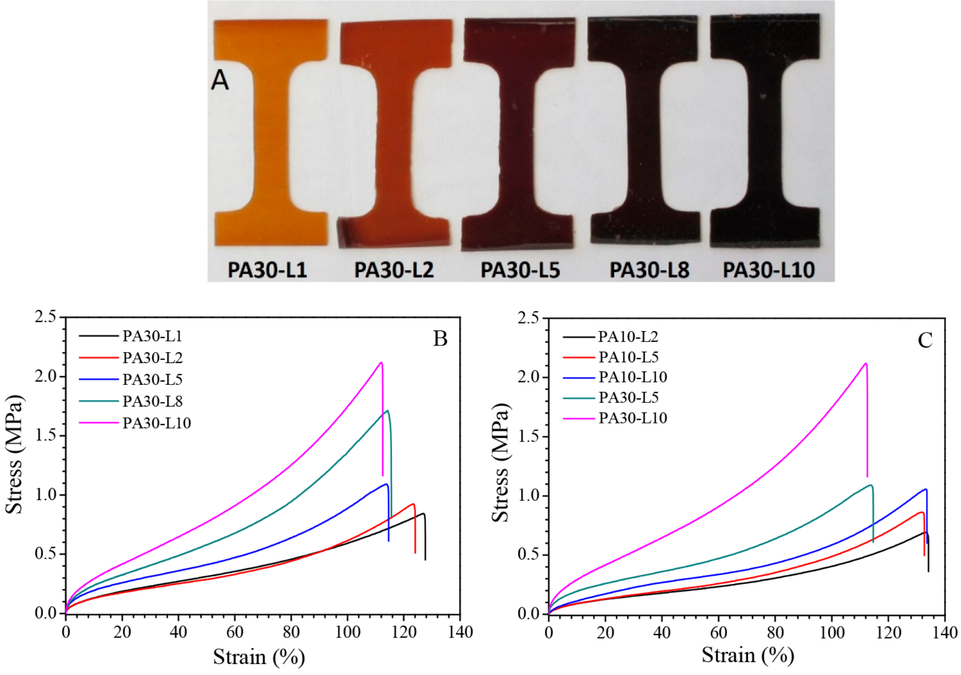


Figure 6. (A) A photo of the dog-bone shaped samples from **PA30**-based elastomers. (B) Stress−strain curves of elastomers from **PA30**. (C) Stress−strain curves of films from **PA10** (**PA10-L2**, **PA10-L5**, and **PA10-L10**) with comparison to films from **PA30** (**PA30-L5** and **PA30-L10**).

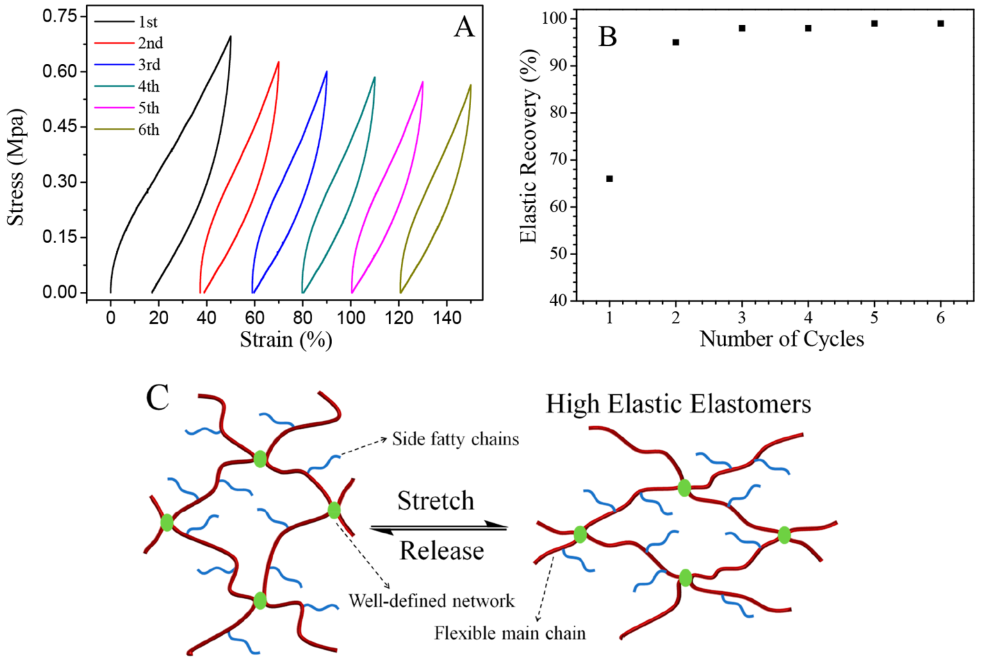


Figure 7. (A) Stress−strain curves of **PA30-L10** during cyclic tensile tests. For clarity, the curves were shifted on the strain axis. (B) Elastic recovery as a function of number of cycles for the **PA30-L10**. (C) Micro structure model for the elastomers at the stretched and relaxed state.

strain recovery (96−100%) and a smaller hysteresis loop were observed afterward. Additional recovery occurred after unloading, and the original size was recovered. The high residual strain during the first cycle comes from the rearrangement of an ill-defined network. After that, better network structures formed and elastomers with good elasticity were then obtained. A similar result was observed from bioelastomer **PA30-L8** (Figure S8). As shown in Figure 7C, the controlled TAAC click reaction led to the formation of well-defined chemical networks. The polymer main chains in between networks are flexible due to the low T_g values. The existence of fatty side chain reduced the chain entanglement as well as interchain friction. All of these structure characteristics endow these elastomers with good elasticity.

CONCLUSIONS

In summary, azide-functionalized soybean oil polymers with $T_g < 5$ °C were successfully prepared, which were suitable for elastomers design. After click cross-linking with alkyne-attached lignin via TAAC, elastomers with a three-dimensional network, long and flexible polymer chain, and low intermolecular friction were obtained. The prepared soybean oil-based elastomers exhibit high mechanical strength and excellent elasticity (96−100% after the first cycle). Moreover, higher azide content in the soy-based polymers and higher content of cross-linker facilitated the increases of tensile strength of elastomers. Given the sustainability, tunability, and elasticity, our approach may open a new avenue to the design of elastomers derived from plant oils.

EXPERIMENTAL SECTION

Materials. Plenish high oleic soybean oil was provided by DuPont Pioneer. Organo-solve lignin (Lignol Corporation), methacrylic anhydride (94%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), sodium azide (Sigma-Aldrich), ammonium chloride (Sigma-Aldrich), trimethylacetic anhydride (99%, Aldrich), and 5-hexynoic acid (97%, Alfa Aesar) were used as received. Azobisisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized from methanol. The soybean oil-derived monomer SBMA was prepared according to the reported method.[23] All other reagents were from commercial resources and used as received unless otherwise mentioned.

Characterization. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. GPC was used to determine molecular weight and molecular weight distribution of polymers. The system was equipped with a 2414 RI detector, a 1525 binary pump, and three Styragel columns. The columns consist of HR 1, HR 3, and HR 5E, with a molecular weight in the range of 1×10^2−5×10^3 g/mol, 5×10^2−3×10^4 g/mol, and 2×10^3−4×10^6 g/mol, respectively. The eluent was tetrahydrofuran (THF) at 35 °C with a flow rate of 1.0 mL/min. Polystyrene standards from Polymer Laboratories were used for calibration. GPC samples were prepared by filtering a 3.0 mg/mL solution in THF through microfilters with an average pore size of 200 nm.

FT-IR spectra were taken on a PerkinElmer spectrum 100 FT-IR spectrometer. The glass transition temperature (T_g) of polymers was tested through DSC conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −70 to 200 °C at a rate of 10 °C/min. After being cooled down to −70 °C at the same rate, the data were collected from the second heating scan. Ten milligrams of each sample was used with nitrogen gas at a flow rate of 50 mL/min. TGA was conducted on a Q5000 TGA system (TA Instruments), ramping from 25 to 700 °C with a rate of 10 °C/min.

Tensile test was carried out with an Instron 5543A testing instrument. Dog-bone-shaped specimens were cut from films with a length of 22 mm and a width of 5.0 mm before being tested at room temperature with the crosshead speed of 10 mm/min. The cyclic tensile test was conducted stepwise to a tensile strain of 50%. In each step, once the specimen reached 50% strain, the crosshead direction was reversed, and the sample strain was decreased at the same rate (1 mm/min) until stress was released to zero. The crosshead was immediately reversed when zero stress was reached, and the sample was then extended again until 50% strain. The cyclic deformation was repeated 5 times.

Synthesis of Epoxy Monomer ESBMA. Epoxidation of fatty amide alcohol (SBOH in Scheme 1) was done by mCPBA. Monomer **2** was obtained by methacrylation of the epoxidized product. Specifically, the epoxidized product (38 g, 0.107 mol), methacrylic anhydride (16.5 g. 0.107 mol), and DMAP (0.12 g, 0.001 mol) were mixed in a 100 mL round-bottom flask. After being stirred at 60 °C for 18 h, 5.0 mL of THF and 5.0 mL of water were added to quench the excess anhydride. $NaHCO_3$ solution was added to neutralize the mixture before the product was extracted by DCM. After being washed by brine solution, the product was dried over anhydrous $MgSO_4$ and concentrated as a light-yellow liquid.

Preparation of Copolymers P30 and P10. Free-radical copolymerization of monomers SBMA and ESBMA was carried out with AIBN as an initiator. The epoxide group in the final polymers could be controlled by changing feed ratios of monomers. Take **P30** as an example, SBMA (9.36 g, 0.023 mol), ESBMA (4.23 g, 0.01 mol), and AIBN (54 mg, 0.33 mmol) were dissolved in 20 mL of toluene and purged with N_2 for 15 min. The polymerization mixture in a flask was placed in an oil bath preheated at 80 °C, and the reaction was stopped after 24 h by placing the flask in an ice−water bath. After being precipitated from cold methanol and dried in a vacuum oven, the polymer was obtained and named as **P30**. Polymer **P10** containing 10 mol % ESBMA was similarly prepared.

Azide-Containing Polymers PA30 and PA10. The pendant oxirane groups in **P30** and **P10** were opened by sodium azide. For example, polymer **P30** (7.8 g, 5.7 mmol oxirane group) was dissolved in 20 mL of THF and 20 mL of DMF. Ammonium chloride (3.8 g, 71 mmol) and sodium azide (1.4 g, 22 mmol) were added to the solution. After being refluxed at 80 °C for 12 h, DCM (100 mL) was added, which was then washed by brine solution 3 times. The organic phase was dried over anhydrous $MgSO_4$, concentrated, and precipitated into cold methanol to get the final product, labeled as **PA30**. The azidation of **P10** led to polymer **PA10**.

Preparation of Multifunctional Cross-linker Lignin-Alkyne. Lignin (2.0 g, 11.2 mmol hydroxyl group), 5-hexynoic acid (1.5 g, 13 mmol), trimethylacetic anhydride (2.4 g, 13 mmol), and DMAP (16 mg, 0.13 mmol) were mixed in 10 mL of dry THF and stirred at 60 °C for 48 h. The product was purified by precipitation from methanol. The solid product was washed with methanol 3 times and dried under vacuum to get the alkyne group-modified lignin as a brittle brown powder, referred to as lignin-alkyne.

Preparation of Thermoset Elastomers through TAAC. Soy-based azide containing polymer (1.0 g, **PA10** or **PA30**) was dissolved in 10 mL of dry THF. Lignin-alkyne with a varied amount was added and stirred for 2 h to make a homogeneous solution. After being degassed and centrifuged, the solution was poured into a Teflon mold. The solution was slowly evaporated for 2 days and dried at 50 °C for 12 h. Then, the film was dried under vacuum for 2 h at room temperature before the temperature was increased to 40, 60, and 80 °C. Each temperature was maintained for 2 h. Finally, the temperature was increased to 120 °C and kept for another 16 h under vacuum. The films were recognized as PA(X)-L(Y), where the number X indicates the percentage of azide-containing side chains, and Y indicates the weight percentage of lignin-alkyne to the polymer. For example, **PA30-L1** means the film was cured using **PA30** (1.0 g) and 1.0 wt % of lignin-alkyne (10 mg).

Soxhlet Extraction. The cured polymer films (around 0.4 g, measured to the exactness of 1.0 mg) were wrapped in a stapled filter paper and extracted in a Soxhlet extractor for 24 h with 300 mL of dichloromethane refluxed at 65 °C. A light yellow-colored solution was observed in the Soxhlet extractor in the beginning and became colorless after several hours. The sample was dried completely under vacuum and measured to the exactness of 1.0 mg.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b05617.

NMR characterization of ESBMA; GPC, solid NMR, and DSC of lignin-alkyne; preparation and NMR characterization of azide-SBOAC; and mechanical test of PA30-L8 (PDF)

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Notes

The authors declare no competing financial interest.

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