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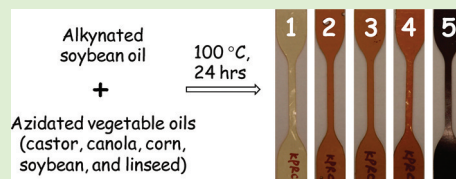
Biopolymers from Vegetable Oils via Catalyst- and Solvent-Free “Click” Chemistry: Effects of Cross-Linking Density

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S Supporting Information

ABSTRACT: New monomers were prepared by introducing the azide groups in castor, canola, corn, soybean, and linseed oils. Polymerization of the azidated oils with alkynated soybean oil under thermal “click” chemistry conditions (without using a solvent or a catalyst) yielded fully cross-linked elastomers (1–5) of almost the same density ($1.05 \times 10^{-3} \text{ kg/m}^3$). The degree of cross-linking gradually increased from the castor-derived polymer (220 mol/m³) to the linseed-derived polymer (683 mol/m³). A systematic correlation between the degree of cross-linking and the thermal and mechanical properties was observed in these biopolymers. Tensile strength (0.62–3.39 MPa) and glass transition temperature (−5 to 16 °C) increased and the linear thermal expansion coefficient decreased in the series from the canola-derived polymer (2) to the linseed-derived polymer (5). The castor-derived polymer (1) that possesses an additional hydroxyl group per fatty acid chain behaved differently.



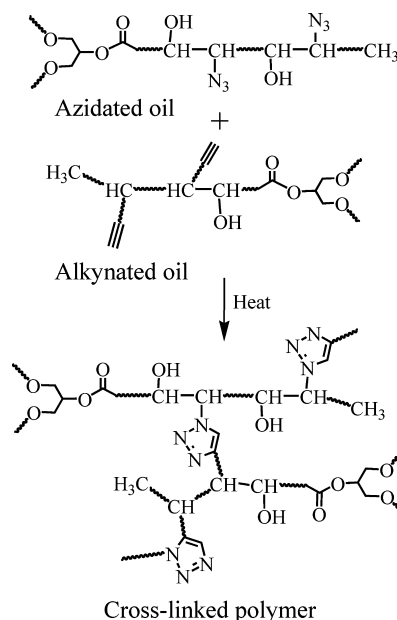
INTRODUCTION

Vegetable oils are environmentally friendly and annually renewable resources and have attracted considerable attention as a raw material for polymers.^{1–11} Some vegetable oils can be directly polymerized into cross-linked polymers.^{12,13} Nonetheless, polymerization of vegetable oils most often requires their conversion into reactive monomers. This is usually achieved through introduction of new polymerizable groups in the fatty acid chains through functionalization of double bonds (e.g., epoxidation, hydroformylation, reaction with maleic anhydride, ring-opening of epoxidized oils with hydrogen active compounds, amidation, and others).^{14–25} Different methods of polymerization (e.g., cationic, radical) have been extensively studied to convert vegetable oil-derived reactive monomers into polymers. Transesterification of saponified triglycerides is another route to produce vegetable oil-based polymers.²⁶ However, most of these methods involve cumbersome conversion and often require expensive reactants, catalysts, or both.

Vegetable oils can be readily epoxidized.²⁷ In fact, certain epoxidized vegetable oils (e.g., soybean, linseed) are available on industrial scales. This makes using epoxidized vegetable oils as the raw material for functional polymers an appealing route. Biswas et al. have shown that the azide functionality can be introduced to the fatty acid chain of the epoxidized soybean oil by ring-opening nucleophilic addition of sodium azide to the epoxy group.²⁸ We have shown that a similar approach can be conveniently used to introduce terminal triple bonds to the fatty acid chains of soybean oil.²⁹ Such azidated and alkynated soybean oils undergo polymerization with each other as well as with diyne or diazide linkers, respectively, under the copper-catalyzed azide–alkyne cycloaddition (“click”) condition. More importantly, we observed that polymerization of the azidated and alkynated soybean oils can also be efficiently performed

under catalyst- and solvent-free conditions.²⁹ The process requires the monomers to be heated at 100 °C, which results in the formation of biopolymers cross-linked via the triazole rings (Scheme 1). The thermal method yields cleaner (no catalyst

Scheme 1



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entrapped) and more homogeneously cross-linked biopolymers than the copper-catalyzed procedure.

Continuing our efforts, we now report the synthesis and characterization of a series of azidated vegetable oils. They readily undergo step-growth polymerization with alkynated soybean oil (ASBO) under the solvent- and catalyst-free “click” chemistry condition, yielding biopolymers without any by-product. The focus of this study was to assess the effects of the degree of cross-linking on the thermal and mechanical properties of this class of biopolymers. As such, several vegetable oils (castor, canola, corn, soybean, and linseed) that have different degrees of unsaturation were chosen for the study.^{30,31} The biopolymers (1–5, respectively) formed by thermally clicking ASBO with the azidated forms of the above-mentioned oils showed almost the same density, but the sol fraction and the degree of swelling decreased as the number of the azide functionality in the monomer increased.

A clear, increasing order in tensile strength, glass transition temperature (T_g), and elongation at break was observed due to an increase in the cross-linking density in polymers 2–5. However, the polymer derived from the azidated castor oil (1) behaved differently. Although it possessed the lower cross-linking density than polymer 2, it showed higher T_g and elongation at break than polymer 2. The behavior is explained on the basis of a higher degree of H-bonding in polymer 1 owing to an additional hydroxyl group per fatty acid chain.

■ EXPERIMENTAL SECTION

Materials. Vegetable oils (castor, canola, and corn) and epoxidized oils (soybean and linseed) were purchased from different suppliers. The epoxy oxygen contents (EOC) of epoxidized soybean and linseed oils were 7.02 and 9.91%, respectively. Sodium azide (NaN_3), propargyl alcohol, tetrafluoroboric acid solution (HBF_4 , 48 wt % in water), toluene, and other reagents were purchased from commercial suppliers and used as received.

Methods. The EOCs and hydroxyl numbers were determined according to the ACS PER-OXI titration method and ASTM D 1899-97, respectively. Element analysis (EA) was conducted at Galbraith Laboratories, Inc. FT-IR spectra were recorded on a Shimadzu IR Affinity-1.

The molecular weights of oils were determined with a vapor pressure osmometer (Osmomat 070, UIC, Inc.). Molecular weight distributions were determined using a Waters gel permeation chromatograph (GPC) consisting of a 515 pump, a 410 differential refractometer, and four phenogel 5 μm 50, 10², 10³, and 10⁴ Å columns. The flow rate of tetrahydrofuran (THF) eluent was 1 mL/min at 30 °C and polystyrene was used as the standard.

Viscosities of oils were measured on an AR 2000 dynamic stress rheometer from TA Instruments at 25 °C with 2° cone plates (25 mm diameter and a truncation height of 55 μm). The densities of polymers were measured by immersing them in water according to ASTM 792.

ASTM D543 was followed to measure the ratios of swelling of the polymers. Soxhlet extraction was used to determine the gel content of the polymers. A polymer sample (1.0 g) was extracted with refluxing toluene (100 mL) for 24 h. The insoluble solid was dried in vacuum oven at 60 °C for 6 h before weighing.

Differential scanning calorimetry (DSC) was performed on TA DSC Q100 at a heating and cooling rate of 10 °C/min under nitrogen. Melting temperature (T_m) and T_g were determined from the first and second scanning curves, respectively. Thermogravimetric analysis (TGA) was performed on a TA TGA Q500. Samples were heated under nitrogen using a heating ramp of 10.0 °C/min from 25 to 600 °C. Thermomechanical analysis (TMA) was carried out on TA Q 400 from TA Instruments with a heating rate of 10 °C/min under nitrogen.

Dynamic mechanical analysis (DMA) was carried out on TA 2980 from TA Instruments. The testing was performed in the tension mode

under nitrogen at a heating rate of 3 °C/min and a mechanical vibration frequency of 1 Hz (amplitude: 15 μm). Tensile properties were measured on Model 3367 from Instron Calibration Lab, according to ASTM D 638-01. Dumbbell-shaped samples punched out from the molded polymer sheets were used.

To correlate the thermal and mechanical properties of the polymers with cross-linking density, the plateau storage modulus (E') from the DMA profiles of the polymers was used to estimate the latter, using the equation: $\nu = E'/3RT$, where ν is the cross-linking density, R is the gas constant, and T is the absolute temperature at which the plateau E' was determined.

Synthesis. The synthesis of alkynated soybean oil (ASBO)²⁹ and azidated soybean oil^{28,29} has been reported previously.

Azidated vegetable oils were synthesized from respective vegetable oils. Castor, canola, and corn oils were first epoxidized following a literature method.²² The azidated forms of castor oil (Az-castor), canola oil (Az-canola), corn oil (Az-corn), and linseed oil (Az-linseed) were synthesized from respective epoxidized oils following an earlier reported procedure of the synthesis of azidated soybean oil (Az-soybean).^{28,29} Briefly, epoxidized oils were treated with NaN_3 in 1-methyl imidazolium tetrafluoroborate (an ionic liquid) at 65 °C for 2 days and subjected to the usual work up. The EOCs of the azidated oils were less than 0.1%. The nitrogen content of the azidated oils was determined by elemental analysis. The values for Az-castor (10.03), Az-canola (13.82), Az-corn (14.62), Az-soybean (14.69), and Az-linseed (17.87) were in a good agreement with the corresponding calculated values (11.04, 14.60, 15.22, 15.37, and 20.44, respectively). The calculated (theoretical) values reflect the nitrogen content of the azidated oils based upon the degree of unsaturation of the respective vegetable oils.

General Procedure for Casting Sheets. Each azidated oil was mixed with ASBO at an equimolar ratio of functional groups. The number of the azide group was calculated from the nitrogen content determined by elemental analysis. The number of the alkyne group was estimated from the difference of the EOCs of ESBO and ASBO. The equimolar mixture was kept at 50–60 °C under vacuum for about 2 h to remove air dissolved in the oils. The mixture was then poured into a steel mold (100 × 100 × 1 mm³) and heated at 100 °C for 24 h.

■ RESULTS AND DISCUSSION

Synthesis and Properties of Azidated Vegetable Oils.

Each of the epoxidized vegetable oils (castor, canola, corn, and linseed) readily underwent nucleophilic addition with sodium azide. The condition used for the reactions was the same employed earlier for the synthesis of the azidated soybean oil.^{28,29} The epoxy oxygen content (EOC), which is a measure of the number of the epoxy functional groups in oils, increased from 4.76 to 9.91 in the following order: castor, canola, corn, soybean, and linseed (see Table S1 in Supporting Information). The EOCs of the azidated oils, however, were less than 0.1, indicating a quantitative ring-opening of the epoxy groups. This was further confirmed by the GPC profiles of the azidated oils, which showed no traces of unreacted epoxidized oils. The addition of the azide groups to the fatty acid chains was reflected in the molecular weights, which were higher for the azidated oils ($M_n = 1202\text{--}1462$ g/mol) than for the corresponding epoxidized oils ($M_n = 936\text{--}1019$ g/mol). The polydispersity of the azidated oils was in the range of 1.02–1.70.

The FT-IR spectra of the azidated oils showed the characteristic, strong azide stretch peak at around 2100 cm^{-1} . In addition, each of the azidated oils also showed a broad peak at 3100–3700 cm^{-1} corresponding to the hydroxyl groups that form during azidation of the epoxidized oils. Elemental analysis of the azidated oils showed their nitrogen contents to be close to the respective theoretical values, clearly indicating the

successful conversion of the epoxy groups into the azide functionalities.

The color of azidated oils varied from light to dark brown in the following order: Az-castor, Az-canola, Az-corn, Az-soybean, and Az-linseed. The number of the azide functionality (N_f) per triglyceride molecule was calculated using the equation $N_f = M_n \times (\text{nitrogen content}) / (42 \times 100)$. The number-average molecular weight of the azidated oils (M_n), the molecular mass of the azide group (42), and the nitrogen content determined by the elemental analysis were used in the above equation. As expected, Az-castor showed the lowest N_f (3.2) and Az-linseed showed the highest N_f (6.2). This number ranged between 3.9 and 4.7 for Az-canola, Az-corn, and Az-soybean (see Table S1 in Supporting Information).

All azidated oils are liquids at room temperature and show similar thermal behaviors. Two or three melting peaks between -35 and 4 °C were observed in each case (see Table S1 in Supporting Information). This can be ascribed to different crystalline structures of oils. Az-castor is an exception, which showed only T_g at -15.3 °C and no melting temperature. The azidated monomers are stable for a long period of time (at least three months) at room temperature. Furthermore, a high yield obtained during polymerization, which was performed at 100 °C without any purging (vide infra), suggests that these monomers remain stable even at higher temperatures.

The azidated oils showed much higher viscosities (11 – 317 Pa·S) than the corresponding epoxidized oils (0.3 – 1.1 Pa·S). This is likely because of the presence of stronger intermolecular hydrogen bonds in the azidated oils that possess both the hydroxyl and azide groups. This is supported by the fact that the Az-castor, which possesses an additional hydroxyl group per fatty acid chain, exhibited about 3–4 times higher viscosity (40.1 Pa·S) than that of Az-canola (11.9 Pa·S) and Az-corn (10.6 Pa·S). Another factor that seems to be affecting the viscosities of the azidated oils is the extent of the oligomeric fraction. For example, the GPC profile of Az-soybean showed it to contain higher fraction of oligomers than that of Az-canola or Az-corn. The viscosity of Az-soybean is almost double that of the latter oils.

Polymerization of Azidated Oils with Alkynated Soybean Oil (ASBO). Polymer sheets were obtained by casting the mixtures of respective azidated oils with ASBO in a steel mold ($100 \times 100 \times 1$ mm³) and heating the mold at 100 °C for 24 h. Because the casting mixtures were free of any solvent or catalyst, all sheets were transparent and reflected the color of the respective azidated oils. Only the sheet from Az-linseed, which was dark brown, was not transparent. The completion of polymerization in each case and the formation of polymers (1–5) were verified by FT-IR spectroscopy.

The FT-IR spectrum of the ASBO monomer has a sharp peak at 3300 cm⁻¹, characteristic of the acetylenic bond ($\text{C}\equiv\text{C}-\text{H}$). No such peak was observed in the spectra of the polymers, clearly indicating the consumption of the triple bonds during polymerization. The intensity of the azide stretch peak at 2104 cm⁻¹ was also hugely decreased in the spectra of the polymers compared to that in the spectra of the azidated oils. The clicking of the triple bond of ASBO and the azide functionality of the azidated oils was further confirmed by the appearance of a small peak at 3140 cm⁻¹ ($\text{C}=\text{C}-\text{H}$) in the polymers spectra. This can be attributed to the triazole rings that form the cross-linking network in the polymers. The spectra of the polymers also showed some residual azide peak at

~ 2100 cm⁻¹. This is because of the small number of the azide groups that remained unreacted in the polymer network.³²

Irrespective of the nature of the azidated oils, the density of polymers 1–5 was found to be the same (Table 1). On the

Table 1. Density, Degree of Swelling, and Sol Fraction of Polymers Derived from the Polymerization of Azidated Oils (Castor, Canola, Corn, Soybean, And Linseed) with ASBO

polymer	monomers	density ($\times 10^{-3}$ kg/m ³)	swelling degree ^a (%)	sol fraction ^a (%)
1	ASBO + Az-castor	1.04 (± 0.03)	71.8	10.4
2	ASBO + Az-canola	1.05 (± 0.02)	80.7	6.1
3	ASBO + Az-corn	1.04 (± 0.03)	76.0	6.9
4	ASBO + Az-soybean	1.06 (± 0.01)	71.8	4.3
5	ASBO + Az-linseed	1.07 (± 0.02)	56.6	4.1

^aSolvent: toluene.

other hand, the degree of swelling decreased gradually from 80.7% for 2 (polymer derived from Az-canola) to 56.6% for 5 (polymer derived from Az-linseed). Interestingly, the degree of swelling was lower (71.8%) for 1 (polymer derived from Az-castor) than that of polymer 2. This is probably because of the additional OH groups of Az-castor, which provides a larger number of H-bonding in the polymer network and decreases the ability of polymer 1 to swell in an organic solvent such as toluene. The low sol fractions observed (<10%) also indicated high polymer conversions. Furthermore, the sol fraction decreased gradually from 10% in the case of 1 to 4% in the case of 5, which is suggestive of an increasing order of the cross-linking density in the series. It was further verified by the DMA data (vide infra). The increase in the cross-linking density is in accordance with the increasing order of the azide functionality in the corresponding monomers.

Because the numbers of the reacting functionalities (the azide groups) were different in the azidated oils studied, it is possible that they exhibit different rates of polymerization with ASBO. Nonetheless, the nature of the reactive functionalities in the individual monomers that these polymers were derived from was the same. The monomers also underwent polymerization under the same condition. Thus, besides an increasing order of cross-linking in polymer 1–5, it can be assumed that there is not much difference in the structural makeup of their networks. It is likely that polymers 1–5 contain both 1,4- and 1,5-disubstituted 1,2,3-triazole rings in the network, because polymerization was performed under a thermal condition, which is believed to be nonstereoselective.^{33,34}

Thermal and Mechanical Properties of Polymers. The T_g of polymers 1–5 were determined by three different methods (DSC, DMA, and TMA) and found to range from -5 to 20 °C (Table 2). Irrespective of the method used, polymer 2 showed the lowest T_g and polymer 5 the highest T_g in the series. For example, DSC showed the T_g of polymers 2–5 to be -4.5 , 1.1 , 9.8 , and 15.9 °C, respectively. The increasing order of the T_g can be attributed to an increase in the degree of cross-linking in 2–5. Polymer 1, on the other hand, did not follow the order shown by 2–5. For example, the T_g of 1 measured by DSC (1.0 °C) was higher than that of 2 (-4.5 °C). This is

Table 2. Thermal and Mechanical Properties of Polymers 1–5

polymer	T_g (°C)			TGA (°C)		decom. at T_{max} (%)	LTEC ^b ($10^{-6}/^{\circ}\text{C}$)	ν^c (mol/m ³)	tensile strength (MPa)	elongation at break (%)
	DSC	DMA ^a	TMA	T_{50}	T_{max}					
1	1.0	6.1	6.9	405	504	96.4	105/411	220	0.62 (± 0.07)	54.1 (± 2.0)
2	−4.5	3.8	−0.9	409	507	93.8	115/478	407	0.89 (± 0.11)	31.1 (± 2.4)
3	1.1	4.3	6.6	406	496	92.7	130/414	376	1.06 (± 0.12)	39.5 (± 1.5)
4	9.8	10.6	5.8	403	511	95.3	101/310	486	1.34 (± 0.06)	39.5 (± 1.0)
5	15.9	18.0	20.5	402	512	90.1	96/268	683	3.39 (± 0.88)	61.0 (± 2.1)

^a T_g was read from the maximum value of the loss modulus (E'') curve. ^bLinear thermal expansion coefficient. The first and second sets of data are the values at $T_g - 50$ °C and $T_g + 50$ °C, respectively. ^cDensity of cross-linking.

most likely because of a larger number of H-bonding in polymer 1 than in polymer 2.

The TGA curves and the DMA profiles of 1–5 are provided in Figures 1 and 2, respectively, and the thermal and

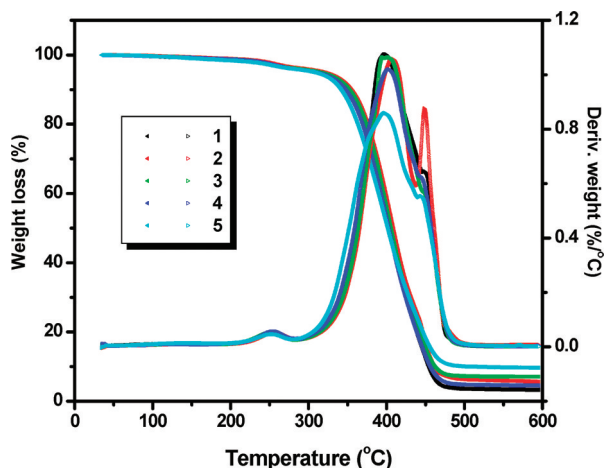
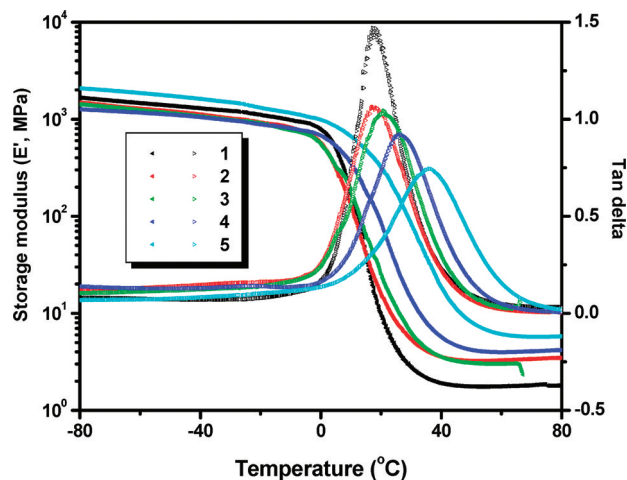


Figure 1. TGA curves of polymers 1–5.

Figure 2. DMA curves of polymers 1–5, showing variation in storage modulus and $\tan \delta$.

mechanical data presented in Table 2. All polymers exhibited similar decomposition behavior. The onset of decomposition was at ~ 300 °C. The decomposition process resulted in the formation of a small char at ~ 500 °C with almost total weight loss (90–96%). An early mass loss of less than 5% was detected at around 260 °C, which could be attributed to the decomposition of the unreacted azide groups.

Linear thermal expansion coefficients (LTEC) of glassy (at $T_g - 50$ °C) and rubbery states (at $T_g + 50$ °C) of 1–5 were calculated from the respective TMA data and found in the range typical for amorphous polymers. The LTEC values gradually decreased in the series from 2 to 5. Polymer 5 exhibited the lowest glassy state LTEC ($96 \times 10^{-6}/^{\circ}\text{C}$) as well as the rubbery state LTEC ($268 \times 10^{-6}/^{\circ}\text{C}$). Polymer 2 showed the highest rubbery state LTECs ($478 \times 10^{-6}/^{\circ}\text{C}$). Polymer 1 again did not follow the trend and showed lower glassy and rubbery state LTECs ($105 \times 10^{-6}/^{\circ}\text{C}$ and $411 \times 10^{-6}/^{\circ}\text{C}$, respectively) than the corresponding LTECs of polymer 2.

The cross-linking density was estimated from the plateau storage modulus (E') and found to increase in the series for polymer 1 (220 mol/m^3) to polymer 5 (683 mol/m^3 ; Table 2). As pointed out earlier, the increasing order of T_g and the decreasing order of LTECs correlate well with the cross-linking density in these polymers.

The DMA curves of 1–5 recorded at a mechanical vibration frequency of 1 Hz between -80 to $+80$ °C revealed only one thermal transition in each case (Figure 2). No minor (β or γ) transitions in the low temperature region were detected. The sharp drop in storage modulus (E') and the concurrent $\tan \delta$ peak in the 5 – 20 °C range are due to glass transition in the respective polymers. The shape and position of a $\tan \delta$ peak are known to be affected by many factors such as cross-link density, orientation of molecular structure, and so on. The $\tan \delta$ not only shifted to higher temperature, but also broadened from polymer 1 to 5. This again is most likely due to the increase in the cross-linking density in these polymers.

Almost linear relationship between stress and strain was observed for 1–5 (Figure 3). Tensile strength varied from a low value (0.62 MPa) to a decent (3.39 MPa) value in the series, and elongation at break was observed in the range of 30–60%. These values suggest that these polymers have relatively short network chains. One of the reasons these polymers showed weak tensile properties could be that their T_g is too close to room temperature (experimental temperature). Nonetheless, there was a gradual increase in tensile strength from 1 to 5, which correlates well with the increasing order of the cross-linking density. Except for polymer 1, which showed higher elongation at break (54.1%) than polymer 2 (31.1%), this property also increased gradually from 2 to 5 (61.0%), indicating improved structure in these imperfect rubbery networks. Increasing strength is usually accompanied with decreasing elongation in cross-linked polymers. However, polymers 2–5 showed an increasing elongation. This is likely because these polymers have T_g below room temperature, meaning they are in the rubbery state. The polymers that have T_g close to room temperature can be in leathery state ($T_g \pm 10$

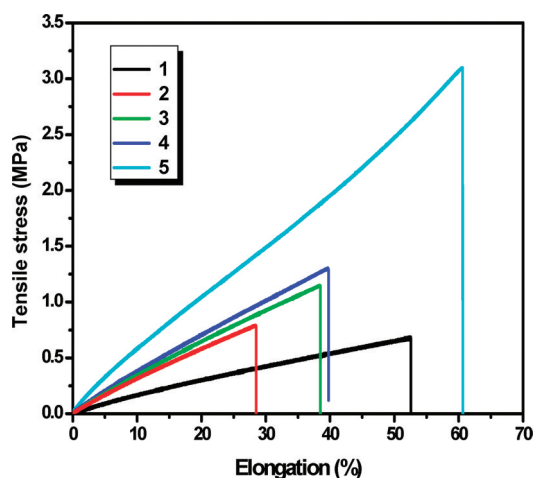


Figure 3. Strain–stress curves of polymers 1–5.

°C) and leathers have higher strength than rubbers and allow higher elongations.^{35,36}

CONCLUSIONS

A series of azidated oils (castor, canola, corn, soybean, and linseed) were prepared and characterized. In accordance with the degree of unsaturation in the oils (from castor to linseed), the number of the azide functionalities in the azidated oils varied from 3.2 to 6.2. Cross-linked elastomeric films (1–5) of almost uniform density ($1.05 \times 10^{-3} \text{ kg/m}^3$) were cast by heating the respective azidated oil with ASBO at 100 °C. The T_g of polymers 1–5 were found in the range of -5 to 20 °C. They exhibited a similar decomposition behavior with the onset of decomposition at ~ 300 °C and almost total weight loss (90–96%) at ~ 500 °C. Nonetheless, the thermal and mechanical properties of the polymers showed a systematic correlation with the density of cross-linking. For example, the tensile strength, T_g , and elongation at break increased in the series from 2 to 5 along with an increase in the degree of cross-linking. Polymer 1 did not follow the order. For example, it had the lower cross-linking density (220 mol/m^3) than polymer 2 (407 mol/m^3), but showed higher T_g (1.0 °C) and elongation at break (54.0%) than polymer 2 (1.0 °C and 31.1%, respectively). The behavior seems related to the presence of an additional hydroxyl group per fatty acid chain that induces a higher degree of H-bonding in polymer 1.

ASSOCIATED CONTENT

Supporting Information

Properties of epoxidized, alkynated, and azidated vegetable oils, GPC profiles, and FT-IR spectra of epoxidized and azidated vegetable oils and DSC, DMA, and TMA curves of polymers 1–5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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