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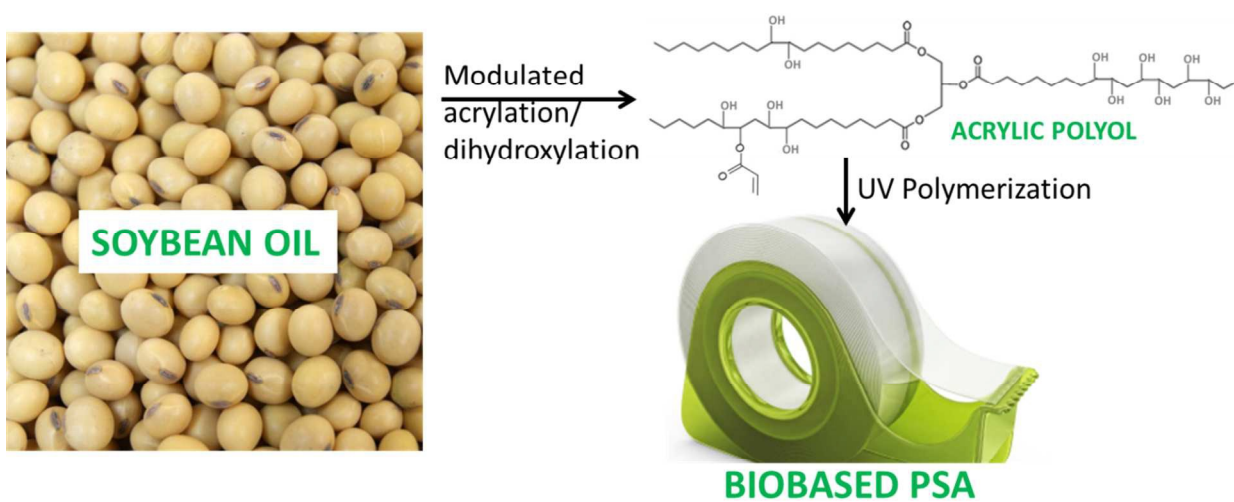
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Table of Contents graphic



SYNOPSIS

Soybean oil based acrylic polyol with modulated acrylate and hydroxyl functionalities was polymerized under UV radiation for biobased pressure-sensitive adhesives (PSA).

Synthesis and characterization of acrylic polyols and polymers from soybean oils for pressure-sensitive adhesives

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Abstract

A new class of acrylic polyols was synthesized from epoxidized soybean oil (ESO) and free-radically polymerized via UV irradiation to form pressure-sensitive adhesives (PSAs). ESO first was partially acrylated, then remaining epoxy groups were dihydroxylated to make acrylic polyols. The acrylic polyols were characterized with Fourier transform infrared spectroscopy, ^1H nuclear magnetic resonance, and hydroxyl value measurements. The degree of acrylation and hydroxyl functionality were carefully controlled to obtain polymers with a good balance of flexibility, crosslinking, and polarity, which are key attributes of PSAs. Glass transition temperature, rubbery plateau modulus, and cross-link density of polymers increased as the amount of acrylic polyol and the acrylate functionality of the resin increased. Biobased PSA with a good balance of peel strength (> 4 N/in), tack (> 7 N/in), and shear resistance ($> 50,000$ min) was achieved. Positive correlations between mechanical performance and viscoelastic responses of frequency sweep of the PSAs were found.

Keywords:

Epoxidized soybean oil, acrylated soybean oil, acrylic polyol, UV polymerization, pressure-sensitive adhesive (PSA), biobased product

1. Introduction

Pressure-sensitive adhesives (PSAs) adhere to a variety of substrates when applied with light pressure.¹ The primary bonding mechanism of PSAs is polar attraction to the substrate surface (e.g., van der Waals interaction, electrostatic forces, and hydrogen bonding).² PSAs have been widely used for tapes, labels, graphics, medical and many other applications, and demand is increasing.³ Many PSAs are made from petroleum-based acrylate monomers, such as 2-ethylhexyl acrylate (2-EHA), butyl acrylate, and isooctyl acrylate.^{3,4} Developing acrylates from renewable resources to partially or fully replace their petrochemical counterparts in PSAs would reduce dependency on limited petroleum resources.

World plant oil production has increased from 90 million metric tons in 2000 to nearly 170 million metric tons in 2013, and production is increasing. Plant oil is one of the most attractive renewable chemicals for potentially adhesive applications.⁵ Plant oils are mixtures of triglycerides with varying compositions of saturated and unsaturated fatty acids. Fatty acid distribution may differ depending on the crop, season, and growing conditions.⁶ Various oil derivatives have been synthesized via oleochemistry and applied in resins, composites, coatings, adhesives, surfactants, lubricants, cosmetic products, as well as biomedical uses,⁷⁻¹⁴ but only a few studies have been carried out to develop PSAs from plant oils.¹⁵⁻²⁰

Plant oil-derived acrylates have been available in the past few years,²¹⁻²³ and several papers have documented polymerization of acrylated epoxidized soybean oil (AESO)^{24,25} and acrylated methyl oleate (AMO)^{15, 26, 27} for PSAs. However, the adhesives were too weak in tack strength and peel adhesion (AESO-based) or in shear resistance (AMO-based) for practical applications. AESO usually had 2-4 acrylate groups per triglyceride, meaning polymerized AESO products were highly cross-linked and did not possess enough softness and flexibility to wet the substrate adequately to form a good bond²⁵ despite their good cohesive strength and shear resistance. Polymerized AMO was a linear polymer with relatively good peel adhesion and initial tack, but its shear resistance was only 10 min.²⁶ Copolymerization of AMO with a multi-functional acrylate increased the

polymer shear resistance to about 6,000 min, but the peel strength was reduced to less than 1 N/in.¹⁵ In addition, obtaining high-purity methyl oleate from natural plant oils is a costly process. Thus, development of new plant oil-derived acrylates suitable for PSA applications is necessary.

Acrylic PSAs are generally copolymers of three types of monomers:^{3, 28} low- T_g acrylate (e.g., butyl acrylate, 2-EHA), the soft monomer, which provides softness and tackiness; high- T_g acrylate (e.g., methyl acrylate, vinyl acetate), the hard monomer, which provides polymer cohesive strength; and unsaturated carboxylic acid (e.g., acrylic acid, methyl acrylic acid), the polar monomer, which adjusts polarity and provides cross-linking sites to improve peel and shear strength. Several technologies can be used to develop acrylic PSAs: solvent-based, water-based, hot-melt, and UV (radiation). UV curing is the most environmentally friendly process because it uses no volatile solvents and consumes less heat energy than other techniques.

Acrylic polyol is a compound that contains both vinyl group and multi-hydroxyl functionalities. Free-radically polymerized acrylic polyols (polymerization through vinyl groups) still possess a large number of hydroxyl groups. The polar nature of such polymers is expected to offer good polar attraction to substrates when used as PSAs. The objectives of this study were to synthesize new types of acrylic polyols from epoxidized soybean oils (ESO) and develop UV-cured PSAs. ESO was first partially acrylated via a ring-opening reaction with acrylic acid to obtain AESO. Remaining epoxides of AESO were then di-hydroxylated with water to obtain acrylic polyols, which were further polymerized and investigated for PSA applications. The degree of acrylation was carefully controlled, so the polymers had both sufficient flexibility to possess good wettability and appropriate cross-linking to maintain adequate cohesive strength.

2. Materials and Methods

2.1 Materials. ESO (VIKOFLEX 7170; epoxy oxygen content 6.7%, molecular weight 1000 g/mol) was provided by Arkema Inc. (King of Prussia, PA). AMC-2 (a solution of 40-60% chromium(III) 2-ethylhexanoate in a mixture of di(heptyl, nonyl, undecyl)

phthalates) was supplied by Ampac Fine Chemicals (Rancho Cordova, CA). Rosin ester (SYLVALITE® RE 80 HP) was obtained from Arizona Chemical (Jacksonville, FL). Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) was provided by BASF (Florham Park, NJ). Perchloric acid (70 wt% solution in water), tetrahydrofuran, ether, ethyl acetate, anhydrous magnesium sulfate, Celite 545, hydroquinone, acrylic acid (99%), 2-ethylhexyl acrylate (2-EHA, 98%), butyl acrylate (>99%), and methyl acrylate (99%) were purchased from Sigma-Aldrich (St. Louis, MO) and Fisher Scientific (Waltham, MA) and used as received. Commercial acrylated epoxidized soybean oil (CAESO, acrylate functionality 2.7, hydroxyl value 156 mg KOH/g) was obtained from Sigma-Aldrich.

2.2 Synthesis of acrylated epoxidized soybean oils (AESO). Acrylation of ESO was carried out in a 250-mL three-neck flask equipped with a mechanical stirrer in a silicone oil bath according to the reference with some modifications.²⁹ Predetermined molar ratios of acrylic acid to epoxide groups were used to obtain AESO with the necessary acrylate functionality. An excess of 0.1 mole acrylic acid per mole of epoxide groups to be acrylated was used to maximize the level of acrylation. Acrylic acid was added in a number of aliquots throughout the reaction to reduce the extent of epoxy homopolymerization. For a typical reaction of synthesizing AESO with 2 acrylate groups per triglyceride, 100.00 g (0.1mol) ESO was charged into the flask, then 0.33 g hydroquinone as an inhibitor of acrylate polymerization and 2.00 g AMC-2 as an acrylation catalyst were added. When the reactant temperature reached 80 °C, 7.20 g (0.1 mol) acrylic acid was pipetted into the flask. This amount corresponds to an addition of 1 mole acrylic acid per mole triglyceride. Two hours later, 7.92 g (0.11 mol) was added to the flask, and the reaction continued for another 4 hours. The product was purified through ether extraction and washed with water to eliminate the hydroquinone inhibitor and excess acrylic acid. The organic phase was dried over anhydrous magnesium sulfate then filtrated and concentrated under vacuum to obtain AESO. AESO with 1, 1.5, and 2 acrylate groups per triglyceride was denoted as AESO1, AESO1.5, and AESO2, respectively.

2.3 Synthesis of acrylated soybean oil polyols (acrylic polyols, DAESO). Acrylic polyols were synthesized from AESO by converting the remaining epoxy groups into dihydroxyl groups with water and acid catalysts. For a typical reaction, 50 g AESO was transferred into a Pyrex flask, and 50 mL tetrahydrofuran was added to dissolve the AESO. 25 mL of distilled water and 1.07 ml perchloric acid (70 wt% solution in water) were mixed in another container then dropped into the flask gradually (within 2 min) while stirring. The reaction continued for 5 hours at room temperature. The product was purified through ethyl acetate extraction, washed with distilled water, neutralized with saturated sodium bicarbonate solution, and finally evaporated using the rotary evaporator under vacuum to remove solvent and water. Acrylic polyols from AESO1, AESO1.5, and AESO2 were denoted as DAESO1, DAESO1.5, and DAESO2, respectively.

2.4 Characterization of AESO and DAESO. Epoxy content was measured according to ASTM D 1652-97 (Test Method A). Hydroxyl value (OHV) was measured according to ASTM D 4274-99 (Test Method A-Acetylation). ^1H nuclear magnetic resonance (^1H -NMR) spectra were acquired at room temperature on a Varian VNMRS 600 MHz SB NMR spectrometer in deuterated chloroform (D1=3 sec, 40 scans). Relative peaks were integrated to quantify the functionality of epoxy and acrylate groups. Fourier transform infrared spectroscopy (FTIR) spectra were acquired with a PerkinElmer Spectrum 400 FT-IR/FT-NIR Spectrometer (Waltham, MA). Spectra were collected in the region of 4000 to 400 cm^{-1} with a spectral resolution of 4 cm^{-1} , and 32 scans were co-added.

2.5 UV polymerization of acrylic polyols

DAESO was mixed with 2-EHA (soft monomer), acrylic acid (polar monomer), and the photoinitiator according to formulas shown in Table 1 to obtain rosin-free polymers (S1-S7). The mixture was thoroughly mixed in a 25-mL glass vial with the aid of a Vortex mixer and sonicator, then spread onto release paper. The resin was free-radically polymerized with a Fusion 300S 6'' UV system (300 W/inch power, D bulb, UVA radiation dose 215-231 mJ/cm^2) equipped with an LC6B bench-top conveyor at conveyor speed of 7 ft/min for 1 pass. The cured specimen was peeled off the release paper and stored for characterization. The ratio of DAESO to 2-EHA and acrylate functionality was

varied in different formulas to study their effects on polymer properties. Formula with AESO1 was prepared as a comparison to DAESO1 formulation, so that we could study how the introduction of extra hydroxyl groups onto triglycerides related to polymer properties. Furthermore, we also prepared polymers from CAESO to compare with our synthesized acrylic polyols.

We further prepared PSAs according to formulas shown in Table 1 (PS1-PS7). The composition of PSA resins was similar to S1-S7, except that 0.5 g rosin ester was added to each formula. For a typical PSA sample preparation, the ingredients were mixed in a glass vial then coated onto PET film using an EC-200 Drawdown Coater with a #20 wire bar (Chem Instruments Inc., Fairfield, OH). The coating amount was calculated to be 48.55 g/m^2 , and wet thickness was 50 microns. The adhesive coating was cured similarly as above and stored for further evaluation. Non-supported PSAs were also prepared for characterization purposes.

2.6 Characterization of polymers and PSAs

Thermal transitions of the polymers were measured with a TA Q200 differential scanning calorimetry (DSC) instrument in an inert environment using nitrogen with a gas flow rate of 50 ml/min. About 10-mg sample was sealed in a stainless steel pan. An empty pan was used as a reference. The sample was heated from $-90 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C/min}$. Phase transition temperatures, including glass transition (T_g), melting (T_m), heat capacity (ΔC_p), and heat of melting (ΔH_m) were obtained.

Dynamic mechanical analysis (DMA) of polymers was conducted using a TA Q800 DMA analyzer equipped with a liquid nitrogen cooling system in a shear sandwich mode at 1 Hz frequency and 0.1% strain (linear viscoelastic region). Specimens (about $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$) were cut from a cured polymer sheet with a blade and heated from -120 to $120 \text{ }^\circ\text{C}$ at a rate of $3 \text{ }^\circ\text{C/min}$ under a nitrogen atmosphere. Storage modulus (G'), loss modulus (G''), and $\tan \delta$ were obtained.

Gel content was measured by immersing the sample in a large amount of toluene.³⁰ Approximately 0.2 g of polymer film was accurately weighed and immersed in 20 mL

toluene for 1 week. The specimen was then taken out and dried at 130 °C for at least 2 hours until a constant weight was achieved. Gel content was measured according equation (1) below:

$$\text{Gel content} = w_1/w_0 \times 100 \quad (1)$$

where w_0 and w_1 are the weights before and after toluene soaking, respectively.

To determine the mechanical performance of PSAs, the PET films coated with adhesive layers were cut into 1-inch \times 5-inch stripes. Peel strength was measured following ASTM D3330/D3330M-04(2010), and loop tack strength was measured following ASTM D6195-03(2011) using IMADA MV-110-S tester (Imada Inc., Northbrook, IL) on 18-gauge, 304 stainless steel test panels (ChemInstruments, Inc., Fairfield, OH) with a stressing clamp moving speed of 5.0 mm/s. Five specimens were measured for each formula. The shear test was conducted following ASTM D3654/D3654M-06 (2011) using Room Temperature 10 Bank Shear (ChemInstruments, Inc., Fairfield, OH) with a specimen size of 1 inch \times 1 inch and test mass of 1000 g on 18-gauge, 304 stainless steel test panels. The time between the application of the load to the specimen and its separation from the panel was recorded.

Viscoelasticity of PSAs was measured using a Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA) with a PP 8 parallel plate. The specimen was cut from non-supported PSA sheets using a lab-made cutter and placed between the two parallel plates. The gap was closed with a set normal force. The strain amplitude was set at 0.1% (within linear viscoelastic region), and an oscillatory frequency sweep was performed from 0.01 to 100 rad/s. Storage modulus (G') and loss modulus (G'') as a function of frequency were recorded to show how the adhesives responded at different time scales.

3. Results and Discussion

3.1 Acrylic polyols

Acrylate functionality was grafted onto triglycerides through the reaction of epoxide ring of ESO with acrylic acid. Converting the epoxy to vinyl ester enables the resin to be free-radically polymerized. The ring-opening reaction of the remaining epoxy groups with water results in acrylic polyols (Figure 1).

The conversion of ESO to AESO then to DAESO was confirmed with FTIR (Figure 2). ESO exhibited a characteristic epoxide peak at 822 and 842 cm^{-1} (inset of Figure 2). Compared with the spectrum of ESO, the intensity of the epoxide peak was reduced in AESO1 due to the conversion of one epoxy group to one acrylate and one hydroxyl. The acrylation was evidenced by the new C=C stretching peaks of the acrylate group at 1635, 1618, and 810 cm^{-1} and the hydroxyl peak at 3450 cm^{-1} . No epoxy peak was observed for DAESO1, whereas the intensity of hydroxyl peak at 3450 cm^{-1} increased greatly, indicating that all the remaining epoxy groups of AESO1 reacted and were mostly or completely converted into hydroxyls. A small shoulder was observed at 1067 cm^{-1} , which was caused by the side reaction of epoxy homopolymerization-generating ether groups.

NMR is another powerful tool to confirm the reaction of triglycerides modification, as well as to quantify the functionality of relative groups (e.g., epoxy, acrylate). Typical spectra of ESO, AESO, and DAESO were presented, and peak assignments of triglyceride protons were noted (Figure 3). The two epoxide protons (peak 3) appeared at 2.8-3.2 ppm in ESO, decreased in area in AESO1, and disappeared in DAESO1. On the other side, three sets of new peaks appeared at 5.7-6.7 ppm in AESO and DAESO, representing the three protons attached to the C=C double bond of acrylate groups (peak 11a-c)³¹. Using methyl protons (0.9-0.98 ppm, peak 8) or an α -methylene proton (2.3 ppm, peak 4) as an internal standard, the functionalities of epoxy and acrylate per triglycerides were calculated (Table 2).³² The acrylate functionality based on NMR was similar to the theoretical functionality based on the amount of acrylic acid addition during synthesis. Protons germinal to hydroxyl groups (peak 12) appeared at 3.26-4.25 ppm; however, these peaks overlapped with the peak of glycerol methylene protons (peak 2, 4.1-4.3 ppm) and the peak of protons vicinal and germinal to possible ether linkages³² caused by epoxy homopolymerization during acrylation and dihydroxylation. Therefore, the relative hydroxyl functionality of resins was evaluated through their respective

hydroxyl value (OHV). The OHV of AESO1 was 107.8 mg KOH/g. More hydroxyl groups were introduced into the triglyceride structure via a dihydroxylation reaction, the OHV of DAESO1 was 260.9, and that of DAESO1.5 and DAESO2 was 255 and 212 mg KOH/g, respectively. The epoxy content of acrylic polyols measured through a titration approach was nearly 0% (Table 2), which was consistent with NMR measurements.

3.2 FTIR and thermal properties of acrylic polyol polymers

When liquid acrylate resins were exposed to UV radiation in the presence of a photoinitiator, free-radical polymerization took place rapidly and led to polymer networks. Typical FTIR spectra of acrylate resins (S2 from Table 1) before and after UV radiation were presented in Figure 4. The completeness of polymerization was confirmed by the disappearance of several acrylate peaks: 1635, 1618, 1406, 984, and 810 cm^{-1} .

Thermal properties of the monomers and polymers confirmed that DAESO1 was a hard monomer and 2-EHA was a soft monomer (Table 3, Figure S1). The T_g of DAESO1 and its homopolymer were $-31.3\text{ }^\circ\text{C}$ and $-27.2\text{ }^\circ\text{C}$, respectively, and T_g of 2-EHA and its homopolymer were $-85\text{ }^\circ\text{C}$ and $-58\text{ }^\circ\text{C}$. With the increase of the amount of DAESO1 in the resin from 0.75 to 1 then to 1.25 g (S1 vs. S2 vs. S3, see formulation in Table 1), the T_g of polymers increased from -46.4 to -41.6 then to $-35.2\text{ }^\circ\text{C}$, and T_m also increased slightly from -0.1 to $4\text{ }^\circ\text{C}$. Since DAESO1 was a relatively hard monomer, it is reasonable that polymer T_g increased and flexibility decreased as more acrylic polyol was added to the resin formulation.

We further studied the effects of acrylate functionality on the T_g of polymers. As the acrylate functionality increased from 1 to 1.5 to 2, T_g of the polymers increased from -41.6 to -38.9 then to $-30.5\text{ }^\circ\text{C}$ (S2 vs. S4 vs. S5, Table 3), indicating higher functionality leading to higher degree of cross-linking, thus higher T_g and less flexibility.³³ This is also why S6, the sample based on commercial AESO with acrylate functionality of 2.7, had the highest T_g of $-22.5\text{ }^\circ\text{C}$ (Table 3). Although the acrylate functionality of DAESO1 was the same as AESO1 (Table 2), the hydroxyl functionality of DAESO1 is much larger than

AESO1 (261 vs. 108 mg KOH/g). As a result, more hydrogen bonding was formed within S2 than in S7, resulting in higher T_g of S2.^{34,35}

3.3 Dynamic mechanical properties of acrylic polyol polymers

Storage modulus (G') and damping factor ($\tan\delta$) of the polymers as a function of temperature were shown in Figure 5. $T_{g, \text{DMA}}$ of polymers was taken as the peak temperature of $\tan\delta$, which is larger than the respective T_g from DSC but changes in the same trend according to polymer composition. The differences between $T_{g, \text{DMA}}$ and T_g from DSC are normal, because $T_{g, \text{DMA}}$ was obtained based on the measurement of mechanical strength and energy loss at 3 °C/min heating rate and 1 Hz, whereas T_g from DSC was obtained based on heat flow (i.e., heat capacity) measurement at heating rate of 10 °C/min.³⁶

The height of peak $\tan\delta$ ($\tan \delta_{\text{peak height}}$) varied according to polymer compositions (Table 4). $\tan \delta_{\text{peak height}}$ decreased as acrylate functionality increased, with S6 of the lowest value of 0.37 and S7 of the highest value of 0.83. Polymers with larger $\tan \delta_{\text{peak height}}$ have better capacity for energy dissipation, which benefits applications such as PSAs. All the seven polymers exhibited a clear rubbery plateau region, indicating that these polymers were cross-linked. With larger amount (S1 vs. S2 vs. S3) or higher acrylate functionality (S2 vs. S4 vs. S5 vs. S6) of acrylic polyols in the composition, G' of polymer was higher at all temperatures except for a few fluctuations in the glassy region. To better understand DMA properties, the experimental cross-link density (ν_e) of the polymer was determined from the rubbery plateau modulus according to equation (2).³⁷

$$\nu_e = \frac{G'}{RT} \quad (2)$$

where G' is the shear storage modulus of the cross-linked polymer in the rubbery plateau region 50 °C above $\tan\delta$ peak temperature ($T_{g, \text{DMA}}$), R is the gas constant, and T is the corresponding absolute temperature ($T_{g, \text{DMA}} + 50$). Molecular weight between cross-links (M_c) was calculated according to equation (3):

$$M_c = \frac{\rho}{v_e} \quad (3)$$

where ρ is the specific gravity of the polymer. The calculated v_e and M_c are also listed in Table 4.

Rubbery plateau modulus and cross-link density increased, whereas molecular weight between cross-links decreased as the amount of DAESO1 acrylic polyol in the resin increased from 0.75 to 1 then to 1.25 g refer to 2-EHA (S1 vs. S2 vs. S3) (Table 4). As a result, the S1 polymer should have little cohesive strength and therefore poor shear properties; however, it easily wet the substrate to achieve good initial tack strength when used as PSA. Acrylic polyol acted as both the polymer backbone and cross-linker, whereas 2-EHA and acrylic acid were linear chain extenders to modify the polymer flexibility and polarity and did not contribute to cross-linking. It is noteworthy to mention that although DAESO1 averaged only 1.1 acrylate per triglyceride based on $^1\text{H-NMR}$ analysis, the factual acrylate functionality of the triglyceride is larger than 1.1, because soybean oil triglycerides also contain 16.1% saturated fatty acids (C14:0, 16:0, and 18:0). These fatty acids/triglycerides could not be functionalized and polymerized and acted as a plasticizer for the polymers.

We also observed that the acrylate functionality had positive effects on rubbery plateau modulus and cross-link density of the polymers (Table 4, samples S2 vs. S4 vs. S5 vs. S6). Higher acrylate functionality created a more cross-linked structure during polymerization, thus a higher modulus. The rubbery plateau modulus, cross-link density, and molecular weight between cross-links are similar for S2 and S7, because AESO1 and DAESO1 had the same acrylate functionality. The molecular weight between cross-links (M_c) of all the polymers met the prerequisite for PSAs except for S6 (with M_c of 4742 g/mol). The M_c value for PSAs needs to be about 10^4 - 10^5 g/mol in order to achieve higher peel energy due to fibrillation during the peeling process.³⁸

Polymers formulated with higher acrylate functionality, such as S6 and S5, displayed higher gel contents than the polymer with lower acrylate functionality (i.e., S1-S3, 4, S7)

(Table 4). Gel content generally correlated well with the rubbery plateau modulus and cross-link density,³⁰ which is also observed in this study.

3.4 Adhesive performance of PSAs

PSA composition was similar to the corresponding polymer discussed above (Table 1), except that the same amount of rosin was added to each formulation to adjust viscoelastic properties and meanwhile improve adhesion performances. Tack, peel, and shear resistance are three fundamental and interconnected adhesion properties of PSAs.⁴ Tack value shows the ability of adhesives to wet the substrate instantaneously, peel strength indicates adhesion to the substrate, and shear resistance reveals the cohesion strength of the polymers as adhesives. All PSAs exhibited excellent shear resistance (>50,000 min), except for PS1 and PS7 (Table 5). As discussed previously, the polymers of PS2, PS3, PS4, PS5, and PS6 have larger rubbery plateau moduli and crosslink densities than PS1 and PS7 polymers, thus stronger polymer cohesive strengths. The shear resistance of PS1 (5,000 min) was larger than PS7 (500 min) because the polymer of PS1 had more hydroxyl groups than that of PS7 in forming physical entanglement through hydrogen bonding. Such physical entanglements contributed to cohesive strength.

PS1 had peel strength of 4.29 N/in and tack of 8.16 N/in, but slight cohesive failure (i.e., adhesive residue remained on substrates after peeling) was observed (Table 5). This is because the polymer backbone was soft and weak due to a large amount of soft monomer (i.e., 2-EHA) in the formulation, and did not form enough crosslinking. By increasing the amount of DAESO1 in the composition, which acted as both a hard monomer and a cross-linker, PS2 had a good balance of peel (4.47 N/in), tack (7.14 N/in), and shear (>50,000 mins) performance. The peel adhesion strength was higher than that of commercial Scotch[®] transparent tape (2.45 N/in).³⁹ Further increasing DAESO1 led to decreased peel and tack properties (i.e., PS3 Table 5), due to less flexibility to wet the adherend sufficiently and form effective bonds, which corresponds to the relatively high glass transition temperature (T_g of -35.2 °C from DSC and $T_{g,DMA}$ of 12.4 °C) and large crosslink density (57.4 mol/m³) of the S3 polymer.

PS2, PS4, PS5, and PS6 PSAs were based on the same amount of acrylic polyols with 1.1, 1.5, 2, and 2.7 acrylates functionality, respectively. Increasing the functionality of acrylic polyols significantly reduced PSA peel and tack values (Table 5). For example, the peel and tack values of PS2 were 4.47 and 7.14 N/in, whereas those of PS6 was only 0.70 and 0.08 N/in. Several reasons attributed to this: first, polymers with high functionality acrylic polyols were highly cross-linked resulted in insufficient flexibility to wetting the substrate and forming bonds; second, high functionality acrylic polyols had less polar hydroxyl groups (i.e., low hydroxyl values). The hydroxyl groups of these polymers acted as a critical adhesion site to improve wetting onto the stainless steel testing panel and accelerate the rate of bond establishment and development via the formation of hydrogen bonding and other noncovalent interactions.

PS2 had much better PSA performance than PS7 (Table 5), even though they were polymerized with the same amount of monomers with identical acrylate functionality (1.1). As mentioned before, DAESO1 of PS2 (OHV of 261 mg KOH/g) had more hydroxyl groups than AESO1 of PS7 (OHV of 108 mg KOH/g). This result further confirms that building extra hydroxyl groups into acrylated triglycerides is critical to developing PSAs in soybean oil system.

The effects of co-monomer type, acrylic acid amount, acrylic polyol to 2-EHA ratio, and rosin amount on PSA adhesion strength were shown in the supporting data (Table S1-S4). In this study, 2-EHA was selected as soft co-monomer against butyl acrylate (BA) and methyl acrylate (MA), because both BA and MA produced rigid polymers (supporting data Table S1). We used acrylic acid (AA) against methyl acrylic acid (MAA), because MAA formulation led to PSA with 100% cohesive failure (supporting data Table S1). Increasing the amount of acrylic acid from 0 g to 0.1 g then to 0.2 g first increased then decreased peel adhesion (supporting data Table S2). An appropriate amount of acrylic acid improved the polarity of the adhesive, resulting in better adhesion; however, excess acrylic acid would decrease polymer flexibility. Increasing the amount of rosin ester in the formulation also led to better adhesion, but when it exceeded a critical amount, adhesive cohesive strength decreased and cohesive failure occurred (supporting data Table S4).

3.5 PSA viscoelasticity

Mechanical performances of PSAs are closely related to their viscoelastic properties. According to Dahlquist's criterion, a PSA needs to have a plateau modulus lower than 3.3×10^5 Pa so it can wet the substrate and exhibit tack during bonding.^{40,41} Correlations between tack, shear and peel adhesion behaviors and viscoelastic responses have been well established.^{3,42} The viscoelastic information at low frequency (~ 0.01 rad/s) describes the bond formation, whereas that at high frequency (~ 100 rad/s) describes the behavior of debonding.⁴³ Therefore, a PSA with good performance should have a low bonding plateau modulus at the bonding frequency (i.e., low G' at 0.01 rad/s) and high energy dissipation at the debonding frequency (i.e., high G'' at 100 rad/s).

Frequency sweep spectra of these PSAs are presented in Figure 6, and characteristic viscoelastic values are summarized in Table 6. The Dahlquist criterion is an important reference because it implies whether a material would be contact efficient (PSA) or deficient (non PSA). Because of the subambient T_g of the PSAs, G' at 0.01 rad/s indicates the value of the plateau modulus.⁴³ The plateau modulus of all the samples except for PS5 and PS6 were much below 3.3×10^5 Pa (Dahlquist's criterion), which met the prerequisite for PSAs. The plateau modulus of PS5 and PS6 were very close to the limit, implying their contact deficiency. Peel performance is dependent upon both bonding efficiency (G' at 0.01 rad/s) and debonding resistance (G' and G'' at 100 rad/s).⁴³ The lower the G' (0.01 rad/s), the more favorable the bonding and the higher the peel strength. Furthermore, G' at 100 rad/s indicates the cohesive strength of adhesive, and G'' at 100 rad/s shows the energy of dissipation. Therefore, the higher G' (100 rad/s) and G'' (100 rad/s), the higher the peel strength.

PS2 had a good balance of relatively low G' (0.01 rad/s) of 36200 Pa and high G' (100 rad/s) and G'' (100 rad/s) of 68600 Pa and 7032 Pa, corresponding to its high peel strength of 4.47 N/in, while the G' (0.01 rad/s) values of PS3, PS4, PS5, and PS6 were all much higher than that of PS2, which limited bonding efficiency and were consistent with lower peel values. Similar to peel correlation, tack performance also depends on bonding efficiency and debonding resistance (G' and G'' at 100 rad/s), except that the bonding

frequency during tack measurement was about 1 rad/s, rather than 0.01 rad/s.⁴³ Comparing the tack values in Table 5 and G' (1 rad/s), G' (100 rad/s), and G'' (100 rad/s) in Table 6 shows that they were also well correlated. Shear performance was correlated with the G' at 0.01 rad/s.⁴³ Generally, the higher the G' (0.01 rad/s), the better the shear. G' (0.01 rad/s) of PS1 and PS7 was smaller than other PSAs, which corresponded to their weak shear resistance.

We further comparatively studied the viscoelasticity of S2 and PS2 of pure polymers and formulated PSAs containing rosin ester tackifier (Figure 7). Tackifier is usually a critical composition of PSA to balance the viscoelastic property of the adhesive suitable for bonding and debonding.⁴⁴ It is obvious that plateau modulus (G' at 0.01 rad/s) was greatly reduced by adding rosin tackifier, which ensured a good wetting and bonding of PS2 at bonding frequency. Moreover, G' and G'' at 100 rad/s were still high enough to achieve adequate cohesive strength and energy dissipation. The viscoelasticity information was consistent with the significantly higher peel adhesion strength of PS2 (4.47 N/in) compared with that of S2 (0.76 N/in). A similar tackifier effect on the viscoelastic properties of polyolefin based PSAs was also reported.⁴⁵

4. Conclusions

Acrylic polyols with 1, 1.5, and 2 acrylates per triglycerides were synthesized, and viscoelastic acrylate polymers were developed via UV polymerization. DSC and DMA measurements revealed that polymers based on a moderate amount of acrylic polyol with lower acrylate functionality (~1) had a better balance of wettability (i.e., T_g) and cohesive strength (i.e., rubbery plateau modulus or cross-link density) and thus were more suitable for PSAs. Compared with polymers from commercial fully acrylated epoxidized soybean oil, the semi-acrylic polyols provide the most potential for PSA applications. This was attributed to the extra polar hydroxyl groups on the polymer backbones, which act as critical adhesion sites to improve wetting onto the substrate and accelerate bonding via polar attraction. The newly developed biobased acrylic polyols are promising alternatives to petrochemical based counterparts for acrylic PSAs.

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Table 1. Composition of ESO derived acrylic polyol polymers and PSAs.

Sample ^a	DAESO1,g	DAESO1.5,g	DAESO2,g	CAESO,g	AESO1,g	2-EHA,g	Sample ^{ab}
S1	0.75	/	/	/	/	1.15	PS1
S2	1	/	/	/	/	0.9	PS2
S3	1.25	/	/	/	/	0.65	PS3
S4	/	1	/	/	/	0.9	PS4
S5	/	/	1	/	/	0.9	PS5
S6	/	/	/	1	/	0.9	PS6
S7	/	/	/	/	1	0.9	PS7

Note: ^aEach formula also contains a fixed amount of 0.1 g acrylic acid and 0.06 g photoinitiator. ^bPS sample composition is similar to the corresponding S sample, except that the PS formula also contains 0.5 g rosin ester.

Table 2. Properties of ESO derived acrylic polyols.

Sample ^a	Epoxy content, %	Hydroxyl value, mg KOH/g	Epoxy functionality -NMR	Acrylate functionality -NMR	Theoretical acrylate functionality
AESO1	4.04±0.07	107.8±7.0	3.7	1.1	1.0
DAESO1	0.13±0.03	260.9±5.5	0	1.1	1.0
DAESO1.5	0.09±0.01	255.0±6.1	0	1.5	1.5
DAESO2	0.12±0.02	212.0±6.5	0	2.0	2.0
CAESO	0.11±0.02	156.0±3.4	0	2.7	/

Note: ^aAESO1 stands for acrylated epoxidized soybean oil with 1 acrylate group per triglyceride; DAESO1, DAESO1.5, and DAESO2 stand for acrylic polyols with 1, 1.5, and 2 acrylate groups per triglyceride, respectively; CAESO stands for commercial acrylated epoxidized soybean oil.

Table 3. DSC thermal properties of ESO derived acrylate monomers and polymers.

Sample	T_g , °C	ΔC_p , J/(g·°C)	T_m , °C	ΔH_m , J/g
DAESO1	-31.3	0.36	7.4	13.1
2-EHA	-85	/	/	/
DAESO1 homopolymer	-27.2	0.41	9.8	10.3
2-EHA homopolymer	-58	/	/	/
S1	-46.4	0.18	-0.1	2.9
S2	-41.6	0.27	2.7	3.6
S3	-35.2	0.30	4.0	4.8
S4	-38.9	0.37	4.7	1.5
S5	-30.5	0.50	/	/
S6	-22.5	0.51	/	/
S7	-59.5	0.37	-9.5	4.1

Table 4. Viscoelastic properties of ESO derived acrylic polyol polymers.

Sample	Density, g/cm ³	T _{g,DMA} , °C	Tan δ _{peak} height	G' @ T _{g,DMA} +50, MPa	T _{g,DMA} +50, °C	Cross-link density, v _e , mol/m ³	Mc, g/mol	Gel content, %
S1	1.26	0.1	0.76	0.07	50.1	26.0	48375.0	73.25±0.33
S2	1.23	5.0	0.76	0.10	55	36.7	33557.3	74.90±0.40
S3	1.26	12.4	0.70	0.16	62.4	57.4	21969.4	75.86±0.41
S4	1.13	6.0	0.66	0.23	56	84.0	13444.8	81.72±0.43
S5	1.11	9.7	0.54	0.29	59.7	104.8	10592.1	87.55±0.22
S6	1.08	20.1	0.37	0.65	70.1	227.8	4741.7	93.32±0.22
S7	1.27	-19.8	0.83	0.09	30.2	35.7	35589.0	70.62±0.37
PSA prerequisite ^a							10 ⁴ -10 ⁵	

Note: ^a prerequisite Mc for PSA is 10⁴-10⁵ g/mol³⁸.

Table 5. Peel, tack, and shear adhesion properties of ESO derived acrylic polyol PSAs.

Sample	Peel strength, N/in	Tack, N/in	Shear resistance, mins
PS1	4.29±0.17 ^a	8.16±0.21	5,300±980
PS2 ^b	4.47±0.13	7.14±0.05	>50,000
PS3	2.87±0.60	4.75±0.95	>50,000
PS4	2.42±0.51	2.03±0.25	>50,000
PS5	0.77±0.27	0.47±0.21	>50,000
PS6	0.70±0.13	0.08±0.01	>50,000
PS7	1.15±0.09	1.56±0.02	500±100

Note: ^asome cohesive failure was noticed. ^bPeel strength of S2 pure polymer (without rosin) was 0.76±0.06 N/in.

Table 6. Characteristic viscoelasticity values of ESO derived acrylic polyol PSAs.

Sample	G'(0.01 rad/s), Pa	G''(0.01 rad/s), Pa	G' (1 rad/s), Pa	G' (100 rad/s), Pa	G'' (100 rad/s), Pa
PS1	15200	66.8	15460	45900	4759
PS2	36100	133.9	36400	68600	7032
PS3	47910	7875	58480	95800	17650
PS4	83650	978	86580	113400	9266
PS5	148500	33830	192200	237000	29510
PS6	238400	28760	298700	386800	51960
PS7	24100	913.3	25690	44060	1075
Dahlquist ^a	<3.3 x 10 ⁵				

Note: ^a According to the Dahlquist criterion, the prerequisite plateau modulus value (G' at 0.01 rad/s) for PSA should be lower than 3.3 x 10⁵ Pa^{40, 41}.

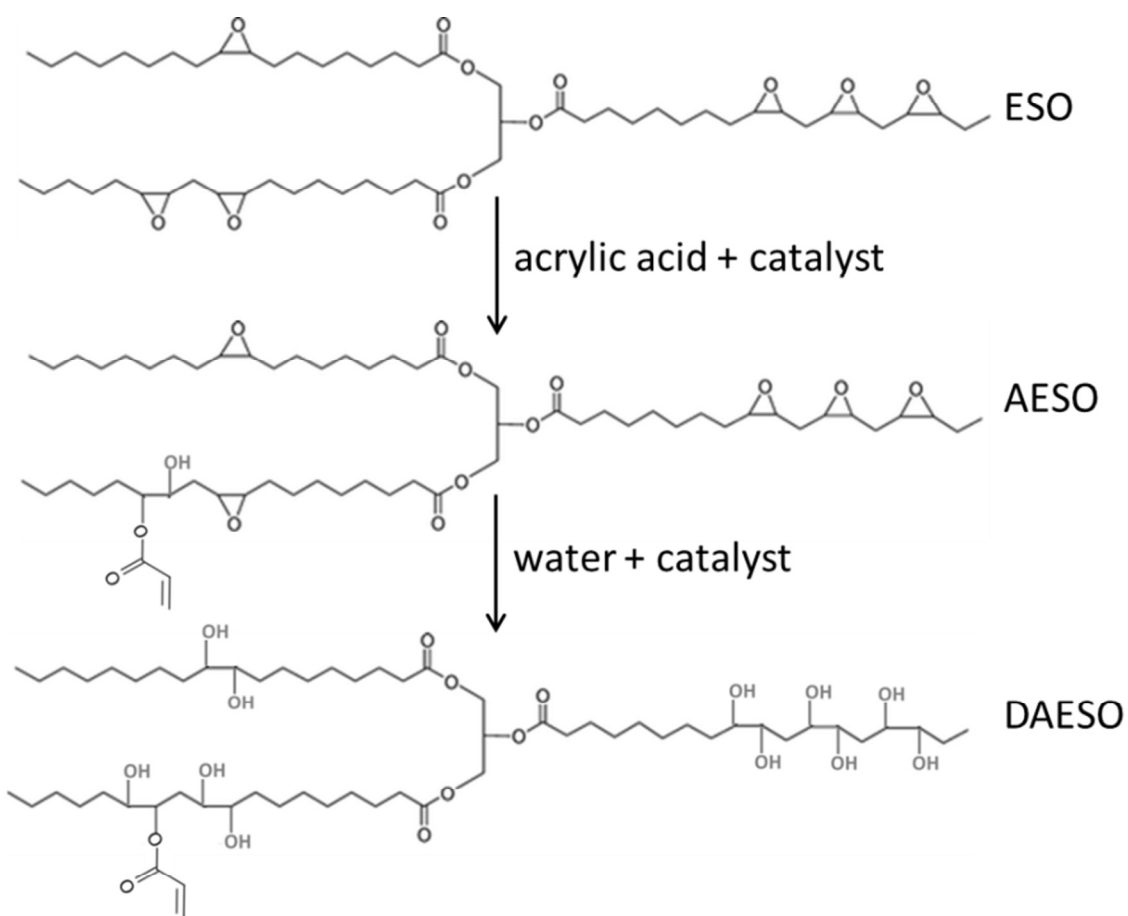


Figure 1. Synthesis of acrylic polyols from ESO (functionality of acrylate, epoxide, and hydroxyl groups of triglycerides may vary depending on reaction conditions).

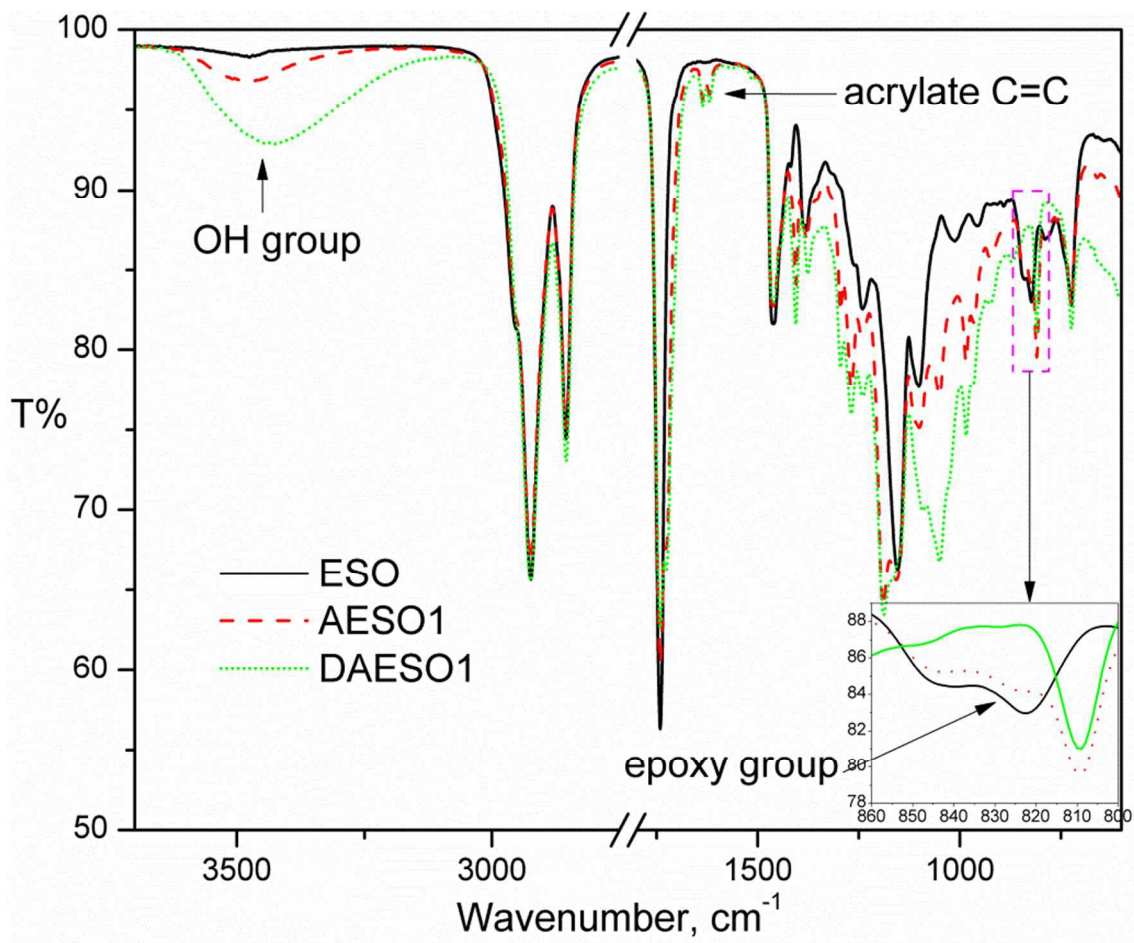


Figure 2. FTIR of ESO, AESO1, and DAESO1. (The inserted graph is enlargement of epoxy area.)

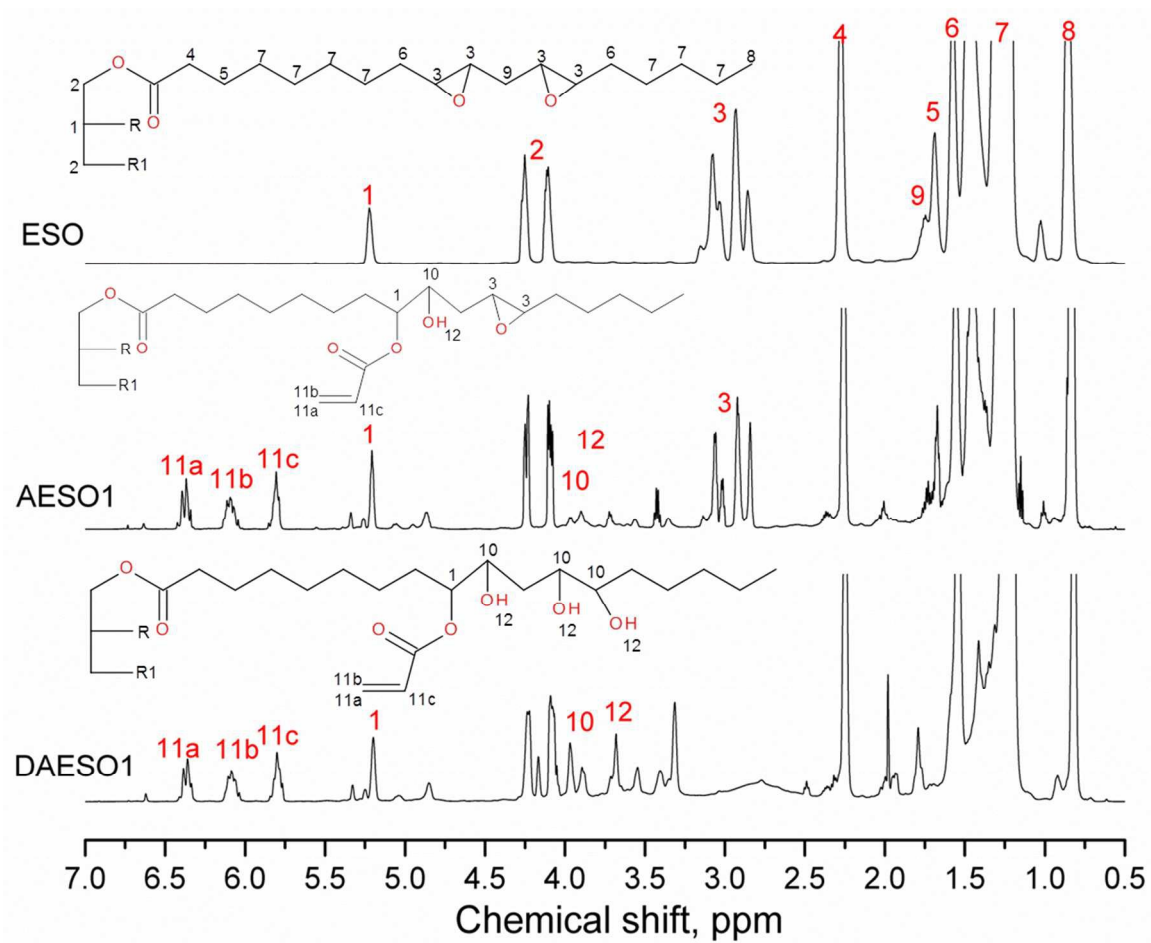


Figure 3. $^1\text{H-NMR}$ (CDCl_3) spectra of ESO, AESO1, and DAESO1.

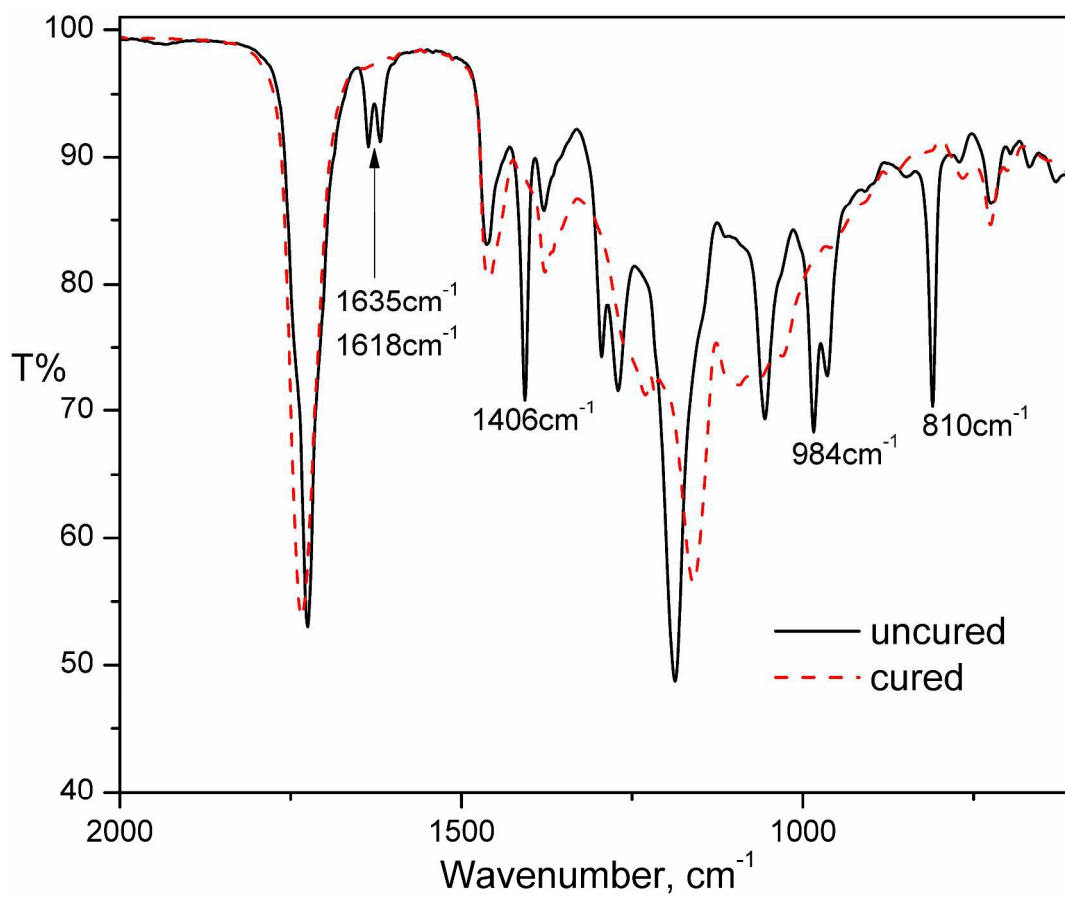


Figure 4. FTIR of sample S2 before (uncured) and after (cured) UV radiation polymerization.

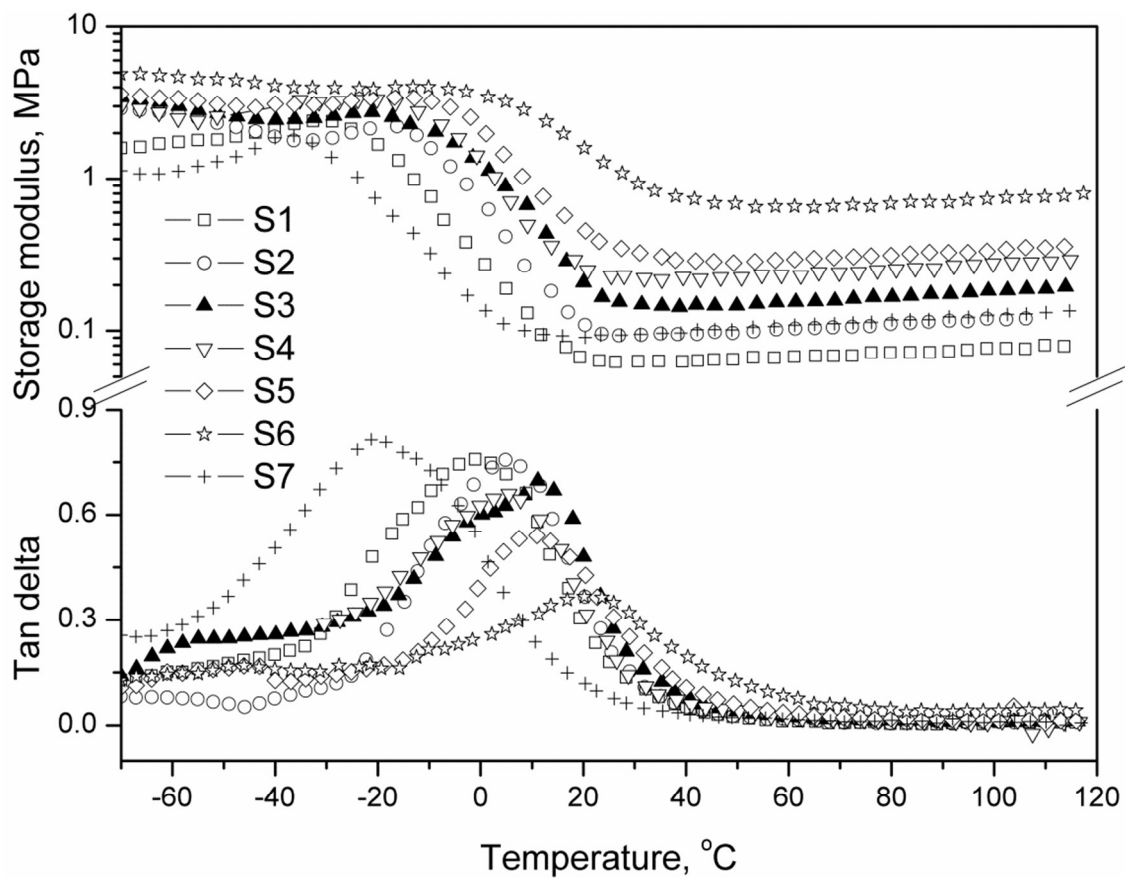


Figure 5. Storage modulus and $\tan\delta$ of the polymers as a function of temperature.

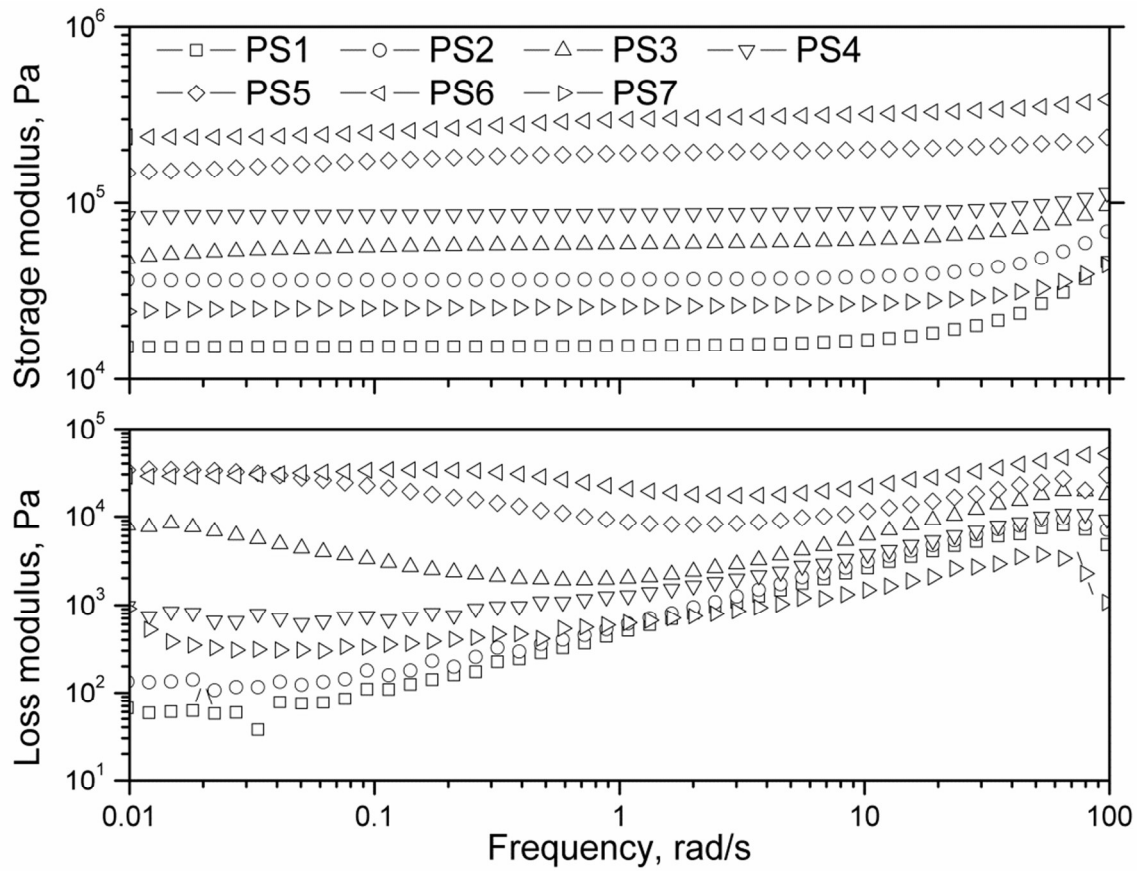


Figure 6. Frequency sweep of the PSAs.

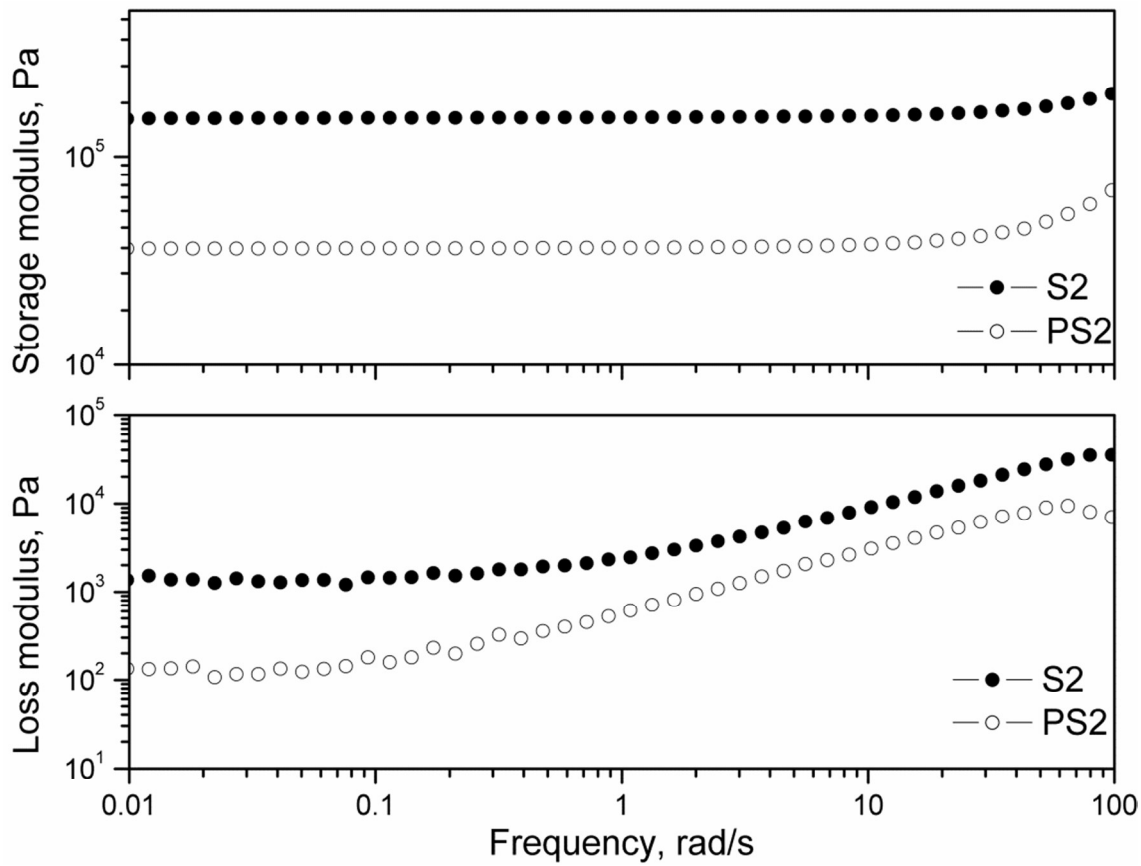


Figure 7. Frequency sweep of samples S2 (pure polymer) and PS2 (with rosin).