

Rapid room-temperature polymerization of bio-based multiaziridine-containing compounds

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Abstract

Successful Michael addition under mild reaction conditions resulted in the grafting of 2-methyl aziridine onto acrylated epoxidized soybean oil, and the aziridine content was titrated as 0.00413 mol g⁻¹. Multiaziridine-containing acrylated epoxidized soybean oil (AESO-AZ) was then subjected to rapid room-temperature polymerization with succinic acid, citric acid, and an isosorbide-based diacid, respectively. The polyacids were added to AESO-AZ at stoichiometric ratios. The resulting polymeric materials were cast into films in order to investigate their thermo-mechanical properties. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and tensile stress–strain tests were performed. The glass transition temperatures (T_g) of the samples suggested that increased functionality of the carboxylic acid groups in the polyacids may have effectively increased T_g, while the rigid rings in isosorbide did not have significant impact on T_g. This work illustrates the feasibility of synthesizing bio-based multiaziridine-containing compounds that can be used as the monomer for rapid polymerization with bio-based polyacids at ambient temperature.

Introduction

Aziridines (AZ) contain a three-membered heterocycle with one amine group (–NH–).¹ Aziridines are known as reactive compounds in nucleophilic ring-opening reactions. There is a considerable amount of published research on multi-functional aziridines as post-curing systems containing free carboxylic acid groups. Xia et al.² employed a triaziridine-based crosslinker (CX-100) to post-cure castor oil-based anionic PU dispersions, utilizing the presence of carboxylic groups as stabilizers. This led to an increase in crosslinking density of the polymer system, higher glass transition temperature (T_g), and higher Young's modulus. Chen et al.³ reported using a mono-aziridine compound as the monomer together with acrylic acid to trigger self-polymerization. The current literature does not report work directly utilizing a multi-aziridine-based compound as the monomer for ring-opening polymerization.

Most of the multi-aziridine-based compounds are derived from petroleum-based molecules via Michael addition, e.g., through the addition of amine onto activated unsaturated groups (e.g., acrylics).⁴ The amine bridges (–NH–) in aziridine and 2-methyl aziridine were used to react with

acrylics.^{5,6} It is worth noting that the acrylics used as the substrates for aziridine addition are mostly small, trifunctional molecules that are not bio-renewable.^{1,2,6,7} For the purpose of developing products with high renewable content, acrylated epoxidized soybean oil (AESO), a derivative product of soybean oil, was selected because it provides multifunctionality. AESO is a known renewable material in a number of applications, such as coatings, adhesives, and others.⁸ Its acrylic group enables the reaction with aziridine and 2-methyl aziridine. In this work, we propose the synthesis of an aziridine-containing compound (AESO-AZ) by reacting bio-based acrylated epoxidized soybean oil with excess 2-methyl aziridine. The structure of the obtained product was confirmed by multiple spectroscopic methods (FTIR, ¹H NMR, ¹³C NMR). Gel permeation chromatography (GPC) and rheometry tests were performed to determine the fundamental properties of AESO-AZ. The aziridine content was 0.00413 mol g⁻¹; it was used to calculate the stoichiometric quantity of polyacids necessary for polymerization.

Succinic acid, citric acid, and an isosorbide-based diacid⁹ were used to polymerize AESO-AZ in a catalyst-free process that took place rapidly at ambient temperature. The effect of both functionality and chemical structure of the polyacids on physical and thermal properties of the polymeric products was analyzed by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and tensile tests. Since the polyacids were bio-based and AESO-AZ was partially bio-based, the resulting polymeric materials had a high bio-content. The fast polymerization rate may trigger the interest of industry to develop applications for this novel polymerization system.

Experimental

Materials

Acrylated epoxidized soybean oil (AESO) containing 4000 ppm monomethyl ether hydroquinone as inhibitor, dichloromethane (CH₂Cl₂), N,N-dimethylformamide (DMF), succinic acid, citric acid, 2-methylaziridine, 0.1 N perchloric acid concentrate (HClO₄), tetrabutylammonium iodide, 0.5% crystal violet solution, chloroform (CHCl₃), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (Milwaukee, WI). Ethanol was purchased from Decon Laboratories Inc., King of Prussia, PA. All materials were used as received without further purification.

Preparation of AESO-AZ

AESO (20 g) was dissolved in 30 mL dichloromethane and placed in a round-bottom flask. Dichloromethane solution (15 mL) of 2-methylaziridine (5 g) was added drop wise (1 drop per s) through an addition funnel in an ice bath. The reaction mixture was kept at ambient temperature for 18 h after addition. Dichloromethane and excess 2-methylaziridine were removed by roto-evaporation at 68 °C under reduced pressure. The obtained AESO-AZ was oven-dried overnight. The resulting AESO-AZ was a brown, viscous liquid at room temperature. This reaction has a 100% yield. The reaction is shown in [Fig. 1](#).

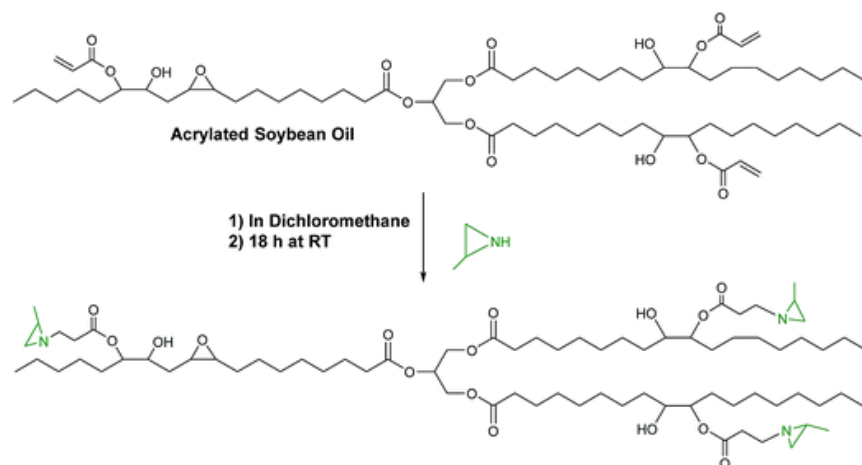


Fig. 1 Synthesis of AESO-AZ.

Succinic acid, citric acid, and an isosorbide-based diacid were used to polymerize AESO-AZ. The structures of the three polyacids are shown in Fig. 2. The isosorbide-based diacid was synthesized according to the protocol published in:⁹ it was derived from the double esterification of isosorbide by succinic anhydride under solvent-free conditions. DMF solution of AESO-AZ (20%) and a corresponding DMF solution of polyacid (20%) were mixed in vials for 10 min. The mixture was then poured into a Teflon mold (5 in \times 5 in) and dried at ambient temperature. The mold was placed in an oven at 60 °C for 24 h. The stoichiometric polymerization between AESO-AZ and diacids has a yield of 99–97%, given that unreacted monomers can be removed in the last oven-drying step. The obtained films were transparent, indicating the amorphous nature of the polymer network.

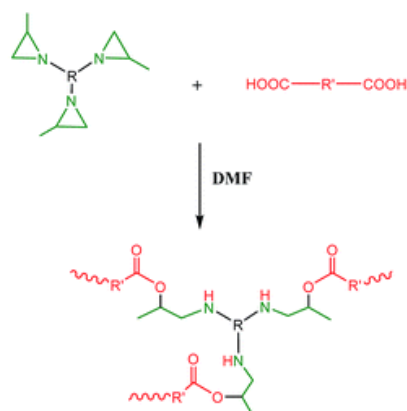
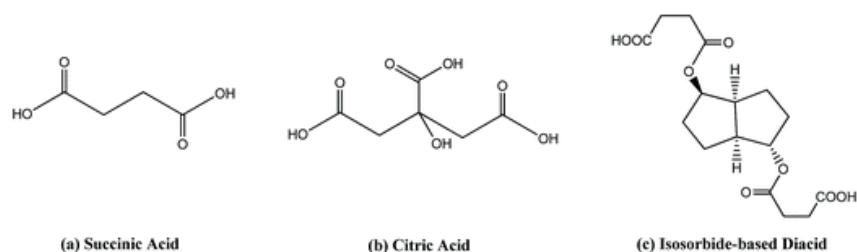


Fig. 2 Demonstration of the polymerization of AESO-AZ with a polyacid.

Characterization

The aziridine content of AESO-AZ was determined according to the titration method published by Jay.¹⁰ Approximately 0.5 g (precisely weighed) of the sample was dissolved in 15 mL chloroform, then 15.00 mL 10% chloroform solution of tetrabutylammonium iodide together with 2 to 3 drops of crystal violet indicator were added. The mixture was titrated with 0.1 N HClO₄. A blank sample was used to eliminate background effects. This titration method is also applicable to epoxy groups; therefore, AESO was titrated as well since it contains some residual epoxy groups resulting from the manufacturing process (acrylation of epoxidized soybean oil). ¹H NMR spectra of AESO and AESO-AZ were recorded on a Varian spectrometer (Palo Alto, CA) at 300 MHz in chloroform-d. The average molecular weight of AESO and AESO-AZ were determined by a Thermo Scientific Dionex Ultimate 3000 GPC (Sunnyvale, CA) equipped with a Shodex Refractive Index (RI) at room temperature. Tetrahydrofuran (THF) was used as eluent solvent and the delivery speed was 1.0 mL min⁻¹. The viscosity of AESO-AZ was measured by varying the shear rate from 10 s⁻¹ to 1000 s⁻¹ on an AR2000 Rheometer (TA Instrument).

The gel content was measured via Soxhlet extraction. A known weight (W_0) of pre-conditioned sample was placed in the Soxhlet extractor with continuous THF extraction for 1 day. The remaining sample was dried and weighed as W_1 . Three tests were performed for each sample. The gel content was calculated as:

$$\text{Gel content\%} = \frac{W_1}{W_0} \times 100\%$$

Differential scanning calorimetry (DSC) was performed on a TA Instrument Q20. Samples were heated to 100 °C in the first ramp in order to eliminate their heat history. The samples were then cooled down to -50 °C and heated to 100 °C at a rate of 10 °C min⁻¹. The heat profile of the second heating ramp was recorded and the glass transition temperature was determined using the midpoint inflection method.

A DMA Q800 (TA Instruments) was implemented to record the dynamic thermal mechanical behavior of the samples. Film-tension mode of 1 Hz was used for testing rectangular samples with a dimension of 15 mm × 10 mm. The samples were kept isothermally for 3 min at -80 °C, followed by a temperature rise to 120 °C at a programmed rate of 3 °C min⁻¹. Tan δ was calculated as the loss modulus divided by the storage modulus and the glass transition temperatures (T_g s) were determined by the peaks of the tan δ curves.

Thermogravimetric analysis (TGA) of the films was conducted on a TA Instrument Q50 (New Castle, DE). At a constant air flow rate of 60 mL min⁻¹, the samples were heated from ambient temperature to 650 °C at a rate of 20 °C min⁻¹. The decomposition profile was recorded as a function of temperature.

The tensile profiles of the samples were determined using an Instron universal testing machine (model 4502). Rectangular samples of 50 mm × 10 mm were subjected to tension at a crosshead

speed of 100 mm min^{-1} . The tests were replicated at least three times for each sample. Toughness was calculated by integrating the area beneath the stress–strain curve.

Results and discussions

Preparation and properties of AESO-AZ

Michael addition of 2-methylaziridine to acrylic groups on AESO was used to prepare AESO-AZ. The synthesis followed a published method with modifications.¹ An excess amount of 2-methylaziridine was added and the unreacted residual was removed via roto-evaporation, an approach possible because of the low boiling point of 2-methylaziridine (b.p. $66\text{--}67 \text{ }^\circ\text{C}$). FTIR spectra of AESO and AESO-AZ are shown in Fig. 3. The disappearance of the peak at 1635 cm^{-1} (blue box) indicated the complete conjugate addition to the acrylic groups. The peak at 3053 cm^{-1} was attributed to the C–H stretching on the aziridine ring. The peaks at 2930 cm^{-1} and 2850 cm^{-1} (C–H stretching in fatty acid chains) and at 1750 cm^{-1} (C=O stretching of ester groups) remained unchanged after the reaction, indicating that the triglyceride structure of AESO was preserved.

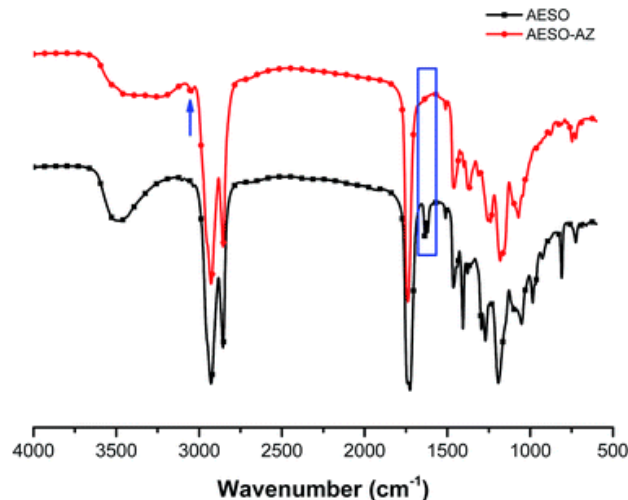


Fig. 3 FTIR spectra of AESO and AESO-AZ.

The $^1\text{H-NMR}$ spectra in Fig. 4 also confirmed the completion of this reaction. Peaks d, e, f, corresponding to the hydrogen atoms on the acrylic group, disappeared after the reaction, which indicated the occurrence of a Michael addition. Peaks g and h in AESO-AZ were attributed to methylene protons that established that the acrylics were saturated after Michael addition. The three hydrogen atoms on the aziridine ring structure could not be clearly observed, but peak i, corresponding to the methyl group of 2-methylaziridine, established that 2-methylaziridine was the nucleophile in the Michael reaction. That the aziridine ring remained intact during the reaction was hard to prove by NMR, but the success of the subsequent polymerization with polyacids provided strong evidence that the aziridine ring was indeed intact. Peaks a, b, and c, associated with the hydrogen atoms labeled on the embedded structure, remained throughout the reaction, further confirming the preservation of the basic structure of AESO.

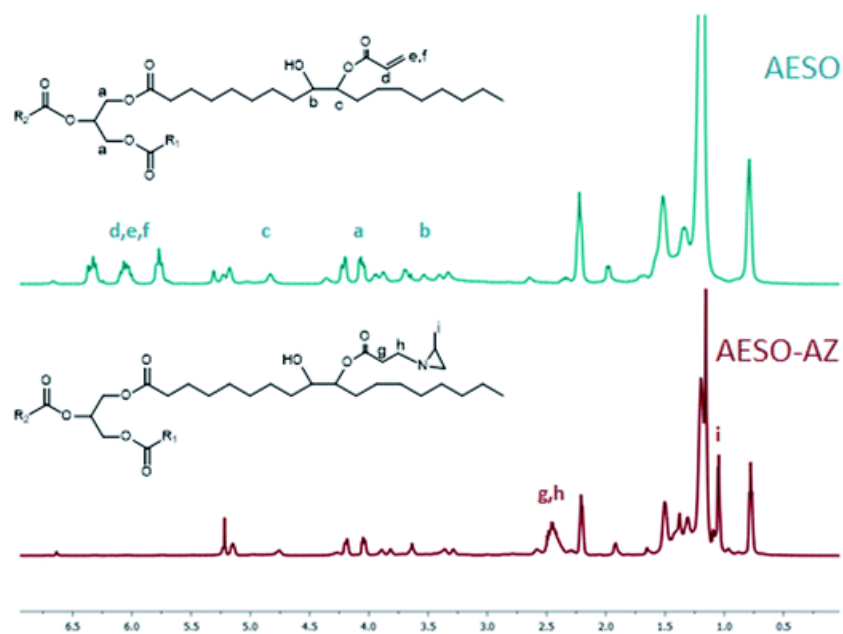


Fig. 4 ^1H -NMR spectra of AESO and AESO-AZ.

^{13}C -NMR spectra were obtained for AESO and AESO-AZ. In [Fig. 5](#), the disappearance of peaks a and b and the appearance of peaks c and d illustrated the fact that the acrylic groups of AESO underwent Michael addition with the $-\text{NH}$ -bridges of the 2-methylaziridine.

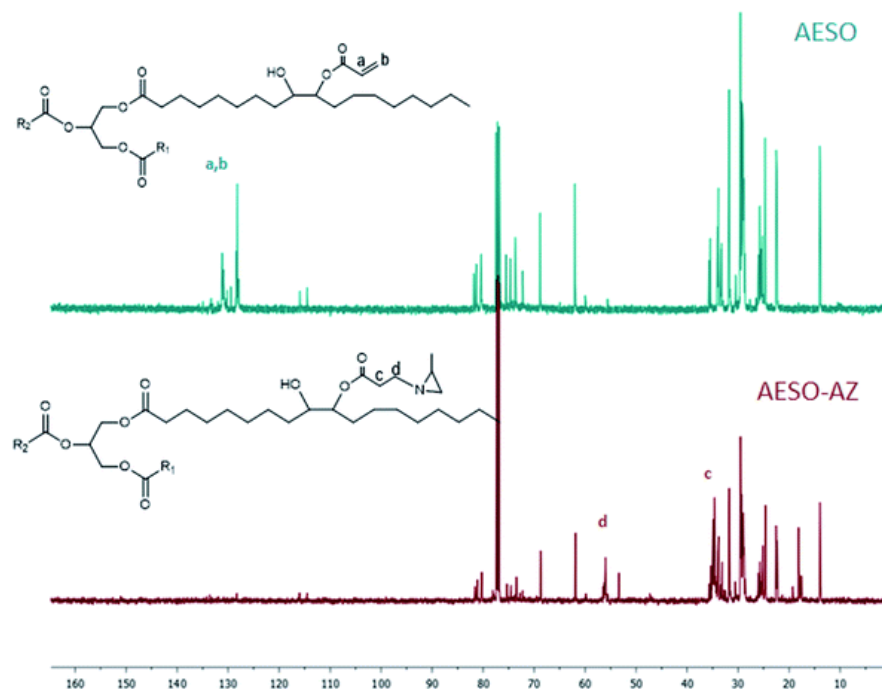


Fig. 5 ^{13}C -NMR spectra of AESO and AESO-AZ.

The viscosities of AESO and AESO-AZ at room temperature and the molecular weights M_n and M_w are summarized in [Table 1](#). There was no distinct difference in viscosity between the two

specimens, indicating that the intermolecular interactions were not remarkably changed after the reaction. The molecular weight of AESO-AZ was slightly higher than that of AESO because of the addition of 2-methylaziridine.

Table 1 Properties of AESO and AESO-AZ

| | Viscosity (Pa s ⁻¹) at 25 °C | M _n (g mol ⁻¹) | M _w (g mol ⁻¹) | PDI |
|---------|--|---------------------------------------|---------------------------------------|------|
| AESO | 27.3 | 1967 | 2165 | 1.10 |
| AESO-AZ | 29.9 | 2492 | 2665 | 1.07 |

Titration of the aziridine content was critical in order to determine the amount of polyacids required for the polymerization step, because the molar ratio of aziridine and carboxylic acid has to be 1 : 1. This titration method is also applicable to epoxy. Upon titration, AESO had an epoxy content of 5.55×10^{-5} mol g⁻¹. Assuming that there was no change in epoxy content after Michael addition, the epoxy content was subtracted from AESO-AZ to get a net content of aziridine. AESO-AZ had an aziridine content of 0.00413 mol g⁻¹.

Polymer properties

Differential scanning calorimetry (DSC) was used to determine the thermal transitions of the polymeric materials and the DSC thermograms of the samples are shown in Fig. 6. Each sample exhibited only one T_g, indicating a homogenous structure. In addition, no melting was observed, so all samples were determined to be amorphous. Notice that the polymer derived from succinic acid and AESO-AZ (succinic-AZ) exhibited the lowest T_g at 12.0 °C. When succinic acid was replaced by citric acid (citric-AZ) or the isosorbide-based diacid (iso-AZ), the T_g of the respective polymer increased to 20.3 °C and 20.8 °C. The increase in T_g of citric-AZ was attributed to a higher crosslinking density.¹¹ Because citric acid had a functionality of 3, while the functionality of succinic acid was 2, the formation of more crosslinking sites in citric-AZ was expected, resulting in a higher crosslinking density. For iso-AZ, the presence of hard segments contributed to the increased T_g.¹² The rigid ring structure introduced by isosorbide remained during polymerization and may have restricted the motion of the polymer chains. The increase in functionality of the citric acid monomer in citric-AZ and the addition of hard segments in iso-AZ had similar effects on T_g.

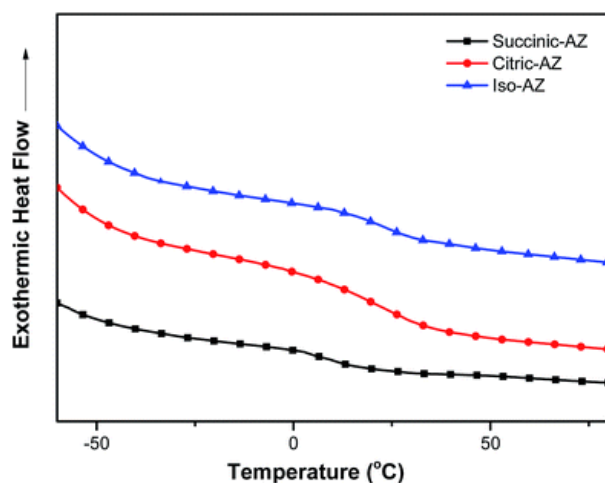


Fig. 6 DSC curves of succinic-AZ, citric-AZ and iso-AZ.

Fig. 7 shows the storage modulus (E') and the loss factor ($\tan \delta$) as functions of temperature. In the low temperature regime, all samples were in a glassy state so that the storage modulus was relatively high because of the low mobility of the polymer chains. In addition, E' dropped slightly before the temperature reached the material's glass transition point at which point the polymer chains were activated. The T_g s obtained by DMA were defined by the peak of $\tan \delta$. Only one $\tan \delta$ was observed for each material, indicating the homogeneity of all investigated samples. The T_g s of succinic-AZ, citric-AZ, iso-AZ were 32.6 °C, 39.7 °C, and 38.9 °C, respectively. It is worth mentioning that the discrepancy between T_g values obtained by DSC and by DMA is a commonly observed phenomenon caused by the different measuring mechanisms. While DSC measures the heat capacity change from frozen to unfrozen chains, DMA measures the change in mechanical response of the polymer chains to heating.¹³ As the temperatures passed the glass transition point, all samples entered into the rubbery state and E' exhibited less dependence on temperature. A rubbery plateau was observed, strongly indicating the presence of a crosslinked network.¹⁴ The value of E' at $T_g + 50$ °C can be used to determine the crosslinking density (v_c):¹⁵

$$E' = 3v_cRT$$

where R is the universal gas constant, and T is the absolute temperature. The calculated crosslinking density for succinic-AZ, citric-AZ, iso-AZ were 287.4 mol m⁻³, 468.5 mol m⁻³, and 107.4 mol m⁻³, respectively, see Table 2. In addition, the height of $\tan \delta$ decreased with increasing crosslinking density, matching the calculated results.^{2,16} The difference in crosslinking density between citric-AZ and succinic-AZ was caused by the difference in functionality (3 vs. 2). The higher functionality created more crosslinking sites, creating a denser network. Although isosorbide-based diacid has the same functionality as succinic acid, iso-AZ exhibited a lower crosslinking density than succinic-AZ, which was attributed to the presence of the rigid isosorbide ring interrupting the crosslinking network. In addition, the rigid ring in isosorbide-based diacid may have restricted the compactness of the network.

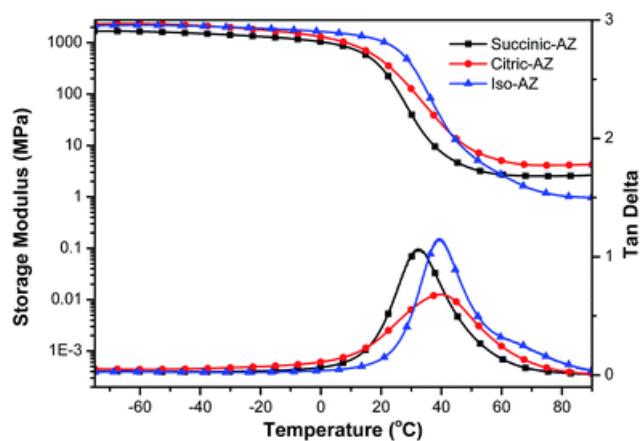


Fig. 7 Storage modulus and loss factor of succinic-AZ, citric-AZ and iso-AZ as functions of temperature.

Table 2 Summary of physical and thermal properties

| | Gel content (%) | T_g (°C) DSC | T_g (°C) DMA | v_c (mol m ⁻³) | T_{10} (°C) | T_{50} (°C) |
|-------------|-----------------|----------------|----------------|------------------------------|---------------|---------------|
| Succinic-AZ | 94.3 | 12.0 | 32.6 | 287.4 | 301.8 | 402.9 |
| Citric-AZ | 93.8 | 20.3 | 39.7 | 468.5 | 293.1 | 400.6 |
| Iso-AZ | 90.9 | 20.8 | 38.9 | 107.4 | 253.3 | 405.6 |

The gel content of all samples was close to or higher than 90% (see [Table 2](#)), indicating the presence of a highly crosslinked polymer network in each sample. The thermosetting behavior of the samples also confirmed successful polymerization.

The thermal resistance of the samples was investigated by TGA, see [Fig. 8](#). All samples underwent three stages of thermal decomposition in air atmosphere. The first weight loss occurred between 100 and 350 °C and was assigned to the dissociation of labile bonds, such as ester groups and secondary amine groups. Succinic-AZ and citric-AZ exhibited similar decomposition profiles, because they were derived from similar, small aliphatic polyacids and differed only in functionality. Decomposition onset of iso-AZ occurred at lower temperatures and was attributed to the instability of isosorbide-based diacid, which underwent ester group dissociation at temperatures above 100 °C. The second thermal degradation stage between 350 and 450 °C was attributed to chain scission in the soybean oil structure.¹⁶ The last stage, above 450 °C, was caused by further thermo-oxidation of the samples due to the presence of oxygen in air atmosphere. The temperatures of 10% and 50% weight loss, T_{10} and T_{50} respectively, are summarized in [Table 2](#). Iso-AZ exhibited the lowest T_{10} because of the low thermal resistance of the ester bond attached to the isosorbide ring. The T_{50} s for all samples were similar as these temperatures reached the regime of chain scission for the triglyceride structures.

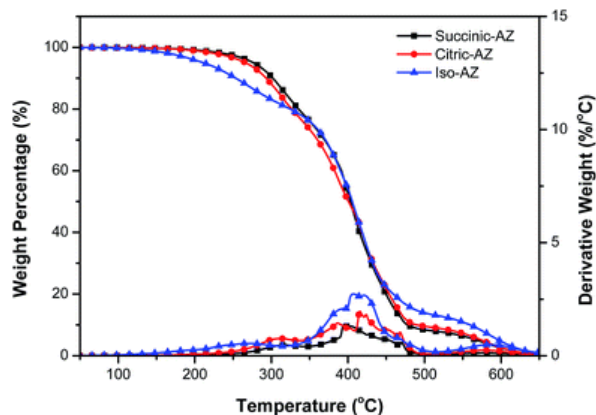


Fig. 8 TGA curves and their derivative curves for succinic-AZ, citric-AZ and iso-AZ.

Tensile profiles for all samples are plotted in [Fig. 9](#). Young's moduli, tensile strength at break, elongation at break, and toughness are summarized in [Table 3](#). Citric-AZ and iso-AZ were stiffer

and stronger compared to succinic-AZ. The relatively higher crosslinking density of citric-AZ provided better resistance to deformation and thus resulted in higher Young's modulus than succinic-AZ. The low crosslinking density of iso-AZ was compensated by the presence of the rigid ring. Succinic-AZ exhibited the highest ductility of all samples, following a common rule that weaker materials exhibit higher ductility.² All samples showed comparable toughness.

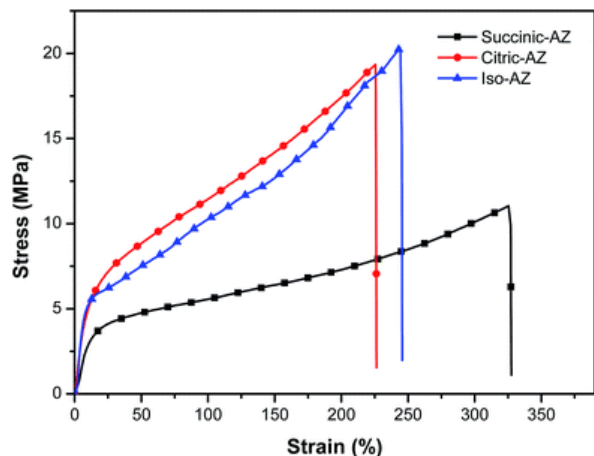


Fig. 9 Stress–strain curves for succinic-AZ, citric-AZ and iso-AZ.

Table 3 Summary of mechanical properties

| | E (MPa) | σ_b (MPa) | ε_b (%) | Toughness (MPa) |
|-------------|-----------|------------------|---------------------|-----------------|
| Succinic-AZ | 35.6 | 11.0 | 327.3 | 22.2 |
| Citric-AZ | 61.0 | 19.4 | 225.9 | 27.2 |
| Iso-AZ | 84.4 | 20.3 | 244.3 | 28.6 |

Conclusions

2-Methylaziridine was grafted onto acrylated epoxidized soybean oil through a Michael addition. The clean and complete incorporation of 2-methylaziridine into the product was confirmed by FTIR, ¹H-NMR and ¹³C-NMR. Polymeric materials were successfully obtained by solution polymerization at room temperature. The process took place rapidly and films were obtained by evaporation of the solvents. Generally, the glass transition temperatures of citric-AZ and iso-AZ were higher than that of succinic-AZ, which was attributed to a difference in functionality of the respective acids. Citric acid has a functionality of 3, while succinic acid has a functionality of 2. High functionality results in higher crosslinking density, which contributes to the higher T_g . Though isosorbide-based diacid has the same functionality as succinic acid, the presence of a rigid ring derived from isosorbide increased the T_g . The higher Young's moduli and higher tensile strength of citric-AZ and iso-AZ were attributed to the same effect. Succinic-AZ was the most ductile polymeric material, resulting from the highest mobility of its polymer chains.

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