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Adipic acid – glutaric anhydride – epoxidised linseed oil biobased thermosets with tunable properties

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ABSTRACT

In this study, the preparation and characterization of biobased thermosets comprising epoxidized linseed oil (ELO), adipic acid and/or glutaric anhydride, initiated by *N*,*N*-4-dimethylaminopyridine (DMAP) is reported. By changing the ratio of adipic acid to glutaric anhydride, the obtained resins changed from soft and flexible to hard and brittle materials. The Young's modulus varied from 25 MPa to 1477 MPa, tensile strength varied from 10.3 MPa to 25.7 MPa, and the elongation at break varied from 2.7% to 67.5%. The maximum toughness was found with the sample containing 20% glutaric anhydride and 80% adipic acid. With the increase of glutaric anhydride content, the total heat released during the curing reaction and the glass transition temperature (T_g) increased. This is the first paper that reports the combination of glutaric anhydride and adipic acid as curing agents for epoxidized plant oils to produce thermosets ranging from flexible to hard.

Keywords: biobased epoxy resin, epoxidized linseed oil, adipic acid, glutaric anhydride, combination

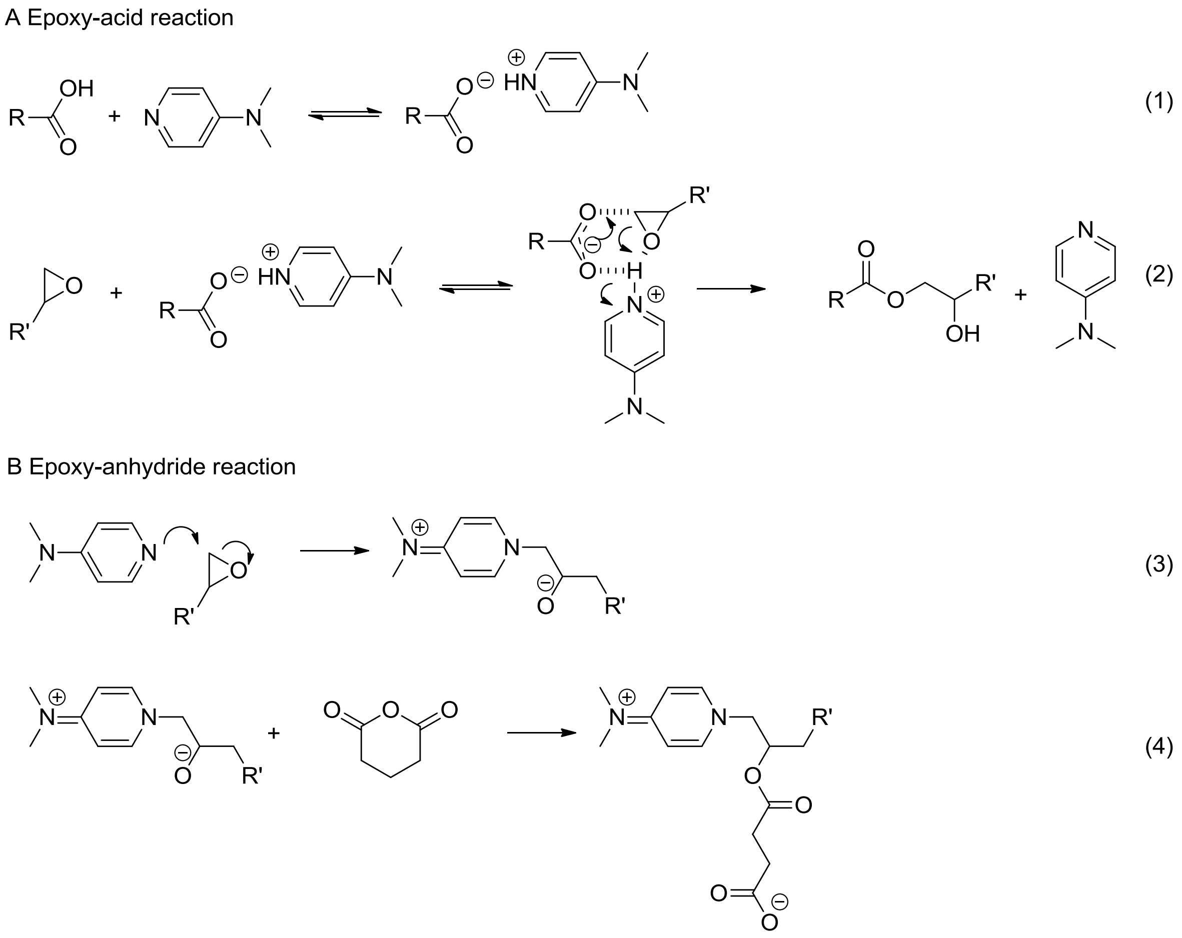
1. Introduction

Epoxidized plant oils (EPOs) are one of the most interesting bio-derived epoxy prepolymers due to their ease of preparation and availability. In industry, EPOs are easily prepared via the Prileshajev-epoxidation process with peracetic or performic acid generated in situ from hydrogen peroxide in the presence of an acid catalyst. EPOs are readily combined with a variety of curing agents, in particular amines and, carboxylic acids and their derivatives, to furnish epoxy thermosets. Carboxylic acids and anhydrides are more easily obtained from renewable materials [1].

Adipic acid (AA) is an important platform molecule in the industry. The global market volume for adipic acid will increase up to 3,747 kilo tons by 2020 [2]. The main applications of adipic acid include: a precursor for the synthesis of Nylon-6,6; polyester production, and polyurethane resins. In industry, adipic acid is synthesized from the oxidation of a mixture of cyclohexanol and cyclohexanone, the unrefined mixture is also known as KA oil, derived from benzene [3]. One serious concern involved in the current industry process is the generation of ozone-depleting greenhouse gas nitrous oxide (N_2O). The production of biobased adipic acid from renewable resources, either from glucose or from long-chain carbon substrates, has already been summarized by several authors [4, 5]. Compared to petroleum-derived adipic acid, biobased adipic acid is both environmentally friendly and cost competitive including lower capital, utilities cost and manufacturing cost [2].

Cyclic anhydrides with 5- and 6-membered rings (succinic anhydride and glutaric anhydride, GA) can be readily synthesized by heating the appropriate diacid in the presence of powerful acylating or dehydrating agents such as acid chloride, phosgene, thionyl chloride, benzenesulfonyl chloride, ketene, or phosphorus pentoxide. However, these methods either involve toxic reagents and harsh conditions or are not effective. In recent years, dialkyl dicarbonates under weak Lewis acid catalysis systems were developed to synthesize cyclic anhydrides from dicarboxylic acids under mild conditions with high yield and selectivity [6]. Biological studies on production of glutaric acid are still in their early stages. Revelles *et al.* showed the production of glutaric acid from the enzymatic conversion of δ-aminovaleric acid which was the degraded product of l-lysine [7, 8]. To the best of our knowledge, glutaric anhydride has not been used as curing agent with plant oil-derived epoxy systems. However, Samper *et al.* studied epoxidised linseed oil (ELO) and/or epoxidised soya bean oil (ESBO) cured with mixtures of maleic anhydride (MA) and phthalic anhydride (PA) and their results showed that at the eutectic point MA/PA mixture had lower melting point than the individual anhydrides, which may decrease the curing temperature [9]. Jain *et al.* studied the curing process of diglycidyl ether of bisphenol A (DGEBA) with mixtures of amines and anhydrides [10, 11]. Their results showed that, through combination of amine and anhydride curing agents, the peak curing temperature (T_P) was decreased without affecting their thermal stability. Rocks *et al.* studied the curing behavior of MA and pyromellitic acid dianhydride (PMDA) cured aminoglycidyl epoxy resins [12]. Different curing behavior was observed with the mixed anhydrides from the individual anhydrides.

The reaction mechanism between epoxy groups an acid/anhydride has been extensively studied [13-17]. A proposed reaction mechanism of ELO cured by adipic acid/glutaric anhydride in the presence of DMAP as initiator is shown in Scheme 1, which only shows the main esterification reactions and other reactions such as etherification, homopolymerization, condensation esterification and hydrolysis reactions are also possible [18].



Scheme 1 Reaction mechanism for the polymerization of ELO using DMAP as an initiator and adipic acid/glutaric anhydride as cross-linker.

We previously reported the effect of systematically increasing chain length of a series of linear α, ω-dicarboxylic acids (DCAs) from C6 to C18 diacids and a cyclic diacid, Pripol 1009F, on thermal and mechanical properties of the resultant epoxy thermosets derived from ELO [19]. The obtained epoxy resins were highly crosslinked polymers with only a small fraction of low molecular weight soluble materials. The glass transition temperature (*T*g), tensile strength, Young's modulus, elongation at break and toughness decreased while the thermal stability increased with respect to increasing chain length of DCAs. Interestingly, strain hardening was only observed for adipic acid (C6) sample for which the best mechanical properties were observed [19]. Thus, herein we study the thermal and physical properties of mixtures of glutaric anhydride and adipic acid as curing agent for ELO aiming to improve the stiffness of the sample.

2. Materials and methods

2.1 Materials

ELO (Lankroflex® L, oxirane content = 9.0%) was obtained from Akcros Chemicals, Eccles, England. Adipic acid (99.5%), glutaric anhydride (95%) and 4-*N*,*N*-Dimethylaminopyridine (DMAP) was purchased from Sigma Aldrich. All chemicals were used as received without further purification.

2.2 Film Preparation

All samples [GAA:AA, 100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100] were prepared with a stoichiometric relationship, R, of 1.0 (R = acid and/or anhydride groups:epoxy groups, one anhydride group for GA and two acid groups for adipic acid). For each formulation, the appropriate amount of DMAP added was calculated based on 1 mol% of epoxy functional groups. The mixture was stirred at 150 ^{o}C for 3-5 min, poured into a hot aluminium pan (internal diameter, 70 mm) and cured in a fan-assisted oven at 180 ^{o}C for 2 h.

2.3 Differential Scanning Calorimetry (DSC)

The DSC analyses were performed with a TA Instruments Q2000 DSC. Premixed samples (7-10 mg), obtained after stirring at 150 ^{o}C for 3 to 5 min as described previously in section 2.2, were hermetically-sealed in Tzero aluminum DSC pans with dry nitrogen flow (50 mL/min). Dynamic runs were performed under four different heating rates, 5, 10, 15 and 20 ^{o}C/min, over a temperature range of 25 ^{o}C to 320 ^{o}C. The results reported are the averages of the three measurements with limited or negligible variation seen between measurements as bulk properties were being determined. Glass transition temperature T_g was obtained by heat-cool cycling (10 ^{o}C/min) of the cured resins (7-10 mg) sealed in Tzero aluminum hermetic DSC pans.

2.4 ATR-IR analysis

ATR-IR (attenuated total reflection infrared) spectra were recorded on a Bruker Vertex 70 Spectrometer equipped with a diamond golden gate ATR cell over a scanning range of 650-4000 cm^{-1} for 32 scans at a spectral resolution of 2 cm^{-1}.

2.5 Mechanical properties

Standard dumb-bell shapes (60 mm × 10 mm) were cut with film thickness in the region of 1–1.5 mm. Tensile studies were conducted in triplicate using an Instron 3367 universal testing machine fitted with 1000 N capacity load cell. The initial grip separation was set at 35 mm and the crosshead speed was 20 mm/min. The results reported were the average of the three measurements.

2.6 Thermal stability

The thermal stability of the cured resins was analyzed using Netzsch STA 409. Approximately 20-30 mg of the sample was heated from room temperature to 600 ^{o}C at a heating rate of 10^{o}C/min under nitrogen gas atmosphere. Only one sample per composition was analysed.

2.7 SEM analysis

Scanning electron micrographs (SEM) analysis of the fracture surfaces of these samples after tensile tests were taken on a JEOL JSM-6490LV (JEOL, Tokyo, Japan). Prior to analysis, samples were mounted on alumina sample holders and coated in a thin film of gold using a high-resolution sputter SC-7640 coating device at a sputtering rate of 1500 V min^{-1}.

3. Results and discussion

3.1 DSC analysis

The DSC thermograms of premixed mixtures of ELO with different compositions of glutaric anhydride and adipic acid are shown in Fig. 1 and thermal properties associated with curing are tabulated in Table 1.

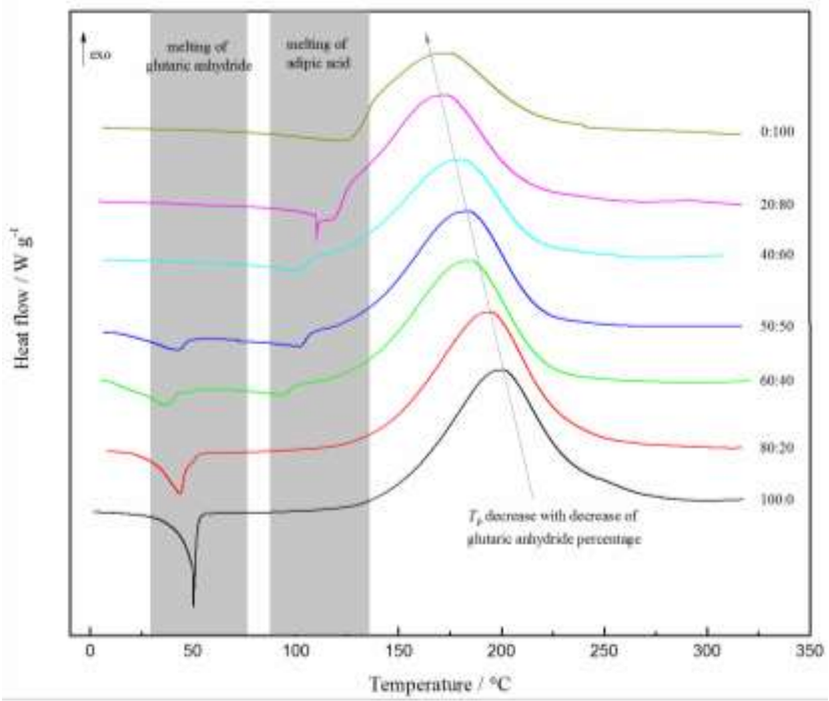


Fig. 1. Thermograms of premixed mixtures of ELO with different compositions of GA:AA at 10 ^{o}C min^{-1}.

All samples show one to two endothermic peaks and one exothermic peak. The first endothermic peak occurring at about 50 ^{o}C was attributed to the melting process of glutaric anhydride. Whilst, the second endothermic peak at about 90 to 120 ^{o}C was attributed to the melting process of adipic acid. The main exothermic peak signified the curing reaction. It's clearly seen that with the incorporation of glutaric anhydride, the melting point of adipic acid was much lower than the pure adipic acid sample.

Table 1. Thermal properties of premixed mixtures and cured resins of ELO cured with different compositions of GA and AA.

GA:AA	**T_{on} (^oC)**	**T_P (^oC)**	**T_g (^oC)**	**ΔH_T ($J.g^{-1}$)**	**ΔH_R ($J.g^{-1}$)**	**Degree of cure[a] (%)**
100:0	344.3	200.3	41.4	405.2	6.3	98.4
80:20	345.9	194.0	40.1	392.5	6.3	98.4
60:40	348.4	185.3	25.1	351.0	9.2	97.4
50:50	350.9	183.5	20.4	330.0	8.4	97.5
40:60	350.6	181.5	15.0	285.6	8.7	97.0
20:80	355.5	172.8	10.6	302.0	6.2	98.0
0:100	359.9	174.1	5.0	228.0	7.1	96.9

[a] Degree of curing = $(\Delta H_T - \Delta H_R) / \Delta H_T$

ΔH_T, total curing enthalpy; ΔH_R, residual curing enthalpy; T_P, peak curing temperature; T_g, glass transition temperature; T_{on}, onset decomposition temperature.

Also, with the increase of adipic acid content, the second endothermic peak and the exothermic peak are not well separated especially for samples containing 100% and 80% adipic acid. As a result, in this case, the enthalpy of the curing process (ΔH_T) is probably slightly lower than the real enthalpy. More importantly, with the increase of adipic acid content, the peak curing temperature (T_P) was decreased gradually from 200.3 ^oC of pure glutaric anhydride sample to 174.1 ^oC of pure adipic acid sample, which was attributed to the higher reactivity of adipic acid compared to glutaric anhydride.

As for the effects of the composition of curing agents on ΔH_T, with the increase of adipic acid content, ΔH_T decreased gradually. ΔH_T of pure glutaric anhydride sample (405.2 J g^{-1}) was 78% higher than that of pure adipic acid sample (228 J g^{-1}).

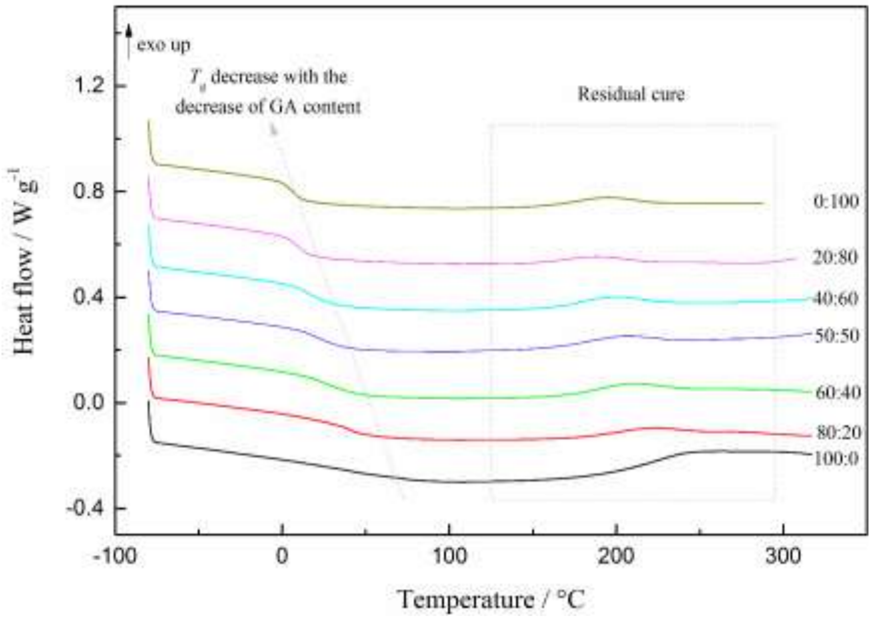


Fig. 2 Thermograms of cured resins of ELO with different compositions of GA:AA at 10 ^{o}C min^{-1}.

Figure 2 shows the thermograms of cured resins of ELO with different compositions of glutaric anhydride and adipic acid. All samples show only one T_g which may indicate that adipic acid and glutaric anhydride were well mixed and all the samples formed are homogeneous. As expected, pure glutaric anhydride sample show the highest T_g of 41.4 ^{o}C and pure adipic acid sample shows the lowest T_g of 5 ^{o}C, which is attributed to the much higher cross-link density of glutaric anhydride samples. By gradually increasing the content of adipic acid, the cross-link density is gradually decreased and thus T_g is gradually decreased. The samples also change from hard plastic (T_g > RT) to soft plastic (T_g near RT), and a soft rubbery polymer (T_g < RT). Therefore, their mechanical properties tested are significantly different from one another. After curing at 180 ^{o}C for 2 h, all samples show high degree of curing over 97%.

3.2 FT-IR analysis

Figure 3 shows the FT-IR spectra of ELO cured with different compositions of glutaric anhydride and adipic acid. All samples show the newly formed O-H groups, ester C=O groups and the disappearance of epoxy groups, which suggested that epoxy groups were ring-opened with acid groups to produce new ester linkages and hydroxyl groups, which was also confirmed by other authors [19-21]. Interestingly, with the change of the composition of curing agents, the relative intensities of the two ester C-O antisymmetric stretch bands at 1166 and 1143 cm^{-1} are different. For glutaric anhydride rich samples, the intensity at 1143 cm^{-1} is higher than the intensity at 1166 cm^{-1}. When the content of adipic acid is over 50%, the relative intensities of these two bands are reversed.

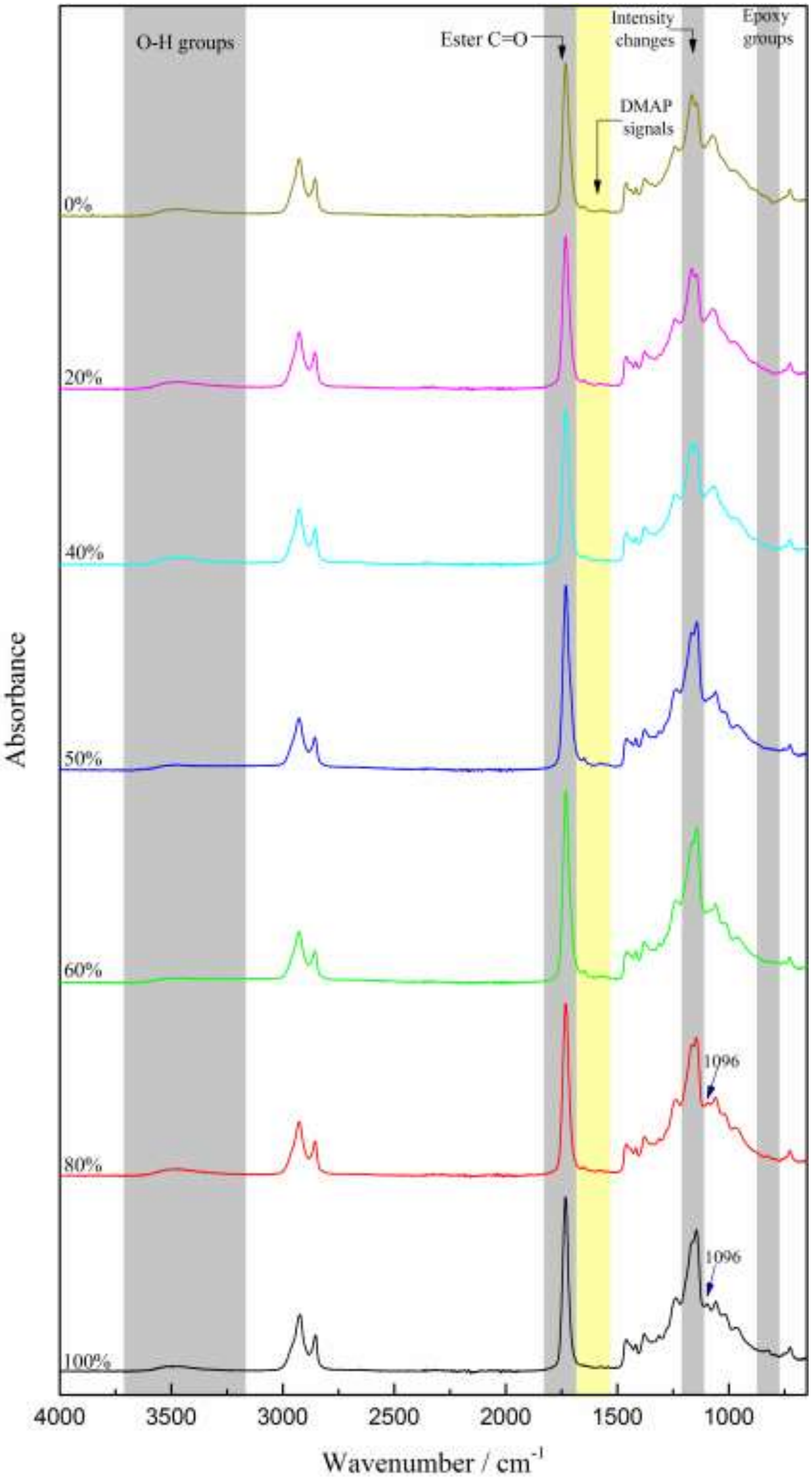


Fig. 3. FT-IR spectra of ELO cured with different composition of GA and AA.

For samples containing 100% and 80% glutaric anhydride, ether antisymmetric stretch band at 1096 cm^{-1} are also observed. The changes in intensity will be associated in differences in bond strength but may also give information with respect to the mechanism as described earlier (Scheme 1), either epoxy-acid or epoxy-anhydride. However, in the scope of this paper a full detailed investigation is not feasible.

3.3 Mechanical properties

Figure 4 shows the stress-strain curves of ELO cured resins with different compositions of glutaric anhydride and adipic acid. Resins with various properties are obtained by easily changing the compositions of curing agents, i.e., ratio of glutaric anhydride and adipic acid. With the decrease of glutaric anhydride content, resins changed from brittle and stiff to soft and flexible, which is well consistent with the trend of their T_g.

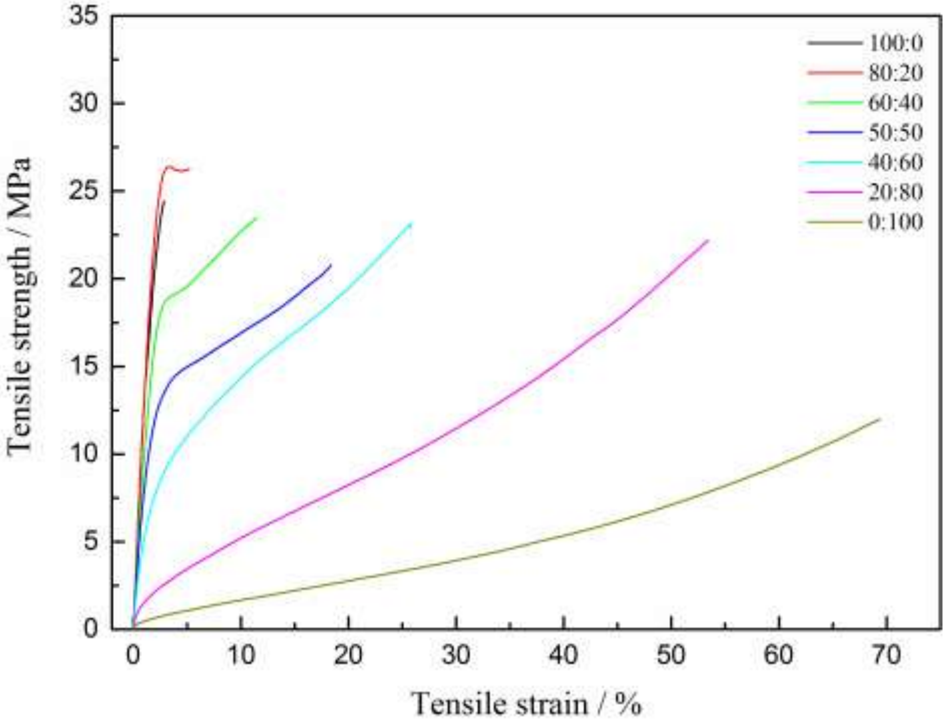


Fig. 4. Stress-strain curves of ELO cured resins with different compositions of GA:AA.

Similar mechanical properties were also observed by Lu *et al.* but in polyurethane films derived from methoxylated soybean oil polyols with different hydroxyl functionalities [22]. With the increase of hydroxyl functionalities, the PU films changed from elastomeric polymers to rigid plastics.

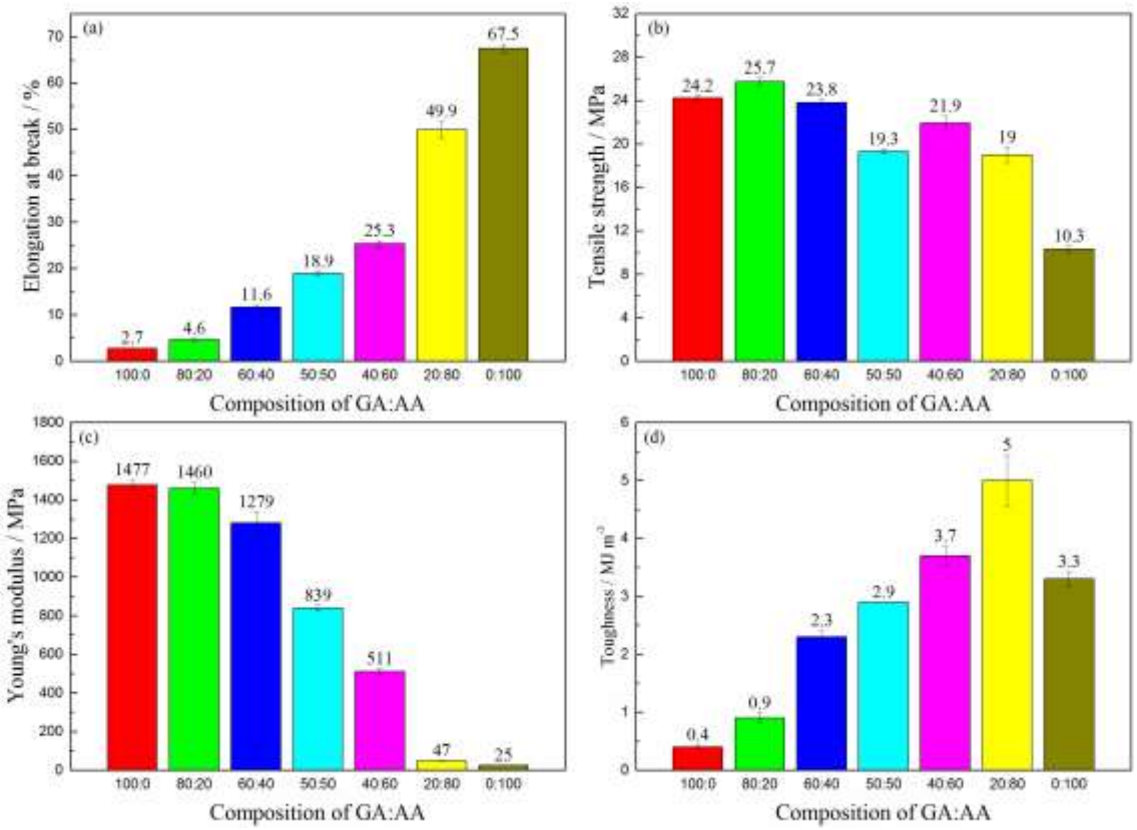


Fig. 5 Mechanical properties of ELO cured with different compositions of GA:AA. (a) elongation at break, (b) tensile strength, (c) Young's modulus and (d) toughness.

Figure 5 shows different mechanical properties including elongation at break, tensile strength, Young's modulus and toughness for ELO cured with different compositions of GA/AA ranging from 100:0 to 0:100. Generally speaking, the higher amount of adipic acid, the higher of elongation at break and toughness but the lower tensile strength and Young's modulus. 100% and 80% glutaric anhydride samples exhibited behavior of rigid plastic and break on the verge of its intrinsic yielding point. These two samples had the highest tensile strength and Young's modulus and poorest elongation at break and toughness.

Toughness, which is defined as the amount of energy per volume that a material can absorb before rupturing, is a material's resistance to fracture when stressed [23]. In a tensile test, the toughness of a material depends on both the tensile strength and the elongation at break. The addition of 20% adipic acid had almost no effect on tensile strength and Young's modulus which were 25 MPa and 1400 MPa, respectively, whilst elongation at break and toughness were improved twice.

Samples containing 60%, 50% and 40% glutaric anhydride exhibited behavior of ductile plastic with a yield point. With the increase of adipic acid content, elongation at break and toughness were improved from 11.6% to 25.3% and from 2.3 MJ m^{-3} to 3.7 MJ m^{-3}, Young's modulus was decreased from 1279 MPa to 511 MPa while tensile strength kept constant about 22 MPa.

Samples containing 80% and 100% adipic acid exhibited behavior of soft rubbery material with quite high elongation at break. Compared to the pure adipic acid sample, the addition of 20% glutaric anhydride doubled tensile strength and Young's modulus without decreasing elongation significantly, which was responsible for its highest toughness of 5 MJ m^{-3}. This may be attributed to possible internal re-ordering of chains, phase change or separation and anisotropic behavior but needs further investigation. Compared to conventional petroleum-based DGEBA epoxy systems cured with glutaric anhydride in the presence of zinc acetyl acetonate [$Zn(acac)_2$] as catalyst, the tensile strength (55 MPa) and modulus (1.8 GPa) were much higher than the findings here [24]. The reason was attributed to the aromatic structures of DGEBA and much higher cross-link density caused by the end epoxy groups within DGEBA molecules.

3.4 Thermal stability

Fig. 6 shows the thermal stability (thermogravimetric analysis) of cured resins of ELO with different compositions of glutaric anhydride and adipic acid in N_2. All films show good thermal stability with onset of decomposition, T_d, at approximately 350 °C (see inset Fig. 6) and a two-stage process, T_{max1} and $T_{max 2}$ (Fig. 6 and Table 2). It's clearly seen from Fig. 6 that, with the increase of adipic acid content, T_d gradually increases from 344.3 °C for pure glutaric anhydride sample to 360.0 °C for pure adipic acid sample. The reason for the increased thermal stability is possibly due to the extra methylene moiety, $-CH_2-$, and associated bond energy contributions to the overall enthalpy of adipic acid compared with glutaric anhydride. Also, the additional methylene moiety introduces more flexibility, has better ability to absorb and thus, better dissipate energy via internal re-ordering.

For all samples, two non-well separated decomposition processes are observed with T_{max} occurring at about 370 °C and 430 °C, respectively (Fig. 6 and Table 2). With the increase of adipic acid content, T_{max1} gradually shifts to higher temperatures from 363 °C for pure glutaric anhydride samples to 385 °C for pure adipic acid sample. Also the second decomposition process becomes more apparent while T_{max2} gradually shifts to lower temperatures from 440 °C for pure glutaric anhydride samples to 427 °C for pure adipic acid sample (Table 2).

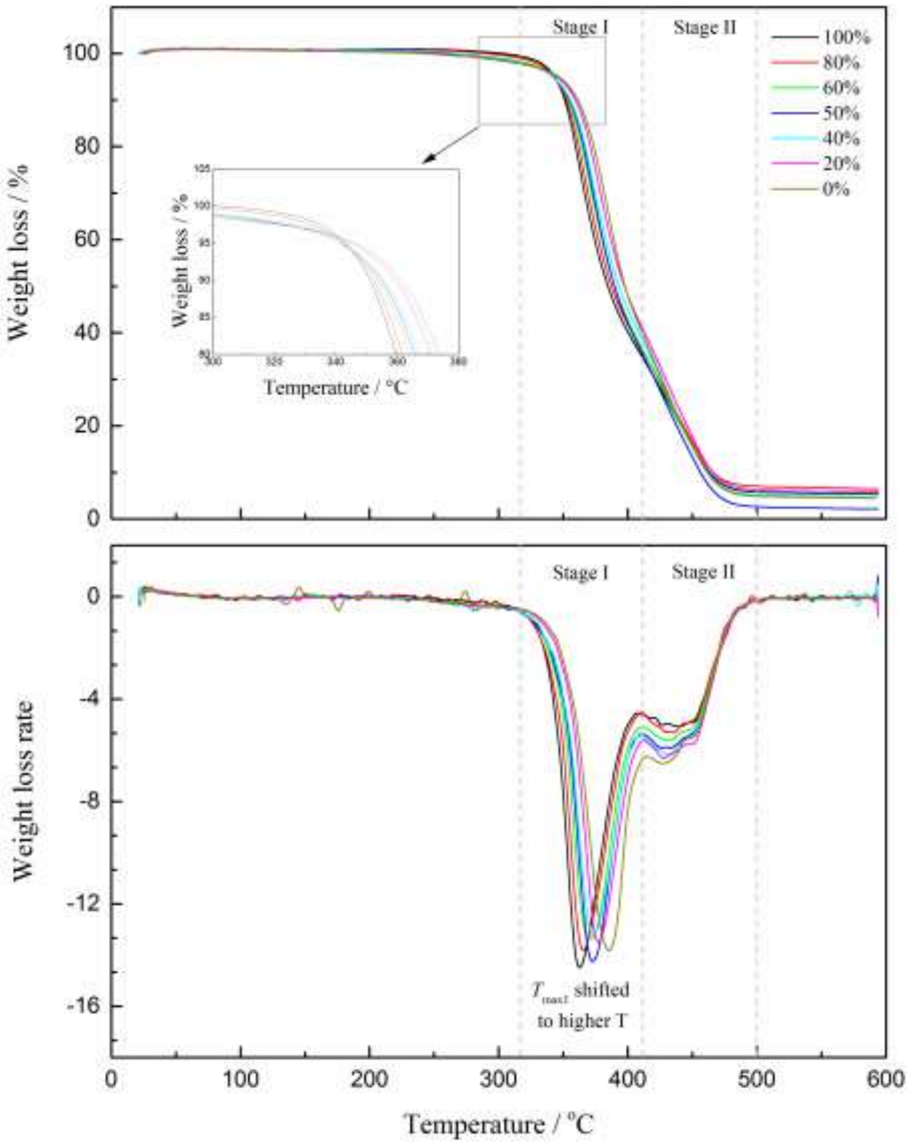


Fig. 6. Thermal stability of ELO cured with different compositions of GA and AA.

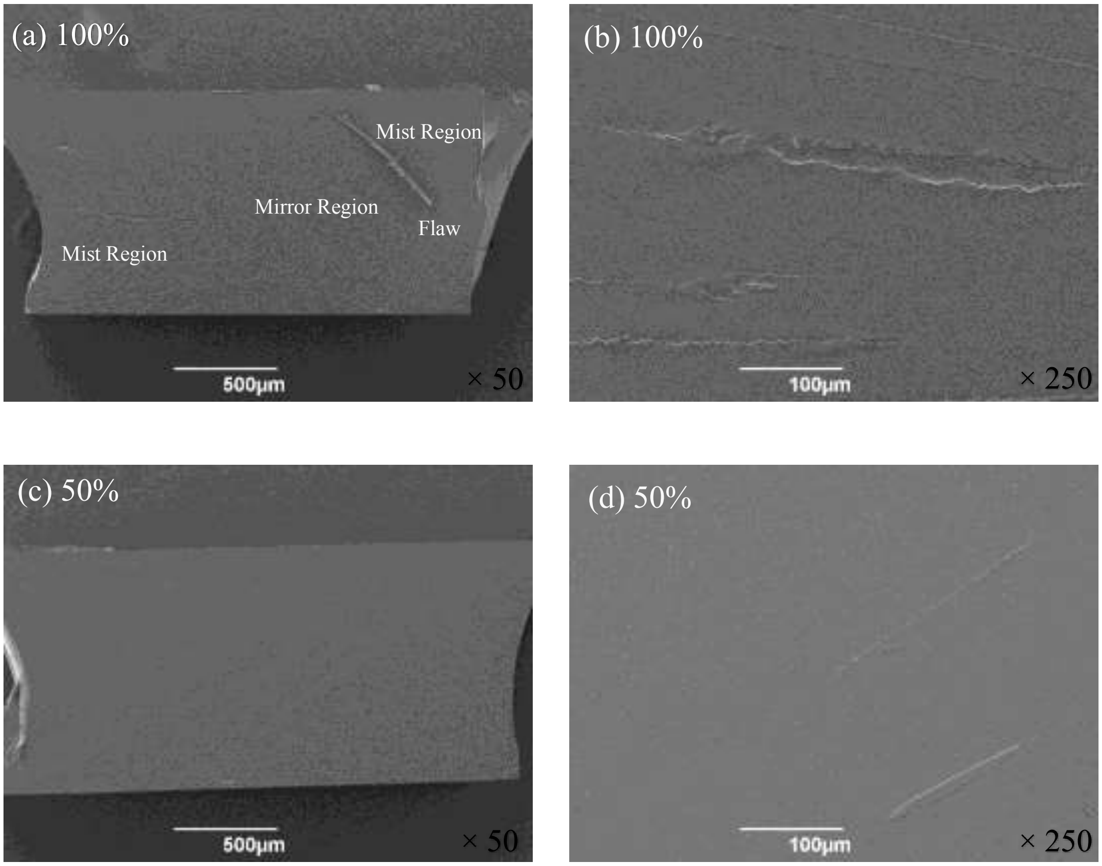
Table 2. **T_{max1} and T_{max2} temperatures for a range of GA and AA mixtures**

GA:AA	T_{max1} (°C)	T_{max2} (°C)
100:0	362.6	439.7
80:20	365.6	435.4
60:40	370.8	432.5
50:50	372.7	432.7
40:60	373.2	430.4

20:80	377.1	427.7
0:100	385.3	427.6

3.5 SEM analysis

Fig. 7(a-f) shows the fracture surfaces of cured resins of ELO cured with different compositions of glutaric anhydride and adipic acid.



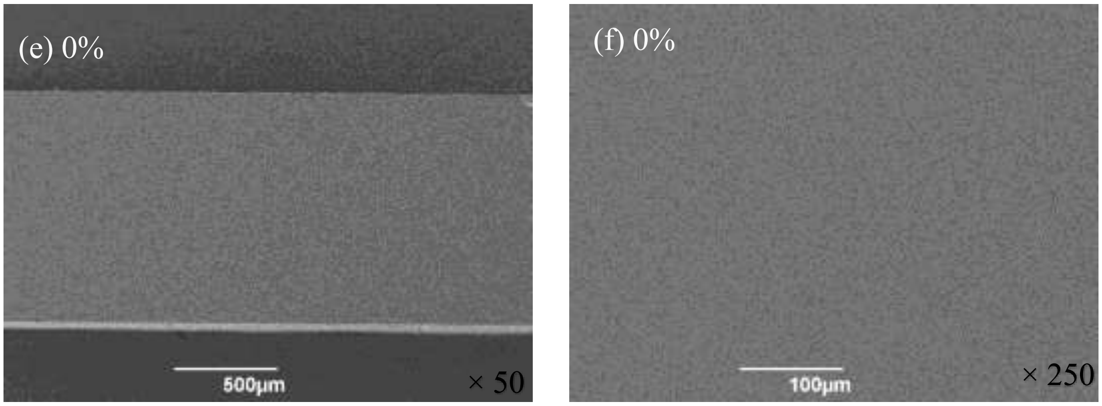


Fig. 7. SEM of fracture surface after tensile tests of ELO cured with different composition of GA and AA. (a, b) 100%GA, (c, d) 50%GA and (e, f) 0%GA.

The findings are well in accordance with soybean oil-styrene-divinylbenzene thermosets synthesized by Li *et al.*.[23] Rigid samples have the roughest fracture surface while rubbery samples showed no fracture features. For example, the tensile fracture surface of the rigid plastic containing 100% glutaric anhydride (Fig. 7 (a) and (b)) is typical for rigid epoxy resins containing flaw region or initiation region, mirror region and mist region [25]. The flaw region is where the cracks generate; the mirror region is an area with a smooth, glossy appearance with relatively slow propagation crack velocity and the mist region is rougher with higher crack velocity compared to the mirror region. Fig. 7 (c) and (d) show the fracture surface of a ductile plastic containing 50% glutaric anhydride. Compared to the rigid sample, the fracture surface is smoother with fewer ridges and furrows. Fig. 7 (e) and (f) show the fracture surface of a rubbery material containing 0% glutaric anhydride. The fracture surface of the rubbery materials appeared to be featureless due to immediate disappearance caused by their elastic nature.

4. Conclusions

This article demonstrates the first combination of ELO with adipic acid and glutaric anhydride to produce biobased thermosets and may serve as potential replacements to petroleum-based polymers. However, further optimization of properties will be needed to extend their range of applications which include coatings and composites [2, 26]. By easily changing the ratio of these two curing agents, the properties can be tuned such that the T_g ranges from 5 to 41 ^{o}C, elongation at break varies from 2.5 to 67.5%, tensile strength can be modulated from 10 to 25 MPa and Young's modulus tuned from 25 MPa to 1477 MPa. The toughness increases from 0.4 to 5.0 MJ m^{-3} with maximum toughness for samples comprising 20% glutaric anhydride.

Acknowledgements

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REFERENCES

[1] T Saurabh, M Patnaik, SL Bhagt, VC Renge, JAET. 3 (2011) 491-50.

[2] Adipic Acid Market Analysis And Segment Forecasts to 2020. Grand View Research, 2014.

[3] S. Van de Vyver, Y. Roman-Leshkov, Cataly. Sci. Technol. 3 (6) (2013) 1465-1479.

[4] T. Polen, M. Spelberg, M. Bott, J. Biotechnol. 167 (2) (2013) 75-84.

[5] J.L. Yu, X.X. Xia, J.J. Zhong, Z.G. Qian, Biotechnol. Bioeng. 111 (12) (2014) 2580-2586.

[6] C. Robert, F. de Montigny, C.M. Thomas, ACS Catal. 4 (10) (2014) 3586-3589.

[7] O. Revelles, M. Espinosa-Urgel, S. Molin, J.L. Ramos, J. Bacteriol. 186 (11) (2004) 3439-3446.

[8] O. Revelles, M. Espinosa-Urgel, T. Fuhrer, U. Sauer, J.L. Ramos, J. Bacteriol. 187 (21) (2005) 7500-7510.

[9] M.D. Samper, V. Fombuena, T. Boronat, D. García-Sanoguera, R. Balart, J. Am. Oil Chem. Soc. 89 (8) (2012) 1521-1528.

[10] R. Jain, P. Kukreja, A.K. Narula, V. Chaudhary, J. Appl. Polym. Sci. 100 (5) (2006) 3919-3925.

[11] R. Jain, V. Choudhary, A.K. Narula, J. Appl. Polym. Sci. 105 (6) (2007) 3804-3808.

[12] J. Rocks, G.A. George, F. Vohwinkel, Polym. Int. 52 (11) (2003) 1758-1766.

[13] N. Supanchaiyamat, A.J. Hunt, P.S. Shuttleworth, C. Ding, J.H. Clark, A.S. Matharu, RSC Adv. 4 (44) (2014) 23304-23313.

[14] P.-J. Madec, E. Maréchal, Kinetics and mechanisms of polyesterifications II. Reactions of diacids with diepoxides. Analysis/Reactions/Morphology, vol. 71: Springer Berlin Heidelberg, 1985. pp. 153-228.

[15] C.E. Hoppe, M.J. Galante, P.A. Oyanguren, R.J.J. Williams, Macromol. Mater. Eng. 290 (5) (2005) 456-462.

[16] I.E. Dell'Erba, R.J.J. Williams, Polym. Eng. Sci. 46 (3) (2006) 351-359.

[17] A. Mahendran, G. Wuzella, A. Kandelbauer, N. Aust, J. Therm. Anal. Calorim. 107 (3) (2012) 989-998.

[18] L. Shechter, J. Wynstra, Ind. Eng. Chem. 48 (1) (1956) 86-93.

[19] C. Ding, P.S. Shuttleworth, S. Makin, J.H. Clark, A.S. Matharu, Green Chem. 17 (7) (2015) 4000-4008.

[20] A. Li, K. Li, ACS Sustainable Chem. Eng. 2 (8) (2014) 2090-2096.

[21] N. Supanchaiyamat, P.S. Shuttleworth, A.J. Hunt, J.H. Clark, A.S. Matharu, Green Chem. 14 (6) (2012) 1759-1765.

[22] Y. Lu, R.C. Larock, Biomacromolecules 9 (11) (2008) 3332-3340.

[23] F. Li, R.C. Larock, J. Polym. Sci., Part B: Polym. Phys. 39 (1) (2001) 60-77.

[24] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, Science 334 (6058) (2011) 965-968.

[25] L. Plangsangmas, J.J. Mecholsky, A.B. Brennan, J. Appl. Polym. Sci. 72 (2) (1999) 257-268.

[26]	F-L. Jin, X. Li, S-J. Park, J Ind Eng Chem. 29 (2015) 1–11.

TABLE OF CONTENT (TOC) GRAPHIC

Adipic acid – glutaric anhydride – epoxidised linseed oil biobased thermosets with tunable properties

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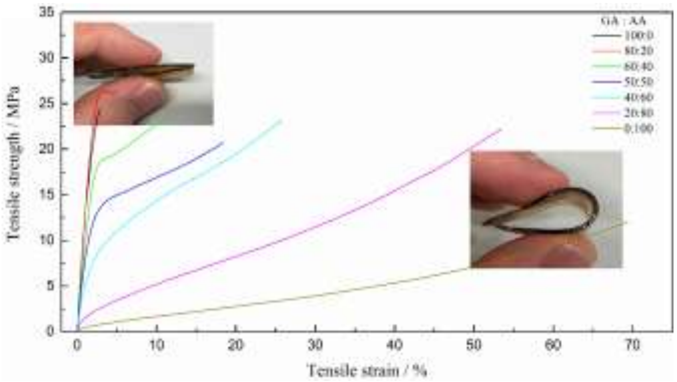

In this graph, it’s shown that the sample changed from hard rigid samples to ductile plastics and then to soft flexible polymers by gradually changing the ratio of glutaric anhydride to adipic acid.