Dynamic Mechanical and Thermal Behavior of Epoxy Resins Based on Soybean Oil

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ABSTRACT: Mechanical and thermal properties of materials prepared by curing epoxidized soybean oil with various cyclic acid anhydrides in the presence of tertiary amines were investigated by dynamic mechanical thermal analysis and thermogravimetry. All samples presented thermoset material characteristics that were dependent upon the type of anhydride, the anhydride/epoxy molar ratio, and epoxy group content. The thermosets obtained from anhydrides with rigid structures as such phthalic, maleic, and hexahydrophthalic showed higher glass transition temperatures (Tg) and cross-linking densities. As expected, the Tg decreased as the anhydride/epoxy ratio decreased. The influence of the degree of epoxidation of soybean oil on the mechanical properties and Tg was also investigated. It was found that the higher the epoxy group amount, the higher the Tg and hardness. Cured resins exhibited thermal stability up to 300°C, except for those prepared with dodecenylsuccinic anhydride, which began to decompose at lower temperature. They presented excellent chemical resistance when immersed in 1% wt/vol NaOH and 3% wt/vol H_2SO_4 solutions but poor chemical resistance in the presence of organic solvents.

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KEY WORDS: Chemical resistance, dynamical mechanical properties, epoxidized soybean oil, epoxy resins, thermogravimetric analysis, thermosetting polymers.

Vegetable oils represent an interesting renewable source for the production of useful chemicals and new materials (1). Soybean oil is readily available in bulk and is mainly composed of TG molecules derived from unsaturated acids, such as oleic acid (22%), linoleic acid (55%), and linolenic acid (7%). Although unsaturated acids possess double bonds, which are the reactive sites for coatings and paints, they need to be functionalized by the introduction of epoxy, hydroxyl, or carboxyl groups in order to be used for preparation of polymeric materials.

Soybean oil can be epoxidized by different methods (2–4) yielding conversions and selectivities higher than 90%. Industrially, it is used mainly as a polyvinyl chloride additive to improve stability and flexibility. New applications have been made possible by the use of photochemically initiated cationic curing (5) and by the preparation of thermosetting materials such as epoxy resins.

Epoxy resins are widely used as adhesives and as matrices in composite materials because of their good physical and chemical properties. Toughness and other properties of epoxy resins can be significantly improved by the modification of classical epoxy resins, such as those based on diglycidylether of bisphenol A (DGEBA). Epoxidized vegetable oils prepared from the most unsaturated oils, e.g., soybean oil or linseed oil, can be used for such purpose.

In this work we report dynamic mechanical properties of different materials prepared by curing fully and partially epoxidized soybean oil (ESO) with various cyclic acid anhydrides in the presence of tertiary amines. Thermal and chemical resistance were also investigated.

MATERIALS AND METHODS

Phthalic anhydride (PA), hexahydrophthalic anhydride (CH), maleic anhydride (MAL), and *N,N′*-dimethylaniline (ARO) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and purified just before use by standard methods. Succinic anhydride (SUC) was purchased from Sigma Co. (St. Louis, MO) and recrystallized from chloroform. Triethylamine (TEA) was purchased from Merck (Darmstadt, Germany) and distilled before use. Dodecenylsuccinic anhydride (DDS) (Sigma Co.) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Aldrich Chemical Co.) were used without further purification.

Fully ESO was supplied by CBM Indústria, Comércio e Distribuição Ltda. (Cachoeirinha, RS, Brazil) and contained 4.1 mmol epoxide/g determined by the oxirane oxygen standard method (AOCS Cd 9-57) (6). On average, ESO has a M.W. of about 929 g/mol and contains about 3.8 epoxy groups per TG.

Partially ESO were prepared using the methyltrioxorhenium-CH_2Cl_2/H_2O_2 system (4). The degree of epoxidation was calculated by integrating the signals in the 2.9–3.1 ppm region of the ^{1}H NMR spectra, corresponding to the *cis* epoxy hydrogens.

Dynamic mechanical properties were measured on Polymer Laboratory–Dynamic Mechanical Thermal Analysis equipment operating in single cantilever mode. The measurements were performed from −60 to 100°C at a heating rate of 2°C/min and frequency of 1 Hz. The glass transition temperature (Tg) was determined as the temperature at the maximum of the tan δ vs. temperature curve.

A TA Instruments model 2050 thermogravimeter was used to measure the weight loss of the polymeric materials in an N_2 atmosphere. The samples were heated from 30 to 800°C at a heating rate of 10°C/min.

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ESO81 (4.1 mmol epoxide/g) and anhydrides were mixed according to the anhydride/epoxy molar ratio (*R*) at the melting temperatures of the anhydrides. Afterward, the amine (3.3 mol% related to epoxide content) was added. The mixtures were placed in an inox mold and cured in an oven under an air atmosphere. The cured cycle was chosen in order to obtain maximal properties without thermal degradation.

Density of epoxy resins was determined according to ASTM D792-91.

Chemical resistance tests were carried out at 1 and 4 wk at 25°C according to ASTM D 543-67.

RESULTS AND DISCUSSION

Dynamic mechanical study. Mechanical and thermal properties of cured epoxy resins are very sensitive to the chemical and structural nature of the curing agent, the type and concentration of cure initiators, cure reaction conditions, and epoxy conversion, which is closely related to the anhydride/epoxy molar ratio. Therefore, a study of the influence of these factors on mechanical and thermal properties is required for successful application of these materials.

Different networks were prepared by curing a fully epoxidized soybean oil (ESO81) with various anhydrides, e.g., SUC, CH, PA, MAL, and DDS, in the presence of TEA, ARO, and DABCO as initiators. Networks obtained from partially epoxidized soybean oil (ESO50, ESO20, and ESO11) cured with DDS using TEA as initiator were also studied.

Mixtures were prepared in two different anhydride/epoxy molar ratios (*R*), 1.0 and 0.5, with the addition of 3.3 mol% of amine related to epoxide content. This proportion is generally used for curing commercial epoxy resins (7). The anhydride cure of ESO81 was usually performed at 150°C for 14 h, but in the case of MAL, a lower temperature was used since it degrades at 150°C.

In Table 1, Tg values and storage moduli (E') obtained at Tg + 40°C are presented for different epoxy resin formulations. As can be seen, materials with Tg from −16 to 65°C can be prepared by changing the anhydride, the epoxidation level of the soybean oil, and the anhydride/epoxy molar ratio (*R*).

Tg values obtained for the systems ESO81/anhydride/amine and *R* = 1 (entries 1–7) are lower than those for the usual commercial resins based on DGEBA (8,11) but close to those of polyester resins based on ESO (12,13). Nevertheless, they are lower than those found for epoxy resins based on epoxidized linseed oil (14), ranging from 109–157°C. This behavior is expected since linseed oil has a higher PUFA content than soybean oil.

The influence of *R* is evident in the ESO81/anhydride/TEA systems. A decrease in Tg was observed when *R* changed from 1.0 (entries 1–5) to 0.5 (entries 8–12). Boquillon and Fringant (14) found higher Tg values for *R*, ranging from 0.6

TABLE 1
Dynamical Mechanical and Thermal Properties of Epoxy Resins Prepared by Curing ESO with Various Dicarboxylic Acid Anhydrides[a]

Entry	Formulation	*R*	Tg (°C)	E' (MPa)	M_c (g/mol)	ν_e ($\times 10^3$ mol/mm^3)
1	ESO81/SUC/TEA	1	27	2.63	3277	0.31
2	ESO81/CH/TEA	1	49	8.59	1094	0.95
3	ESO81/PA/TEA	1	65	15.89	585	1.68
4	ESO81/MAL/TEA[b]	1	35	15.02	590	1.75
5	ESO81/DDS/TEA	1	25	16.83	493	1.98
6	ESO81/DDS/ARO	1	28	14.60	586	1.71
7	ESO81/DDS/DABCO	1	31	16.95	519	1.95
8	ESO81/SUC/TEA	0.5	16	1.61	5199	0.20
9	ESO81/CH/TEA	0.5	40	4.05	2234	0.46
10	ESO81/PA/TEA	0.5	33	23.58	352	2.76
11	ESO81/MAL/TEA[b]	0.5	34	10.98	919	1.25
12	ESO81/DDS/TEA	0.5	17	2.68	2942	0.32
13	ESO81/DDS/ARO	0.5	16	1.04	7210	0.12
14	ESO81/DDS/DABCO	0.5	19	3.97	2236	0.47
15	ESO81/DDS/TEA[c]	1	31	16.90	508	1.97
16	ESO50/DDS/TEA[c]	1	20	6.68	1698	0.80
17	ESO20/DDS/TEA[c]	1	−8	20.22	441	2.65
18	ESO11/DDS/TEA[c]	1	−5	6.85	1121	0.90
19	SO[c]	—	−16	4.78	1717	0.64

[a] *R* = anhydride/epoxy molar ratio; E' = storage modulus at elastic region (Tg + 40°C); M_c = M.W. between crosslinks; ν_e = cross-linking density; ESO*x*, epoxidized soybean oil with *x*%, of epoxidation; SO = soybean oil; SUC = succinic anhydride; CH = hexahydrophthalic anhydride; PA = phthalic anhydride; MAL = maleic anhydride; DDS = dodecenylsuccinic anhydride; TEA = triethylamine; ARO = *N,N′*-dimethylaniline; DABCO = 1,4-diazabicyclo[2.2.2]octane. Mixtures were cured at 150°C for 14 h.
[b] Cured at 120°C.
[c] Cured for 48 h.

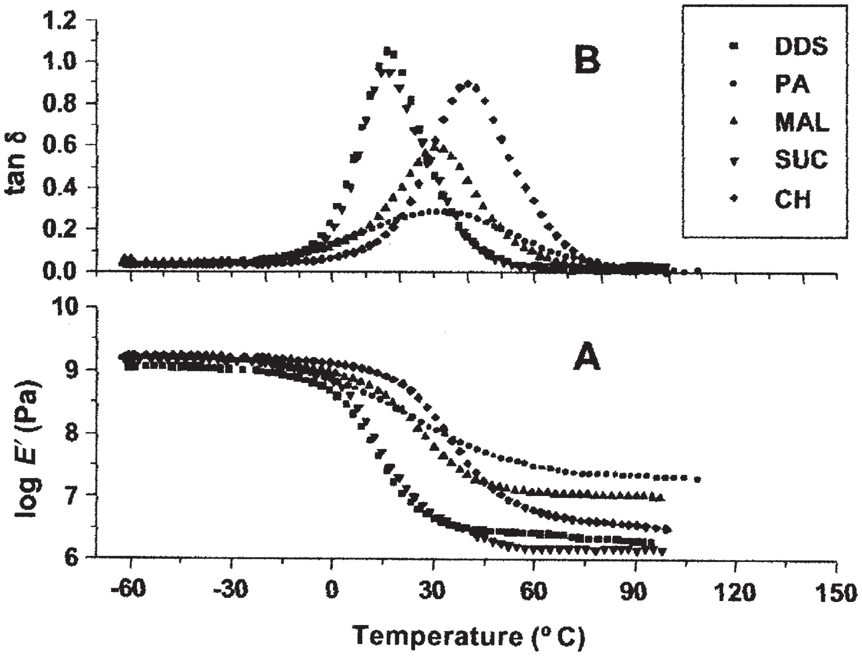

FIG. 1. Temperature dependence of the storage modulus E' (A) and of the loss factor tan δ (B) for ESO81/anhydride/TEA thermosets ($R = 0.5$). ESO81, epoxidized soybean oil, 4.1 mmol epoxide/g; TEA, triethylamine; DDS, dodecenylsuccinic anhydride; PA, phthalic anhydride; MAL, maleic anhydride; SUC, succinic anhydride; CH, hexahydrophthalic anhydride.

to 1.0, when studying systems based on epoxidized linseed oil. The authors reported that curing reactions were completed when R was about 0.8. Therefore, they suggested that, for $R < 0.8$, the unreacted epoxy groups lead to mobile pendant chain ends and account for the decrease in Tg.

In the data presented in Table 1, it is possible to verify the importance of the anhydride type. In both anhydride/epoxy molar ratios, the more rigid dicarboxylic acid anhydrides, MAL, PA, and CH, resulted in stiffer polyesters with Tg varying between 35 and 65°C for $R = 1.0$, and 33 and 40°C for $R = 0.5$.

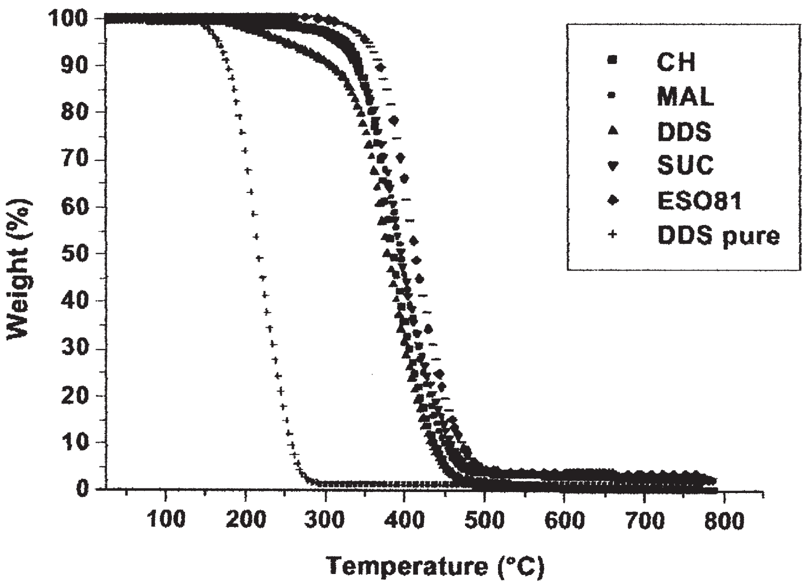

FIG. 2. Thermogravimetric analysis (TGA) thermograms of the ESO81/anhydride/TEA, $R = 0.5$, epoxidized soybean oil (ESO81), and DDS in a nitrogen atmosphere at a rate of 10°C/min. R = anhydride/epoxy molar ratio; for other abbreviations see Figure 1.

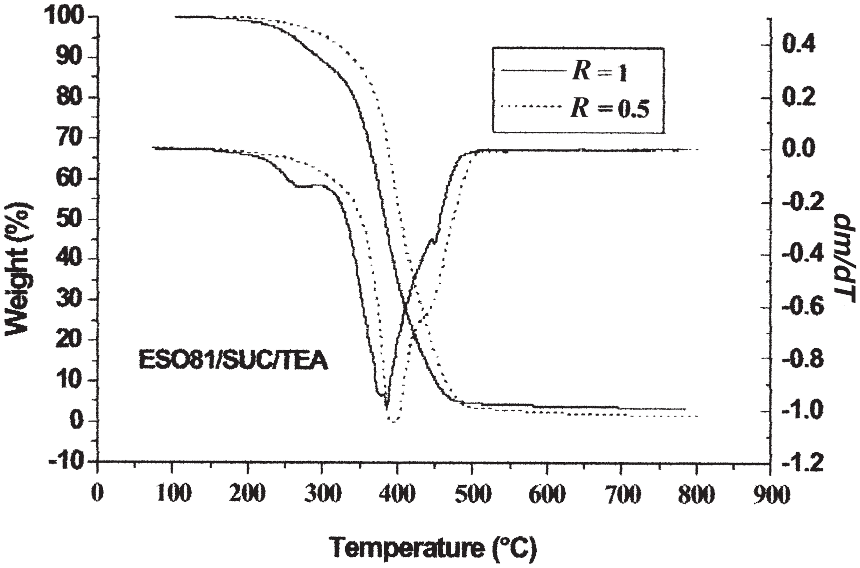

FIG. 3. TGA thermograms of ESO81/SUC/TEA at two molar ratios *R* in a nitrogen atmosphere at a rate of 10°C/min. *dm/dT*, change of mass with change of temperature; for other abbreviations see Figures 1 and 2.

No major influence of the initiator type on the final properties of the systems ESO81/DDS containing the amines TEA, ARO, or DABCO was observed (Table 1, entries 5–7 and 12–14).

Figure 1 shows the temperature dependence of the storage modulus (E') and loss factor tan δ for the networks obtained with the ESO81/anhydride/TEA systems for $R = 0.5$. In Figure 1A, E' modulus remains constant at lower temperatures for all formulations. As temperature increases, the storage modulus falls in the region between 0 and 70°C. At still higher temperatures, the appearance of a relatively constant modulus indicates that stable cross-linked networks exist in the bulk polymer. Stiffer materials are obtained with the more rigid anhydrides, PA and MAL; they have storage moduli in the range of 11 to 23 MPa (entries 10 and 11, Table 1) at an elastic plateau, whereas materials based on anhydrides SUC and DDS have poor thermomechanical properties and lower storage moduli (entries 8 and 12, Table 1). Generally, the storage modulus is also higher for systems prepared with higher anhydride/epoxy molar ratios ($R = 1$).

In Figure 1B, the tan δ vs. temperature curves for the ESO81/anhydride/TEA ($R = 0.5$) systems are presented. A single tan δ peak was observed for all formulations and associated with the α relaxation corresponding to the glass transition of the cross-linked polymer network. Although Boquillon and Fringart (14) reported the appearance of a secondary β relaxation at −75°C for the epoxy resin based on epoxidized linseed oil, no peak related to this relaxation could be observed in our systems, even when the dynamical mechanical curves were obtained at temperatures from −100 to 180°C.

The broader transition range observed for the system ESO81/PA/TEA indicates that the segmental movements in these cross-linked molecules are rather extensive upon cross-linking.

The cross-linking density (ν_e) for networks prepared with different types of anhydrides (Table 1) was calculated by the following equation, derived from the theory of rubber elasticity (15):

$$E' = 3\nu_e RT \qquad [1]$$

where E' is the storage modulus of the thermoset in the rubbery plateau region at Tg + 40°C, R is the gas constant, and T is the absolute temperature.

By using the density of the material, it is also possible to estimate the M.W. between crosslinks (M_c), which are presented in Table 1. Cross-linking densities in the bulky polymers ($R = 1$) are lower than those of conventional thermosets (16) but similar to those of polymer networks derived from cured epoxidized linseed oil (14). The degree of cross-linking is generally improved when more anhydride (higher R) is used in the original formulation. However, this behavior was not observed for PA. One possible explanation is the rigidity of the diester segment formed, containing a carbon–carbon

TABLE 2
Dimensional Changes of Cured Films[a] Immersed in Different Solutions at 28°C for 1 wk

Solvent	Δa (mm^2) $R = 0.5$	Δa (mm^2) $R = 1.0$
Acetone	3.0	2.9
Ethanol	1.2	1.9
Toluene	6.3	3.0
Gasoline	8.5	4.8
NaOH 1%	—	—
H_2SO_4 3%	—	—
Soybean oil	—	—

[a] ESO81/DDS/TEA systems cured for 14 h at 150°C. For abbreviations see Table 1.

double bond, thus reducing molecular motions during cure and favoring the formation of trapped entanglements.

Owing to the different chemical structure of the cross-linking agent, there is no clear relationship between cross-linking densities and Tg. For example, the ESO81/DDS/TEA (entry 5) system, in spite of presenting the lowest Tg, has the highest cross-linking density compared with the other systems in the same molar ratio.

To study the influence of the epoxidation level on the dynamical mechanical properties, partially ESO were cured with DDS using TEA as initiator. Longer reaction times were necessary in order to obtain a suitable film for the dynamical mechanical measurements. Therefore, a reaction time of 48 h at 150°C was chosen by taking into account the reaction time needed to polymerize pure soybean oil (SO—entry 19). In the case of SO, a film was formed because of the well-known oxidative polymerization process through the methylene groups between two carbon–carbon double bonds. When partially ESO was used in the epoxy resin formulation, both the cross-linking process and the reaction between the epoxy group and the anhydride should be taken into consideration. The extension of each process depends on the reactivity and relative content of the epoxy groups and double bonds.

The networks obtained with partially ESO have lower Tg and cross-linking densities (entries 16–19). The data presented in Table 1 show that the higher the epoxidation level of the soybean oil, the higher the Tg of the network. This result is in agreement with the expected higher reactivity of the epoxy group.

Thermal stability. The thermal stability of the ESO/anhydride/amine systems was studied by thermogravimetric analysis (TGA). The curves of weight loss against temperature for the systems ESO81/anhydride/TEA, $R = 0.5$, are shown in Figure 2.

The cured epoxy resins studied are generally thermally stable up to 300°C, followed by decomposition in one step (300–420°C). The same thermal behavior was reported for DGEBA epoxy resin/epoxidized oil mixtures (16) and other epoxy resins such as *N,N,N′,N′*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane (18) and brominated epoxy resins (19). However, our results are lower than those obtained for fish (20) and tung oil (21) thermosetting polymers (400–560°C), which present three different decomposition stages in air.

In Figure 2, the initial temperature of the polymer decomposition and the TGA curve profiles of the different systems are quite similar to that of ESO81, except for the DDS system. This behavior suggests that the anhydride nature has little influence on the thermal stability of the thermosetting polymer.

In all formulations with DDS, the thermal decomposition occurs in two steps, 180–320°C (stage I) and 320–420°C (stage II). Stage I could be associated with the presence of unreacted DDS, since the TGA curve of this anhydride shows that decomposition starts at 200°C. Nevertheless, when a Soxhlet extraction was carried out, the presence any unreacted anhydride in the IR spectrum of the CH_2Cl_2-soluble fraction was not detected. Even when the DDS systems were cured in longer reactions, 18 h, the resultant TGA curves presented thermal decomposition in two stages. These results suggest that the first decomposition step is associated with side-chain degradation of the anhydride.

In general, a decrease in the thermal stability of the films was observed when the molar ratio R of anhydride/epoxy increased. Figure 3 shows the TGA and differential thermogravimetry curves of the ESO81/SUC/TEA, $R = 0.5$ and 1.0, systems cured for 14 h at 150°C. For the sample prepared with $R = 1$, an initial weight loss was observed before that corresponding to the resin degradation. This was attributed to the presence of unreacted anhydride since when this system was cured for a longer time, 18 h, the initial weight loss disappeared, indicating a complete anhydride conversion.

Chemical resistance. Chemical stability of the cured resins based on ESO81/DDS/TEA systems was also studied. First, dimensions of films of cured resins were measured and then they were immersed in NaOH 1% wt/vol and H_2SO_4 3% wt/vol solutions; in organic solvents (acetone, ethanol, toluene, gasoline); and in SO. They were measured again after 1 wk and then 4 wk in order to verify the dimension changes and physical characteristics. The dimensions of films immersed in NaOH 1% wt/vol and H_2SO_4 3% wt/vol solutions and in SO did not change during 4 wk and presented good physical resistance as well. The dimensions of those immersed in organic solvents changed after 1 wk, as shown in Table 2. After 4 wk they could not be measured due to their fragility. Moreover, the systems with the higher anhydride/epoxy ratio, $R = 1$, presented smaller dimension changes as a result of higher cross-linking density.

In addition, our results showed that epoxy resins made with ESO presented higher chemical resistance in polar organic solvents (acetone and ethanol) than in nonpolar organic solvents (toluene and gasoline). This fact indicates that the solvents clearly interacted with the resin as a consequence of their similar polarity.

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