

Influence of Cure Schedule on the Viscoelastic Properties and Thermal Degradation of Crosslinked Mono- and Diepoxides Obtained During the Reaction of Hydrogen Peroxide and Divinylbenzene

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ABSTRACT: The present work investigates the influence of cure schedule on the dynamic mechanical behavior and thermal degradation of crosslinked mono- and diepoxides obtained in epoxidation of commercially available divinylbenzene by 60% hydrogen peroxide as the oxidant in the presence of organic solvents (acetonitrile and methanol) and the catalyst magnesium oxide. The crosslinking process of the obtained mono- and diepoxides was accomplished using three different hardening agents: glutaric anhydride, 2,4,6-tri(dimethylaminomethyl)phenol, and maleic anhydride. The influence of cure schedule and hardening agent on the dynamic mechanical properties like

storage modulus, $\tan \delta$, glass transition temperature (T_g), and thermal stability of cured epoxides has been studied by dynamic mechanical analyzer (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The variations obtained in the elastic modulus in the rubber region above the glass transition have been used to analyze the crosslink density of the networks. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 462–469, 2007

Key words: epoxidation; hydrogen peroxide; olefins; viscoelastic properties; curing agents

INTRODUCTION

Epoxidation of olefinic compounds to corresponding epoxides is a simple and efficient method for introducing a new reactive group (an oxirane group) into the compound. The reaction of peroxyacids (peracids) and olefinic or aromatic double bonds leads to new and useful properties and wide use in a variety of applications, especially in polymer blending, in the production of a large number of bulk, fine, and pharmaceutical-grade chemicals, intermediates for synthesizing other organic compounds.^{1–9} Epoxidation of double bonds using organic peracids or peroxides such as hydrogen peroxide has been studied extensively ever since oxiranes were prepared by reacting ethylenic compounds with perbenzoic acid.⁸ Epoxidation of double bonds by hydrogen peroxide in the presence of nitrile (e.g., acetonitrile, benzonitrile) and under strongly alkaline conditions is well documented.^{10–17} This reaction generally required the presence of the catalyst, e.g., metal oxides, titania silica mixed oxides,^{15,16} and hydrotalcites.^{18,19} Epoxy

groups in obtained products become reactive sites for further modification and can be also used as crosslinking sites. They can be cured with a number of nucleophilic and electrophilic reagents. Among the curing agents of greatest technological importance are polycarboxylic acid anhydrides, amines, and imidazoles.²⁰ This crosslinking reaction with di- or polycarboxylic acid anhydrides is based on the reaction of an epoxy group with an anhydride group to produce ester linkages (hydroxylalkyl esters) via an ionic mechanism at first stage. The reaction of acid anhydrides with epoxides often require the presence of a basic catalyst or activator or temperatures above 120–180°C, because the uncatalyzed reaction at room temperature is very slow. In addition to the ester-forming reaction an ether-forming reaction is also possible because the epoxy groups can react with secondary hydroxyl groups obtained at first stage at higher temperatures and in the presence of catalytic activation of carboxylic acids. In this way, the formation of ether linkages (polyether linkages) is observed. In contrast, primary, secondary, and tertiary amines are used as curing agents of the epoxides. In the epoxide/tertiary amine system, the initial step in the polymerization is the formation of a tertiary amine, epoxide zwitterion. The zwitterion (the negatively charged oxygen) then attacks another

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epoxy ring to form an oligomer (polymer) via an anionic step growth mechanism. In this system, only the ether-forming reaction was expected to occur. The tertiary amines (e.g., Lewis basis) caused the formation of polyether linkages in the cured materials.^{21–31}

In the present work, the influence of cure schedule on the dynamic mechanical behavior and thermal degradation of crosslinked mono- and diepoxides obtained in epoxidation of commercially available divinylbenzene by 60% hydrogen peroxide as the oxidant in the presence of organic solvents (acetonitrile and methanol) and the catalyst-magnesium oxide was studied. The crosslinking process of the obtained mono- and diepoxides was accomplished with three different hardening agents: glutaric anhydride, 2,4,6-tri(dimethylaminomethyl)phenol, and maleic anhydride. The influence of cure schedule and hardening agent on the dynamic mechanical properties like storage modulus, $\tan \delta$, glass transition temperature (T_g), and thermal stability of cured epoxides has been studied by dynamic mechanical analyzer (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The variations obtained in the elastic modulus in the rubber region above the glass transition have been used to analyze the crosslink density of the networks.

EXPERIMENTAL

Materials

Commercial-grade divinylbenzene (65 wt % DVB, 35 wt % ethylvinylbenzene (EVB) stabilized with 4-*tert*-butylpyrocatechol, methanol (99.8 wt %), and acetonitrile (99.9 wt %) was obtained from Merck. Aqueous hydrogen peroxide (60 wt %) was bought from the Azoty Nitrogen Plant (Puławy, Poland). Magnesium oxide (MgO) was from POCh (Gliwice, Poland) and was used as an active catalyst. Maleic anhydride and glutaric anhydride was from Aldrich (Milwaukee, WI), and 2,4,6-tri(dimethylaminomethyl)phenol was from Anchor Chemical Co. (Westlake, OH). All chemicals were used without further purification.

Preparation of epoxides

The typical experiment was performed under air in a batch reactor containing condenser, thermometer, stirrer, and the required amounts of chemicals. Epoxidation was carried out at 50°C. Magnesium oxide was used as the catalyst in the presence of water adjusted to pH 10 with sodium hydroxide. Commercial-grade divinylbenzene (0.192 mol), acetonitrile (1.46 mol), distilled water (50 ml), and magnesium oxide (1.25 g) were charged to the reactor. The reactor was allowed to attain the reaction temperature in a thermostat bath and the mixture of 60% hydrogen

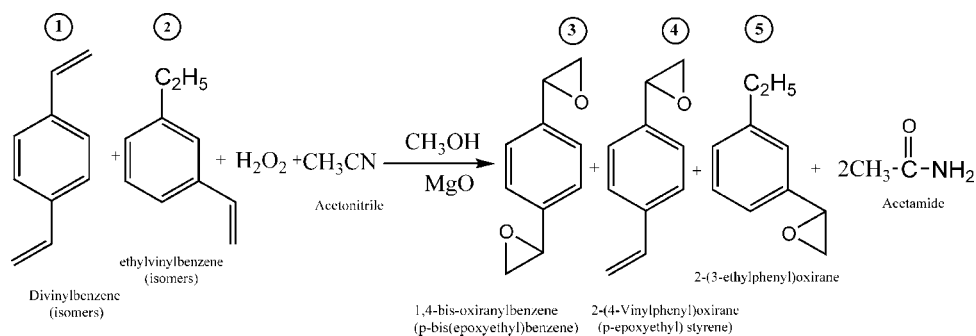
peroxide (1.77 mol) and methanol (1.90 mol) was slowly dropped at the reaction temperature while stirring over a period of 2 h. With the 60% hydrogen peroxide, the reaction was almost immediately exothermic. The reaction mixture was stirred for a predetermined time (5 h). After completion, the liquid product was cooled down to room temperature and the catalyst was separated by filtration. The raw product was washed several times with distilled water. The epoxides were separated from the solvents and byproduct (acetamide), extracted with three portions of diethyl ether, and dried.

Characterization of the products

All the liquid organic products were identified by GC-MS analysis (GCQ, Thermo-Finnigan, Oakland, CA). The samples were dissolved in dichloromethane and quantified using a gas chromatograph with capillary column (Restec RTX-5, 18 m \times 18 mm \times 0.2 μ m; injector PTV 35–300°C 10°C/s) and FID detector at the temperature program 35°C–1 min/ 10°C/min to 300°C and were analyzed by mass spectrometry with EI = 70 eV and temperature ion volume 220°C. Proton nuclear magnetic resonance (¹H-NMR) spectra were obtained using a NMR Bruker 300 MSL (Rheinstetten, Germany) spectrometer at 300 MHz with deuterated chloroform (CDCl₃) as the solvent. ¹H-NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference. The infrared (IR) spectra were recorded on a Fourier transform infrared (FTIR) Perkin-Elmer 1700 spectrometer in the 400–4000-cm⁻¹ wavenumber range using KBr pallets.

Crosslinking procedure

The obtained epoxides were crosslinked with maleic anhydride, glutaric anhydride and 2,4,6-tri(dimethylaminomethyl)phenol with stoichiometric ratios of anhydrides r 0.85, where r was defined as anhydride groups/epoxy groups. Maleic anhydride or glutaric anhydride was dissolved in prepared product at 40°C to obtain a homogenous solution. This solution was stored at room temperature for 2 days for samples with maleic anhydride and for 10 days for samples with glutaric anhydride to obtain crosslinked products. The composition of the epoxy product (100 g) and 2,4,6-tri(dimethylaminomethyl)phenol (15 g) was stored at room temperature for 3 days. After crosslinking at room temperature, the samples were subjected to the following cure schedules: 120°C for 4 h (schedule 1); further curing at 120°C for 8 h after schedule 1 (schedule 2), and 140°C for 4 h after schedule 2 (schedule 3), in the case of samples crosslinked with 2,4,6-tri(dimethylaminomethyl)phenol. The postcuring conditions for epoxides/



Scheme 1 Theoretical model of epoxidation of commercial-grade divinylbenzene.

glutaric anhydride (schedule 1A–5A) and epoxides/maleic anhydride (schedule 1B–5B) were the same, respectively: at 80°C for 4 h (schedules 1A and 1B); further curing at 100°C after 1A and 1B (schedules 2A and 2B); at 120°C for 4 h (schedules 3A and 3B); at 150°C for 5 h (schedules 4A and 4B); and finally at 180°C for 3 h (schedules 5A and 5B). Postcuring above 180°C for samples cured with anhydrides and above 150°C for samples with tertiary amine lead to a change in color in the samples from orange to deep red, possibly because significant epoxide isomerization and/or oxidation occurred within the samples at such a high cure temperature.

Characterization of the crosslinked samples

DMA measurements were performed using a dynamic mechanical analyzer Q 800 TA Instruments (Kenilworth, NJ) provided with a cantilever device with a span length of 35 mm. Runs at 10 Hz were performed at a heating rate of 3°C/min over the temperature ranges 25–200°C (for samples 1–3 and 1A–5A)

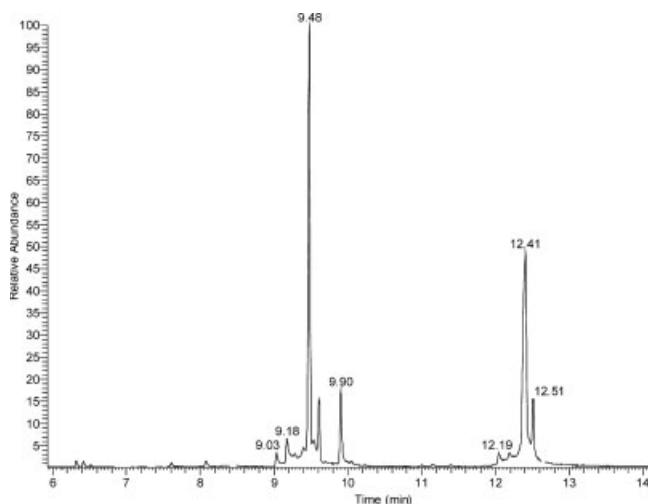


Figure 1 GC chromatogram of the obtained product during the epoxidation process of divinylbenzene with hydrogen peroxide and acetonitrile in the presence of magnesium oxide.

and 25–300°C (for samples 1B–5B). The size of the samples was 35×10×4 mm; T_g was identified as the maximum of the $\tan \delta$; and T_g was also determined using a DSC 204 produced by Netzsch (Günzburg, Germany) with heating run 20–200°C and temperature increase rate 10°C/min. All DSC measurements were carried out in aluminum pans with a pierced lid with sample weight of ~ 10 mg in nitrogen atmosphere.

Thermal stability was examined by means of derivative MOM (Budapest, Hungary) within the temperature range 20–1000°C with the sample weight 100 mg and heating rate 10°C/min.

RESULTS AND DISCUSSION

Characterization of epoxides

The theoretical model of the epoxidation of commercial grade of divinylbenzene is given in Scheme 1. The characterization of the products (the structure and molecular weight of obtained epoxides) was confirmed by GCMS analysis (Fig. 1). It was found that the epoxidation process of commercial grade of divinylbenzene permits us to obtain the mixture of epoxides: 45.2% of bis(epoxyethylbenzene (retention

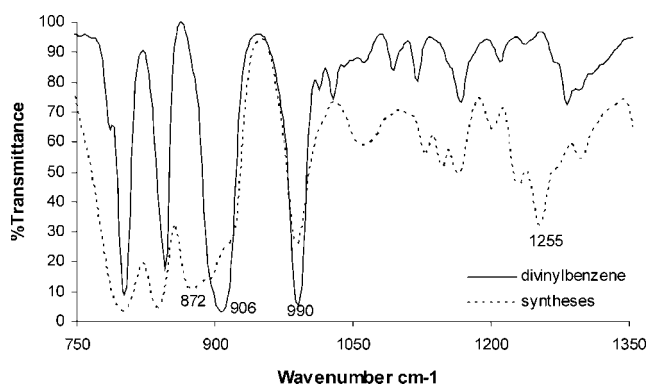


Figure 2 FTIR spectra within the range of 750–1350 cm^{-1} of divinylbenzene and obtained product during the epoxidation process of divinylbenzene with hydrogen peroxide and acetonitrile in the presence of magnesium oxide.

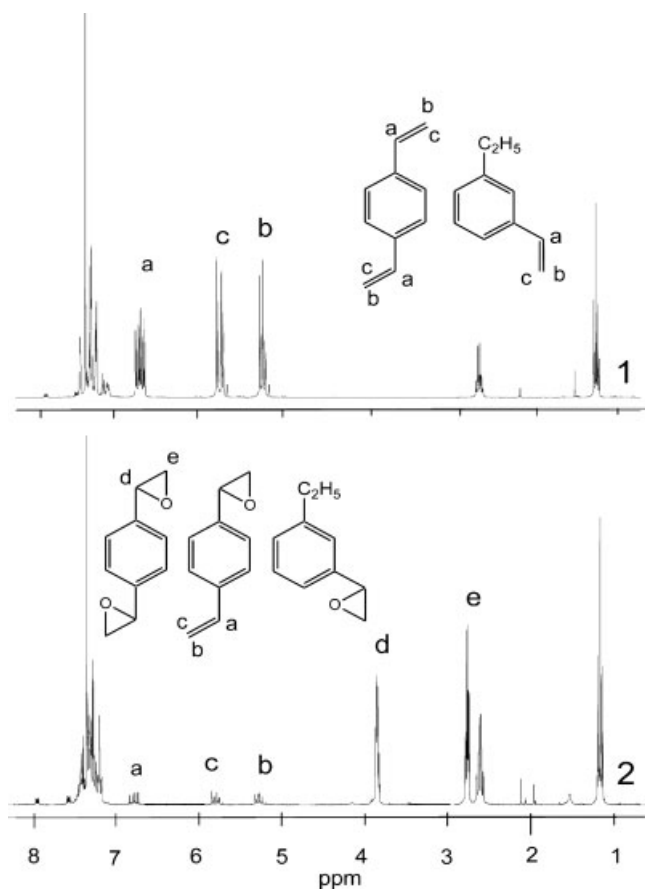


Figure 3 $^1\text{H-NMR}$ spectra of divinylbenzene (1) and obtained product during the epoxidation process of divinylbenzene with hydrogen peroxide and acetonitrile in the presence of magnesium oxide (2).

time 12.41 min) – 3, 8.4% of epoxyethylstyrene (retention time 9.90min) – 4, 46.4% of 2-(3-ethylphenyl)oxirane (retention time 9.48min) – 5. The typical IR spectra of the reactant and products obtained during the epoxidation reaction is shown in Figure 2. It can be seen that there are obvious differences between them. It was found that during the epoxidation reaction double bonds of divinylbenzene and ethylvinylbenzene can be transformed into epoxy functional groups. The IR signal at 906 cm^{-1} and 990 cm^{-1} characteristic for double bonds decreased and the new signals, which are characteristic bands for oxirane groups at 872 cm^{-1} (the oxirane ring vibration) and 1255 cm^{-1} (ring breathing of epoxy group), were observed. From the $^1\text{H-NMR}$ spectrum of the mixture of divinylbenzene and ethylvinylbenzene, the characteristic chemical shifts for the vinyl protons from double bonds were observed at $\delta = 6.63\text{ ppm}$ (internal single hydrogen; a) and 5.18 and 5.61 ppm (two terminal hydrogens; b and c). The analysis of $^1\text{H-NMR}$ spectra of the obtained products shows the disappearance of the chemical shifts for double bonds and appearance of new proton signals at δ

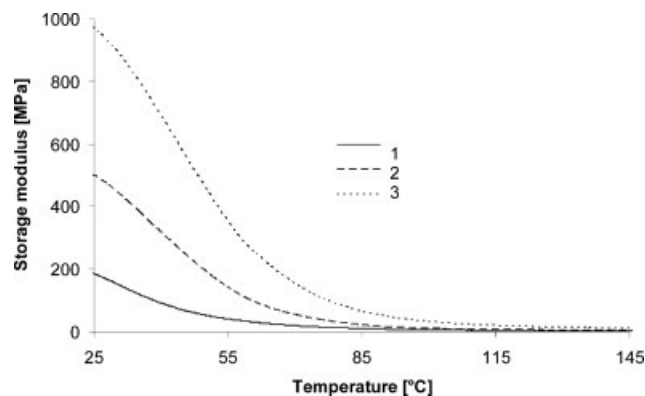


Figure 4 Variation of the storage modulus (E'), of the samples crosslinked with 2,4,6-tri(dimethylaminomethyl)-phenol (samples 1–3) as a function of temperature.

= 2.83 ppm (e) and 3.82 ppm (d) which can be attributed to protons attached to the epoxy group (Fig. 3). The degree of epoxidation was above 90% and was calculated by integration of the epoxide resonance from the $^1\text{H-NMR}$ spectrum.

Viscoelastic properties of crosslinked samples with maleic anhydride, glutaric anhydride, and 2,4,6-tri(dimethylaminomethyl)phenol

The mechanical behavior of crosslinked samples is commonly studied by DMA, a technique in which the modulus and damping of the materials, under an oscillating load, are monitored against time, temperature, or frequency of oscillation. This technique has been widely used to study the dynamic mechanical properties of a variety of materials, such as elastomers, thermoplastics, viscous thermosets, and composites. It is particularly useful for evaluating polymeric materials, which exhibit temperature and time effects on the mechanical properties because of their viscoelastic nature. The glass/secondary transi-

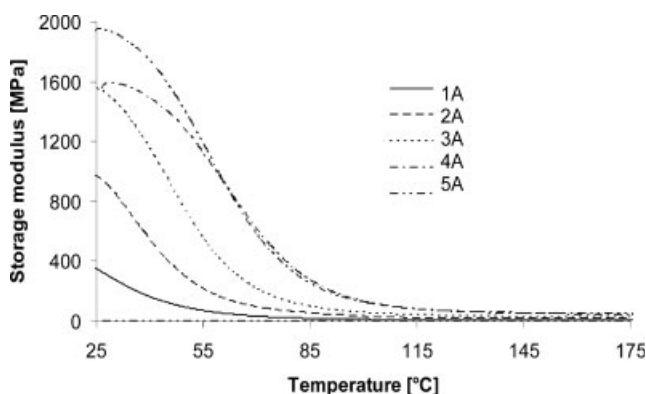


Figure 5 Variation of the storage modulus (E'), of the samples crosslinked with glutaric anhydride (samples 1A–5A) as a function of temperature.

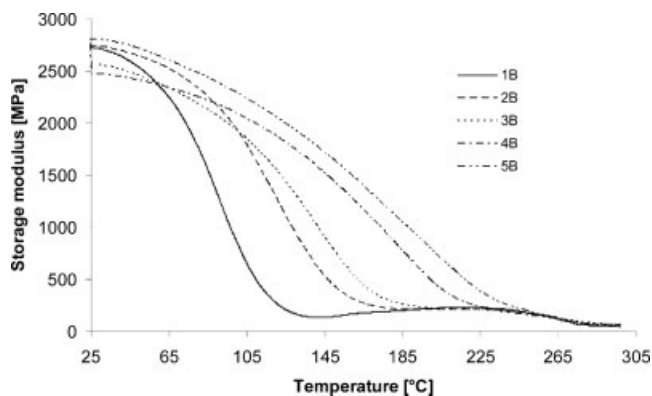


Figure 6 Variation of the storage modulus (E'), of the samples crosslinked with maleic anhydride (samples 1B–5B) as a function of temperature.

tions, crosslinking, creep, and stress relaxation can be investigated. The storage modulus (E') connects with the elastic modulus of the materials, and the loss modulus (E'') relates to the energy loss due to polymer chain movement. The ratio E''/E' is the loss tangent ($\tan \delta$); this loss factor is very sensitive to the structural transformation of the materials. The maximum in the loss factor at high temperatures corresponding to the α relaxation is associated with the T_g of the mixture. Figures 4–6 show the variation of the storage modulus (E') as a function of temperature for crosslinked samples with 2,4,6-tri(dimethylaminomethyl)phenol (Fig. 4), glutaric anhydride (Fig. 5) and maleic anhydride (Fig. 6), respectively, at various temperature conditions. The storage modulus at 25°C of all the compositions is significantly increased particularly for postcured samples at high temperatures. Additionally, the moduli increased from 337.2 MPa (sample 1A) to 1947.2 MPa (sample 5A) when the composition was crosslinked with glutaric anhydride. When the 2,4,6-tri(dimethylaminomethyl)phenol was used as the crosslinking agent the

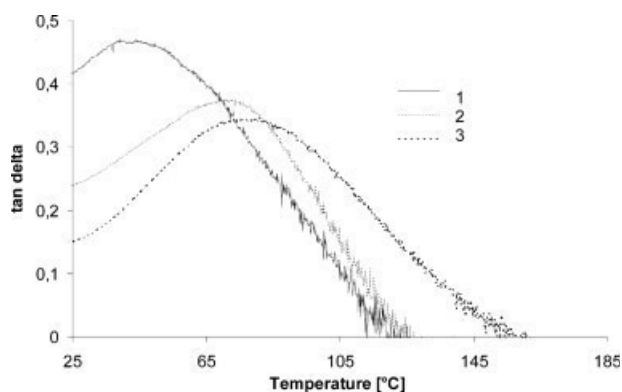


Figure 7 $\tan \delta$ vs temperature for epoxides cured with 2,4,6-tri(dimethylaminomethyl)phenol (samples 1–3).

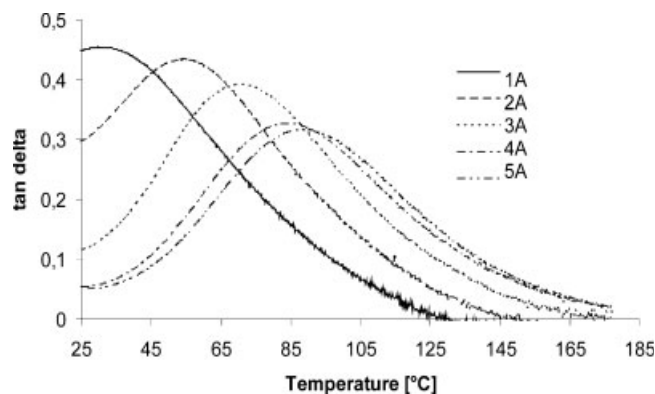


Figure 8 $\tan \delta$ vs temperature for epoxides cured with glutaric anhydride (samples 1A–5A).

storage modulus were within the range 180.2 MPa (sample 1) to 951.0 MPa (sample 3), respectively. The obtained values of E' for samples 1A–5A are significantly higher than those for samples 1–3, but the highest values of E' were observed for the epoxide/maleic anhydride system from 2723.1 (sample 1B) to 2800.0 (sample 5B) (Table I). As can be seen from Figures 4–6 for all crosslinked samples the storage modulus decreases rapidly when the compositions are heated through the glass-to-rubber transition region (the loss modulus and $\tan \delta$ go through a maximum). It was apparent that the changes in the E' values showed significant fall at temperatures between 25–90°C for the compositions 1–3 and 1A–5A and at 25–180°C for samples 1B–5B. The relaxation behavior within the range 25°C to 200°C or 300°C for mixtures cured at different temperature conditions is shown in Figures 7–9. The mechanical loss factor ($\tan \delta$) showed only one peak in the examined range of temperatures. The maximum in $\tan \delta$ moves to a slightly higher temperature by increasing the temperature conditions in which the samples were stored. The maximum of the $\tan \delta$ in the loss factor corresponding to the T_g showed an increasing trend with the increase of curing temperature. When

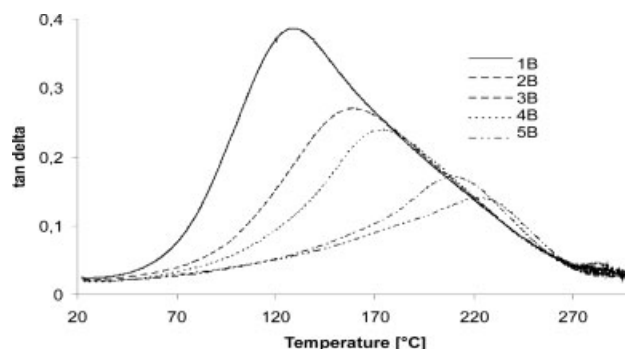


Figure 9 $\tan \delta$ vs temperature for epoxides cured with maleic anhydride (samples 1B–5B).

TABLE I
Results of DMA and DSC Analysis of Crosslinked Samples with
2,4,6-tri(dimethylaminomethyl)phenol (1–3), Glutaric Anhydride (1A–5A),
and Maleic Anhydride (1B–5B)

Sample no.	$E'_{25^\circ\text{C}}$ (MPa)	Damping parameter $\tan \delta_{\text{max}}$	Temperature ($^\circ\text{C}$)		ΔH_{res} (J/g)
			$\tan \delta_{\text{max}}$ (DMA)	T_g (DSC)	
1	180.2	0.466	45.1	40.4	48.6
2	488.5	0.371	73.7	66.3	30.1
3	951.0	0.342	80.6	75.2	—
1A	337.2	0.453	33.0	51.8	42.1
2A	954.7	0.432	55.8	62.3	22.3
3A	1538.9	0.391	71.5	68.7	5.8
4A	1586.7	0.326	85.6	71.4	2.4
5A	1947.2	0.316	90.6	90.9	—
1B	2723.1	0.386	130.3	92.4	32.4
2B	2737.0	0.269	161.0	118.6	15.3
3B	2548.5	0.238	175.9	132.8	4.7
4B	2473.0	0.170	211.7	158.8	—
5B	2800.0	0.144	224.3	166.7	—

maleic anhydride was used as hardening agent the highest values of $\tan \delta$ from 130.3 $^\circ\text{C}$ to 224.3 $^\circ\text{C}$ were observed. In contrast, the variation of T_g for samples 1–3 (45.1–80.6 $^\circ\text{C}$) was quite similar to samples 1A–5A (55.8–90.6 $^\circ\text{C}$). For all samples, the subsequent cure steps above 150 $^\circ\text{C}$ increase the T_g (although not by much), thus indicating the completion of cure reactions. Surprisingly, for samples crosslinked with maleic anhydride the glass transition temperatures reached after the 100 $^\circ\text{C}$ cure step was higher than the cure temperature used. This behavior could be related to etherification and/or more esterification reactions that occur among unreacted epoxide and formed hydroxyl groups and the unreacted acid esters: the exothermy of the cure reactions in the mixtures could increase the temperature of the bulk mixtures inside the mold, so promoting other reactions because of the proximity of these reacting groups in the forming network.³² In the case of epoxides cured with maleic anhydride, the further cure steps clearly increase the T_g , possibly because of copolymerization of double bonds of hardening agent. In contrast, the epoxides crosslinked with 2,4,6-tri(dimethylaminomethyl)phenol or glutaric anhydride showed the loss peak at lower temperatures, possibly due to the highly loose nature of the network so obtained. To confirm that observation, the crosslinking density (ρ) was calculated from the equilibrium storage modulus E' in the rubbery region over the α relaxation temperature according to the equation $\rho = E'/\phi RT$, where ϕ , R , and T are the front factor (usually equal to unity), the gas constant, and the absolute temperature in the rubbery region, respectively.^{33,34} From Table II, one can see that calculated crosslinking densities in the rubbery region of all the cured samples are increased with the cure temperature. As was expected, the lowest

crosslinking densities were obtained for samples cured with tertiary amine, where only the ether-forming reaction was occurred. The highest values of ρ were obtained for samples cured with acid anhydrides.

The tendency of T_g to vary with $\tan \delta$ is consistent with that obtained from DSC analysis. The T_g determined by DSC proceeds in the same order. With the increased curing temperature, the T_g values of the samples increase. The higher T_g values were observed for epoxides cured with maleic anhydride (92.4–166.7 $^\circ\text{C}$) than for those obtained for epoxides crosslinked with glutaric anhydride (51.8–90.9 $^\circ\text{C}$) and 2,4,6-tri(dimethylaminomethyl)phenol (50.4–75.2 $^\circ\text{C}$) (Table I). Figure 10 shows the DSC thermograms for the partially cured and fully cured materials with acid anhydrides and tertiary amine. It was observed that as the material was more crosslinked, its T_g

TABLE II
Crosslinking Density (ρ) of Epoxides Cured at
Different Temperature Conditions

Sample no.	T (K)	E' (MPa)	ρ (mol/cm ³)
1	316.8	75.2	2.85×10^{-2}
2	344.4	81.4	2.84×10^{-2}
3	351.7	92.7	3.17×10^{-2}
1A	306.2	154.2	6.06×10^{-2}
2A	327.5	171.4	6.29×10^{-2}
3A	344.4	182.6	6.37×10^{-2}
4A	357.9	196.0	6.66×10^{-2}
5A	362.8	200.5	6.65×10^{-2}
1B	404.3	163.2	4.85×10^{-2}
2B	432.7	285.8	7.94×10^{-2}
3B	448.8	299.5	8.02×10^{-2}
4B	484.2	327.4	8.05×10^{-2}
5B	497.5	362.9	8.77×10^{-2}

increased and its residual heat of curing (ΔH_{res}) decreased. The values of ΔH_{res} were presented in Table I. The partial cure of the samples could be a consequence of insufficient curing temperature. It can be seen that the complete cure for epoxides/tertiary amine system have been reached at curing temperatures above 120°C. In contrast, the epoxides/acid anhydrides system the curing process can be completed at temperatures above 150°C, no residual heat was observed.

Thermal degradation

Parameters like the initial (T_i), maximum (T_{max}), and final (T_k) decomposition temperatures evaluated from TG and DTG thermograms of the crosslinked samples are summarized in Table III. The TG thermograms indicated that epoxides crosslinked with acid anhydrides had higher initial degradation temperatures 220–260°C for samples crosslinked with maleic anhydride and 240–285°C for samples crosslinked with glutaric anhydride and lower final decomposition temperatures 850–860°C and 865–875°C, respectively, in comparison with samples crosslinked with

TABLE III
Parameters Evaluated from TG and DTG Thermograms of the Crosslinked Samples with 2,4,6-Tri(dimethylaminomethyl)phenol (1–3), Glutaric Anhydride (1A–5A), and Maleic Anhydride (1B–5B)

Sample no.	T_i (°C)	$T_{\text{max}1}$ (°C)	$T_{\text{max}2}$ (°C)	$T_{\text{max}3}$ (°C)	T_k (°C)
1	185	237	—	435	930
2	200	241	—	440	932
3	210	250	—	442	934
1A	245	345	372	437	868
2A	260	350	375	440	870
3A	265	354	375	440	872
4A	275	355	378	442	873
5A	285	355	380	443	875
1B	220	330	360	438	850
2B	230	330	365	440	850
3B	245	335	368	440	850
4B	250	336	370	444	855
5B	260	338	370	446	860

2,4,6-tri(dimethylaminomethyl)phenol ($T_i = 155$ – 210 °C and $T_k = 910$ – 934 °C). The initial and final decomposition temperatures for all crosslinked samples shifted to higher temperature values with increasing the temperature in which the samples were cured. It can be seen that the thermal degradation pattern of crosslinked epoxides with acid anhydrides contained three separated degradation stages with three maximum rate peaks in the differential thermogravimetric (DTG). The main maximum decomposition temperature ($T_{\text{max}1}$) occurred at the highest temperatures 330–338°C and 340–355°C when temperature and time of crosslinking process increased. The second ($T_{\text{max}2}$) and third ($T_{\text{max}3}$) maximum decomposition temperatures at 360–370°C (for samples 1B–5B) and 370–380°C (for samples 1A–5A) and 435–446°C were expected to be the ester and ether bond breakdown, respectively, formed by crosslinking reaction of epoxy groups with anhydride groups. The thermal degradation pattern of samples crosslinked with 2,4,6-tri(dimethylaminomethyl)phenol was indicated at two degradation stages. The main maximum decomposition temperature ($T_{\text{max}1}$) occurred at 237–250°C. The second maximum decomposition peaks at about 435–442°C were expected to be associated with the breakdown reaction of ether linkages because in this system, only the ether-forming reaction between epoxide groups was expected to occur.

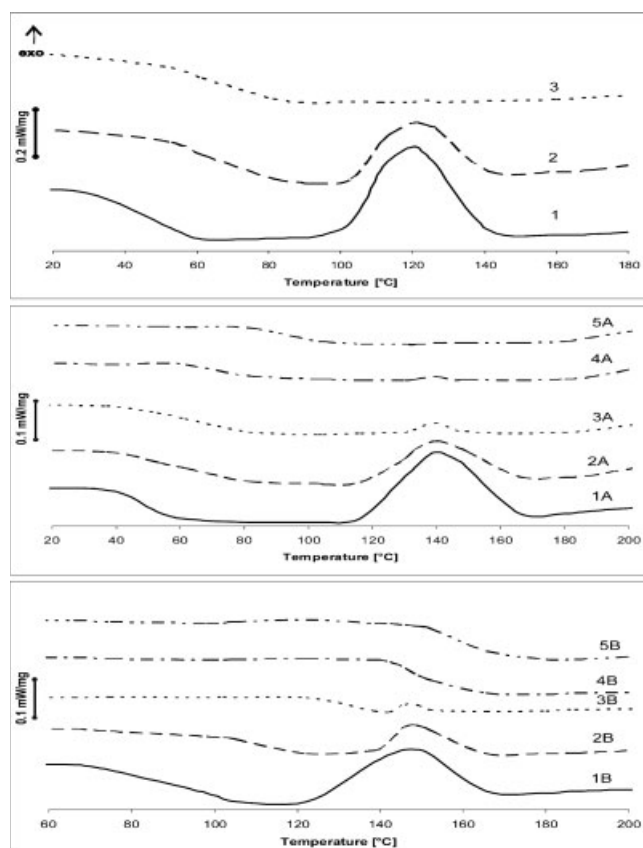


Figure 10 DSC thermograms of samples crosslinked with 2,4,6-tri(dimethylaminomethyl)phenol (1–3), glutaric anhydride (1A–5A), and maleic anhydride (1B–5B) at different curing conditions.

CONCLUSIONS

The results presented indicate that obtained mono- and diepoxides during epoxidation of commercially available divinylbenzene using 60% hydrogen peroxide over magnesium oxide and acetonitrile are reactive compounds for further modification. The

crosslinking reaction with maleic anhydride, glutaric anhydride or 2,4,6-tri(dimethylaminomethyl)phenol give rise to receive polyepoxide materials with different viscoelastic properties and thermal stability. For the curing of epoxides obtained during the epoxidation process of commercial-grade divinylbenzene, the use of maleic anhydride was found to be more interesting than other curing agents. The use of maleic anhydride as the crosslinking agent of prepared epoxides produced materials with higher values of elastic modulus, glass transition temperature, crosslinking density in comparison with samples cured with glutaric anhydride or tertiary amine. This has been related to competitive esterification and etherification reactions occurring during cure of the epoxides which was compared by thermogravimetric analysis. Thermal degradation process of crosslinked samples with acid anhydrides indicated on ester (at temperatures 360–380°C) and ether (437–446°C) bond breakdown. In contrast, during degradation process of samples cured with tertiary amine only ether bond breakdown was observed. Postcuring at high temperatures increases the conversion of epoxy groups and modifies the crosslink density of these epoxide/crosslinking agent networks. The effects of postcuring on the viscoelastic properties and initial decomposition temperature become more significant for epoxides/acid anhydride system due to additional etherification reactions between unreacted epoxy groups or copolymerization reaction of double bonds of hardening agent (maleic anhydride). The stronger the intermolecular interactions and the crosslinking densities at high cure temperatures resulting in increasing dynamic mechanical properties of epoxides crosslinked with acid anhydrides compared with epoxides cured only with tertiary amine.

In conclusion, the prepared epoxides can be cured with different hardening agents like saturated or unsaturated acid anhydrides or tertiary amines. The unsaturated acid anhydride (maleic anhydride) was found to be more efficient than others. The use of maleic anhydride should be considered to accelerate the rate of reaction and lead to an excellent network structure and resulted in better viscoelastic and thermal properties of the cured materials.

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