

Synthesis, Characterization, Thermal, and Viscoelastic Properties of an Unsaturated Epoxy Polyester Cured with Different Hardeners

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ABSTRACT: The chemical modification of the structure of the unsaturated polyester obtained in poly condensation process of 1,2,3,6-tetrahydrophthalic anhydride, maleic anhydride, and ethylene glycol by well known conventional method of epoxidation with peracetic acid in mild conditions has been presented. The new material containing both epoxy groups and unsaturated double bonds in polyester chain was characterized by FTIR and ^1H NMR spectra. The prepared unsaturated epoxy polyester was suitable material for further chemical modification. Both epoxy groups and unsaturated double bonds can be used as cross-linking sites. Curing behavior, thermal, and visco-

elastic properties of the unsaturated epoxy polyester cured with different hardeners: 1,2,3,6-tetrahydrophthalic anhydride (THPA), hexahydrophthalic anhydride (HHPA), and/or with vinyl monomer (styrene) using radical initiator—benzoyl peroxide (BPO) were studied by differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), and dynamic mechanical analysis (DMA). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3582–3589, 2008

Key words: curing of polymers; differential scanning calorimetry (DSC); polyesters; thermal properties; viscoelastic properties

INTRODUCTION

Epoxy resins are widely used in the electronic industry, advanced composites, coatings, structural adhesives, paints, varnishes, construction materials, and some other advanced fields because of their superior thermal, mechanical and electronic properties like high stiffness, high strength, good impact resistance, dimensional stability, etc.^{1–9} Epoxy resins are real polyethers based on a condensation reaction between epichlorhydrin and dian (the most common is bisphenol A). This compound can be replaced with glycerol or other aliphatic polyols in the preparation of epoxy resins. Additionally, higher molecular weight epoxy resins contained pendent hydroxyl groups can be esterified with fatty acids or used in conjunction with urea, melamine, formaldehyde, acrylic, polyester or phenolic resins or crosslinked with isocyanate, polyamine, polysulfides, polyamide, etc. hardeners which lend themselves to two component or multi-component application.^{10–12} The development of new epoxy resins has been carried out on two aspects of the epoxy resins namely, development and modification of newer epoxy resins and their application in different fields.¹³ The literature

describes many methods for chemical modification of the polymeric materials by introducing a functional groups either stoichiometric or catalytic.^{14–16} One of methods of chemical modification is the method based on the direct oxidation of unsaturated cyclo-aliphatic compounds with isolated double-double bonds by ready peracids or peracids formed *in situ* in the addition of hydrogen peroxide to an organic acid.^{17–19} The performic and peracetic acids are the most often applied peracids in the epoxidation reactions of the esters of fatty acids and cycloaliphatic resins like dicyclopentadiene-type in industry.^{20–22} This resins have low viscosity and their cured resins have high glass transition temperatures, high crosslinking density but they are poor in mechanical elongation and toughness.^{7,23} A few articles described the chemical modification of high-molecular compounds useful for powder UV-curable coating application prepared by the condensation of 1,2,3,6-tetrahydrophthalic anhydride, glycols and dicyclopentadiene or 1,2,3,6-tetrahydrophthalic acid or anhydride, cycloaliphatic polyols, saturated polycarboxylic acid and alcohol with acid solutions such as peracetic or performic acids generated separately or *in situ* from organic acid and hydrogen peroxide.^{24–26} To this time no article describes selective oxygenation of the unsaturated polyesters prepared in polycondensation of 1,2,3,6-tetrahydrophthalic anhydride, maleic anhydride, and glycols by peracetic acid. In this article, the chemical structure of the

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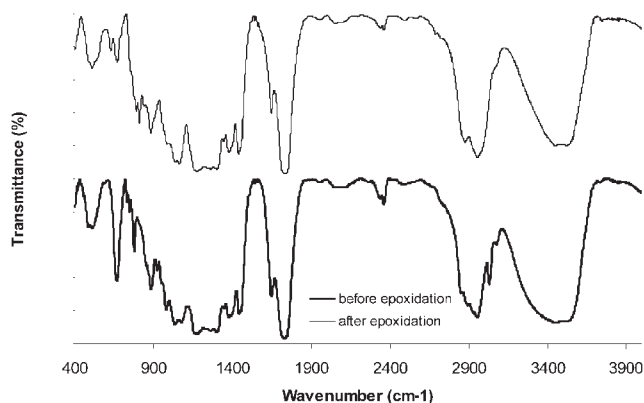


Figure 1 FTIR spectra of the unsaturated polyester before and after epoxidation.

unsaturated polyester obtained in polycondensation process of THPA, MA, and EG at 1 : 0.5 : 2.1 molar ratio of substrates was modified by well known conventional method of epoxidation with 38–40% peracetic acid in mild conditions. The modified unsaturated polyester which contains both epoxy groups in cyclohexenyl rings and the unsaturated double bonds in the polyester chain suitable for further chemical modification has been prepared. Its structure was confirmed by FTIR and ^1H NMR spectra. Both epoxy groups and unsaturated double bonds can be used as cross-linking sites. The modified unsaturated polyester (unsaturated epoxy polyester) can be cured by means of common curing agents suitable for epoxy resins e.g., nucleophilic and electrophilic agents like polycarboxylic acid anhydrides, amines, etc. via ionic mechanism²⁷ and/or with vinyl monomer using organic peroxides via free-radical copolymerization mechanism.²⁸ Therefore, in this work, curing behaviors, thermal stabilities and dynamic mechanical properties of the unsaturated epoxy polyester cured with different hardeners: 1,2,3,6-tetrahydrophthalic anhydride (THPA), hexahydrophthalic anhydride (HHPA) and/or with vinyl monomer (styrene) using radical initiator-benzoyl peroxide (BPO) were studied by differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

1,2,3,6-tetrahydrophthalic anhydride (THPA), hexahydrophthalic anhydride (HHPA), maleic anhydride (MA), methylene chloride, tetrahydrofuran Lichrosolv (chromatographic grade) were purchased from Merck-Schuchardt (Hohenbrunn, Germany). 38–40% solution of peracetic acid was from Merck-Schu-

chardt (Hohenbrunn, Germany) and was used as the oxidising agent. Ethylene glycol was from Fluka (Buchs, Switzerland). Other reagents such as sodium carbonate, sodium hydroxide, sodium chloride, magnesium sulfate, benzoyl peroxide (BPO) and styrene (ST) were delivered by POCh (Gliwice, Poland). All reagents were used without further purification.

Epoxidation of the unsaturated polyester

The unsaturated polyester was obtained in polycondensation process of 1,2,3,6-tetrahydrophthalic anhydride, maleic anhydride, and ethylene glycol at 1 : 0.5 : 2.1 molar ratio of substrates. The acid number of initial polyester, defined as the number of mg KOH required for the titration of 1 g of polyester was 14.8. This corresponds to 0.264 mmol of COOH groups per g of polyester. The average molecular weight (determined by means of the osmometer KNAUER GmbH, Germany) was 940 g/mol. Additionally, the chemical structure of the unsaturated polyester was confirmed by FTIR and ^1H NMR spectra (Figs. 1 and 2).

The chemical structure of the initial unsaturated polyester was modified by well known conventional method of epoxidation with 38–40% peracetic acid in mild conditions to obtain the new unsaturated epoxy polyester containing both epoxy groups and unsaturated double bonds in polyester chain. The unsaturated polyester was placed in the three-necked flask equipped with a water condenser, a thermometer and a glass stirrer. It was dissolved in methylene chloride and the resulting solution was heated to the reaction temperature of 40°C. Then 38–40% solution of peracetic acid was added under vigorous stirring

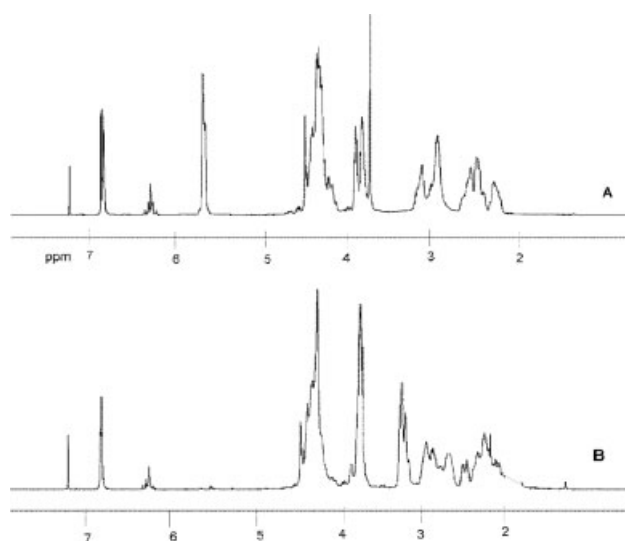


Figure 2 ^1H NMR spectra of the unsaturated polyester (A) and unsaturated epoxy polyester (B).

and reacted at 40°C for a predetermined time of 2 h. With peracetic acid the reaction was almost immediately exothermic, so the reaction mixture had to be cooled down with an ice bath to attain the reaction temperature. After completion, the reaction mixture was cooled down and washed with the aqueous solution of sodium carbonate and sodium hydroxide saturated with sodium chloride to neutrality. Then, the mixture was placed in the separator and the organic phase was thoroughly washed two times with aqueous solution of sodium hydroxide and distilled water, dried over anhydrous MgSO_4 . Then, the solvent was removed by vacuum distillation. The residue was diluted with tetrahydrofuran, dried and distilled off under reduced pressure. The average molecular weight of obtained unsaturated epoxy polyester was 990 g/mol and epoxy value (determined by the dioxane/HCl titration method) was 0.275 mol/100 g. The new unsaturated epoxy polyester was also characterized by FTIR and ^1H NMR spectra (Figs. 1 and 2). Then, the curing behavior, thermal and viscoelastic properties of the different hardeners (THPA, HHPA, and/or BPO) cured material have been studied.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer 1725 X FTIR spectrophotometer in the 400–4000 cm^{-1} wave number range using KBr pallets.

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained by using a NMR Bruker-Avance 300 MSL (Germany) spectrometer at 300 MHz with deuterated chloroform (CDCl_3) 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.

Differential scanning calorimetry (DSC) thermograms were obtained using a DSC Netzsch 204 calorimeter (Netzsch, Günzburg, Germany). All DSC measurements were done in aluminum pans with a pierced lid with sample weight ~ 10 mg in nitrogen atmosphere (30 mL/min). Isothermal curing tests were conducted at 100, 140, and 200°C until no further heat flow can be detected. A dynamic scans were done at a heating rate of 10 K/min in the temperature range of 20–300°C. Curing characteristic such as temperature of the cure initiation (T_{onset}), peak maximum temperature (T_{max}), final cure temperature (T_{end}), and the heat generated during the cure reaction (ΔH) were evaluated. The glass transition temperatures- α relaxation (T_g) of fully cured samples were also determined.

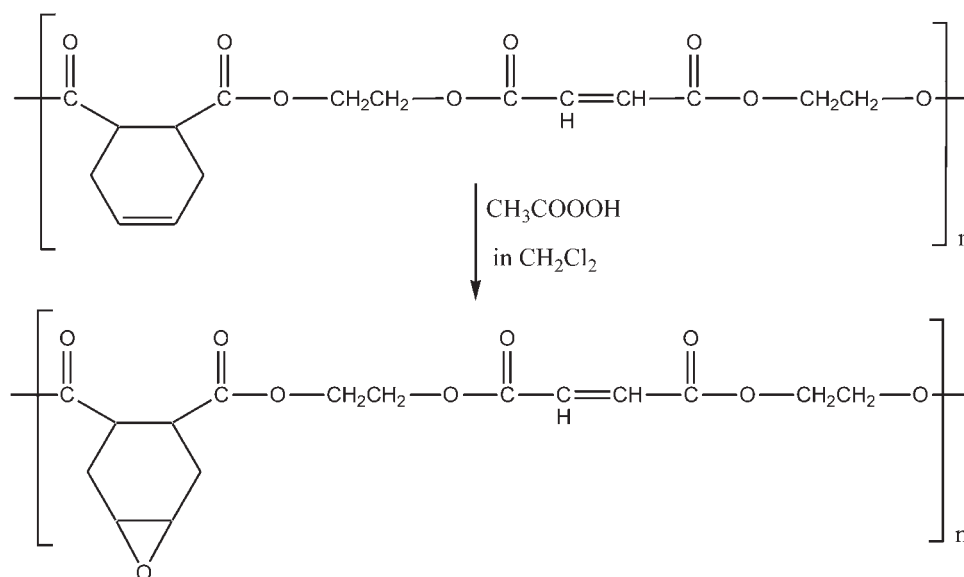
Thermo gravimetric analysis (TGA) was performed on a MOM 3427 derivatograph (Paulik, Pau-

lik and Erdey, Budapest, Hungary) at a heating rate of 10°C/min in air, in the temperature range of 20–1000°C with the sample weight of 100 mg. The IDT (initial decomposition temperature), the maximum rate of weight loss (T_{max}) and final decomposition temperature (T_k) were determined.

DMA measurements were performed using dynamic mechanical analyzer (DMA) Q 800 TA Instruments (USA) provided with a dual cantilever device with a span length of 35 mm, calibrated according to the producer's recommendation. Runs at 10 Hz were performed at a constant heating rate of 4°C/min over the temperature ranges 25–300°C. The size of the samples was 35 \times 10 \times 4 mm. Viscoelastic properties of the cross-linked material were estimated from the changes of storage modulus (E'), mechanical loss (E'') as well as from the changes of $\tan \delta$ at constant frequency depending on temperature. The T_g was identified as the maximum of the $\tan \delta$. From the $\tan \delta$ curves also the width across the curve when it dropped to half of its peak value (FWHM or full-width at half-maximum) was determined.

Sample preparation

The unsaturated epoxy polyester was cured with different acid anhydrides—THPA, HHPA via ionic mechanism and/or with vinyl monomer (styrene) using radical initiator—BPO via free-radical copolymerization mechanism. The stoichiometric ratio of an anhydride r 0.85, where r was defined as anhydride/epoxy groups and/or the subsequent concentrations of vinyl monomer (styrene) 20 wt % and radical initiator—BPO 1 wt % were used, respectively. The samples used for DSC experiments were prepared as follows: the unsaturated epoxy polyester and the stoichiometric ratio of a suitable anhydride were mixed and heated up above the melting point for suitable anhydride to obtain a homogeneous solution. Then, the samples were quenched in cold water. In the case of the curing reaction initiated by BPO, the styrene and BPO were firstly mixed and then the unsaturated epoxy polyester was added. All samples were tested immediately after mixing. For thermal and viscoelastic testing, the samples were prepared as for calorimetric experiments. They were placed in a glass mold under reduced pressure at 80°C for 4 h to remove any air. Then, the curing cycle for each formulation was 5 h at 100°C, 5 h at 140°C, 15 h at 180°C and finally 1 h at 200°C. The used curing cycle allowed to obtain stable and maximum properties of the material without damage connected with thermal degradation.



Scheme 1 The epoxidation route of the unsaturated polyester.

RESULTS AND DISCUSSION

Characterization of the unsaturated epoxy polyester

The chemical structure of the unsaturated polyester obtained in polycondensation process of 1,2,3,6-tetrahydrophthalic anhydride, maleic anhydride, and ethylene glycol was modified through the well known conventional method of epoxidation. The epoxidation reaction of the unsaturated polyester with 38–40% peracetic acid in mild conditions allowed obtaining the material which contains both epoxy groups in cycloaliphatic rings and the unsaturated double bonds in the polyester chain. The epoxidation route of the unsaturated polyester was shown in Scheme 1. It can be explained by different reactivity of the double bonds in cyclohexenyl rings and the double bonds from maleic anhydride in the polyester chain. It is well known that the presence of carboxyl, carbonyl or ester groups in the double bonds environment reduces the rate of epoxidation reaction while the presence of e.g., alkyl groups near the double bonds increase the efficiency of epoxidation.¹¹

The FTIR spectra of the unsaturated polyester before and after epoxidation is given in Figure 1. The characteristic absorption bands in the range of 666–775 cm⁻¹ related to the double bonds in cyclohexenyl rings (C–H out-of-plane deformation vibration) and at 3031 cm⁻¹ (=C–H stretching vibration) for the unsaturated polyester are observed. Moreover, in this spectrum the absorption bands at 960–990 cm⁻¹ (trans –HC=CH wagging) and at 1640 cm⁻¹ (C=C stretching vibration for double bonds) are indicated. After epoxidation, the almost totally decrease of the absorption bands in the range of 666–775 cm⁻¹ and completely disappearance of the

absorption bands at 3031 cm⁻¹ was the indication that the oxidation process occurred. Additionally, the new absorption bands at 789–836 cm⁻¹ corresponding to oxirane ring vibration groups were indicated. In addition, no changes at 960–990 cm⁻¹ and 1640 cm⁻¹ were observed. The analysis of ¹H NMR spectra of the unsaturated polyester showed the presence of the characteristic chemical shifts for the protons on the double bonds of cyclohexenyl rings at 5.67–5.7 ppm and for the protons on the double bonds from maleic units at 6.29–6.35 ppm (*cis*-form) and 6.90–6.93 (*trans*-form). In the synthesis of the unsaturated polyester from maleic anhydride the isomerization of maleate (*cis*) polyester to fumarate (*trans*) happened. It depends on condensation time, medium acidity, the reactants (glycol, acid) or catalysts. It has some advantageous, generally speaking it is easier to crosslink the prepolymer to form a network structure if the unsaturated acid exists in the *trans* form.¹¹ In this case, the degree of isomerization calculated from the ¹H NMR spectra by the integration of the signals area for maleate and fumarate forms^{29–31} was above 80%. From the ¹H NMR spectra of the unsaturated epoxy polyester, the total disappearance of the signals at $\delta = 5.67\text{--}5.7$ ppm and the presence of the unchanged signals for maleic units were observed. The conversion of the double bonds in cycloaliphatic rings calculated from ¹H NMR spectra was above 98% in synthesis conditions. It confirmed that the oxidation reaction was successful and the double bonds in cyclohexenyl rings have been converted into epoxy groups. The new proton signals at 2.65–2.78 ppm appeared in the spectrum after oxidation and can be attributed to the protons attached to the epoxy groups, (Fig. 2).

TABLE I
The Data Obtained from DSC Thermograms

Curing agent	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)	ΔH (kJ/mol)
BPO	66.0	118.5	182.2	101.9
THPA	66.3	165.2	207.3	205.9
HHPA	65.4	167.6	210.0	211.7
THPA/BPO	64.6	120.3/166.1	265.4	353.2
HHPA/BPO	65.2	121.2/170.2	260.4	359.8

Calorimetric study of the cure reaction

The cure behavior of the unsaturated epoxy polyester with different hardener systems was investigated with DSC. Isothermal curing tests were conducted at different isothermal temperatures (100, 140, and 200°C). The mixture of the unsaturated epoxy polyester with suitable hardener was heated to the isothermal curing temperature and held at this temperature until no further heat flow can be detected. The integration of the isothermal curve was rather imprecise due to the asymptotic character of the heat curve. Dynamic runs were carried out under nitrogen atmosphere at a heating rate of 10 K/min, the sample was heated from 20 to 300°C. The reaction was considered to be complete when the rate curve returned to a baseline. Curing characteristic such as temperature of the cure initiation (T_{onset}), peak maximum temperature (T_{max}), final cure temperature (T_{end}) and the heat generated during the cure reaction (ΔH) were evaluated. The ΔH values were obtained by the integration of the exothermic peak. The data obtained from dynamic DSC thermograms were summarized in Table I. The exemplary isothermal DSC thermograms of the curing reaction of the unsaturated epoxy polyester with different hardeners conducted at 140°C were given in Figure 3. The isothermal tests conducted at different temperatures showed similar trends. The isothermal experiments confirmed that the cure reaction of the unsaturated epoxy polyester was much faster when BPO was used as an initiator. Thus, it is highly likely that BPO would accelerate the rate of the cure reaction. These observations were in accordance with dynamic DSC experiments. The dynamic DSC measurements showed that the cure reaction initiated by BPO was less exothermic and was characterized through lower ΔH values (101.9 kJ/mol). This low heat of reaction can be associated with the lowest T_{max} and T_{end} values indicating high reactivity of the reaction mixture but probably lower crosslink density of the obtained polymer network. The heat generated during the cure reaction was attributed to the chain-growth process-copolymerization between vinyl monomer (styrene) and the unsaturated double bonds³² when the cure was initiated by radical ini-

tiator (BPO). The broad asymmetric exothermic peak was characteristic for the cure reaction performed with acid anhydrides (THPA and HHPA). It can be attributed to the epoxy/anhydride copolymerization. In this system, the reaction between epoxy and anhydride groups promoted by hydroxyl compounds to produce ester linkages was expected. Alternatively, at higher temperatures in the presence of catalytic activation of carboxylic acid the etherification process may happen.^{33–39} The ΔH values for the cure reaction with THPA, HHPA hardeners were comparable 205.9 kJ/mol and 211.7 kJ/mol, respectively. Curing process initiated by the dual initiator system: acid anhydride/BPO was more exothermic. The values of ΔH were in the range of 353.2–359.8 kJ/mol depending on the type of acid anhydride. They were 45.4–46.2 kJ/mol higher than the sum of ΔH of the cure reaction initiated by BPO or suitable acid anhydride. This can be indication that the more cross linked polymer network structure was obtained. Additionally, in this case, the broad exothermic peak with two maxima had been observed. It suggests the occurrence of two reaction process, which are not clearly time/temperature separated. The first maxima with T_{max} in the range 120.3–121.2°C can be related to the radical polymerization, the second with T_{max} 166.1°C for THPA/BPO system and 170.2°C for HHPA/BPO has been taken to indicate polyaddition reaction. So, it is not able to separate the radical polymerization from polyaddition reaction when the dual initiator system acid anhydride/BPO was employed. Moreover, the final cure temperatures were higher (260.4–265.4°C) when the dual hardener system was used. This could be due to the increase of the crosslink density of the matrix as curing progress and the liquid state are faster transformed to glassy state via rubbery state. The movement of reacting groups (due to the steric hindrance) is greatly limited, and the cure reaction

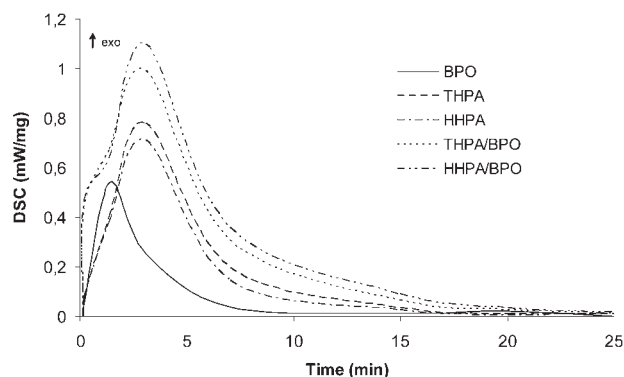


Figure 3 The exemplary isothermal DSC thermograms of the cure reaction of the unsaturated epoxy polyester with different hardeners.

TABLE II
The Parameters Evaluated from TG and DTG
Thermograms of Cured Material

Curing agent	IDT (°C)	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	T_k (°C)
BPO	270	370	520	600
THPA	280	380	560	620
HHPA	280	380	560	615
THPA/BPO	290	380	580	640
HHPA/BPO	290	380	575	635

slows down as further possible reactions are only due to diffusion.

Thermal stabilities of cured material

Thermal stability and thermal degradation behaviors of the acid anhydride and/or BPO cured material were investigated by means of thermo gravimetric analysis. The parameters evaluated from TG and DTG thermograms in static air atmosphere were reported in Table II. The anhydride/BPO cured epoxy polyester was considerably more thermally stable than anhydride or BPO cured material. The increase of IDT as well as the maximum rate of weight loss ($T_{\max 2}$) and T_k for acid anhydride/BPO cured samples were observed. The IDT temperatures were about 10–20°C higher than those obtained for anhydride or BPO cured material. Similarly, the final degradation temperatures for anhydride/BPO cured samples were about 10–40°C higher compared to others. This can be a consequence of more cross-linked network structure obtained when the both acid anhydride and radical initiator were used. Moreover, the degradation of the cured samples exhibited two separated degradation steps with $T_{\max 1}$ and $T_{\max 2}$ in the range of 370–380°C and 520–580°C, respectively, depending on hardeners. The

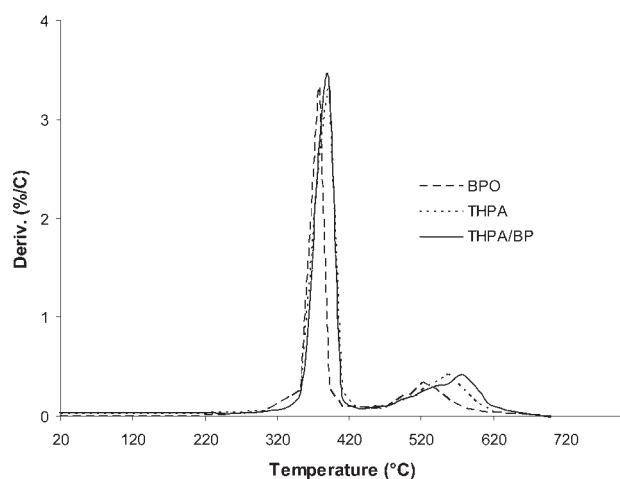


Figure 4 The exemplary DTG thermograms of THPA and/or BPO cured material.

second maximum can be attributed to the total degradation of the cured samples. The first maximum could be due to the degradation of the ester bonds of polyester or formed during epoxy/anhydride polymerization as reported by some authors.⁴⁰ The cure mechanism of epoxy/anhydride is generally known. Ring opening of an acid anhydride is promoted by hydroxyl groups to form an acid. The acid then ring-opens the epoxy group, thereby yielding another hydroxyl moiety to help propagate the polymerization reaction in which the ester bonds are formed.^{3,41} The exemplary DTG thermograms of THPA and/or BPO cured samples are given in Figure 4.

Dynamic mechanical analysis

One of the most important characteristics of the amorphous state is the behavior of a polymer during its transition from solid to liquid.³ A DSC study and DMA analysis in the glassy state and in rubbery region were done to determine how the different parameters influence on the polymer network. The viscoelastic properties of acid anhydride and/or BPO cured material were measured in a wide temperature range 30–250°C at a heating rate of 4°C/min. Variation of storage modulus as a function of temperature for all cured materials is presented in Figure 5. The storage modulus changed in the function of temperature. The use of acid anhydride/BPO system had the considerable effect in stiffness behavior of the cured material. The acid anhydride/BPO cured epoxy polyester was characterized through the higher values of storage modulus ($E'_{30^\circ\text{C}}$) compared to acid anhydride cured samples, Table III. The storage modulus in a glassy state is increased by 24.3% (from 2300 MPa to 2860 MPa) for THPA/BPO cured material and by 32.2% (from 2061 MPa to 2726 MPa) for HHPA/BPO cured. The loss modulus (E'') shifted toward the higher temperature for acid

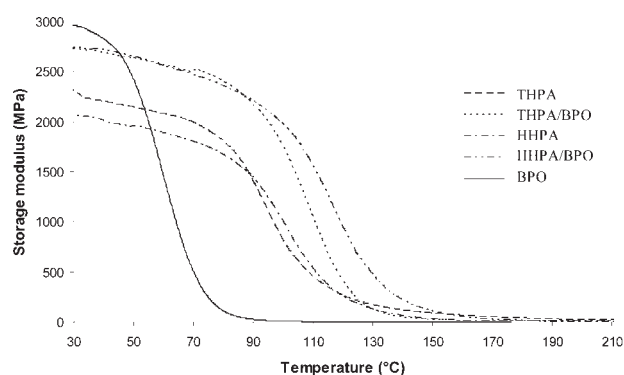


Figure 5 Variation of the storage modulus as a function of temperature for all cured samples.

TABLE III
The Data Obtained from DMA and DSC Curves

Curing agent	$E'_{30^\circ\text{C}}$	FWHM	Temperature ($^\circ\text{C}$)		
			$\tan \delta_{\text{max}}$	E''_{max}	T_g (DSC)
BPO	2960	35	81.3	66.4	86.6
THPA	2300	65	104.8/195.8	96.5	108.6
HHPA	2061	70	127.7/157.9	103.0	110.2
THPA/BPO	2860	75	136.2/185.6	122.4	122.8
HHPA/BPO	2726	65	140.7/166.2	119.4	120.4

anhydride/BPO cured material, Figure 6. The E''_{max} values were in the range of 119.4–122.4 $^\circ\text{C}$ for dual initiator system, 96.5–103 $^\circ\text{C}$ for acid anhydride and 66.4 $^\circ\text{C}$ for BPO cured epoxy polyester. The relaxation behaviour of cured material with different hardeners is shown in Figure 7. The observation revealed that the $\tan \delta_{\text{max}}$ corresponding to the glass transition temperature had higher values for THPA/BPO and HHPA/BPO cured samples than others. Additionally, the changes profile of glass transition temperature determined by means of DSC was in accordance to those obtained from DMA analysis. Moreover, the BPO cured material displayed a single transition course (one symmetrical peak) in the examined range of temperatures. On the other hand, the broad asymmetrical peak of $\tan \delta$ with two maximum for acid anhydride and acid anhydride/BPO cured material had been observed. This could suggest structural constituent and more spatially heterogeneous networks obtained for acid anhydride or acid anhydride/BPO cured material (higher FWHM values) compared to BPO cured material.

CONCLUSIONS

The chemical modification of the structure of the unsaturated polyester prepared from THPA, MA, and EG allowed to obtain the unsaturated epoxy polyester containing both epoxy groups and unsaturated

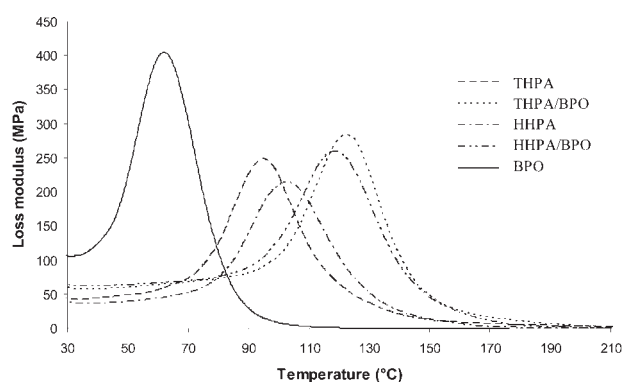


Figure 6 Variation of the loss modulus as a function of temperature for all cured samples.

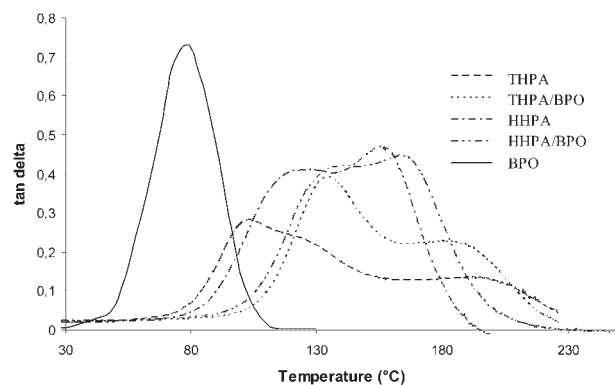


Figure 7 The $\tan \delta$ for the cured material as a function of temperature.

double bonds in the polyester backbone. The cure behaviors, thermal, and viscoelastic properties of acid anhydride (THPA, HHPA) and/or BPO cured material were studied. The cure reaction initiated by the dual initiator system (THPA/BPO and HHPA/BPO) was more exothermic and characterized through higher ΔH values than that of acid anhydride (THPA, HHPA) or BPO. In this system, the heat generated during the cure reaction was attributed to both the chain-growth process: copolymerization of styrene and the unsaturated double bonds of epoxy polyester and to the epoxy/anhydride copolymerization. The better thermal properties, including initial decomposition temperature, final decomposition temperature, glass transition temperature and viscoelastic properties of THPA/BPO and HHPA/BPO cured materials were observed. It could be attributed to the more cross-linked polyester network obtained for acid anhydride/BPO cured material.

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