

Chemical Modification of Unsaturated Polyesters Influence of Polyester's Structure on Thermal and Viscoelastic Properties of Low Styrene Content Copolymers

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ABSTRACT: In this study, the chemical modification of unsaturated polyesters and the influence of polyester's structure on thermal and viscoelastic properties have been presented. The structure of unsaturated polyesters obtained in polycondensation of cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride and only one suitable symmetrical glycol: ethylene glycol or 1,4-butanediol (BDO) or 1,6-hexanediol has been modified by peracetic acid. The selective oxidation of unsaturated polyesters conducted in mild time and temperature conditions was a successful and effective method to prepare new materials/unsaturated epoxy polyesters/containing epoxy groups in cycloaliphatic rings and carbon-carbon double bonds in polyester chain. The unsaturated epoxy polyesters were capable of both copolymerization with vinyl

monomer and polyaddition reactions with suitable curing agent. Therefore, they were successfully used as a component of low styrene content copolymers. As was confirmed by DSC, DMA, and TGA analyses, polyester's structure had significant influence on thermal and viscoelastic properties of styrene copolymers. The properties of styrene copolymers prepared from unsaturated epoxy polyesters were considerably better compared with those obtained for styrene copolymers from unsaturated polyesters. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 720–731, 2009

Key words: unsaturated polyesters; unsaturated epoxy polyesters; chemical modification; thermal properties; viscoelastic properties

INTRODUCTION

Unsaturated polyesters are becoming increasingly popular and widely produced industrially because of their low cost, easy processing, and extremely versatile in properties and applications.^{1–3} They are usually prepared by polycondensation, typically of a dihydroxyl compound or mixtures of dihydroxy compounds (diols) with maleic anhydride (MA) and/or together with other dicarboxylic acids, such as aromatic or aliphatic dicarboxylic acids under elevated temperature.^{4–7} Unsaturated polyesters are largely employed as laminates, construction materials, adhesives, coatings, in the building industry, the electrical industry, etc.^{8–10} Despite those many advantages, such as room temperature capability, transparency, low densities, etc.¹¹, the typical polyesters have some disadvantages. They are not tough enough, highly flammable, and their impact strength is lower than of other thermoset polymers like epoxy.¹² Therefore, their properties are often improved and modified in two commonly used

methods: physical blending and compounding^{13,14} and chemical modification. The second method is very intensively studied. It allows to introduce modifying monomers to synthesis of unsaturated polyesters or replace carbon-carbon double bonds in polyester backbone with epoxy, hydroxyl, or carboxyl groups.^{15–18} The literature describes many methods for chemical modification of polymeric materials by introducing a functional group either stoichiometric or catalytic.^{19–21} One of those is a direct oxidation of unsaturated polyesters by peracids generated separately or peracids formed *in situ* during addition of hydrogen peroxide to an organic acid. Oxidation of the unsaturated polyesters to the corresponding epoxide derivatives containing a large number of epoxide groups offered considerable interest. Epoxidation of polyesters having pendent allyl groups prepared from succinic anhydride and allyl glycidyl ether by *m*-chloroperbenzoic acid lead to obtain the multifunctional epoxy-polyester resins.^{22,23} *In situ* oxidation process of polyesters from tetrahydrophthalic anhydride and different glycols or unsaturated alkyd resin using a cation exchange resin of the styrene-divinyl benzene sulfonic acid type permit to modify the polyesters structure and synthesize molecules containing several epoxide groups (polyepoxides).^{24,25} The aliphatic-cycloaliphatic

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epoxy compounds contain different epoxy groups in molecule: 2,3-epoxypropyl groups and 1,2-epoxycyclopentane or 1,2-epoxycyclohexane rings prepared by epoxidation of carbon-carbon double bonds in cycloolefins by peracetic acid are reported.²⁶ Also, a few articles describe the chemical modification of high-molecular weight compounds prepared by the polycondensation of tetrahydrophthalic anhydride, glycols and dicyclopentadiene or tetrahydrophthalic acid or anhydride, at least one cycloaliphatic polyols, at least one saturated polycarboxylic acid and alcohol by peracetic or performic acid generated separately or *in situ*. In this way, the solid epoxidized polyesters useful for powder coating applications were obtained.²⁷⁻³⁰

In this study, the structure of unsaturated polyesters obtained in polycondensation of cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), MA and only one suitable symmetrical glycol: ethylene (EG) or 1,4-butanediol (BDO) or 1,6-hexanediol (HDO) has been modified by 38-40% peracetic acid in mild time and temperature conditions. The selective oxidation of unsaturated polyesters allowed to obtain the new unsaturated epoxy polyesters containing both epoxy groups in cycloaliphatic rings and carbon-carbon double bonds in polyester backbone, which was confirmed by FTIR and ¹H NMR analyses. The modified polyesters are suitable materials for further modification. They are capable of both copolymerization with vinyl monomer and polyaddition reactions with suitable hardener. Therefore, both unsaturated polyesters and unsaturated epoxy polyesters were dissolved in vinyl monomer (styrene) and cured with suitable curing agent: benzoyl peroxide (BPO) or the mixture of benzoyl peroxide and tetrahydrophthalic anhydride (BPO/THPA). The influence of polyester's structure on thermal and viscoelastic properties of cured low styrene content copolymers prepared from modified polyesters as well as from unmodified polyesters were studied and compared.

EXPERIMENTAL

Materials

Tetrahydrophthalic anhydride (THPA, cyclohex-4-ene-1,2-dicarboxylic anhydride) and MA were obtained from Merck-Schuchardt (Hohenbrunn, Germany). Ethylene glycol (EG), BDO, and HDO were from Fluka (Buchs, Switzerland). Hydroquinone and styrene (ST) were from POCh (Gliwice, Poland). 38-40% peracetic acid containing 1 wt % of sulphuric acid, methylene chloride, tetrahydrofuran Lichrosolv (chromatographic grade) were purchased from

Merck-Schuchardt (Hohenbrunn, Germany). Other reagents, such as sodium carbonate, sodium hydroxide, sodium chloride, and magnesium sulfate were delivered by POCh (Gliwice, Poland). All reagents were used without further purification.

Unsaturated polyesters and their chemical modification

The unsaturated polyesters were obtained in polycondensation process of tetrahydrophthalic anhydride (THPA), MA, and only one suitable symmetrical glycol: EG or BDO or HDO in the presence of 0.015 wt % of hydroquinone as an inhibitor. The reaction was performed at the ratio of 1.5 mol of THPA, 1 mol of MA and 3.15 mol of suitable glycol. All reagents were placed in the three-necked flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer, and heated up to 130-140°C for 2 h. Then, 10 wt % xylene was added and subjected the polycondensation. The condensation water was being removed by simultaneous azeotropic distillation. The process was performed at temperatures not exceeding 180°C, preferably in the temperature range of 150-180°C. The reaction course extent was controlled by determining acid number (defined as a number of mg KOH required for the titration of 1 g of a sample) of the reaction mixture. The drop of an acid number to final value 30 mg KOH/g was an indication of the process completion. Then, solvent xylene was removed by distillation under reduced pressure. The structure of unsaturated polyesters was confirmed by FTIR and ¹H NMR analyses. The prepared unsaturated polyesters were subjected to chemical modification with 38-40% peracetic acid in mild conditions to produce the new materials, which are capable of both copolymerization and polyaddition reactions. The preliminary studies exhibited higher efficiency of the oxidation process in mild time and temperature conditions where the maximum conversion of double bonds in cyclohexenyl rings and minimum influence of side reactions of epoxy groups like hydrolysis or acidolysis have been expected.³¹ Therefore, unsaturated polyester was placed in a three-necked round-bottomed flask equipped with thermometer, reflux condenser, and glass stirrer, dissolved in methylene chloride and heated up to reaction temperature (40°C). After dissolution, peracetic acid was slowly added under vigorous stirring. The oxidation reaction was exothermic, so the mixture had to be cooled down with ice bath to keep up the reaction temperature. After 2 h, the mixture was washed with an 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 . The solvent, methylene chloride, was removed by vacuum distillation. To purify, the residue was diluted with tetrahydrofuran, dried and distilled off under reduced pressure.³¹ The structure of unsaturated epoxy polyesters was confirmed by FTIR and ^1H NMR analyses. Basic properties of unsaturated polyesters and unsaturated epoxy polyesters in the non-cross-linked state, e.g., viscosity (determined by means of a rotating spindle rheometer), density, average molecular weight (determined by osmometric method), and epoxy value (determined by dioxane/HCl titration method) were presented in Tables I and II, respectively.

Curing procedure

All unsaturated polyesters were dissolved in 20 wt % of polymerizable monomer – styrene to obtain styrenated polyesters solutions. Such prepared solutions (resins) are characterized by large content of “dry” mass and low styrene monomer content, which is desirable thing due to the toxicity of styrene solutions of polyesters. Then, 0.5 wt % of benzoyl peroxide (BPO) or the mixture of stoichiometric ratio of tetrahydrophthalic anhydride (THPA) and 0.5 wt % of benzoyl peroxide (BPO) were added to styrene solutions of unsaturated epoxy polyesters. On the contrary, 0.5 wt % of benzoyl peroxide (BPO) were mixed with styrene solutions of unsaturated polyesters. The compositions were mixed and heated up above melting point of hardeners to obtain homogeneous solutions. After deaeration, the compositions were placed in glass mold and the thermal curing was performed at 100–140°C for 10 h, and then postcured at 180°C for 10 h and 200°C for 1 h. Conditions temperatures were appointed from the DSC curves, the position of the exothermic peak was the indication of chosen the postcuring temperatures. The applied curing cycle allowed to total cure of the compositions (no additional exothermic peak was appeared in DSC thermograms) and to obtain stable materials without damage connected with thermal degradation.

TABLE I
Properties of Unsaturated Polyesters before Curing

Properties	Glycol		
	EG	BDO	HDO
Viscosity (mPa s)	3010	1560	150
Density (g/cm ³)	1.14	1.13	1.11
Molecular weight (g/mol)	990	1050	1020

TABLE II
Properties of Unsaturated Epoxy Polyesters before Curing

Properties	Glycol		
	EG	BDO	HDO
Viscosity (mPa s)	3420	1730	240
Density (g/cm ³)	1.16	1.15	1.13
Epoxy value (mol/100 g)	0.27	0.25	0.23
Molecular weight (g/mol)	1040	1100	1050

Characterization

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on 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.

Fourier transform infrared (FTIR) spectra were obtained by using a Perkin–Elmer 1725 X FTIR spectrophotometer in the 400–4000 cm^{-1} wavenumber range using KBr pellets.

The calorimetric measurements of unsaturated polyesters, unsaturated epoxy polyesters, and obtained low styrene content copolymers were performed in the Netzsch DSC 204 calorimeter (Germany) operating in a dynamic mode. The non-isothermal scans were performed at a heating rate of 10 K/min from room temperature to a maximum of 500°C under nitrogen atmosphere (30 mL/min). As a reference an empty aluminum crucible was used. Thermal characteristic: temperature of thermal cross-linking (T_{max}), temperature of thermal degradation (T_d) was done.

Thermogravimetric analysis (TGA) was performed on a MOM 3427 derivatograph Paulik and Erdey (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. $\alpha\text{-Al}_2\text{O}_3$ was used as a reference. The IDT (initial decomposition temperature), the temperature of the maximum rate of weight loss (T_{max}) and final decomposition temperature (T_f) were determined.

DMA measurements were performed using Dynamic Mechanical Analyzer (DMA) Q 800 TA Instruments (USA). Tests were conducted with a double Cantilever device with a support span of 35 mm, calibrated according to the producer's recommendation. Temperature scanning from –135 to 300°C was performed with a constant heating rate of 4°C/min at an oscillation frequency of 10 Hz. The rectangular profiles of the samples was used (35 × 10 × 4 mm). Thermomechanical properties of the cross-linked low styrene content copolymers 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. Glass transition temperature (α relaxation) for obtained copolymers was determined from the dependence of the $\tan\delta$ on temperature and 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) and cross-linking density (ν_e) were determined.

RESULTS AND DISCUSSION

Characterization of unmodified and modified unsaturated polyesters

The unsaturated polyesters obtained in polycondensation of THPA, MA, and only one suitable symmetrical glycol were yellow soft solids or viscous liquids, well soluble in common organic solvents, such as chloroform, methylene chloride, acetone, tetrahydrofuran and after heating in xylene, toluene and insoluble in water, methanol, ethanol. However, the unsaturated epoxy polyesters obtained by chemical modification were light green soft solids or viscous liquids, soluble in chloroform, methylene chloride, acetone, tetrahydrofuran, dioxane, and insoluble in methanol, ethanol, xylene, toluene. As can be seen from Table I, the unsaturated polyesters and the unsaturated epoxy polyesters were characterized by considerably different viscosities depending on the chemical structure. The polyesters obtained from glycols with longer aliphatic chain length (CH_2) were characterized by lower viscosity, which was in accordance reported by other authors.³² The viscosities of the unsaturated epoxy polyesters were a bit higher than those obtained for unsaturated polyesters. Both unsaturated polyesters and unsaturated epoxy polyesters possess hydroxyl, carboxyl and esters groups in polyester chain. The presence of those groups can be the reason of the intermolecular and/or intramolecular interactions. Probably, due to the stronger intermolecular interactions of hydroxyl groups and carboxyl groups with ester groups/carbonyl groups of polyesters prepared from glycols with shorter aliphatic chain, the higher values of viscosity were obtained. In the case of unsaturated epoxy polyesters, the presence of the additional oxygens /epoxy groups/ in polyester backbone resulted stronger intermolecular interactions of epoxy groups with above mentioned groups in polyester and caused their higher viscosity.³³

The structure of unsaturated polyesters and unsaturated epoxy polyesters was confirmed by FTIR and ^1H NMR analyses. The FTIR spectra of unmodified

polyesters and modified polyesters was presented in Figure 1(a,b), respectively. The FTIR spectra of unsaturated polyesters [Fig. 1(a)] showed three characteristic absorption peaks at $662\text{--}664\text{ cm}^{-1}$, $728\text{--}729\text{ cm}^{-1}$, and $775\text{--}778\text{ cm}^{-1}$ related to the C—H out-of-plane deformation vibration and $3029\text{--}3031\text{ cm}^{-1}$ due to the =C—H stretching vibration of cyclohexenyl rings. Moreover, the absorption bands at $960\text{--}990\text{ cm}^{-1}$ were attributed to the trans —CH=CH wagging. The characteristic absorption peaks at $1646\text{--}1648\text{ cm}^{-1}$ were assigned to C=C stretching vibration for carbon-carbon double bonds from MA. Other absorption bands characteristic for polyesters were appeared in the spectrum e.g. at $1728\text{--}1732\text{ cm}^{-1}$ responsible for carbonyl C=O stretching vibrations of ester groups, 748 cm^{-1} skeletal vibration of —CH₂— groups, at $1355\text{--}1440\text{ cm}^{-1}$ attributed to deformation vibration of C—H in esters (sym. and asym.), at $2851\text{--}2954\text{ cm}^{-1}$ due to the C—H stretching of CH₂ groups (sym. and asym.) $1100\text{--}1300\text{ cm}^{-1}$, which were attributed to C—O stretching vibration of esters groups $3445\text{--}3450\text{ cm}^{-1}$ associated with the stretching of —OH groups. After chemical modification of unsaturated polyester's structure with peracetic acid, the considerable differences in FTIR spectra were observed, Figure 1(b). The disappearance of the absorption peaks at $728\text{--}729$, $775\text{--}778\text{ cm}^{-1}$ and $3029\text{--}3031\text{ cm}^{-1}$ and significant decrease of the intensity of the absorption peaks at $662\text{--}664\text{ cm}^{-1}$ characteristic for double bonds in cyclohexenyl rings were observed. The appearance of the new absorption peaks at 787 , $810\text{--}812$, and 867 cm^{-1} characteristic for oxirane ring vibration groups was seen. Moreover, no changes at $960\text{--}990\text{ cm}^{-1}$ and $1646\text{--}1648\text{ cm}^{-1}$ were indicated. It confirmed that oxidation process run inside cyclohexenyl rings, during when carbon-carbon double bonds from MA remained unaltered in polyester backbone.

^1H NMR analysis allowed to additional confirmation that oxidation process of unsaturated polyesters was successful and selective. The fragment of ^1H NMR spectra before and after chemical modification of unsaturated polyester's structure were presented in Figure 2(a,b), respectively. The characteristic chemical shifts for the protons on the double bonds of cyclohexenyl rings at $\delta = 5.67\text{--}5.7\text{ ppm}$ and for the protons on carbon-carbon double bonds from MA at $\delta = 6.29\text{--}6.35\text{ ppm}$ (*cis* form) and $\delta = 6.90\text{--}6.93\text{ ppm}$ (*trans* form) for unsaturated polyesters were indicated. In the spectrum of unsaturated epoxy polyesters, the disappearance of the resonance signals assigned to the double bonds in cyclohexenyl rings were observed. Additionally, the resonance signals attributed to carbon-carbon double bonds (*cis-trans* units) of MA showed no changes. Therefore, it was the complete confirmation that the

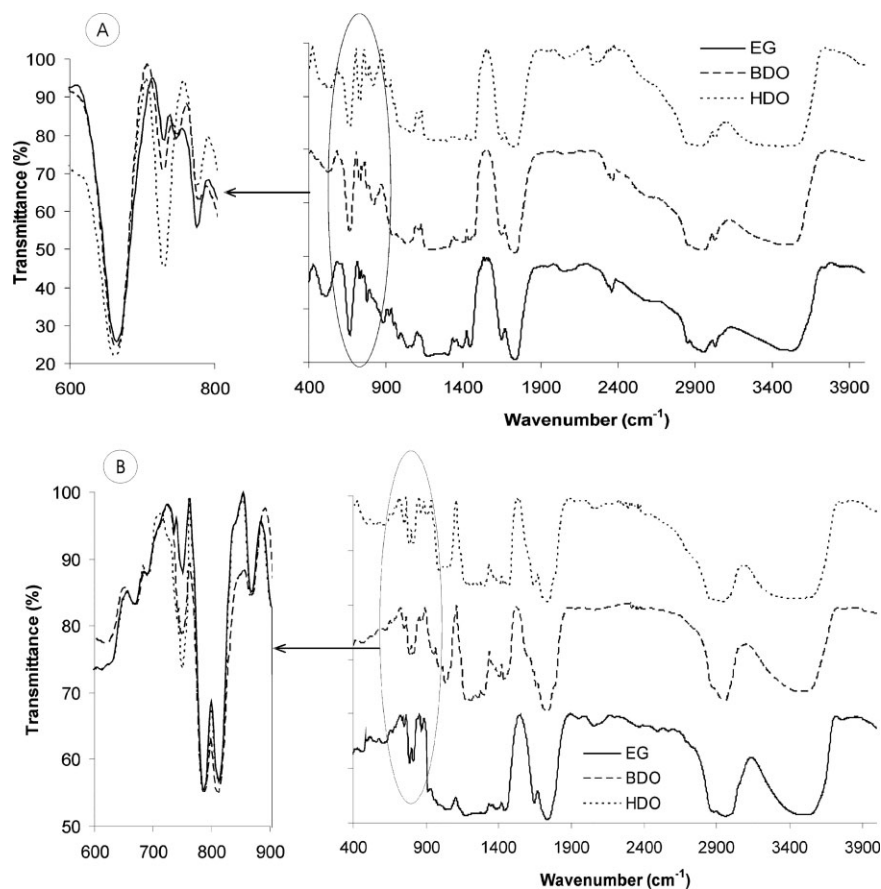


Figure 1 FTIR spectra of unsaturated polyesters (A) and unsaturated epoxy polyesters (B).

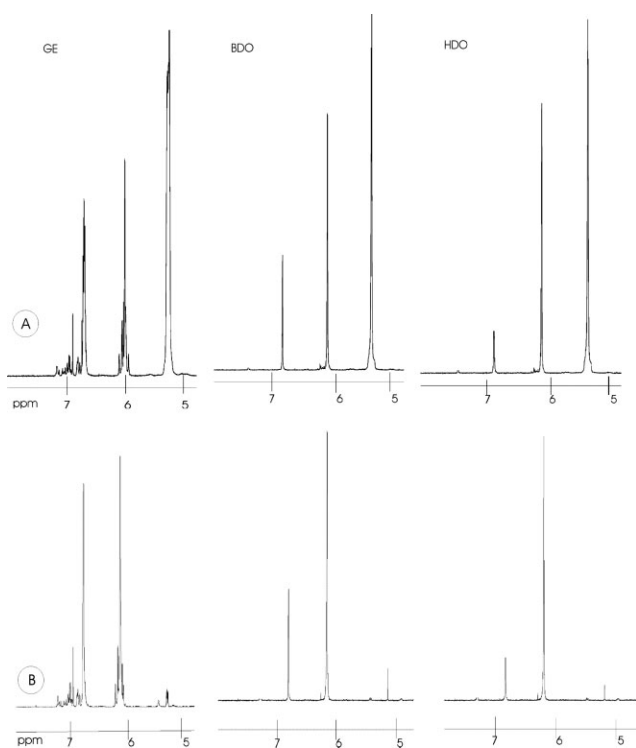


Figure 2 ¹H NMR spectra of unsaturated polyesters (A) and unsaturated epoxy polyesters (B).

chemical modification of unsaturated polyesters was selective and happened inside cyclohexenyl rings. The conversion of double bonds in cyclohexenyl rings calculated from ¹H NMR spectra was in the range 95–98% and was independent of polyester's structure. The used glycol had no influence on the conversion of double bonds during chemical modification. However, the used glycol's type for syntheses of unsaturated polyesters influenced on the degree of isomerization of maleate units to fumarate units. The isomerization of maleate to fumarate forms took place during the polycondensation process and the degree of isomerization depended from reactive environment, acid, glycols, catalyst, etc.^{34,35} The degree of isomerization (ISO%) of unsaturated polyesters was calculated from the following equation: $ISO\% = (\text{trans}/\text{trans}+\text{cis}) \times 100\%$ where *trans* and *cis* were the relative amount of the peak area for maleate and fumarate forms.³⁶ In this case, the ISO% was 52.5% for unsaturated polyester prepared with EG, 27.6% for unsaturated polyester prepared with BDO and 17.4% for unsaturated polyester from HDO. It was distinctly seen that when glycol's chain length increased the degree of isomerization decreased. Those results were in accordance with data reported in literature.³² It has some advantages, if the

unsaturated acid exists in *trans* form its easier to crosslink the prepolymer to form network structure and the cross-linked materials are characterized through better thermomechanical properties.^{32,36}

Additionally performed DSC analysis showed the differences in thermal behavior of the unsaturated polyesters and unsaturated epoxy polyesters. Figure 3 presents the DSC thermograms of unsaturated polyesters prepared with different glycols. The two nondistributed asymmetrical peaks were observed. The exothermic peak at 350–360°C can be attributed to double bonds copolymerization, whereas the endothermic peak at 400–412°C described the thermal degradation (T_d) of polyesters. The used glycol's type for preparation of unsaturated polyesters imperceptibly influenced on observed degradation temperature. The T_d of the unsaturated polyesters increased with the increase of aliphatic chain length in glycols used. The DSC thermograms after chemical modification were presented in Figure 4. It showed significant changes compared with the thermal behavior of unsaturated polyesters. The small exothermic peak at 200–210°C and broad asymmetrical peak at 292–312°C were attributed to the addition reaction of epoxy groups to terminal hydroxyl groups on polyester to form ether linkages and to a thermal cross-linking reaction of epoxide groups with carboxylic acid groups in polyester or formed by the random chain scission.^{37,38} The endothermic peak at 376–406°C demonstrated the thermal degradation process of formed cross-linked polyesters. All the conducted analyses proved that the chemical modification of unsaturated polyester's structure with peracetic acid allowed to obtain unsaturated epoxy polyesters containing both epoxy groups in cycloaliphatic rings and carbon-carbon double bonds in polyester chain. In this way, the materials that capable of both copolymerization and polyaddition reactions were prepared.

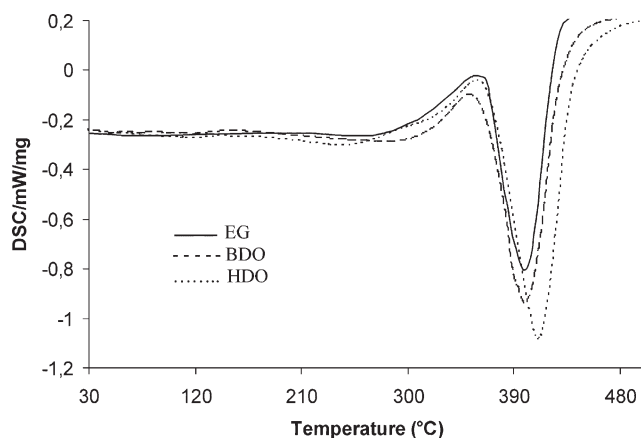


Figure 3 DSC curves of unsaturated polyesters.

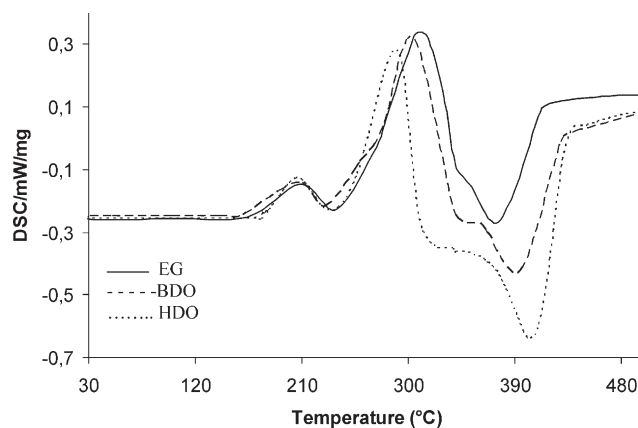


Figure 4 DSC curves of unsaturated epoxy polyesters.

Characterization of cured low styrene content copolymers

The obtained unsaturated epoxy polyesters can be cured by means of different curing agents. The unsaturated epoxy polyesters as was proved contain both epoxy groups in cycloaliphatic rings and carbon-carbon double bonds (*cis-trans* units) in polyester chain. They can be cured via free-radical copolymerization mechanism using organic peroxides and/or via ionic mechanism using both nucleophilic or electrophilic hardeners suitable for epoxy resins like polycarboxylic acid anhydrides, amines, etc.^{39,40} In the current article, all unsaturated epoxy polyesters were dissolved in styrene monomer and were cross-linked using organic peroxide-benzoyl peroxide (BPO) and the mixture of BPO and tetrahydrophthalic anhydride (THPA). Also, the unsaturated polyesters containing carbon-carbon double bonds in polyester backbone were dissolved in styrene monomer and cross-linked using BPO. The thermal and viscoelastic properties of cured low styrene content copolymers obtained from modified and unmodified polyesters were compared. The influence of polyester's structure on thermal and viscoelastic properties of cured low styrene content copolymers was evaluated by means of DSC, TGA, and DMA analyses.

Dynamic mechanical analysis of cured low styrene content copolymers

The viscoelastic properties of fully cured low styrene content copolymers obtained from modified and unmodified polyesters were studied in a wide range of temperatures from -135.0 to 250°C at constant heating rate of 4°C/min. The temperature dependence of the storage modulus (E') and loss factor ($\tan\delta$) for BPO cured low styrene content copolymers obtained from unmodified polyesters was presented in Figure 5. However, the variation of E' and

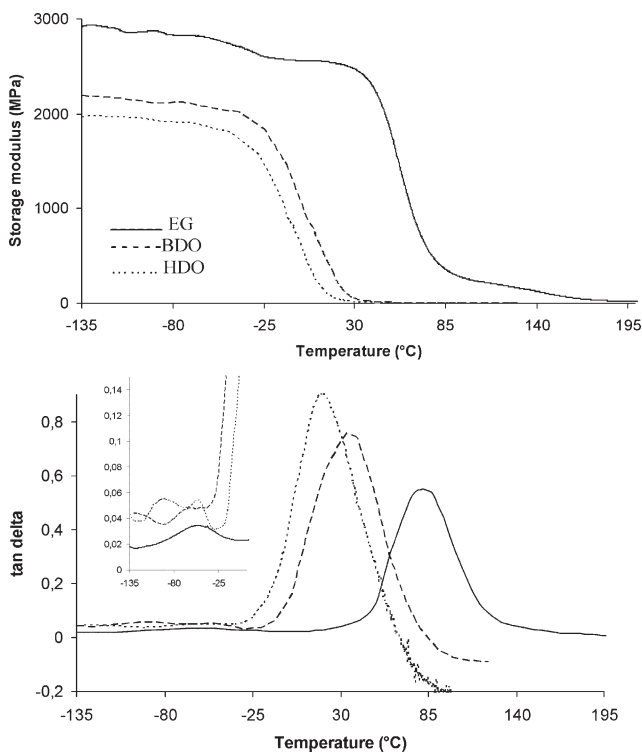


Figure 5 Variation of storage modulus (E') and tan delta ($\tan\delta$) of BPO cured low styrene content copolymers from unsaturated polyesters.

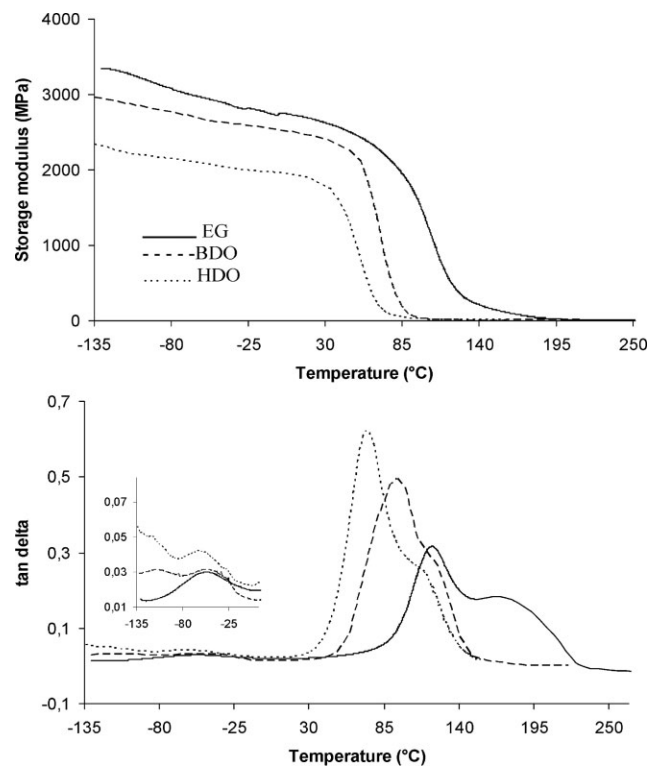


Figure 7 Variation of storage modulus (E') and tan delta ($\tan\delta$) of BPO/THPA-cured low styrene content copolymers from unsaturated epoxy polyesters.

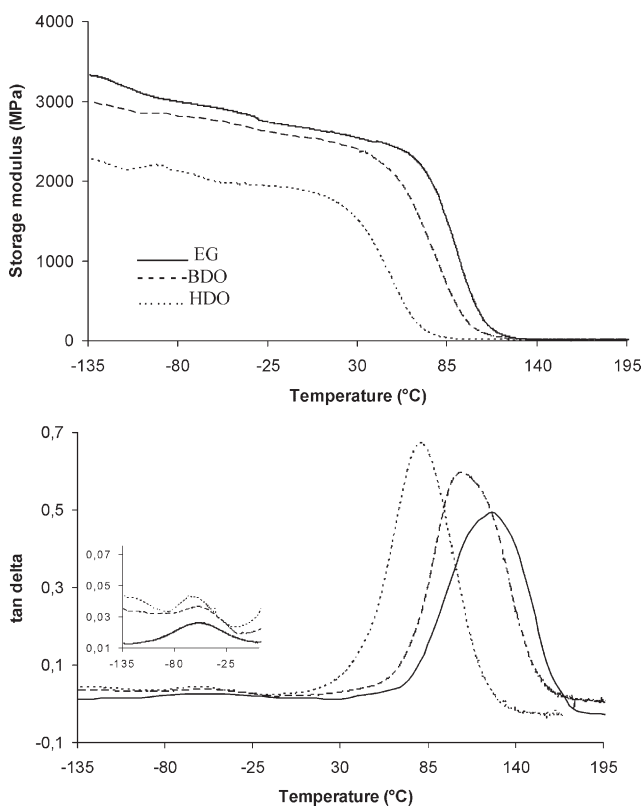


Figure 6 Variation of storage modulus (E') and tan delta ($\tan\delta$) of BPO cured low styrene content copolymers from unsaturated epoxy polyesters.

$\tan\delta$ in the function of temperature for BPO and BPO/THPA-cured low styrene content copolymers prepared from modified polyesters were presented in Figures 6 and 7, respectively. As can be seen from presented curves, the polyester's structure as well as used curing agent had a considerable effect on the stiffness behavior of styrene copolymers. The storage modulus for all styrene copolymers uniformly decreased with the increasing temperature in studied area. The largest changes of E' values between temperatures 0–150°C when the cured materials were transformed from a glassy state to the rubbery state were observed. The highest values of $E'_{20^\circ\text{C}}$ especially for BPO/THPA-cured low styrene content copolymers prepared from unsaturated epoxy polyesters were obtained. It may be due to more cross-linked polymer networks obtained. The both, free-radical copolymerization between carbon-carbon double bonds of unsaturated epoxy polyester and styrene and polyaddition reaction of epoxy groups to anhydride groups were expected. Such copolymers were characterized by higher stiffness compared with copolymers obtained from unsaturated polyesters and styrene where only copolymerization between carbon-carbon double bonds of polyester and styrene was expected. Additionally, the storage modulus of styrene copolymers at room temperature (Tables III–V) decreased with increase

TABLE III
Data Obtained from DMA Curves for BPO-Cured Low Styrene Content Copolymers from Unsaturated Polyesters

Glycol	$E'_{20^{\circ}\text{C}}$ (MPa)	$\text{tg}\delta_{\text{max1}}$	$\text{tg}\delta_{\text{max2}}$	$\text{tg}\delta_{\text{max1}}$ ($^{\circ}\text{C}$)	$\text{tg}\delta_{\text{max2}}$ ($^{\circ}\text{C}$)	E''_{max1} ($^{\circ}\text{C}$)	E''_{max2} ($^{\circ}\text{C}$)	$v_e \cdot 10^{-3}$ (mol/cm ³)	FWHM ($^{\circ}\text{C}$)
Ethylene glycol	2530	0.035	0.538	-53.5	76.6	-53.4	58.5	0.30	43
1,4-Butanediol	194	0.055	0.755	-52.5	33.5	-53.0	10.5	0.24	46
1,6-Hexanediol	37	0.060	0.895	-54.5	18.5	-55.0	-2.0	0.20	45

of glycol's aliphatic chain length in polyesters. Generally, the highest values of $E'_{20^{\circ}\text{C}}$ for styrene copolymers prepared from polyesters containing only $(\text{CH}_2)_2$ units were obtained. From the curves presented, the relaxation behavior ($\text{tan}\delta$) versus temperature, two distinct peaks for low styrene content copolymers were observed. The low temperature peak ($\text{tan}\delta_{\text{max1}}$) usually noted as the secondary β -relaxation appeared centered from -50.5 to -56.0°C . The position of β -relaxation peak was almost independent on the chemical structure of polyesters and used curing agent. This relaxation could be related to the molecular motions of end ester groups in polyesters chain $(-\text{COO}^-(\text{CH}_2)_n-\text{OH})$ and/or to the motions of new diester segments formed between two crosslinks.^{41,42} However, the β -relaxation peak height changed in dependence on the chemical structure of polyesters and hardener's type. The β -relaxation peak height increased with the increase of glycol's chain length applied for polyester's synthesis. The higher molecular mobility of end ester groups in polyester chain were observed when glycol's chain length increased. On the other hand, the only BPO cured styrene copolymers from modified polyesters were characterized through higher $\text{tan}\delta_{\text{max1}}$ values compared with BPO/THPA-cured styrene copolymers. The new diester segments formed between two crosslinks for BPO/THPA-cured styrene copolymers caused the formation of more stiffness network structure and restriction of molecular mobility. The second relaxation peak at higher temperatures generally called the α relaxation was associated with the glass transition temperature (T_g) of obtained copolymers. The position of α -relaxation peak as well as loss modulus (E'') clearly depended on polyester's structure and used curing agent (Tables III-V). All styrene copolymers

obtained from polyesters with longer glycol's chain were characterized through lower values of T_g . The higher values of T_g were obtained for low styrene content copolymers prepared from modified polyesters. Moreover, BPO/THPA-cured styrene copolymers exhibited the transition from the glassy state to the rubbery state at higher temperatures. It can be connected with more cross-linked polymer network structure obtained. Additionally, the molecular mobility of main chains of polyester in BPO/THPA-cured styrene copolymers from modified polyesters was more restricted (lower values of $\text{tan}\delta_{\text{max2}}$) compared with others. This behavior may be connected with larger rigidity of polymer network formed when both copolymerization and polyaddition reactions took place. The BPO cured styrene copolymers from unmodified polyesters exhibited larger values of $\text{tan}\delta_{\text{max2}}$ in relation to BPO cured styrene copolymers from modified polyesters. In both cases, only the copolymerization process between carbon-carbon double bonds on polyester and styrene initiated by BPO was suspected. This was an unusual feature and could be attributed to additional etherification reaction between epoxide groups and initial or reaction formed hydroxyl groups or to esterification process between epoxy groups and carboxyl groups in modified polyesters at higher postcure temperatures.⁴³⁻⁴⁶ So, more cross-linked polymer networks were obtained and lower molecular mobility of ester groups in BPO cured styrene copolymers from modified polyesters had been observed. To confirm those observations, the cross-linking density (v_e) for the obtained networks was calculated (Tables III-V). In this article, the cross-linking density was calculated by applying the equation derived from the theory of rubber elasticity: $E' = 3v_eRT$, where E' is the storage modulus in the rubbery plateau

TABLE IV
Data Obtained from DMA Curves for BPO-Cured Low Styrene Content Copolymers from Unsaturated Epoxy Polyesters

Glycol	$E'_{20^{\circ}\text{C}}$ (MPa)	$\text{tg}\delta_{\text{max1}}$	$\text{tg}\delta_{\text{max2}}$	$\text{tg}\delta_{\text{max1}}$ ($^{\circ}\text{C}$)	$\text{tg}\delta_{\text{max2}}$ ($^{\circ}\text{C}$)	E''_{max1} ($^{\circ}\text{C}$)	E''_{max2} ($^{\circ}\text{C}$)	$v_e \cdot 10^{-3}$ (mol/cm ³)	FWHM ($^{\circ}\text{C}$)
Ethylene glycol	2590	0.026	0.493	-54.5	119.0	-54.5	93.0	0.59	41
1,4-Butanediol	2505	0.037	0.595	-55.5	106.0	-55.5	82.0	0.55	38
1,6-Hexanediol	1695	0.045	0.673	-56.0	80.0	-56.5	50.5	0.50	39

TABLE V
Data Obtained from DMA Curves for BPO/THPA-Cured Low Styrene Content Copolymers from Unsaturated Epoxy Polyesters

Glycol	$E'_{20^\circ\text{C}}$ (MPa)	$\text{tg}\delta_{\text{max1}}$	$\text{tg}\delta_{\text{max2}}$	$\text{tg}\delta_{\text{max1}}$ ($^\circ\text{C}$)	$\text{tg}\delta_{\text{max2}}$ ($^\circ\text{C}$)	E''_{max1} ($^\circ\text{C}$)	E''_{max2} ($^\circ\text{C}$)	$v_e \cdot 10^{-3}$ (mol/cm ³)	FWHM ($^\circ\text{C}$)
Ethylene glycol	2680	0.030	0.317/0.185	-50.5	120.5/170.0	-53.0	108.5	0.97	65
1,4-Butanediol	2560	0.032	0.485	-53.0	93.0	-55.0	73.0	0.84	55
1,6-Hexanediol	1890	0.042	0.623	-54.0	73.0	-55.5	55.0	0.73	53

region, R is a gas constant, and T is the absolute temperature.⁴⁷⁻⁵⁰ Moreover, the molecular weight between cross-links in the polymer network increased when the cross-linking density decreased.⁵¹ As was expected, higher cross-linking density values for BPO/THPA-cured styrene copolymers from modified polyesters were observed. Additional diester segments formed in reaction of epoxy groups with THPA groups reduced the molecular motions and created more stiffness network structure with higher cross-linking density and lower molecular weight between crosslinks. Moreover, the cross-linking density decreased with increase of the aliphatic glycol's chain length in polyesters. The highest v_e values for low styrene content copolymers prepared from polyesters with glycol containing less CH_2 units were obtained. There was clear relationship between cross-linking density and T_g . When the glass transition temperature decreased, the cross-linking density of polymer networks obtained also decreased. The width of the $\text{tan}\delta$ curves was connected with the degree of structural heterogeneity of polymer networks. The broader the $\text{tan}\delta$ peak implied a more heterogeneous polymer network with a wide distribution of relaxation times.⁵²⁻⁵⁵ As can be seen from Tables III-V, more homogeneity networks structure were obtained for BPO-cured copolymers from modified and unmodified polyesters. However, the highest values of the peak width of $\text{tan}\delta$ (FWHM) were observed for BPO/THPA-cured low styrene content copolymers from modified polyesters. Additionally, the α relaxation peak was broader, asymmetrical with two faintly marked maxima, indicating more heterogeneous network structure and testified about structural constitu-

ent in BPO/THPA-cured low styrene content copolymers, Fig. 7.

Thermogravimetric and differential scanning calorimetry analyses

The thermal stability of cured low styrene content copolymers was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA analysis was performed in static air atmosphere in the temperature range of 20-1000 $^\circ\text{C}$ at a heating rate of 10 K/min. The DSC analysis was conducted in inert atmosphere (nitrogen) in the temperature range of 20-500 $^\circ\text{C}$ at a heating rate of 10 K/min. The parameters evaluated from TG, DTG and DSC curves were presented in Tables VI-VIII. Moreover, the exemplary DSC curves of styrene copolymers prepared from polyesters containing EG and cured with different hardeners were given in Figure 8. However, the exemplary TG and DTG thermograms were presented in Figure 9. Based on DSC analysis, the preliminary studies concerning the thermal stability of cured low styrene content copolymers were performed. The single asymmetrical endothermic peak with the maximum at about 400 $^\circ\text{C}$ for all cured copolymers was appeared in DSC curves conducted in inert atmosphere. This peak started at about 330 $^\circ\text{C}$ was associated with the thermal degradation of cured copolymers. Based on DSC analysis, the thermal stability of cured styrene copolymers were comparable. However, the performed thermogravimetric analysis showed the differences in thermal stability of cured styrene copolymers. The TG thermograms indicated that

TABLE VI
Parameters Evaluated from TG, DTG, and DSC Curves for BPO-Cured Low Styrene Content Copolymers from Unsaturated Polyesters

Glycol	IDT ($^\circ\text{C}$)	T_{max1} ($^\circ\text{C}$)	T_{max2} ($^\circ\text{C}$)	T_k ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)
Ethylene glycol	280	380	555	600	400
1,4-Butanediol	260	375	550	600	410
1,6-Hexanediol	250	380	550	590	410

TABLE VII
Parameters Evaluated from TG, DTG, and DSC Curves for BPO Cured Low Styrene Content Copolymers from Unsaturated Epoxy Polyesters

Glycol	IDT ($^\circ\text{C}$)	T_{max1} ($^\circ\text{C}$)	T_{max2} ($^\circ\text{C}$)	T_k ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)
Ethylene glycol	280	370	520	610	400
1,4-Butanediol	275	370	530	600	400
1,6-Hexanediol	270	360	520	600	390

TABLE VIII
Parameters Evaluated from TG, DTG, and DSC Curves for BPO/THPA-Cured Low Styrene Content Copolymers from Unsaturated Epoxy Polyesters

Glycol	IDT (°C)	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	T_k (°C)	T_d (°C)
Ethylene glycol	285	370	520	630	400
1,4-Butanediol	280	365	510	625	400
1,6-Hexanediol	270	370	520	620	405

cured styrene copolymers obtained from unsaturated epoxy polyesters were characterized by higher thermal stability than styrene copolymers prepared from unsaturated polyesters. The initial degradation temperatures (IDT) and final degradation temperatures (T_k) were in the range of 270–285°C and 600–630°, respectively. The IDT and T_k values for all cured styrene copolymers shifted to lower temperatures with increasing the glycol's chain length in polyester. Similarly, BPO/THPA-cured styrene copolymers were characterized by higher thermal stability compared with others. It confirmed that both chemical structure of polyesters and hardener's type influenced on the thermal stability of cured styrene copolymers. The more cross-linked polymer network was obtained for BPO/THPA-cured copolymers containing shorter glycol's chain in polyester. Additionally, the chemical modification of polyesters allowed to obtain cured styrene copolymers with better thermal stability. Moreover, the thermal degradation pattern of all cured low styrene content copolymers exhibited two almost separated degradation steps with two maximum rate peaks in DTG curves, Figure 9. The main maximum decomposition temperature peak ($T_{\max 1}$) observed at 360–380°C could be associated with the ester bonds breakdown

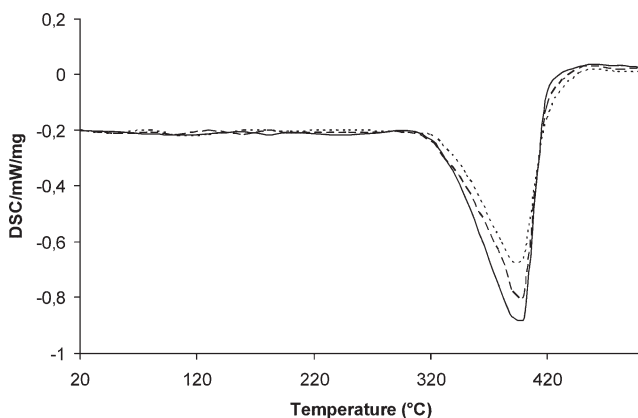


Figure 8 DSC curves of: (·····) BPO-cured copolymer from unsaturated polyester, (---) BPO-cured copolymer from unsaturated epoxy polyester, (—) BPO/THPA-cured copolymer from unsaturated epoxy polyester.

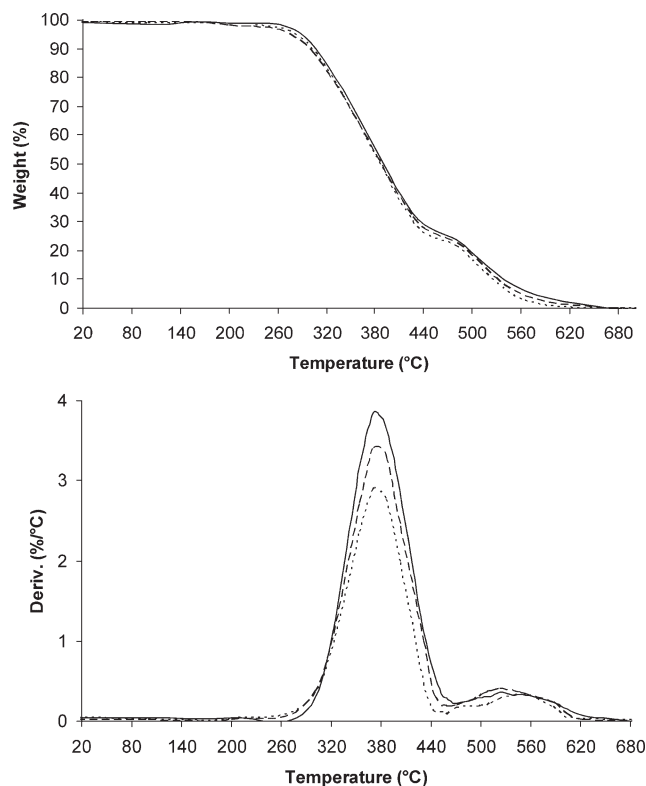


Figure 9 TG and DTG thermograms of: (·····) BPO-cured copolymer from unsaturated polyester, (---) BPO-cured copolymer from unsaturated epoxy polyester, (—) BPO/THPA-cured copolymer from unsaturated epoxy polyester.

in polyesters and/or ester bonds breakdown formed during the epoxy/anhydride polymerization as reported by other authors.^{37,38} The second small degradation peak at 510–555°C could be attributed to the total degradation of low styrene content copolymers.

CONCLUSIONS

In this study, the chemical modification of unsaturated polyesters and the influence of polyester's structure on thermal and viscoelastic properties of low styrene content copolymers were presented. The selective oxidation of unsaturated polyesters obtained in polycondensation of THPA, MA and only one suitable symmetrical glycol: EG or BDO or HDO allowed to introduce epoxy groups in polyester backbone in easy and simple way, as was proved. The unsaturated polyesters containing cyclohexenyl rings and carbon-carbon double bonds in polyester chain were converted into unsaturated epoxy polyesters by peracetic acid in mild time and temperature conditions. The double bonds in cyclohexenyl rings were oxidized, whereas carbon-carbon double bonds in polyester chain were not changed.

The obtained unsaturated epoxy polyesters were capable of both copolymerization and polyaddition reactions with suitable curing agent. As was confirmed by means of DSC, DMA, and TGA analyses, depending on polyester's structure, various thermal and viscoelastic properties of cured low styrene content copolymers were obtained. The properties of BPO cured low styrene content copolymers from unsaturated polyesters differed considerably from BPO-cured low styrene content copolymers from unsaturated epoxy polyesters and were directly connected with polyester's structure. The exchange of double bonds in cyclohexenyl rings on epoxy groups caused higher thermal stability and better viscoelastic properties of BPO cured low styrene content copolymers from modified polyesters. As was proved, BPO cured low styrene content copolymers from modified polyesters were more cross-linked compared with BPO cured low styrene content copolymers from unmodified polyesters. It was due to the presence of epoxy groups in modified polyesters backbone. Therefore, the additional etherification between epoxy groups and hydroxyl groups or esterification between epoxy groups and carboxyl groups in polyesters at higher postcure temperatures were expected. The higher values of cross-linking density, glass transition temperatures, storage modulus as well as larger rigidity of polymer network obtained from unsaturated epoxy polyesters were observed. The BPO/THPA-cured low styrene content copolymers were characterized through the best properties which was due to both copolymerization of carbon-carbon double bonds in polyester chain and vinyl monomer and polyaddition reaction of epoxy groups and anhydride groups to form additional diester segments and more cross-linked polymer networks. Moreover, the studied properties were largely depended on glycol used for polyester's synthesis. The thermal and viscoelastic properties of cured low styrene content copolymers increased with decreasing glycol's chain length in polyesters. The storage modulus, glass transition temperatures, thermal stability as well as cross-linking density for cured low styrene content copolymers increased for polyesters obtained from glycol with shorter aliphatic chain.

Recapitulating, based on conducted analyses, the correlation between the polyester's structure and the resulting thermal and viscoelastic properties of cured low styrene content copolymers were found. Moreover, it was shown, that selective oxidation of studied unsaturated polyesters was successful and effective method which allowed to modify their structure. The prepared unsaturated epoxy polyesters were successfully used as a component of low styrene content copolymers. They considerably improved the thermal and viscoelastic properties of

cured copolymers compared with copolymers obtained from unsaturated polyesters.

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