

THE INFLUENCE OF CHEMICAL MODIFICATION OF UNSATURATED POLYESTERS ON VISCOELASTIC PROPERTIES AND THERMAL BEHAVIOR OF STYRENE COPOLYMERS

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The influence of chemical modification of unsaturated polyesters on viscoelastic properties and thermal behavior of styrene copolymers has been investigated by DMA and TG analyses. Chemical modification of unsaturated polyesters obtained in polycondensation of cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA) and suitable glycol: diethylene glycol (DEG) or triethylene glycol (TEG) was performed using 38–40% peracetic acid. It allowed to selective and successful oxidation of carbon-carbon double bonds in unsaturated polyesters giving modified unsaturated polyesters/unsaturated epoxyesters/containing both carbon-carbon double bonds in polyester chain and new functional groups-epoxy groups in cycloaliphatic rings. Both unsaturated polyesters and unsaturated epoxyesters were used as a component of styrene copolymers cured with different hardeners. It has been demonstrated that the use of modified unsaturated polyesters as a component of styrene copolymers allowed obtaining more stiffness and more cross-linked network structure compared to styrene copolymers based on unmodified polyesters. The higher values of storage modulus, glass transition temperatures and better thermal stability for styrene copolymers based on unsaturated epoxyesters were obtained.

Keywords: DMA, TG, unsaturated epoxyesters, unsaturated polyesters

Introduction

Chemical modification of polymeric materials allows the introduction of modifying monomers to synthesis of unsaturated polyesters or replace carbon-carbon double bonds in polyester backbone with epoxy, hydroxyl or carboxyl groups [1–5]. The literature describes many methods for chemical modification of polymeric materials. One of those is catalytic or non-catalytic epoxidation of polymers having a carbon-carbon double bonds. It allows the introduction of epoxy functionality into polymer backbone. Hydrogen peroxide, iodobenzene, sodium hypochlorite or *tert*-butyl hydroperoxide are usually used in catalytic reactions. However, organic peroxy acids generated separately or peroxy acids formed in situ during addition of hydrogen peroxide to an organic acid are the oxidant agents for non-catalytic reactions [6–8]. Oxidation of unsaturated polyesters to the corresponding epoxide derivatives containing a large number of epoxide groups offered considerable interest. The multifunctional epoxy-polyester resins can be obtained by epoxidation of polyesters having pendent allyl groups prepared from succinic anhydride and allyl glycidyl ether by *m*-chloroperbenzoic acid [9, 10]. 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 permitted to modify the polyesters structure and synthesize molecules containing several epoxide groups (polyepoxides) [11, 12]. The preparation of solid epoxidized polyesters obtained from tetrahydrophthalic anhydride, glycols, dicyclopentadiene and alternatively saturated polycarboxylic acids with peracetic or performic acids is reported [13–16]. Also, the aliphatic-cycloaliphatic epoxy compounds contain different epoxy groups: 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 known [17].

In the present study, the influence of chemical modification of unsaturated polyesters on viscoelastic properties and thermal behavior of styrene copolymers has been presented. The unsaturated polyesters obtained in polycondensation of cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride and suitable glycol: diethylene glycol or triethylene glycol were oxidized by 38–40% peracetic acid at 40°C during 2 h. It allowed to selective and successful oxidation giving modified unsaturated polyesters containing both epoxy groups in cycloaliphatic rings and unchanged carbon-carbon double bonds in polyester chain, which was confirmed by FTIR, ¹H NMR analyses. Thermal behavior of unsaturated polyesters and

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unsaturated epoxypolyesters has been studied by means of DSC analysis. The viscolstic properties and thermal behavior of styrene copolymers obtained from unmodified and modified unsaturated polyesters have been investigated by DMA and TG analyses. For the applications of these materials to be successful, the knowledge of their properties is required.

Experimental

Materials

Unsaturated polyesters were obtained from cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA, Merck-Schuchardt, Germany), maleic anhydride (MA, Merck-Schuchardt, Germany) and suitable glycol: diethylene glycol (DEG, Fluka, Switzeland) or triethylene glycol (TEG, Fluka, Switzerland) according to procedure described in [18]. The polycondensation was carried out at the ratio of 1.5 mol of THPA, 1 mol of MA and 3.15 mol of suitable glycol. Basic properties of unsaturated polyesters were presented in Table 1.

Hexahydrophthalic anhydride (HHPA), 38–40% peracetic acid, methylene chloride, tetrahydrofuran were purchased from Merck-Schuchardt (Germany). Other reagents such as sodium carbonate, sodium hydroxide, sodium chloride and magnesium sulphate were delivered by Polish Chemical Reagents-POCH (Gliwice, Poland). All reagents were used as received.

Chemical modification of unsaturated polyesters

Unsaturated polyesters based on DEG or TEG were subjected to chemical modification with 38–40% peracetic acid to produce modified unsaturated polyesters (unsaturated epoxypolyesters) which were able to both polyaddition and polymerization reactions. The preliminary studies exhibited higher efficiency of the oxidation process in mild conditions where the maximum conversion of double bonds in cyclohexenyl rings and minimum influence of side reactions of epoxy groups like hydrolysis have been ex-

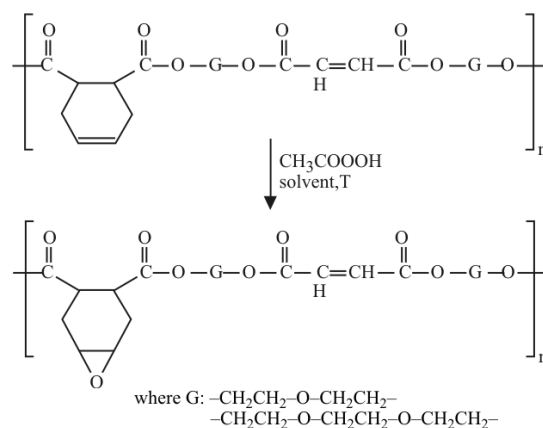


Fig. 1 The theoretical structure of unsaturated polyesters and unsaturated epoxypolyesters

pected [18]. Therefore, chemical oxidation of unsaturated polyesters was performed at 40°C during 2 h. First, they were dissolved in methylene chloride and heated up to reaction temperature. Then, peracetic acid was slowly added under vigorous stirring. After predetermined time, reaction mixture was washed with an aqueous solution of sodium carbonate and sodium hydroxide saturated with sodium chloride to neutrality. The mixture was placed in the separator and organic phase was thoroughly washed two times with aqueous solution of sodium hydroxide and distilled water, dried over anhydrous MgSO_4 . The solvent was removed by vacuum distillation. To purify, the residue was diluted with tetrahydrofuran, dried and distilled off under reduced pressure [19]. The theoretical structure of unsaturated polyesters and unsaturated epoxypolyesters based on DEG or TEG is presented in Fig. 1.

Curing procedure

Unsaturated polyesters and modified unsaturated polyesters were dissolved in 20 mass% of styrene monomer to obtain styrenated polyesters solutions containing large content of ‘dry’ mass and low styrene monomer content. It was desirable thing due to the toxicity of styrene solutions of polyesters. Then,

Table 1 Basic properties of unsaturated polyesters (UP) and unsaturated epoxypolyesters (UEP) before curing

Properties	Polyesters			
	GDE		TGE	
	UP	UEP	UP	UEP
Viscosity/mPa s	240	730	175	620
Density/g cm ⁻³	1.12	1.14	1.12	1.13
Epoxy value/mol/100 g	–	0.23	–	0.21
Mñ/g mol ⁻¹	1180	1220	1260	1310

GDE – diethylene glycol, TGE – triethylene glycol

0.5 mass% of benzoyl peroxide (BPO) or the mixture of stoichiometric ratio of suitable acid anhydride (THPA or HHPA or MA) and 0.5 mass% of BPO were added to styrene solutions of unsaturated epoxypolyesters. On the contrary, 0.5 mass% of BPO were mixed with styrene solutions of unsaturated polyesters. The compositions were mixed and heated up above melting point of the hardeners to obtain homogeneous solutions. Thermal curing was carried out at 100–140°C for 10 h, and then post-cured at 180°C for 10 h and 200°C for 1 h. Condition temperatures were determined from the DSC curves, the position of the exothermic peaks was indicative of the post-curing temperatures. The applied curing cycle allowed obtaining fully cured copolymers (no additional exothermic peak was appeared in DSC curves).

Methods

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

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.

Viscosity (mPa s) was measured by means of a rotating spindle rheometer (Brookfield, model DV-III).

Epoxy value (mol/100 g) was determined by dioxane/HCl titration method.

Average molecular mass M_n (g mol^{-1}) was determined by osmometric method (osmometer KNAUER GmbH, Germany).

Density (g cm^{-3}) was evaluated by means of a glass pycnometer with capillary fuse Gay/Lussaca (25 mL).

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Germany) operating in a dynamic mode. The dynamic scans were performed at a heating rate of 10 K min^{-1} from room temperature to a maximum of 500°C under nitrogen atmosphere (30 mL min^{-1}). The mass of the sample was ~10 mg. As a reference an empty aluminum crucible was used.

Thermogravimetric analysis (TG) of cured styrene copolymers was carried out on a MOM 3427 derivatograph Paulik and Erdey (Hungary) at a heating rate of 10°C min^{-1} in air, in the temperature range of 20 to 1000°C with the sample mass of 100 mg. As a reference $\alpha\text{-Al}_2\text{O}_3$ was used. The initial decomposition temperature (IDT), $T_{10\%}$, $T_{20\%}$, $T_{50\%}$ of mass loss, final decomposition temperature (T_k) and temperature of the maximum rate of mass loss (T_{max}) were determined.

DMA measurements were performed using Dynamic Mechanical Analyzer Q 800 from TA Instruments (USA). Tests were conducted using a dual Cantilever clamp with a support span of 35 mm, calibrated according to the producer's recommendation. Analysis was performed from -135 to 250°C with a heating rate of 4°C min^{-1} at an oscillation frequency of 10 Hz. A rectangular specimen was used (35×10×4 mm). The mechanical properties of the cured styrene copolymers were estimated from the changes of storage modulus (E') and mechanical loss (E'') as well as from the changes of $\tan\delta$ at constant frequency depending on temperature. The glass transition temperature (α -relaxation) for the copolymers were determined from the dependence of the $\tan\delta$ on temperature and was identified as the maximum of the $\tan\delta$. Also, from the $\tan\delta$ curves the full-width-at-half-maximum (FWHM) values were determined.

Results and discussion

Characterization of unsaturated polyesters before and after chemical modification

The structure of unsaturated polyesters before and after chemical modification was confirmed by FTIR, ^1H NMR analyses. Thermal behavior of unsaturated polyesters and unsaturated epoxypolyesters has been studied by means of DSC analysis. Additionally, basic properties of polyesters before curing were presented in Table 1. The exemplary IR spectra of unsaturated polyester and unsaturated epoxypolyester is shown in Fig. 2. The total disappearance of the characteristic absorption bands at 664, 728 and 777 cm^{-1} (C–H out-of-plane deformation vibration) related to double bonds in cyclohexenyl rings and appearance of the new absorption peaks at 787, 806 and 876 cm^{-1} characteristic for oxirane ring vibration groups were observed. Additionally, no changes at 960–990 cm^{-1} (–CH=CH wagging from maleic anhydride) and

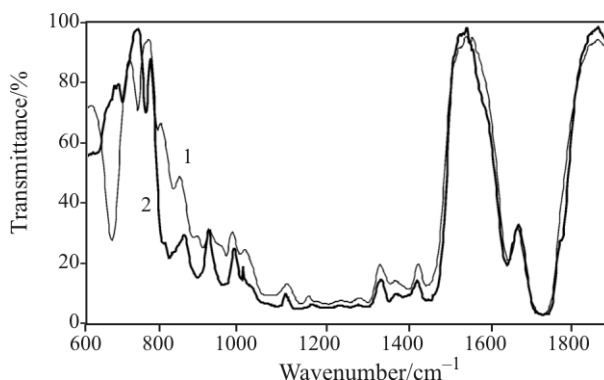


Fig. 2 FTIR spectra of 1 – unsaturated polyester and 2 – unsaturated epoxypolyester

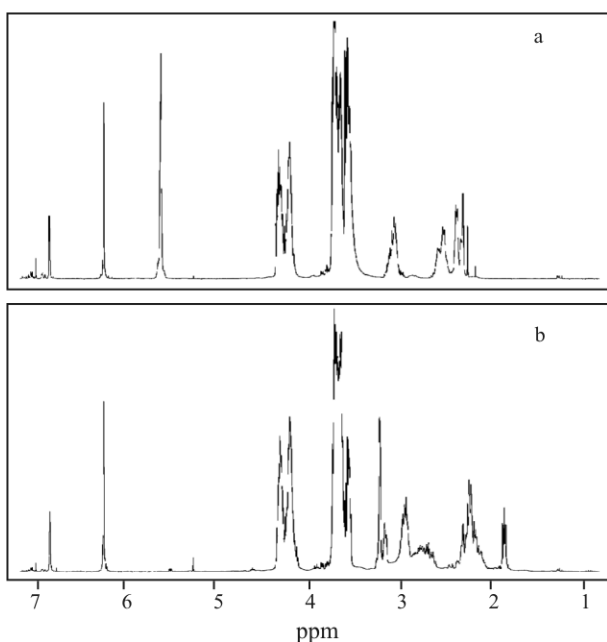


Fig. 3 ^1H NMR spectra of a – unsaturated polyester and b – unsaturated epoxy polyester

1646–1648 cm^{-1} ($\text{C}=\text{C}$ stretching vibration for carbon–carbon double bonds from maleic anhydride) were observed. Moreover, from ^1H NMR spectra the disappearance of the resonance signals assigned to double bonds in cyclohexenyl rings ($\delta=5.67\text{--}5.7$ ppm) were observed. The resonance signals attributed to carbon–carbon double bonds (*cis-trans* units) of maleic anhydride ($\delta=6.29\text{--}6.35$ ppm *cis*-form and $\delta=6.90\text{--}6.93$ ppm *trans*-form) showed no significant changes, Fig. 3. It confirmed that the oxidation process was successful selective and took place inside cyclohexenyl rings.

DSC analysis showed the differences in thermal behavior of unsaturated polyesters and unsaturated epoxy polyesters, Fig. 4. DSC curves of unsaturated polyesters showed two asymmetrical peaks. The exothermic peak at 360°C was attributed to carbon–carbon double bonds copolymerization whereas the en-

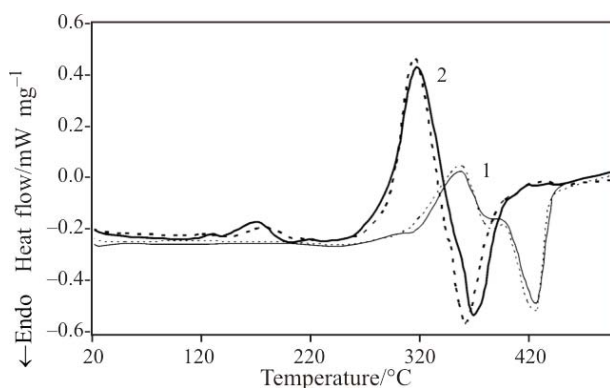


Fig. 4 DSC curves of 1 – unsaturated polyesters and 2 – unsaturated epoxy polyesters

dothermic peak at 429°C described the thermal degradation of polyesters. On the other hand, from DSC curves of unsaturated epoxy polyesters, the small exothermic peak at $176\text{--}188^\circ\text{C}$ and broad asymmetrical peak at $318\text{--}320^\circ\text{C}$ were attributed to the 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 [20–22]. The endothermic peak at $360\text{--}370^\circ\text{C}$ demonstrated the degradation process of thermally cured polyesters.

Based on performed analyses, it was confirmed that chemical modification of unsaturated polyesters obtained from THPA, MA and DEG or TEG with peracetic acid allowed to prepare unsaturated epoxy polyesters containing epoxy groups in cycloaliphatic rings and carbon–carbon double bonds in polyester chain which can be able to both copolymerization with vinyl monomer (styrene) initiated with benzoyl peroxide (BPO) and polyaddition reaction of epoxy groups to anhydride groups (THPA, HHPA, MA).

Viscoelastic properties of styrene copolymers

The viscoelastic properties of styrene copolymers obtained from unmodified and modified polyesters were measured in a wide range of temperatures (from -135 to 250°C). The data obtained from DMA curves for copolymers prepared from styrene and polyesters based on DEG and TEG cured with different hardeners were presented in Tables 2 and 3, respectively. The BPO cured styrene copolymers based on unmodified polyesters were characterized by significantly lower values of storage modulus ($E'_{20^\circ\text{C}}$) compared to BPO cured styrene copolymers based on modified polyesters. Unsaturated polyesters containing polymerizable units: carbon–carbon double bonds in polyester chain from maleic anhydride were only able to copolymerize with the double bonds of styrene. In the case of unsaturated epoxy polyesters containing both carbon–carbon double bonds in polyester chain and epoxy groups in cycloaliphatic rings, copolymerization with styrene and thermal curing between epoxide groups and initial or reaction formed hydroxyl groups or carboxyl groups in modified polyesters at higher post-cure temperatures should be taken into consideration [23–26]. So, more stiff structure of BPO cured styrene copolymers based on modified polyesters were produced. The highest values of storage modulus for BPO/acid anhydride cured styrene copolymers based on modified polyesters were obtained. It was due to the both copolymerization and additional polyaddition reaction of epoxy groups to

anhydride groups [1]. The additionally formed diester linkages caused to produce a more stiff network of copolymers. Moreover, considerably higher values of $E'_{20^\circ\text{C}}$ for styrene copolymers from polyesters based on DEG compared to styrene copolymers from polyesters based on TEG were obtained.

The position of α -relaxation peak ($\tan\delta$) as well as loss modulus (E'') clearly depended on polyester's structure and used curing agent, as noted in Tables 2 and 3. The BPO cured styrene copolymers based on modified polyesters were characterized by significantly higher values of $\tan\delta$ and E'' compared to BPO cured copolymers from unmodified polyesters. Moreover, BPO/acid anhydride cured styrene copolymers exhibited the transition from the glassy state to the rubbery state at higher temperatures compared to others. The α -relaxation peak height associated with molecular mobility, decreased for styrene copolymers prepared from unsaturated epoxy polyesters. The molecular mobility of those copolymers was more restricted, lower values of $\tan\delta_{\text{max}}$ were obtained. This behavior was connected with larger rigidity of polymer network formed when unsaturated epoxy polyesters were used as a component of styrene copolymers. From the curves presented the dependence of loss modulus (E'') vs. temperature for styrene copolymers, Fig. 5, the asymmetrical peak at lower temperatures usually noted as the secondary β -relaxation [27], from -100 to -10°C was observed. Similarly, the small asymmetrical peak at lower temperatures (ca. -60°C) from the curves presented the dependence of relaxation behavior ($\tan\delta$) vs. temperature was indicated, Fig. 6. It could be associated with the molec-

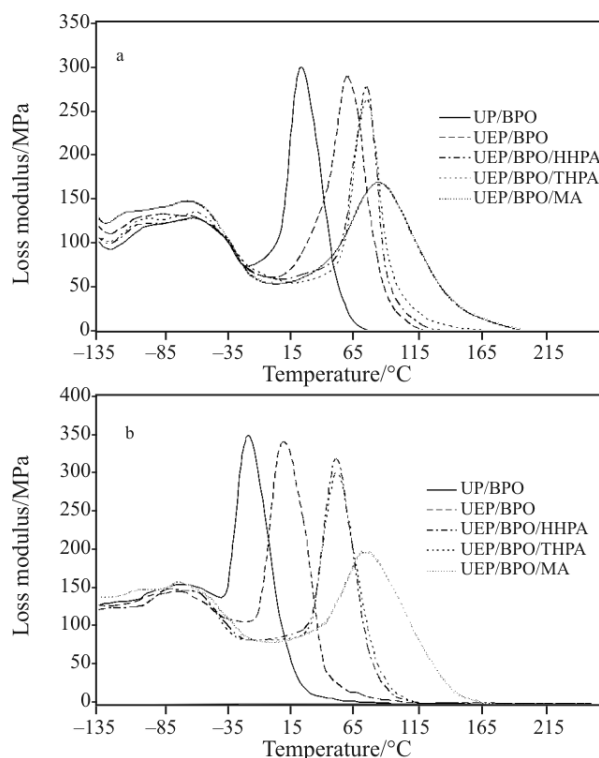


Fig. 5 Loss modulus (E'') vs. temperature curves for styrene copolymers

ular motions of end groups in polyester chain ($-\text{G}-\text{OH}$) and/or to the motions of diester segments formed between two cross-links [28, 29]. Additionally, the second transition peak – the α -relaxation peak was broader, asymmetrical with two faintly marked maxima for styrene copolymers based on modified polyesters. The width of the $\tan\delta$ curves was

Table 2 Data obtained from DMA curves of styrene copolymers based on unsaturated polyesters from diethylene glycol (DGE)

Formulation	$E'_{20^\circ\text{C}}/\text{MPa}$	$\text{tg}\delta_{\text{max}}$	$\text{tg}\delta_{\text{max}}/^\circ\text{C}$	$E''/^\circ\text{C}$	FWHM/ $^\circ\text{C}$
UP/BPO	1110	0.789	44	24	32
UEP/BPO	2290	0.609	80	59	66
UEP/BPO/HHPA	2350	0.427	98	74	80
UEP/BPO/THPA	2430	0.405	109	76	82
UEP/BPO/MA	2500	0.257	118	85	110

UP – unsaturated polyester, UEP – unsaturated epoxy polyester, BPO – benzoyl peroxide, THPA – tetrahydrophthalic anhydride, HHPA – hexahydrophthalic anhydride, MA – maleic anhydride

Table 3 Data obtained from DMA curves of styrene copolymers based on unsaturated polyesters from triethylene glycol (TGE)

Formulation	$E'_{20^\circ\text{C}}/\text{MPa}$	$\text{tg}\delta_{\text{max}}$	$\text{tg}\delta_{\text{max}}/^\circ\text{C}$	$E''/^\circ\text{C}$	FWHM/ $^\circ\text{C}$
UP/BPO	510	0.928	19	-18	28
UEP/BPO	1110	0.789	55	7	63
UEP/BPO/HHPA	1560	0.546	63	48	76
UEP/BPO/THPA	1790	0.504	65	50	78
UEP/BPO/MA	2180	0.366	85	74	100

UP – unsaturated polyester, UEP – unsaturated epoxy polyester, BPO – benzoyl peroxide, THPA – tetrahydrophthalic anhydride, HHPA – hexahydrophthalic anhydride, MA – maleic anhydride

connected with the degree of structural heterogeneity of polymer networks. The broader the $\tan\delta$ peak implied a more heterogeneous polymer network with a wide distribution of relaxation times [30–33]. More homogeneous network structures were obtained for BPO cured copolymers based on unmodified poly-

esters, the lowest values of the peak width of $\tan\delta$ (FWHM) were observed. The heterogeneity of the polymer networks considerably increased when unsaturated epoxyesters were used as a component of styrene copolymers. Moreover, asymmetrical peak with two faintly marked maxima could testify about phase's separation (structural constituent) in cured styrene copolymers from modified polyesters.

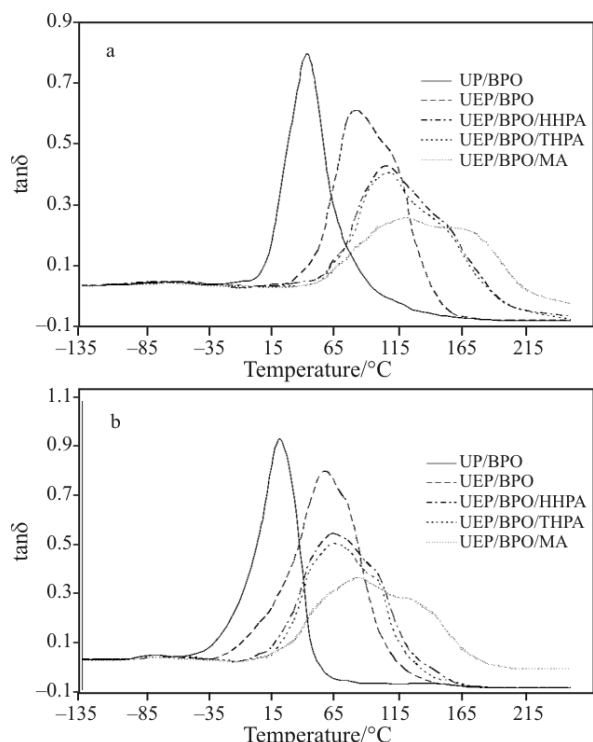


Fig. 6 Tangent δ ($\tan\delta$) vs. temperature curves for styrene copolymers

Thermal behavior of styrene copolymers

Thermogravimetric analysis (TG) showed the differences in thermal behavior of cured styrene copolymers. The TG curves indicated that cured styrene copolymers based on unsaturated epoxyesters were characterized by higher thermal stability than styrene copolymers based on unsaturated polyesters, as seen in Tables 4 and 5. Moreover, BPO/acid anhydride cured styrene copolymers were characterized by higher values of IDT, $T_{10\%}$, $T_{20\%}$ and T_k compared to others. It definitely confirmed, that both chemical structure of polyesters and hardener's type influenced the thermal stability of cured styrene copolymers. The chemical modification of polyesters allowed obtaining styrene copolymers which were characterized by better thermal stability. The more cross-linked polymer network was obtained for BPO/acid anhydride cured copolymers containing shorter glycol's chain in polyester. Moreover, the thermal degradation pattern [34] of all copolymers exhibited two almost separated degradation steps with two maximum rate peaks in DTG curves, as noted in Tables 4, 5. The main maxi-

Table 4 Data obtained from TG and DTG curves of styrene copolymers based on unsaturated polyesters from diethylene glycol (DGE)

Formulation	IDT/°C	$T_{10\%}$ /°C	$T_{20\%}$ /°C	$T_{50\%}$ /°C	T_k /°C	T_{max1} /°C	T_{max2} /°C
UP/BPO	260	290	320	375	600	370	565
UEP/BPO	270	310	330	375	610	365	565
UEP/BPO/HHPA	275	305	335	370	610	370	565
UEP/BPO/THPA	280	310	340	370	630	370	565
UEP/BPO/MA	280	315	340	370	620	365	560

UP – unsaturated polyester, UEP – unsaturated epoxyester, BPO – benzoyl peroxide, THPA – tetrahydrophthalic anhydride, HHPA – hexahydrophthalic anhydride, MA – maleic anhydride

Table 5 Data obtained from TG and DTG curves of styrene copolymers based on unsaturated polyesters from triethylene glycol (TGE)

Formulation	IDT/°C	$T_{10\%}$ /°C	$T_{20\%}$ /°C	$T_{50\%}$ /°C	T_k /°C	T_{max1} /°C	T_{max2} /°C
UP/BPO	230	260	300	370	570	375	560
UEP/BPO	245	290	300	360	590	370	555
UEP/BPO/HHPA	260	280	300	365	600	370	555
UEP/BPO/THPA	265	290	320	370	610	370	550
UEP/BPO/MA	265	280	310	375	615	365	550

UP – unsaturated polyester, UEP – unsaturated epoxyester, BPO – benzoyl peroxide, THPA – tetrahydrophthalic anhydride, HHPA – hexahydrophthalic anhydride, MA – maleic anhydride

imum decomposition temperature peak ($T_{\max 1}$) observed at 360–375°C could be associated with ester bonds breakdown in polyester and/or ester bonds breakdown formed during the polyaddition of epoxy to anhydride groups as reported by other authors [20, 21]. The second degradation peak ($T_{\max 2}$) at 550–565°C was associated with the total degradation of styrene copolymers.

Conclusions

Chemical modification of unsaturated polyesters obtained in polycondensation of cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA) and suitable glycol: diethylene glycol (DEG) or triethylene glycol (TEG) had considerably influence on viscoelastic properties and thermal behavior of styrene copolymers. Selective oxidation of unsaturated polyesters with 38–40% peracetic in mild conditions allowed to obtain unsaturated epoxy polyesters containing epoxy groups in cycloaliphatic rings and unchanged carbon-carbon double bonds in polyester chain. The viscoelastic properties and thermal behavior of styrene copolymers based on unmodified and modified unsaturated polyesters were studied by DMA and TG analyses. It was found, that styrene copolymers based on modified unsaturated polyesters were characterized by significantly higher values of storage modulus ($E'_{20^\circ\text{C}}$), loss modulus (E''), $\tan\delta$ and better thermal stability compared to styrene copolymers based on unmodified unsaturated polyesters. It was connected with different polyester's structure. The unsaturated polyesters containing polymerizable units: carbon-carbon double bonds from maleic anhydride were able to copolymerization reaction with vinyl monomer-styrene. However, copolymerization of carbon-carbon double bonds in polyester with styrene, thermal cross-linking reaction of epoxy groups with carboxyl or hydroxyl groups in polyester at higher post-cure temperature and polyaddition reactions of epoxy groups to anhydride groups for styrene copolymers based on unsaturated epoxy polyesters should be taken into consideration. In this way, the more cross-linked and stiff network of copolymers based on unsaturated epoxy polyesters was produced.

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Received: December 7, 2008

Accepted: December 17, 2008

DOI: 10.1007/s10973-008-9852-y