

Succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters

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Abstract The influence of the structure of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters on the course of the cure reaction with styrene initiated by benzoyl peroxide (BPO) or the mixture of benzoyl peroxide/tetrahydrophthalic anhydride (BPO/THPA) or benzoyl peroxide/maleic anhydride, as well as viscoelastic properties and thermal behavior of their styrene copolymers have been studied by DSC, DMA, and TGA analyses. Additionally, mechanical properties: flexural properties using three-point bending test and Brinell's hardness for studied copolymers were evaluated. It was confirmed that the structure of used polyesters had a considerable influence on the course of the cure reaction with styrene, viscoelastic, thermal, and mechanical properties of prepared styrene copolymers. Generally, one or two asymmetrical peaks for the cure reaction of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters with styrene were observed. They were connected with various cure reaction, e.g., copolymerization of carbon–carbon double bonds of polyester with styrene, thermal curing of epoxy groups, polyaddition reaction of epoxy to anhydride groups in dependence of used curing system. In addition, only one asymmetrical, exothermic peak attributed to the copolymerization process of succinic or glutaric anhydride modified linear unsaturated polyesters with styrene was visible. Moreover, the obtained styrene copolymers based on succinic or glutaric anhydride modified linear unsaturated epoxy polyesters were characterized by higher values of $E'_{20^\circ\text{C}}$, T_g , E'' , ν_e , E_{mod} , F_{max} , hardness, IDT, FDT but lower $\varepsilon - F_{\text{max}}$ compared to those

values observed for styrene copolymers prepared in the presence of succinic or glutaric anhydride modified linear unsaturated polyesters. This supported to the production of stiffer and more thermally stable polymeric structure of copolymers based on unsaturated epoxy polyesters. Moreover, the copolymers prepared in the use of glutaric anhydride modified linear unsaturated (epoxy) polyesters were described by lower values of $E'_{20^\circ\text{C}}$, T_g , E'' , ν_e , E_{mod} , F_{max} , hardness, IDT, FDT but higher $\varepsilon - F_{\text{max}}$ than those based on succinic anhydride modified linear unsaturated (epoxy) polyesters. The presence of longer aliphatic chain length in polyester's structure leads to produce more flexible network structure of styrene copolymers based on glutaric anhydride modified linear unsaturated (epoxy) polyesters than those based on succinic anhydride modified linear unsaturated (epoxy) polyesters.

Keywords Unsaturated polyesters · Thermal properties · Viscoelastic properties · Mechanical properties · Curing of polymers

Introduction

Chemical modification of the unsaturated polyesters allows preparation of the new materials with entirely different properties and potential industrial applications [1–4]. Recently, the epoxide derivatives of unsaturated polyesters containing a large number of epoxy groups are intensively studied [5–13]. The unsaturated polyesters are usually prepared by polyesterification process of linear or branched dihydroxyl compounds with unsaturated, polymerizable dicarboxylic acids or acid anhydrides and/or with the addition of saturated, non-polymerizable dicarboxylic acids or acid anhydrides under elevated temperature [14–19].

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The suitable selection of the individual components allows preparation of the polyesters designed for their specific cost and performance purposes. The polycondensation process of two acid anhydrides: one saturated, non-polymerizable acid anhydride: cyclohex-4-ene-1,2-dicarboxylic anhydride and other unsaturated, polymerizable acid anhydride: maleic anhydride and only one suitable linear dihydroxy compound leads to prepare the unsaturated polyesters suitable for further chemical modification with peracetic acid. The selective oxidation of the unsaturated polyesters to the corresponding epoxide derivatives containing both epoxy groups and carbon-carbon double bonds in their backbone offers considerable interest. The new materials (unsaturated epoxy polyesters) due to the presence of epoxy groups in cycloaliphatic rings and carbon-carbon double bonds in polyester chains are susceptible to both polyaddition and copolymerization reactions with vinyl monomer in the presence of suitable curing agent [20–23]. Moreover, their basic skeletal structure can be additionally modified by other reagents. The use of additional saturated, non-polymerizable acid anhydrides: cycloaliphatic acid anhydride, e.g., NADIC anhydride or aromatic acid anhydride: phthalic anhydride to polyester's synthesis leads to prepare the polyesters with considerably different properties. As was shown, their structure had a direct influence on the viscoelastic properties and thermal behavior of their cured copolymers [24]. It is therefore considered of interest to investigate systematically the curing behavior and dynamic mechanical properties of copolymers based on polyesters obtained in the presence of other modified acid anhydrides.

In this article, the course of the cure reaction of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) with styrene initiated by BPO or the mixture of BPO/acid anhydride (BPO/THPA or BPO/MA) as well as the thermal and viscoelastic properties of obtained cured styrene copolymers have been studied by means of DSC, DMA, and TGA analysis. The obtained results were compared to those for BPO initiated cure reaction of succinic or glutaric anhydride modified linear unsaturated polyesters (UP). The influence of polyester's structure as well as used curing agent on the studied properties has been evaluated.

Experimental

Materials

Succinic or glutaric anhydride modified linear unsaturated polyesters (UP) were prepared in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), succinic anhydride (S) or glutaric

anhydride (G) and ethylene glycol (EG). The reaction was carried out by a molar ratio of 1 mol of THPA, 0.5 mol of MA, 0.5 mol of S or 0.5 mol of G and 2.65 mol of EG in the presence of 0.015 wt% of hydroquinone as a radical polymerization inhibitor. The polycondensation was performed at the temperature range of 150–180 °C with simultaneous azeotropic distillation with xylene (10 wt%) to remove condensation water. The reaction course extent was controlled by determining acid number of the reaction mixture. The acid number was defined as a number of mg KOH required for the titration of 1 g of a sample. The drop of an acid number to final value 30 mg KOH/g was indication of the process completion.

Succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) were obtained by chemical modification of above-mentioned UP with 38–40% peracetic acid according to Refs. [20–24].

Cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), succinic anhydride (S), glutaric anhydride (G), 38–40% peracetic acid were obtained from Merck-Schuchardt, Hohenbrunn, Germany. Benzoyl peroxide (BPO) and ethylene glycol (EG) were supplied by Fluka, Buchs, Switzerland. Hydroquinone and styrene (ST) were delivered by POCh, Gliwice, Poland.

The basic properties of succinic or glutaric anhydride modified linear unsaturated polyesters (UP) and succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) in the non-crosslinked state: viscosity (mPas), density (g cm^{-3}), epoxy value (mol/100 g) as well as average molecular weight (g mol^{-1}) were determined. The obtained values were given in Tables 1 and 2.

Characterization of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters and their styrene copolymers

Fourier transform infrared (FTIR) spectra were obtained by using a Perkin-Elmer 1725 X FTIR spectrophotometer in the 400–4,000 cm^{-1} range using KBr pellets.

Proton nuclear magnetic resonance ($^1\text{H NMR}$) spectra were recorded on an NMR Bruker-Avance 300 MSL

Table 1 Basic properties of succinic anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP) before curing

Properties	Polyesters	
	UP	UEP
Viscosity/mP s	2,240	2,480
Density/ g cm^{-3}	1.14	1.15
Epoxy value/mol/100 g	–	0.26
Molecular weight/ g mol^{-1}	680	710

Table 2 Basic properties of glutaric anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP) before curing

Properties	Polyesters	
	UP	UEP
Viscosity/mP s	1,820	2,010
Density/g cm ⁻³	1.12	1.14
Epoxy value/mol/100 g	–	0.27
Molecular weight/g mol ⁻¹	660	680

(Germany) spectrometer at 300 MHz with deuterated chloroform (CDCl₃) as the solvent. ¹H NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference.

Viscosity was measured at 25 °C by means of rotating spindle rheometer, Brookfield, model DV-III. Density was evaluated using a glass pycnometer with capillary fuse Gay/Lussaca (25 mL) at 25 °C. Epoxy value was estimated by dioxane/HCl titration method. The average molecular weight was determined by osmometric method (osmometer KNAUER GmbH, Germany).

The calorimetric measurements were carried out 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⁻¹ 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 characteristics: the temperature of the cure initiation (T_{onset}), the peak maximum temperature (T_{max}), the final cure temperature (T_{end}), the heat generated during the cure reaction (ΔH), as well as the thermal degradation temperature (T_d) were evaluated.

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 room temperature until the sample become too soft to be tested (180–200 °C) with a constant heating rate of 4 °C min⁻¹ at an oscillation frequency of 10 Hz was performed. Rectangular samples 10 mm wide and 4 mm thick were used. Dynamic mechanical properties of the cured styrene 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 temperatures (α -relaxation) for the experimental copolymers were taken as the maximum of the $\tan \delta$ versus temperature curves. From the $\tan \delta$ curves also the width across the curve when it dropped to half of its peak value (full width at half

maximum: FWHM) and cross-linking density (ν_c) were determined. The cross-linking density (ν_c) for obtained networks was calculated by applying the equation derived from the theory of rubber elasticity: $E' = 3 \nu_c RT$, where E' is the storage modulus in the rubbery plateau region, R is a gas constant, and T is the absolute temperature ($T = T_g + 50$ °C) [25–27].

Thermogravimetric analysis (TGA) 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 20–1,000 °C with the sample weight of 100 mg. α -Al₂O₃ was used as a reference. The initial decomposition temperature (IDT), the temperature of 10, 20, and 50% of weight loss (T_{10} , T_{20} , and $T_{50\%}$), the temperature of the maximum rate of weight loss (T_{max}) and the final decomposition temperature (FDT) were determined.

Hardness according to Brinell was determined by means of a hardness tester HPK.

Flexural properties were measured in a three-point bending test using a Zwick/Roell Strength Machine (model Z010, Germany). The specimen dimensions were 10 mm wide and 4 mm thick. The measurements were carried out at room temperature with a crosshead speed of 2 mm/min using a support span of 64 mm. At least five specimens were tested for each sample to evaluate flexural properties. The flexural modulus at bending (E_{mod}), maximum force at bending (F_{max}), deflection (extension) at maximum force ($\varepsilon - F_{\text{max}}$) were qualified.

Curing procedure

Succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) were mixed with styrene in order to obtain the resins which were characterized by large content of “dry” mass and low styrene monomer content (4:1). To study the course of the cure reaction, the suitable curing agent was used. As curing agents: 0.5 wt% of benzoyl peroxide (BPO) or the mixture of 0.5 wt% of BPO and suitable acid anhydride (THPA or MA) were applied. To compare the course of the cure reaction and the properties of cured styrene copolymers, the styrene solutions of succinic or glutaric anhydride modified linear unsaturated polyesters (UP) prepared in the same concentrations were cured using 0.5 wt% of BPO. The samples for DSC experiments were prepared by mixing styrene with BPO to obtain homogeneous solutions. Then, BPO/styrene solutions were added to succinic or glutaric anhydride modified linear UP or UEP and tested immediately after mixing. On the contrary, BPO/THPA or BPO/MA compositions were prepared as follows: THPA or MA and suitable acid anhydride modified linear UEP were mixed and heated up above the melting point of an anhydride, quenched in cold water and after cooling, BPO/styrene solution was added,

mixed, and tested. The samples used for DMA and TGA experiments were prepared in the same way as for DSC experiments. The compositions after degassing were placed in glass mold and cured at 100–140 °C and then, additionally conditioned in the temperature range 160–180 °C for 10 h to obtain the fully cured styrene copolymers (no additional exothermic peak was appeared in DSC curves).

Results and discussion

Characterization of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters

As was presented in Tables 1 and 2, both succinic anhydride modified linear unsaturated polyester (SUP) and succinic anhydride modified linear unsaturated epoxy polyester (SUEP) were characterized by higher viscosities compared to glutaric anhydride modified linear unsaturated polyester (GUP) and glutaric anhydride modified linear unsaturated epoxy polyester (GUEP). It was in accordance reported by other authors [19] and probably connected with stronger intermolecular interactions of hydroxyl groups and carboxyl groups with ester groups/carbonyl groups or epoxy groups in polyesters containing less methylene groups in the backbone. Moreover, the values of viscosity for succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters (UEP) were a bit higher than those obtained for succinic or glutaric anhydride modified linear unsaturated polyesters (UP). It was due to additional intermolecular interactions of formed epoxy groups with other polar groups in polyester's structure [28].

The structure of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters was confirmed by spectroscopic methods. The FT IR spectra of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters showed the disappearance of absorption bands characteristic for double bonds in cyclohexenyl rings (665–776 cm^{-1} , C–H out of plane deformation vibration) and appearance of new absorption bands responsible for epoxy ring vibration groups (790–808 cm^{-1}). Moreover, the absorption band for carbon–carbon double bonds in polyester chain (1,648 cm^{-1} , C=C stretching vibration) was apparent in the spectra for both types of polyesters: UP and UEP. Based on ^1H NMR spectra for succinic or glutaric anhydride modified linear unsaturated epoxy polyesters, the disappearance of the resonance signals attributed to the protons attached to cyclohexenyl rings (5.67–5.7 ppm) was clearly observed. Moreover, the existence of the resonance signals for the protons assigned to carbon–carbon double bonds in polyester chains (6.29–6.35 and 6.90–6.93 ppm, *cis*–*trans* forms) was indicated before and after chemical modification process (Figs. 1, 2; Scheme 1). Those results

were in accordance to our previous studies and confirmed earlier observations concerning the selectivity of the oxidation reaction of the unsaturated polyesters [20–24].

Curing reaction of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters with styrene using different curing agents

The course of the cure reaction of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters with styrene using different curing agents was monitored by DSC. The cure reaction of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) with styrene was initiated by following curing systems: 0.5 wt% of diacyl peroxide: benzoyl peroxide (BPO) or the mixture of 0.5 wt% of BPO/suitable acid anhydride: cyclohex-4-ene-1,2-dicarboxylic anhydride (BPO/THPA) or maleic anhydride (BPO/MA). Also, the course of the cure reaction of succinic or glutaric anhydride modified linear unsaturated polyester (UP) with styrene initiated by 0.5 wt% BPO was presented to compare. The obtained results from DSC curves were presented in Tables 3 and 4. BPO initiated cure reaction of succinic or glutaric anhydride modified linear unsaturated polyesters (UP) with styrene was described by one, asymmetrical, exothermic peak ($T_{\text{max}1}$). Similarly, the comparable exothermic peak ($T_{\text{max}1}$) for BPO initiated cure reaction of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) with styrene was observed. The presence of this peak was associated with the copolymerization process of carbon–carbon double bonds of polyester with styrene. Moreover, the second, exothermic peak at higher temperatures ($T_{\text{max}2}$ 312 or 314 °C) for BPO initiated cure reaction of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) was indicated. The presence of this exothermic signal was directly connected with the reaction of epoxy groups with hydroxyl or carboxyl groups in polyester which resulted the formation of ether or ester linkages at higher temperatures [29–31].

The cure process of succinic or glutaric acid anhydride modified linear unsaturated epoxy polyesters (UEP) with styrene initiated by the mixture of BPO/acid anhydride (BPO/THPA or BPO/MA) was described by one, asymmetrical, exothermic peak with two maxima. Additionally, BPO/acid anhydride initiated cure reaction of UEP with styrene was more exothermic (described by higher ΔH values) compared to those only BPO initiated cure reaction of UEP with styrene. Those results indicated on simultaneous running cure processes: copolymerization of carbon–carbon double bonds of polyester with styrene and polyaddition reactions of epoxy to anhydride groups. Those observations were in accordance with earlier studies presenting the course of the cure reaction of different types of

Table 3 DSC data of the cure reaction of succinic anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP) with styrene

Formulation	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{max1}}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$T_{\text{max2}}/^{\circ}\text{C}$	$T_d/^{\circ}\text{C}$	$\Delta H_d/\text{kJ mol}^{-1}$
UP/BPO	92	127	198	75	–	423	172
UEP/BPO	84	128	204	74	312	392	–
UEP/BPO/THPA	65	130/175	268	307	–	398	205
UEP/BPO/MA	52	91/160	251	327	–	399	215

Table 4 DSC data of the cure reaction of glutaric anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP) with styrene

Formulation	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{max1}}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$T_{\text{max2}}/^{\circ}\text{C}$	$T_d/^{\circ}\text{C}$	$\Delta H_d/\text{kJ mol}^{-1}$
UP/BPO	92	126	199	76	–	427	169
UEP/BPO	80	127	205	75	314	394	–
UEP/BPO/THPA	65	125/179	258	314	–	399	202
UEP/BPO/MA	52	88/159	249	324	–	393	211

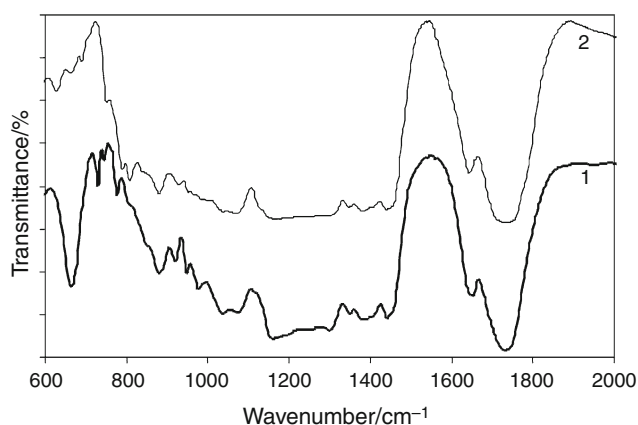
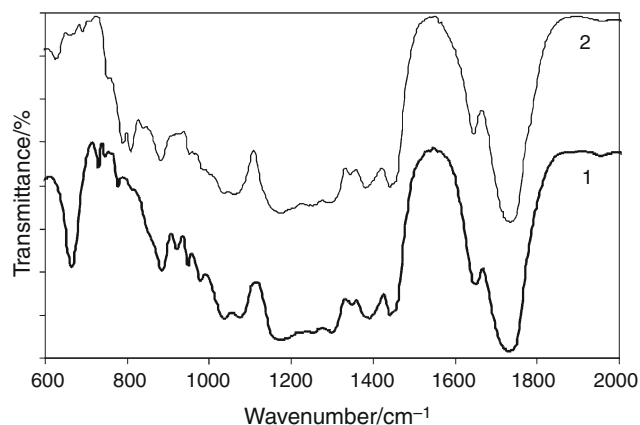
unsaturated (epoxy) polyesters with styrene in the presence of chosen curing agents [20–24].

Furthermore, the use of the mixture of BPO and polymerizable acid anhydride: maleic anhydride as a curing system of succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) caused significantly decrease of T_{onset} and T_{max1} values of the cure reaction compared to those values observed when BPO and non-polymerizable acid anhydride: cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA) was applied. This behavior could be attributed to the simultaneous copolymerization of carbon–carbon double bonds of polyester and styrene, polyaddition of epoxy to anhydride groups and additional copolymerization of carbon–carbon double bonds of maleic anhydride with styrene or carbon–carbon double bonds of polyester. Those interactions might accelerate the rate of the cure reaction of studied unsaturated epoxy

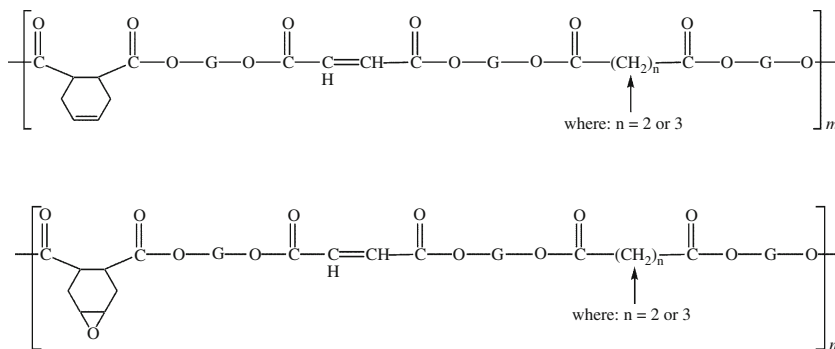
polyesters causing the production of more cross-linked network structure of their styrene copolymers (Tables 3, 4). However, the comparable T_{onset} , T_{max} , and T_{end} temperatures for the cure reaction of both succinic anhydride modified linear unsaturated (epoxy) polyesters as well as glutaric anhydride modified unsaturated (epoxy) polyesters with styrene in the presence of the same curing agent were obtained. This observation confirmed that the presence of both succinic or glutaric anhydride residues in polyester's structure had a little influence on the course of the cure reaction with styrene.

Dynamic mechanical properties, mechanical properties, and thermal stability of cured styrene copolymers

DMA data of cured styrene copolymers based on succinic or glutaric anhydride modified linear unsaturated (epoxy)

**Fig. 1** IR spectra of succinic anhydride modified linear: unsaturated polyester (1) and unsaturated epoxy polyester (2)**Fig. 2** IR spectra of glutaric anhydride modified linear: unsaturated polyester (1) and unsaturated epoxy polyester (2)

Scheme 1 The structure of studied linear unsaturated (epoxy) polyesters



polyesters were presented in Tables 5 and 6, respectively. The data obtained from mechanical studies for cured styrene copolymers prepared in the presence of succinic or glutaric anhydride modified linear unsaturated (epoxy) polyesters were collected in Tables 7 and 8. The BPO cured styrene copolymers based on succinic or glutaric anhydride modified linear unsaturated epoxy polyester (UEP) were characterized by significantly higher values of storage modulus ($E'_{20^\circ\text{C}}$), loss modulus (E''), glass transition temperature (T_g), cross-linking density (ν_e), modulus at bending (E_{mod}), maximum force at bending (F_{max}), hardness but lower values of deflection (extension) at maximum force ($\varepsilon - F_{\text{max}}$) compared to BPO cured styrene copolymers prepared from succinic or glutaric anhydride modified linear unsaturated polyesters (UP). The differences were directly connected with polyester's structure. As it was shown, based on DSC studies on the cure process, the presence of both carbon-carbon double bonds and epoxy groups in unsaturated epoxy polyester's structure allowed both: copolymerization reactions with styrene and

additional etherification and/or esterification reactions at higher temperatures. It resulted to obtain stiffer network structure for styrene copolymers based on unsaturated epoxy polyesters (UEP) compared to those based on unsaturated polyesters (UP). Moreover, considerable improvement of studied properties (the highest values of $E'_{20^\circ\text{C}}$, T_g , E'' , ν_e , E_{mod} , F_{max} , hardness and lower values of $\varepsilon - F_{\text{max}}$ and $tg\delta_{\text{max}}$ height) for BPO/acid anhydride cured styrene

Table 7 Mechanical properties of styrene copolymers based on succinic anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP)

Formulation	$E_{\text{mod}}/\text{GPa}$	F_{max}/N	$\varepsilon - F_{\text{max}}/\%$	Hardness/MPa
UP/BPO	0.95	90	4.86	–
UEP/BPO	2.43	145	4.03	98
UEP/BPO/THPA	2.67	187	2.35	140
UEP/BPO/MA	3.12	224	0.76	165

Table 5 DMA data of styrene copolymers based on succinic anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP)

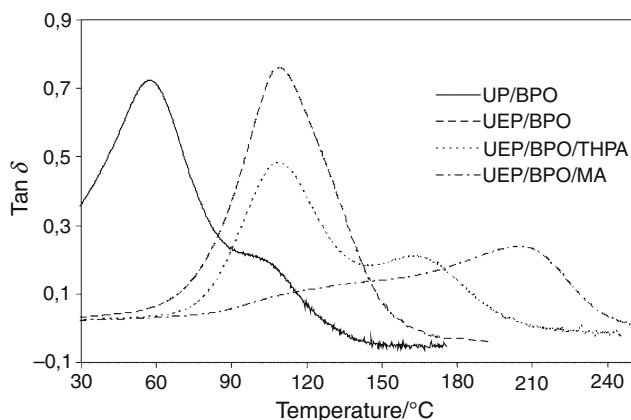
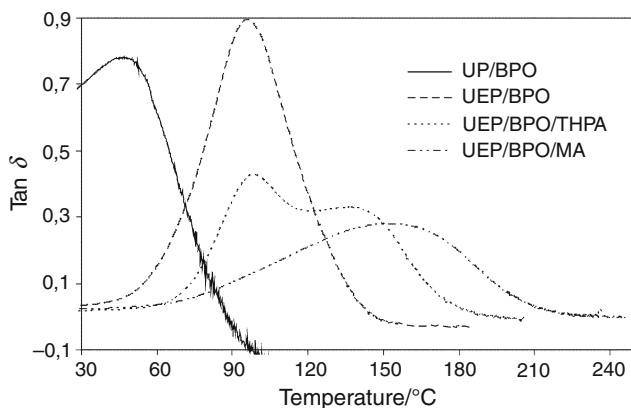
Formulation	$E'_{20^\circ\text{C}}/\text{MPa}$	$tg\delta_{\text{max}}$	$tg\delta_{\text{max}}/^\circ\text{C}$	$E''/^\circ\text{C}$	FWHM/ $^\circ\text{C}$	$\nu_e \times 10^{-3}/\text{mol}/\text{cm}^3$
UP/BPO	840	0.721	57	–	–	0.28
UEP/BPO	2,165	0.753	110	84	42	0.57
UEP/BPO/THPA	2,462	0.481/0.207	110/163	92	–	0.93
UEP/BPO/MA	2,875	0.238	204	109	94	1.85

Table 6 DMA data of styrene copolymers based on glutaric anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP)

Formulation	$E'_{20^\circ\text{C}}/\text{MPa}$	$tg\delta_{\text{max}}$	$tg\delta_{\text{max}}/^\circ\text{C}$	$E''/^\circ\text{C}$	FWHM/ $^\circ\text{C}$	$\nu_e \times 10^{-3}/\text{mol}/\text{cm}^3$
UP/BPO	700	0.779	48	–	–	0.25
UEP/BPO	2,017	0.889	96	69	40	0.52
UEP/BPO/THPA	2,350	0.426/0.327	98/142	85	–	0.90
UEP/BPO/MA	2,663	0.277	152	96	86	1.80

Table 8 Mechanical properties of styrene copolymers based on glutaric anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP)

Formulation	$E_{\text{mod}}/\text{GPa}$	F_{max}/N	$\varepsilon - F_{\text{max}}/\%$	Hardness/MPa
UP/BPO	0.80	85	5.08	–
UEP/BPO	2.36	136	4.22	87
UEP/BPO/THPA	2.60	180	2.41	135
UEP/BPO/MA	2.95	217	0.80	160

**Fig. 3** $\tan \delta$ versus temperature curves for styrene copolymers based on succinic anhydride modified linear unsaturated polyesters (UP) and unsaturated epoxy polyesters (UEP)**Fig. 4** $\tan \delta$ versus temperature curves for styrene copolymers based on glutaric anhydride modified linear unsaturated polyesters (UP) and unsaturated epoxy polyesters (UEP)

copolymers prepared in the presence of succinic or glutaric anhydride modified linear UEP was indicated. The additionally formed linkages during the reaction of epoxy groups with anhydride groups allowed producing stiffer networks of mentioned copolymers compared to BPO cured styrene copolymers of UEP (Tables 5, 6, 7, 8; Figs. 3, 4). Additionally, the values of $E'_{20^\circ\text{C}}$, T_g , E'' , v_e , E_{mod} , F_{max} , hardness decreased for copolymers prepared in the presence of glutaric anhydride modified linear unsaturated (epoxy) polyesters compared to styrene copolymers based on succinic anhydride modified linear unsaturated (epoxy) polyesters. It suggested to produce more flexible polymeric network structure for copolymers based on polyesters containing more methylene groups ($-\text{CH}_2-$) in their chains.

The TGA data of obtained styrene copolymers were shown in Tables 9 and 10. The thermogravimetric analysis (TGA) showed the differences in thermal stability of cured styrene copolymers. The cured styrene copolymers based on succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) were characterized by higher thermal stability than styrene copolymers prepared from succinic or glutaric anhydride modified linear unsaturated polyesters (UP). The initial decomposition temperatures (IDT) and final decomposition temperatures (FDT) were in the range 270–320 °C and 610–640 °C for copolymers based on studied UEP, which was due to the formation of more highly crosslinked networks. Additionally, the styrene copolymers prepared in the presence of glutaric anhydride modified linear unsaturated (epoxy) polyesters were generally less thermally stable (lower values of IDT, FDT) (Tables 9, 10) than those based on succinic anhydride modified unsaturated (epoxy) polyesters. It confirmed earlier observations regarding to the production of less crosslinked and thus more flexible network structure for glutaric anhydride modified linear unsaturated (epoxy) polyesters. In addition, the thermal degradation pattern of all styrene copolymers exhibited two separated degradation steps ($T_{\text{max}1}$ and $T_{\text{max}2}$). The first maximum of weight loss ($T_{\text{max}1}$) was observed at 365–375 °C, the second ($T_{\text{max}2}$) at relatively higher temperatures exceeded 540 °C. They were directly connected with degradation of ester/ether/other bonds in formed polymeric network structure [20–24, 32].

Table 9 TG and DTG data of styrene copolymers based on succinic anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP)

Formulation	IDT/°C	$T_{10\%}/^\circ\text{C}$	$T_{20\%}/^\circ\text{C}$	$T_{50\%}/^\circ\text{C}$	FDT/°C	$T_{\text{max}1}/^\circ\text{C}$	$T_{\text{max}2}/^\circ\text{C}$
UP/BPO	260	275	305	360	630	365	550
UEP/BPO	270	290	310	370	640	370	545
UEP/BPO/THPA	300	310	320	370	630	370	550
UEP/BPO/MA	320	340	350	375	640	370	550

Table 10 TG and DTG data of styrene copolymers based on glutaric anhydride modified linear unsaturated polyester (UP) and unsaturated epoxy polyester (UEP)

Formulation	IDT/°C	$T_{10\%}/^{\circ}\text{C}$	$T_{20\%}/^{\circ}\text{C}$	$T_{50\%}/^{\circ}\text{C}$	FDT/°C	$T_{\text{max}1}/^{\circ}\text{C}$	$T_{\text{max}2}/^{\circ}\text{C}$
UP/BPO	250	280	300	365	600	365	545
UEP/BPO	270	300	320	370	610	375	540
UEP/BPO/THPA	290	300	325	365	610	370	540
UEP/BPO/MA	310	325	330	375	620	370	540

Conclusions

Those all presented results confirmed that both the chemical structure of polyesters as well as used curing agent had a considerable influence on the cure behavior, thermal, viscoelastic, and mechanical properties of their styrene copolymers. The styrene copolymers based on succinic or glutaric anhydride modified linear unsaturated epoxy polyesters (UEP) were generally characterized by better viscoelastic, mechanical, and thermal properties compared to those for styrene copolymers based on succinic or glutaric anhydride modified linear unsaturated polyesters (UP). It was connected with possible, various cure reactions of UEP due to the presence of both carbon-carbon double bonds and epoxy groups in their structure, e.g., copolymerization of carbon-carbon double bonds of polyester with styrene, polyaddition of epoxy to anhydride groups, thermal curing of epoxy groups using suitable curing system. It leads to produce of more cross-linked polymer network structure and thus stiffer and more thermally stable styrene copolymers based on UEP. Moreover, the present studies confirmed that styrene copolymers prepared in the presence of glutaric anhydride modified linear unsaturated (epoxy) polyesters were described by lower values of $E'_{20^{\circ}\text{C}}$, T_g , E'' , ν_e , E_{mod} , F_{max} , hardness, IDT, FDT but higher $\varepsilon - F_{\text{max}}$ values compared to those obtained for styrene copolymers based on succinic anhydride modified linear unsaturated (epoxy) polyesters. This supported to the production of more flexible polymer networks for styrene copolymers obtained in the presence of polyesters containing more methylene groups ($-\text{CH}_2-$) in their chains.

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