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Studies on the cure reaction and thermal properties of NADIC/phthalic anhydride modified unsaturated (epoxy) polyesters

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Abstract The cure reaction of NADIC/PA modified unsaturated (epoxy) polyesters with styrene initiated by benzoyl peroxide (BPO) or the mixture of benzoyl peroxide/tetrahydrophthalic anhydride (BPO/THPA) and the thermal properties of obtained styrene copolymers have been studied. Based on non-isothermal DSC analysis, it was proved that the course of the cure reaction clearly depended on the structure of polyesters as well as used curing agent. Generally, one or two asymmetrical peaks for the cure reaction of NADIC/PA modified unsaturated epoxy polyesters with styrene were observed. They were attributed to the copolymerization process of carbon–carbon double bonds of polyester and styrene and/or to the thermal curing of epoxy groups or polyaddition reaction of epoxy groups to anhydride groups, in dependence of used hardener. In addition, only one asymmetrical peak connected with the copolymerization process for the cure reaction of NADIC/PA modified unsaturated polyesters and styrene was observed. Moreover, the cure process of NADIC/PA modified unsaturated epoxy polyesters with styrene initiated with BPO/THPA was more exothermic (higher values of ΔH) compared to the cure process initiated only with BPO.

The obtained styrene copolymers based on NADIC/PA modified unsaturated epoxy polyesters were characterized by better thermal properties compared to copolymers based on NADIC/PA modified unsaturated polyesters. It has manifested by higher $E'_{20\,°C}$, E''_{max}, $tg\delta_{max}$, T_g as well as higher IDT, $T_{10\%}$, $T_{20\%}$, $T_{50\%}$ and T_k temperatures. Moreover, the introduction of non-polymerizable cycloaliphatic anhydride (NADIC anhydride) into unsaturated (epoxy) polyester structure caused improvement of the thermal properties of cured copolymers compared to copolymers based on non-polymerizable, aromatic (PA) modified unsaturated (epoxy) polyesters.

Keywords Unsaturated polyesters · Unsaturated epoxy polyesters · Thermal properties · Copolymers

Introduction

Unsaturated polyesters are low-molecular-weight maleate or fumarate esters containing various chemical structures designed for their specific coast and performance purposes [1, 2]. The commonly used unsaturated polyesters are based on maleic anhydride which provides a site for cross-linking. Moreover, appreciable *cis* and *trans* isomerization generally occurs during the polycondensation process and in polyester chain maleic anhydride is incorporated mostly as fumarate groups. This is desirable phenomenon, as fumarate forms are more reactive in copolymerization process with vinyl monomer. It has a favorable effect on thermal and mechanical properties of obtained materials [3–5]. In the unsaturated polyester chemistry the number and position of double bonds is an important factor responsible for their properties. Unsaturated polyesters are often prepared with the addition of saturated acids/anhydrides. They act as a spacer to reduce the number of double bonds and thus the cross-linking density [6]. The most often applied saturated, non-polymerizable acids/anhydrides are phthalic anhydride, sebacic acids or cyclo-olephinic acids or anhydrides used for polyesters for special applications [7].

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The present paper describes the studies on the cure reaction of NADIC/PA modified unsaturated (epoxy) polyesters with styrene initiated by BPO or the mixture of BPO and THPA. Moreover, the thermal properties of copolymers based on those prepared polyesters have been studied by means of DSC, TG and DMA analyses. The NADIC/PA modified unsaturated polyesters were prepared in conventional polycondensation process of THPA, maleic anhydride, NADIC/phthalic anhydride and ethylene glycol. The obtained unsaturated polyesters contained carbon–carbon double bonds and cyclohexenyl rings in polyester backbone. They were suitable for further chemical modification. By the use of peracids as the oxidant reagents of polyesters, their epoxy derivatives can be prepared [8–12]. Moreover, as previously described, the epoxidation reaction performed in mild temperature and time conditions allowed to selective oxidation of unsaturated polyesters based on maleic anhydride and THPA. In this process the polyesters containing carbon–carbon double bonds in polyester chain and epoxy groups in cycloaliphatic rings can be prepared [13–15]. The selective oxidation of NADIC/PA modified unsaturated polyesters by the use of peracetic acid allowed to obtain NADIC/PA modified unsaturated epoxy polyesters. The structure of polyesters before and after oxidation process was confirmed by FT IR, ^{1}H NMR and DSC analyses.

Experimental

Materials

Tetrahydrophthalic anhydride (THPA), maleic anhydride (MA), nadic anhydride (NADIC) and phthalic anhydride (PA) were obtained from Merck–Schuchardt (Hohenbrunn, Germany). Ethylene glycol (EG) was from Fluka (Buchs, Switzeland). 38–40% peracetic acid, methylene chloride, tetrahydrofuran were purchased from Merck-Schuchardt (Hohenbrunn, Germany). Hydroquinone, styrene (ST) were delivered by POCh (Gliwice, Poland). All reagents were used without further purification.

Preparation of NADIC/PA modified unsaturated (epoxy) polyesters

The modified unsaturated epoxy polyesters were prepared in two stage process. In the first stage, the modified unsaturated polyesters were obtained during polycondensation process of THPA, maleic anhydride (MA), nadic anhydride (NADIC)/phthalic anhydride (PA) and ethylene glycol (EG). The 0.015 wt% of hydroquinone as an inhibitor was used. The reaction was carried out at the ratio of 1 mol of THPA, 0.5 mol of MA, 0.5 mol of NADIC or PA and 2.65 mol of EG in the temperature range of 150–180 °C. 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. In the second stage the NADIC/PA modified unsaturated polyesters were oxidized using 38–40% peracetic acid. The oxidation reaction was performed at 40 °C for 2 h in methylene chloride as the solvent. The raw product was purified as described in [12]. The epoxy value (determined by dioxane/HCl titration method) was 0.23 mg KOH/g or 0.24 mg KOH/g for NADIC/PA modified unsaturated epoxy polyesters, respectively.

Characterization of NADIC/PA modified unsaturated (epoxy) polyesters and their copolymers

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

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a NMR Brucker-Avance 300 MSL (Germany) spectrometer at 300 MHz with deuterated chloroform ($CDCl_3$) as the solvent. ^{1}H NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference.

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}). As a reference an empty aluminium crucible was used. Curing characteristic such as temperature of the cure initiation (T_{onset}), peak maximum temperature (T_{max}), final cure temperature (T_{end}), the heat generated during the cure reaction (ΔH), the glass transition temperature (T_g) and the decomposition temperature (T_d) were evaluated.

Thermogravimetric analysis (TG) 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. The IDT, $T_{10\%}$, $T_{20\%}$, $T_{50\%}$ of weight loss, final decomposition temperature (T_k) and temperature of the maximum rate of weight loss (T_{max}) were determined.

DMA measurements of cured copolymers were performed using Dynamic Mechanical Analyzer Q 800 TA Instruments (USA). Tests were conducted with a dual Cantilever device with a support span of 35 mm, calibrated according to the producer's recommendation. Temperature scanning from −135 to 250 °C was performed with a constant heating rate of 4 °C min^{-1} at an oscillation frequency of 10 Hz. The rectangular profile of the samples was used (35 × 10 × 4 mm). Viscoelastic properties of cured copolymers were estimated from the changes of storage modulus (E′), mechanical loss (E″) as well as from the changes of tan δ at constant frequency depending on temperature. Glass transition temperature (α-relaxation) for obtained copolymers was determined from the dependence of the tan δ on temperature and was identified as the maximum of the tan δ.

Curing procedure

The styrene solutions of NADIC/PA modified unsaturated epoxy polyesters by mixing polyester and styrene in the ratio of 4:1 were prepared. Then, to cure those styrene solutions, 0.5 wt% of BPO or the mixture of the stoichiometric ratio of THPA and 0.5 wt% of BPO were added. Also, to compare the course of the cure reaction and the properties of cured copolymers, the styrene solutions of NADIC/PA modified unsaturated polyesters prepared in the same concentrations, were cured using 0.5 wt% of BPO. The samples used for DSC, DMA and TGA experiments were prepared by mixing styrene with BPO to obtain homogeneous solutions. Then, the BPO/styrene solutions were added to modified unsaturated epoxy polyesters or modified unsaturated polyesters and tested immediately after mixing. On the contrary, THPA/BPO compositions were prepared as follows: THPA and modified unsaturated epoxy polyesters were mixed and heated up above the melting point of anhydride, quenched in cold water and after cooling the solution of BPO and styrene were added, mixed and tested. The samples used for DMA and TGA experiments were conditioned in the temperature range of 100–180 °C. The condition temperatures were appointed from the position of the exothermic peaks at DSC curves. In this way, the fully cured styrene copolymers without damage connected with thermal degradation were prepared.

Results and discussion

Characterization of NADIC/PA modified unsaturated (epoxy) polyesters

The structure of NADIC/PA modified unsaturated epoxy polyesters and NADIC/PA modified unsaturated polyesters was confirmed by ^{1}H NMR, IR and DSC analyses. The fragment of ^{1}H NMR spectra of NADIC modified unsaturated polyester and NADIC modified unsaturated epoxy polyester has been presented in Fig. 1. Figure 2 showed the ^{1}H NMR spectra of PA modified unsaturated polyester and PA modified unsaturated epoxy polyester. The differences of resonance signals attributed to the protons attached to double bonds in cyclohexenyl rings were observed. The spectra analysis of NADIC/PA modified unsaturated epoxy polyesters indicated disappearance of peaks for protons assigned to double bonds at cyclohexenyl rings (5.67–5.7 × 10^{-6}). The presence of protons assigned to carbon–carbon double bonds in polyester chain before and after oxidation process was indicated (6.3 × 10^{-6} and 6.9 × 10^{-6}). The IR spectra of NADIC/PA modified unsaturated epoxy polyesters and unsaturated polyesters were given in Figs. 3 and 4, respectively. Significant differences in IR spectra before and after oxidation process were showed. The absorption bands at 665, 727 and 775 cm^{-1} (C–H out of plane deformation vibration) characteristic for double bonds in cyclohexenyl rings were observed. Moreover, the absorption bands for carbon–carbon double bonds in polyester chain (C=C stretching vibration) at 1,645–1,648 cm^{-1} appeared in the spectra before oxidation. The performed selective oxidation process caused the disappearance of absorption bands for double bonds in cyclohexenyl rings. However, the appearance of new absorption bands at 788–790, 807–808 and 836–851 cm^{-1} responsible for oxirane ring vibration groups was indicated. The C=C stretching vibration in polyester chain before and after oxidation process were observed. It confirmed that the oxidation of NADIC/PA modified unsaturated polyesters was selective. The double bonds in cyclohexenyl rings were converted into epoxy groups whilst carbon–carbon double bonds in polyester chain were not oxidized. Moreover, DSC analysis showed the differences in thermal behavior of NADIC/PA modified unsaturated (epoxy) polyesters, Figs. 5 and 6. The exothermic peak at 352.2 or 354.4 °C for NADIC/PA modified unsaturated polyesters was observed. It may be due to the double bonds copolymerization. The exothermic peaks at 175.3 or 177.9 °C and 308.2 or 296.7 °C were characteristic for NADIC/PA modified unsaturated epoxy polyesters. They were attributed to the reaction of epoxy groups with hydroxyl groups in polyester or to a thermal cross-linking process of epoxy groups with carboxylic groups, as reported by other authors [16–18]. The temperatures of degradation process (T_d) of studied polyesters before oxidation reaction were 36–43.4 °C higher then those obtained for polyesters after oxidation. It was connected with different structure of cured polyesters.

Curing process of NADIC/PA modified unsaturated (epoxy) polyesters

The cure reaction of NADIC/PA modified unsaturated (epoxy) polyesters was monitored by means of DSC. The DSC curves of the cure reaction of NADIC/PA modified unsaturated epoxy polyesters (UEP) with BPO or BPO/THPA and modified unsaturated polyesters (UP) with BPO were presented in Figs. 7 and 8, respectively. As can be

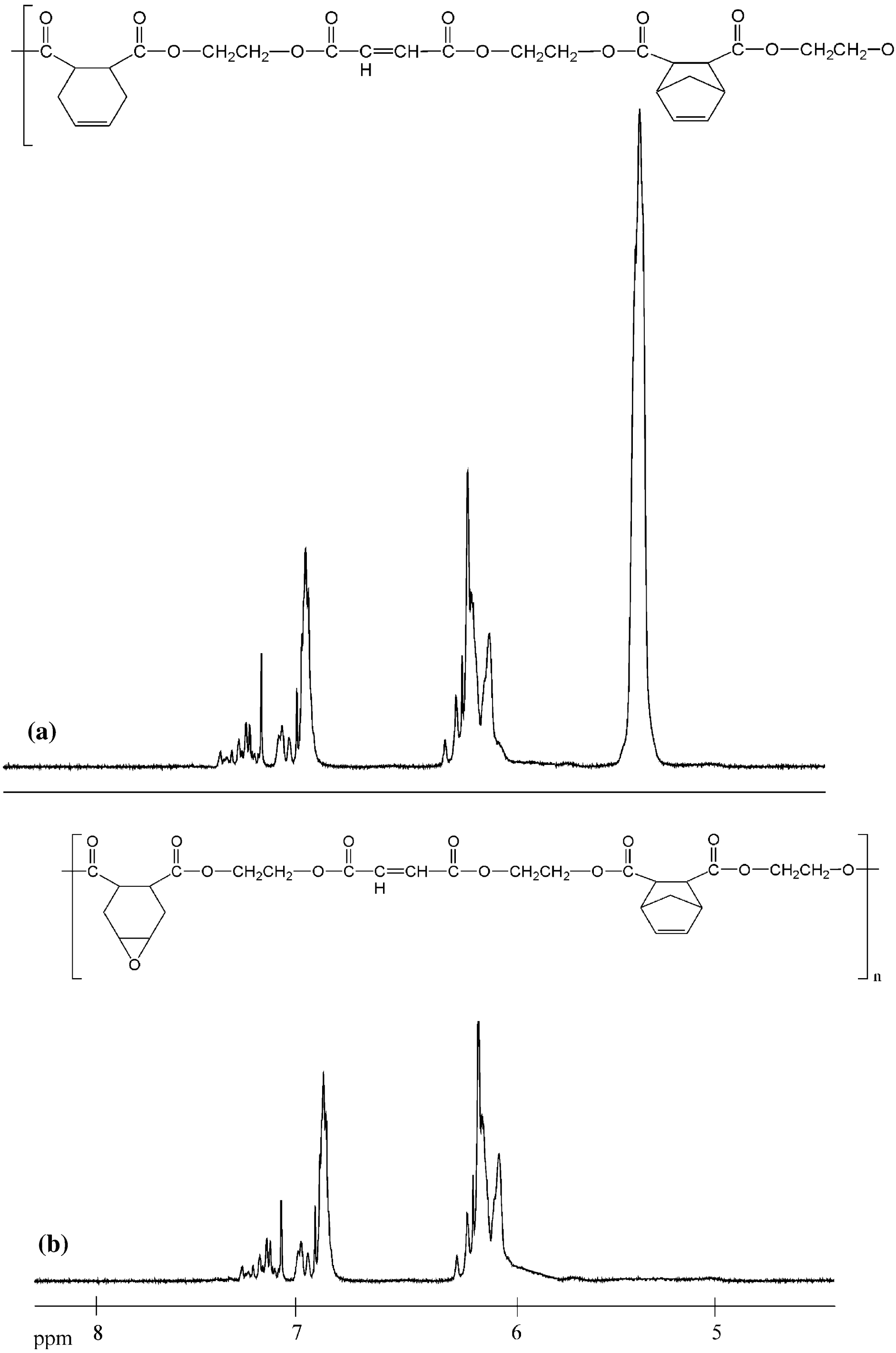

Fig. 1 ^{1}H NMR spectra of NADIC modified unsaturated polyester (**a**) and NADIC modified unsaturated epoxy polyester (**b**)

seen from those figures, the course of the cure reaction depended on the structure of used polyesters as well as used curing agent. The one asymmetrical exothermic peak (at T_{max} 125.3 or 124.2 °C) for the cure reaction of NADIC/PA modified unsaturated polyesters initiated with BPO was observed. It was associated with the copolymerization process of carbon–carbon double bonds in polyester chain and vinyl monomer-styrene [14, 19]. Similarly, the exothermic peak (at T_{max} 124.7 or 120.0 °C) for the cure reaction of NADIC/PA modified unsaturated epoxy polyesters with styrene initiated by BPO was appeared. The heat generated during the cure reaction (ΔH) of polyesters before and after oxidation was comparable, Tables 1 and 2. It indicated on the similar amount of unsaturated units in modified epoxy polyesters and modified unsaturated polyesters. This observation additionally confirmed that the unsaturated double bonds in polyester chain did not change during the oxidation process.

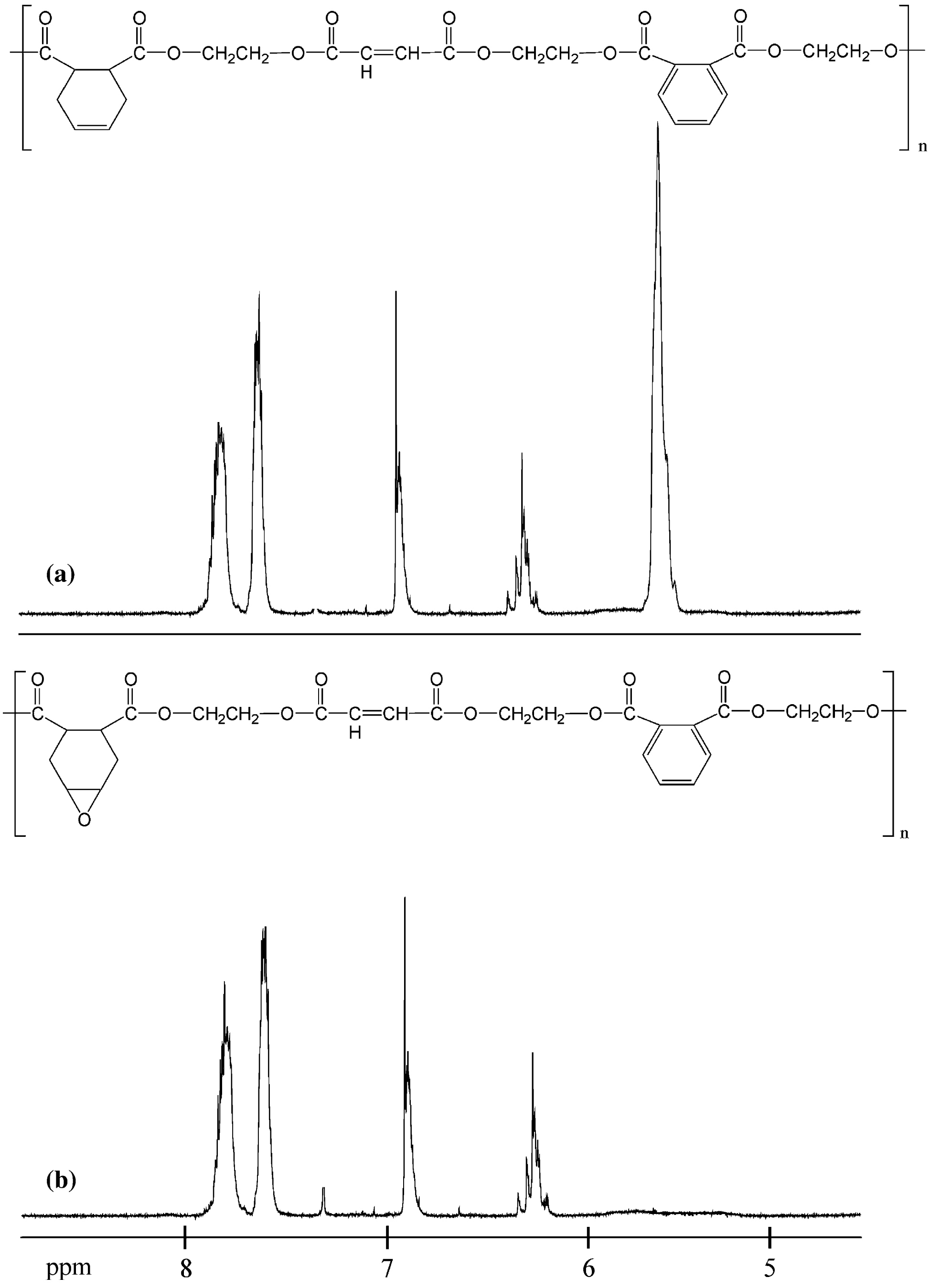

Fig. 2 ^{1}H NMR spectra of PA modified unsaturated polyester (**a**) and PA modified unsaturated epoxy polyester (**b**)

Moreover, the second exothermic peak (at T_{max} 307.3 or 272.3 °C) for the cure reaction of NADIC/PA modified unsaturated epoxy polyesters with styrene initiated by BPO was indicated. It can be attributed to the thermal curing of epoxy groups to the hydroxyl or carboxyl groups in polyester resulting in forming ether or ester linkages [20, 21]. The broad asymmetric exothermic peak was characteristic for the cure reaction of NADIC/PA modified unsaturated epoxy polyesters with styrene initiated by the mixture of BPO/THPA. The cure process was more exothermic compared to the cure reaction initiated with BPO. The ΔH values were 296.8 and 287.9 kJ mol^{-1} indicating that copolymerization process of carbon–carbon double bonds and styrene and polyaddition reaction of epoxy groups to anhydride groups happened simultaneously. Moreover, the cure reaction of NADIC/PA modified unsaturated epoxy polyesters started at lower temperatures (T_{onset}) compared to those initiated only with BPO, Tables 1 and 2. However, higher final cure temperatures (T_{end}) were observed (230.4 and 235.2 °C). This could be caused by increasing the

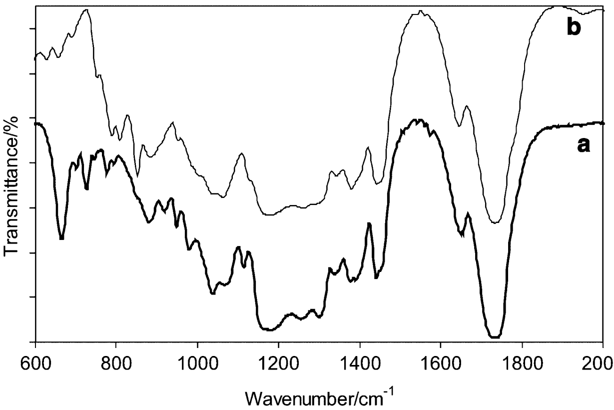

Fig. 3 IR spectra of NADIC modified unsaturated polyester (a) and NADIC modified unsaturated epoxy polyester (b)

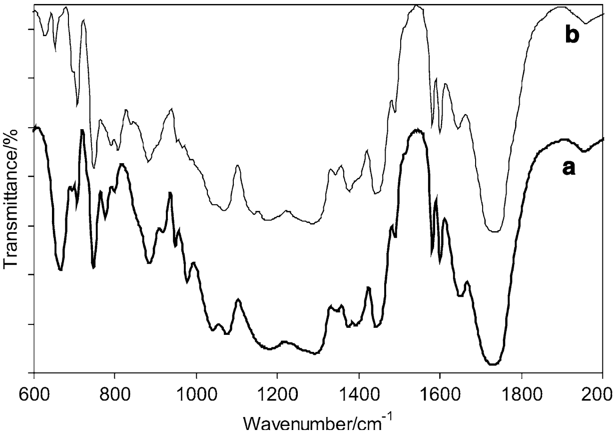

Fig. 4 IR spectra of PA modified unsaturated polyester (a) and PA modified unsaturated epoxy polyester (b)

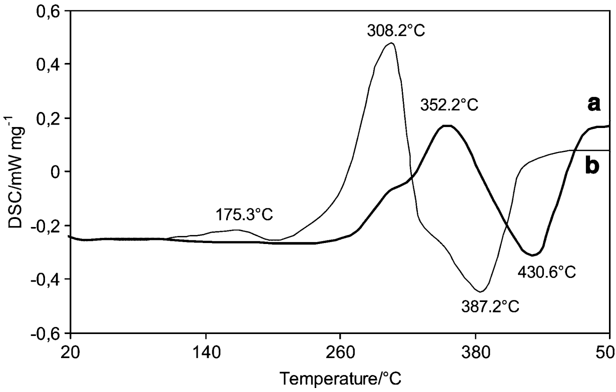

Fig. 5 DSC curves of NADIC modified unsaturated polyester (a) and NADIC modified unsaturated epoxy polyester (b)

cross-links density of the matrix as the curing process progress. So, due to the steric hindrance, the movement of reacting groups was reduced. It resulted in decreasing of

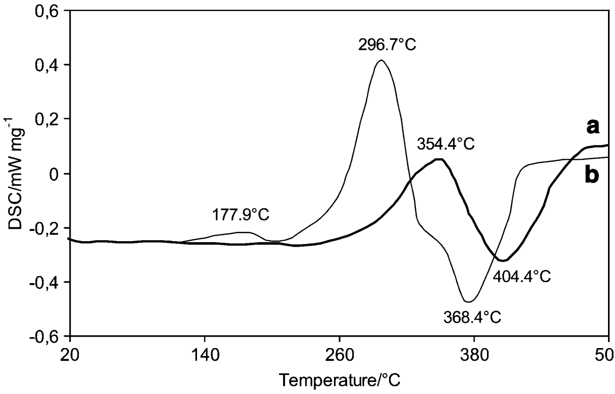

Fig. 6 DSC curves of PA modified unsaturated polyester (a) and PA modified unsaturated epoxy polyester (b)

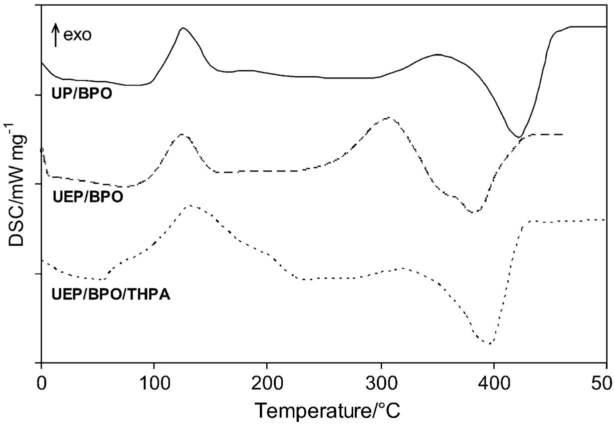

Fig. 7 DSC curves of the cure reaction of NADIC modified unsaturated polyester (UP) and epoxy polyester (UEP) with styrene initiated with BPO and BPO/THPA

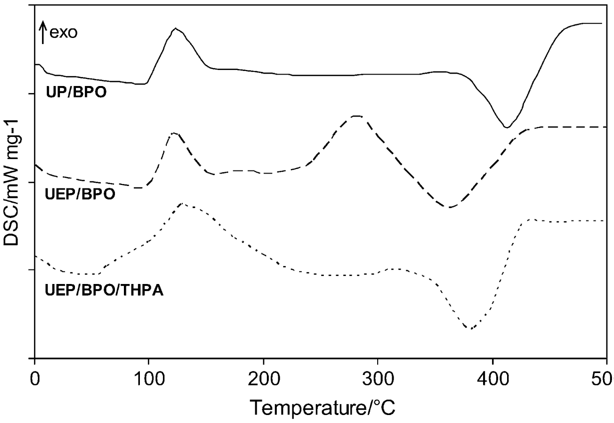

Fig. 8 DSC curves of the cure reaction of PA modified unsaturated polyester (UP) and epoxy polyester (UEP) with styrene initiated with BPO and BPO/THPA

Table 1 DSC data of the cure reaction of NADIC modified unsaturated (epoxy) polyesters with styrene

Formulation	T_{onset} (°C)	T_{max1} (°C)	T_{end} (°C)	ΔH (kJ mol^{-1})	T_{max2} (°C)	T_d (°C)	ΔH_d (kJ mol^{-1})
UP/BPO	89.4	125.3	170.2	79.0	–	420.3	173.3
UEP/BPO	76.8	124.7	174.8	75.1	307.3	380.5	–
UEP/BPO/THPA	58.4	130.2	230.4	296.8	–	400.4	202.8

Table 2 DSC data of the cure reaction of PA modified unsaturated (epoxy) polyesters with styrene

Formulation	T_{onset} (°C)	T_{max1} (°C)	T_{end} (°C)	ΔH (kJ mol^{-1})	T_{max2} (°C)	T_d (°C)	ΔH_d (kJ mol^{-1})
UP/BPO	90.8	124.2	160.5	76.0	–	408.0	158.7
UEP/BPO	75.2	120.0	168.2	72.2	272.3	362.5	–
UEP/BPO/THPA	59.3	128.4	235.2	287.9	–	383.7	187.6

Table 3 DMA data of the viscoelastic properties of styrene copolymers based on NADIC modified unsaturated (epoxy) polyesters

Formulation	E'_{20} (MPa)	$tg\delta_{max1}$	$tg\delta_{max1}$ (°C)	$tg\delta_{max2}$	$tg\delta_{max2}$ (°C)	E'_1	E'_1 (°C)	T_g (°C)
UP/BPO	1637	0.112	−59.8	1.086	57.2	−58.7	28.2	–
UEP/BPO	2193	0.035	−56.2	1.008	120.3	−60.3	100.5	80.9
UEP/BPO/THPA	3085	0.029	−57.7	0.765	138.7	−55.4	113.5	91.8

UP modified unsaturated polyester, *UEP* modified unsaturated epoxy polyester

Table 4 DMA data of the viscoelastic properties of styrene copolymers based on PA modified unsaturated (epoxy) polyesters

Formulation	E'_{20} (MPa)	$tg\delta_{max1}$	$tg\delta_{max1}$ (°C)	$tg\delta_{max2}$	$tg\delta_{max2}$ (°C)	E''_1	E''_1 (°C)	T_g (°C)
UP/BPO	1059	0.071	−54.7	1.356	48.7	−53.8	22.5	–
UEP/BPO	2085	0.032	−56.8	1.172	108.4	−57.5	87.6	71.0
UEP/BPO/THPA	2966	0.028	−57.2	0.717	129.5	−59.2	102.8	84.6

UP modified unsaturated polyester, *UEP* modified unsaturated epoxy polyester

the rate of cure process. The degradation temperatures of cured copolymers based on NADIC/PA modified unsaturated polyesters were higher (420.3 and 408.0 °C) with lower values of ΔH_d compared to those obtained based on NADIC/PA modified unsaturated epoxy polyesters. It can be connected with different type of formed linkages during the cure process. The formed additional ether and ester linkages were decomposed at lower temperatures (T_d were in the range of 362.5–400.4 °C).

Thermal properties of styrene copolymers based on NADIC/PA modified unsaturated (epoxy) polyesters

Thermal properties of styrene copolymers based on NADIC/PA modified unsaturated (epoxy) polyesters were investigated using DSC, DMA and TG analyses. The data obtained from DSC and DMA curves were presented in Tables 3 and 4. The values of storage modulus ($E'_{20\ °C}$) of fully cured styrene copolymers significantly depended on the structure of studied polyesters and used curing agent. Generally, the styrene copolymers based on NADIC modified unsaturated (epoxy) polyesters have demonstrated better thermo-mechanical properties compared to styrene copolymers based on PA modified unsaturated (epoxy) polyesters. Moreover, BPO cured styrene copolymers based on NADIC/PA modified unsaturated epoxy polyesters were characterized by higher values of storage modulus ($E'_{20\ °C}$), higher values of glass transition temperatures qualified by DSC and DMA analyses and larger rigidity of formed polymer network (lower values of

$tg\delta_{max}$) compared to BPO cured styrene copolymers based on NADIC/PA modified unsaturated polyesters. It was due to the different structure of used polyesters. As was proved, based on the study of the cure reaction by means of DSC, the copolymerization process of carbon–carbon double bonds of polyester and styrene and thermal curing process of epoxy groups for BPO cured styrene copolymers based on NADIC/PA modified unsaturated epoxy polyesters were expected. On the contrary, the copolymerization of carbon–carbon double bonds of polyester and styrene for BPO cured styrene copolymers based on NADIC/PA modified unsaturated polyesters generally happened. For that reason, the properties of styrene copolymers based on NADIC/PA modified unsaturated epoxy polyesters differed from the properties of styrene copolymers based on NADIC/PA modified unsaturated polyesters. Moreover, the improvement of examined properties for styrene copolymers based on NADIC/PA modified unsaturated epoxy polyesters cured with the use of the mixture of BPO/THPA has been observed. The additionally formed diester linkages during the reaction of epoxy groups and anhydride groups caused the production of more cross-linking network structure with more stiffness. Consequently, the amplification of storage modulus values and glass transition temperatures was indicated, Tables 3 and 4. The asymmetrical peak noted as the secondary β-relaxation [22] at lower temperatures (from −53.8 to −60.3 °C) was visible. It testified about the molecular motions of end polyester groups or motions of diester segments formed between two cross-links in cured copolymers [23, 24] (Figs. 9, 10).

The styrene copolymers based on NADIC modified unsaturated (epoxy) polyesters were generally more thermally stable (based on TG analysis) than those based on PA modified unsaturated (epoxy) polyesters. They were characterized by higher values of IDT, $T_{10\%}$, $T_{20\%}$, $T_{50\%}$ and T_k, Tables 5 and 6, respectively. Moreover, the styrene copolymers based on NADIC/PA modified unsaturated epoxy polyesters were characterized by higher thermal stability. It was connected with more cross-linked polymer networks obtained for those copolymers. The formation of additional linkages between epoxy groups or epoxy and anhydride groups were expected. The thermal degradation pattern of all styrene copolymers exhibited two separated degradation steps. The T_{max1} could indicated on ester bond breakdown in polyester or new diester segments formed during the cure process [16, 17]. The T_{max2} was probably connected with the total degradation process of styrene copolymers.

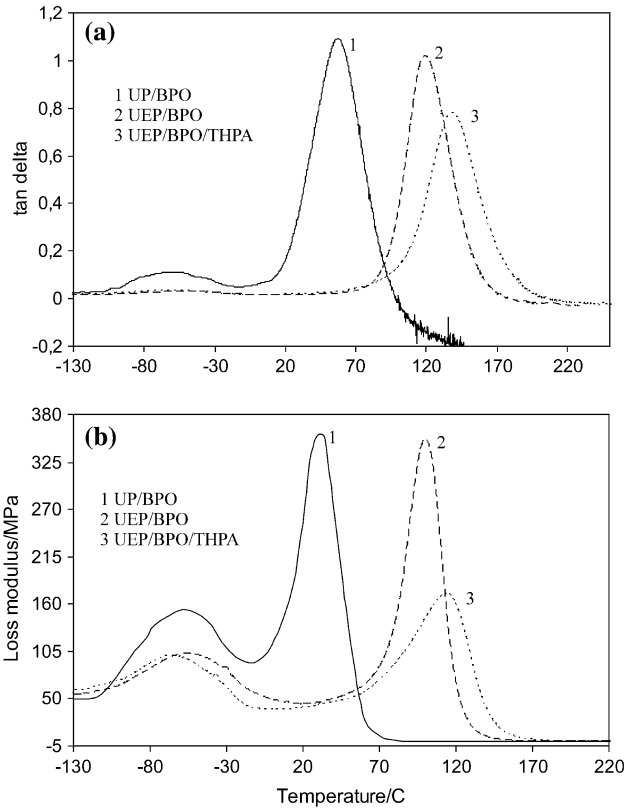

Fig. 9 Tan δ (**a**) and loss modulus (**b**) versus temperature curves for styrene copolymers based on NADIC modified unsaturated (epoxy) polyesters

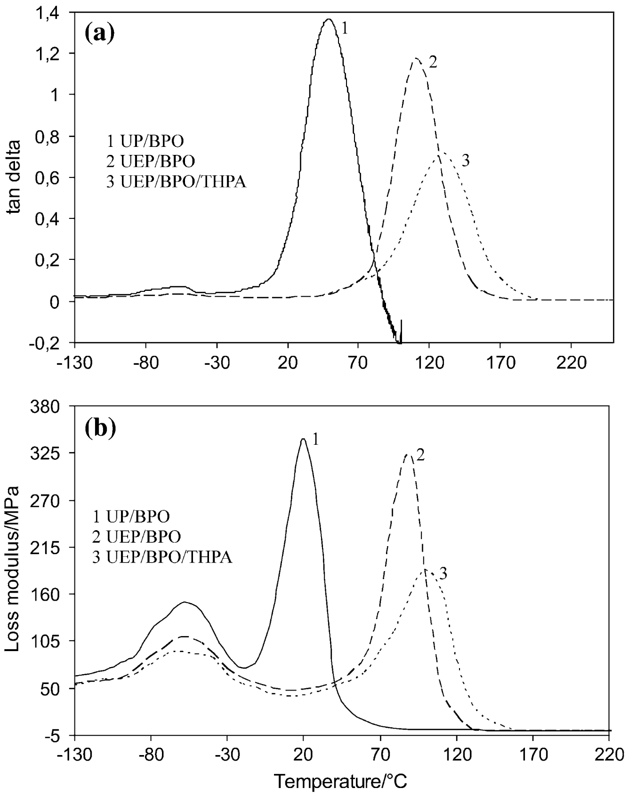

Fig. 10 Tan δ (**a**) and loss modulus (**b**) versus temperature curves for styrene copolymers based on PA modified unsaturated (epoxy) polyesters

Table 5 TG and DTG data of the thermal degradation of styrene copolymers based on NADIC modified unsaturated (epoxy) polyesters

Formulation	IDT (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_k (°C)	T_{max1} (°C)	T_{max2} (°C)
UP/BPO	235	265	315	360	595	360	555
UEP/BPO	260	285	320	360	600	360	520
UEP/BPO/THPA	270	300	325	370	620	370	520

Table 6 TG and DTG data of the thermal degradation of styrene copolymers based on PA modified unsaturated (epoxy) polyesters

Formulation	IDT (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_k (°C)	T_{max1} (°C)	T_{max2} (°C)
UP/BPO	225	250	300	360	580	360	540
UEP/BPO	250	280	310	360	595	360	520
UEP/BPO/THPA	270	300	320	365	600	370	520

Conclusions

Based on performed analyses, it was proved that both the chemical structure of polyesters and used curing agent influenced on the cure behavior and thermal properties. The cure reaction of NADIC/PA modified unsaturated epoxy polyesters with styrene initiated by the mixture of THPA/BPO was more exothermic and started at lower temperatures than those initiated with only BPO. Significantly higher values of $E'_{20\,°C}$, E'', $tg\delta_{max2}$, T_g and larger rigidity of formed polymer networks (lower values of tan δ_{max}), better thermal stability for copolymers based on NADIC/PA modified unsaturated epoxy polyesters were observed. It was connected with simultaneous copolymerization of carbon–carbon double bonds of polyester and styrene, thermal curing of epoxy groups to hydroxyl or carboxyl groups in polyester and polyaddition reaction of epoxy groups to anhydride groups. Consequently, the production of more cross-linked polymer networks for copolymers based on NADIC/PA modified unsaturated epoxy polyesters was expected.

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