Thermal and dynamic mechanical properties of IPNS formed from unsaturated polyester resin and epoxy polyester

Marta Worzakowska

Abstract The interpenetrating polymer networks (IPNs) were formed by unsaturated polyester resin (UPR) polymerized by free radical initiators: benzoyl peroxide (BPO) or cumene hydroperoxide (CHP) and epoxy polyester (EP), cured with acid anhydrides: tetrahydrophthalic anhydride (THPA) or maleic anhydride (MA). IPNs consisting 10, 30, 50, 70, 90 wt% of EP were prepared. The effect of the EP component in the IPNs and the type of curing agent on the cure behavior, thermal, and viscoelastic properties have been investigated. The results showed that both EP content and used curing system influenced on studied properties. As the EP content increased, the glass transition temperatures (T_g) also increased. Moreover, higher values of $\tan\delta_{max}$ and lower values of cross-linking density in a rubbery state (v_e) of IPNs containing higher EP content, probably due to plasticization effect of EP component were observed. Additionally, more heterogeneous network structure (higher values of the full-width at half-maximum (FWHM) as the EP content decreased was prepared. The thermal and viscoelastic properties of the blends cured with BPO/MA or CHP/MA system were considerably better than those cured with BPO/THPA or CHP/THPA. The higher stiffness, v_e, T_g and lower $\tan\delta_{max}$ values were obtained. It was probably connected with the interactions of carbon–carbon double bonds of MA with vinyl monomer (styrene), UPR and radical initiators causing to obtain more cross-linked polymer network structure. This supposition was confirmed on basis of the cure reaction monitored by DSC. The chemical interactions between two components of the blends and epoxy hardener caused that the BPO/MA or CHP/MA cure systems influenced on the cure behavior of UPR and EP components in the IPNs. The exotherm peak temperature (T_{max1}) shifted to lower values compared to these in the neat UPR whilst T_{max2} shifted to higher values than in the neat EP. However, the cure behavior of the UPR was not greatly affected by the presence of EP component when BPO/THPA or CHP/THPA cure systems were used due to the lack of chemical interactions between the components and their curatives.

Introduction

Unsaturated polyesters have been widely used as resin components for composites in the building industry, the electrical industry, as the matrix of glass fibre reinforced composites, etc. They are very popular because of their low manufacturing cost, easy processing, low densities. However, the typical unsaturated polyester resins (UPR) have some drawbacks such as polymerization shrinkage, inherent brittleness, low resistance to crack propagation due to the high degree of cross-linking [1–7]. Therefore, in recent years, the chemical modification by reactive blending of UPR and other thermosets to form interpenetrating polymer networks (IPNs) is a promising way to extend the range of properties of those thermosets and hence increase the number of applications for the polymer product in the industrial demands [8]. IPNs obtained by blending of unsaturated polyesters and epoxy resin have been extensively studied [9–11]. Unsaturated polyester–bismaleimide modified epoxy matrix systems [12], vinyl ester oligomer modified unsaturated polyester with varying percentages of

M. Worzakowska (✉)
Department of Polymer Chemistry, Faculty of Chemistry, MCS University, Gliniana 33 Street, 20-614 Lublin, Poland
e-mail: marta.worzakowska@poczta.umcs.lublin.pl; mworzako@op.pl

bismaleimide [13], unsaturated polyester–polyurethane prepolymers [14–18], unsaturated polyester–epoxidized novolac resins have been developed. Chemical bonding between elastomer and unsaturated polyester resin using methacrylate end-capped nitrile rubber or epoxy-terminated nitrile rubber or isocyanate end-capped polybutadiene [19] and IPNs based on poly(ethylene glycol) diacrylate and epoxy [20] have been also studied. IPNs are ideally compositions of two or more chemically distinct polymer networks held together exclusively by their permanent mutual entanglements [21]. They can be formed by one of two methods as sequential or simultaneous IPNs. A sequential IPN is one where the first network is formed and then swollen with a second cross-linking system, which is subsequently polymerized. The second type is the simultaneous IPN in which the two network components are polymerized together [22].

In the present study, curing behavior and thermal properties of IPNs have been studied. The unsaturated polyester resin (maleic type) and epoxy polyester (EP) prepared by oxidation of polyester based on tetrahydrophthalic anhydride and ethylene glycol by 38–40% peracetic acid [23–25] were blended. The IPNs were formed by UPR polymerized by free-radical initiators: benzoyl peroxide (BPO) or cumene hydroperoxide (CHP) and EP cured with acid anhydrides: tetrahydrophthalic anhydride (THPA) or maleic anhydride (MA). The effects of the epoxy component in the IPNs and the type of cross-linking agent on cure behavior, thermal and dynamic mechanical properties were investigated. The final properties of the cured polyesters as well as the prepared blends depended on various factors such as the nature of the curing agent, curing conditions, chemical interactions between both components, etc. Through these studies we aim to form a more detailed understanding of the chemical interactions between initiating systems, the influence of each reactant on the development of the other network and their thermal and dynamic mechanical properties. For the practical and potential applications of those materials to be successful, the knowledge of their possible interactions and properties is required.

Experimental

Materials

Unsaturated polyester prepared in polycondensation process of maleic anhydride (MA) and ethylene glycol (E.G) was dissolved in 40 wt% of vinyl monomer (styrene) to obtain the UPR. The polycondensation reaction was carried out at the molar ratio of 1 mol MA and 1.2 mol E.G in the temperature range of 150–200 °C.

Epoxy polyester (EP) was prepared in two stage process. First, the polyester containing cyclohexenyl rings in the polycondensation of tetrahydrophthalic anhydride (THPA) and E.G was obtained. The reaction was carried out at the molar ratio of 1 mol THPA and 1.2 mol E.G in the temperature range of 150–220 °C. Further chemical modification of the polyester with 38–40% peracetic acid allowed the introduction of the oxirane rings into polyester structure [23, 26]. Two different types of radical initiator were used to cure the UPR component. Benzoyl peroxide (BPO) and cumene hydroperoxide (CHP) were supplied by Fluka, Switzerland. They were used separately as initiators at a concentration of 1 wt% of the UPR component.

Tetrahydrophthalic anhydride (THPA) and maleic anhydride (MA) obtained from Merck-Schuchardt, Hohenbrunn, Germany were used to cure the EP component. The stoichiometric ratio of an anhydride r 0.85, where r was defined as anhydride/epoxy groups was applied. The epoxy value (determined by dioxane/HCl titration method) of prepared epoxy polyester was 0.3 mgKOH/g.

IPNs preparation

The unsaturated polyester resin and epoxy polyester were mixed in a 90:10; 70:30; 50:50; 30:70; 10:90 (wt%:wt%) and stirred well to give a homogeneous liquid. Then, the suitable anhydride THPA or MA was added with continuous stirring at slightly elevated temperature until a clear mixture was obtained. After cooling in cold water, the radical initiator (BPO or CHP) was added. The prepared mixtures were tested immediately after mixing by non-isothermal DSC. For thermal and viscoelastic testing, the samples were prepared as for calorimetric experiments. They were placed in a glass mould and cured in an oven at 80 °C for 5 h followed by successive post-curing at 100 °C for 5 h, at 140 °C for 5 h and finally at 180 °C for 5 h. The used post-curing procedure allowed to obtain fully cured simultaneous IPNs (based on DSC experiments, no additional curing peak was observed). Also, the neat unsaturated polyester resin cured with BPO or CHP and neat epoxy polyester cured with THPA or MA and post-cured according to the procedure employed for IPNs were studied to estimate and compare the examined properties.

Techniques

Differential scanning calorimetry (DSC) thermograms were obtained using a DSC Netzsch 204 calorimeter (Netzsch, Germany). All DSC measurements were done in aluminum pans with a pierced lid and sample weight of ∼10 mg in nitrogen atmosphere (30 mL/min). Dynamic scans were done at a heating rate of 10 K/min in the temperature range of 20–300 °C. Curing characteristic such as temperature of

the cure initiation (T_{onset}), peak maximum temperature (T_{max}), final cure temperature (T_{end}), and the heat generated during the cure reaction (ΔH) were evaluated. The glass transition temperatures-α relaxation (T_g) of fully cured samples were also determined.

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 20–1,000 °C with the sample weight of 100 mg. The initial decomposition temperature (IDT), the maximum rate of weight loss (T_{max}), and final decomposition temperature (T_k) were determined.

DMA measurements were performed using Dynamic Mechanical Analyzer (DMA) Q 800 TA Instruments (USA) provided with a dual Cantilever clamp with a support span of 35 mm. Runs with a frequency at 10 Hz were performed at a constant heating rate of 4 °C/min over the temperature ranges from −135 °C to 270 °C until the sample become soft to be tested. A rectangular specimen was used ($35 \times 10 \times 4$ mm). Viscoelastic properties of the fully cured materials were estimated from the changes of storage modulus (E'), mechanical loss (E'') as well as from the changes of tanδ at constant frequency depending on temperature. The T_g was identified as the maximum of the tanδ. From the tanδ curves also the full-width at half-maximum (FWHM) and cross-linking density (ν_e) were determined.

Results and discussion

Curing behavior of IPNs

The simultaneous IPNs were prepared by mixing two components together (UPR and EP) with their curatives and were studied by non-isothermal DSC. IPNs consisting 10, 30, 50, 70, 90 wt% of epoxy polyester were prepared.

The neat UPR component in the blends were polymerized by two types of free-radical initiators—benzoyl peroxide (BPO) and cumene hydroperoxide (CHP), Scheme 1. The neat EP component in the blends was cured using acid anhydrides: tetrahydrophthalic anhydride (THPA), Scheme 2 and maleic anhydride (MA), respectively. The effect of the epoxy component in the IPNs as well as the type of cross-linking agent on the cure behavior was studied. The DSC curves of the cure reaction of BPO initiated neat UPR, THPA cured neat EP as well as BPO/THPA cured blends were shown in Fig. 1. The cure reaction of UPR initiated by BPO exhibited a sharp single exotherm at 113.0 °C, which was associated with the chain-growth copolymerization process of carbon–carbon double bonds in polyester chain and vinyl monomer–styrene [26, 27]. Similarly, the cure reaction of EP with THPA was represented by one, broad, asymmetrical peak at 194.6 °C. The presence of these peaks could be attributed to polyaddition reaction of epoxy groups to anhydride groups [28, 29]. The DSC curves of the cure reaction of the blends appeared to show two non-entirely divided exothermic peaks. Based on the close correspondence of peak temperatures in the neat and blended systems the existence of two exotherms can be attributed in part to the UPR and EP component cure. The curing exotherm peak of UPR was shifted to a bit higher temperatures, particularly for the blends consisting above 50 wt% of EP component (50:50 and 30:70 UPR:EP), than in the parent resin. It was possibly due to dilution of the reactants by the other component which therefore reduced the cure reaction rates and raised the temperature peak of UPR [30, 31]. The similarity of the cure behavior of the UPR and EP components in the blends and in the neat resins suggested that the curing mechanism of each component was not greatly affected by the presence of the other, probably due to the lack of chemical interactions between the components of the parent resins. The overall heat of polymerization (ΔH)
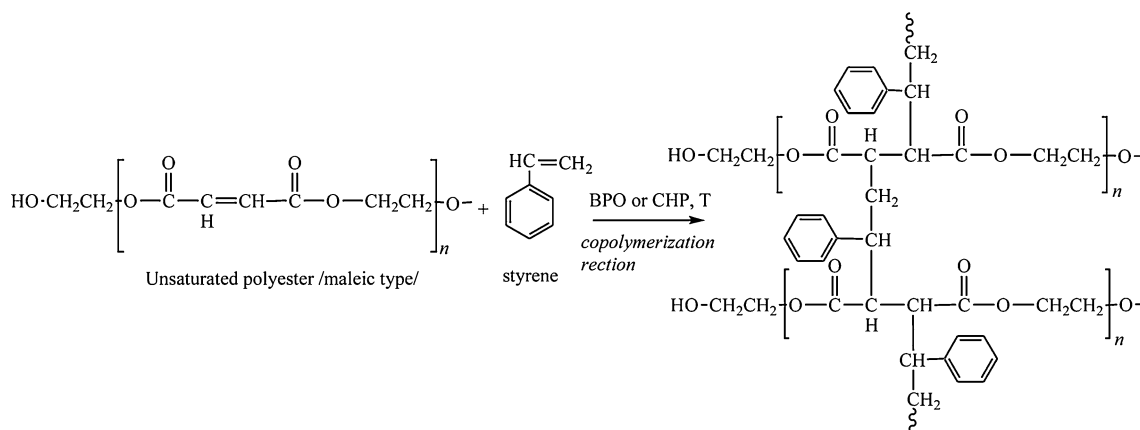
Scheme 1 Structures of unsaturated polyester (UP), styrene and their copolymerization product
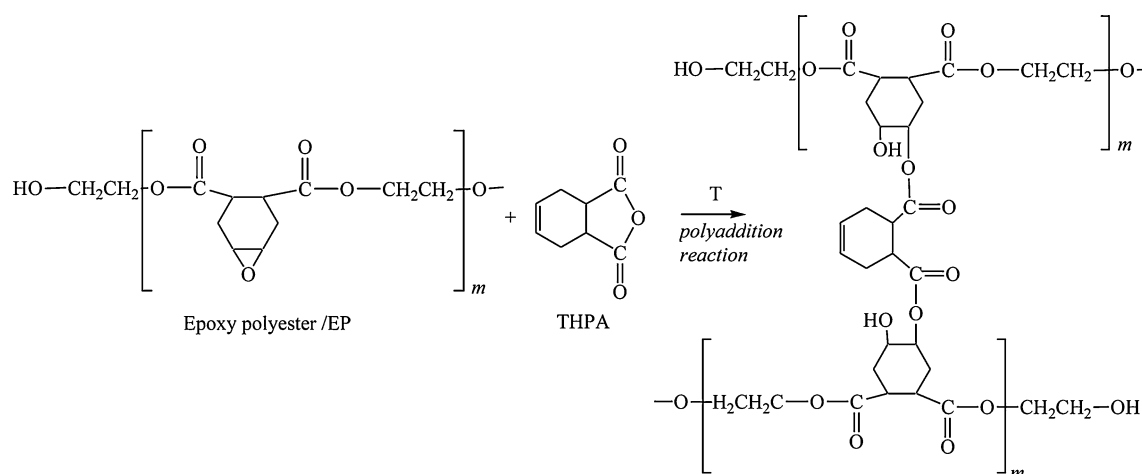
Scheme 2 Structures of epoxy polyester (EP), tetrahydrophthalic anhydride (THPA) and their cured product
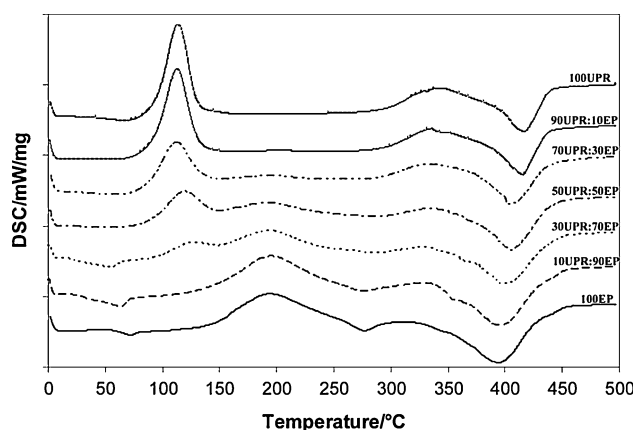

Fig. 1 DSC curves of the BPO/THPA cure reaction of the blends, BPO cure reaction of UPR and THPA cure reaction of EP

associated with the peaks in the IPN were approximately proportional to the weight fractions of UPR and EP components in the IPN. As shown in Table 1, the total polymerization heat for the 90:10, 70:30, 50:50, 30:70 and 10:90 blends of UPR/BPO:EP/THPA were 207.7, 220.5, 226.8, 240.7 and 249.5 kJ/mol, respectively. They were comparable with the weighted averages of the ΔH values for individual components of 200.0, 211.9, 223.9, 235.8, and 247.8 kJ/mol, respectively. It could suggest that blending had not impaired the curing ability of each component. The curing reaction of neat UPR with BPO was more exothermic (higher ΔH values) and happened at relatively lower temperatures (lower values of T_{onset}, T_{max}, and T_{end}) compared to these initiated with CHP. Probably, relatively lower temperature of thermal decomposition of BPO to radicals compared to decomposition temperature of CHP caused the accelerating effect and increasing the rate of cure of UPR. Similarly, for the 50:50 blends of UPR/BPO:EP/THPA the exothermic peak indicating the copolymerization process of UPR and styrene at lower

temperatures (119.9 °C) compared to UPR/CHP:EP/THPA (137.3 °C) was observed. The second exothermic epoxy peak occurred at similar temperatures independently of used radical initiator. It indicated that the cure reaction of epoxy component in the blends was not affected by the presence of other component and used radical initiator.

The use of polymerizable acid anhydride—maleic anhydride (MA)—as a hardener of epoxy component in the blends caused the considerable decrease of T_{max1} and increase of T_{max2} values compared to those obtained when non-polymerizable acid anhydride—THPA—was applied. The exothermic UPR peak in the blends had significantly lower values than in the neat resin cured with BPO or CHP. It could be attributed to the simultaneous copolymerization of the carbon–carbon double bonds of polyester and styrene and additional copolymerization of carbon–carbon double bonds of maleic anhydride with styrene or carbon–carbon double bonds of polyester, Scheme 3. Those interactions might accelerate the rate of the cure reaction of UPR causing the significant change in viscosity of the blends, which influenced the curing behavior of the second component (EP). The developing skeletal structure of UPR network with additional connections through MA double bonds might exert a topological restraint on the development of the other EP network due to steric hindrance. The reduction of chain mobility of maleic anhydride groups might cause the decrease of the reaction rate of EP component. In this way, the cure of EP component happened at significantly higher temperature (191.6 and 206.5 °C) than in the parent resin (159.7 °C). The IPNs formed using radical initiator and maleic anhydride probably showed complex cure behavior due in part to reactions of epoxy hardener with UPR, styrene and radical initiators. It led to obtain more cross-linked polymer network where the epoxy hardener had considerably influence on UPR component, their curatives and indirectly on the EP component. The

Table 1 Data obtained from DSC curves of the BPO/THPA cure reaction of the blends, BPO cure reaction of UPR and THPA cure reaction of EP

Composition	Curing agent	T_{onset}/°C	T_{max1}/°C	T_{max2}/°C	T_{end}/°C	ΔH/J/g	T_d/°C	ΔH_d/J/g
100UPR	BPO	68.5	113.0	–	169.4	193.9	415.9	160.6
90UPR:10EP	BPO/THPA	60.2	112.3	190.0	230.6	207.7	415.4	176.0
70UPR:30EP	BPO/THPA	57.8	112.3	189.8	247.5	220.5	405.2	188.7
50UPR:50EP	BPO/THPA	62.5	119.9	189.5	267.3	226.8	402.3	191.6
30UPR:70EP	BPO/THPA	54.2	128.4	193.2	275.3	240.7	400.1	200.5
10UPR:90EP	BPO/THPA	62.8	194.7	–	278.5	249.5	394.7	241.3
100EP	THPA	72.5	194.6	–	283.4	253.8	394.4	243.2
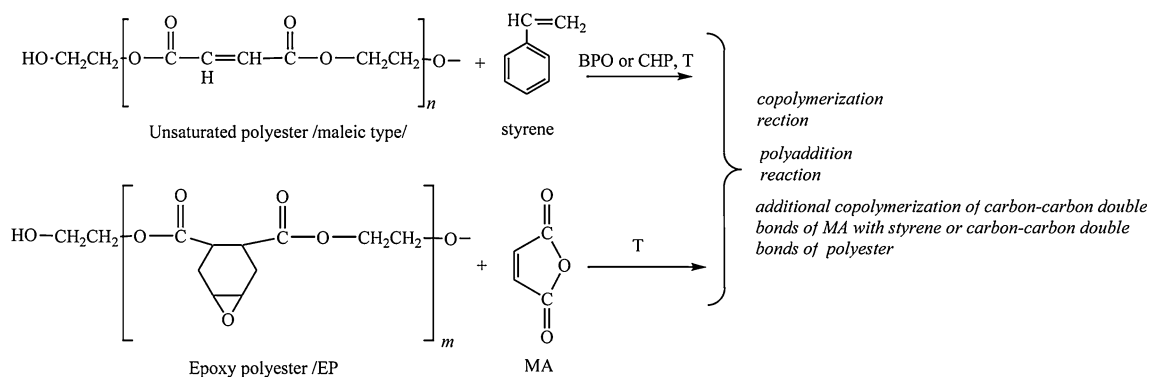
Scheme 3 The scheme of possible cure reactions of the UPR/EP blends initiated by BPO/MA or CHP/MA system

chemical connections between two components of the blends and polymerizable epoxy hardener were suspected.

The lower initial temperatures (T_{onset}) for the cure reaction of the blends compared to those for the neat UPR were observed. However, the end cure temperatures (T_{end}) were higher for the cure reaction of the blends (Tables 1 and 2). This could be caused by increasing the cross-links density of the matrix as the curing process progressed. So, due to the steric hindrance, the movement of reacting groups was reduced which resulted in decreasing of the rate of cure process.

The degradation temperatures (T_d) of IPNs were lower compared to those obtained for neat UPR. The decrease of T_d with the increasing weight fraction of EP was indicated. It can be connected with different type of formed linkages during the cure process. The formed additional ether and ester linkages were probably decomposed at lower temperature than other bonds in formed networks.

Dynamic mechanical properties

The storage modulus (E') in the function of temperature for neat UPR, neat EP, and obtained IPNs consisting of 10, 30, 50, 70, 90 wt% of epoxy polyester were presented in Fig. 2. As can be seen there was no indication of additional post-curing reaction during the temperature scan.

The changes of storage modulus from a glassy state to the rubbery state were clearly observed for all studied blends as well as the neat resins. The E' uniformly decreased as the temperature increased over the range of temperature investigated. The largest changes of E' values in the temperature range of 0–150 °C were observed. Moreover, below T_g the storage modulus imperceptibly decreased with EP content up to 30 wt% in the blends, which may be the result of plasticization effect of EP component. At higher concentrations of EP (above 30 wt%), E' in a glassy state increased regularly with EP content. It may be the result of additionally formed diester linkages during the reaction of epoxy groups and anhydride groups which consequently caused the production of a more stiff network structure of the blends in a glassy state. The higher content of EP acted as reinforcement to the blends. However, above T_g lower values of the storage modulus for all studied blends than those of the neat UPR were observed. This could be due to lower cross-linking density of polymer network of the blends in a rubbery region. To confirm those observations, the cross-linking density (v_e) for the obtained networks was calculated (Table 3). The cross-linking density was calculated by applying the equation derived from the theory of rubber elasticity: $E' = 3 v_e RT$, where E' is the storage modulus in the rubbery plateau region, R is a gas constant, and T is the absolute

Table 2 Data obtained from DSC curves of the cure reaction of the blends containing 50:50 wt% UPR:EP with different hardener systems, CHP cure reaction of UPR and MA cure reaction of EP

Composition	Curing agent	T_{onset}/°C	T_{max1}/°C	T_{max2}/°C	T_{end}/°C	ΔH/J/g	T_d/°C	ΔH_d/J/g
100UPR	CHP	75.2	134.6	–	225.4	180.5	412.3	134.3
50UPR:50EP	CHP/THPA	70.3	137.3	188.7	252.2	221.2	400.5	178.1
50UPR:50EP	BPO/THPA	62.5	119.9	189.5	267.3	226.8	402.3	191.6
50UPR:50EP	CHP/MA	58.5	123.1	196.1	240.5	204.6	400.2	186.9
50UPR:50EP	BPO/MA	50.3	91.4	206.5	248.6	205.6	400.8	193.5
100EP	MA	70.3	159.7	–	262.4	203.3	393.8	251.3
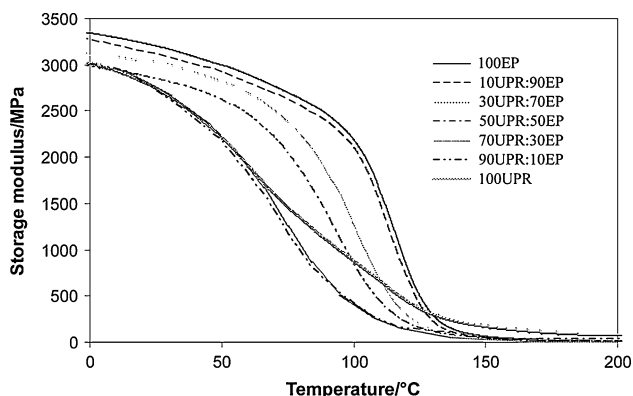
Fig. 2 Storage modulus (E') versus temperature of the BPO/THPA cured IPNs, BPO cured UPR and THPA cured EP

temperature [32–35]. Moreover, the molecular weight between cross-links in the polymer network increased when the cross-linking density decreased [36]. As was expected, higher cross-linking density values with consistently lower molecular weight between cross-links for the neat UPR cured with BPO (8.58×10^{-3}) were obtained. The addition of 10 wt% of EP to the blends caused the considerable decreasing of the cross-linking density of formed IPN (3.88×10^{-3}). Additionally, it can be seen from Table 3, that the cross-linking density (v_e) decreased regularly with EP content in the blends. In a rubbery state, the lowering of cross-linking density and the plasticization effect of EP component led to decrease in the storage modulus.

Figure 3 illustrated the tanδ from dynamic mechanical analysis of BPO cured UPR, THPA cured EP, as well as BPO/THPA cured blends with different weight fractions of UPR and EP components, respectively. Two distinct transition peaks (tanδ_{max1} and tanδ_{max2}) of the IPNs and neat UPR and neat EP were observed. The first, asymmetrical peak at lower temperatures was noted as the secondary β-relaxation [37] and might testify about the molecular motions of the end polyester groups or motions of the segments formed between two cross-links in cured UPR, EP and IPNs [38, 39]. The second tanδ peak was slightly shifted to higher temperatures with increasing EP concentration in the IPNs but remained close to that of the pure components. More changes of the glass transition temperature (T_g) were visible based on performed DSC analysis. T_g increased with the EP content in the blends, but T_g values did not exceed temperature characteristic for the neat EP. The values were in the range of 45.8–99.3 °C (Table 3). The differences in T_g may be explained by the copolymerization effect which was a result of merely changing the fractions and types of the components that were copolymerized [40, 41]. Moreover, the existence of single composition-dependent T_g intermediate between those of the pure components suggested that prepared blends were homogeneous in the amorphous phase [42].

The α-relaxation peak height associated with molecular mobility, increased for obtained IPNs with the increase of EP content. The molecular mobility of those blends was less restricted, higher values of tanδ_{max} were obtained. This behavior was connected with lower rigidity of polymer

Table 3 Data obtained from DMA and DSC curves of the BPO/THPA cured IPNs, BPO cured UPR and THPA cured EP

| Composition	Curing agent	tgδ_{max1}/°C	tgδ_{max2}	tgδ_{max2}/°C	E''_2/°C	T_g/°C	FWHM/°C	v_e/mol/cm³ $\times 10^{-3}$
100UPR	BPO	−56.6	0.235	126.3	66.0	50.3	81	8.58
90UPR:10EP	BPO/THPA	−55.9	0.351	120.5	56.2	45.8	68	3.88
70UPR:30EP	BPO/THPA	−53.9	0.386	122.1	74.8	62.3	63	2.96
50UPR:50EP	BPO/THPA	−53.0	0.422	124.1	94.6	70.0	62	2.70
30UPR:70EP	BPO/THPA	−52.4	0.531	125.7	103.1	84.7	54	2.12
10UPR:90EP	BPO/THPA	−50.4	0.576	131.3	115.7	99.3	44	1.72
100EP	THPA	−46.6	0.667	132.2	117.1	101.8	44	1.20
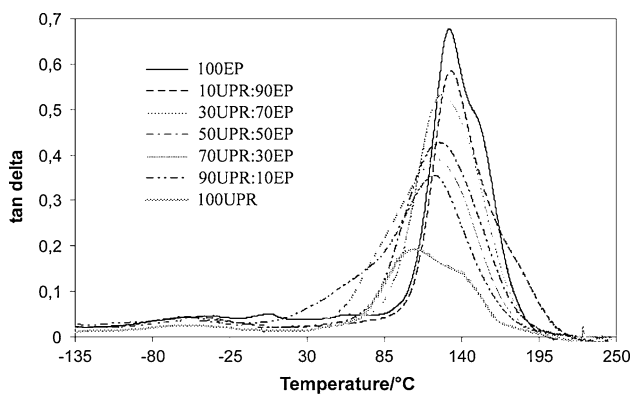
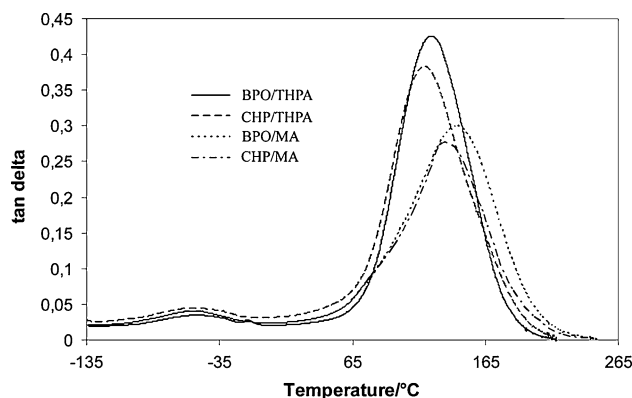**Fig. 3** Tanδ versus temperature of the BPO/THPA cured IPNs, BPO cured UPR and THPA cured EP

Fig. 4 Tanδ versus temperature for obtained IPNs containing of 50:50wt% UPR:EP cured with different hardener system

network formed when higher weight fractions of EP component were used. There was clear relationship between cross-linking density and molecular mobility. The blends with lower cross-linking density were characterized by higher molecular mobility of created polymer network.

The width of the tanδ curves was connected with the degree of structural heterogeneity of polymer networks. The broader the tanδ peak implied a more heterogeneous polymer network with a wide distribution of relaxation times [43–46]. More homogeneous network structures were obtained for blends containing more EP component, the lowest values of the peak width of tanδ (FWHM) were observed. The heterogeneity of the polymer networks considerably increased for IPNs formed with lower weight fractions of EP component. The formation of microgels in the blends containing more UPR and consequently more styrene could be responsible for the evolution of more heterogeneous network structure.

The 50:50 wt% UPR:EP blends cured with CHP were characterized by higher cross-linking density and lower molecular mobility of polymer chains compared to those values obtained for BPO cured blends (Table 4, Fig. 4). It could suggest that a more stiff network structure for blends cured with CHP was obtained. Similarly, the use of MA in place of THPA allowed obtaining more cross-linked polymer networks of the blends. Such blends were

characterized by higher stiffness, cross-linking density, lower values of tanδ_max, and higher values of glass transition temperature. The free-radical copolymerization of the double bonds of unsaturated polyester and styrene, additional copolymerization of MA carbon–carbon double bonds and styrene or unsaturated polyester and polyaddition reaction of maleic anhydride groups to epoxy groups in EP were expected.

Thermogravimetric analysis

Thermogravimetric analysis (TG) of obtained IPNs as well as the neat resins was performed in the temperature range of 20–1,000°C in air. The data obtained from TG and DTG curves were presented in Tables 5 and 6. It can be seen that the neat UPR and the neat EP as well as all the blends exhibited a two-step weight loss mechanism (T_{max1} and T_{max2}). The first maximum decomposition temperature peak (T_{max1}) observed at 365–375 °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 [47, 48]. The second degradation peak (T_{max2}) at 530–550 °C could be associated with the degradation process of other bonds. The TG curves indicated that BPO or CHP cured UPR was characterized by higher thermal stability than BPO/THPA

Table 4 Data obtained from DMA and DSC curves for obtained IPNs containing of 50:50 wt% UPR:EP cured with different hardener system, CHP cured UPR and MA cured EP

Composition	Curing agent	tgδ_max1/°C	tgδ_max2	tgδ_max2/°C	E''_2/°C	T_g/°C	FWHM/°C	v_e/mol/cm³ × 10⁻³
100UPR	CHP	−55.8	0.210	120.3	60.5	52.4	78	7.98
50UPR:50EP	CHP/THPA	−57.0	0.381	118.8	89.7	69.4	63	3.57
50UPR:50EP	BPO/THPA	−53.0	0.422	124.1	94.6	70.0	62	2.70
50UPR:50EP	CHP/MA	−51.4	0.280	133.2	92.4	78.9	75	4.87
50UPR:50EP	BPO/MA	−50.2	0.302	146.0	96.6	80.5	72	4.51
100EP	MA	−51.6	0.315	168.6	135.3	128.0	50	2.84

Table 5 Data obtained from TG and DTG curves of the BPO/THPA cured IPNs, BPO cured UPR and THPA cured EP

Composition	Curing agent	IDT/°C	T_{max1}/°C	T_{max2}/°C	T_k/°C
100UPR	BPO	285	375	550	650
90UPR:10EP	BPO/THPA	275	375	545	640
70UPR:30EP	BPO/THPA	270	370	540	630
50UPR:50EP	BPO/THPA	270	370	540	630
30UPR:70EP	BPO/THPA	265	375	540	620
10UPR:90EP	BPO/THPA	270	365	530	620
100EP	THPA	270	370	530	620

Table 6 Data obtained from TG and DTG curves for obtained IPNs containing of 50:50 wt% UPR:EP cured with different hardener system, CHP cured UPR and MA cured EP

Composition	Curing agent	IDT/°C	T_{max1}/°C	T_{max2}/°C	T_k/°C
100UPR	CHP	285	365	550	645
50UPR:50EP	CHP/THPA	275	370	535	630
50UPR:50EP	BPO/THPA	270	370	540	630
50UPR:50EP	CHP/MA	295	365	540	650
50UPR:50EP	BPO/MA	300	375	540	650
100EP	MA	290	375	535	640

or CHP/THPA cured blends. The higher values of initial decomposition temperature (IDT) and final decomposition temperature (T_k) were observed. It could be connected with more cross-linked polymer network obtained for BPO or CHP cured UPR. Moreover, the IDT and T_k values were comparable for all prepared blends. Only, the BPO/MA or CHP/MA cured blends exhibited higher values which were connected with additional cure reaction of MA double bonds with styrene or unsaturated polyester which led to more cross-linked polymer network. Imperceptibly, higher T_k values for blends containing lower concentrations of EP component were observed (Table 5). Based on TG analysis, it can be considered that no dramatic change of thermal stability for prepared blends was observed.

Conclusions

The polymerization behavior, thermal, and viscoelastic properties of IPNs formed from radically initiated unsaturated polyester resin (maleic type) (UPR) and acid anhydride-cured EP as well as the neat UPR and EP have been studied by non-isothermal DSC, DMA, and TG analyses. The IPNs consisting of 10, 30, 50, 70, 90 wt% of epoxy polyester component were prepared. The effect of the epoxy component in the IPNs and the type of cross-linking agent on characteristic cure temperatures: T_{onset}, T_{max}, T_{end}, the heat generated during cure (ΔH), glass transition temperature (T_g), initial decomposition temperature (IDT),

final decomposition temperature (T_k), storage modulus (E'), loss modulus (E''), $\tan\delta_{max}$, full-width at half-maximum (FWHM) and cross-linking density (v_e) have been investigated. It was found that both EP content and used curing system influenced on examined properties. The DSC studies showed the similarity of the cure behavior of the UPR and EP components in IPNs and in the neat resins suggested that the curing mechanism of each component was not greatly affected by the presence of the other. It was probably due to the lack of chemical interactions between the components of the parent resins when BPO/THPA or CHP/THPA cure systems were applied. The ΔH values were dependent on the EP content in the blends and were comparable with the weighted averages of the ΔH values for individual components. It suggested that blending had not impaired the curing ability of each component. The use of BPO/MA or CHP/MA systems in place of BPO/THPA or CHP/THPA systems as hardeners of the blends caused the considerable decrease of T_{max1} but increase of T_{max2} values, probably due to the chemical connections between two components of the blends and epoxy hardener. The interactions of double bonds of MA and styrene, UPR and radical initiator might accelerate the rate of the cure reaction of UPR component causing the significant change in viscosity of the IPN which influenced the curing behavior of second component (EP). The thermal and viscoelastic properties of fully cured blends showed that the glass transition temperatures increased with EP content in the blends. Moreover, lower rigidity (higher values of $\tan\delta$) and lower v_e values of IPNs containing more EP content have been observed. It could be connected with plasticization effect of EP component. Additionally, more heterogeneous IPN network structures were prepared when EP content decreased (higher FWHM values). The use of BPO/MA or CHP/MA curing systems allowed to obtain more cross-linked polymer networks compared to those cured with BPO/THPA or CHP/THPA systems. The higher stiffness, cross-linking density, glass transition temperature and lower $\tan\delta_{max}$ values were received. Moreover, thermal behavior of the blends and the neat resins were comparable indicated on the two-step weight loss mechanism associated with ester and carbon–carbon bonds breakdown.

References

1. Burns R (1982) Polyester molding compounds. Marcel Dekker, New York
2. Lubin G (ed) (1969) Handbook of fiber glass and advanced plastics composites. Van Nostrand Reinhold, New York
3. Riew CK, Gillham K (eds) (1984) Rubber modified thermoset resins. Advances in chemical science. American Chemical Society, Washington DC, p 208
4. Paul DR, Newman S (eds) (1978) Polymer blends, vol 2. Academic Press, New York

5. Qipeng G, Haifeng Z, Sixun Z, Yongli M, Wei Z (1999) J Mater Sci 34:123. doi:10.1023/A:1004486129169
6. Mouritz AP, Mathys Z (1999) Compos Struct 47:643
7. Egglestone GT, Turley DM (1994) Fire Matter 18:255
8. Lubin G (ed) (1982) Handbook of composites. Van Nostrand, New York, p 17
9. Liu M-S, Liu Ch-Ch, Lee Ch-T (1999) J Appl Polym Sci 72:585
10. Shaker ZG, Browne RM, Stretz HA, Cassidy PE, Blanda MT (2002) J Appl Polym Sci 84:2283
11. Park SJ, Park WB, Lee JR (1999) Polym J 31:28
12. Dinakaran K, Alagar M (2002) J Appl Polym Sci 85:2853
13. Dinakaran K, Alagar M (2002) J Appl Polym Sci 86:2502
14. Chou YC, Lee LJ (1994) Polym Eng Sci 34:1239
15. Ludovic V, Hsu Ch-P (1999) Polymer 40:2059
16. Xu MX, Xiao JS, Zhang WH, Yao KD (1994) J Appl Polym Sci 54:1659
17. Xu MX, Liu WG, Guan YL, Bi ZP, DeYao K (1995) Polymer Int 38:205
18. Benny CA, Abraham Beena T, Thomas TE (2006) J Appl Polym Sci 100:449
19. Suspene L, Show Yang Y, Pascault J-P (1993) In: Keith Riew C, Kinloch AJ (eds) Rubber toughened plastics. Advances in chemistry. American Chemical Society, Washington, DC, p 168
20. Lin MS, Jeng KT, Huang KY, Shin YF (1993) J Polym Sci Polym Chem Ed 31:3317
21. Sperling LH, Mishra V (1995) Polym Adv Technol 7:197
22. Dean K, Cook WD, Zipper MD, Burchill P (2001) Polymer 42:1345
23. Worzakowska M (2008) J Therm Anal Calorim 93:799
24. Penczek P, Bończa-Tomaszewski Z, Bańkowska A (2002) Macromol Symp 187:243
25. Bończa-Tomaszewski Z, Penczek P, Bańkowska A (2006) Surf Coat Int B Coat Trans 89:157
26. Worzakowska M (2008) J Appl Polym Sci 110:3582
27. Yang H, Lee J (2000) J Appl Polym Sci 79:1230
28. Stevens GC (1981) J Appl Polym Sci 26:4256
29. Park WH, Lee JK, Kwan KI (1996) Polym J 28:407
30. Yang YS, Lee LJ (1987) Macromolecules 20:1490
31. Jin SR, Widmaier JM, Meyer GC (1988) Polymer 29:346
32. Ward IM (1971) Mechanical properties of solid polymer. John Wiley& Sons, London, p 77
33. Tobolsky AV, Carlson DW, Indicator NJ (1961) J Polym Sci 54:175
34. Charlesworth JM (1988) Polym Eng Sci 28:230
35. Treloar LRG (1958) The physics of rubber elasticity. Oxford University Press, London
36. Elliot JE, Nie J, Bowman CN (2002) Polymer 44:327
37. Barral L, Cano J, López J, López-Bueno I, Nogueira P, Abad MJ, Ramirez C (2000) J Therm Anal Cal 60:391
38. Shimbo M, Ochi M, Iesako H (1984) J Polym Sci Polym Phys Edn 22:1461
39. Ochi M, Iesako H, Nakajima S, Shimbo M (1984) J Polym Sci Polym Phys Edn 24:251
40. Fox TG, Loshaek S (1955) J Polym Sci 15:371
41. Bicerano J, Sammler RL, Carriere CJ, Seitz JT (1996) J Polym Sci B: Polym Phys 34:2247
42. Zheng H, Zheng S, Guo Q (1997) J Polym Sci Polym Chem Ed 35:3161
43. Cook WD, Forsythe JS, Scott TF, Quay-Thevenon S (2004) J Appl Polym Sci 93:1348
44. Simon GP, Allen PEM, Wiliams DRG, Cook WD (1991) Polymer 32:2577
45. Allen PEM, Wiliams DRG, Clayton AB (1994) Eur Polym J 30:427
46. Kannurpatti AR, Anseth JW, Bowman CN (1998) Polymer 39:2507
47. Park WH, Lenz RW, Goodwin S (1999) Polym Degrad Stabil 63:287
48. Grassie N, Murry EJ, Holmes PA (1984) Polym Degrad Stabil 6:95