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Curing reaction of unsaturated (epoxy) polyesters based on different aliphatic glycols

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Abstract The cure behavior of the unsaturated (epoxy) polyesters based on different aliphatic glycols with styrene initiated by various types of organic peroxides or the mixture of an acid anhydride/organic peroxide has been studied by means of differential scanning calorimetry. unsaturated polyesters (UP) prepared from cyclohex-4-ene-1,2-dicarboxylic anhydride, maleic anhydride, and suitable aliphatic glycol: ethylene glycol or 1,4-butanediol or 1,6-hexanediol and unsaturated epoxy polyesters (UEP) obtained by chemical modification of UP were dissolved in vinyl monomer (styrene). The styrene solutions of polyesters were subjected to the cure reaction with suitable curing agent. The different organic peroxides: diacyl peroxide: benzoyl peroxide (BPO), dialkyl peroxide: dicumyl peroxide (DCP), and alkyl hydroperoxide: cumene hydroperoxide (CHP) were used. In addition, to cure the UEP, the mixture of the stoichiometric ratio of an acid anhydride (tetrahydrophthalic anhydride or hexahydrophthalic anhydride)/organic peroxide were applied. The 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) were evaluated. It has been found that the course of the cure reaction of studied polyesters with styrene significantly depended on their structure and used initiating system. The presence of both carbon–carbon double bonds and epoxy groups in polyester backbone led to obtain more cross-linked materials where the copolymerization, thermal curing of epoxy groups with hydroxyl or carboxyl groups and polyaddition reaction of epoxy to anhydride groups have been expected. The use of BPO allowed to cure the polyesters at relatively lower temperatures with higher exothermic effect compared to DCP and CHP which was directly connected with lower thermal stability and significant higher ΔH values obtained during decomposition of diacyl peroxide used. In addition, the curing exotherm peak of polyesters based on glycol containing more $–CH_2–$ units with styrene was shifted to a bit higher temperatures which was probably due to lower molecular mobility of polyester's chain caused the production of less stiff network structure.

Keywords Unsaturated polyester · Unsaturated epoxy polyester · DSC · Radical initiators · Cure reactions

Introduction

The cure of thermoset resins like unsaturated polyester resin (UPR) or epoxy resin, in general is complete transformation from liquid to gel, to rubber, to glass formed a rigid cross-linked molecular structure that occurs as a result of cure reaction with suitable hardener [1]. The curing reaction is highly exothermal and can be easily monitored by DSC, a conventional one of the experimental techniques in the determination of the heat of reaction, kinetics, and mechanism of curing process [2, 3]. The curing of an UPR is a free radical chain-growth copolymerization between the low molecular weight vinyl monomer, e.g., styrene, methyl met(acrylate), divinylbenzene, etc., which acts as cross-linking agent and the unsaturated double bonds of the α, β acid residues along the repeat unit of the polyester chain [4, 5]. To induce the cure of UPR, the suitable initiating system is needed. The various types of organic compounds are commonly used as initiators. Generally,

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they have specific types of covalent bonds: oxygen–oxygen, oxygen–nitrogen, or sulfur–sulfur bonds. The most useful compounds used to cure the UP resins are organic peroxides such as ketone or alkyl hydroperoxides, diacyl or dialkyl peroxides. Free radicals can be formed by homolytic decomposition of covalent peroxide bonds by energy absorption at elevated temperatures or electron transfer from ions or atoms containing unpaired electrons followed by bond dissociation in the acceptor molecule in ambient temperature applications [6–8].

On the contrary, other thermosets: epoxy resins due to the presence of epoxy groups can be cured with a number of nucleophilic and electrophilic reagents. Amongst the curing agents of greatest technological importance are polycarboxylic acid anhydrides, amines, and imidazoles [9]. The cross-linking reaction with di- or polycarboxylic acid anhydrides is based on the reaction of epoxy group with acid anhydride group to produce ester linkages (hydroxylalkyl esters) via an ionic mechanism. The reaction of acid anhydrides with epoxides often require the presence of a basic catalyst, activator, or temperatures above 120–180 °C, because the uncatalysed reaction at room temperature is very slow. In addition to the ester-forming reaction, in the presence of catalytic activation of carboxylic acids at higher temperatures, the formation of ether linkages (polyether linkages) is observed [10–12].

This work presents the studies on the cure reaction of unsaturated (epoxy) polyesters based on different aliphatic glycols with styrene initiated by various types of organic peroxides or the mixture of a stoichiometric ratio of an acid anhydride/organic peroxide by means of differential scanning calorimetry. The diacyl peroxide: benzoyl peroxide (BPO), dialkyl peroxide: dicumyl peroxide (DCP), and alkyl hydroperoxide: CHP were used as free-radical initiators. As hardener of epoxy groups acid anhydrides, such as tetrahydrophthalic anhydride (THPA) or hexahydrophthalic anhydride (HHPA) were applied. The influence of polyester's structure as well as used curing agent on the course of the cure reaction of studied polyesters with styrene has been qualified.

Experimental

Materials

Unsaturated polyesters (UP) were obtained from cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), Merck-Schuchardt (Germany) and suitable glycol: ethylene glycol (EG) or 1,4-butanediol (BDO) or 1,6-hexanediol (HDO), Fluka, Chemika (Switzerland). The polycondensation was carried out at the ratio of 1.5 mol of THPA, 1 mol of MA and 3.15 mol of suitable glycol according to procedure described in Ref. [13]. Unsaturated epoxy polyesters (UEP) were prepared by chemical modification of unsaturated polyesters performed using 38–40% peracetic acid, Merck-Schuchardt (Germany) at 40 °C during 2 h according to procedure described in Ref. [13–15]. The epoxy value (determined by dioxane/HCl titration method) was 0.27 mg KOH/g; 0.25 mg KOH/g or 0.23 mg KOH/g for UEP based on EG, BDO or HDO, respectively.

Hexahydrophthalic anhydride (HHPA), BPO, purum (% peroxide 98%) were purchased from Merck-Schuchardt (Germany). DCP, purum, (% peroxide > 97%), CHP, solution in cumene (% peroxide 80%) were from Fluka, Chemika (Switzerland). Styrene was delivered by Polish Chemical Reagents-POCH (Gliwice, Poland). All reagents were used as received.

Curing procedure

The styrene solutions of unsaturated polyesters (UP) and unsaturated epoxy polyesters (UEP) based on EG, BDO, or HDO by mixing polyester and styrene in the molar ratio of 4:1 were prepared. Then, 1.0 mass% of suitable organic peroxide: BPO or DCP or CHP were added to cure the styrene compositions. Also, the mixture of a stoichiometric ratio of THPA or HHPA and 1.0 mass% of organic peroxide were used to cure the styrene solutions of UEP. The experimental samples were prepared by mixing styrene with suitable organic peroxide and added to unsaturated (epoxy) polyesters, mixed to obtain homogeneous solutions. They were tested immediately after mixing by means of DSC. On the contrary, an acid anhydride/organic peroxide cured compositions were prepared as follows: an acid anhydride and UEP were mixed and heated up above the melting point of an anhydride, quenched in cold water and after cooling, the solution of styrene and organic peroxide was added, mixed and tested.

Techniques

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Germany). 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 aluminum crucible was used. Moreover, isothermal scans were conducted at 60, 80, 100, 120, 140, and 160°, respectively. The sample was rapidly heated to a predetermined isothermal temperature and tested until no further heat flow can be detected.

Results and discussion

The cure behavior of the unsaturated (epoxy) polyesters based on different aliphatic glycols with styrene using various types of curing agents was studied by DSC analysis. Unsaturated (epoxy) polyesters were dissolved in styrene in the molar ratio of 4:1 to prepare the resins which were characterized by large content of "dry" mass and low styrene monomer content. It was desirable thing due to the toxicity of styrene solutions of polyesters. To study the curing reaction of obtained styrene compositions, the suitable organic peroxide: diacyl peroxide: BPO or dialkyl peroxide: DCP or alkyl hydroperoxide: CHP or the mixture of a stoichiometric ratio of an acid anhydride (THPA or HHPA)/organic peroxide were applied. The samples were heated from 20 to 500 °C, in order to evaluate the thermal effects due to cross-linking and decompose the cured material under nitrogen. The curing characteristics 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) obtained by the integration of the exothermic peaks and also the decomposition temperature (T_{d}) were evaluated. Tables 1 and 2 contain the DSC data of the cure reaction of UP and UEP based on EG, BDO, or HDO with styrene using organic peroxides: BPO or DCP or CHP, respectively. The DSC data of the cure process of UEP initiated with the mixture of an acid anhydride (THPA or HHPA)/organic peroxide were given in Tables 3 and 4. In addition, the examplary curves presented the course of the cure process of unsaturated (epoxy) polyesters based on BDO with styrene were shown in Figs. 2, 3, 4, respectively. The one, exothermal asymmetrical peak for organic peroxides initiated cure process of UP with styrene was clearly observed. The formation of the three-dimensional network for the UP resins might have resulted from the competition of various reactions. It was mainly the result of copolymerization of carbon–carbon double bonds of vinyl monomer: styrene with carbon–carbon double bonds in polyester chain for studied UP. Although, according to the literature data, except this process, the additional homopolymerization of styrene should be taken into consideration [5, 16]. Moreover, it was brightly seen that BPO cure reaction of UP was described by lower values of T_{onset}, $T_{\max}$, and T_{end} compared to those initiated with DCP or CHP. It was directly connected with thermal stability of the used organic peroxides, Fig. 1. As it was known, their thermal decomposition by energy absorption allowed to produce active species (radicals) which after induction period promoted the polymerization process. The DSC analysis of all used radical initiators confirmed that DCP and CHP were more thermally stable owing to the lower dissociation enthalpy compared to BPO, Fig. 1. The rapid decomposition of pure BPO happened at relatively lower temperature about 99 °C with $T_{\max}$ 108 °C and significant higher ΔH values (1,090 J g^{-1}). The onset decomposition temperature of DCP were near 122 °C with $T_{\max}$ 175 °C and lower ΔH values (753 J g^{-1}). However, the decomposition of CHP was less exothermic (251 J g^{-1}) and occurred at 148 °C with $T_{\max}$ 194 °C in studied conditions. Those studies were in accordance with earlier observations reported by other authors [17–22]. In addition, isothermal curing test for the cure reaction of unsaturated (epoxy) polyesters with styrene initiated by organic peroxides conducted at different isothermal temperatures 60, 80, 100, 120, 140, and 160 °C were performed. No exothermal peak described the curing reaction of UP initiated with BPO or

Table 1 DSC data of the cure reaction of unsaturated polyesters based on EG, BDO, or HDO using different organic peroxides

Polyester	Curing agent	T_{onset}/°C	$T_{\max 1}$/°C	T_{end}/°C	ΔH_1/J g^{-1}	T_{d}/°C
EG	BPO	87.5	120.5	160.2	118.4	410.5
	DCP	118.5	149.7	235.3	95.3	407.8
	CHP	110.8	153.2	228.4	78.6	404.2
BDO	BPO	88.9	125.4	161.8	119.7	411.3
	DCP	121.2	158.5	238.2	96.5	408.2
	CHP	111.3	165.7	229.3	79.4	403.5
HDO	BPO	90.2	130.2	164.3	116.4	412.3
	DCP	120.3	168.7	241.2	94.5	408.5
	CHP	115.4	178.9	230.4	72.9	404.2

Table 2 DSC data of the cure reaction of unsaturated epoxy polyesters based on EG, BDO, or HDO using different organic peroxides

Polyester	Curing agent	T_{onset}/°C	$T_{\max 1}$/°C	$T_{\max 2}$/°C	T_{end}/°C	ΔH_1/J g^{-1}	ΔH_2/J g^{-1}	T_{d}/°C
EG	BPO	85.4	121.3	250.3	154.2	117.5	155.3	365.9
	DCP	116.4	149.5	255.2	280.2	94.6	150.2	368.4
	CHP	115.2	150.2	260.8	288.6	77.8	138.4	360.5
BDO	BPO	86.2	122.5	262.7	155.0	118.5	159.2	373.2
	DCP	115.3	157.9	258.3	284.2	95.4	156.8	374.5
	CHP	115.2	163.4	261.2	289.7	76.5	136.9	368.9
HDO	BPO	88.4	127.3	273.8	150.2	114.5	152.7	405.9
	DCP	117.4	169.1	271.2	291.2	93.7	152.4	404.2
	CHP	114.8	175.3	264.3	298.7	71.3	140.8	400.8

Table 3 DSC data of the cure reaction of unsaturated epoxy polyesters based on EG, BDO, or HDO using the mixture of different organic peroxides/THPA

Polyester	Curing agent	T_{onset}/°C	$T_{\max 1}$/°C	T_{end}/°C	ΔH_1/J g^{-1}	T_{d}/°C
EG	BPO/THPA	61.2	123.3	230.8	366.2	370.5
	DCP/THPA	63.2	150.2	228.5	341.8	369.4
	CHP/THPA	65.9	150.1	225.4	325.4	365.8
BDO	BPO/THPA	63.8	124.2	231.5	368.5	374.3
	DCP/THPA	64.2	154.8	225.4	342.8	374.6
	CHP/THPA	66.3	163.5	228.3	320.2	373.9
HDO	BPO/THPA	62.8	129.4	235.2	365.1	385.4
	DCP/THPA	66.9	168.5	230.8	343.7	380.2
	CHP/THPA	68.4	179.2	230.5	327.3	378.8

Table 4 DSC data of the cure reaction of unsaturated epoxy polyesters based on EG, BDO, or HDO using the mixture of different organic peroxides/HHPA

Polyester	Curing agent	T_{onset}/°C	$T_{\max 1}$/°C	T_{end}/°C	ΔH_1/J g^{-1}	T_{d}/°C
EG	BPO/HHPA	62.3	121.4	225.3	371.2	375.5
	DCP/HHPA	65.8	154.3	230.7	348.4	370.2
	CHP/HHPA	63.4	162.7	220.8	330.5	373.8
BDO	BPO/HHPA	61.8	127.6	228.9	373.2	379.2
	DCP/HHPA	64.3	156.0	230.1	349.7	376.9
	CHP/HHPA	62.1	165.5	225.7	325.6	376.8
HDO	BPO/HHPA	60.5	131.8	230.7	368.1	386.4
	DCP/HHPA	62.4	169.4	231.2	345.4	385.2
	CHP/HHPA	64.3	178.4	229.4	320.5	381.4

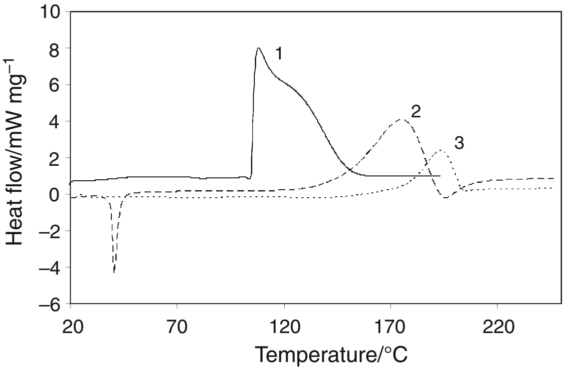

Fig. 1 Thermal decomposition of organic peroxides: 1—BPO, 2—DCP, 3—CHP

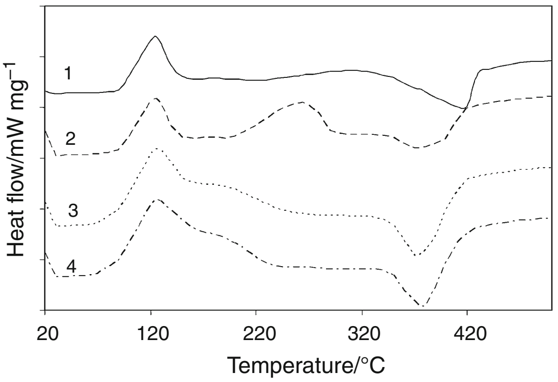

Fig. 2 The cure reaction of polyesters based on BDO: 1—UP/BPO, 2—UEP/BPO, 3—UEP/BPO/THPA, 4—UEP/BPO/HHPA

DCP or CHP was observed at 60 and 80 °C after 1 h during the isothermal scans. The quite violent exothermic reaction happened in a very short period, (after 3–5 minutes) was observed for BPO initiated samples heated at 100 and 120 °C. The exothermal peak in isothermal tests was indicated at relatively higher isothermal temperature for DCP cure reaction. The applying temperatures above 140 °C increased significantly the rate of the cure reaction initiated with DCP and consequently decreased time of the cure reaction to about 2–3 min. Moreover, just temperature of 160 °C allowed to observe the small exothermal curing peak when CHP was applied. It confirmed that the rapid production of highly reactive radicals from BPO allowed to decrease time and temperature of the cure reaction of UP and UEP with styrene.

The exothermal effect of the cure reaction of UEP based on EG, BDO, or HDO with styrene was split into two peaks, one at comparable temperatures observed for cure reaction

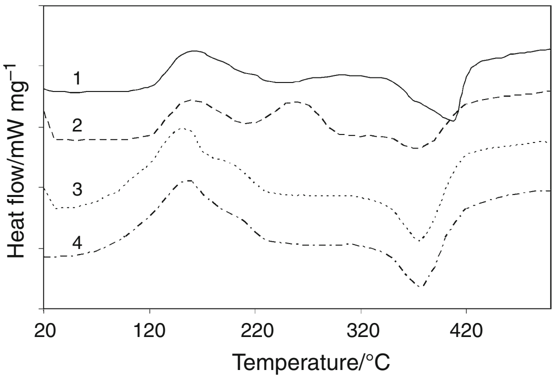

Fig. 3 The cure reaction of polyesters based on BDO: 1—UP/DCP, 2—UEP/DCP, 3—UEP/DCP/THPA, 4—UEP/DCP/HHPA

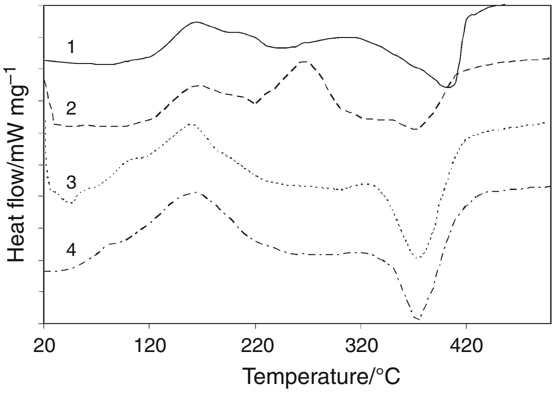

Fig. 4 The cure reaction of polyesters based on BDO: 1—UP/CHP, 2—UEP/CHP, 3—UEP/CHP/THPA, 4—UEP/CHP/HHPA

of UP and the other at significantly higher temperatures exceeding 250 °C, Table 2. These results suggested that in the presence of organic peroxides two cross-linking mechanisms were involved, one was due to the double bonds, the other to the epoxy groups. The thermal curing of epoxy groups with hydroxyl or carboxyl groups in polyester resulting in forming ether or ester linkages at higher temperatures was expected [5, 11, 23]. Additionally, the second exothermic peak ($T_{\max 2}$) occurred at similar temperatures independently of the used organic peroxide. It was a confirmation that the thermal curing of epoxy groups in polyesters was not affected by the presence of organic peroxide.

The differences of ΔH_1 values definitely depended on the type of the organic peroxide used. The cure reaction initiated by BPO was more exothermic compared to others due to lower activation energy of decomposition of this peroxide and the production of high reactivity of active species. In the case of more thermally stable CHP, the production of less reactivity radicals caused the obtaining lower ΔH values, Table 1 and 2. It confirmed earlier observations indicating higher reactivity of the reaction mixture initiated by BPO. Moreover, the ΔH_1 values of the cure process of unsaturated (epoxy) polyesters using the same organic peroxide were comparable indicating the similar amount of unsaturated units in studied polyesters.

The curing exotherm peak of unsaturated (epoxy) polyesters was shifted to a bit higher temperatures, particularly for the polyesters containing longer aliphatic glycol's chain length. It could be due to the lower molecular mobility of polyester chains obtained based on glycols containing more –CH_2– units in their structure which consequently increased $T_{\max 1}$ values.

The use of dual initiator system: an acid anhydride/organic peroxide allowed to obtain the excellent network structure where both the free-radical copolymerization and polyaddition reaction were expected. The cure process of unsaturated epoxy polyesters in this system was described by one, asymmetrical broad exothermic peak started at relatively lower T_{onset} temperatures independently of used organic peroxide and acid anhydride, Tables 3, 4. It could be a confirmation that the presence of acid anhydride might accelerate of the cure reaction and promote the copolymerization process. Moreover, $T_{\max 1}$ values were similar to those obtained for the cure reaction of unsaturated epoxy polyesters initiated with only organic peroxide. Hence, it was not possible to separate the radical polymerization from polyaddition reaction for the used curing system. Both processes run simultaneously, but the increase of cross-linking density of the matrix with progressing curing caused significantly higher T_{end} values for an acid anhydride/BPO initiating system compared to BPO cure process of UEP. The movement of reacting groups due to the steric hindrance was reduced so the decreasing of the rate of cure process was expected [24]. Moreover, longer aliphatic glycol's chain length caused the steric hindrance which consequently led to the considerable increasing of $T_{\max 1}$ temperature for cure process of polyesters based on HDO with styrene. The cure reaction of UEP with styrene initiated by an acid anhydride/organic peroxide system was more exothermic related to both copolymerization and polyaddition processes. It could suggest to produce more cross-linked polymer network structure.

As can be seen based on Tables 1, 2, 3, 4, the cured initial polyesters based on EG, BDO, or HDO were characterized by relatively higher decomposition temperatures (T_d) compared to epoxy-modified cured polyesters. It was directly connected with different type of formed linkages during the cure process. The formed additional ether and ester linkages were decomposed at lower temperatures compared to decomposition of carbon–carbon linkages.

Conclusions

Curing reaction of unsaturated (epoxy) polyesters with styrene initiated by different types of organic peroxides or the mixture of an acid anhydride/organic peroxide was studied by DSC analysis. It was proved that the course of the cure reaction of polyesters with styrene significantly depended on the polyester's structure as well as the used curing system. The presence of carbon–carbon double bonds from maleic anhydride in UP structure and both carbon–carbon double bonds from maleic anhydride and epoxy groups in cycloaliphatic rings in UEP structure caused to observe one or two exothermal effects during the organic peroxide initiated cure process with styrene. The first exothermal signal was due to the copolymerization process, and their position was depended on the used organic peroxide as well as on the aliphatic chain length in polyester backbone. The second exothermal peak at relatively higher temperature described the thermal curing of epoxy groups with hydroxyl or carboxyl groups in polyester. The cure process of UEP initiated by the mixture of an acid anhydride/organic peroxide was characterized by one exothermal effect indicating on simultaneous copolymerization and polyaddition reactions. Moreover, the use of BPO allowed to cure the studied polyesters at relatively lower temperature with higher exothermal effect compared to DCP and CHP. It was directly connected with the thermal stability of the applied organic peroxides. In addition, it was proved that the cure process of polyesters containing more $-CH_2-$ units in their structure with styrene happened at a bit higher temperatures, probably due to the lower molecular mobility of longer polyester's chains. The results presented above additionally confirmed that calorimetric analysis is a powerful and sensitive method to investigate and estimate the differences in the cure behavior of unsaturated (epoxy) polyesters based on different aliphatic glycols with styrene.

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