Thermal and viscoelastic properties of novel epoxy-dicyclopentadiene-terminated polyesters-styrene copolymers

Marta Worzakowska

Abstract This article presents the studies on the thermal and viscoelastic properties of novel epoxy-dicyclopenta-diene-terminated polyesters-styrene copolymers. The novel materials were prepared during a three step process including the addition reaction of maleic acid to norbone-nyl double bond of dicyclopentadiene; polycondensation of acidic ester of dicyclopentadiene, cyclohex-4-ene-dicar-boxylic anhydride, maleic anhydride, and suitable glycol: ethylene, diethylene, or triethylene glycol; and the epoxi-dation process of prepared polyesters. It allowed obtaining novel epoxy-dicyclopentadiene-terminated polyesters which were successfully used as a component of different styrene content (10–80 mass%) copolymers. The influence of the structures of polyester and styrene content on the cross-linking density (v_e), $tg\delta_{max}$, $tg\delta_{max}$ height, storage modulus ($E'_{20\ °C}$), FWHM values as well as the thermal stability of copolymers was evaluated by TG, DSC, and DMA analyses and discussed.

Keywords Dicyclopentadiene · Polyesters · Thermal properties · Viscoelastic properties

Introduction

The chemical structure of the starting polymer, the type of monovinyl monomer and the polymer/monovinyl monomer ratio significantly influences the thermal and mechanical properties of manufactured copolymers. The suitable selection of the individual components during the synthesis of polymers leads to the preparation of different materials suitable for many applications [1, 2]. The presence of aromatic units in the structure of polymer allows the for-mation of materials with higher glass transition tempera-ture, hardness, and chemical resistance comparing to those aliphatic based [3, 4]. The incorporation of cycloaliphatic rings into polymer backbone surely improves the thermal stability, transparency, glass transition temperature, and the flexibility of prepared copolymers [5–7]. In addition, the presence of a rigid structure in the polymer skeleton, e.g., bisphenyl or dicyclopentadiene, influences on the improv-ing mechanical elongation and toughness of the products [8, 9]. Dicyclopentadiene is one of the most popular reagents used for synthesis because of its reactivity, accessibility, and low cost. It is utilized for the preparation of, e.g., acidic esters, secondary alcohols which serves as intermediate compounds for polymer preparation [10–12]. The chemical modification of dicyclopentadiene-based products with organic peracids allows obtaining high reactive epoxy derivatives during cure due to the high ring strain of epoxycyclopentenyl groups. Consequently, the materials with excellent rigidity, thermal and dimensional stability, and good mechanical properties suitable for many applications are formed [13, 14].

Those studies are a part of general work connecting with the preparation of new epoxy polyester materials. This paper presents the studies on the thermal and viscoelastic properties of novel epoxy-dicyclopentadiene-terminated polyesters-styrene copolymers. The influence of the struc-ture of polyester and styrene content on the cross-linking density (v_e), $tg\delta_{max}$, $tg\delta_{max}$ height, storage modulus ($E'_{20\ °C}$), FWHM values as well as the thermal stability of prepared copolymers was evaluated by TG, DSC, and DMA analyses and discussed.

M. Worzakowska (✉)
Department of Polymer Chemistry, Maria Curie-Skłodowska University, Gliniana 33 str, 20-614 Lublin, Poland
e-mail: marta.worzakowska@poczta.umcs.lublin.pl

Experimental

Materials

Dicyclopentadiene (DCPD), maleic acid (MA), cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (BM), hexahydrophthalic anhydride (HHPA), and 40% peracetic acid were supplied by Merck-Schuchardt, Germany. Ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and benzoyl peroxide (BPO) were obtained from Fluka, Buchs, Switzerland. Styrene, hydroquinone, and xylene were delivered by POCh, Poland. Butylstannoic acid (catalyst) was delivered by Alkema Inc., USA. All the reagents were used without further purification.
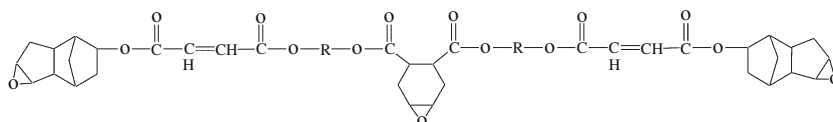
Synthesis of novel epoxy-dicyclopentadiene-terminated polyesters

DCPD (1.07 mol), maleic acid (1 mol), and hydroquinone (0.035 mass%) were placed into a 500 ml three-neck flask equipped with a mechanical stirrer, a thermometer, and a condenser. The mixture was heated to 135 °C, and stirred for 2.5 h. In this stage, the acidic ester of DCPD was prepared. Then, the polycondensation process of the acidic ester of DCPD, cyclohex-4-ene-1,2-dicarboxylic anhydride (0.5 mol), catalyst (0.01 mass%), maleic anhydride (0.5 mol), and suitable glycol: ethylene glycol (EG), diethylene glycol (DEG) or triethylene glycol (TEG) was performed. The reaction mixture was heated at 150 °C for 1 h and then at 180 °C, until the drop of an acid value below 3 mgKOH g^{-1} was observed. The reaction water was removed by azeotropic distillation with xylene. After completion, xylene was removed by distillation under reduced pressure. Then, the obtained product was chemically modified with 40% peracetic acid according to the procedure described in Ref. [15–17]. In this way, novel epoxy-dicyclopentadiene-terminated polyesters were obtained, Scheme 1.

Characterization of novel epoxy-dicyclopentadiene-terminated polyesters

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an 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.

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

Characterization of styrene copolymers

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Germany). The dynamic scans were performed at a heating rate of 10 °C min^{-1} under nitrogen atmosphere (40 mL min^{-1}). The copolymers were heated from room temperature to 500 °C. As a reference, an empty aluminum crucible was used. The characteristic maximum temperatures during degradation (T) were evaluated.

Thermogravimetric (TG) experiments were carried out on a STA 449 Jupiter F1, Netzsch (Germany). The conditions were as follows: heating rate 10 °C min^{-1}, a helium atmosphere (40 mL/min), the temperature range of 30–800 °C, and sample mass ∼10 mg. Empty Al_2O_3 crucible was used as a reference. The temperatures of 5, 10, and 50% of mass loss ($T_{5\%}$, $T_{10\%}$, and $T_{50\%}$) and the temperatures of the maximum rate of mass loss (T_{max}) were determined.

Dynamic mechanical analysis (DMA) was performed using Dynamic Mechanical Analyzer Q 800 TA Instruments (USA). Tests were conducted using a double Cantilever device with a support span of 35 mm. Apparatus was calibrated according to the producer's instruction. The rectangular profiles of the samples 10-mm wide and 4-mm thick were applied The measurements were made from room temperature to the temperatures at which the sample was too soft to be tested at a constant heating rate of 4 °C min^{-1} and an oscillation frequency of 10 Hz. The storage modulus ($E'_{20\ °C}$), glass transition temperature (α-relaxation) identified as a maximum of the $tg\delta$ ($tg\delta_{max}$), $tg\delta_{max}$ height, cross-linking density (v_e), and FWHM values were determined. Cross-linking density was calculated based on the equation: $E' = 3v_eRT$, where E' is the storage modulus in the rubbery plateau region, R is the gas constant, T is the absolute temperature at which the experimental modulus was determined ($T = T_g + 50$ °C) [18, 19].

Scheme 1 The theoretical structure of novel epoxy-dicyclopentadiene-terminated polyesters

Where R: —CH_2CH_2—
—CH_2CH_2—O—CH_2CH_2—
—CH_2CH_2—O—CH_2CH_2—O—CH_2CH_2—

Curing procedure

The polyesters were dissolved in styrene to prepare the resins containing 10, 20, 40, 60, and 80 mass% of monovinyl monomer. The curing system: the mixture of stoichiometric amount of hexahydrophthalic anhydride and 1.0 mass% of benzoyl peroxide was applied. The compositions after degassing were placed in a glass mold, conditioned in the temperature range of 60–120 °C, and then post-cured at 160–180 °C, until no additional exothermic peak was seen from DSC curves.

Results and discussion

Characterization of novel epoxy-dicyclopentadiene-terminated polyesters

The structure of prepared materials was confirmed based on spectroscopic methods. The analysis of ^{1}HNMR spectra of polyesters shows the presence of the characteristic resonance signals for protons at the epoxide groups (2.8–3.2 ppm) and for protons attributed to *cis–trans* units of maleic residue, at 6.20–6.40 ppm (*cis* unit) and at 6.80–6.95 ppm (*trans* unit), respectively, as shown in Fig. 1. Figure 2 presents the example FTIR spectra of novel epoxy-dicyclopentadiene-terminated polyesters. The strong absorption bands at 783–880 cm^{-1} (oxirane ring vibration groups) and the absorption bands at 1,646 cm^{-1} (C=C stretching vibration bonds) are visible, which confirms the formation of desirable product.
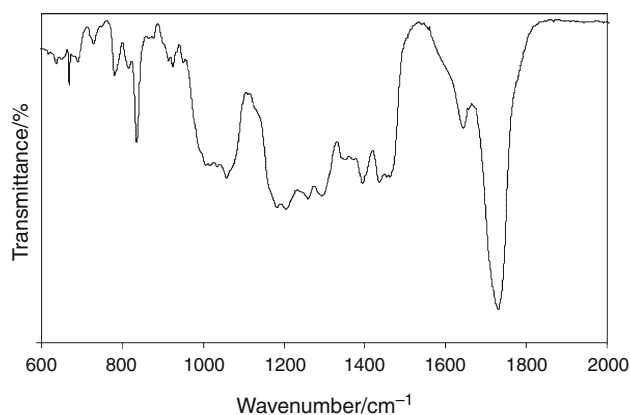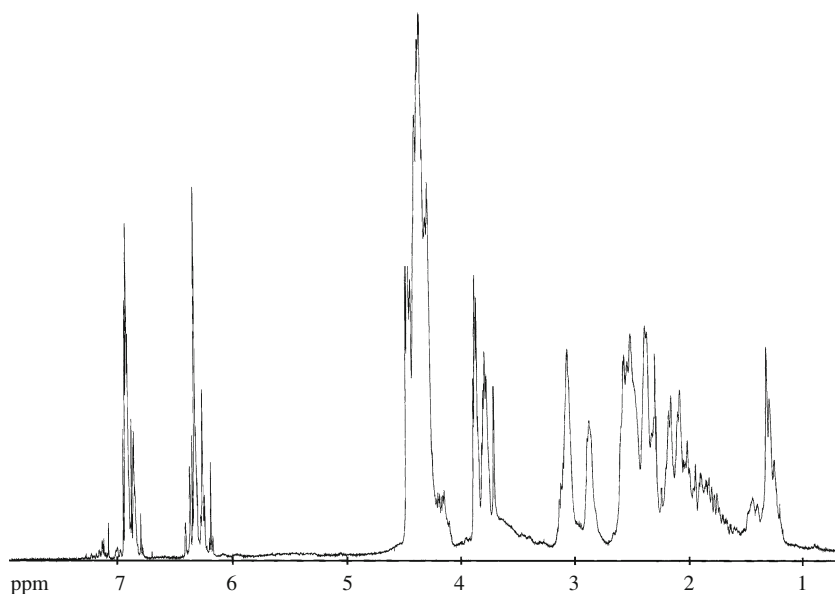

Fig. 2 Example FTIR spectra of novel epoxy-dicyclopentadiene-terminated polyesters

Thermal and viscoelastic properties of styrene copolymers

The results obtained based on DMA analysis are summarized in Tables 1, 2, 3. Also, the representative DMA curves for copolymers containing different styrene content are presented in Fig. 3. The results show that the properties of copolymers strongly depended on the structure of polyesters and styrene content. In general, the decrease in molecular mobility of the polymer chains ($tg\delta_{max}$ height) of each copolymer is determined by the cross-linking density (v_e) [20, 21]. The copolymers prepared in the presence of polyesters based on diethylene or triethylene glycols exhibited lower values of cross-linking density (v_e), glass transition temperature identified as a $tg\delta_{max}$, storage modulus ($E'_{20\,°C}$), and higher values of $tg\delta_{max}$ height than those

Fig. 1 Example ^{1}H NMR spectra of novel epoxy-dicyclopentadiene-terminated polyesters

Table 1 Viscoelastic properties of copolymers (based on ethylene glycol)

Styrene content/%	$E'_{20\,°C}$/ MPa	$tg\delta_{max}$	$tg\delta_{max}$/ °C	$v_e \times 10^{-3}$/ mol/cm³	FWHM/ °C
10	1,800	1.123	74.5	0.398	37
20	2,700	0.306	129.1	0.652	45
40	2,700	0.615	128.5	0.512	40
60	2,700	0.795	129.2	0.469	38
80	2,620	1.003	131.5	0.458	38

Table 2 Viscoelastic properties of copolymers (based on diethylene glycol)

Styrene content/%	$E'_{20°C}$/ MPa	$tg\delta_{max}$	$tg\delta_{max}$/ °C	$v_e \times 10^{-3}$/ mol/cm³	FWHM/ °C
10	1,280	1.280	42.2	0.386	33
20	2,300	0.613	85.3	0.602	40
40	2,250	0.784	84.5	0.494	33
60	2,245	0.947	85.3	0.448	32
80	2,180	1.225	86.7	0.421	30

Table 3 Viscoelastic properties of copolymers (based on triethylene glycol)

Styrene content/%	$E'_{20°C}$/ MPa	$tg\delta_{max}$	$tg\delta_{max}$/ °C	$v_e \times 10^{-3}$/ mol/cm³	FWHM/ °C
10	620	1.354	32.0	0.395	30
20	1,250	0.722	55.4	0.600	38
40	1,200	0.865	56.8	0.502	35
60	1,180	1.145	57.3	0.450	34
80	1,150	1.384	56.5	0.433	32

Fig. 3 Storage modulus (E') and $tg\delta$ versus temperature for ethylene glycol based copolymers containing 10, 20, 40, 60, and 80 mass% of styrene

ethylene glycol-based copolymers. It indicated on formation of more flexible polymer networks for copolymers based on polyesters with longer glycol's chain length in their structure [22, 23].

Moreover, as the styrene content in the copolymers is varied from 20 to 80 mass%, the significant increase in molecular mobility of the polymer chains ($tg\delta_{max}$ height), decrease in cross-linking values (v_e) and the storage modulus ($E'_{20\,°C}$) and almost constant $tg\delta_{max}$ were observed. It was expected since reduced v_e values usually lower $E'_{20\,°C}$ of the materials. It suggests that less densely cross-linked networks are produced for copolymers containing lower polyester content, probably due to the plasticizing action of styrene monomer. Also, the heterogeneity of prepared copolymers was evaluated qualitatively by examining the width of the tangent delta peak (FWHM). Physically, the FWHM values provide a measure of the range of mobilities in the network. Their higher values imply better

interactions between the phases and a more heterogeneous structure [24–26]. The results clearly indicate that FWHM values slightly decreases as the styrene content increases from 20 to 80 mass%. It can be an indication on higher degree of structural heterogeneity of the copolymers containing higher content of polyester.

The TG and DSC data for prepared copolymers are shown in Tables 4, 5, and 6. The representative TG curves are presented in Fig. 4. The differences in the thermal behavior of copolymers are indicated. The ethylene glycol-based copolymers are characterized by a little higher thermal stability (higher values of $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$) than those diethylene or triethylene glycols based. It was due to the formation of more rigid and cross-linked networks. In addition, the presence of two degradation peaks with T_{max1} at ~362–371 °C and T_{max2} at ~405–425 °C for all copolymers suggests that the degradation process run through at least two steps. The degradation of linkages present in the polyester structure and formed during the cure process is mainly expected [27].

Moreover, the increase of styrene content in copolymers causes an increase of the $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$ values. When the percentage of styrene is increased, the number of

**Table 4** Thermal properties of copolymers (based on ethylene glycol)

Styrene content/%	$T_{5\%}/$ °C	$T_{10\%}/$ °C	$T_{50\%}/$ °C	$T_{max1}/$ °C	$T_{max2}/$ °C	$T_1/$ °C	$T_2/$ °C
10	255	277	363	368	412	366	410
20	280	306	368	365	420	368	412
40	295	320	372	368	425	363	415
60	302	324	370	366	422	365	418
80	308	325	365	365	423	363	422

Table 5 Thermal properties of copolymers (based on diethylene glycol)

Styrene content/%	$T_{5\%}/$ °C	$T_{10\%}/$ °C	$T_{50\%}/$ °C	$T_{max1}/$ °C	$T_{max2}/$ °C	$T_1/$ °C	$T_2/$ °C
10	253	274	365	366	408	361	405
20	280	305	368	370	412	365	408
40	285	308	368	371	412	363	410
60	292	315	370	368	420	360	418
80	300	318	370	365	425	358	421

Table 6 Thermal properties of copolymers (based on triethylene glycol)

Styrene content/%	$T_{5\%}/$ °C	$T_{10\%}/$ °C	$T_{50\%}/$ °C	$T_{max1}/$ °C	$T_{max2}/$ °C	$T_1/$ °C	$T_2/$ °C
10	238	254	365	365	405	358	401
20	270	295	365	362	408	362	403
40	274	298	368	371	410	360	405
60	283	302	372	368	410	356	412
80	285	310	370	369	420	359	418
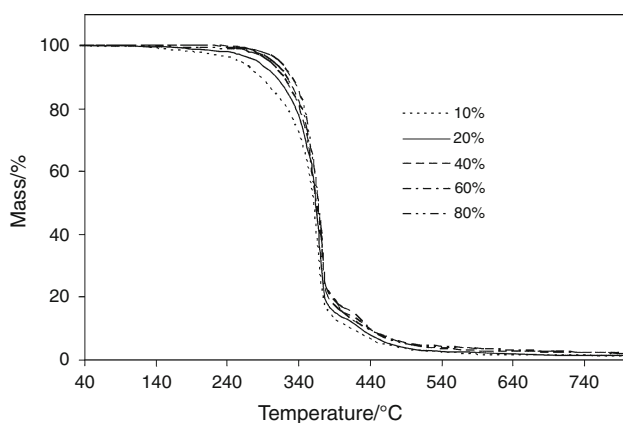
Fig. 4 TG curves for ethylene glycol based copolymers containing 10, 20, 40, 60, and 80 mass% of styrene

aromatic rings and new carbon–carbon linkages due to the homopolymerization of styrene increases, whereas the number of ester groups in the polymer network decreases. This is probably the reason that can be responsible for better thermal stability of higher styrene content. Besides, as was already discussed, the higher degree of cross-linking density should also increase the thermal stability of copolymers. However, in those studies copolymers with lower v_e were characterized by better thermal stability. This observation confirms that the presence of higher content of styrene allows producing copolymers with lower $E'_{20 \,°C}$, $tg\delta_{max}$, v_e, and FWHM values due to the plasticizing effect of styrene but more thermally stable due to the presence of higher content of aromatic rings in prepared networks.

Conclusions

The performed analyses showed that the thermal and viscoelastic properties of copolymers strongly depended on the chemical structure of polyester as well as the styrene content. The ethylene glycol-based copolymers were generally more rigid and more thermally stable than those diethylene or triethylene glycols based. The increase in styrene content in copolymers resulted in obtaining less densely cross-linked networks probably due to the plasticizing action of monovinyl monomer but more thermally stable due to higher content of aromatic rings in the prepared polymer networks. Those studies confirmed that the novel epoxy-dicyclopentadiene-terminated polyesters can be successfully applied as components for the preparation of styrene copolymers and due to their properties are promising materials for practical applications.

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