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THERMAL ANALYSIS OF POLYESTERS CONTAINING OXIRANE GROUPS

Marta Worzakowska[*]

Faculty of Chemistry MCS University, Department of Polymer Chemistry, Gliniana 33 street, 20-614 Lublin, Poland

The preliminary studies of the thermal behaviour of polyester obtained in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride and ethylene glycol and its new epoxidized form have been performed. The thermal characterization of initial polyester and its completely oxidized form was done by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The non-isothermal DSC was applied to determine the influence of time and the temperature on the chemical modification of initial polyester using 38–40% solution of peracetic acid. On the basis of DSC profiles it has been found that the endothermic transition, due to the degradation process of initial polyester was characteristic feature under controlled heating program.

The two characteristic transitions for the new epoxidized polyester, the exothermic peak corresponded to the thermal crosslinking of epoxidized polyester (322.8–336.4°C) and the endothermic decomposition peak of the cured material (363.8–388.9°C) were observed. The peak maximum temperatures (T_{max}) and the heat of cross-linking reaction (ΔH_{c}) for epoxypolyester prepared at 20–60°C under 1–4 h were evaluated. The T_{max1} were almost independent from epoxidation conditions, while, the values of ΔH_{c} were dependent from conditions of synthesis. The ΔH_{c} values of this process decreased when time of oxidation increased. The highest values of ΔH_{c} at 40°C were obtained. Additionally, TG experiments confirmed two separated degradation steps of the new epoxidized polyester indicating the ester (370–380°C) and ether (450–460°C) bond breakdown.

Keywords: *DSC, epoxidation, epoxypolyester, peracetic acid, TG*

Introduction

Epoxy resins, one of the most important thermosetting polymers are currently used in advanced composites, coatings, structural adhesives and microelectronics due to their high stiffness, high strength, good chemical resistance and dimensional stability [1–5]. To this time, the widely used method of synthesis of the epoxy resins is the method based on polycondensation process of dian and epichlorohydrin under normal or higher pressure in the presence of sodium hydroxide as a catalyst [6–8]. This process has several disadvantages, the most significant is due to the toxic properties of epichlorohydrin. And so, the new ways of preparation of the polymeric materials contained the epoxy groups are still investigated. The chemical modification of polymeric structure can be achieved by introducing a functional group. The literature describes many methods for preparing epoxidized polymers either stoichiometric or catalytic [9–12]. Usually, peracids generated separately or in situ formed peracids by the addition of hydrogen peroxide to an organic acid are the oxidant agents for non-catalysed reactions while hydrogen peroxide, iodosylbenzene, sodium hypochloride and *tert*-butylhydroperoxide may be used in catalytic reactions [4, 13, 14]. Epoxidation of polymers having an olefinic carbon-carbon double bonds include olefinic polydienes such as polybutadiene or polyisoprene or block copolymers which contains a polymer block of a diene, poly(vinyl chloride), rubber seed oil can be performed using organic peracids [15–17]. A few articles described the chemical modification of high-molecular compounds useful for powder UV-curable coating application prepared by the condensation of tetrahydrophthalic anhydride, glycols and dicyclopentadiene or tetrahydrophthalic acid or anhydride, cycloaliphatic polyols, saturated polycarboxylic acid and alcohol with acid solutions such as peracetic acid, performic acid generated separately or in-situ from organic acid and hydrogen peroxide [18–20].

In this study the thermal analysis was applied to monitor the epoxidation process of polyester prepared in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride and ethylene glycol by use the well-known conventional method. The initial polyester containing cyclohexenyl units has been successfully epoxidized with 38–40% solution of peracetic acid. The new epoxypolyester was identified by FTIR, ^{1}H NMR, DSC and TG analysis. The influence of time and the temperature on efficiency of the oxidation process of the initial polyester was determined by meaning of DSC. The thermal stability and

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[*] marta.worzakowska@poczta.umcs.lublin.pl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

enthalpy changes (ΔH_c) of the epoxypolyester under controlled heating program were determined. Additionally, the thermal degradation pattern of new material were estimated by TG analysis.

Experimental

Materials

Tetrahydrophthalic anhydride (cyclohex-4-ene-1,2-dicarboxylic anhydride) was obtained from Merck-Schuchardt (Hohenbrunn, Germany). Ethylene glycol was from Fluka (Buchs, Switzerland). Methylene chloride, tetrahydrofuran Lichrosolv (chromatographic grade) were purchased from Merck-Schuchardt (Hohenbrunn, Germany) and were used as the solvents. 38–40% solution of peracetic acid was from Merck-Schuchardt (Hohenbrunn, Germany) and was used as the oxidizing agent. Other reagents such as sodium carbonate, sodium hydroxide, sodium chloride and magnesium sulphate were delivered by POCh (Gliwice, Poland). All reagents were used without further purification.

Polyester synthesis

The polyester was obtained in the polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride and ethylene glycol. The reaction was carried out at 1:1.2 molar ratios of cyclohex-4-ene-1,2-dicarboxylic anhydride and ethylene glycol to obtain a polyester with end hydroxyl groups. Firstly, the addition reaction was performed at temperatures 130–150°C for 2 h and when the addition reaction was completed 10 mass% xylene was added and subjected the polycondensation. The reaction was carried out in the temperature range of 150–230°C with simultaneous azeotrophic removal of condensation water from the reaction medium. The course of the process was controlled by determining the acid number. The drop of an acid number of the reaction mixture compared to assumed value was taken as an indicator of the process completion. The solvent-xylene was removed by distillation under reduced pressure at elevated temperature. The obtained polyester containing cyclohexenyl rings was analyzed and used for further chemical modification to produce the epoxidized polyester.

Epoxidation of polyester

Epoxidation of obtained polyester with 38–40% peracetic acid was carried out in solution (methylene chloride or chloroform) at 20, 40 and 60°C for different times. The initial polyester was dissolved in the solvent and the resulting solution was heated to the reaction temperature. Then 38–40% solution of peracetic acid in acetic acid was added in two portions under vigorous stirring. With peracetic acid the reaction was almost immediately exothermic. After completion, the reaction mixture was cooled down and washed with aqueous solution of sodium carbonate and sodium hydroxide to neutralize acetic acid. Then the organic phase was thoroughly washed two times with aqueous solution of sodium hydroxide and water and dried over $MgSO_4$. The solvent was removed by distillation under reduced pressure. The residue was diluted with tetrahydrofuran, dried and distilled off under reduced pressure. The chemical structure of initial polyester and its epoxidized form have been presented in Fig. 1.

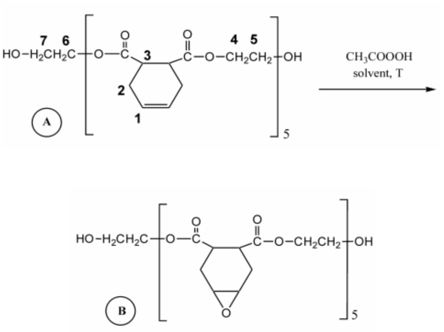

Fig. 1 The chemical structure of A – polyester and B – epoxidized polyester

Methods

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

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

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Germany) operating in a dynamic mode. The non-isothermal scans were performed at a heating rate of 10 K min^{-1} from room temperature to a maximum of 500°C under nitrogen atmosphere (30 mL min^{-1}). As a reference an empty aluminium crucible was used.

Thermogravimetric analysis (TG) was performed on a MOM 3427 derivatograph (Hungary) at a heating rate of 10°C min^{-1} in air, in the temperature range of 20–1000°C with the sample of 100 mg.

Results and discussion

Characterization of the initial polyester and its epoxidized form

The chemical modification of polyester obtained during the polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride and ethylene glycol was led at 20–60°C in different times (1–4 h) to obtain epoxidized polyester. The oxidation of the initial polyester by 38–40% solution of peracetic acid allowed to obtain the completely epoxidized polyester. Its structure was confirmed by FTIR and ^{1}H NMR spectra. From the ^{1}H NMR spectrum of initial polyester the characteristic chemical shifts for the protons on the double bonds of cyclohexenyl rings were observed at δ=5.67–5.7 ppm (H_1). The increase in epoxidation degree could be followed by the decrease of double bonds peaks areas and the appearance of new proton signals at δ=2.65–2.78 ppm which can be attributed to protons attached to the epoxy groups. Moreover, a new proton signals at 3.25 ppm were also identified. It is an indication that another functionality was being introduced in the polyester backbone probably an alcohol formed by the opening of the epoxide [21, 22], Fig. 2. The exemplary IR spectra of initial polyester and epoxidized polyester is shown in Fig. 3. The IR spectra of initial polyester showed the characteristic absorption bands in the range of 660 cm^{-1} related to the double bonds in the cyclohexenyl rings (m, C–H out-of-plane deformation vibration). After epoxidation process the disappearance of the signals at 660 cm^{-1} were observed and the new absorption signals at 807 and 836 cm^{-1} appeared in the spectrum, which are characteristic bands for oxirane ring vibration groups.

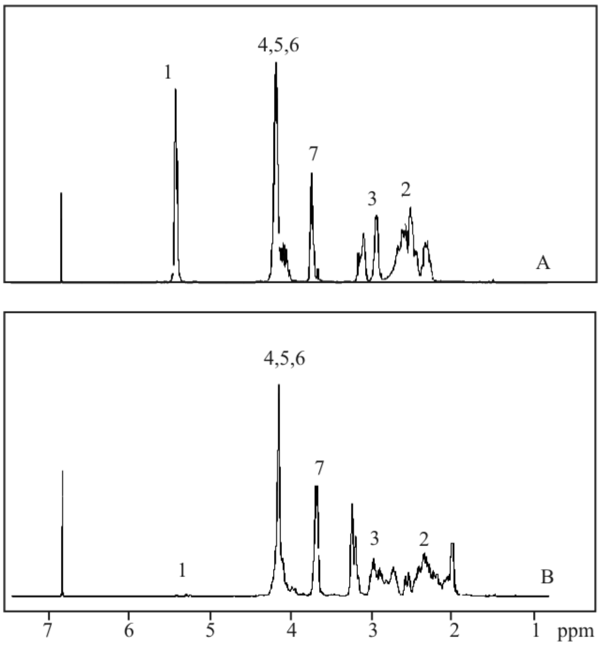

Fig. 2 ^{1}H NMR spectra of A – initial polyester and B – epoxidized polyester

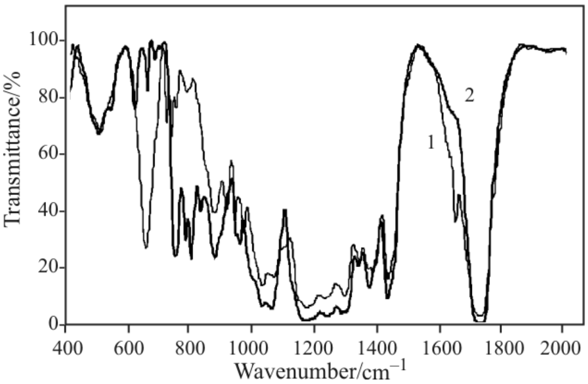

Fig. 3 FTIR spectra of 1 – initial polyester and 2 – epoxidized polyester

DSC and TG characterization

In order to understand the course of the epoxidation process of initial polyester the reaction was carried out at various temperatures 20–60°C and times 1–4 h. The initial polyester and the epoxidized polyester obtained at 20–60°C were characterized by both differential scanning calorimetry and thermogravimetric analysis at a heating rate of 10 K min^{-1}. The DSC was performed in a nitrogen atmosphere from 20 to 500°C. The thermogravimetric analysis was conducted in air from 20–1000°C.

Figure 4 shows DSC curves for initial polyester and its epoxidized form obtained at 40°C in different times 1–4 h. DSC curve of the polyester presented a single asymmetrical endothermic peak at 425°C which resulted from their thermal degradation. In contrast DSC curves of the epoxidized polyester showed two peaks. First, the exothermic peak at temperatures from 322.8 to 333.6°C can be ascribed to a thermal crosslinking reaction of epoxide groups

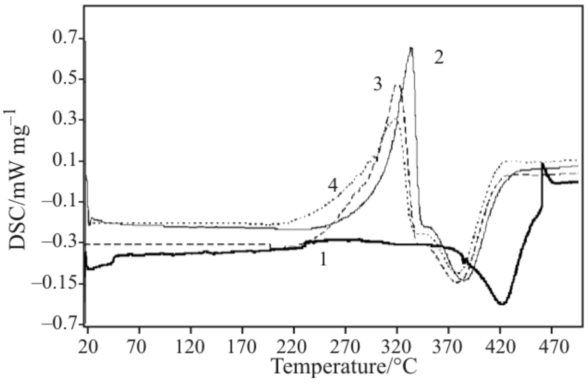

Fig. 4 DSC curves of 1 – initial polyester and 2 – epoxidized polyester obtained at 40°C for 2 – 1, 3 – 2 and 4 – 4 h

Table 1 Peak maximum temperatures (T_{max}) and the ΔH_c values obtained from DSC curves

Condition parameters	20°C			40°C			60°C		
	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h
T_{max1}/°C	333.6	327.8	329.6	336.4	324.7	322.8	325.5	331.4	331.5
ΔH_c/J g^{-1}	166.8	150.3	98.2	210.6	198.4	154.8	130.3	120.6	85.7
T_{max2}/°C	384.8	383.9	363.8	388.9	382.6	381.9	369.9	369.0	385.6

with carboxylic acid groups which are formed by the random chain scission at higher temperatures [23, 24] or to addition reaction of epoxy groups to terminal hydroxyl end groups on polyester at lower temperatures to form ether linkages. From Table 1 it can be seen that the heat of crosslinking reaction (ΔH_c) decreased when the time of epoxidizing reaction increased. It was found that the heat of crosslinking reaction was directly proportional to the amount of epoxide groups in polyester. When the time of epoxidation reaction increased the fall of ΔH_c values at constant temperature was observed. The maximum values of ΔH_c were reported when the time of epoxidation process was shorter (1 h). The ΔH_c were 166.8 J g^{-1} at 20°C, 210.6 J g^{-1} at 40°C and 130.3 J g^{-1} at 60°C, respectively. As can be seen from Table 1 the highest values of ΔH_c were obtained at 40°C (210.6–154.8 J g^{-1}) comparing to those obtained at 20°C (166.8–98.2 J g^{-1}) and at 60°C (130.3–85.7 J g^{-1}). The optimum time and the temperature of the epoxidation process when the side reactions were the slowest have been defined (40°C at 1 h). This observation were confirmed by determination of epoxy number. When the time of epoxidation increased the lower values of epoxy number were assigned. The maximum values of epoxy number (0.3 mg KOH/g) were determined at 40°C. Below this temperature the oxidation reaction of initial polyester was slower and the longer time of synthesis was required. On the other hand, above the temperature of 40°C the probability of the side reactions increased due to the high acidity of the reaction medium. The formation of alcoholic and ester groups bounded to the polyester backbone caused by opening the oxirane rings were observed. Additionally, the T_{max1} (peak max. temperature of the thermal crosslinking reaction) were almost independent from epoxidation conditions and it were in the range of 322.8–336.4°C. The second transition from DSC curves, the endothermic decomposition peak at 363.8–388.9°C may result from the thermal degradation of the newly formed ester and ether bonds during the thermal crosslinking reaction. To test this supposition the thermogravimetric analysis was conducted. The thermal decomposition patterns [25] of the new epoxypolyester followed a considerably different pattern from the single-step reaction of initial polyester. When the epoxide content increased their thermal stability as measured by mass loss also increased,

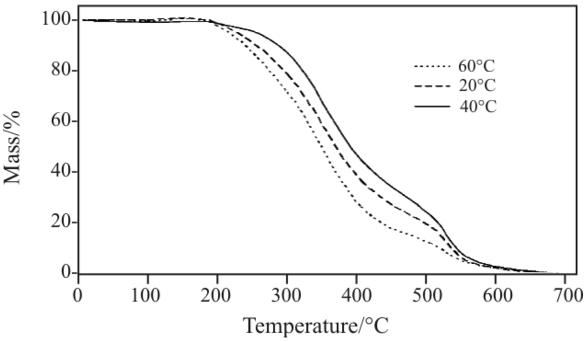

Fig. 5 TG curves of epoxidized polyester at 20, 40 and 60°C for 2 h

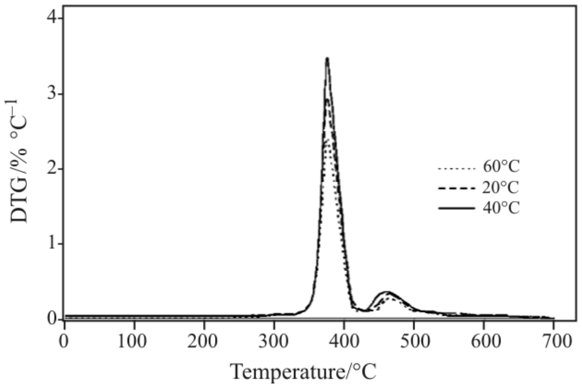

Fig. 6 DTG curves of epoxidized polyester at 20, 40 and 60°C for 2 h

Table 2 Parameters evaluated from TG and DTG curves of the epoxidized polyester obtained at different conditions

Condition parameters	20°C			40°C			60°C		
	1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h
IDT	280	278	275	285	280	278	278	270	270
T_{max1}/°C	370	372	370	375	375	380	378	376	378
T_{max2}/°C	450	452	460	455	460	460	450	453	458

Fig. 5. The highest values of initial decomposition temperatures (IDT) were observed for samples prepared at 40° (the IDT were in the range of 278–285°C), Table 2. The DTG curves for the epoxidized polyester contained two separated degradation steps and when the epoxide content increased the decomposition peaks increased in size, Fig. 6. The thermal degradation process indicated on ester ($T_{\max1}$ 370–380°C) and ether ($T_{\max2}$ 450–460°C) bond breakdown.

Conclusions

The adopted method of epoxidation of polyester obtained in polycondensation process of cyclohex-4-ene-1,2-dicarboxylic anhydride and ethylene glycol has been effective way to introduce a new functional groups into polyester chain containing cyclohexenyl rings. The polyester and its epoxidized form were analysed by FTIR and ^{1}H NMR spectra and DSC, TG analysis. The thermal analysis can be a valuable method for the determination of the influence of time and the temperature conditions on the efficiency of the epoxidation process of initial polyester. It has confirmed that the ΔH_c values decreased with reaction time and temperature above 40°C. Under controlled heating program, the thermal crosslinking process of epoxy groups with carboxyl or hydroxyl groups were observed. It was confirmed by TG analysis where the ester and ether bond breakdown were identified.

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