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Crosslinking of microbial copolyesters with pendant epoxide groups by diamine

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Abstract

The poly(3-hydroxyoctanoate-co-3-hydroxy-10,11-epoxyundecanoate)s, PHOEs, with epoxide pendant units of 10, 22 and 34 mole% were prepared. The PHOEs were crosslinked with a stoichiometric hexamethylene diamine (HMDA) at 90°C for 0.5–24 h. The crosslinking reaction of PHOE–HMDA system was verified from the glass transition temperature (T_g) increment and the relative storage modulus increment. Higher increment in T_g and relative modulus with increasing the amount of epoxide group in the initial PHOE was observed. Activation energies of the crosslinking reaction were determined by use of the Kissinger and the Ozawa methods. The activation energies for the crosslinking reactions have similar values for each sample, regardless of epoxide content in the PHOEs. The values obtained from the Ozawa method were slightly higher than those from the Kissinger method.

Keywords: Poly(3-hydroxyalkanoate)s; crosslinking; glass transition temperature

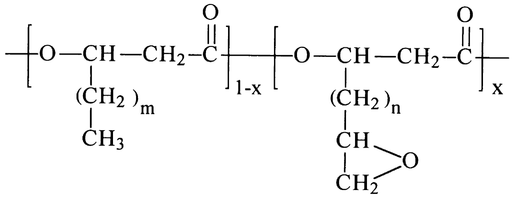
1. Introduction

Until now, various types of poly(3-hydroxyalkanoate)s, PHAs, were biosynthesized by microorganisms. Of the micro-organisms capable of producing PHAs, *Pseudomonas oleovorans* can produce the PHAs with relatively long pendant side chains. The long pendant side chain in the PHAs would often contain a functional unit (olefin [1–4], halogen [5–8], nitrile [8]) at its terminus when a carbon source with unusual functional group is cofed on fermentation. Many of the PHAs produced by *P. oleovorans* have the properties of thermoplastic elastomers, although the elastic response of these materials were relatively poor [9]. Therefore, to specially improve their elastomeric properties, PHAs should be crosslinked by an appropriate chemical method.

Poly(3-hydroxyoctanoate-co-3-hydroxyundec-10-enoate), PHOU, which is produced when *P. oleovorans* is fed a mixture of sodium octanoate and 10-undecylenic acid, has a reactive unsaturated group located at the terminus of pendant chain. As reported previously [10,11], PHOU can be crosslinked by peroxide or sulfur vulcanization methods. Peroxides and sulfur-based systems were used successfully as crosslinking agents for PHOU, but the materials showed little or no tensile or tear resistance as well as little increment of their glass transition temperature after crosslinking. The substantial decrease in material integrity may have been caused in part by chain scission and molecular weight loss caused either by the radical reactions involved or by the thermal degradation at the high cure temperature.

Recently, the epoxidation procedure of PHOUs was developed for the quantitative conversion of the unsaturated groups to epoxide groups [12–14]. Resultant epoxide groups can be used as reactive intermediates for further crosslinking reaction with an appropriate crosslinking agent.

In the present study, the use of a diamine crosslinking agent was attempted with the epoxide-containing copolyesters, poly(3-hydroxyoctanoate-co-3-hydroxy-10,11-epoxyundercanoate)s. PHOEs, as shown later.



$$\left[\mathrm{O{-}\underset{\underset{\underset{CH_3}{|}}{(CH_2)_m}}{\overset{|}{CH}}{-}CH_2{-}\overset{\overset{O}{\|}}{C}}\right]_{1-x}\left[\mathrm{O{-}\underset{\underset{CH(O)CH_2}{|}}{(CH_2)_n}{CH}{-}CH_2{-}\overset{\overset{O}{\|}}{C}}\right]_x$$

m = 2, 4, 6 n = 4, 6, 8

x = 0.10, 0.22, 0.34

As a crosslinker for PHOE sample, hexamethylene diamine (HMDA) was employed. The PHOE–HMDA

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Table 1
Epoxide contents and properties of the PHOE samples used

Polymers	Epoxide content (mole%)	M_n(×10^{-3})	M_w/M_n	T_g (°C)	T_{max}[a] (°C)
PHOE(90/10)	10	97	2.5	−33	301
PHOE(78/22)	22	112	2.2	−34	298
PHOE(66/34)	34	101	2.4	−32	292

[a] Maximum decomposition temperatures determined from TGA thermograms

crosslinking system needs no catalyst because the crosslinking reaction between them is relatively fast. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to analyze the crosslinking behavior of the PHOE–HMDA system. The degree of crosslinking was evaluated quantitatively from the exothermic heats on DSC thermograms, or qualitatively from the increase in glass transition temperature, T_g, and relative storage modulus. The activation energies of the crosslinking reaction were determined by the Kissinger [15] and Ozawa [16] methods.

2. Experimental

2.1. Materials

Production and epoxidation of PHOU was carried out as described in previous reports [13,14].

The PHOE samples with three different epoxide group contents were evaluated as follows: 90/10, 78/22 and 66/34, in which the first number indicates the molar percentage of saturated O, repeating units $(1-x)$ and the second number indicates the molar percentage of epoxide E, repeating units (x) [5,6]. The molecular weights and characterization results of PHOE samples are listed in Table 1.

2.2. Crosslinking procedure

The PHOE samples were crosslinked with HMDA in the absence of a catalyst. Reagents were dissolved in chloroform for 30 min at 40°C to obtain a 10 wt% homogeneous solution, and this solution was stored in a refrigerator maintained at −20°C to prevent any reaction. The composition in solution of epoxy/HMDA reactants by mole ratio was 100/50 corresponding to a stoichiometric ratio. The solution was evacuated under the reduced pressure to remove chloroform for 1 h before crosslinking. Sample were crosslinked either in the DSC sample cell under nitrogen atmosphere or in a drying oven for a pre-specified period of time, 30 min to 24 h, at 90°C. After the isothermal crosslinking at 90°C, the samples were quenched to room temperature.

2.3. Polymer characterization

Molecular weights of PHOEs were determined by gel permeation chromatography (GPC) using polystyrene standards. The compositions of the PHOE copolymers were determined from ^{1}H-NMR spectra [13].

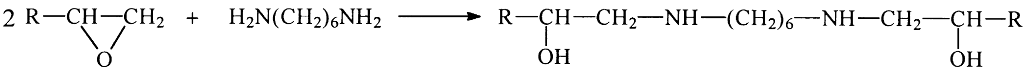
2.4. Crosslinking monitoring techniques

IR spectra were obtained on a Jasco 300E FT-IR Spectrometer. Differential scanning calorimetry (DSC) was conducted using TA Instruments 2910. The temperature scale was calibrated with mercury and indium. Samples were tested from −70°C to 220°C at a heating rate of 10°C/min. To determine the activation energy of the crosslinking reaction. DSC scans were conducted at heating rates of 2.5, 5.0, 10, and 20°C/min. The glass transition temperature was taken as the inflection point. Dynamic mechanical analysis (DMA) was conducted with a Dupont 983 Dynamic Mechanical Analyzer. The sample ($10.1 \times 0.15 \times 12$ mm^3) supported on a glass fabric was run with a measuring frequency of 1 Hz under nitrogen atmosphere.

3. Results and discussion

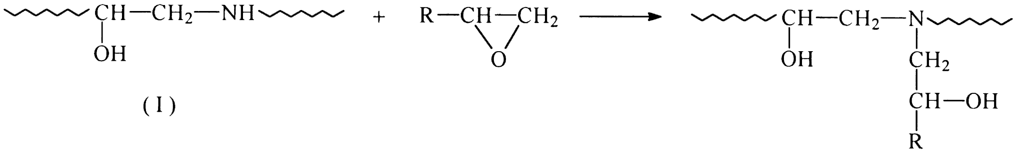
3.1. Crosslinking reaction

The uncatalyzed crosslinking reaction of diamine with epoxide group is expected to proceed as shown in the following reaction [17].



$$2\ R{-}\underset{\diagdown O \diagup}{CH{-}CH_2} + H_2N(CH_2)_6NH_2 \longrightarrow R{-}\underset{OH}{CH}{-}CH_2{-}NH{-}(CH_2)_6{-}NH{-}CH_2{-}\underset{OH}{CH}{-}R \quad (1)$$

(I)



$$\sim\sim\underset{OH}{CH}{-}CH_2{-}NH\sim\sim + R{-}\underset{\diagdown O \diagup}{CH{-}CH_2} \longrightarrow \sim\sim\underset{OH}{CH}{-}CH_2{-}\underset{\underset{\underset{R}{|}}{CH-OH}}{\underset{|}{\underset{CH_2}{|}}}{N}\sim\sim \quad (2)$$

(I)

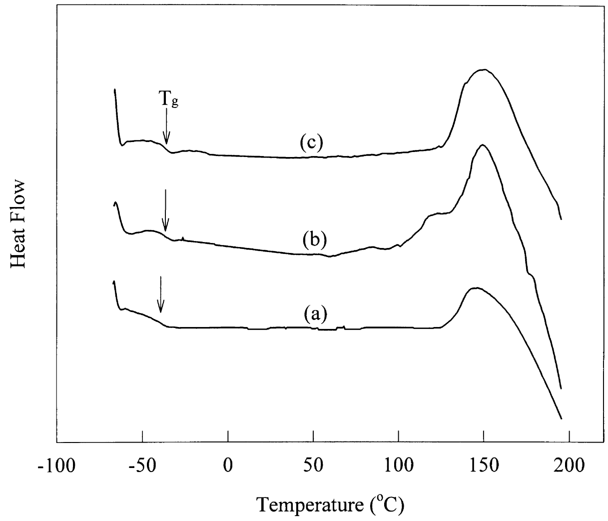


Fig. 1. DSC thermograms for three PHOE–HMDA samples at a heating rate of 10°C/min: (a) PHOE(90/10), (b) PHOE(78/22), (c) PHOE(66/34).

An epoxide group in the polymer is opened by attack of primary amine group to form a secondary alcohol and a secondary amine, which reacts with another epoxide group to form a crosslink (Eq. (1)). The secondary amine so formed, in turn, also reacts with an epoxide group to give a tertiary amine and two secondary hydroxyl groups (Eq. (2)). It is well known that no competitive reaction is detectable between a secondary hydroxyl group and an epoxide group to afford an ether linkage, provided a stoichiometric equivalent or excess amine maintained [18]. In this study, the mole ratio of reactants, epoxy (difunctional)/HMDA (tetrafunctional), was used in a stoichiometric ratio (100/50) for the formation of principal crosslinks.

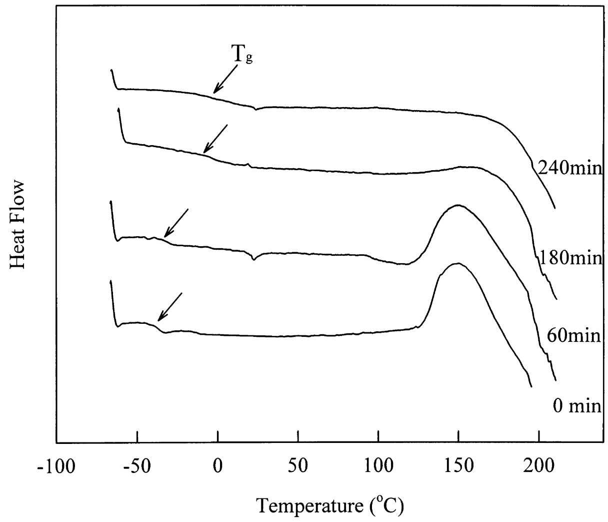


Fig. 2. DSC thermograms of the PHOE(66/34)– HMDA sample crosslinked for various times at 90°C.

3.2. DSC and IR study of crosslinking behavior

Fig. 1 shows the dynamic DSC thermograms for three PHOE–HMDA original samples at a heating rate of 10°C/min. The T_g and one principal exotherm, which was attributed to the crosslinking reaction of the epoxide group in PHOE with the HMDA, is seen in the thermograms. The higher the amount of epoxide content in the PHOE samples, the larger the exothermic heat. The PHOE(66/34)– HMDA system showed the largest exothermic heat, as expected because this sample had the highest amount of crosslinkable epoxide units. In Fig. 2, the change of DSC thermograms with crosslinking time is shown for the PHOE(66/34) sample. The exotherm with a maximum rate at 151°C decreased gradually with crosslinking time and almost disappeared after the crosslinking time of 180 min, indicating the almost completion of the crosslinking reaction. Fig. 3 shows the IR spectra of PHOE(66/34)– HMDA sample with crosslinking time. The doublet peaks at 3375 and 3315 cm^{-1}, which were assigned to the absorption of primary amine in the original sample, changed into a singlet peak at 3320 cm^{-1} because of the absorption of the secondary amine after 90 min. After the crosslinking for 180 min, no band at $\sim$ 3300 cm^{-1} was detected because of the formation of tertiary amine, indicating near completion of the crosslinking reaction in agreement with the result from DSC thermograms in Fig. 2. Also, the absorption of an epoxide group at 850 cm^{-1} decreased in the intensity with crosslinking time, almost disappeared after 180 min.

However, the exotherms in Figs. 1 and 2 seemed to overlap with a endothermic thermal degradation reaction, which occurred in the vicinity of 180°C and which diminished the exothermic enthalpy value. As a result the dynamic DSC temperature scan at 10°C/min was not suitable for measuring accurately the total or residual heat of the crosslinking reaction (Even at slower scanning rates of 5 and 2°C/min, the crosslinking exotherm was complicated by the degradation reaction). Moreover, this overlapping was also confirmed by TGA measurement, in which shows that weight loss started at around 180°C (not shown).

The total heat of the crosslinking reaction could, however, be measured by carrying out an isothermal DSC scan at 90°C for all samples. The total exothermic heats (ΔH_{total}) of the isothermal crosslinking reactions at 90°C, obtained by this procedure with the PHOE(90/10), PHOE(78/22) and PHOE(66/34) samples, were 58, 87 and 104 J/g, respectively.

The degree of crosslinking, α(%), in the isothermal process was estimated by the following equation:

$$\alpha(t) = \frac{\Delta H_t}{\Delta H_{\text{total}}} \tag{3}$$

in which $\alpha(t)$ is the degree of crosslinking as estimated by the extent of reaction at time t, and ΔH_t is the exothermic heat up to time t. The degree of crosslinking was calculated using Eq. (3) by estimating the amount of heat released up to

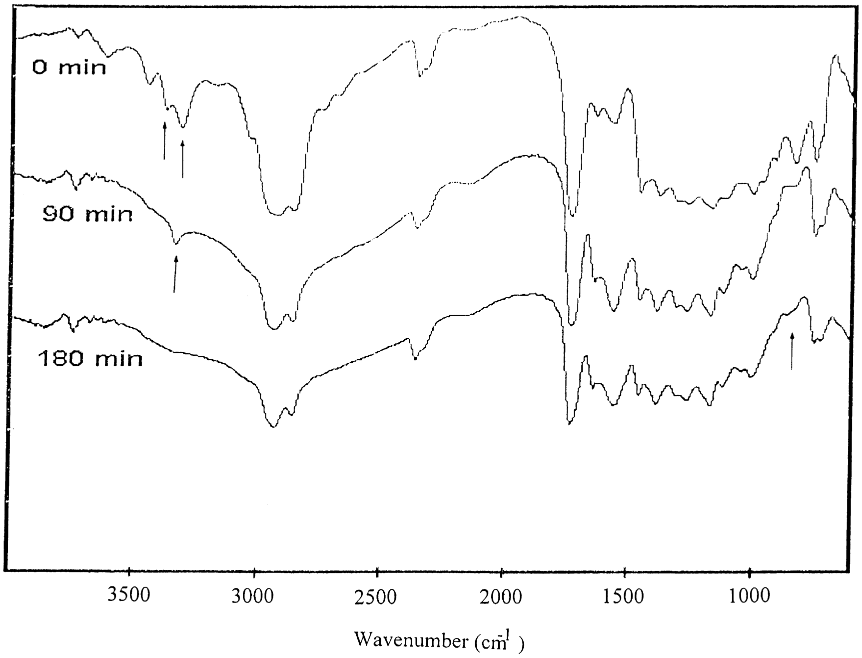


Fig. 3. IR spectra of the PHOE(66/34)– HMDA sample crosslinked for various times at 90°C.

selected time interval, and the relative areas of those sections were estimated to be a measure of ΔH_t. The degree of crosslinking, α, as a function of time for the epoxy–diamine reaction, as determined by this isothermal crosslinking reaction data at 90°C is shown in Fig. 4. The PHOE(66/34)– HMDA system with the highest amount of epoxide units showed the fastest crosslinking reaction rate, as seen in Fig. 1. The degree of crosslinking was higher than 80% at 3 h and almost 100% after 5 h for all samples.

The T_g is a sensitive and practical parameter for the crosslinking systems. Crosslinking caused an increase in the T_g of the system. The T_g values of PHOE–HMDA systems, which were crosslinked for various periods of time at 90°C, are shown in Figs. 5(a)–(c). The increments of T_g for the PHOE samples, which were completely crosslinked at 90°C, were 6, 18 and 44°C for PHOE(90/10), PHOE(78/22) and PHOE(66/34), respectively. The increase in the T_g on crosslinking leveled off at longer time-periods, owing to completion of the crosslinking reaction. The dotted lines in Fig. 5 indicate the maximum glass transition temperature of the fully crosslinked sample obtained in the isothermal reaction for 24 h.

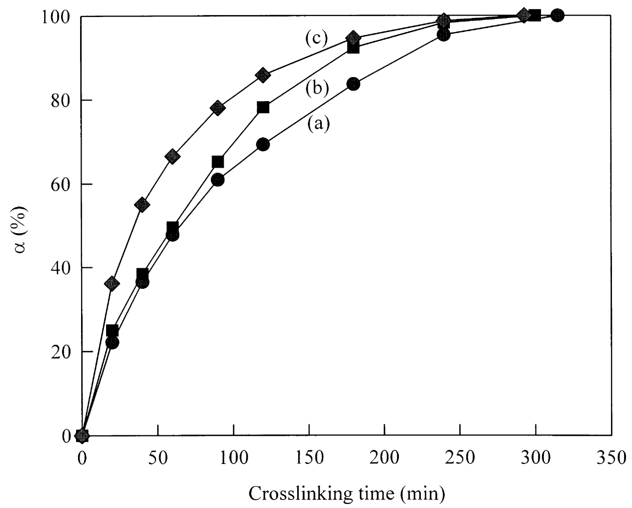


Fig. 4. Variation of the degree of crosslinking (α) as a function of crosslinking time: (a) PHOE(90/10), (b) PHOE(78/22), (c) PHOE(66/34).

3.3. DMA study of crosslinking behavior

The crosslinking behavior of PHOE–HMDA system could be also detected from dynamic mechanical data. A sample specimen was supported on a glass fabric for the test. Fig. 6 shows the variation of relative storage modulus with crosslinking time for PHOE–HMDA systems. As the epoxide content of PHOEs increased, the final modulus attained at the plateau also increased. The higher modulus (or larger modulus increment) reflects the higher crosslinking density achieved with more reactive epoxide groups available for crosslinking. Gelation time can be determined from the loss peak of an isothermal dynamic mechanical spectrum [19]. Fig. 6(b) shows the variation of relative loss modulus as a function of time for PHOE–HMDA systems. The peak maximum on spectra corresponds to the gelation time of each sample. The gelation became faster, from 252 min to 144 min, with increasing the crosslinking density (or epoxide content) in the PHOE–HMDA system. Therefore, the results from dynamic mechanical

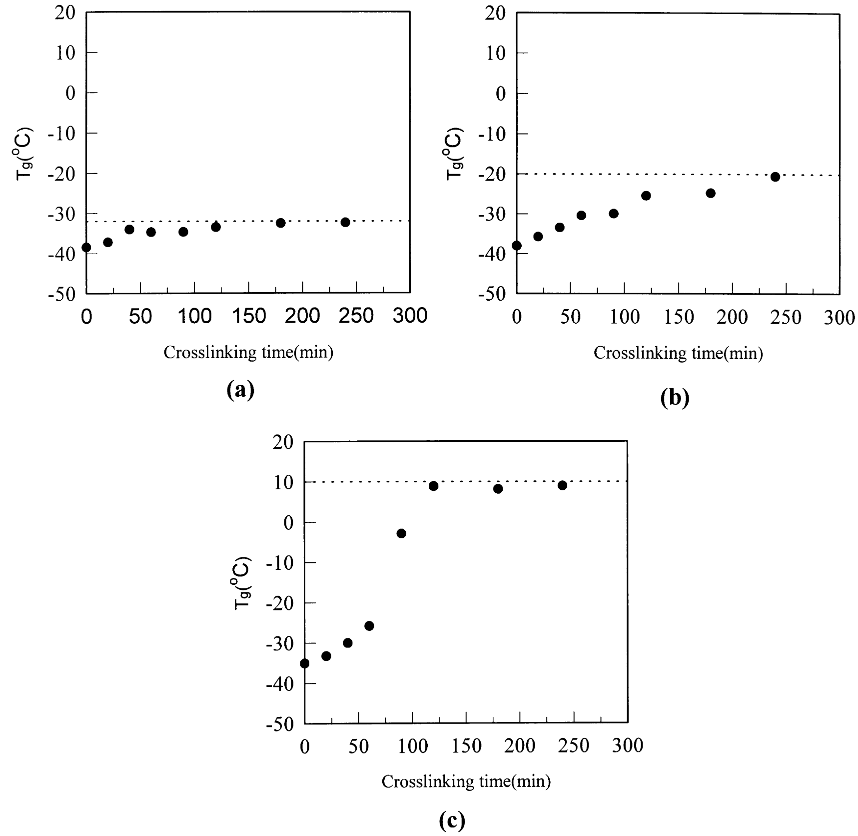


Fig. 5. Variation of glass transition temperature as a function of crosslinking time: (a) PHOE(90/10), (b) PHOE(78/22), (c) PHOE(66/34).

data further confirm the quantitative results obtained by DSC.

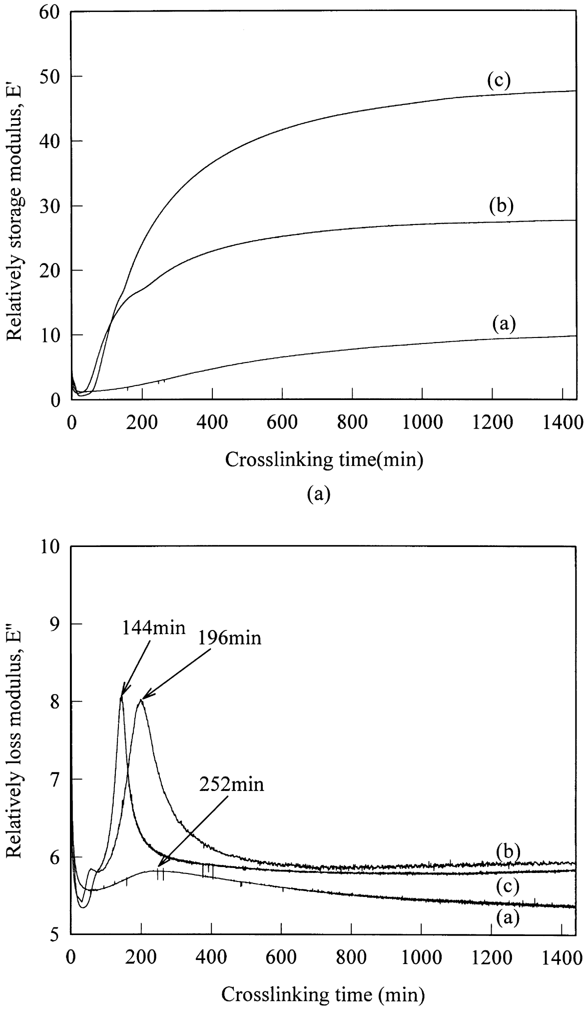
The dynamic mechanical spectra of the completely crosslinked samples as a function of temperature are given in Fig. 7. Fig. 7(a) shows that crosslinking has little effect on the modulus of polymer below T_g, where the material is rigid. However, at temperature above the T_g, modulus was strongly dependent upon the extent of crosslinking. The slight decrease in modulus at about 200°C was attributed to the initial thermal degradation of polymer, as mentioned previously. In addition to the differences in modulus at plateau region, Fig. 7(b) shows that the tanδ peak, which is associated with the glass transition region, was shifted to higher temperatureas as the crosslinking density increased from PHOE(90/10) to PHOE(66/34). There was also a slight broadening in peak width and a slight decline in peak height with the crosslinking density. This broadening is known to be caused by heterogeneity in the crosslinked structure [20].

3.4. Activation energy of crosslinking reaction

The peak exotherm temperature on DSC thermogram for the crosslinking reaction varied in a predictable manner with the heating rate, so several methods for determining the activation energy could be used. Simple but accurate relationships between activation energy, heating rate and peak exotherm temperature were derived by Ozawa [8] and by Kissinger [7]. The activation energies obtained from both the Kissinger and Ozawa methods are listed in Table 2. As seen from the data in Table 2, activation energies were identical for each sample within the error limits. These identical values of activation energies possibly reflect the same type of the crosslinking reaction involved in the PHOE–HMDA systems. The value (18.3 kcal/mol) of ΔE_a obtained from Ozawa method was slightly higher than that (17.6 kcal/mol) from the Kissinger method.

Table 2
Activation energies for PHOE–HMDA systems determined by the Kissinger and Ozawa methods

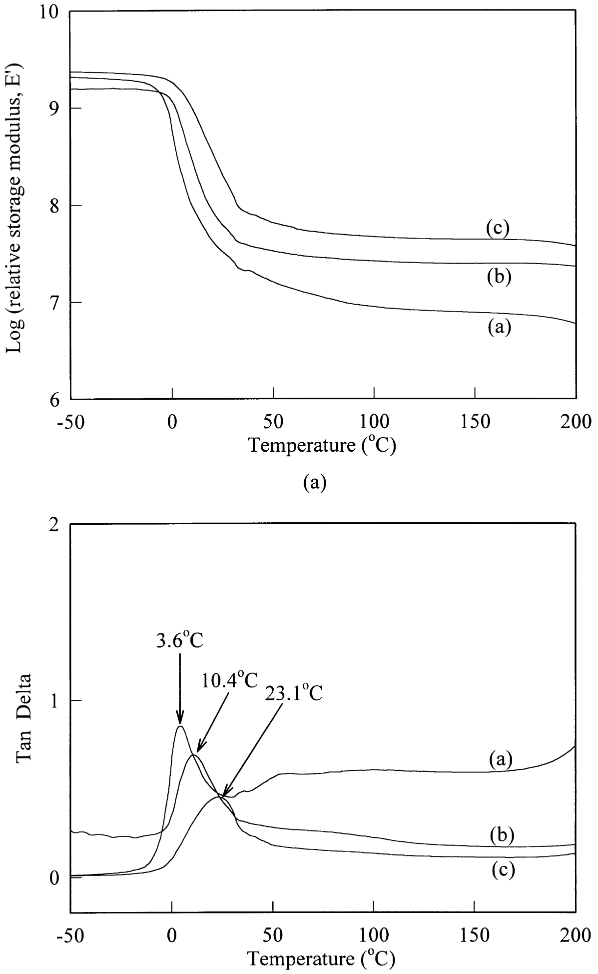
Crosslinking system	Kissinger method (kcal/mol)	Ozawa method (kcal/mol)
PHOE(90/10)–HMDA	17.7	18.5
PHOE(78/22)–HMDA	17.5	18.2
PHOE(66/34)–HMDA	17.6	18.3



(a)

(b)

Fig. 6. Variation of (a) relative storage modulus and (b) relative loss modulus with crosslinking time for the PHOE–HMDA samples: (a) PHOE(90/10), (b) PHOE(78/22), (c) PHOE(66/34).



(a)

(b)

Fig. 7. Variation of (a) relative storage modulus and (b) tanδ with temperature for the completely crosslinked PHOE samples: (a) PHOE(90/10), (b) PHOE(78/22), (c) PHOE(66/34).

4. Conclusions

Poly(3-hydroxyoctanoate-co-3-hydroxy-10,11-epoxyundecanoate)s, PHOEs with 10, 22, and 34 mole% of epoxide units were crosslinked with a stoichiometric hexamethylene diamine at 90°C for 0.5–24 h.

The PHOE(66/34)–HMDA system with the highest amount of epoxide units showed the fastest crosslinking reaction rate. The degree of crosslinking was higher than 80% at 3 h and almost 100% after 5 h for all samples. The increments of T_g for the PHOE samples, which were completely crosslinked at 90°C, were 6, 18, and 44°C for PHOE(90/10),PHOE(78/22) and PHOE(66/34), respectively. The increase in T_g on crosslinking leveled off at longer time-periods, owing to completion of crosslinking reaction.

As the epoxide content was increased, the PHOE sample showed a higher increment of the relative storage modulus with crosslinking time, and a higher final modulus attained at the plateau. The gelation time also became faster with increasing crosslinking density (or the epoxide content) in PHOE–HMDA system.

The activation energies obtained from both the Kissinger and Ozawa methods were identical for each sample within the error limits. These identical values in the activation energy possibly reflect the same type of crosslinking reaction involved in PHOE–HMDA systems.

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