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Study of cure kinetics of DGEBA with optically active curing agents

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Abstract 3-Deoxy-D-*erythro*-hexos-2-ulose bis (thiosemicarbazone) (**I**) readily obtained from D-glucose reacts with copper acetate hydrate to give the corresponding chelate (**II**). The complex (**II**) was acetylated to give the corresponding tri-*O*-acetyl derivative (**III**). The (**I**), (**II**), and (**III**) were used as optically active curing agents for diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin, and the cure reaction was studied by the non-isothermal DSC method. The maximum exothermic temperature (T_p) of curing of DGEBA-(**III**) system shifted about 313 K toward lower temperature in comparison with the T_p of DGEBA/(**II**) system. The average E_a values obtained by using Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), and isoconversional methods for non-isothermal curing of DGEBA-(**I**), DGEBA-(**II**), and DGEBA-(**III**) systems are 95.8, 135.5, and 85.8 kJ mol^{-1}, respectively. The higher reactivity of (**III**) toward epoxide groups can be due to better solubility of the (**III**) in DGEBA as a result of acetylation of hydroxyl groups.

Keywords Curing of polymers · DSC · Epoxy resin · Kinetics · Optically active curing agents

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Introduction

In recent years, optically active polymers have attracted much attention due to their unique function such as molecular recognition, catalytic activity in asymmetric transformation, and optical resolution for racemates as well [1–4]. One of the most practical and widely accepted applications of chiral polymers is the use as chiral stationary phase (CSP) for HPLC for the separation of racemic compounds [5]. Epoxy resins are one of the most important products used widely in the polymer industries, and curing of the most commonly used epoxy resin, DGEBA, with variety of curing agents was extensively reported in the literatures [6–9]. Extensive work has been carried out into the use of metals and their salts in the formulation of epoxy resin systems, and this has included the use of organo-transition metal complexes as catalysts for epoxy resins when co-cured with amines [10–14]. There have been reports that application of complex of metal with different curing agents improved physical properties such as adhesion, bending strength, viscosity, water absorption, and thermal stability of the cured epoxy resin [15–21].

The objective of this study was to cure DGEBA with new optically active curing agents. From our previous studies [10], we expected that application of metal complex of the curing agents must have a significant effect on the mechanism of cure reaction. Different non-isothermal kinetic methods such as KAS, FWO, and isoconversional were applied to DSC data to test their applicability in the new epoxy-hardener systems. To improve the solubility of the optically active complex curing agent, the effect of structural change (acetylation) in the curing agent on the cure reaction was also studied.

Experimental

Materials

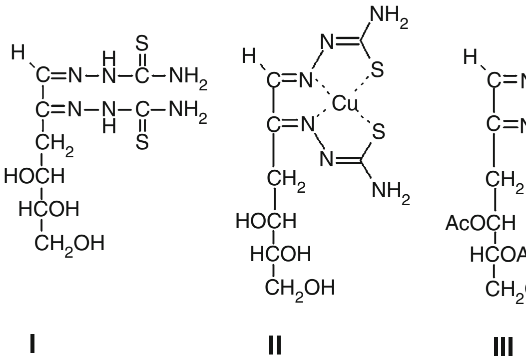
D-Glucose, *p*-toluidine, and thiosemicarbazide were purchased from Fluka and used without purification. Acetic anhydride and copper acetate monohydrate were also obtained from Fluka. The epoxy compound used in this study was a diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin, Epidian5, provided by the Iran Petrochemical Co: Epoxide equivalent 196–208, clear liquid, viscosity (at 298 K) 25,000 Mpas. The curing agents were synthesized according to the procedure given in the literature.

Apparatuses

A Mettler Toledo differential scanning calorimeter (DSC822^e), a Bruker vector 22 FT-IR spectrometer, and an elemental analyzer of Thermofinnigan Flash EA 1112 were used.

Synthesis of curing agents

Scheme 1 displays the structure of the curing agents used in this study. The curing agent 3-deoxy-D-*erythro*-hexos-2-ulose bis(thiosemicarbazone) (**I**) [22] was prepared by the reaction of monosaccharide D-glucose (0.011 mol) with *p*-toluidine (0.011 mol) in a slightly acid (1.2 mL of glacial acetic acid) hydroalcoholic solution (3:1) at 373 K for 30 min. After addition of thiosemicarbazide (0.022 mol, 2:1 mol ratio) to the mixture, the reaction was maintained at 373 K for 5 h and then refrigerated at 273 K overnight, affording a pale-brown precipitate. Twice recrystallization from a mixture of 2:1 water–ethanol led to pale-yellow needles with melting point of 502 K and yield of 40%. FT-IR (KBr, cm^{-1}): υ 3386, 3265, and 3170 (NH_2, OH); 1608 (C=N); 837 (C=S). ^{1}H NMR [DMSO-d_6, δ ppm]: δ 10.7 (s, 1H, NH), 11.7 (s, 1H, NH), 7.78–8.33 (4H, $2NH_2$), 7.65 (s, 1H, H − 1), 4.67–5.43 (s, 3H, 3OH), 2.8 (d, 2H, H − 3). Elemental analysis calculated for (**I**) ($C_8H_{16}N_6O_3S_2$): C, 31.16%; H, 5.19%; N, 27.27%; S, 20.77%. Found: C, 31.30%; H, 5.12%; N, 27.10%; S, 20.74%.



Scheme 1 Chemical structures of the curing agents

The copper (**II**) complex of (**I**) was prepared [22] by dissolving Cu (II) acetate and compound (**I**) in a 1:1 M ratio in hot methanol. The mixture was stirred for 3 h, left to cool, and then filtered and washed several times with ethanol. The brown color solid product was dried in a vacuum oven at 323 K which yielded 80% with melting point of 481 K. FT-IR (KBr, cm^{-1}): υ 3339, 3163 (NH_2, OH); 1587 (C=N); 701 (C=S). Elemental analysis calculated for (**II**) ($C_8H_{14}N_6O_3S_2Cu$): C, 25.98%; H, 3.79%; N, 22.73%; S, 17.32%; Cu, 16.19%. Found: C, 26/12%; H, 3/85%; N, 22/58%; S, 17.45%; Cu, 16.32%.

The complex (**II**) was acetylated under standard condition [23] to give the corresponding tri-*O*-acetyl derivative (**III**) that the thiosemicarbazone moiety remained intact and the hydroxyl groups protected. The compound (**III**) was obtained in 68% yield with melting point of 463–465 K. FT-IR (KBr, cm^{-1}): υ 3339, 3303, 3180 (NH_2); 1736 (C=O), 1575 (C=N); 715 (C=S). Elemental analysis calculated for (**III**) ($C_{14}H_{20}N_6O_6S_2Cu$): C, 33.90%; H, 4.04%; N, 16.95%; S, 12.92%; Cu, 12.82%. Found: C, 33.72%; H, 4.09%; N, 16.85%; S, 12.86%; Cu, 12.76%.

Sample preparation

The curing agents were well dried in a vacuum oven and were completely powdered to obtain fine particles. The epoxy resin was thoroughly mixed with the curing agents and, to facilitate the mixing, a small amount of acetone was added to the mixing composition. The stoichiometric amounts of the curing agents were calculated through the number of active amino hydrogen, and the values for (**I**), (**II**), and (**III**) were 25, 45, and 65 phr, respectively.

DSC measurement

The thermal curing data were obtained by using a Mettler Toledo instrument (DSC 822^e), which was heated from room temperature to 623 K at different heating rates (5, 10, 15, and 20 K min^{-1}) under nitrogen atmosphere. The instrument was first calibrated with pure indium for thermal response with the heat of fusion and the temperature with the melting point. A small quantity (5 mg) of well-mixed and uniform viscous liquid was sealed in a DSC aluminum sample pan covered with an aluminum lid and closed tightly under pressure. An identical empty pan was taken as reference.

Results and discussion

Synthesis and characterization of the curing agents

3-Deoxy-D-*erythro*-hexos-2-ulose bis(thiosemicarbazone) (**I**) was synthesized by the reaction of D-glucose with *p*-toluidine in a slightly acid solution using a procedure given in the literature [22], a rearrangement of Amadori takes place with the loss of a molecule of water. The reaction mixture was maintained at 373 K for 5 h after addition of thiosemicarbazide, during which condensation of thiosemicarbazide with carbon 1 and 2 as well as reduction of carbon 3 to a CH_2 group takes place and compound (**I**), shown in Scheme 1, is formed. In this reaction, *p*-toluidine may be viewed as a catalyst promoting the rearrangement and elimination reactions, and the thiosemicarbazide as the trapping agent. The (**I**) can act as a tetradentate ligand in the formation of Cu(II) coordination complex. The complex (**II**) was prepared according to the procedure given in the literature [22]. In order to investigate the effect of solubility of the curing agent on the curing activity of the complex, the complex (**II**) was acetylated under standard condition [23] to give the corresponding tri-*O*-acetyl derivative (**III**) that the thiosemicarbazone moiety remained intact and the hydroxyl groups were protected. FT-IR spectra of the curing agents are illustrated in Fig. 1. The FT-IR and elemental analysis data for the curing agents are in good agreement with results reported in the literatures [22, 23]. The absence of any bands in the 2,600–2,800 cm^{-1} region suggests the absence of any thiol tautomer in solid state. The IR spectrum of the ligand (**I**) shows a band at 837 cm^{-1}, assignable to the thioamide band, which is the only band involving $\upsilon(C{=}S)$ that is easily assignable in this spectrum. In the IR spectra of the metal complexes of (**II**) and (**III**), the thioamide vibration shifts to lower frequencies indicating loss of double bond character and coordination via the thiolato sulfurs. The $\upsilon(C{=}N)$ vibration region is complicated by the appearance of a second band due to $\upsilon\{N{=}C(S)\}$. Compared to $\upsilon(C{=}N)$ in the free ligand, the $\upsilon\{N{=}C(S)\}$ band is usually found at slightly higher energies in the complexes. Thus, we assign $\upsilon(C{=}N)$ in the 1,560–1,590 cm^{-1} in the spectra of the complexes, consistent with previous studies [22]. The metal ligand bands $\upsilon(Cu–S)$ and $\upsilon(Cu–N)$, are found in the 450 and 430 cm^{-1} region, respectively, consistent with the results of other bisthiosemicarbazone complexes [24, 25]. The IR spectra of both complexes show the band assigned to azomethine nitrogen shifted to lower wave number. Coordination of these nitrogen is confirmed with the presence of new bands assigned to $\upsilon(M–N{=}C)$ in the spectra of complexes. In the IR spectra of complexes, the band assigned to $\upsilon(NH_2)$ remains in the same position as in the free ligand, so the primary amines are not bonded to the copper ion. In addition, coordination via sulfur atoms is indicated by a decrease in the frequency of the thioamide band. The presence of a new band assignable to $\upsilon(Cu–S)$ confirms that the sulfur atoms are involved in the coordination. Finally, in the case of complex (**III**) there is a new peak at 1,736 cm^{-1} and also the number of peaks in the region of 3,000–3,400 cm^{-1} related to the hydroxyl groups decreased that confirm the formation of ester linkage.

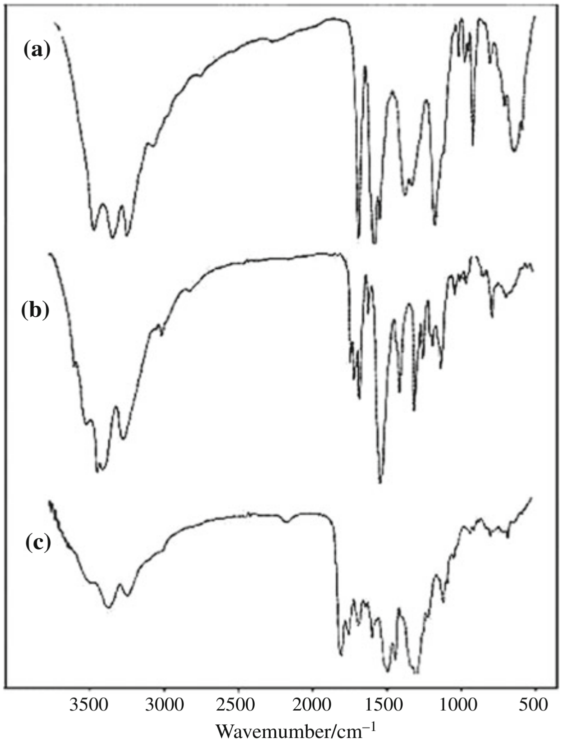
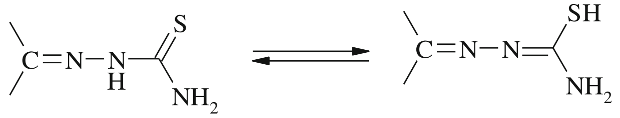


Fig. 1 FT-IR spectra of the curing agents: (*a*) (**I**), (*b*) (**II**), and (*c*) (**III**)

Curing behavior

The curing behavior of DGEBA-(**I**), DGEBA-(**II**), and DGEBA-(**III**) systems were studied by using DSC at different heating rates (5, 10, 15, and 20 K min^{-1}). DSC thermograms of curing DGEBA with these curing agents are shown in Figs. 2, 3, and 4. From DSC thermograms, it can be clearly observed that the initial curing temperature (T_i) and the maximum peak temperature (T_p) increased with increasing heating rate. The exothermic peak is due to polymerization and etherification reactions of the epoxide groups with the amine and hydroxyl groups. DSC thermograms of curing DGEBA-(**I**) system, in Fig. 2, show a shoulder peak when the heating rate increases. The two steps curing of DGEBA-(**I**) system can be attributed to the possible tautomerization in the curing agent, which may occur at the higher temperatures, and formation of thiol groups which can compete with the primary amine groups in reaction with the epoxide groups:



The appearance of shoulder peak indicates that there are two competing reactions between functional groups in the curing agent with the epoxide groups. However, formation of complex between ligand (**I**) and Cu(II) and acetylation of the complex (**III**), shown in Scheme 1, had a significant effect on the mechanism of cure reaction with DGEBA. DSC thermograms of DGEBA-(**II**) and DGEBA-(**III**) systems in Figs. 3 and 4 show one sharp exothermic peak in all the heating rates. These results confirm the absence of tautomerization in the complexes of (**II**) and (**III**) and they have only one type of functional group, –NH_2, which reacts with the epoxide group and generate one single exothermic peak in DSC test. The data obtained from DSC thermograms of the curing systems are listed in Table 1. The T_p of curing of DGEBA-(**III**) system shifted toward lower temperature in comparison with T_p of DGEBA-(**I**) system which can be due to lower melting temperature and better solubility of the (**III**) in DGEBA because of the acetylation of the hydroxyl groups.

Cure kinetics

DSC method assumes that for a cure process the measured heat flow (dH/dt) is proportional to the conversion rate, $d\alpha/dt$. Non-isothermal DSC methods can be used as single-heating rate and multi-heating rate methods. Two multiple-heating rate methods that have been shown to be effective are KAS [26, 27] and FWO given by Flynn and Wall [28] and Ozawa [29]. According to the KAS method based on Coats–Redfern approximation [30], E_a is obtained from the maximum reaction rate where $d(d\alpha/dt)/dt$ is zero under a constant heating rate condition. The basic equation of the method in the integral form is:

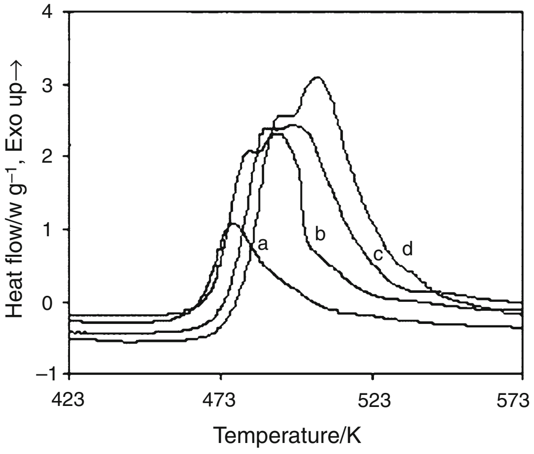


Fig. 2 DSC thermograms of cure reaction of DGEBA/(**I**) system at: (*a*) 5, (*b*) 10, (*c*) 15, and (*d*) 20 K min^{-1}

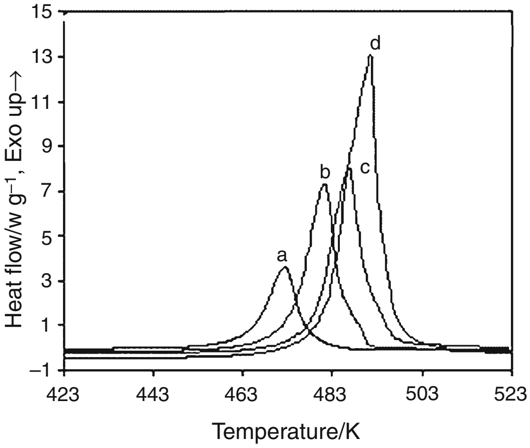


Fig. 3 DSC thermograms of cure reaction of DGEBA/(**II**) system at: (*a*) 5, (*b*) 10, (*c*) 15, and (*d*) 20 K min^{-1}

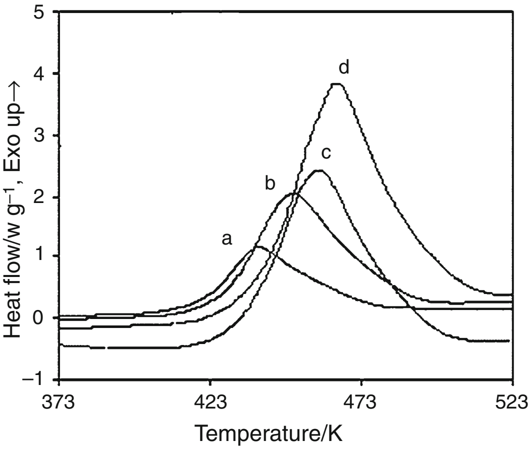


Fig. 4 DSC thermograms of cure reaction of DGEBA/(**III**) system at: (*a*) 5, (*b*) 10, (*c*) 15, and (*d*) 20 K min^{-1}

$$\mathrm{Ln}\left(\beta_i/T_{p,i}^2\right) = \mathrm{Ln}(AR/E_a) - E_a/RT_{p,i} \tag{1}$$

where β_i is the heating rate and $T_{p,i}$ is the peak temperature at different heating rates. The activation energy E_a and the pre-exponential factor A can be calculated from the slope and y intersect of the linear plot of $-\mathrm{Ln}\left(\beta/T_{p,i}^2\right)$ against ($1/T_p$), respectively.

The FWO method based on Doyle's approximation [31] is an alternative method for the calculation of E_a and is expressed in the integral form as follows:

$$\mathrm{Ln}(\beta_i) = \mathrm{Const.} - 1.052E_a/RT_p \tag{2}$$

A plot of $\mathrm{Ln}\beta$ versus $1/T_p$ should give a straight line with a slope of $1.052E_a/R$. The obtained values of E_a by KAS and FWO methods are listed in Table 2.

Table 1 Curing data from DSC thermograms

Heating rate/°C min^{-1}	DGEBA/(**I**)		DGEBA/(**II**)		DGEBA/(**III**)	
	T_p/K	ΔH_r/J g^{-1}	T_p/K	ΔH_r/J g^{-1}	T_p/K	ΔH_r/J g^{-1}
5	477.15	347.7	472.15	389.7	439.15	373.0
10	491.15	380.1	481.15	386.6	450.15	361.1
15	496.15	352.5	486.15	356.6	458.15	380.0
20	505.15	343.9	491.15	351.2	465.15	387.1

Table 2 E_a values obtained by using DSC data and different kinetic equations

Curing system	E_a, KAS method/ kJ mol^{-1}	E_a, FWO method/ kJ mol^{-1}	E_a, isoconversional method/kJ mol^{-1}
DGEBA/(**I**)	94.2	97.4	95.8
DGEBA/(**II**)	135.5	136.4	134.6
DGEBA/(**III**)	84.3	87.2	85.9

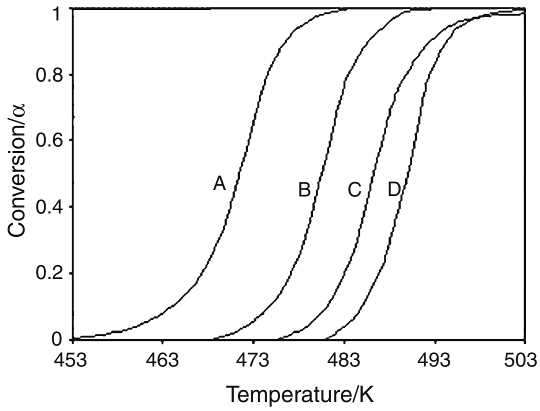


Fig. 5 Plots of α_i versus T_i for curing of DGEBA/(**II**) system at: (*a*) 5, (*b*) 10, (*c*) 15, and (*d*) 20 K min^{-1}

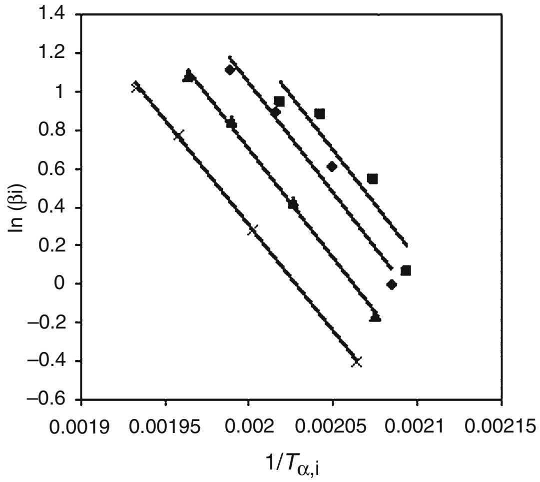


Fig. 6 Plots of Lnβ_i versus $1/T_i$ for curing DGEBA/(**I**) system at different conversions of: $\alpha = 0.2$ (*filled diamond*), $\alpha = 0.4$ (*filled triangle*), $\alpha = 0.6$ (*times*), $\alpha = 0.8$ (*filled square*)

The above methods have a limitation because they produce a single value of E_a for the whole process which is a sign of a single-step process. A more complete determination of E_a at any selected conversion can be calculated by the most popular isoconversional Eq. 3 [32–35] of FWO that is similar to Eq. 2 except in $T_{\alpha,i}$ that is the temperature at different conversions at different heating rates:

$$\mathrm{Ln}(\beta_i) = \mathrm{Const.} - 1.052E_a/RT_{\alpha,i} \quad (3)$$

The isoconversional method allows complex processes to be detected by a variation of E_α with α. The basic idea of this type of analysis is that the reaction rate at a constant conversion depends only on the temperature. To perform isoconversional analysis, the original DSC data in Figs. 2, 3, and 4 were transformed into the form α_i versus T_i for each *i*th heating rate. Conversions were determined as fractional areas of a DSC peak. The isoconversional temperatures were obtained from the conversion curves at any selected conversion. The resulting dependence of α_i versus T_i for each heating rate is shown in Fig. 5 for the representative DGEBA-(**II**) system. Figure 6 shows a typical Arrhenius plots of Ln(β_i) versus $1/T_i$, using Eq. 3, for the DGEBA-(**I**) system in a range of $0.2 \leq \alpha \leq 0.8$. The E_a value for each conversion was obtained from the slope of the straight line and the resulting dependence of E_a on conversion (α_i) is presented in Fig. 7. The E_a values remain constant up to $\alpha = 0.6$ and then started to decrease slightly for DGEBA-(**I**) and DGEBA-(**II**) systems with increasing α. This rule was accordance with the hypothesized mechanism of an amino epoxy. The decrease in activation energy can be due to the autocatalytic role of hydroxyl groups in the curing reaction. The average values of E_a obtained from isoconversional studies for DGEBA-(**I**), DGEBA-(**II**), and DGEBA-(**III**) systems are 95.8, 134.6, and 85.9 kJ mol^{-1}, respectively, which are close with those obtained by KAS and FWO methods. The higher reactivity of complex (**III**) can be due to lower melting point and also better solubility in DGEBA which can be related to the acetylation of the hydroxyl groups.

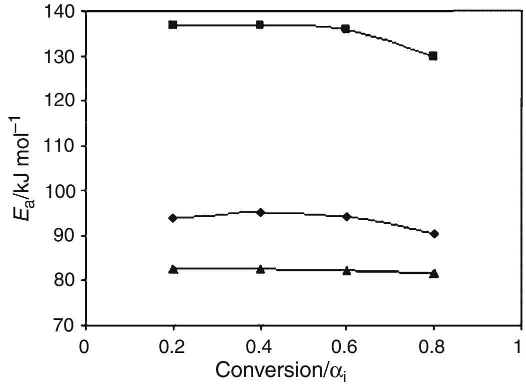


Fig. 7 Plots of E_a versus α_i for curing of DGEBA with different curing agents of: *filled triangle* (**III**), *filled diamond* (**I**), *filled square* (**II**)

Conclusions

Optical active curing agents (**I**), (**II**), and (**III**) based on D-glucose were prepared, and their characteristic properties were measured and checked with those reported in the literature. The exothermic peak of curing of DGEBA with (**I**), (**II**), (**III**) appeared in the ranges 473–423, 463–503, and 423–483 K, respectively. DSC thermograms of curing DGEBA-(**I**) system showed a shoulder peak due to reaction of epoxide group with the thiol group which is formed as a result of tautomerization. The E_a values of curing by using KAS, FWO, and isoconversional methods were found to be in the ranges 94.2–97.4, 135.5–136.4, and 84.3–87.2 kJ mol^{-1} for DGEBA-(**I**), DGEBA-(**II**), and GEBA-(**III**) systems, respectively. The order of reactivity of the curing agents toward epoxide group is: (**III**) > (**I**) > (**II**). The higher reactivity of complex (**III**) can be attributed to the structural change in the curing agent as a result of acetylation of hydroxyl groups which reduced the melting temperature and also improved its solubility in DGEBA.

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