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STUDY OF THE REACTION MECHANISM OF THE COPPER CHELATE WITH DGEBA USING DSC

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Abstract

The reaction mechanism of metal-containing and complex compound with epoxy oligomer of diglycidyl ether of bisphenol A (DGEBA) was studied using dynamic DSC technique. It is shown that cure reaction of the epoxy oligomers with copper acetate proceeds at two stages: through coordination of cation with the epoxy group, and through ionic polymerization at high temperatures. Mechanism of curing of DGEBA with copper chelate depends on equilibrium process of dissociation of the chelate which, in turn, depends not only on temperature of curing but also on concentration of the hardener. At the dissociation temperature of the hardener, polymerization proceeds according to ionic mechanism. Hardening of the epoxy oligomers due to interaction of epoxy groups with unconnected amine groups predominate at higher temperatures or at higher concentrations of the hardener. At low temperatures and small concentrations of the hardener, polymerization proceeds according to catalytic ionic mechanism.

Keywords: copper, curing, DSC, epoxy resins, mechanism

Introduction

A vast number of compounds have been screened for their suitability as curing agents. Many compounds used in the early years of the technology have now been superseded by more sophisticated materials, though some still retain their popularity. There are several factors on which the choice of curing agent to be used with an epoxide resin will depend upon: *a*) handling characteristics; *b*) cure, post-cure time and temperature requirements; *c*) properties of the cured system; and *d*) cost of the curing agent. The extent and nature of the intermolecular cross-linking will, therefore, be determined in part by the correct choice of curing agent. Linear epoxy resins are converted into a three-dimensional network during cure reaction.

Various studies, using different experimental techniques, report efforts to evaluate the rate and mechanism of cure reaction. It was reported by Kurnoskin [1, 2] to use metal chelates of different structures to cure epoxy oligomers of diglycidyl ether of bisphenol-A(DGEBA).

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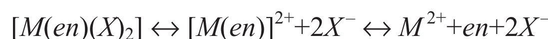
The properties of the metalliferous epoxy chelate polymers and the dependence of their strength on the content of the chelates were examined. It was also suggested that the optimum set of strength, water resistance and thermal stability were reacted by using 0.17, 0.11 and 0.07 mol of a chelate per 1 mol of DGEBA regardless of the chelate stucture (1). When DGEBA is hardened with the metal chelates of the same molar concentration, then the type of cation is considered to be of prime importance for the formation of matrix structure. It was also considered that the dissociation of chelates is an equilibrium process and depends not only on temperature but also concentration of the complex dissolved in oligomer (Scheme I).



$$[M(en)(X)_2] \leftrightarrow [M(en)]^{2+}+2X^{-} \leftrightarrow M^{2+}+en+2X^{-}$$

Scheme I

where M is the metal cation; *en*, alkyl amine and X, the anion of an organic acid. A variety of experimental techniques including differential scanning calorimeter (DSC) has been developed to follow the cure reaction of thermosetting systems. DSC technique is used in polymers in determining transition temperatures (T_g and T_m), degree of crystallinity, reaction kinetics and materials purity [3–7] . DSC technique has also been used by several workers [8–14] to study the mechanism and kinetics of curing reactions of epoxy resins with different types of curing agents. In order to contribute in explaining the mechanism of cure reaction of DGEBA with one of metal chelates, such as copper chelate with an amine, the following work has been carried out using DSC.

Experimental

Materials

The epoxy compound used was a diglycidyl ether of bisphenol A based epoxy resin: Epon 828 obtained from Shell Co. with epoxy equivalent weight of about 185. Ethylene diamine and copper acetate monohydrate of decomposition temperature of 240°C were obtained from Fluka.

Syntheses

The metal chelate of structure $Cu(en)(OAc)_2$ was prepared according to the following modified procedure[15, 16]: For the dehydration, copper acetate was heated at 110°C for 12 h in a vacuum oven. Ethylene diamine (0.01 mol) was added gradually to copper acetate (0.01 mol) in dry acetone and it was thoroughly mixed with stirring for 20 min. The mixture was then filtered and the filtrate was washed several times with mixture of acetone and diethyl ether. After drying in a vacuum oven, a green solid product decomposing at 140–151°C was obtained. IR measurements, Fig. 1, showed a band at 1250 cm^{-1} assigned to C–O, and bands at 1640 and 3550 cm^{-1} assigned to N–H bending and stretching, respectively, and band at 1720 cm^{-1} related to C=O of acetate group.

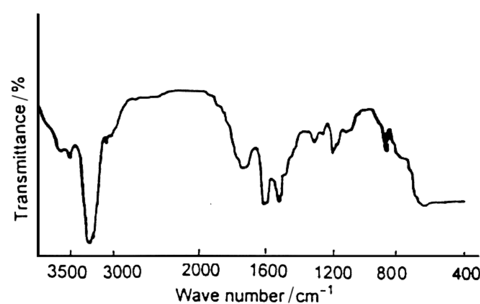


Fig. 1 IR Spectrum of the complex compound Cu(*en*)$(OAc)_2$

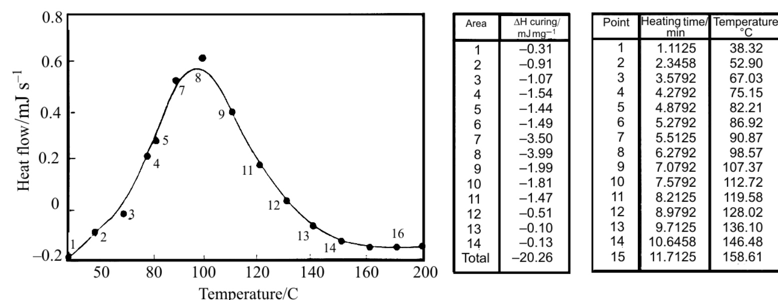
Apparatus

DSC instrument of polymer Laboratory was used to monitor the dynamic curves of cross-linking reaction at a heating rate of 10ºC min^{-1}. Based on calculations made using epoxy equivalent weight, 8–12 g of ethylene diamine must be used as a hardener per 100 g of resin. Different concentrations of copper chelate complex of 12, 20, 24, 28, and 30 phr (or 0.05, 0.080, 0.100, 0.115 and 0.124 moles, respectively) were used as hardener. Dynamic DSC curves obtained from reaction of metal chelate with epoxy oligomers were compared with those obtained using ethylene diamine and copper acetate alone as a hardener.

Results and discussion

As epoxy resin can be cured with ethylene diamine (*en*) alone, it was decided to compare the DSC curves with those obtained from employing copper chelate. A typical curve of dynamic DSC run for DGEBA/*en* system of 10 phr of hardener at a heating rate of 10°C min^{-1} is shown in Fig. 2.

The total area under the curve, based on the extrapolated base line of the reaction, was used to calculate the total heat of reaction which is strongly dependent on the concentration of curing agent. Replicate experiments were performed at each concentrations of the hardener and the kinetic parameters i.e., activation energy (E_a), frequency factor



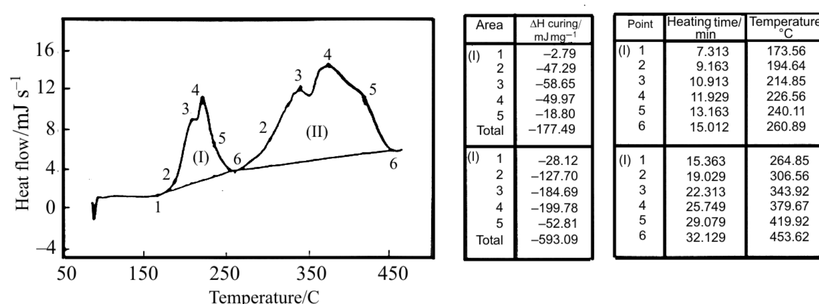
Area	ΔH curing/ mJ mg^{-1}
1	–0.31
2	–0.91
3	–1.07
4	–1.54
5	–1.44
6	–1.49
7	–3.50
8	–3.99
9	–1.99
10	–1.81
11	–1.47
12	–0.51
13	–0.10
14	–0.13
Total	–20.26

Point	Heating time/ min	Temperature/ °C
1	1.1125	38.32
2	2.3458	52.90
3	3.5792	67.03
4	4.2792	75.15
5	4.8792	82.21
6	5.2792	86.92
7	5.5125	90.87
8	6.2792	98.57
9	7.0792	107.37
10	7.5792	112.72
11	8.2125	119.58
12	8.9792	128.02
13	9.7125	136.10
14	10.6458	146.48
15	11.7125	158.61

Fig. 2 DSC curves of curing DGEBA with 10 phr of ethylene diamine

Table 1. Kinetic parameter of curing of DGEBA with parameters

Hardener	Concentration/(phr)	Peak	n	E_a/ kJ mol^{-1}	A (1 s^{-1})
Ethylene diamine (*en*)	8	–	1.4	71.1	$3.7 \cdot 10^7$
	10	–	1.4	67.4	$5.1 \cdot 10^7$
$Cu(OAc)_2$	20	1st	1.4	154.8	$1.36 \cdot 10^{14}$
		2nd	1.0	331.3	$1.84 \cdot 10^3$
$Cu(en)OAc)^2$	12	1st	1.8	262.0	$2.24 \cdot 10^{29}$
		2nd	0.95	325.4	$3.68 \cdot 10^{23}$
	20	1st	1.7	254.5	$5.07 \cdot 10^{29}$
		2nd	0.85	331.3	$2.60 \cdot 10^{37}$
	24	–	1.7	277.8	$2.62 \cdot 10^{30}$
	28	–	1.8	271.7	$6.04 \cdot 10^{31}$
	30	–	1.3	202.0	$3.66 \cdot 10^{22}$



Area		ΔH curing/ mJ mg^{-1}
(I)	1	–2.79
	2	–47.29
	3	–58.65
	4	–49.97
	5	–18.80
	Total	–177.49
(I)	1	–28.12
	2	–127.70
	3	–184.69
	4	–199.78
	5	–52.81
	Total	–593.09

Point		Heating time/ min	Temperature/ °C
(I)	1	7.313	173.56
	2	9.163	194.64
	3	10.913	214.85
	4	11.929	226.56
	5	13.163	240.11
	6	15.012	260.89
(I)	1	15.363	264.85
	2	19.029	306.56
	3	22.313	343.92
	4	25.749	379.67
	5	29.079	419.92
	6	32.129	453.62

Fig. 3 DSC curves of curing of DGEBA with 20 phr of $Cu(OAc)_2$

(A), and reaction order (n) are given in Table 1. As it is seen in Fig. 2, the single maximum of the exotherm peak for DGEBA/*en* system appears at about 100ºC for 10 phr of hardener. The exotherm peaks are shown in Fig. 3 for DGEBA/copper acetate system and in Figs. 4–8 for DGEBA/copper chelate system at different concentrations. These data indicate that DGEBA/ethylene diamine system cures at a lower temperature and faster than DGEBA/copper chelate and copper acetate systems. According to the classic Barretts's method [17] the reaction rate dα/dt is directly proportional to the rate of heat generation dH/dt (which is the ordinate of a DSC trace):

$$d\alpha/dt = 1/\Delta H dH/dt \tag{1}$$

where, ΔH=H_t mass of sample

The extent of reaction, α, is given by:

$$\alpha=\Delta H_t / \Delta H \quad (2)$$

where ΔH_t is partial area under a DSC trace up to a temperature. The reaction rate can also be expressed in differential forms:

$$d\alpha/dt = Kf(\alpha) \quad (3)$$

where K is the Arrhenius rate constant, and $f(\alpha)$ a functional form of α, that depends on the reaction mechanism. By incorporating the Arrhenius form of the rate constant K. $K = A \exp(-E_a/RT)$, Eq. 3 can be rearranged in the following form:

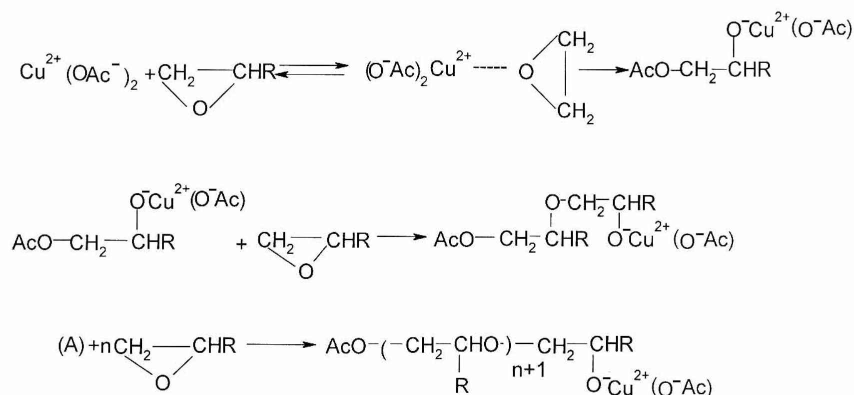
$$d\alpha/dt = A \exp(-E_a / RT) f(\alpha) \quad (4)$$

where A is frequency factor, E_a activation energy, R gas constant and T temperature in K. Integration of Eq. 4 yields :

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln K = \ln A - E_a/RT \quad (5)$$

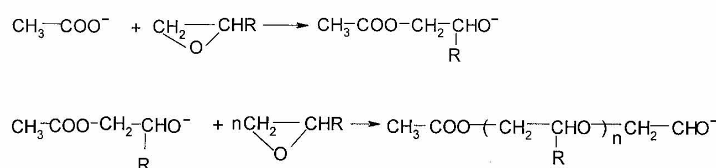
which forms the starting equation for derivative analysis of the dynamic data. The computer program reads in dynamic data from data file and calculates $\ln[(d\alpha/dt)f(\alpha)]$ for each conversion point using the functional form for chosen model. A plot of the left-hand side of the above equation *vs.* $1/T$ should give a straight line with a slope of $-E_a/R$ for the correct functional form $f(\alpha)$. The intercept is $\ln A$ from which the frequency factor can be evaluated.

The mechanism of curing of epoxy resin with amines is given in the literature [18]. Copper acetate as a hardener is an ionic compound which can react with epoxy oligomers through the coordination of the cations with epoxy groups and is accompanied by formation of a transition complex or an ionic associate which acts as an initiator of ionic mechanism for ring opening polymerization of the oxirane [1, 15], as depicted in Scheme II, where *R* in this Scheme is an alkyl group; and *n* a whole number.



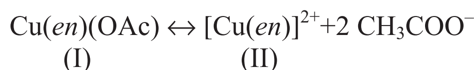
Scheme II

Figure 3 shows DSC curve of cure reaction of DGEBA with 20 phr of copper acetate. The first exotherm peak can be related to the mechanism of curing by ionic polymerization. Further growth of temperature of curing process is accompanied by decomposition of metal salt into acetate anion and copper cation. The second large exotherm peak, as in Fig. 3, can be related to further ionic polymerization of oxirane by this new species where its mechanism is shown in Scheme III.



Scheme III

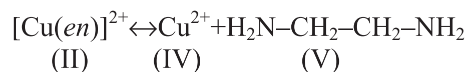
Reaction of metal-containing complex with epoxy oligomers has been examined in several works [1–2]. Temperature of the beginning of active reaction between chelate and epoxy oligomer is defined by temperature of decomposition of the complex into acetate anion and complex cation(II) as shown in Scheme IV. It is seen in Fig. 4 that this temperature for copper chelate complex of structure Cu(*en*)$(OAc)_2$ is higher than 140°C.



$$\mathrm{Cu}(en)(\mathrm{OAc}) \leftrightarrow [\mathrm{Cu}(en)]^{2+} + 2\ \mathrm{CH_3COO^-}$$
(I) (II)

Scheme IV

Reaction of oligomers with anions are determined by functionality of the later, i.e. by the number of active groups capable of chemical bonding in interaction with epoxy group. In case of the acetate, the reaction proceeds according to ionic mechanism as in Scheme III. This mechanism of formation of cross-linkages can be related to first exotherm peak with a maximum of 159°C which appears in the DSC curve of DGEBA / Cu(*en*)$(OAc)_2$ system at a concentration of 12 phr of the hardener (Fig. 4). The complex cation (II) possesses high stability and further growth of temperature is accompanied by breaking the donor-acceptor bonds into unconnected ethylene diamine and copper cation (Scheme V). It is seen in Fig. 4 that this temperature for copper cation is higher than 360°C.



$$[\mathrm{Cu}(en)]^{2+} \leftrightarrow \mathrm{Cu}^{2+} + \mathrm{H_2N{-}CH_2{-}CH_2{-}NH_2}$$
(II) (IV) (V)

Scheme V

Hardening of oligomers at temperature equal to or higher than temperature of dissociation of the complex cation (II), according to Scheme V, occurs due to interaction of aliphatic amines that have lost coordinate bonds with the metal. Curing of epoxy oligomer with aliphatic amine groups can be related to the second exotherm

Area	ΔH curing/ mJmg^{-1}
1	−16.55
2	−0.60
3	−51.34
4	−49.61
5	−25.26
Total	−11.47
1	−14.91
2	−29.55
3	−41.41
4	−19.73
5	−2.49
Total	−108.09

Point	Heating time/ min	Temperature/ °C
1	6.179	119.02
2	8.863	149.77
3	9.613	158.87
4	10.579	169.41
5	12.046	185.87
6	13.729	204.86
1	27.379	359.34
2	29.063	378.16
3	30.029	389.14
4	31.212	402.15
5	32.746	419.27
6	33.929	432.44

Fig 4. DSC curves of curing of DGEBA with 12 phr of Cu(en)$(OA)_2$

peak with a maximum of 388°C which is seen in Fig. 4. It is necessary to take into consideration that dissociation of the chelates, as in Scheme IV and V, is an equilibrium process and depends not only on temperature but also on concentration of the complex dissolved in the oligomer. Decrease in the hardener concentration shall reduce content of the complex cation (II) and acetate anion in the system and, in turn, that of copper cation (IV) and ethylene diamine (V). On the contrary, introduction of additional amount of the hardener would shift the chemical equilibrium to the right. Thus, at low temperatures and small concentrations, the polymerization proceeds mainly according to the catalytic ionic mechanism, as presented in Scheme VI.

[Cu(*en*)($CH_3COO)_2$] + CH_2---CHR (O) ⇌ RCH / >O----[Cu(*en*)($CH_3COO)_2$] (δ + CH_2) ⟶

CH_3-COO-CH_2-CHR-O^-[Cu(*en*)$^{2+}$ (CH_3COO^-)]
(A)

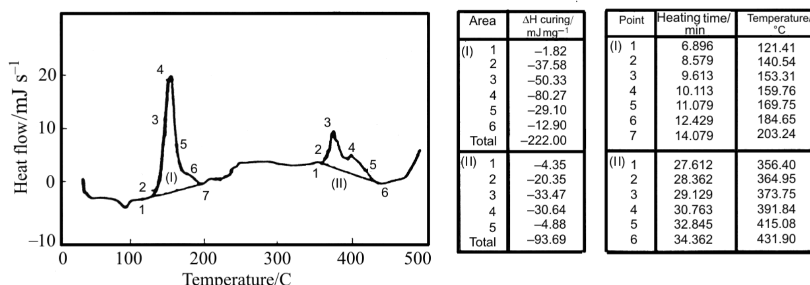
(A) + CH_2---CHR (O) ⇌ CH_3-COO-CH_2-CHR-O^-[Cu(*en*)$^{2+}$ (CH_3-COO^-)] (RCH---CH_2 δ+, Oδ-)

CH_3-COO-CH_2-CHR-O^-[Cu(*en*)]$^{2+}$$O^-$-CHR-$CH_2$-OOC-$CH_3$
(B)

(B) + *n* CH_2---CHR (O) ⟶ R, CH, CH_2-(-O-RCH-CH_2-)-OOC-CH_3; H_2N, O, NH_2, Cu; CH_2 —|— CH_2; O; CH, R; CH_3-COO-(-CH_2-CH_2-O-)- CH_2
(C)

Scheme VI

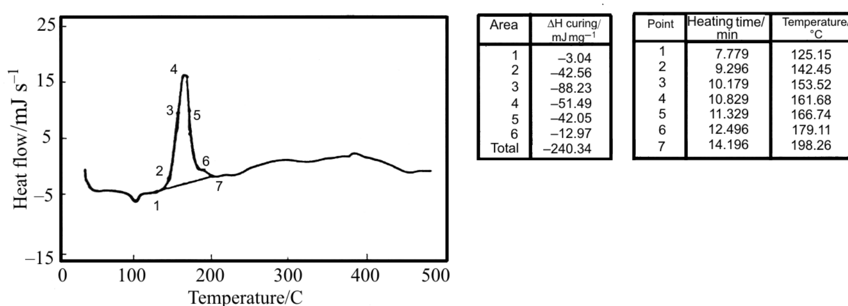
With shift of the chemical equilibrium to the right, which results from either temperature rise or addition of hardener concentration, hardening of the epoxy oligo-



Area		ΔH curing/ mJ mg^{-1}
(I)	1	–1.82
	2	–37.58
	3	–50.33
	4	–80.27
	5	–29.10
	6	–12.90
	Total	–222.00
(II)	1	–4.35
	2	–20.35
	3	–33.47
	4	–30.64
	5	–4.88
	Total	–93.69

Point		Heating time/ min	Temperature/ °C
(I)	1	6.896	121.41
	2	8.579	140.54
	3	9.613	153.31
	4	10.113	159.76
	5	11.079	169.75
	6	12.429	184.65
	7	14.079	203.24
(II)	1	27.612	356.40
	2	28.362	364.95
	3	29.129	373.75
	4	30.763	391.84
	5	32.845	415.08
	6	34.362	431.90

Fig 5. DSC curves of curing of DGEBA with 20 phr of Cu(*en*)$(OAc)_2$



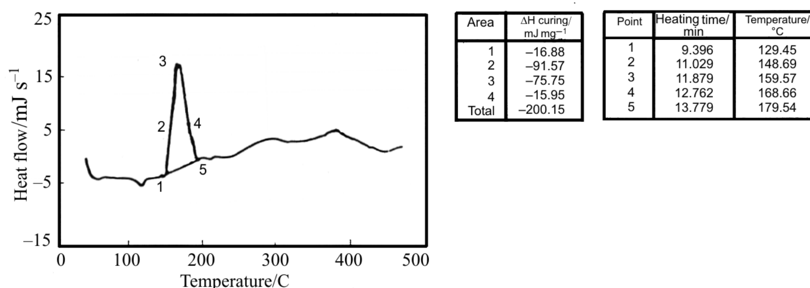
Area	ΔH curing/ mJ mg^{-1}
1	–3.04
2	–42.56
3	–88.23
4	–51.49
5	–42.05
6	–12.97
Total	–240.34

Point	Heating time/ min	Temperature/ °C
1	7.779	125.15
2	9.296	142.45
3	10.179	153.52
4	10.829	161.68
5	11.329	166.74
6	12.496	179.11
7	14.196	198.26

Fig 6. DSC curves of curing of DGEBA with 24 phr of Cu(*en*)$(OAc)_2$

mers will be realized at expense of its interaction with the complex cation (II) and acetate anion, and also with the loose of amino groups.

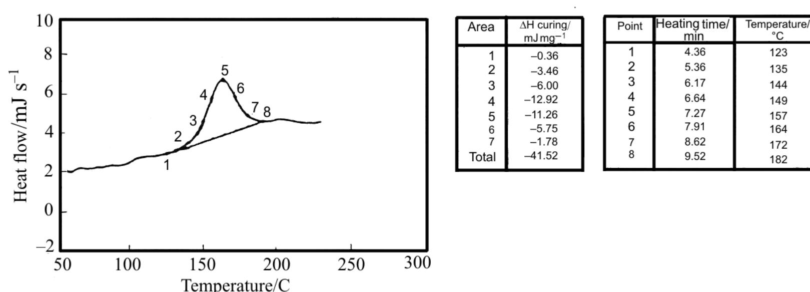
Further increase of the hardener concentration in an epoxy composition would shift the chemical equilibrium, as in Scheme IV and V, up to formation of ethylene diamine at lower temperatures and yields the same structure as those obtained in DGEBA hardening at temperature exceeding temperature of dissociation of the complex cation (II). This has been shown in Figs 5–8, where the hardener concentration is 20, 24, 28 and 30 phr, respectively. Thus, in conditions where hardener concentration exceeds the optimum quantity a predominant formation of epoxy-amine network results from reaction between epoxy oligomer and unconnected amine groups. As hardener concentration rises from 12 to 20 phr the chemical equilibrium shifts further to the right (Schemes IV and V) and contribution of loose amine groups in formation of the cross-linked polymer becomes predominant and the second exotherm peak becomes smaller and completely disappears at higher concentrations. These are evident as in Figs 6, 7 and 8 for hardener concentrations of 24, 28 and 30 phr, respectively. The kinetic parameters of curing of DGEBA with copper chelate at different concentrations are given in Table 1. Thus, the first exotherm peak of DSC curves of curing process with copper chelate can be mainly related to: ionic polymerization of epoxy groups with acetate anion and/or interaction of epoxy groups with unconnected amino groups which depends on concentration of the hardener. The second exotherm peak exists only at low concentration of the hardener and it comes into effect when a driving force such as temperature causes complex cation (II) to dissociate into free amino group.



Area	ΔH curing/ mJ mg^{-1}
1	–16.88
2	–91.57
3	–75.75
4	–15.95
Total	–200.15

Point	Heating time/ min	Temperature/ °C
1	9.396	129.45
2	11.029	148.69
3	11.879	159.57
4	12.762	168.66
5	13.779	179.54

Fig 7. DSC curves of curing of DGEBA with 28 phr of Cu(*en*)(OAc)$_2$



Area	ΔH curing/ mJ mg^{-1}
1	–0.36
2	–3.46
3	–6.00
4	–12.92
5	–11.26
6	–5.75
7	–1.78
Total	–41.52

Point	Heating time/ min	Temperature/ °C
1	4.36	123
2	5.36	135
3	6.17	144
4	6.64	149
5	7.27	157
6	7.91	164
7	8.62	172
8	9.52	182

Fig 8. DSC curves of curing of DGEBA with 30 phr of Cu(*en*)(OAc)$_2$

Conclusion

The results show that DSC can be applied successfully to study the mechanism of curing of epoxy oligomers with the metal-containing compounds and complexes. The epoxy oligomers can be cured by metal salt through coordination of cation with epoxy group. But with further growth of curing temperature, the metal salt dissociates into an organic anion and the polymerization proceeds through ionic mechanism.

Curing of epoxy oligomers with the metal chelate is described by the dissociation temperature of the complex.This is an equilibrium process which depends not only on the temperature of curing but also no the concentration of the complex dissolved in the epoxy oligomers. At the dissociation temperature of the hardener, the polymerization proceeds according to ionic mechanism at the expense of interaction of acetate anion with epoxy groups. At further growth of temperature or increasing concentration of the hardener, the coordination bonds between donor-acceptor in the complex cation will be broken and unconnected aliphatic amine groups will be produced.

Thus, hardening of the oligomers proceeds according to interaction of epoxy groups with the loose amine. On the contrary, at lower temperatures and/or reduced quantity of hardener the equilibrium process shifts to the left and polymerization proceeds mainly according to the catalytic ionic mechanism and a structure of epoxy-chelate polymer matrix fragment of (C) shown in Scheme VI is created. It is, therefore, concluded that if a high concentration of the hardener (i.e. >20 phr or 0.08 mol) is used, the equilibrium process shifts to the right and it yields free aliphatic amine which reacts with epoxy oligomers at low temperatures and produces a cross-linked polymer.

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