

*Archive of SID***Study of the Reaction Mechanism of the Copper Chelate with DGEBA Using DSC**

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Received: 22 August 1998; accepted 5 July 1999

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 the coordination of the cation with the epoxy group, and through ionic polymerization at high temperatures. The mechanism of curing of DGEBA with the copper chelate depends on the equilibrium process of dissociation of the chelate which, in turn, depends not only on the temperature of curing but also on the concentration of the hardener. At the dissociation temperature of the hardener, the polymerization proceeds according to ionic mechanism. Hardening of the epoxy oligomers due to interaction of the epoxy groups with the unconnected amine group predominates at higher temperatures or at higher concentrations of the hardener. At low temperatures and small concentrations of the hardener, the polymerization proceeds according to the catalytic ionic mechanism.

Key Words: epoxy resins, curing, copper, mechanism, DSC

INTRODUCTION

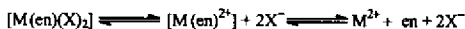
A vast number of compounds have been screened for their suitability as curing agents. Many compounds used in the early years of the technology have now been superseded by more sophisticated materials, though some still retain their popularity. There are several factors on which the choice of curing agent 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 reached by using 0.17, 0.11 and 0.07 mol of a chelate per 1 mol of DGEBA regardless of the chelate structure (I). 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 the matrix structure. It was also considered that the dissociation of chelates is an equilibrium process and depends not only on the temperature but also the concentration of the complex dissolved in the oligomer (Scheme I).



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. The DSC technique is used in polymers in determining the transition temperatures (T_g and T_m), degree of crystallinity, reaction kinetics and materials purity [3-7].

The 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 the metal chelates, such as copper chelate with an amine, the following work has been carried out using DSC. The purpose of this work is to delineate the reaction mechanism of DGEBA with copper acetate ethylene diamine complex.

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.

Synthesis

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:

$Cu(en)(OAc)_2$	C(%)	H(%)
Found	29.5	5.5
Calculated	29.7	5.7

The IR measurements 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.

The IR spectrum of compound $Cu(en)(OAc)_2$ is shown In Figure 1.

Apparatus

DSC instrument of Polymer Laboratory was used to

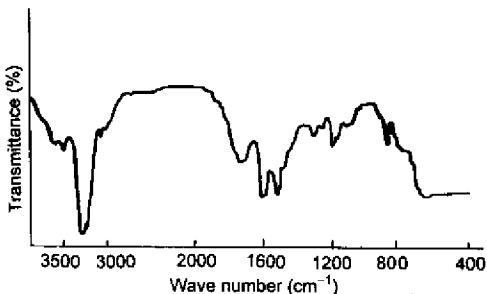


Figure 1. IR Spectrum of the complex compound $Cu(en)(OAc)_2$.

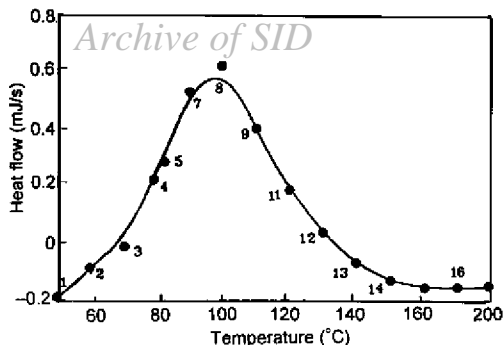


Figure 2. DSC Thermogram of curing of DGEBA with 10 phr of ethylene diamine.

Area	ΔH curing (mJ/mg)
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	4.2782	75.15
5	4.8782	82.21
6	5.2792	86.92
7	5.6125	90.87
8	6.2792	98.57
9	7.0782	107.37
10	7.5782	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

monitor the dynamic thermograms of cross-linking reaction at a heating rate of 10 °C/min. Based on the calculations made by using epoxy equivalent weight, 8–12 g of ethylene diamine must be used as a hardener per 100 g of the resin. Different concentrations of copper chelate complex of 12, 20, 24, 28 and 30 phr (0.050, 0.080, 0.100, 0.115 and 0.124 mols, respectively) were used as hardener. Dynamic DSC thermograms obtained from the reaction of metal chelate with epoxy oligomers were compared with those obtained using ethylene diamine and copper acetate alone as a hardener.

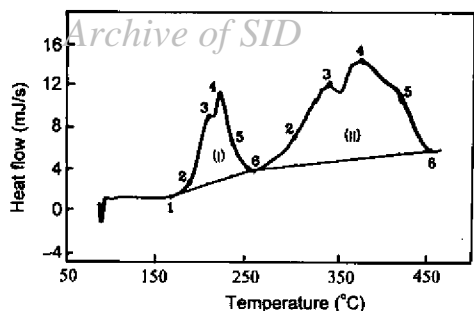
RESULTS AND DISCUSSION

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

The total area under the thermogram, based on the extrapolated base line at the end of the reaction, was used to calculate the total heat of reaction which is strongly dependent on the concentration of curing

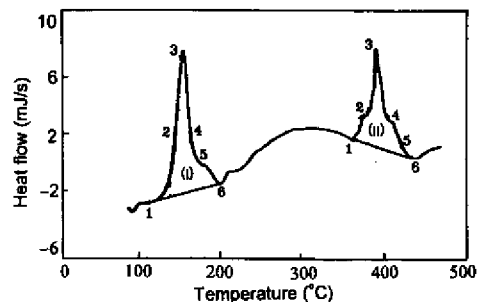
Table 1. Kinetic parameter of curing of DGEBA with hardeners.

Hardener	Concentration (phr)	Peak	n	E_a (kJ/mol)	A (1/s)
Ethylene diamine (en)	8	–	1.4	71.1	3.7×10^7
	10	–	1.4	67.4	5.1×10^7
Cu(OAc) ₂	20	1 st	1.4	154.8	1.36×10^{14}
		2 nd	1.0	74.5	1.84×10^3
Cu(en)(OAc) ₂	12	1 st	1.8	262.0	2.24×10^{29}
		2 nd	0.95	325.4	3.68×10^{23}
	20	1 st	1.7	254.5	5.07×10^{29}
		2 nd	0.85	331.3	2.60×10^{37}
	24	–	1.7	277.8	2.62×10^{30}
	28	–	1.8	271.7	6.04×10^{31}
30	–	1.3	202.0	3.66×10^{22}	


 Figure 3. DSC Thermogram of curing of DGEBA with 20 phr of $\text{Cu}(\text{OAc})_2$.

agent. Replicate experiments were performed at each concentrations of the hardener and the kinetic parameters i.e., activation energy (E_a), frequency factor (A), and reaction order (n) are given in Table 1. As it is seen in Figure 2, the single maximum of the exotherm peak for DGEBA/en system appears at about 100 °C for 10 phr of hardener. The exotherm peaks are shown in Figure 3 for DGEBA/copper acetate system and in Figures 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 Barrett's method [17] the reaction rate da/dt is directly proportional to the rate of heat generation dH/dt (which is the ordinate of a DSC trace):

$$da/dt = 1/\Delta H \times dH/dt \quad (1)$$


 Figure 4. DSC Thermogram of curing of DGEBA with 12 phr of $\text{Cu}(\text{en})(\text{OAc})_2$.

Area	ΔH curing (mJ/mg)
(i) 1	-2.79
2	-47.29
3	-58.65
4	-49.97
5	-18.80
Total	-177.49
(ii) 1	-28.12
2	-127.70
3	-184.89
4	-199.78
5	-52.81
Total	-593.09

Point	Heating time (min)	Temperature (°C)
(i) 1	7.313	173.58
2	9.163	194.64
3	10.913	214.85
4	11.929	228.58
5	13.183	240.11
6	15.012	260.89
(ii) 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	32.128	453.62

Where, $\Delta H = \Delta H_i \times \text{wt}$ of sample

The extent of reaction, a , is given by:

$$a = \Delta H_i / \Delta H \quad (2)$$

Where ΔH_i is the partial area under a DSC trace up to a temperature. The reaction rate can also be expressed in differential forms (13):

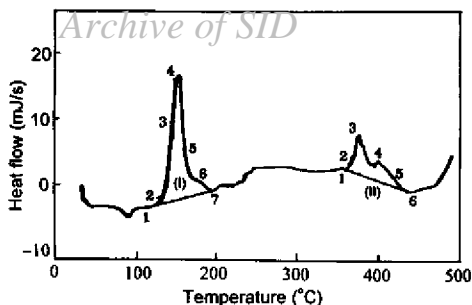
$$da/dt = kf(a) \quad (3)$$

Where k is the arrhenius rate constant, and $f(a)$ a functional form of a , that depends on the reaction mechanism. By incorporating the Arrhenius form of the rate constant k , i.e. $k = A \exp(-E_a/RT)$, eqn (3) can be rearranged in the following form:

$$da/dt = A \exp(-E_a/RT) \times f(a) \quad (4)$$

Area	ΔH curing (mJ/mg)
(i) 1	-16.58
2	-8.60
3	-51.34
4	-49.61
5	-25.26
Total	-114.47
(ii) 1	-14.91
2	-29.55
3	-41.41
4	-19.73
5	-2.49
Total	-108.09

Point	Heating time (min)	Temperature (°C)
(i) 1	6.179	119.02
2	8.863	149.77
3	9.813	158.87
4	10.579	169.41
5	12.046	185.87
6	13.729	204.88
(ii) 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	33.829	432.44



Area	ΔH curing (mJ/mg)
(I) 1	-1.82
2	-37.88
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	-30.84
5	-4.88
Total	-93.89

Point	Heating time (min)	Temperature (°C)
(I) 1	6.898	121.41
2	8.579	140.54
3	9.613	153.31
4	10.113	159.78
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	373.76
4	30.763	391.84
5	32.846	415.08
6	34.392	431.90

Figure 5. DSC Thermogram of curing of DGEBA with 20 phr of Cu(en)(OAc)_2 .

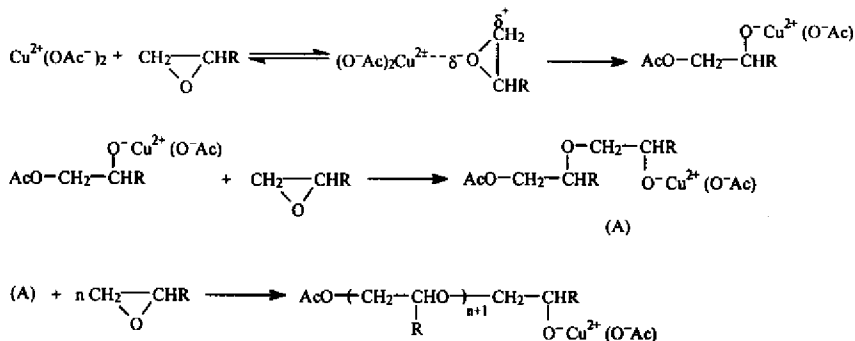
Where A is the frequency factor, E_a the activation energy, R the gas constant and T the temperature in K .

Integration of eqn (4) yields:

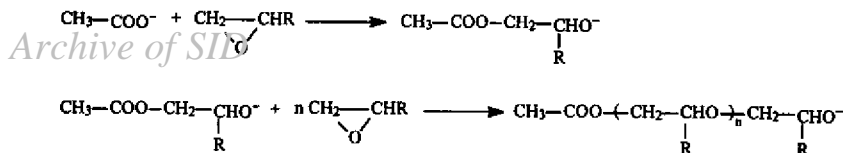
$$\ln[(da/dt)/f(a)] = \ln k = \ln A - E_a/RT \quad (5)$$

which forms the starting equation for the derivative analysis of the dynamic data. The computer program reads in the dynamic data from the data file and calculates $\ln[(da/dt)/f(a)]$ for each conversion point using the functional form for the chosen model. A plot of the left-hand side of the above equation against $1/T$ should give a straight line with a slope of $-E_a/R$ for the correct functional form $f(a)$. 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 the formation of a transition complex or an ionic associate which acts as an initiator of ionic mechanism for the ring opening polymerization of the oxirane [1, 15], as depicted in Scheme II, where R in this scheme an alkyl group; and n a whole number. Figure 3 shows the DSC thermogram 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. The further growth of the temperature of curing system of epoxy/copper salt is accompanied by decomposition of the metal salt into acetate anion and copper cation. The second large exotherm peak,



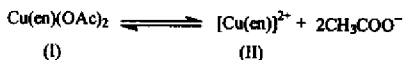
Scheme II



Scheme III

as in Figure 3, can be related to further ionic polymerization of oxirane by this new species where its mechanism is shown in Scheme III.

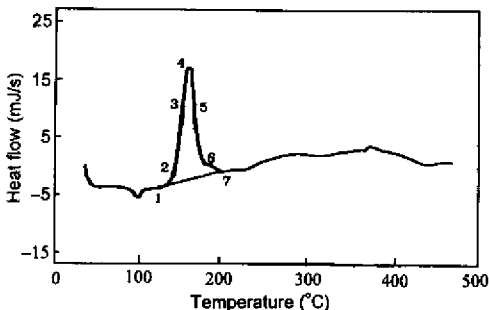
The reaction of metal-containing complex with epoxy oligomers has been examined in several works [1, 2]. The temperature of the beginning of the active reaction between the chelate and the epoxy oligomer is defined by the temperature of the decomposition of the complex into acetate anion and complex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



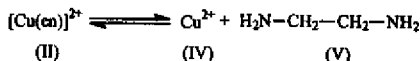
Scheme IV

The reaction of the oligomer with an anion is determined by the functionality of the latter, i.e., by the number of the active groups capable of chemical bonding in the interaction with the epoxy group.

In case of the acetate, the reaction proceeds

Figure 6. DSC Thermogram of curing of DGEBA with 24 phr of Cu(en)(OAc)_2 .

according to the ionic mechanism as in Scheme III. This mechanism of formation of cross-linkages can be related to the first exotherm peak with a maximum of 159 °C which appears in the DSC thermogram of DGEBA/ Cu(en)(OAc)_2 system at a concentration of 12 phr of the hardener (Figure 4). The complex cation (II) possesses high stability and further growth of the temperature is accompanied by breaking the donor-acceptor bonds into unconnected ethylene diamine and copper cation (Scheme V). It is seen in Figure 4 that this temperature for the copper cation is higher than 360 °C.



Scheme V

Hardening of the oligomer at temperature equal to or higher than the temperature of the dissociation of the complex cation (II), according to Scheme V, occurs due to the interaction of the aliphatic amine that has lost coordinate bonds with the metal. The

Area	ΔH curing (mJ/mg)
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	7.775	125.16
2	9.298	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

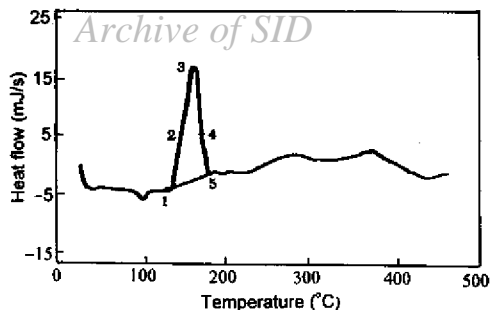


Figure 7. DSC Thermogram of curing of DGEBA with 28 phr of Cu(en)(OAc)_2 .

Area	ΔH curing (mJ/mg)
1	-16.88
2	-91.57
3	-75.75
4	-15.95
Total	-200.15

Point	Heating time (min)	Temperature (°C)
1	9.398	126.45
2	11.029	148.09
3	11.879	159.57
4	12.762	188.66
5	13.776	179.54

curing of epoxy oligomer with the aliphatic amine groups can be related to the second exotherm peak with a maximum of 388 °C which is seen in Figure 4. It is necessary to take into consideration that the dissociation of the chelates, as in Schemes IV and V, is an equilibrium process and depends not only on the temperature but also on the concentration of the complex dissolved in the oligomer. The decrease in the hardener concentration shall reduce the 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, the introduction of the additional amount of the hardener would shift the chemical equilibrium to the right. Thus, at low temperatures and small concentrations of the hardener, the polymerization proceeds mainly according to the catalytic ionic mechanism, as presented in

Scheme VI.

With the shift of the chemical equilibrium to the right, which results from either the temperature rise or addition of the hardener concentration, hardening of the epoxy oligomers will be realized at the expense of its interaction with the complex cation (II) and acetate anion, and also with the loose amino groups.

The further increase of the hardener concentration in an epoxy composition would shift the chemical equilibrium, as in Schemes IV and V, up to the formation of ethylene diamine at lower temperatures and yields the same structure as those obtained in DGEBA hardening at the temperature exceeding the temperature of the dissociation of the complex cation (II). This has been shown in Figures 5–8, where the hardener concentration is 20, 24, 28 and 30 phr in

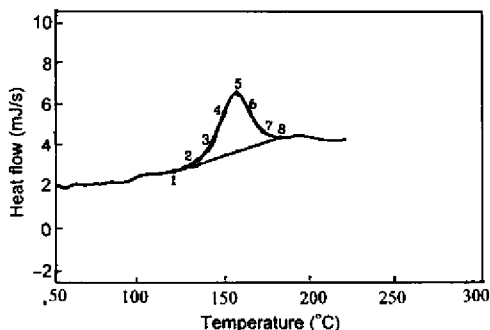


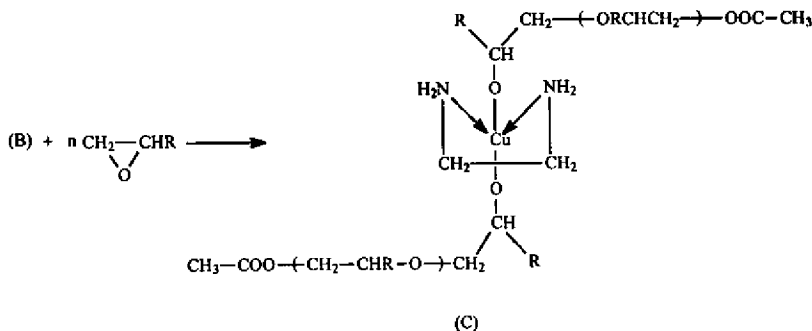
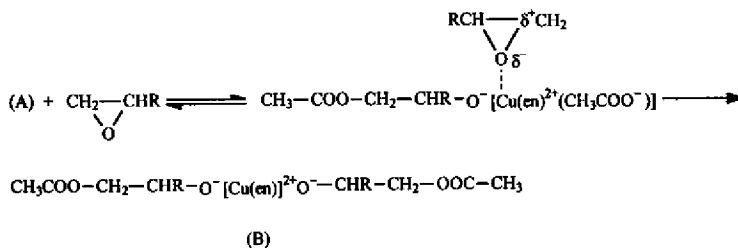
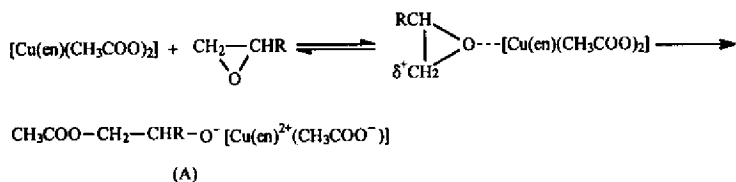
Figure 8. DSC Thermogram of curing of DGEBA with 30 phr of Cu(en)(OAc)_2 .

Area	ΔH curing (mJ/mg)
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	4.3625	123.81
2	5.3625	135.12
3	6.1792	144.42
4	6.6458	149.87
5	7.2782	157.21
6	7.9125	164.35
7	8.8292	172.41
8	9.5282	182.61

each, respectively. Thus, in the conditions where the hardener concentration exceeds the optimum quantity a predominant formation of the epoxy-amine network results from the reaction between the epoxy oligomer and unconnected amine groups. As the hardener concentration rises from 12 to 20 phr the chemical equilibrium shifts further to the right (Schemes IV and V) and the contribution of loose amine groups in the 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 Figures 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 thermograms of the 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 the 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.



Scheme VI

CONCLUSION

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

Curing of epoxy oligomer 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 on 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 the further growth of temperature or increasing concentration of the hardener, the coordination bonds between donor-acceptor in the complex cation will be broken and an 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 the hardener the equilibrium process shifts to the left and the 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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