Thermochimica Acta, 94 (1985) 105–112
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

REACTION ENTHALPIES DURING THE CURING OF EPOXY RESINS WITH ANHYDRIDES

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ABSTRACT

The enthalpy of reaction during the curing of epoxy resins with anhydrides is determined by differential scanning calorimetric(DSC) methods. Based on thermochemical laws, a mean molar reaction enthalpy of -(65 ± 3) kJ/mol is calculated for the formation of ester by polyaddition in stoichiometric proportions. This value is almost independent of the chemical structure of epoxy resins and dicarboxylic acid anhydrides. It is used in determining the concentration of structural elements in the polymeric networks that are obtained by curing epoxy resins with a deficit of dicarboxylic acid anhydride.

The pertinent DSC curves are multipeaked. From the reaction enthalpy assigned to the polyaddition, it follows that over 95 % of the possible ester groups are formed at starting molar ratios up to 1 : 0.6 of epoxy resin to dicarboxylic acid anhydride. The approximate data of ether/ester molar ratios show the clear change in the chemical structure of the network of epoxy resin moulding materials.

INTRODUCTION

The curing of epoxy resins with dicarboxylic acid anhydrides in the presence of basic accelerators leads under exothermic reaction to high grade electrical insulation materials (ref. 1). Using differential scanning calorimetric methods the time and temperature dependent conversion of the reaction is obtained from the increase in reaction enthalpy (ref. 2, 3, 4). In developmental work the epoxy resin can thus be adapted to the technical processes. Moreover, further data regarding the polymer reactions can also be derived from the reaction enthalpy.

In this paper the mean molar reaction enthalpies of ester groups formed during the curing reactions of epoxy resins and dicarboxylic acid anhydrides in stoichiometric proportions will be calculated from the emerging reaction enthalpies per unit weight. Thence, the multipeaked thermograms which are obtained during the curing of non-stoichiometric reactions can be evaluated. Moreover, it is possible to make statements regarding the structural configuration of polymeric networks.

THERMOCHEMICAL BASIS

In DSC investigations of chemical reactions, reaction enthalpies per unit weight ΔH are obtained. They reproduce the energy balance between the initial components and the end products on complete conversion of the reaction. The reaction enthalpy per unit weight can be represented as the sum of molar reaction enthalpies ΔH^o of each reaction product i that is formed:

$$\Delta H = \sum a_i \, \Delta H_i^o,$$

where a_i signifies the concentration of reaction products. On the other hand, the molar reaction enthalpy for the formation of a reaction product results from the molar enthalpies of formation ΔH_i^F of the participants:

$$\Delta H^o = \sum \nu_i \, \Delta H_i^F,$$

where ν_i signifies the stoichoimetric coefficient of the reaction equation; it denotes the mathematical expression of Hess's law. It is also applicable to polymer reactions since only the conversion of reactive groups contributes mainly to the reaction enthalpy. At an assumed reaction mechanism, the reaction enthalpies of molecular groups in gas state at 25°C can be approximately calculated from the tabulated increments of the enthalpies of formation. The change in values with respect to the temperature of reaction is stated by Kirchhoff's law:

$$\frac{\partial \Delta H^o}{\partial T} = \sum \nu_i \, Cp_i,$$

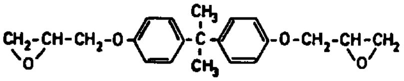
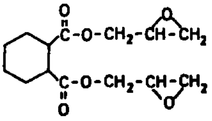
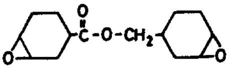
where Cp_i denotes the heat capacity of the reactants. A transition from 25°C to the reaction temperature results generally in a slight decrease in the reaction enthalpy. The energetic transformation of the gas state into the condensed phase can not be performed since the enthalpies of vaporization or condensation are not known. This leads to a certain error in the calculated values of reaction enthalpies. The reaction enthalpies which can also be calculated for polymer reactions in the same manner, contribute to a sound interpretation of the experimental results.

MATERIALS

Commercially available bisphenol-A-bisglycidyl ether (BADGE), hexahydrophthalic acid diglycidyl ester (HHPDGE) and 3,4-epoxy cyclohexyl-methyl -3',4'-epoxy cyclohexane carboxylate (OEP) were used as epoxy resin components. The analytical characteristics are listed in Table 1. The curing components hexahydrophthalic acid anhydride (HHPA), methyl tetrahydrophthalic acid anhydride (MTHPA) and methyl hexahydrophthalic acid anhydride (MHHPA), are listed in Table 2. Alkyl substituted imidazoles were used as accelerators.

TABLE 1

Analytical characteristics of epoxy resins

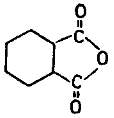
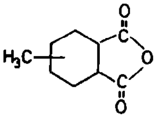
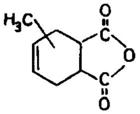
	Concentration of functional groups			
	EP mol/kg	OH mol/kg	Cl mol/kg	H_2O mol/kg
 Bisphenol-A-bisglycidyl ether (BADGE)	5.75	0.20	0.06	0.10
 Hexahydrophthalic acid diglycidyl ester (HHPDGE)	6.64	0.52	0.27	0.06
 3.4-Epoxy cyclohexyl methyl-3!4-epoxy cyclohexane carboxylate (OEP)	7.18	0.60	---	0.12

EXPERIMENTAL

Epoxy resins (EP) and dicarboxylic acid anhydrides (AA) were mixed in molar ratios at about 50°C and degassed. After cooling to room temperature, the accelerator was added unter stirring. Roughly 10 mg of the sample were weighed in an aluminium micropan, cold welded and measured by differential scanning calorimetry (Thermal Analyzer 910/1090, Du Pont) at a heating rate of 10 K/min. For calculating the reaction enthalpy, a straight base line was set in such a manner that it crosses the thermoanalytical curve tangentially before and after the reaction. Extremely pure indium was used for the calibration of enthalpy. In all experiments the second run of measurement showed no residual enthalpy of reaction. All experiments were repeated several times. There was an accuracy of ± 3% in the enthalpy measurement.

TABLE 2

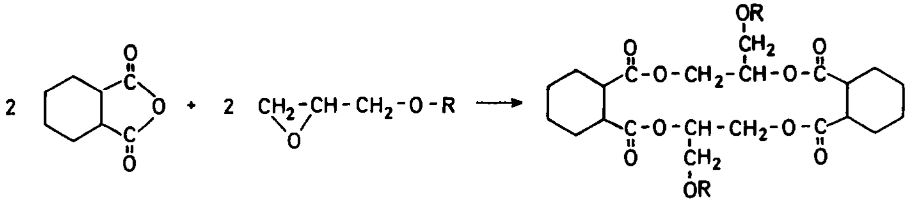
Analytical characteristics of dicarboxylic acid anhydrides

	Concentration of functional groups	
	A A mol/kg	COOH mol/kg
 Hexahydrophthalic acid anhydride (HHPA)	6.49	0.06
 Methyl hexahydrophthalic acid anhydride (MHHPA)	5.94	0.06
 Methyl tetrahydrophthalic acid anhydride (MTHPA)	6.02	0.04

RESULTS AND DISCUSSION

In stoichiometric reactions, polyaddition of epoxy resins with dicarboxylic acid anhydrides takes place preferentially. Initially, a secondary hydroxyl group reacts with an anhydride group under the formation of monoester. Subsequently, the monoester gets converted to a diester by an epoxy group. At the same time, a secondary hydroxyl group is formed (ref. 5,6). From the increments of the enthalpies of formation, the reaction enthalpies for the formation of monoester and diester were calculated to be -82 kJ/mol and -66 kJ/mol respectively. A mean reaction enthalpy of -74 kJ/mol results for an ester group in gas state at 25°C (ref. 7, see Fig. 1). The reaction of hydroxyl groups in the epoxy resins causes an accelerating effect. However, it does not contribute to the reaction enthalpy since the hydroxyl groups are present in the same concentration when the reaction is completed.

The DSC investigations regarding curing of reactions in stoichiometric proportions yield different values for reaction enthalpies per unit weight. A mean molar reaction enthalpy of -(65 ± 3) kJ/mol was found in all cases for the ester formation, taking into account the concentrations of reactive groups in the reactions set. This value is comparable with the one calculated from the



-C(=O)-O-C(=O)-	-429.40	CH_2	- 20.62			
		CH	- 4.56	4 -C(=O)O-	-1336	
cis 1.2	- 6.24	-O-	-113.80	2 CH2	- 41.24	
5-ring	- 24.36	ring	+ 53.83	2 CH	- 9.12	
ΔH^F_i	-460 x 2 = -920		- 85.15 x 2 = -170.3		-1386.36	in kJ/mol

$$\Delta H^0 = \sum_{1}^{I} \nu_i \, \Delta H_i^F$$

$$\Delta H^0 = -74 \text{ kJ/mol ester}$$

Fig. 1. Reaction enthalpy calculated from the increments of the enthalpies of formation in gas state at 25°C

enthalpies of formation and shows a good agreement between the theory and the experiment. The molar reaction enthalpy is slightly dependent on the chemical structure of epoxy resin components (Table 3). Its amount increases in the order BADGE, OEP, HHPDGE from -62 kJ/mol to -67 kJ/mol. The rate of reaction increase in the same order as shown by the decrease in temperature at maximum heat flow (T_{max}) from 174 °C to 166 °C. The glass transition temperatures (T_g) obtained in the second run of measurement show, on the contrary, the clear influence of epoxy resin structure on the network density (ref. 8, 9). If dicarboxylic acid anhydrides are changed slight differences in reaction enthalpies become equally noticeable (Table 4). The density of the network, however, is influenced only insignificantly.

TABLE 3

Calorimetric values after the complete curing of different epoxy resins with MTHPA (molar ratio 1:1, 1,5% imidazole containing accelerator)

epoxy resin	epoxide groups mol/kg	T_{max} °C	ΔH J/g	ΔH^o_{ester} kJ/mol	T_g °C
BADGE	2.88	174	- 359	- 62	130
OEP	3.23	171	- 419	- 65	172
HHPDGE	3.12	166	- 416	- 67	114

TABLE 4

Calorimetric values after the complete curing of different dicarboxylic acid anhydrides with BADGE (molar ratio 1:1, 0,75% 1-ethylimidazole)

acid anhydride	an-hydride mol/kg	T_{max} °C	ΔH J/g	ΔH^o_{ester} kJ/mol	T_g °C
HHPA	3.03	151	- 380	- 63	135
MHHPA	2.90	150	- 381	- 66	128
MTHPA	2.91	152	- 372	- 64	125

The proportions of reactants in a technical reaction set have a deficiency in dicarboxylic acid anhydrides (ref. 10,11). In DSC investigations, multipeaked thermograms are obtained with imidazole accelerators (Fig. 2). Since endothermic reactions can be ruled out the separation in time of polyaddition from the reaction of excess epoxy groups is partially achieved with dynamic conduct of the

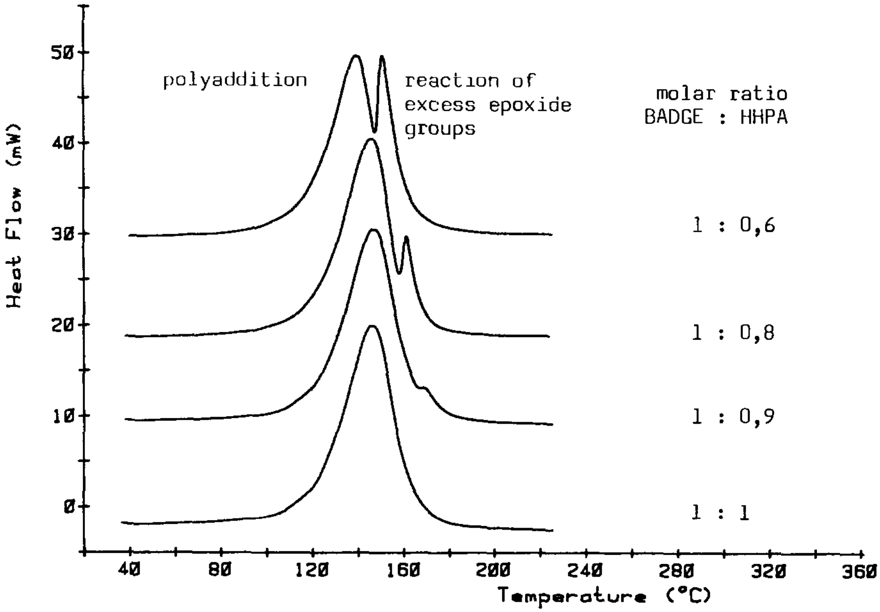


Fig. 2. DSC curves obtained during the reaction of BADGE with HHPA at different molar ratios (accelerator: 0,75% 1-ethylimidazole, sample weight: 10 mg, heating rate: 10 K/min)

TABLE 5

Influence of the molar ratio BADGE: HHPA in the reaction set on the structural configuration of epoxy moulding materials

Molar ratio set	Concentrations of functional groups		Concentration of structural elements in the network		
BADGE : HHPA	epoxide mol/kg	anhydride mol/kg	ester mol/kg	ether mol/kg	$\frac{\text{ether}}{\text{ester}}$ mol/mol
1 : 1	3.03	3.03	6.03	-	-
1 : 0.9	3.18	2.86	5.42	0.47	0.09
1 : 0.8	3.34	2.87	5.11	0.79	0.15
1 : 0.6	3.72	2.24	4.37	1.54	0.35

experiment. The evaluation can still be made although the enthalpy of reaction for polymerisation of epoxy groups is not accessible due to the lack of a well-defined reaction mechanism. For that purpose, the partial area of the preceding polyaddition was matched by superimposing of distribution functions and the pertinent reaction enthalpy per unit weight thus determined. Using the mean molar enthalpy of reaction for the formation of ester it was found that more than 95% of the possible ester groups result even at an increasing initial molar ratio of epoxide to anhydride (Table 5). Altogether, the concentration of ester groups decreases in the polymeric network. The increasing change of the polyester network is evident from the concentration proportions mentioned in Table 5. If the residual epoxy groups react to ether groups, there results an ether concentration of 1.54 mol/kg and a ether/ester ratio of 0.35, for instance, at a starting molar ratio of 1 : 0.6. In this case, every fourth structural constituent forming the network is an ether group. Thus, a contribution can be made in elucidating the structural configuration of polymeric networks by determining the reaction enthalpies.

REFERENCES

1 H. Möhler and M. Schwab, Kunststoffe, 71, 245-252 (1981)
2 H.J. Booss, Angew. Makromol. Chem., 45, 65-76 (1975)
3 K. Horie, H. Hiura, M. Sawada, I. Mita and H. Kambe, J. Polym. Sci., Part A-1, 8, 1357-1372 (1970)
4 W. Fisch, W. Hofmann and R. Schmid, J. Appl. Polym. Sci., 13, 295-308 (1969)
5 W. Fisch and W. Hofmann, Makromol. Chem., 44, 8-23 (1961)
6 H.J. Booss and K.R. Hauschildt, Angew. Makromol. Chem., 84, 51-65 (1980)
7 Landolt-Boernstein, "Zahlenwerte und Funktionen", Vol. 2, Part 4, p. 15-21 (1961), 6th Edition, Springer Publishers, Berlin, Goettingen, Heidelberg, 1961
8 H. Batzer, F. Lohse and R. Schmid, Angew. Makromol. Chem., 29/30, 349-411 (1973)
9 M. Fischer, F. Lohse and R. Schmid, Makromol. Chem., 181, 1251-1287 (1980)
10 M. Saure and W. Dunkel, Kunststoffe, 66, 422-427 (1976)
11 G.C. Stevens, J. Appl. Polym. Sci., 26, 4279-4297 (1981)