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THE DIFFERENTIAL SCANNING CALORIMETRIC STUDY ON POTENTENTIAL MID-TEMPERATURE CURING REAGENT SYSTEM FOR EPOXY RESINS

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ABSTRACT

DSC study of a mixture containing epoxy resin E-51, DICY and 805 catalyst showed that optimal ratios for curing are 100:3-4:2-3 parts (wt). Activation energy and reaction order were calculated.

INTRODUCTION

Dicyandiamine (DICY) is a widely used potential curing reagent for epoxy resins. Epoxy resin cured with DICY gives a product with excellent mechanical properties and resistance to various mediums. However, the known exposy-DICY compound generally requires 170°C or even higher temperatures to cure completely. Therefore, many laboratories in different parts of the world are involved in a study on how to lower the curing temperature of this system. The present paper describes some of the studies which were done in our laboratory.

The paper, is based on past work, related to the epoxy-DICY-805 catalyst system on its thermal character, optimum ratio, optimum curing temperature range, and its apparent activation energy and reaction order, so as to provide relevant parameters for its application in one-packed adhesives, casting materials, and coating industry, etc.

EXPERIMENTAL

The experiments were carried out under the following conditions, except in a few cases which will be indicated in the text.

Sample weight, 10 mg; reference, air; heating rate, 10c/min; DTA, ±100 μv; DSC, ±10 mCal/sec.

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Apparatus:

The Differential Scanning Calorimeter was provided by Shanghai Balance Apparatus Factory (CDR-1).

Reagents:

Epoxy resin E-51 (epoxy approximately to Epon 828).

Dicyandiamine, chemical pure.

805 catalyst (tertiary amine) was synthesized in our laboratory.

RESULTS AND DISCUSSION

The system concerned was investigated for its thermal characteristics by DSC. The experimental results are shown separately as follows:

1. DSC curves of 805 catalyst, DICY and E-51 resin.
   Curves A,B,C in Fig.1 show the DSC of E-51 resin, 805 catalyst and DICY, respectively. E-51 resin is stable below 250°C and does not yield any thermal effect. (Fig 1A). 805 catalyst shows endothermic peaks at 186°C and 260°C respectively. There is one endothermic peak at 216°C and one exothermic peak at 260°C in the DTA curve of DICY (curve C).
2. DSC curves of mixtures of two of the three components of 805 catalyst, DICY and E-51 resin .

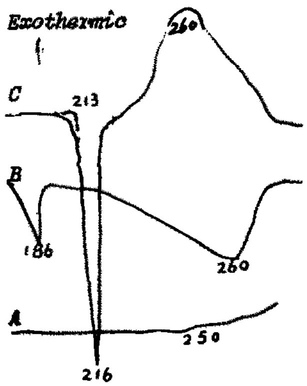

Fig. 1

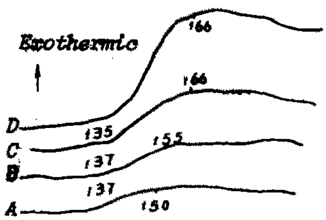

Fig. 2

Fig. 1. DSC curves of(A)-51 resin,; (B) 805 catalyst and (C) DICY.

Fig. 2. DSC curves of mixtures containing E-51 resin (100 parts) and 805 catalyst, A, 1 part, B, 2 parts, C, 3 parts and D, 4 parts.

In Fig. 2, curves A,B,C and D show the DSC results of E-51 resin (100 parts) mixed with 1, 2, 3 and 4 parts (wt) of 805 catalyst, respectively.

As the amount of 805 catalyst increases, the exothermic effect produces an obvious exothermic peak, proving that that the 805 catalysts react with E-51 resin.

Fig. 3 shows the DSC curves of mixture of 805 catalyst and DICY in the weight ratio 1: 7 and 1:1. Comparing Figs. 1 and 3 it is obvious that the mixture shows a new endothermic peak at 135°C. On curve A, two peaks at 213°C and 260°C can be seen, which are characteristic for DICY itself, showing that this mixture contains an excess of DICY.

Fig. 4 shows the DSC curve of a mixture of E-51 resin and DICY in the ratio 100:10 (wt). From the curve, we can see that the mixture in this ratio begins to crosslink at 181°C and form a peak at 206°C, indicating a sharp reaction.

The experimental results prove that the mixture, as above mentioned, requires a temperature higher than 170°C to cure completely.

3. **Effect of 805 catalyst on E-51 resin and DICY**

Fig. 5 shows the DSC curves of the mixture of E-51 resin with DICY to which different amounts of 805 catalyst were added. Compared with Fig. 4, it can be seen that the initial curing temperature drops down from 181°C to 164, 136, 135, and 135°C, whereas the peak temperature decreases from 206°C to 186, 174, 160,

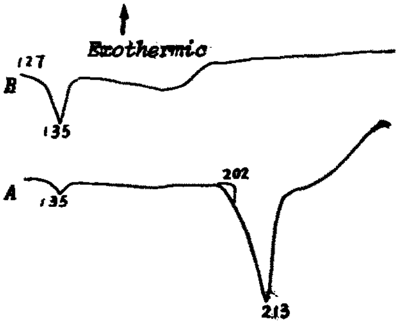

Fig. 3

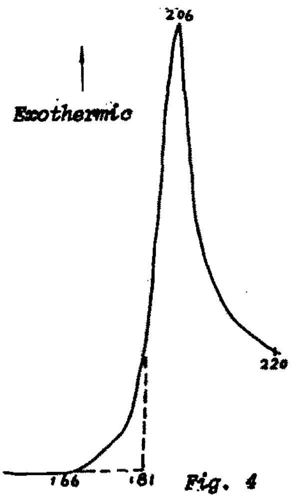

Fig. 4

Fig. 3. DSC curves of mixtures containing 805 catalyst and DICY, A, weight ratio 1:7, B, weight ratio 1:1.

Fig. 4. DSC curve of a mixture containing E-51 resin (100 parts) and DICY (10 parts).

and 155°C, respectively. The effect of 805 catalyst on E-51 resin-DICY system is obvious. This proves that the 805 catalyst really has an effect on lowering the curing temperature of expoxy resin with DICY.

A small endothermic peak at 208°C can be seen in Fig. 5. It is caused by excess amounts of DICY in the mixture. After crosslinking, the excess DICY easily dissolves in water and in other solvents.It probably makes the resistance of the product to be medium inferior. This is very noticeable. Generally speaking, adding 2-3 parts of 805 catalyst to the E-51 resin-DICY system will satisfy the need of mid-temperature crosslinking.

4. Effect of DICY on E-51 resin-805 catalyst system

The DSC curves in Fig. 6 refer to the mixture of E-51 resin 100 parts, wt, 805 catalyst /2 parts, to which increasing amounts of DICY were added. Fig .6, shows that 5 parts of DICY added to the system form a small endothermic peak at 210°C which means that the amount of DICY is excessive. The initial curing temperatures from curves A to B are about 133°C. The peak temperature rises slightly as the amount of DICY increases. Curing samples described in A or C of Fig.6, at 130°C cooling them to room temperature, then remeasuring them by DSC with more sensitivity, we get Fig. 7. We may conclude that the optimum ratio for E-51 resin:805 catalyst is 100;3-4:2-3 parts (wt).

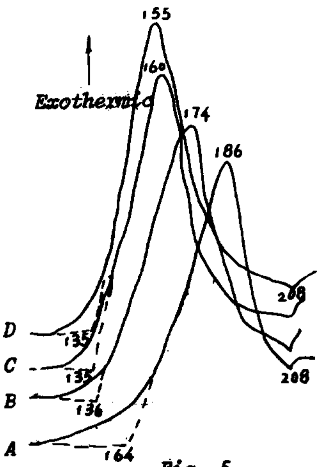

Fig. 5

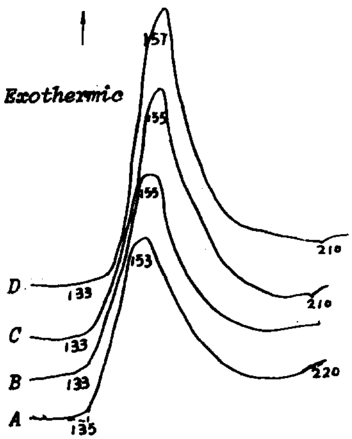

Fig. 6

Fig. 5. DSC curves of a mixture containing E-51 resin (100 parts) and DICY (10 parts) to which 805 catalyst is added, A, B, C and D, 1, 2, 3 and 4 parts (wt).

Fig. 6. DSC curves of mixtures of E-51 resin (100 parts) 805 catalyst (2 parts) and DICY, A, B, C and D, 3, 4, 5 and 6 parts (wt), respectively.

5. The curing temperature range in the optimum ratio.

Summing up the above results, we investigated the optimum ratio: E-51 resin, 100 parts, DICY 3 parts, 805 catalyst 2 parts (wt).

A-D curves in Fig.8, give the different results at different heating rates. In order to eliminate the effect of the heating rate, we extropolated the curves to get the temperature at the heating rate 0°C/min.

Dealing with experimental data by one-place linear regression, we get Fig. 9, where Tb is the regression curve of the initial curing temperature, Tm is the peak temperature for crosslinking. The calculated Tb and Tm are 115.5 and 130°C, respectively.

According to above experiments, the optimum curing temperature range is 116 to 130°C. The temperature to be chosen depends on the curing time and other curing conditions.

Our study has proved that the 805 catalyst E-51 resin DICY system is a

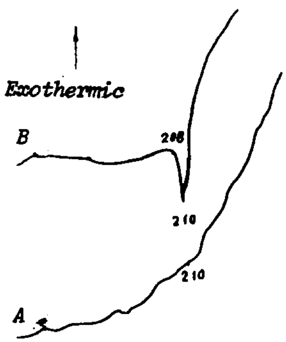

Fig. 7

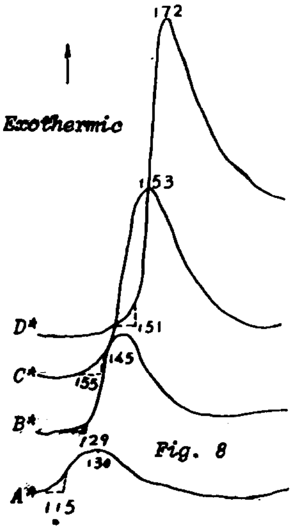

Fig. 8

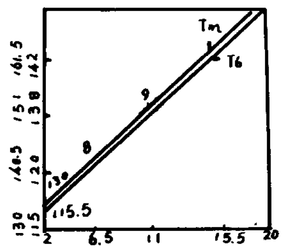

Fig. 9

Fig 7. DSC curve of sample described in Fig 6 A or C, after it had been cured at 130° and recooled to room temperature.

Fig 8 .DSC curves of mixtures containing E-51 resin; DICY: 805 catalyst = 100:3:2 parts (wt) at different heating rates: A, 2; B, 5; c, 10 and D, 20°/min.

Fig 9. Regression curve of the initial curing temperature (tb) and of peak temperature for crosslinking (Tm). Adding 5 parts (wt) of DICY to the mixture of E-51 resin (100 parts), 805 catalyst (2 parts) is shown to be excessive, but 3 parts is not. Therefore, it is appropriate not to add more than 5 parts of DICY.

potential mid-temperature curing system, which can be used in many relevant fields.

Activation energy E is one of the factors which determines whether or not a reaction may take place. Studying by DSC is different from isothermal process, since the former is completed under conditions of rising temperature at uniform rate.

The apparent activation energy and reaction order of the above system are calculated by Kissinger's analytic equation:..

Kissinger analytic equation:

$$\frac{d(\ln\beta/Tm)}{d(1/Tm^2)} = \frac{-E}{R}$$

where: β is heating rate °C/min., Tm is the peak temperature °K, R is ideal gas constant. E is apparent activation energy KCal/mol.

From Fig.8, the peak temperatures corresponding to different heating rates are as follows:

β (°C)	2	5	10	20
Tm (°C)	130	145	153	172
Tm' (°K)	403	418	426	445
$1/Tm \times 10^3$	2.4814	2.3923	2.3474	2.2472
$\ln\beta/Tm^2$	-11.30	-10.45	-9.81	-9.20

Drawing a curve with 1/Tm vs.ln(f/Tm), we obtained a one-place linear regression equation:

$$Y = 11.4977 - 9.1592\ x$$

$$B = \frac{-E}{R}$$

$$E = 9.1592 \cdot 1.9870$$

$$= 18.2\ \text{KCal/mol}$$

$$|r| = |-0.98786| = 0.99 \text{ (interrelation coefficient)}$$

Then we obtained the shape index from A, C curves in Fig. 8.

$$b = 7.1 \quad a = 12.1$$

$$S = a/b = 12.1/7.1 = 1.704$$

and

$$n = 1.26 \quad S = 1.64$$

CONCLUSION

1. The optimum ratio for the E-51 resin-dicyandiamine-805 catalyst system is 100:3-4:2 -3(wt).
2. The optimum range of the curing temperature is 116°C to 130°C.
3. Calculations with the Kissinger analytic equation gave the apparent energy for the system, E = 18.2 KCal/mol, and the reaction order, n ≈ 1.64.
4. The system concerned is a potential, mid-temperature curing one, which may be used in casting materials, compound materials coating materials and structural adhesives. Our work provides basic parameters for further research.

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