Thermochimica Acta, 111 (1987) 115–120
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC INVESTIGATION OF CURING OF SOME NEW POLYHYDROXY EPOXY RESINS

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(Received 4 June 1986)

ABSTRACT

The curing reactions of two new polyhydroxy epoxy resins, i.e. 1,3-bis(2,4,6-trimethylol phenoxy)propan-2-ol (I) and 1,3-bis[4-(3,5-dimethylol-4-hydroxyphenyl trichloroethylidenyl)-2,6-dimethylol phenoxy]propan-2-ol (II) were investigated with differential scanning calorimetry (DSC) either isothermally or at a constant heating rate. The thermosetting characteristics were studied at several different temperatures (110–150°C). The activation energies of the setting reactions were determined; these were equal to 60.14 and 89.12 kJ mol^{-1} for the resins I and II, respectively. Two types of curing reactions were observed; dehydration and dehydroformylation reactions.

INTRODUCTION

There has been increasing interest in the synthesis and study of new cross linked resins prepared from the condensation of phenols and formaldehyde; several papers and patents have been published in this field [1]. In an earlier research program we synthesised and studied several new polyhydroxy epoxy resins made from the condensation of several phenols and bisphenols with formaldehyde and epichlorohydrin in a one-pot reaction system [2,3]. The thermosetting characteristics of two of these new resins have been studied by DSC. In thermosetting polymer technology, determining the degree of cure or the degree of the thermosetting reaction is a common problem. The DSC technique is a valuable tool for studying such reactions [4].

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0040-6031/87/$03.50

EXPERIMENTAL

Instruments

The Du Pont Thermoanalyser model 1090 with the DSC unit (model 910) connected to a microprocessor data station unit was used in this study after being calibrated with standard materials.

Materials

Two new resins were synthesised and characterised in our laboratories in a one-pot reaction system as previously reported [2,3]. They are: (I) 1,3-bis(2,4,6-trimethylol phenoxy)propan-2-ol; (II) 1,3-bis[4-(3,5-dimethylol-4-hydroxyphenyl trichloroethylidenyl)-2,6-dimethylolphenoxy]propan-2-ol.

The two resins were prepared by condensation of phenol or the 1,1-bis(4-hydroxyphenyl trichloroethane) (III) with formaldehyde and epichlorohydrine at a definite temperature and pH.

Thermosetting study

Three types of setting experiments were carried out: (a) by heating the samples isothermally in the DSC calorimetric cell at different temperatures and for different periods of time the DSC thermograms were recorded; typical curves are shown in Fig. 1. (b) The thermally setted samples in step (a) were examined by DSC at a heating rate of 20° min^{-1}, the complete DSC thermograms being recorded over a temperature range (ambient −280°C). Typical thermograms are shown in Figs. 2 and 3. (c) The setting characteristics were also studied by heating the samples at a low heating rate (2°C min^{-1}) in order to investigate the number and position of curing reactions. A typical thermogram is shown in Fig. 4.

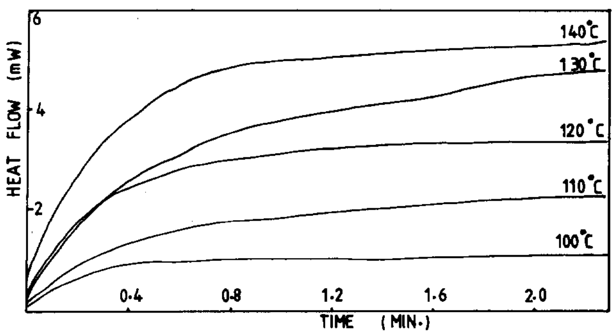


Fig. 1. Typical isothermal DSC curves for the resin I.

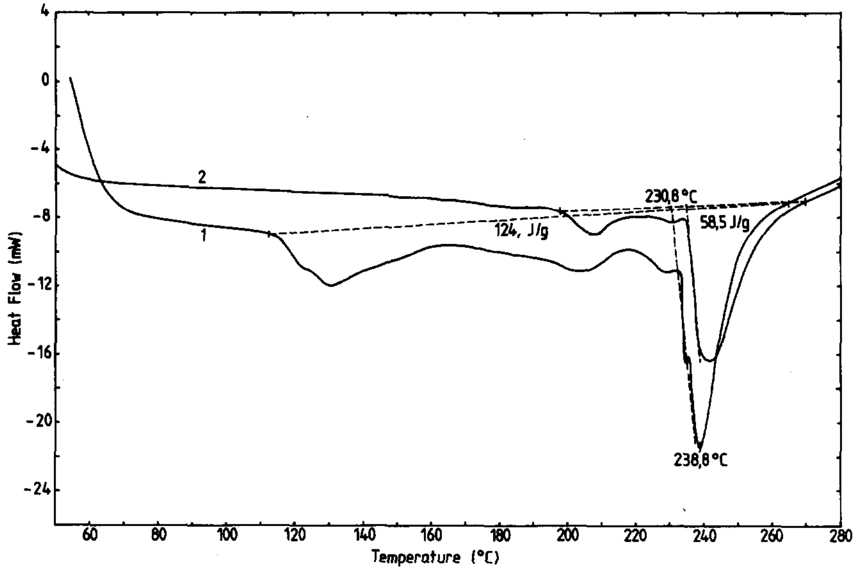


Fig. 2. DSC thermograms: (1) polyhydroxy epoxy resin I (untreated); (2) heated at 130 °C for 15 min.

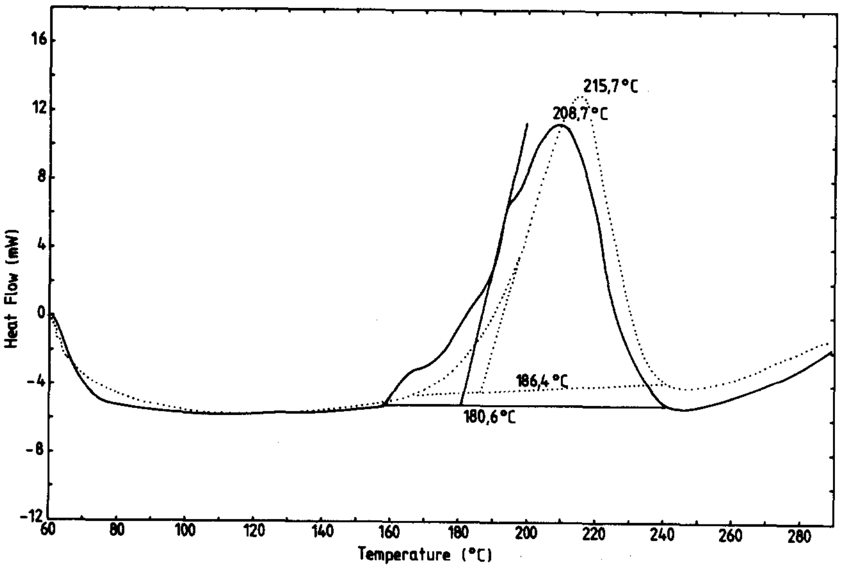


Fig. 3. DSC thermograms for the resin II: (———) heated at 120 °C for 15 min, curing energy = 215 J g^{-1}, degree of curing = 53.8%; (······) heated at 140 °C for 15 min, curing energy = 92.3 J g^{-1}, degree of curing = 80.2%

RESULTS AND DISCUSSION

From the DSC thermograms obtained via isothermal settings at different temperatures, the rate of setting was determined from the slopes of the

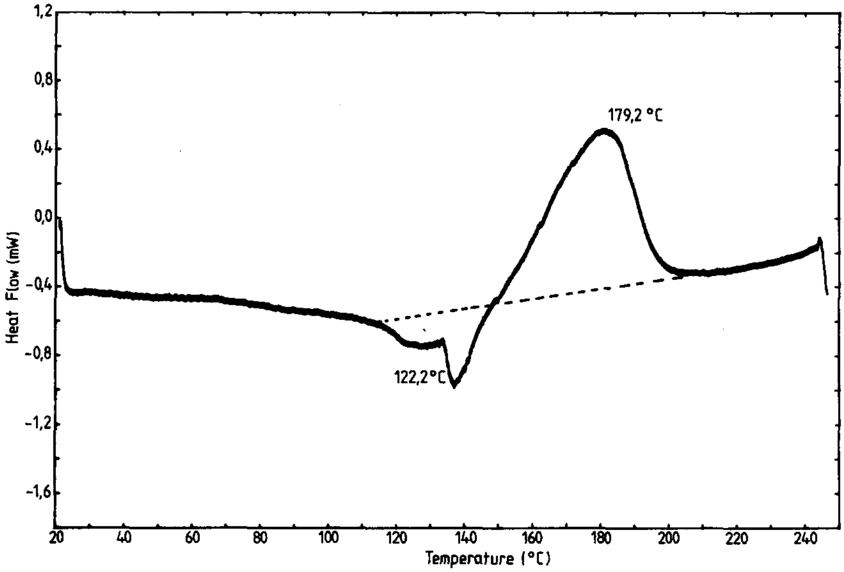


Fig. 4. DSC thermogram of the resin II at a heating rate of 2° min^{-1} showing the endothermic and the exothermic curing reactions.

initial parts of the curves. The rate of setting varies with temperature and typical Arrhenius plots are shown in Fig. 5. The activation energies determined from Arrhenius plots were found to be 60.14 and 89.12 kJ mol^{-1} for the resins I and II, respectively.

On the other hand the percentage of curing was determined by comparing the energy required for partial setting with the energy required for complete setting. The degree of curing varies linearly with temperature as shown in Fig. 6.

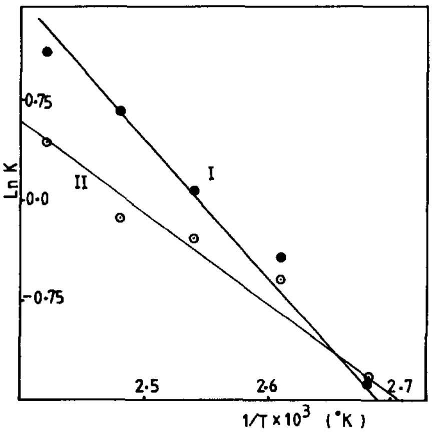


Fig. 5. Arrhenius plots for the setting reactions for resins I and II.

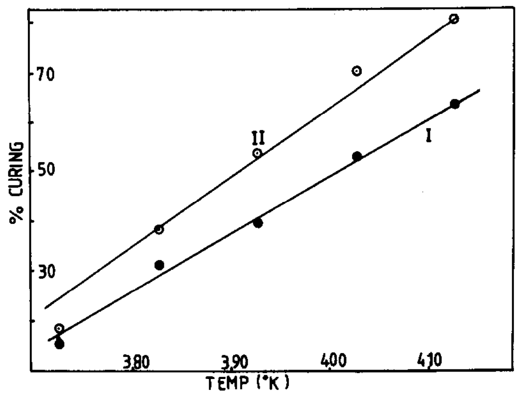
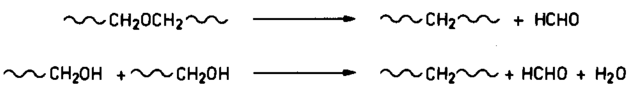


Fig. 6. Effect of temperature on the degree of curing.

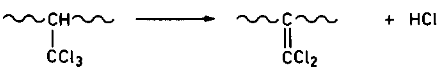
The DSC thermograms obtained at low heating rates showed that two types of curing reactions takes place. The first type is endothermic at about 120 °C which can be related to a dehydration reaction leading to etherial interlinkage groups:

The second type of curing reaction can be related to dehydroformylation:



The two types of curing reactions are familiar in the technology of the setting of phenolic resins [5].

The dehydroformylation reaction was found to be endothermic for resin (I), but exothermic for resin (II), although we have no concrete explanation for this unexpected behaviour. We think it could be related to a side reaction which has been observed by Faiz et al. [6,7] during the study of some polymers derived from the monomer (III), i.e. the compound undergoes dehydrochlorination at elevated temperatures:



Thus the HCl evolved from such a side reaction could behave as a catalyst for the curing reactions leading to an exothermic reaction instead of an endothermic reaction, since we have found that these new polyhydroxy epoxy resins set catalytically at room temperature. On the other hand all the other polyhydroxy resins derived from non-chlorinated bisphenols behave similarly to resin (I) [8].

The dehydration curing reactions were studied in detail by the moisture evolution analysis technique [9,10], the activation energy for this reaction being determined by studying the rate of setting at several different temperatures (120–160 °C). The values obtained by this technique were 57.12 and 74.34 kJ mol^{-1} for resins I and II, respectively. On the other hand we have found that thermosetting treatments lead to an increase in the glass transition temperature of the cured resins [11], but this behaviour was not observed with these two resins, probably because their glass transition temperatures are below the ambient temperature which was not covered in this study.

ACKNOWLEDGEMENTS

We would like to thank Mr. S. Abdula and Mr. F. Radhi for their support and technical assistance.

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