

Curing of Epoxy Resins with Citric Acid–Piperazine Salt

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Abstract: Citric acid–piperazine salt was prepared with a molar ratio of acid–piperazine of 2.9. The salt was characterized by thermal calorimetry, ^{13}C NMR and IR spectroscopy. The piperazine content in the salt was 52%. A typical formulation was achieved by mixing the salt with the diglycidyl ether of bisphenol A (DGEBA). The heat of reaction was measured by a calorimeter and the evaluated peak resulted from the simultaneous endothermic salt decomposition and exothermic network formation. The heat of reaction value was $-\Delta H = 18 \text{ kJ/eq.}$ for the stoichiometric ratio, and the glass transition temperature, T_g , was 95°C . The heat of reaction evolved and the T_g value of piperazine–epoxy were determined for comparison with the salt–epoxy system.

Key words: latent catalyst, epoxy, piperazine, salts, citric acid.

INTRODUCTION

The citric acid–amine salts constitute a promising family of latent curing agents for epoxies. Piperazine salts of polycarboxylic acids have been shown to function as curing agents for epoxy resins. Succinic, adipic, phthalic and isophthalic acids have been used as diacids. Using these systems, the shelf-life of the epoxy was increased from 2 h to 35–70 days. The piperazine salts cure epoxy resins more rapidly than does dicyandiamide.¹

Chiao² has patented a salicylic acid–piperazine system for adhesive purposes. Galego *et al.*³ analysed the formulation of citric acid–diethylenetriamine salts. A very small heat of reaction was observed ($\Delta H \sim -10 \text{ kJ/eq.}$). A stoichiometric formulation for

the epoxy–salt system showed a higher glass transition temperature value ($T_g = 180^\circ\text{C}$) than the usual epoxy–diethylenetriamine system ($T_g = 120^\circ\text{C}$).

This work deals with the citric acid–piperazine system and its application to the network reaction of epoxy resin.

EXPERIMENTAL

Differential scanning calorimetry (DSC) runs were carried out using a Dupont 990 thermal analyser at a heating rate of 10°C/min under nitrogen atmosphere.

^{13}C NMR spectra were recorded on a Bruker AC-250 F instrument. The spectra were obtained in deuterated water (D_2O) with DMS/diozane as internal reference at 300 K. The instrument was used to characterize the piperazine and the salt.

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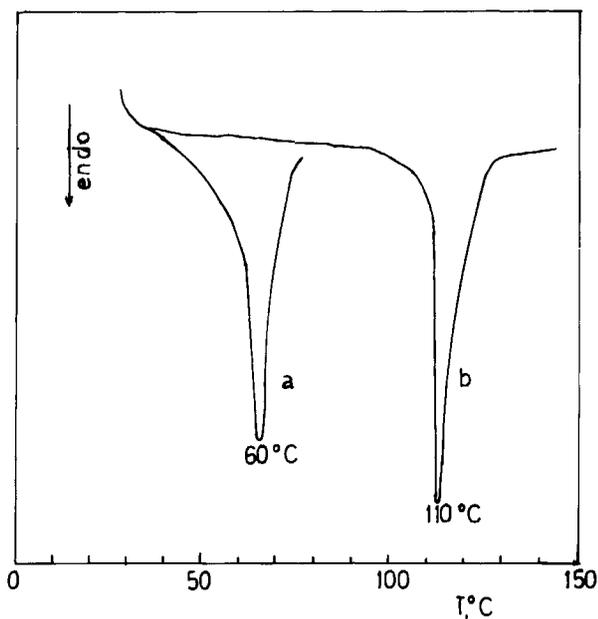


Fig. 1. DSC runs of piperazine amine at 10°C/min: (a) as received; (b) after sublimation under vacuum.

Infrared spectra were determined on a Perkin Elmer 599 FTIR spectrophotometer, using KBr pellets mixed with solid sample and for characterizing the salt.

Citric acid Chemapol ($M_{\text{CA}\cdot\text{H}_2\text{O}} = 210 \text{ g/mol}$) was used as received. Piperazine hexahydrate ($M_{\text{PIPE}\cdot 6 \text{ H}_2\text{O}} = 194 \text{ g/mol}$) from Merck was sublimated under vacuum before use. The thermogram of piperazine was obtained at a heating rate of 10°C/min (Fig. 1). The melting point before sublimation was 60°C and after sublimation it was 110°C.

The epoxy resin used was the diglycidyl ether of bisphenol A (DGEBA) from Ciba-Geigy. The epoxy resin was carefully dehydrated at 90°C under vacuum before use. The epoxy equivalent was determined by acid titration as 185 g/eq. epoxy.

RESULTS AND DISCUSSION

Salt preparation and characterization

The salt preparation was carried out using an excess of one of the reagents to avoid gelation of the poly-electrolyte. It was experimentally determined that a formulation containing a piperazine–citric acid molar ratio (R) of ≤ 1.8 leads to gelation.

Citric acid was dissolved in piperazine at 100°C to give a solution with $R = 2.9$. The piperazine excess was removed from the salt after 1 h, by washing with ethanol–methanol solution several times. A white powder was obtained.

The final ratio of piperazine–citric acid in the salt, after removing the unreacted piperazine, was calculated.

The amine–acid initial ratio (r) was 0.5. Supposing that the amine groups have equal reactivity, the probability of finding a free amine group when the base–acid reaction is completed is

$$A/A_0 = (1 - r)^2 = 0.25 \quad (1)$$

where A is the amine groups concentration remaining free at the end of the reaction and A_0 is the initial amount of amine. Then

$$A = 2 \times 0.25 = 0.5 \quad (2)$$

The final salt has the following equivalents:

$$r = (2 - 0.5)/1 = 1.5 \quad (3)$$

The percentage of amine that could be lost when heating the mixture is as follows:

$$\% \text{free amine} = \left[\frac{(1.5 \times 86/2)}{(1.5 \times 86/2) + (1 \times 192/3)} \right] = 50.2 \quad (4)$$

The salt was heated at 150°C (close to the piperazine boiling point, $\sim 145^\circ\text{C}$) in an open tube and the mass loss was determined by weighing as 52% after 1 h. This value agrees with the estimated piperazine mass fraction in the salt (50.2%). The hydrogen equivalent in the salt was calculated as follows:

$$\frac{1 \text{ gsalt}}{0.5 \text{ gPIPE}} \times \frac{86 \text{ gPIPE}}{2 \text{ eq. H}} = 86 \frac{\text{gsalt}}{\text{eq. H}} \quad (5)$$

The fresh salt was studied by DSC in dynamic mode from 25 to 300°C under nitrogen. The main peaks were observed at 125, 180 and 210°C (Fig. 2). A sample was run in the DSC until 140°C. The capsule was weighed before and after the DSC run and no weight loss was determined. Thus the first peak at 125°C was

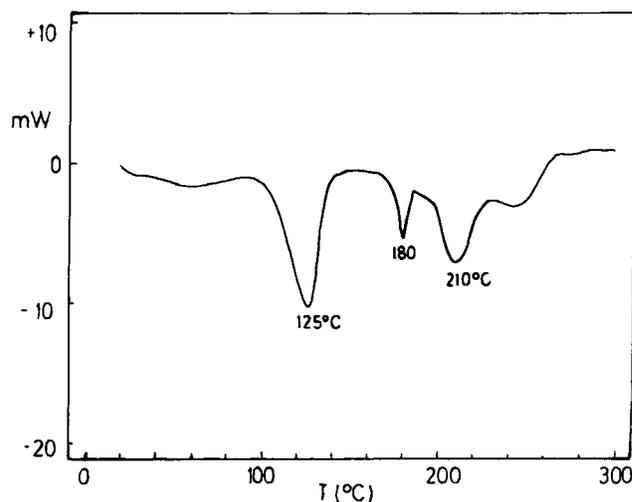


Fig. 2. DSC thermogram of citric acid–piperazine salt under nitrogen at 10°C/min.

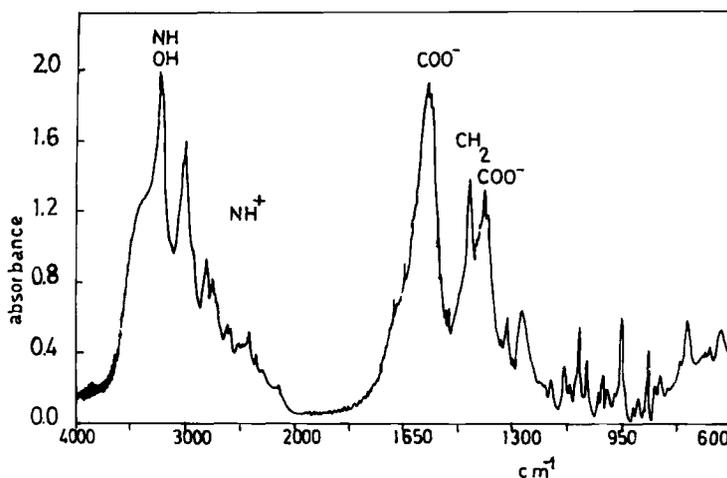
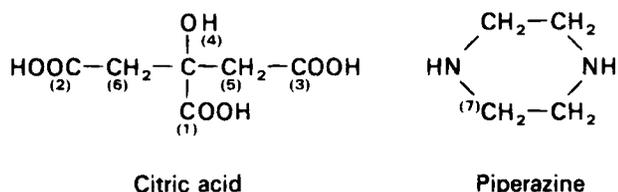


Fig. 3. FTIR spectrum of citric acid-piperazine salt in KBr pellets.

attributed to the salt melting point and the peak at 210°C was associated with volatilization of citric acid. The peak at 180°C was not identified.

The FTIR of the salt is shown in Fig. 3. The salt is characterized by bands assigned to COO⁻ and NH⁺ groups. The absence of bands due to free carboxylic acid confirm the salt formation.

¹³C NMR spectra were obtained for citric acid, piperazine and the salt. The ¹³C NMR spectrum of citric acid has four different peaks, because the carboxyls (2) and (3) are equivalents as are the carbons from the CH₂ groups. The citric acid and piperazine chemical structures are as follows:



C	δ (ppm)
(1)	177.5
(2), (3)	174.2
(4)	74.2
(5), (6)	44.2
(7)	47.39

During salt formation, ionization of the carboxyl (+3.5 ppm) and a shift of the amine carbon (-7 ppm) occur. Table 1 shows the results for the fresh and the heated salt. The values demonstrate the salt stability at the temperatures and times studied.

The ¹³C NMR spectrum for the salt heated at 180°C for 30 min is shown in Fig. 4. Several peaks appear in the carboxylic region and also in the CH₂ region, as a consequence of side reactions of the salt.

TABLE 1. ¹³C NMR study of the citric acid-piperazine salt

	Fresh salt (δ (ppm))	Heated salt, 130°C/30 min δ (ppm)	Heated salt, 140°C/30 min δ (ppm)
—COO ⁻ (1)	181.46	181.49	182.93
—COO ⁻ (2),(3)	178.51	178.53	179.94
—C ⁽⁴⁾	74.96	74.99	76.44
—CH ₂ ^{(5),(6)}	45.64	45.73	47.06
—CH ₂ ⁽⁷⁾	40.34	40.30	41.85

Epoxy-salt and epoxy-piperazine thermal analysis

Thermal analysis of the epoxy-piperazine reaction was done for comparison purposes. The heat evolved for the stoichiometric ratio was $-\Delta H = 86 \text{ kJ/eq.}$ and the T_g value determined by a second run was $T_g = 90^\circ\text{C}$ (Fig. 5).

Different formulations of $r =$ equivalent amine hydrogen in the salt/equivalent epoxy were heated in DSC at 10°C/min under a nitrogen atmosphere. Figure 6 shows two thermograms for different r values. No change occurs until the salt melts; consequently a long shelf-life at room temperature is expected. When the salt to epoxy ratio increases two exothermic peaks appear due to the piperazine-epoxy reaction and the piperazine boiling point at 145°C. The endothermic peak at 212°C increases due to the increase of free citric acid. Above 260°C, degradation reactions could appear. The exothermic reaction peak at 193°C for the excess of epoxy ratio is associated with the homopolymerization reaction. Higher temperature and excess of epoxy are the conditions for producing this reaction;^{4,5} the other peaks appear as shoulders on the main peak.

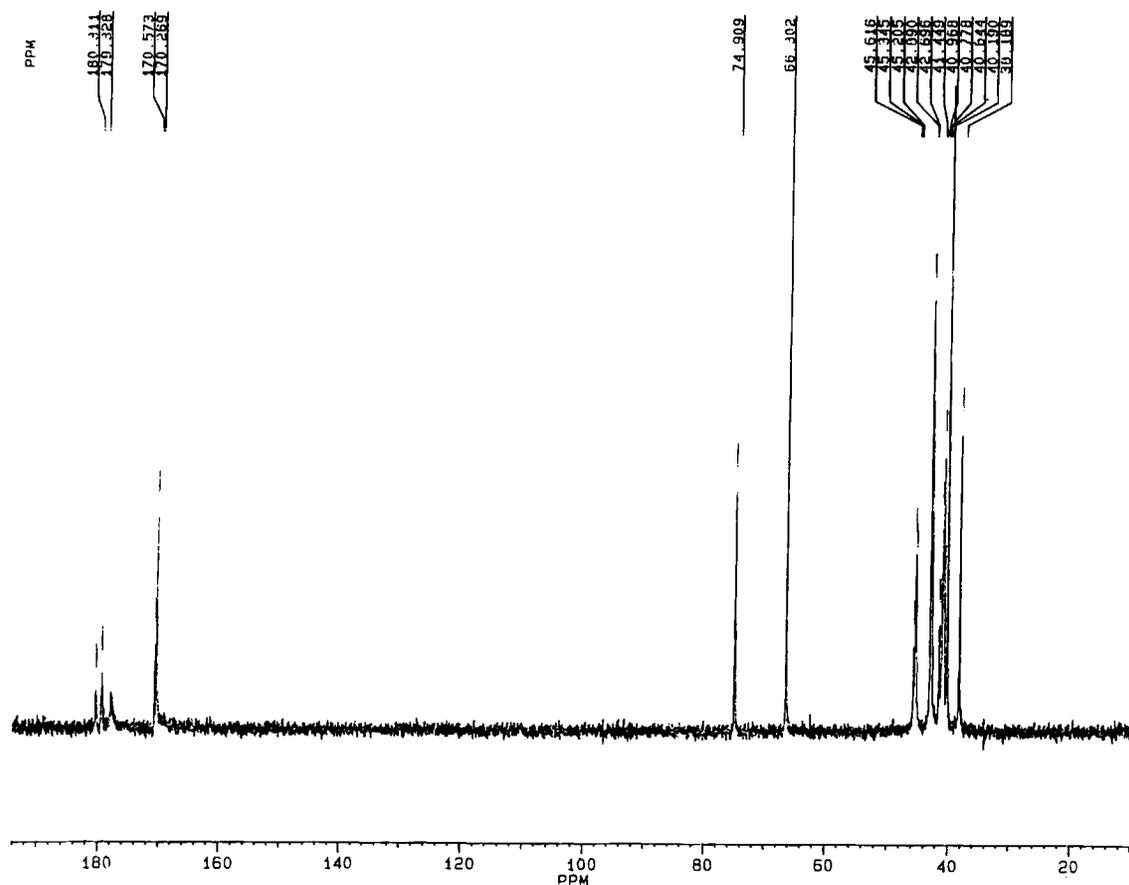


Fig. 4. ^{13}C NMR spectrum of citric acid-piperazine salt heated at 180°C for 30 min.

A second run was done to determine the glass transition temperature (T_g); the thermogram presents no residual heat (Fig. 7).

Table 2 shows the evolved heat, calculated as the area under the reaction exothermic peak, as a function of the

epoxy equivalent. The heat evolved for the salt-epoxy system is lower than when substituted urea is used as latent initiator ($-\Delta H = 61 \text{ kJ/eq.}$),⁶ the epoxy-amine reaction ($-\Delta H = 105 \text{ kJ/eq.}$),^{7,8} or the epoxy homo-

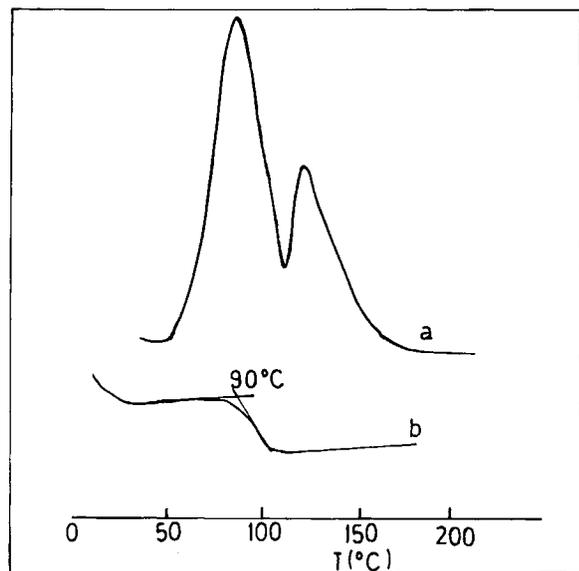


Fig. 5. DSC runs of epoxy-piperazine system for stoichiometric ratio, $r = \text{eq. H/eq. epoxy}$: (a) at a heating rate of $10^\circ\text{C}/\text{min}$, $r = 0.99$, $m = 15 \text{ mg}$; (b) second run of (a).

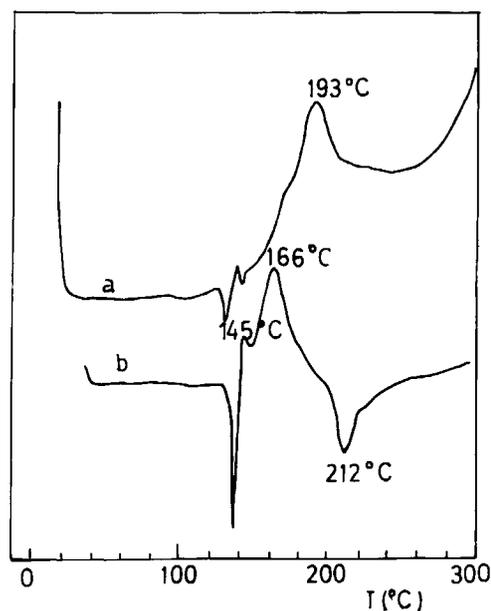


Fig. 6. DSC runs of salt-epoxy system for different stoichiometric ratio, $r = \text{equiv.H in the salt/eq. epoxy}$: (a) $r = 0.01$; (b) $r = 0.1$.

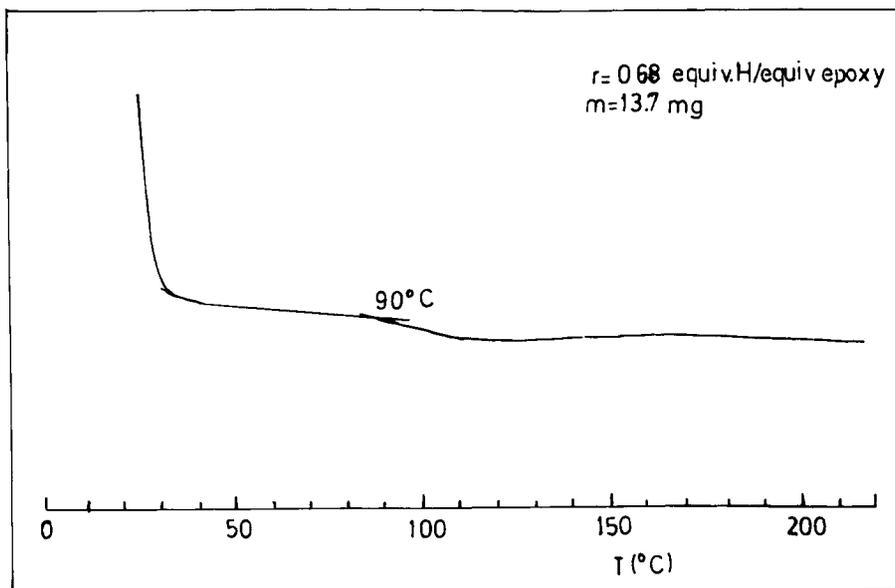


Fig. 7. Second run for the DSC thermogram at 10°C/min showing the T_g value.

polymerization reaction ($-\Delta H = 92 \text{ kJ/eq.}$).⁹ The mass loss is from the citric acid and piperazine; consequently the heat of reaction evolved is not constant. Figure 8 shows the glass transition temperatures (T_g) determined for different epoxy-salt formulations and epoxy-

piperazine. The T_g value should decrease with excess amine or epoxy.³ However, as a consequence of secondary reactions involved in the system at high temperature, the T_g value is almost constant.¹⁰ To explain the T_g behaviour would require further study of the several possible reactions and network formation in the system.

TABLE 2. Reaction heat of epoxy-salt system

g salt g epoxy	$r = \frac{\text{equiv.H}}{\text{equiv.epoxy}}$	% Weight loss	ΔH (kJ/eq.)
0.10	0.21	0.6	12
0.32	0.68	7.8	31
0.46	0.99	12.6	18
0.70	1.51	14.1	18

CONCLUSIONS

The salt from citric acid and piperazine amine was prepared and characterized. The salt can be used as a latent catalyst. The heat of reaction evolved has a lower value ($-\Delta H = 18 \text{ kJ/eq.}$) than the piperazine-epoxy system ($-\Delta H = 86 \text{ kJ/eq.}$) as a result of endothermic and exothermic reactions, and the T_g values are a little higher. The T_g values are almost constant with the hydrogen-epoxy equivalents in the range studied, due to the reactions involved in the system.

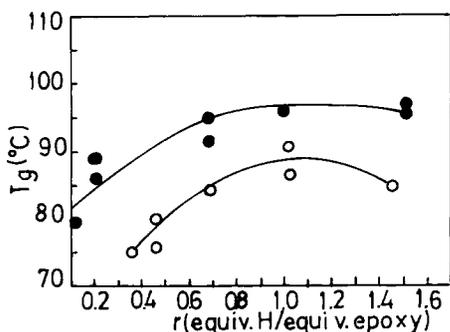


Fig. 8. Glass transition temperatures of samples with different stoichiometric ratios: (●) epoxy-salt formulation and (○) epoxy-piperazine system.

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