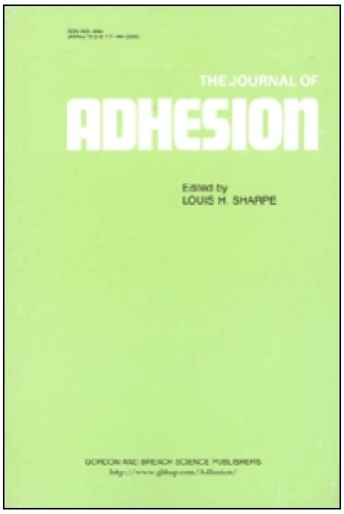

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Aspects of Latency in Epoxy Film Adhesives

B. C. Ennis[a]; R. G. Davidson[a]; P. J. Pearce[a]; C. E. M. Morris[a]
[a] Materials Research Laboratory, Melbourne, Australia

To cite this Article Ennis, B. C. , Davidson, R. G. , Pearce, P. J. and Morris, C. E. M.(1992) 'Aspects of Latency in Epoxy Film Adhesives', The Journal of Adhesion, 37: 1, 131 — 141

To link to this Article: DOI: 10.1080/00218469208031256

URL: http://dx.doi.org/10.1080/00218469208031256

J. Adhesion, 1992, Vol. 37, pp. 131–141
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Aspects of Latency in Epoxy Film Adhesives

B. C. ENNIS, R. G. DAVIDSON, P. J. PEARCE and C. E. M. MORRIS

Materials Research Laboratory, P.O. Box 50, Ascot Vale, Melbourne, Australia 3032.

(Received September 4, 1991; in final form September 27, 1991)

Studies have shown that the cure of epoxy resins with urea hardeners, either alone or in conjunction with dicyandiamide, is influenced by the ability of adventitious agents, products, or by-products to volatilise from the reacting system. Although a generalised mechanism has not been identified, the phenomenological findings are important in evaluation and characterisation of adhesives and cure schedules, particularly by thermal analysis, and need to be considered in any detailed chemical study of these systems. Propenal has been identified as a significant by-product of cure under certain conditions.

KEY WORDS Epoxy, DGEBA, TGMDA, ureas, Monuron, latent hardener, thermal analysis, evolved gas analysis, cure kinetics.

INTRODUCTION

Latent catalysts and/or hardeners are used in order to avoid room temperature advancement in one part epoxy systems—such as film adhesives—which need to have a reasonable shelf (or pot) life at ambient conditions and also viscosity (flow) controlled within a narrow range. In common systems formulated from resins based on diglycidyl ether of bisphenol A (DGEBA), inhibition of reaction at low temperature is often achieved by the use of dicyandiamide (dicy) as hardener and the latency of the formulation and attendant high cure temperatures (170°C) can be attributed to the low solubility of dicy in the resin.[1] The addition of a small amount of an accelerator, for example the urea Monuron (I) or TDI-DMA (II), can lower the cure temperature to around 100°C without compromising the room temperature latency of the formulation.[2]

$$\mathrm{Ar.NCO + R_2NH = Ar.NH.CO.NR_2}$$

I Monuron: p-chlorophenylisocyanate, dimethylamine.
II TDI/DMA: tolyl 2,4-diisocyanate, dimethylamine.
III PDI/DMA: phenyl 1,4-diisocyanate, dimethylamine.

The mixes of dicy and the urea have been recognised as synergistic,[3] and cure DGEBA more readily (faster, or at lower temperature) than either agent alone. In some cases the combination can lead to a formulation where the cured properties are unexpectedly temperature dependent.[4] Although dicy is frequently used without accelerators, the ureas are less often used alone as curing agents. Nevertheless, we have studied a commercial adhesive in which PDI-DMA (III) was the sole hardener,[5] and have used urea derivatives as latent sources of piperidine when preparing tougher matrix materials based on tetraglycidyl methylene dianiline (TGMDA) resins.[6] The reaction of dicy with DGEBA is complex and not fully understood[7,8] and even the functionality of the dicy is subject to some ambiguity. It is therefore not surprising that the way in which the urea (itself capable of curing the resin and formally at least able to dissociate into secondary amine and isocyanate) acts as an accelerator has been little studied under practical conditions.

We have noted from time to time that the thermal analysis of this type of system can be different in open and hermetically sealed pans.[9] This paper examines the effect of volatile restraint in more detail, but since this work has been incidental to other studies[4,5,6] over several years, in different systems using different instrumentation, it is perforce largely anecdotal. It is a cautionary tale relevant to evaluation and characterisation of these epoxy systems, particularly by thermal methods, and emphasises the need to reproduce the constraints of application.

EXPERIMENTAL

Materials

DGEBA Resins: various grades of DGEBA resin were used at different times: X22 (mw 340), Shell Chemicals, and DER 332 (mw 340–350), Dow, are essentially monomeric; Epon 828 (mw 370–384), Shell, has low oligomer content, and Epon 1001 (mw 900–1100), Shell, slightly more.

TGMDA resin: MY720, Ciba Geigy.

Hardeners: Commercial dicy and Monuron were used without further purification, the other ureas were prepared by standard methods and recrystallised to constant m.p. (DSC) before use.

Generally the mixes were prepared in small quantity at room temperature by hand in a mortar and pestle. No attempt was made to dry the reactants.

Thermal analysis A range of Dupont thermal analysers (Models 900, 1090, 2000) has been used to control a differential scanning calorimeter (DSC910) and thermobalance (TGA950). Samples were typically in the range 10–20 mg weighed into appropriate (open, crimped or hermetic) aluminium pans. The latter are said to withstand an internal pressure of three atmospheres. Usually Dupont software was used to evaluate the data, most often in the 1090 version, although integration of the Model 900 runs used a purpose built integrator. Relevant experimental details are given in the text.

Evolved gas I-R analysis Most of the work reported here was performed with a custom built tube furnace, a multi-pass gas cell (Specac) and a Perkin-Elmer 580B ratio recording infra-red spectrometer.[10] Samples (10–20 mg) were placed in standard DSC pans and heated from ambient to the required temperature at 5°C/min. For isothermal work the samples were inserted into the preheated furnace. Evolved gases were purged through the gas cell with nitrogen (50 ml/min) and spectra recorded at 2 min intervals.

RESULTS AND DISCUSSION

In DSC studies of DGEBA/dicy mixes it was found that the course of the reaction was determined by the choice of an open or hermetic pan, and particularly under isothermal conditions the heat of reaction was significantly greater in a closed pan (Table I). Under dynamic conditions the DSC curves show that the major difference was in the vigour of reaction during its early stages. It was difficult to get reproducible results, particularly in dynamic runs, because of leakage from the sealed pans. This was attributed to the relatively low pressure capability of the swage and the ease of contaminating the mating surfaces with the syrupy mix. Hermetic pans, opened after reaction, smelled transiently ammoniacal.

The dynamic DSC curves for X22/PDI-DMA (Figure 1) show a similar dependence on pan configuration. An initial reaction accelerated rapidly above 140°C and was substantially complete at 200°C although polymerisation continued. The reaction was slower in the open than in the sealed pan, the maximum rate shifted to a higher temperature (for 828/dicy the maximum did not shift) and the heat of reaction during the initial reaction was reduced (Table I). The urea III is relatively

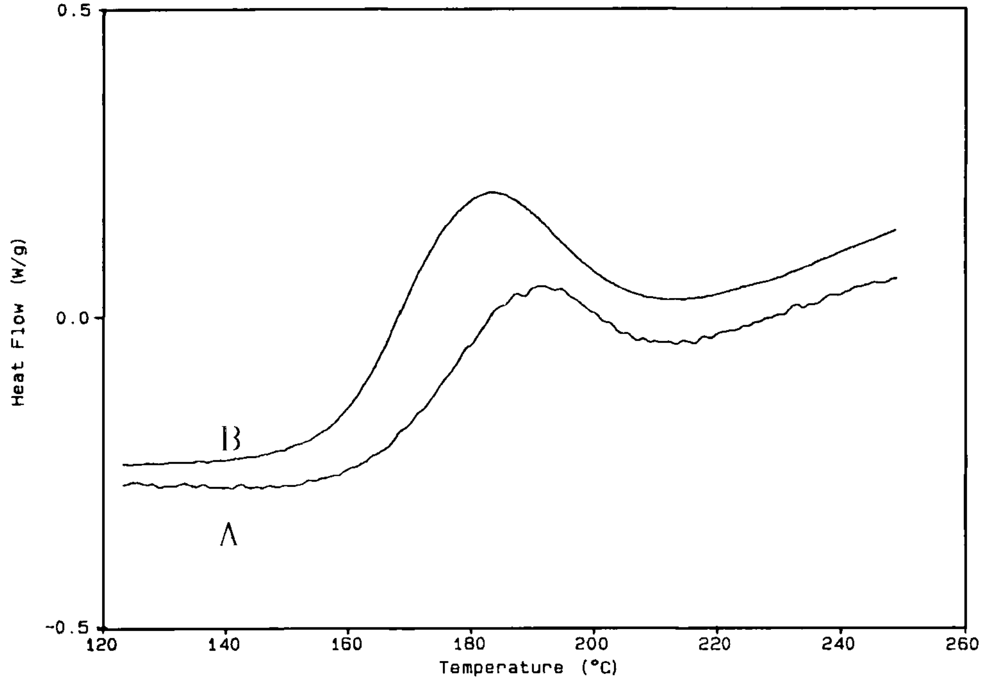

FIGURE 1 DSC curves of X22/PDI-DMA (3.15phr) at 5°C/min showing the effect of pan configuraton; A, open; B, hermetic pan.

TABLE I
The effect of sample container on the thermal analysis of some epoxy systems

System	Condition	Parameter	Open pan	Closed pan
828/dicy (10phr)	160°C/2h	Heat of reaction (J/g)	360	460
X22/PDI-DMA (3.15phr)	5°C/min	Partial heat of reaction* (J/g)	64	185
332/TDI-DMA (6phr)	130°C/3h	T_g (°C)	106	102
	150°C	Heat of reaction (J/g)	325	587
		Time to max. (min)	10	7
		Time to end (min)	2	1
MY720/TDI-DMA (8phr)	5°C/min	Exotherm max (°C)	151	158
		Heat of reaction (J/g)	480	550

*The heat of initial reaction, tangential baseline, Figure 1.

insoluble[5] and slow to dissolve but the Monuron which is easily soluble behaved in the same way. (Figure 1 also shows that the DSC curve is noisier for the open pan; this is probably largely accounted for by the greater pan/sample mass ratio of the hermetic pans decreasing the sensitivity, but is not inconsistent with evolution of volatiles from the open pan).

The effect of volatilisation of reactants and products in thermal analysis is obvious; most manufacturers of DSC instrumentation provide pans with at least some pressure resistance (massive pans degrade sensitivity) and pressure cells are available with some instruments. It has, for example, been shown that the kinetics of phenolic cure are accessible if the evolution of water is suppressed in pressure DSC,[11] although there can be some problems associated with the generation of appropriate baselines (and thus quantitative measurement) when there is a volatile reactant in a closed system.[12] We are not aware of any reports of the effect of pan closure on standard epoxy cure reactions and open pans are often used; although the volatilisation of piperidine from DGEBA has been frequently invoked to explain higher cure temperature leading to products of lower glass transition temperature, T_g, other explanations are more convincing.[13]

Table I shows that there is a range of effects in these systems when the degree of constraint of the sample is changed by using a hermetic pan rather than an open one. Generally it appears that the reaction proceeds more readily and to a greater extent in closed systems, the kinetics are changed, and the properties of the product, for example T_g, are different but not predictably.

There are several possibilities which explain these observations; (i) the evaporation of an adventitious catalyst, for example water, (ii) the volatilisation of a major reactant, or (iii) the volatilisation or decomposition of an intermediate product or catalyst. The loss could be by sublimation or dissociation as well as by evaporation. It is also possible that the loss of a reactant allows an alternative reaction not otherwise favoured.

Water is claimed to be a catalyst—among other hydroxyl compounds—in amine epoxy reactions;[14] we have found no pronounced sensitivity to encapsulation in thermal analysis of most film adhesives aged under moist conditions, and in one case where a urea curing agent was present and a sensitivity to moisture was found (at a lower temperature so that evaporation was less likely),[15] the effects were not as great as those reported here. Encapsulation had no significant effect on the DSC curves of the 828/DDS reaction (also see below). It seems unlikely that the results in Table I can be attributed to the presence of water.

The heat of reaction for X22/PDI-DMA (3.15phr) during isothermal cure in a sealed pan, 3h/170°C, was at least 430 J/g (Figure 2), and the partial heat of reaction associated with the initial reaction was 90 J/g (up to maximum rate, compared to 185 J/g in Table I). If it is assumed that there is approximately constant heat of reaction for the epoxide ring opening (102.5 kJ/mol for phenyl glycidyl ether with n-butylamine),[16] the expected heat of complete reaction of the epoxy groups in this mix is close to 600 J/g. Since the molecular ratio of the reactants is 12:1, even if the urea exhibits polyfunctionality, there must be extensive and effective homopolymerisation facilitated in some way by volatile product retention.

Ureas are seldom used in isolation, but are often used to lower the practical cure temperatures for dicy hardened formulations. When dicy (8phr) was sprinkled on the mix of X22 and PDI-DMA the strong synergism is expressed by an onset of reaction well below that of either curing agent alone[5] and there was a marked effect of open and closed pans. We observed that the relative effectiveness (measured by the heat of initial reaction, and the reduction in the onset temperature of initial exothermic peak) of TDI-DMA, PDI-DMA and Monuron at the same molar concentration depended on the pan configuration. Factors affecting urea cure include the parent isocyanate[8] and particularly the secondary amine.[17] (Dimethylamine derived ureas are the most active and are effective as accelerators; those from

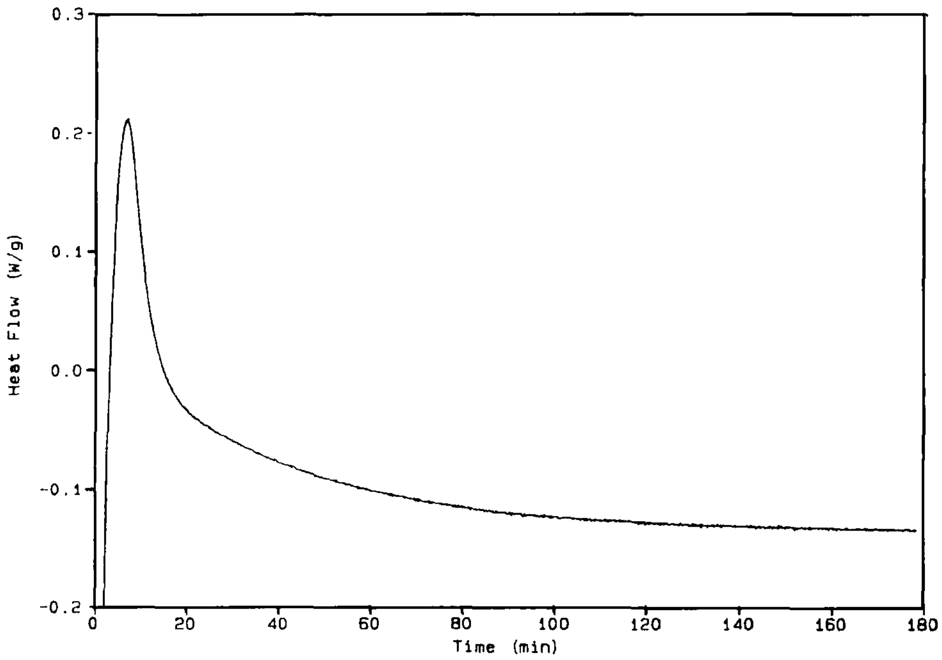

FIGURE 2 DSC curve of the isothermal cure at 170°C of X22/PDI-DMA (3.15phr), hermetic pan.

piperidine are less reactive and give more controllable cure of TGMDA systems at higher temperatures).[6]

Both thermogravimetric analysis (TG) and evolved gas analysis (EGA) have been applied to the problem but, because the chemical composition in open and closed systems will vary, the balance of reactions may be different and care should be taken in extending these results to closed systems.

The weight losses from 332/TDI-DMA mixes, under conditions essentially the same as open pan DSC, are shown in Figure 3. The resin was relatively nonvolatile below 200°C but increasingly rapid evaporation at higher temperatures left virtually no residue. It was surprising that the addition of TDI-DMA—itself relatively involatile—substantially increased the weight loss below 200°C (Table II).

The coincidence of low temperature weight loss and cure of 332 at higher levels of TDI-DMA is clearly shown in the DSC and TG curves (Figure 4), and the weight losses depended on the amount of hardener/catalyst present. The weight lost below 200°C appears to be associated with the urea, whereas that lost at higher temperatures is associated with unreacted monomer, and this accounts for the small losses in the DDS and dicy cures. The use of TG in association with epoxy cure has received little attention although Levy et al.[18] studied an anhydride cure of DGEBA and the competitive volatilisation of hardener and resin.

It is possible that the differences in heat of reaction of 828/dicy or MY720/TDI-DMA in open and closed pans could be explained by volatilisation of monomer but the weight change in the open pan (and consequent heat of vaporisation and the heat of reaction foregone) is insufficient to account for the difference.

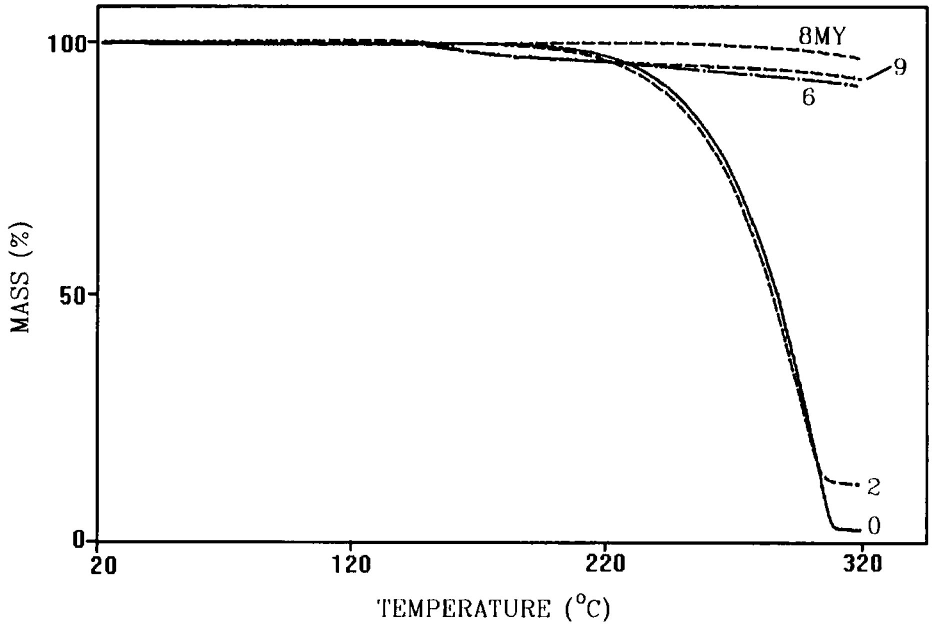

FIGURE 3 Weight loss from mixes of 332 (and MY720) with TDI-DMA heated in nitrogen at 10°C/min. The accelerator concentration (phr) is indicated.

TABLE II
Thermogravimetric analysis of some epoxy mixes in nitrogen; 5°C/min and isothermal

Sample	Weight loss at 200°C (%)	T_{max} (°C)	Weight loss at 300°C (%)	Weight loss after 10min (%, at °C)
332	<1		98	
TDI-DMA	1	182 (m.p.)		7 (186)*
332/TDI-DMA (2phr)	1	broad	86	1 (150°C)
(6phr)	3	160	12	2.5
(9phr)	4	162	7	3.5
332/DDS (36phr)	<1		3	
332/dicy (9phr)	<1		4	3 (230°C)**
MY720/TDI-DMA (8phr)	<1			4 (230°C)**

*Constant rate (zero order) weight loss (= sublimation?) above m.p., for mixes the rate of isothermal loss decreases quite rapidly. During dynamic heating of virgin TDI-DMA there is negligible loss below m.p.

**Weight losses from open DSC pans.

Evolved gas analysis of these reactive mixtures reveals further complexity and is summarised in Table III.

The evolution of propenal during cure is interesting but does not correlate with the sensitivity to pan configuration, for example 332/dicy shows a strong pan effect but does not evolve propenal; TGMDA/DDS does yield the aldehyde although it is no more reactive in a closed pan.

Grayson and Wolf[19] observed propenal, together with other carbonyl compounds, during low temperature heating of cured MY720/DDS and considered that it originated from small amounts of thermally unstable products from homopolymerisation or cyclisation (although the possibility of mechano-chemical degradation should always be considered for small amounts of product from finely ground sample).[20] It has been speculated that the propenal and the other carbonyl compounds are

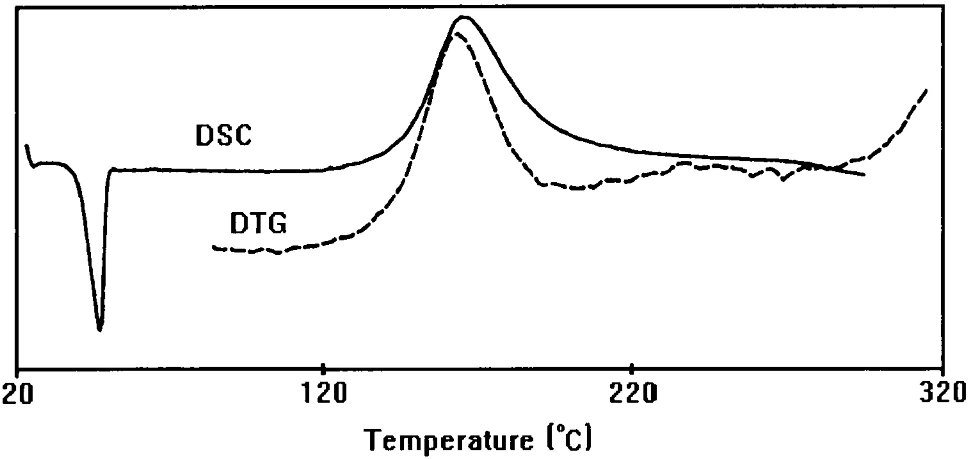

FIGURE 4 DSC and derivative TG curves for 332/TDI-DMA (9phr), 10°C/min, nitrogen.

TABLE III
Products identified during evolved gas analysis of epoxy mixes heated at 5°C/min

Sample	Products (appear at °C)
332	DGEBA (260), negligible decomposition
332/TDI-DMA (6,9phr)	Propenal (140–220), CO_2 (130–210) DGEBA (220)—only at 6phr Decomposition of cured resin (>330)
332/Monuron (9phr)	As above
1001/TDI-DMA	Small amount of propenal evolved below 200
332/DDS (36phr)	DGEBA, trace (220) Decomposition (>320)
332/dicy (7phr)	DGEBA (220) Decomposition (>320)
TGMDA	Propenal (250)
TGMDA/TDA-DMA	Propenal, trace (180)
TGMDA/DDS	Propenal (230)

formed as a result of secondary reactions of the primary products.[21] Grassie *et al.*[22] found that the low temperature (280°C onset) thermal degradation of monomeric DGEBA yields propenal as a result of isomerisation of terminal epoxide groups. The relative paucity of these in the higher oligomers would account for the lack of propenal from 1001/TDI-DMA.

The evolution of propenal demonstrates the complexity of these reactions. Figure 5 shows the effect of cure conditions on the yield of propenal as 332/TDI-DMA

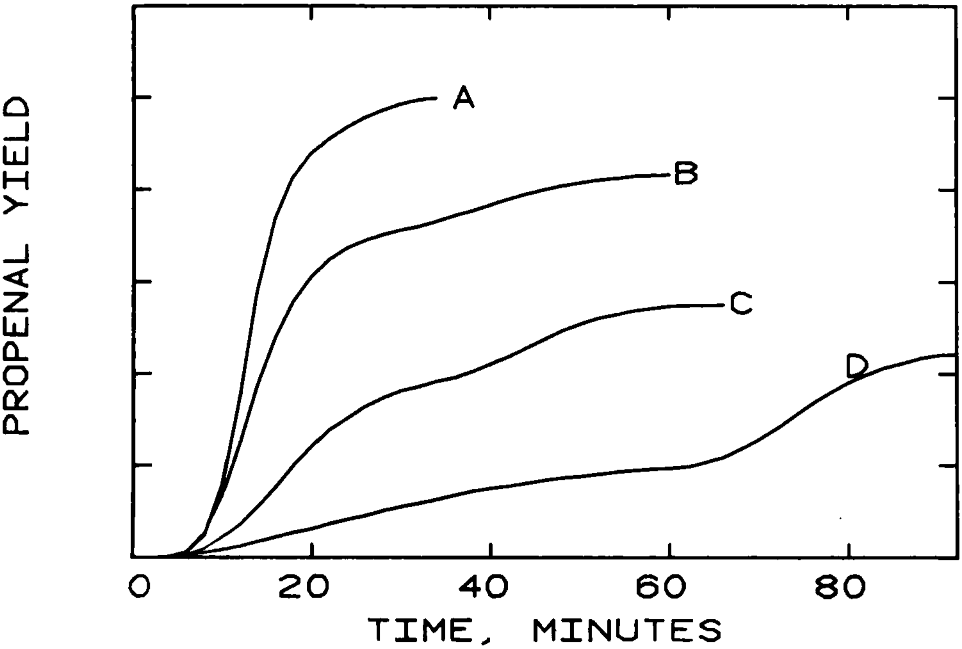

FIGURE 5 Normalised yield of propenal from 332/TDI-DMA (6phr) heated at 5°C/min in nitrogen, sample temperature 120°C at zero time: A, continuous heating; B, held 20 min at 160°C; C, held 30 min at 140°C: D, held 60 min at 120°C.

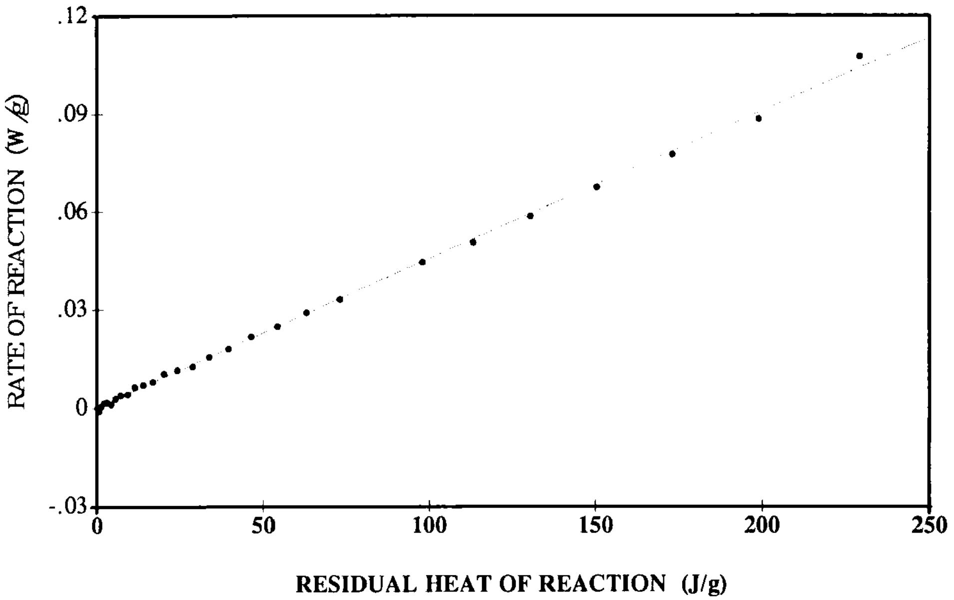

FIGURE 6 The data in Figure 2 after maximum rate appear to follow 1st order kinetics. A plot of residual reactivity (J/g) against rate of reaction (w/g).

(6phr) mixes were heated at 5°C/min to cure temperature, held for a set time and then further heated to 220°C. The total yield and the yield during cure and post-cure stages each depend on the cure temperature, with longer times at lower temperature decreasing the overall yield. Both these results, and those given in Table II, suggest that the resin is reacting at higher temperatures, but, since the resin alone does not give detectable amounts of propenal, the cure reaction itself must be intimately involved. This would be consistent with the observation that TGMDA, which is capable of self-polymerisation without added catalyst, yields propenal when heated.

Evidence implicating dimethylamine as the escaping catalyst has been fragmentary. It has not been detected in EGA experiments of 1,1-dimethylurea-containing mixes, with the exception that when 332/TDI-DMA (9phr) was plunged into the preheated furnace (150°C) there was a transient trace of the amine. Odours remaining in DSC capsules (ammonia from dicy, amine from ureas) after heating to higher temperatures could be ascribed to decomposition of remnant reactant at high temperature (after cure) rather than before or during cure. It should be noted that during cure of MY720 with TDI-PIP (a piperidine based urea) significant gas evolution and "blowing" of castings could occur at moderate heating rates and temperatures.

Although we have found very small amounts of the dissociation products (dimethylamine, isocyanate, and carbon dioxide produced by reaction of the isocyanate with traces of H_2O in the nitrogen) just before the melting when TDI-DMA is heated alone in EGA-IR, the rapid weight loss after melting appears to be mainly sublimation rather than decomposition. In a resin mix at any moderate temperature the reaction of the secondary amine would be expected to be rapid and it is unlikely that the amine would have an appreciable independent life under normal conditions. The putative isocyanates will also react with epoxides[23] but are rather less reactive than secondary amines. They have not been detected in EGA-IR and although the difunctional types would not be volatile (unless both functionalities were simultaneously reacted) strong container effects have been seen for both TDI and PDI derivatives.

The reaction of X22/PDI-DMA (3.15phr) under isothermal conditions was initially auto-catalytic (Figure 2, but seen much more clearly at lower isothermal temperatures). It is interestng that a large part of this reaction (55%) apparently followed simple first order kinetics (Figure 6), although DSC curves obtained at different heating rates indicate complex kinetics for adhesives based on this accelerator.[5]

SUMMARY AND CONCLUSIONS

The cure of model epoxy systems, representative of latent formulations, has been found to be sensitive to the degree of containment during reaction. A range of reactions can be postulated during cure of urea accelerated epoxy/dicy mixes;

epoxy/dicy (dicy itself is multifunctional),
epoxy/urea,
epoxy decomposition giving propenal,
urea dissociation,
epoxy/secondary amine,
epoxy/isocyanate,
epoxy/any of the above primary products (in some cases giving very effective homopolymerisation).

It is suggested that the actual reactions taking place depend on the specific conditions of temperature, pressure (restraint), and concentration in the particular application. Instrumental analysis of cure reactions and evaluation of materials and processes should take this into account. For example in studies[6] of toughening MY720 resins, where the materials were cast in open moulds, open pans were used in DSC investigations of urea hardeners, but for film adhesives crimped pans were used to more truly represent a joint. Model reactions in solution need to be interpreted with care. It should be recognised that it is not only the thermoanalytical results that are different, but that the cured adhesive itself is different and can have different properties as a result of different cure conditions.[14] Head space analysis in constrained systems may be informative, certainly with available instrumentation and capability more definitive results could be expected than these reported here.

References

1. G. L. Hagnauer and D. A. Dunn, *J. Appl. Polym. Sci.* **26,** 1827 (1981).
2. C. A. May and Y. Tanaka, *Epoxy Resins* (Marcel Dekker, New York, 1973), p. 297.
3. P-N. Son and C. N. Weber, *J. Appl. Polym. Sci.* **17,** 1305 (1973).
4. B. C. Ennis, P. J. Pearce and C. E. M. Morris, *J. Appl. Polym. Sci.* **37,** 15 (1989).
5. P. J. Pearce and B. C. Ennis, submitted to *J. Appl. Polym. Sci.*

6. P. J. Pearce, B. C. Ennis and C. E. M. Morris, *Polym. Comm.*, **29**, 90 (1988).
7. S. A. Zahir, *Org. Coatgs. Sci and Technol. 6th Int. Conf. Proc.*, Athens, Greece, 1980, p. 475.
8. H. Brockmann and J. Barwich, in *Fertigungssyst. Kleben '89* DECHEMA Monogr., **119,** (1990), p. 177.
9. C. E. M. Morris, P. J. Pearce, B. C. Ennis and V-T. Truong, in *Progress in Pacific Polymer Science,* B. C. Anderson and Y. Imanishi Eds. (Springer Verlag, Berlin, 1991), p. 165.
10. R. G. Davidson and G. I. Mathys, *Anal. Chem.*, **54,** 837 (1986).
11. R. B. Prime in *Thermal Characterisation of Polymeric Materials,* E. A. Turi, Ed. (Academic Press, N.Y., 1981), pp. 447 *et seq.*
12. W. Balcerowiak, W. Jerzykiewicz and H. Szewcyzk, *Tenside Detergents,* **21,** 1 (1984).
13. V-T Truong, B. Y. Truong and B. C. Ennis, *Polym. Comm.*, **32,** 275 (1991).
14. H. Lee and K. Neville in *Handbook of Epoxy Resins* (McGraw Hill, N.Y., 1967), 5–6.
15. B. C. Ennis, P. J. Pearce and C. E. M. Morris, *Thermochim. Acta,* **134,** 187 (1988).
16. K. Horie, H. Hiura, M. Sawada, I. Mita and H. Kambe, *J. Polym. Sci., A-1,* **8,** 1357 (1970).
17 B. R. LaLiberte, J. Bornstein and R. E. Sacher, *Ind. Eng. Chem. Prod. Res. Dev.*, **22,** 261 (1983).
18. J. H. Levy, W. I. Stuart, and R. N. Whitten, *J. Thermal Anal.*, **25,** 359 (1982).
19. M. A. Grayson and C. J. Wolf, *J. Polym. Sci., Polym. Chem.*, **22,** 1897 (1984).
20. R. G. Davidson, *J. Anal. and Appl. Pyrolysis,* **21,** 181 (1991).
21. J. A. Bornmann, *J. Polym. Sci., C Polym Lett.*, **26,** 409 (1988).
22. N. Grassie, M. I. Guy and N. H. Tennent, *Polym. Degradn. and Stab.*, **13,** 11 (1985).
23. N. Kinjo, S. Numata, T. Koiyana and T. Narahara, *J. Appl. Polym. Sci.*, **28,** 1729 (1983).