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THERMAL ANALYSIS OF EPOXIDE FILM ADHESIVES

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ABSTRACT

Thermal analysis (DSC, TMA, TG) has been used in the study of batch variation, optimisation of cure conditions, and water absorption of a film adhesive. The advantages of TA arise from rapid measurement of reactivity of the sample and Tg of the product, not from predictive kinetic parameters.

INTRODUCTION

Thermoanalytic techniques are well suited to evaluation and quality control of structural film adhesives widely used in aerospace applications. Most film adhesives are premixed epoxy formulations supported on a suitable carrier and, as reactive mixtures with a limited shelf life, must be stored and transported at sub-ambient temperatures. The quality of the materials, which are imported to Australia, is affected by a thermal history which may not be known in detail, and is rendered more uncertain by usage, which is largely repair and maintenance rather than prime manufacture. These applications are likely to result in curing conditions which are not so strictly controlled, or which deviate from those recommended because of the proximity of heat sensitive components or large heat sinks. There is therefore a need to evaluate both adhesives and cure schedules.

The relevance of thermal analysis is obvious, and there is an extensive and well reviewed literature (e.g. Prime[1]) of these techniques for epoxy polymers and model compounds. This shows that it is easy to generate data during the exothermic cure but, because the DSC response is the summation of consecutive and sequential reactions, interpretation of that data can be difficult.

DSC has been used to evaluate film adhesives, and several approaches have been made to kinetic models of the cure reaction[2-5]. These papers identify three factors which need to be considered in a commercial material, namely the stoichiometry[5], the extent of initial reaction (B-staging)[2] and the extent to which the mechanism of cure changes with temperature[4]. If more than one of

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these is important it will be very difficult to develop any kinetic model for the reaction. In addition, the formulations can be complex[6] with more than one resin and hardener present. The utility of predictive methods for these materials is therefore questionable. We have studied numerous film adhesives[6,7,8] and have found wide variations in cure and aging properties, and differences in the immediate relevance of thermal analysis.

In this paper we use one commercial adhesive to exemplify the range of TA techniques (some novel) usefully applicable to film adhesives. The interpretation of the results, and their relevance to the choice of a suitable adhesive for a specific application, involving off-optimum cure, will be reported elsewhere.

INSTRUMENTATION AND MATERIAL

A Dupont Model 1090 Thermal Analyzer was used. DSC samples (10-15 mg) were in crimped aluminium pans. Isothermal samples were dropped into the preheated DSC cell and reached reaction temperature within 1 to 1.5 minutes. The TMA sample configuration is described later.

The film adhesive used was FM73 (American Cyanamid) a relatively simple formulation on a light polyester support (either knit or random mat). Various batches were obtained as normal commercial supplies, but not always directly. It is emphasised that the thermal history of these materials, before we received them, is uncertain. The results reported here are representative of the material as used, not necessarily ex-factory.

RESULTS AND DISCUSSION

Batch Variation

DSC curves of FM73 are shown in Figures 1 and 2. The dynamic curves can show two maxima, and the isothermal curves at 120°C clearly indicate two processes. There are variations in the significant times and temperatures identifiable in these curves which are not matched by the glass transition (Tg) of the cured material (Table 1), by the composition of the samples as shown by liquid chromatography[9], or by the strength of lap-shear joints[9].

Absorbed Water

The recent samples (6 and 7) showed a single peak in dynamic DSC curve and less differentiation in isothermal DSC. These curves are similar to, but not the same as, those recently published for this adhesive[5].

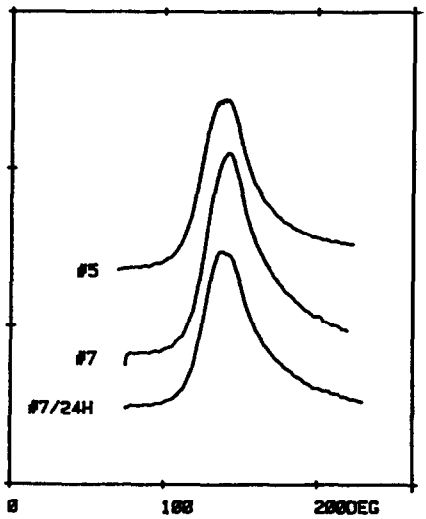

FIG 1 DSC curves of FM73, 5°C/min

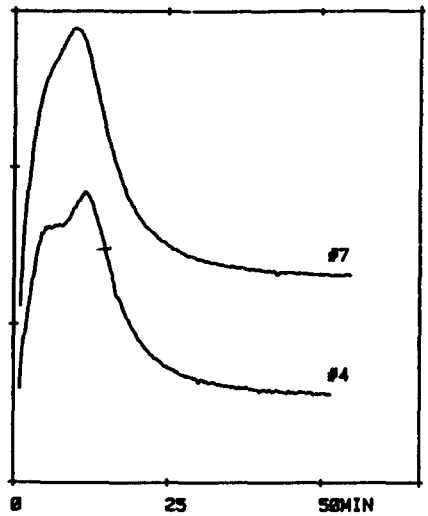

FIG 2 DSC curves of FM73, isothermal 120°C

TABLE 1

Sample variation in FM73 - DSC cure

	5°C/min			120°C/60 min		
Sample*	T_{max} (°C)		ΔH(J/g)	t_{max} (min)	ΔH(J/g)	Tg(°C)
1	137	(142)	176	9.5	190	98
2	137	(142)	207	10.9	228	105
3	138	(142)	179	11.2	199	104
4	(137)	142	188	10.7	216	105
5	137	142	188	-	-	-
6	138.5		180	10.1	227	-
7		142	193	8.0	220	105

T_{max}, temperature of maximum exotherm, ( ) secondary maximum; ΔH, heat of reaction; t_{max}, time to maximum exotherm; Tg, extrapolated end of transition, 10°C/min. *The support was of random mat construction, except in samples 6 and 7 which contained a knit.

The changed support would not contribute to the DSC curves, and the differences are not what would be expected for acceptable quantitative[10] or qualitative[11] batch variability. Exposure of the recent samples in the laboratory for 24 h produced bimodal curves (Figure 1). The effect was largely reversed by desiccation. Obviously the "anomolous" curves are the result of absorption of small amounts of water. (This reversible effect on the cure kinetics is in marked contrast to the more subtle but permanent effect of moisture on a more complex adhesive comprised in part of very similar materials[6]).

A Simple "Rheometer"

The samples on the knit support tended to give joints with increased porosity. Since thermogravimetry showed no difference in volatile loss at the cure temperature, an indication of the physical changes during cure was required. A small "beam" (6-8 x 2-3 mm) of a single ply of FM73 sandwiched between discs (~10 mm diameter) of Teflon coated glass release cloth was supported on silica rings (Dupont Flexure kit, circa 1970) in the TMA. The beam was loaded via the hemispherical probe with a constant load (~ 0.1 g) and an additional load (1 g) was applied intermittently, using a simple hand windlass, as the temperature was raised at 5°C/min to the cure temperature (120°C). Typical curves are shown in Figure 3, in this case of a sample of FM73 fresh from the freezer and then after aging in the laboratory.

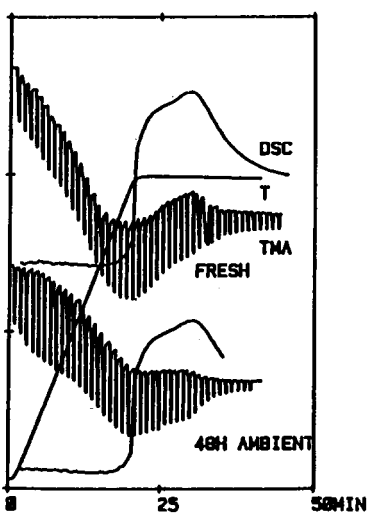

FIG 3 TMA of FM73 between release cloth; 5°C/min, 120°C; 1g intermittent load

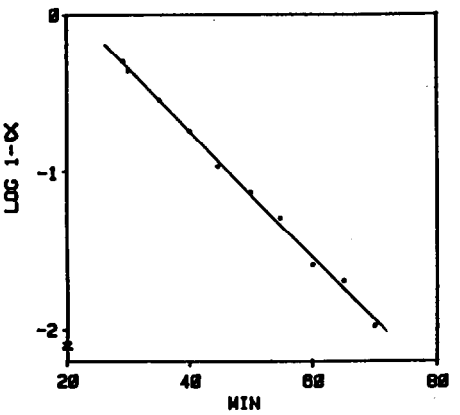

FIG 4 Residual reactivity (1-α) after t_{max}, FM73 at 101°C

In this temperature range the glass cloth is elastic and shows no transitions. In the initial stages, the curves show flow of the adhesive and flex of the support, and extra flow at each application of the intermittent load. Flow ceases before the cure temperature is reached in one case. The DSC curves do not discriminate as well as flow curves. At the cure temperature there is a period of relative constancy before a rapid increase in viscosity/stiffness limits deflection and recovery; this corresponds to the DSC maximum.

The use of release cloth allows examination of the cured sample for resin flow and void formation whether the load is intermittent or static. The support in flexure extends the utility of TMA for studying adhesives and prepregs, and the simple apparatus could be easily automated for variable dwell time[12]. The results are qualitative, because of the difficulty of reproducing the sample and stress geometry, but can offer useful insights into material properties.

Low Temperature Cure

FM73 is tolerant of cure conditions and "cure cycles may be varied over a broad range from 200°F (93°C) to over 350°F (177°C)"[13]. Samples cured isothermally in the DSC cell were subsequently cooled and reheated to determine Tg and the residual heat of reaction (ΔH_r). Materials cured at different temperatures are not the same (Table 2). While further heating at 120°C raised the Tg (to 114°C) of the undercured (70 and 80°C) materials, the others were not affected.

TABLE 2
The Effect of Temperature on DSC Cure of FM73

Cure Conditions (°C/min)	ΔH (J/g)	t_{max} (min)	t_{end} (min)	Tg (°C)	ΔH_r (J/g)
76/900	190	235	600	103	12
86/900	194	108	400	105	4
101/150	200	37	100	116	0
121/60	190	10	50	98	0
141/30	200	1	20	93	0

t_{end}, completion of reaction; ΔH_r residual heat of reaction

This approach is not rigorous, as in any application of the adhesive the temperature is ramped to the cure temperature. In most adhesives press-cured and DSC cured samples have the same Tg but for FM73 at temperatures above 100°C the press cured sample had a higher Tg, because of the increased time at lower temperature when cure is occurring (Figure 3).

Kinetics and Prediction

Clearly the cure of this adhesive is complex and the structure of the cured material dependent on the temperature of cure. It can readily be shown, following Barton[14], that the basic "Arrhenius" expression -

$$d\alpha/dt = k f(\alpha)$$

is not applicable : the "activation energy" is not constant for the first half of the reaction (Table 3). Thereafter the reaction approximates closely to first order (Figure 4). It is clear that the predictive methods can be of little use to extrapolate to other temperatures[4,5], or indeed in view of the batch variations (whether acquired during or post manufacture) at a particular temperature[2].

TABLE 3

Relative rates of reaction (r) at the same conversion (α) of FM73 cured at 101° and 121°C.

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
r101 / r121	4.0	3.0	2.5	1.8	2.1	2.0	2.0	2.0	2.1

CONCLUSIONS

We have shown that while the various techniques of TA are useful in the assessment of adhesive quality and cure schedules, at least for this adhesive the temperature programs should match those expected in practice. Because the Tg at full cure depends on both the isothermal cure temperature and the manner in which it was reached, kinetic parameters derived from DSC curves are of limited value and the direct experiment cannot be avoided. The greatest value is obtained from direct measurement of the properties of interest (e.g. extent of cure, reactivity, time to cure, Tg) which will be determined by the particular adhesive and circumstances.

This approach may be well served by non-standard qualitative techniques and in this context we have shown that useful results can be obtained from TMA samples sandwiched between release cloth and subject to static or intermittent stress.

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