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Thermal analysis in the development of self validating adhesives[1,2]

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Abstract

Zero volume unbonds (ZVU), or kissing bonds, cannot be detected by the conventional non-destructive testing (NDE) techniques. These unbonds can cause premature failure in adhesive joints. Self-validating adhesives are being developed which detect and remove zero volume unbonds. It is hoped that this can be achieved by the addition of a secondary component to the primary adhesive. This material will be able to migrate through the matrix and 'fill' the ZVU and then cure or solidify over time, repairing the joint in situ. In order to determine the structure of the 'smart' adhesive, dynamic mechanical thermal analysis and differential scanning calorimetry have been employed. These have indicated the presence of multiple phases in certain formulations and the lack of them in others, as well as physical ageing of the amorphous polymer. Crown copyright © 1997 Published by Elsevier Science B.V. All right reserved.

Keywords: Epoxy resin; Zero volume unbond; Kissing bond; Physical ageing; Smart materials

1. Introduction

Current adhesive joints are limited in their ultimate strength by the presence of zero-volume unbonds (ZVUs) or 'kissing bonds'. These unbonds are formed where the adhesive and substrate are in close proximity but no adhesive forces are formed, leaving a void of approximately 0.5 nm depth and which may extend in the interfacial plane over a wide area. Such a ZVU is shown in Fig. 1.

The presence of such defects has been discussed elsewhere [1]. Repair of defects formed throughout the service life of composites has been carried out [2]. This repair has involved the filling of hollow fibres with a polymer resin which then fracture under excessive loading of the structure and as such these techniques are aimed at the repair of macroscopic defects.

In a self-validating adhesive, we are looking to address the problems caused by ZVUs. In order to do this we are introducing secondary systems to the primary adhesive which are capable of migrating to and repairing the ZVU, providing improved adhesion and durability. This case is shown in Fig. 2.

In this study we have used an epoxy resin of <700 g mol^{-1} molecular weight and a polyoxypropyl diamine hardener to make our adhesive system. This discussion considers the use of methacrylates as blend components.

Dynamic mechanical thermal analysis and differential scanning calorimetry have been used to study the phase morphology and cure behaviour of these systems. It is a premise of a self-validating adhesive that the secondary component can be made to cure or polymerise within the bulk adhesive and at an interface. In particular we have been looking

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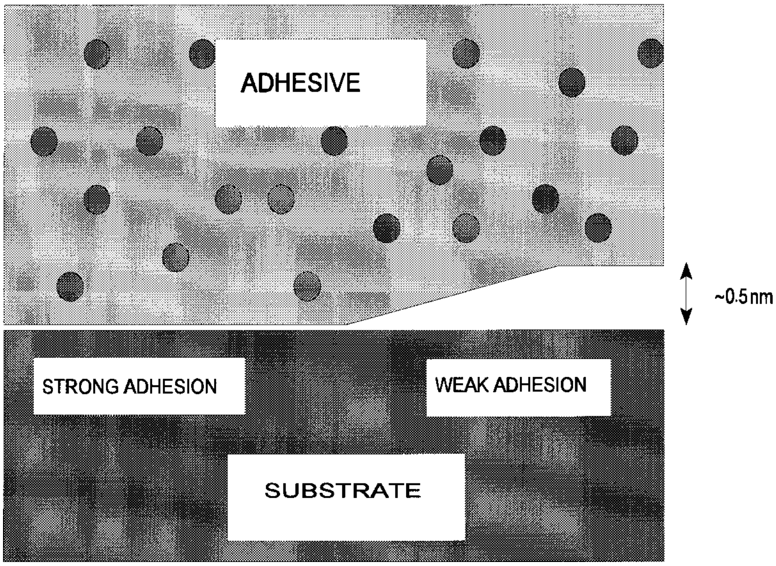

Fig. 1. Adhesive joint showing zero volume unbond.

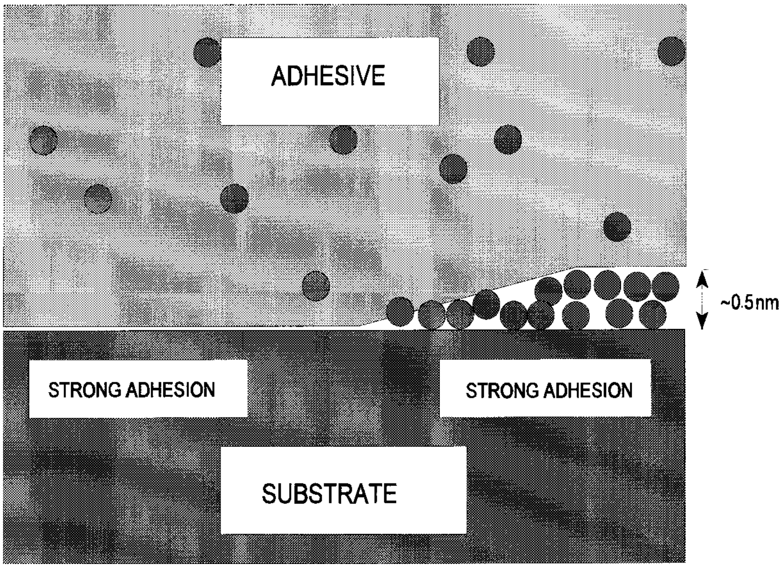

Fig. 2. Adhesive joint showing zero volume unbond after migration of secondary phase.

for the evidence of the curing/polymerisation of the secondary components. DMTA has been used to detect the development of phase morphology within the blends with heat treatment. DSC allowed us to study cure and physical ageing behaviour.

Scanning electron microscopy and contact angle measurements were also used to investigate the blend morphology. X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) have also been employed but this will be reported elsewhere.

2. Experimental

2.1. Adhesive preparation

The epoxy resin was the diglycidel ether of bisphenol A, produced under the name Epikote 828 (Shell Chemicals U.K.) and the hardener was a polyoxypropyl diamine, known as Jeffamine D230 (Texaco Incorporated, TX).

The adhesive was prepared by mixing three parts by weight of epoxy with one part amine and stirring thoroughly. Secondary components were added at 10 weight percent of the formulation, the compounds used being: methyl methacrylate, 2-ethyl hexyl methacrylate, tertiary butyl amino ethyl methacrylate and lauryl methacrylate (supplied by Permabond Europe, UK). Formulation compositions are summarised in Table 1. Material was cast into polypropylene dishes and allowed to cure at room temperature (293±1 K).

2.2. Specimen preparation

DMTA specimens were cut out from the cured castings to the approximate dimensions: 30 mm×

Table 1
Formulation compositions and designations

Composition (% w/w)	Designation
75% Epoxy, 25% amine	CR
67% Epoxy, 22% amine, 10% methyl methacrylate	CR10MMA
67% Epoxy, 22% amine, 10% 2-ethyl hexyl methacrylate	CR10EHMA
67% Epoxy, 22% amine, 10% lauryl methacrylate	CR10LMA
67% Epoxy, 22% amine, 10% *tertiary* butyl amino ethyl methacrylate	CR10BAEMA

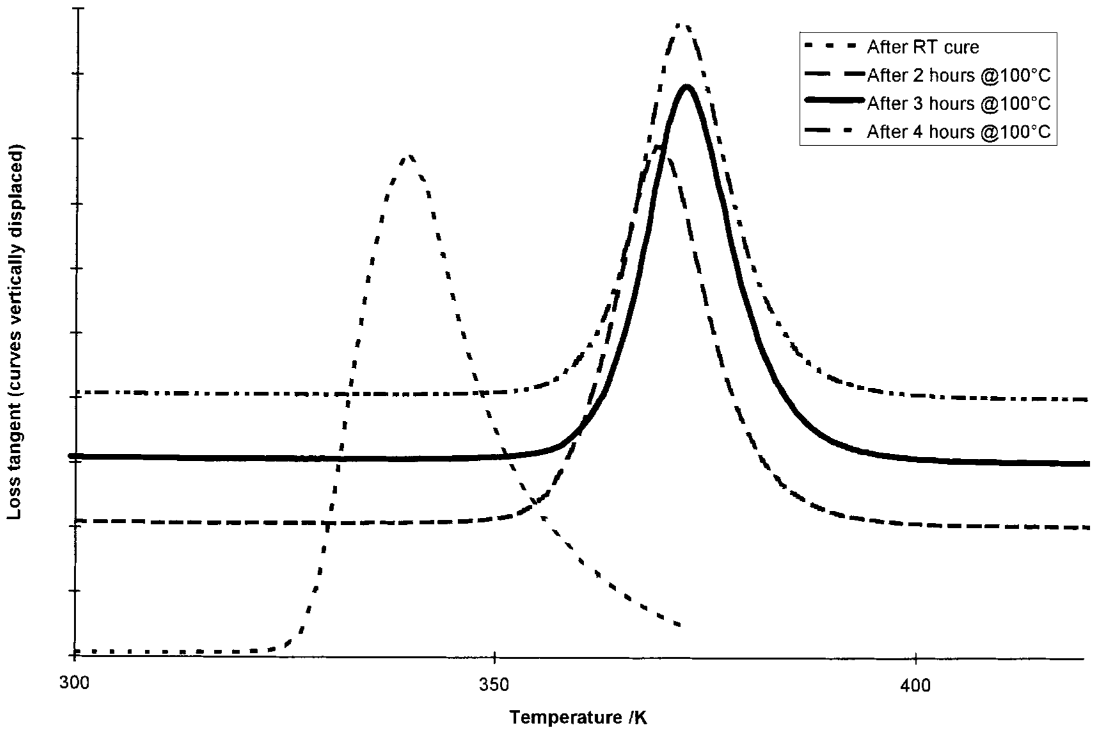

Fig. 3. DMTA traces showing development of T_g in CR specimen.

10 mm×3 mm, this corresponded to a single cantilever bending test piece with a clamped free length of 8 mm. Surfaces were smoothed by P800 grade wet and dry paper.

DSC specimens were cut from the same castings as cubes of approximately 1 mm in all dimensions. One face was smoothed with P600 paper to ensure a level surface for contact with the aluminium DSC pan.

2.3. Thermal analysis

The DMTA used was a Polymer Laboratories Mk II bending/shear head and analyser. After an initial ramp, each sample was subjected to a series of alternating isothermals and ramps. All ramps were carried out at 2 K min^{-1} from 303 to 398 K. Isothermal scans were carried out at 373 K for 60 min. The nominal amplitude of displacement was 64 μm and the frequency of test, 10 Hz.

DSC analysis was carried out on a DuPont 9900 and a TA 2920 MDSC. Ramping scans were conducted at a heating rate of 10K min^{-1} and from a start temperature of between 273 and 303 K to a final temperature of around 450 K.

2.4. Surface analysis

Scanning Electron Microscopy (SEM) was carried out on a Hitachi S450. The Dynamic Contact Angle analyser (DCA) was a Cahn 322, test liquids being bromonaphthalene, di-iodomethane, formamide, ethylene glycol, glycerol and distilled water.

3. Results and discussion

DMTA studies have shown that, for all formulations, the glass transition temperature of the primary epoxy phase increased with the number of heating cycles. CR10MMA and CR10EHMA formulations developed a secondary peak over the course of the heat treatment. It is suggested that this was due to the polymerised methacrylate formed during heating. For CR10MMA, this would correspond to a relative mole-

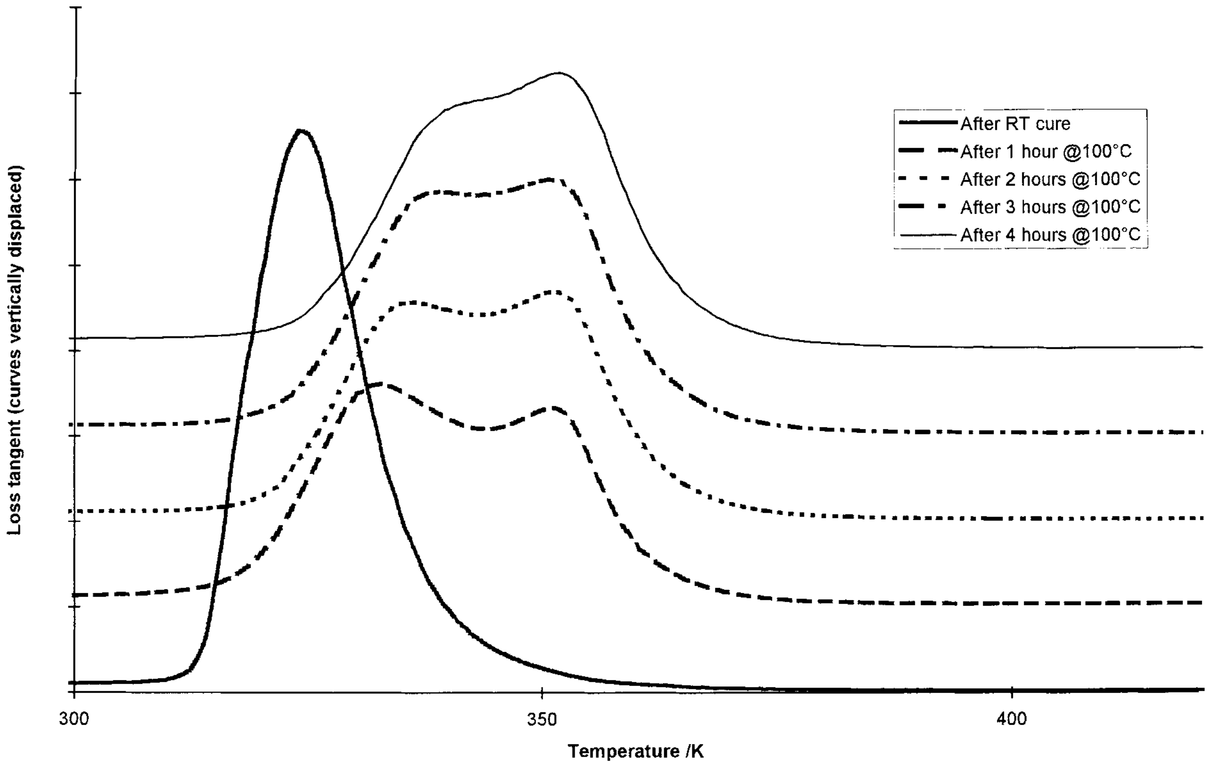

Fig. 4. DMTA traces showing development of T_g in CR10MMA specimen.

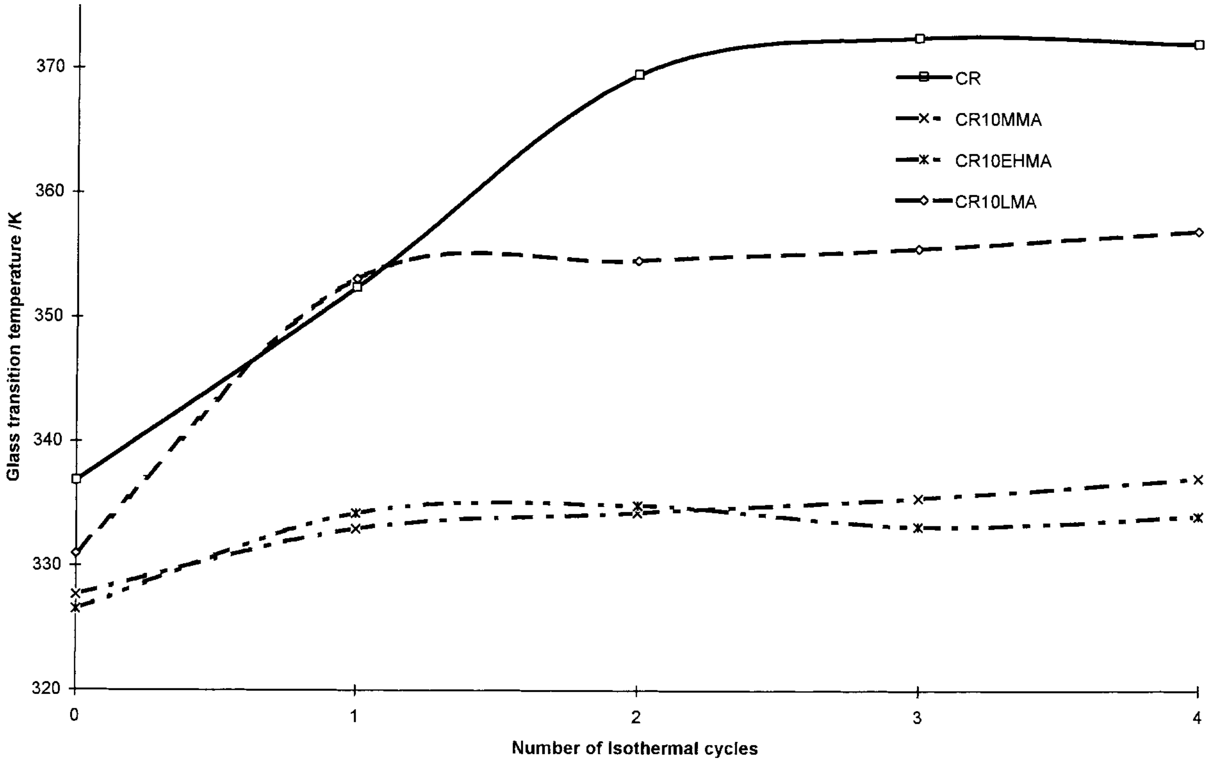

Fig. 5. Variation of T_g of primary phase with heat treatment.

cular mass of 15 000 [3]. Figs. 3 and 4 show the DMTA curves of CR and CR10MMA specimens respectively as a function of heat treatment. An increasing glass transition temperature with heat treatment was observed with the CR10MMA sample.

Specimens of CR10LMA and CR10BAEMA did not show any indication of forming a secondary phase, although both showed a broadening of the glass transition, suggesting that these components produced a broader range of cross-link densities in the epoxy matrix compared with the unblended system.

The changes in the epoxy glass transition temperature with isothermal cycling are shown in Fig. 5 for all the formulations in this study. Similarly, the development of secondary peaks, where applicable, are shown in Fig. 6.

The presence of further cure is also shown in the DSC traces. Fig. 7 shows two traces for a CR specimen. These were run sequentially. The large endotherm is thought to be due to the physical ageing of amorphous polymer within the specimen, as has been seen before in partially cured epoxy resin [4]. Physical ageing can adversely affect the mechanical properties of polymers used below their T_g [5]. As such, knowledge of its presence is important in interpreting the results.

The specimen was removed from the casting, three months after manufacture, accounting for the large physical ageing peak. Cure is thought to be indicated by the steady exotherm after the epoxy T_g. Studies of CR10MMA samples, before and after heat treatment, have not revealed a secondary transition that could be ascribed to a phase, such as poly (methyl methacrylate) (PMMA), though such a transition could be obscured by the cure exotherm. In order to resolve this, a CR10MMA sample has been studied using modulated temperature DSC (MDSC), as shown in Fig. 8. The derivative reversing heat signal revealed

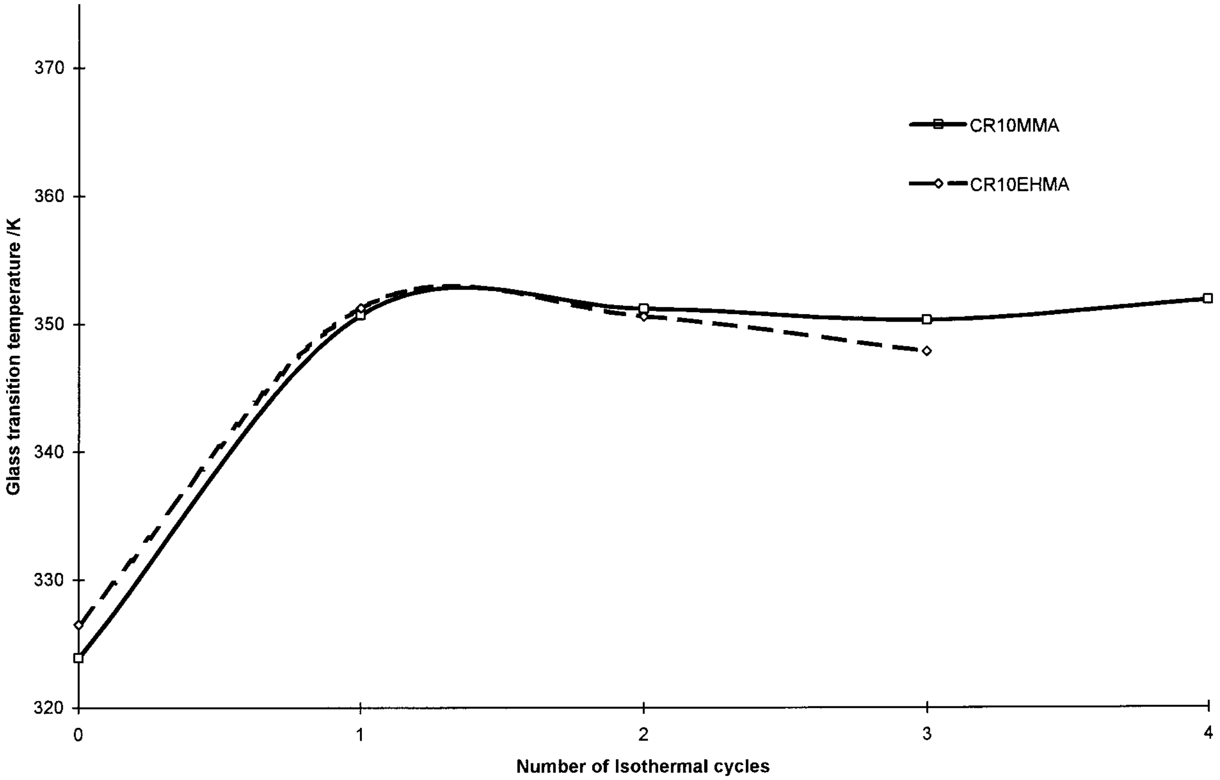

Fig. 6. Variation of T_g of secondary phase with heat treatment.

two glass transitions. The second transition appears to have been obscured by the first in the previous DSC experiments. The MDSC experiments were carried out at 2 K min^{-1} with a modulation of ±2 K and a period of 80 s.

The presence of a secondary phase in CR10MMA and CR10EHMA was supported by SEM. Fig. 9–12 show several scanning electron micrographs. Fig. 9 shows a specimen of CR10MMA before heat treatment. Two domains can be seen in the specimen, with some dendritic pattern. Fig. 10 shows a specimen after heating at 373 K for 4 h. The domains and dendritic patterning become more common, but contrast less sharply with the matrix. Fig. 11 is a CR10EHMA specimen after heating at 373 K for 4 h. Fig. 12 is a detail of this region. Domains of secondary phase can be seen.

Further results to indicate the presence of these secondary components in the first molecular layer of the formulations have been obtained from the contact angle analysis. Samples of all the formulations described in Table 1 have been tested.

The use of the DCA gave the surface energy (γ) of each sample as two components: the dispersive (γ^D) and the polar (γ^P). Each test gives us two readings of surface energy: one derived from the advancing contact angle and the other from the receding contact angle. With all the samples γ has remained largely constant, but the proportions of components γ^P and γ^D have changed.

DMTA has already shown that heat treatment of certain methacrylate bearing systems yields a polymerised secondary phase and the DCA data on these formulations indicate that these secondary components are present at the surface of the formulations. The decrease in advancing γ^P and increase in receding γ^P when data from heat treated CR and CR10MMA samples are compared has shown that there is a larger

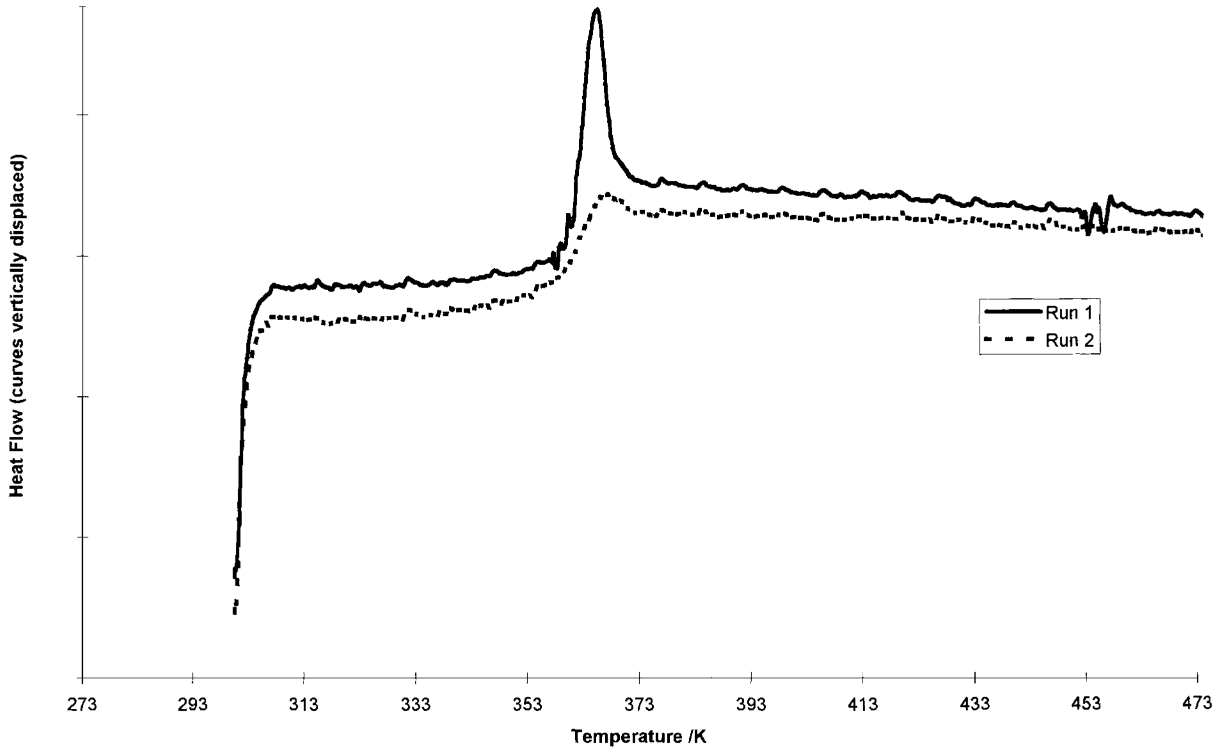

Fig. 7. DSC traces of CR specimen, showing physical ageing.

Table 2
Surface energy (polar component) data for CR and CR10MMA samples

Formulation	Cure conditions		Surface energy (polar component) (mJm^{-2})	Error
	Temperature (K)	Time (h)		
CR	293	48	Advancing: 2.565 Receding: 15.849	±2.052 ±5.471
CR	393	24	Advancing: 1.605 Receding: 20.552	±1.551 ±6.409
CR10MMA	293	48	Advancing: 4.252 Receding: 13.654	±3.330 ±4.815
CR10MMA	393	24	Advancing: 1.151 Receding: 26.769	±0.943 ±8.790

amount of polar functionality at the surface of CR10MMA which can be explained by the presence of PMMA. These data are shown in Table 2. Other methacrylate bearing formulations have shown the same trend.

4. Conclusions

It was found that DMTA and MDSC could be used to identify useful secondary components for self-validating adhesive formulations. Material that was

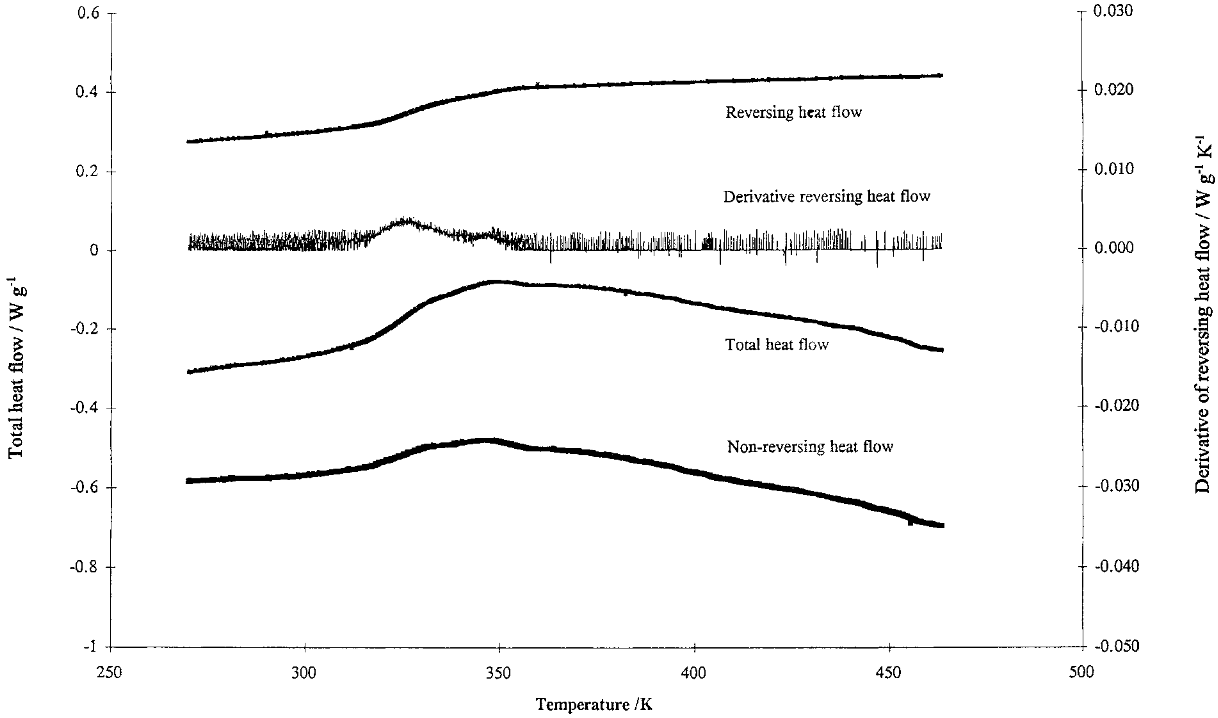

Fig. 8. MDSC traces of CR10MMA specimen after 4 h heating at 373 K and 24 h at 323 K.

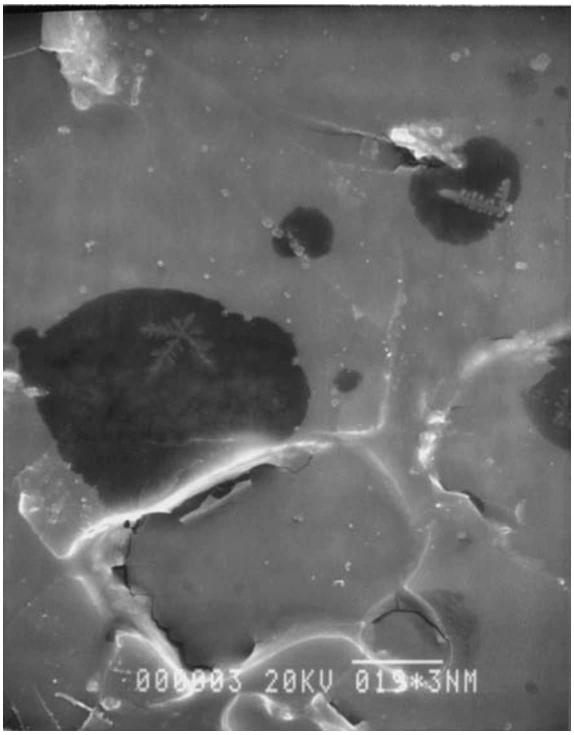

Fig. 9. SEM micrograph of CR10MMA before heat treatment.

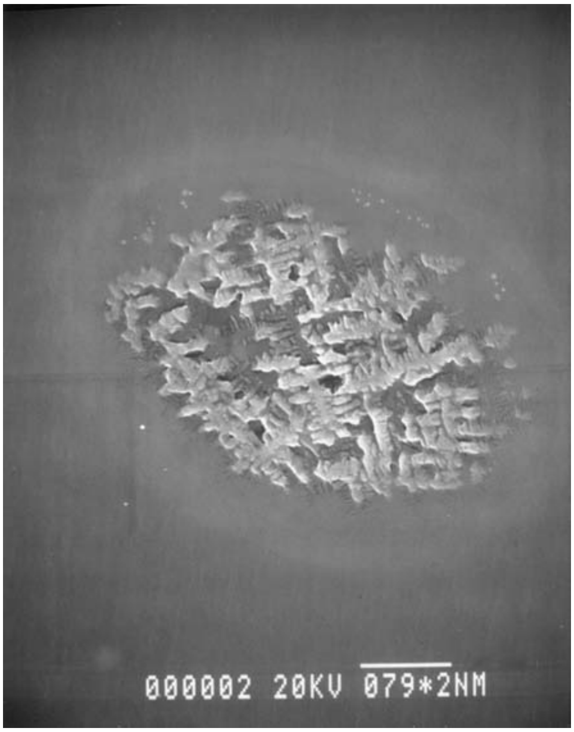

Fig. 10. SEM micrograph of CR10MMA after 4 h heating at 373 K.

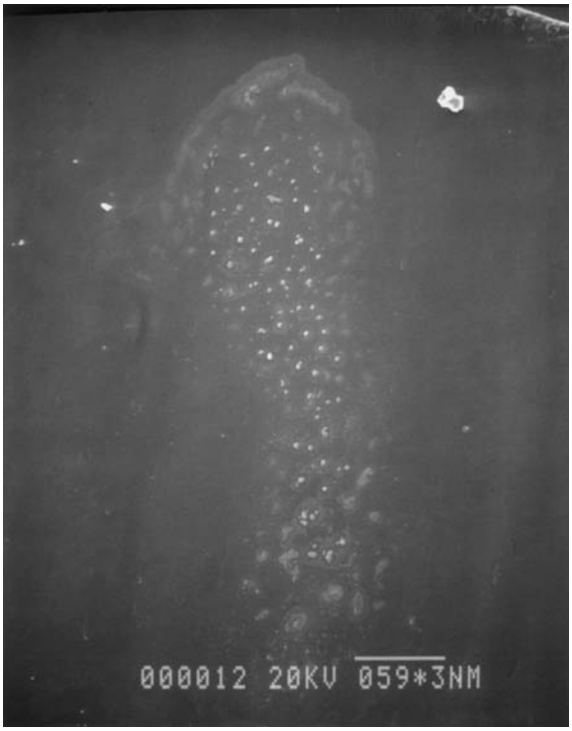

Fig. 11. SEM micrograph of CR10EHMA after 4 h heating at 373 K.

Fig. 12. SEM micrograph of CR10EHMA after 4 h heating at 373 K; detail of Fig. 11.

unable to form a solid phase within the epoxy matrix would not fulfill the criteria for the self-validating adhesive system.

Acknowledgements

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