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THERMAL BEHAVIOUR OF SILVER-FILLED EPOXY ADHESIVES
Technological implications in microelectronics

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Abstract

One-component silver-filled epoxy adhesives electrically conductive with low extractable ionic content have been used in microelectronics for attach applications. For the specific application described here there was evidence showing that adhesive polymerisation was not complete with negative consequences for the electronic devices. The present study aimed at understanding the causes of such disadvantages and setting up the best conditions to make the epoxy adhesive perfectly suitable for the required applications.

The work was carried out mainly by means of differential scanning calorimetry (DSC) and with the help the dynamic mechanical thermal analysis (DMTA) technique. The study succeeded in determining that the technological problems were due to incomplete polymerisation that caused solvent and monomer retention. These residues produced a leakage of the insulating properties of some capacitors present in the devices jeopardising the sensor working. Moreover, the study also showed that it was possible to avoid these difficulties adjusting the polymerisation temperature to 130°C and respecting curing time of 3 h: with these new curing conditions excellent results were achieved.

Keywords: curing, DSC, DMTA, epoxy adhesives, polymerisation, T_g

Introduction

The application of epoxy adhesives in industry is very wide and many formulations have been developed in order to solve particular technological problems [1–2]. One of the most critical aspects associated with these polymers concerns the curing mechanisms that are responsible for the transformation from low molecular mass monomers into a polymeric network [3]. The curing process determines the mechanical and physicochemical properties that make epoxy resins excellent adhesives for many purposes [4]. In order to understand these curing mechanisms DSC calorimetry and

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DMTA analysis have been extensively used both in the isothermal and non-isothermal mode to evaluate important parameters, such as extent and rate of chemical conversion, glass transition temperature T_g, etc. [2, 5–10]. This last parameter, T_g, is particularly important for determining the thermomechanical properties, but also to ascertain the degree of conversion monomer → polymer in the range above 95%, where it revealed itself much more sensitive than DSC [2]. For technological applications one of the most desired requirement is to maximise T_g in the shortest time in order to avoid any adverse effects associated with the insufficient epoxy polymer performance [2].

Normally these epoxy systems present excellent insulation properties [1, 2, 4], but some formulations have also been developed to produce conductive adhesives for ‘die attach’ applications where very low extractable ionics are required. These epoxy adhesives are one component, silver filled (up to 70 mass/mass), microelectronic grade, offering good bond strength and good thermal stability allowing the usage of the adhesives in die attach and component of electronic devices bonding. In particular, some of these compounds have been recently selected to link up electronic devices – polycells – in the manufacture of a γ-rays sensor called ISGRI that will be placed in Integral satellite of the European Space Agency (ESA). During the preliminary operations of the build up of some electronic parts constituting the sensor several technological problems have arisen concerning the performances of the microelectronics. More specifically, after the thermal annealing at 110°C that was performed to the devices to stabilise their performances, a strong leakage of the insulating properties of the capacitors present in the polycells in proximity of the adhesive junctions jeopardised the operation of the device [11]. Curing of the adhesive used for such an application (150°C for 1 h) has been selected with no scientific investigation, but only in analogy with other applications of similar adhesives.

The aim of the present study was to understand the causes of such disadvantages and to set up the best curing conditions to make the epoxy adhesive perfectly suitable for the required applications. Therefore, in that stage we were not interested in determining the kinetic mechanism of the polymerisation, this could be the subject of a next study.

The work was carried out by means of DSC calorimetry and DMTA technique. DSC calorimetry was performed both in isothermal and dynamic modes to check the thermal effects associated with polymerisation, enthalpy changes, and the degree of polymerisation as a function of the curing conditions (temperature and time). DMTA measurements were made to control the performance of the polymerised epoxy adhesive, above all in relationship to the glass transition temperature T_g.

Experimental

One-component silver-filled microelectronic grade epoxy adhesive Amicon C990J® was supplied from Emerson & Cuming S.P., United Kingdom; the content of silver powder (mass/mass) was in the range 69–73%. This adhesive was used as received and stored at –18°C.

DSC curves were carried out by means of a Perkin Elmer (PE) DSC 7 power compensation differential scanning calorimeter equipped with PE pc Pyris 3.52 software. The measurements were performed both in isothermal and dynamic mode with a dry nitrogen flow of 16 cm^3 min^{-1}. The scanning rate β was 4 or 8°C min^{-1} depending on the sample type. The calibration of the apparatus was made through the melting of biphenyl and tin and then tested with NH_4NO_3 125°C transition and the melting of indium [12]. Before each DSC measurement Amicon C990J® adhesive was allowed to reach room temperature and was vigorously stirred to homogenise it in order to avoid silver particle settling. A certain amount of the adhesive was weighed (ca 10 mg) in the standard aluminium sample pan. The pans were also weighed immediately after the end of the measurement to calculate possible mass changes in percent with respect to the initial mass.

DMTA measurements were made by means of a Perkin Elmer 7e instrument. The procedure to prepare the samples for DMTA measurements was the following. After the adhesive reached the room temperature, it was vigorously stirred and small amounts of it were poured into a teflon mould with cylindrical cavities to obtain pellets (6 mm diameter, 6 mm height). Each teflon mould was able to produce three pellets; the bottom of every mould was created by applying an adhesive kapton film. Then the curing was performed in a forced-air oven according to the selected time and temperature. It was possible to directly control the temperature of the adhesive during curing plunging a K-type thermocouple in one of the cylindrical cavity through a small lateral hole in the mould. At the end of the curing samples of the

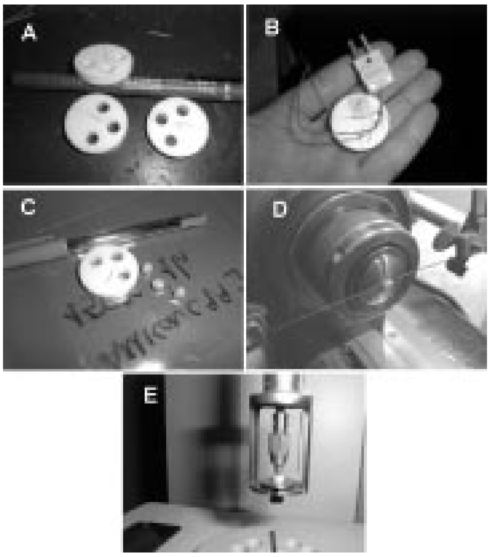

Fig. 1 Steps of the procedure to prepare the samples for DTMA measurements. A – teflon made moulds; B – adhesive in the mould with the K-type thermocouple wire coming out from one of the holes; C – pellets of the cured adhesive after de-moulding; D – view of the saw cutting a thin slice of the cured adhesive from the pellet; E – slice of the cured adhesive under the DTMA probe

cured adhesive were easily removed from their teflon mould. The DMTA scan at 5°C min^{-1} was run in ultra pure helium flow on a thin slice of the cured adhesive that had been cut away from a pellet by means of a saw: in this way, it was possible to increase the number of DMTA scans on a single pellet to check the reproducibility of the data. Figure 1 schematically reports the steps of this procedure. DMTA measurements in the compression mode were carried out under the following experimental conditions: static stress 4.150 mN, dynamic stress 3.458 mN, dynamic stress frequency 1 Hz. For the DMTA run, a slice of the cured adhesive was placed under a 0.9 mm diameter penetration probe, performing a scanning of the temperature with simultaneous measurement of the storage modulus E' and the tanδ parameter. We recall that due to the very small size of our samples the absolute values of the storage modulus E' were not reliable; therefore, we focused our attention on the differences of this parameter. Some DMTA measurements were also made directly on samples coming from the DSC runs (isothermal or non-isothermal) after removing the aluminium pan and cover.

Results and discussion

The DMTA curve shown in Fig. 2 refers to a sample of the epoxy adhesive Amicon C990J® cured at 150°C for 1 h. The behaviour of the tanδ and the storage modulus E' as a function of temperature inferred a glass transition temperature T_g of ca 53°C. This low value of T_g could be considered a possible source of the undesired effects caused by the epoxy adhesive in the microelectronics devices as discussed in the previous section. Moreover, a poor polymerisation degree as a result of curing at 150°C for 1 h would have produced this low T_g-value. In fact, for a good polymerisation degree, in relationship to the technological applications of the adhesive, T_g should be at least 100°C [13]. Figure 2 also shows an interesting E' peak located at around 230°C:

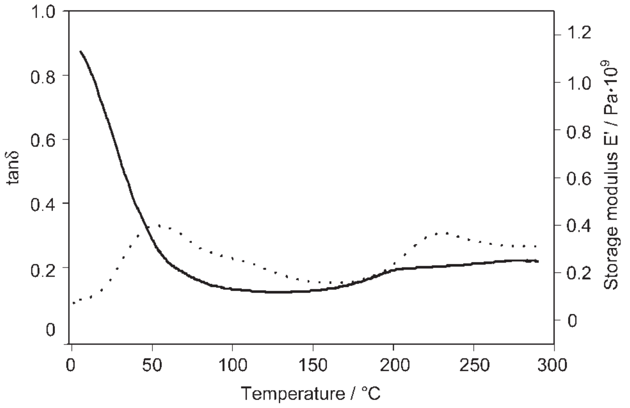

Fig. 2 DMTA curve of the silver-filled epoxy adhesive Amicon C990J® cured at 150°C for 1 h. Scan speed: 5°C min^{-1}. Full line: behaviour of the tanδ parameter; dotted line: trend of the storage modulus E'

this second peak is probably due to the prosecution of the polymerisation associated with the heating ramp during the DMTA measurement. It was also interesting to notice that an incomplete polymerisation is associated with partial retention of volatile products in the adhesive that can migrate and diffuse in the microelectronics devices after the hardening of the adhesive. This diffusion can be particularly enhanced during the thermal annealing to which the electronic devices must be subjected during the production cycle.

In order to investigate the polymerisation mechanism of this one-component epoxy adhesive, we carried out DSC measurements in the isotherm mode at 130°C for 5 h. Figure 3 shows the DSC curve obtained using these last curing conditions. The polymerisation occurred in two steps, as deduced from the two exothermic peaks that appear in Fig. 3. The first quite sharp started ca. 5 min after beginning the curing at 130°C and lasted about 30 min. This first peak is very similar for both shape and time duration to the results found by other authors [2, 4]. The enthalpy change evaluated from the area of the first peak was $\Delta H = -64 \pm 2$ J g^{-1}. Taking into account that our sample contained ca. 70% by mass of Ag, that was inert in relationship to the polymerisation, we calculated ΔH per gram of epoxy polymer and the result was -237 ± 7 J g^{-1}. This value is very close the enthalpy change for other epoxy systems [2, 4, 14]. The second peak was broader and much less enhanced (magnification in Fig. 3) and started ca. 1 h after beginning the curing lasting a very variable time from 40 min up to 1.5 h. This high variability of the second peak duration was probably due both to the mass of the sample in the DSC pan (the duration is proportional to the mass to be polymerised), and to the fact that the second stage of the polymerisation occurred in a heterogeneous solid matrix that can hinder either the polymerisation re-

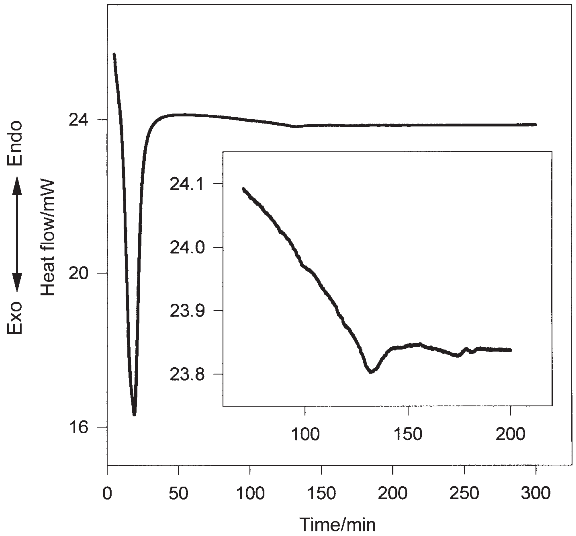

Fig. 3 Isotherm DSC curve of the silver-filled epoxy adhesive Amicon C990J® at 130°C; in the inset magnification of the second exothermic peak

action, or the escape of low molecular mass – volatile – compounds associated with it. The enthalpy change for this small exothermic peak evaluated in the same way as above gave a value of $\Delta H = -2.0 \pm 0.4$ J g^{-1}. The presence of multiple exothermic peaks in these polymerisation reactions involving epoxy monomers has been already recognised [4, 14–16]. In particular, the satellite peaks with respect to the main transition can be before and/or after the main transition: we never observed the shoulder before the main transition attributed to adduct formation steps [4, 14–16], but always a small peak after the main transition well separated from this. We checked also the mass decrease due to the partial loss of some volatile products that accompanies the polymerisation. For this sample cured at 130°C for 5 h the mass difference (mass before curing minus mass after curing) in percent with respect of the initial mass sample was 8.70±0.05%.

The polymerisation was also followed in the dynamic mode (scan speed of 4°C min^{-1}) instead of the isotherm mode and both enthalpy change ($\Delta H = -64 \pm 2$ J g^{-1}) and mass decrease (8.68±0.05%) perfectly matched the corresponding values found in the isotherm mode. Figure 4 shows a part (the region 100–200°C) of this DSC curve performed in the dynamic mode from which it was possible to observe also in this case a mechanism in two stages (155 and 160°C) as illustrated by two peaks (that at higher temperature detectable as a shoulder of the main peak) in the DSC curve. While the isotherm mode allowed to separate the two steps well, the dynamic mode did not permit to resolve the two peaks and, therefore, they appeared superimposed. The comparison of this result with the scanning curves obtained by Ooi *et al.* [4] for another epoxy system, showed that our polymerisation peak temperatures were above those of these authors [4] and this was in agreement with the isothermal results (our curing temperature of 130 *vs*. 80°C [4]).

DSC curves in the scan speed mode (4 and 8°C min^{-1}) from room temperature up to 250°C (data not reported) were carried out on these samples cured at 130°C for 5 h

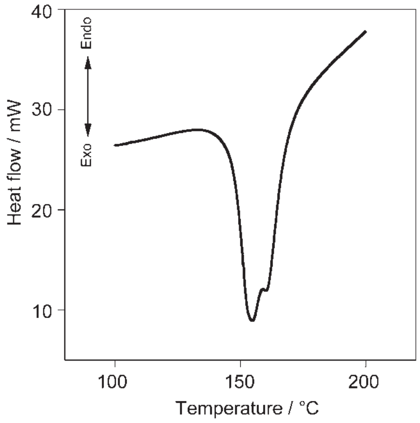

Fig. 4 Dynamic DSC curve of the silver-filled epoxy adhesive Amicon C990J® performed from 25 to 200°C at 4°C min^{-1}: portion of the DSC curve from 100 to 200°C

and no exothermic peaks associated with polymerisation were detected, indicating that this curing gave a 100% polymerisation degree. Even the mass decrease as above defined was practically zero, supporting a complete polymerisation. In fact, we recall that a good polymerisation of the adhesive should produce a material where the volatile content must be almost zero. Indeed, to confirm the complete curing both FTIR spectra and measure of the insoluble fraction of the cured polymer–gel percentage – could be carried out, but for the aims of the present study it was sufficient to adopt the thermal and mass loss criteria, as above described. This result was not in agreement with that found by Ooi *et al.* [4], who has already found some residue ΔH associated with incomplete polymerisation: the reason for this discrepancy could probably be attributed either to our higher time of curing in the isothermal mode, or to the lower amount of the polymer (our 10 mg contained only ca 30% of material to be polymerised). The DMTA curve performed on the sample cured at 130°C for 5 h confirmed that the polymer obtained with this curing had thermomechanical properties (T_g=147°C, DMTA curve in Fig. 5) suitable for its application as adhesive in microelectronics devices.

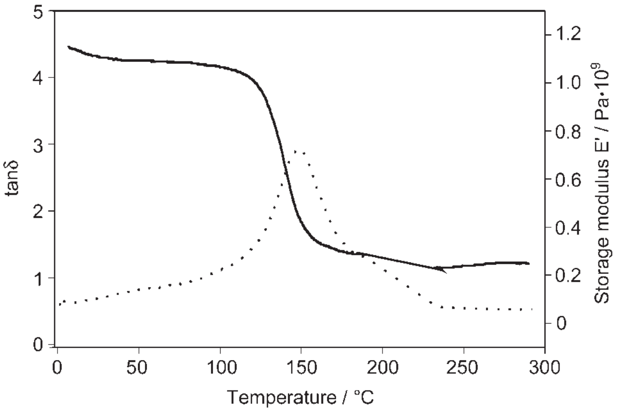

Fig. 5 DMTA curve of the silver-filled epoxy adhesive Amicon C990J® cured at 130°C for 5 h. Scan speed: 5°C min^{-1}. Full line: behaviour of the tanδ parameter; dotted line: trend of the storage modulus V

Then we tried to reduce the curing time from 5 to 3 and 2.5 h respectively, since the best conditions, as requested by the technological requirements for microelectronics use, would have had to be *'complete polymerisation in the shortest time'* [2]. Indeed, we could take into account also the possibility to change the curing from isothermal conditions to programmed heating ramps (either linear or not) [17], but we preferred to consider isothermal curing due to application reasons. Curing 3 h at 130°C produced a DSC curve similar to that observed in Fig. 2 (Fig. 6, top). The same result was also obtained with curing conditions of 130°C for 2.5 h (Fig. 6, bottom). The shape of the two curves in Fig. 6 presented the same features of the other curing curve reported in Fig. 3 and the calculated ΔH associated with the first peak was -62 ± 2 J g^{-1} for 3 h and -61 ± 2 J g^{-1} for 2.5 h, according to the previous results. The

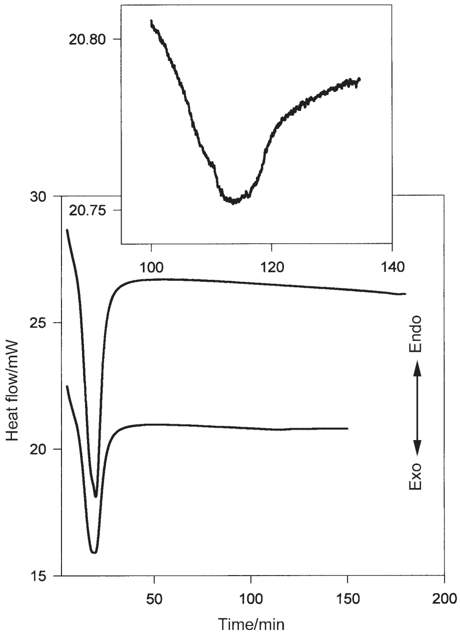

Fig. 6 Isotherm DSC curves of the silver-filled epoxy adhesive Amicon C990J® at 130°C. Top: total time (curing time) 3 h; bottom: total time 2.5 h. In the inset magnification of the second exothermic peak of the bottom curve

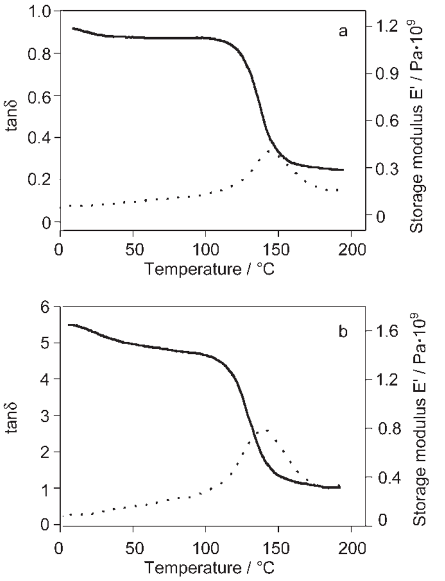

Fig. 7 DMTA curves of the silver-filled epoxy adhesive Amicon C990J® cured at 130°C for 3 h (a) and 2.5 h (b). Scan speed: 5°C min^{-1}. Full line: behaviour of the tanδ parameter; dotted line: trend of the storage modulus *E′*

second broad peak was incomplete for 3 h sample while it was complete and well resolved for the 2.5 h specimen (the magnification in the inset of Fig. 6). The mass in percent with respect of the initial sample was 8.65±0.04% for 3 h and 8.50±0.04% for 2.5 h. This last value was slightly less than the previous values, supporting a not perfectly completed polymerisation with partial retention of volatile products in the case of curing time of 2.5 h, according to a shorter curing time. Concerning the gravimetric behaviour of the samples during curing a detailed study by TG could be interesting in order to understand the curing mechanism better. DMTA curves reported in Fig. 7 confirmed that the polymer obtained with 3 h curing at 130°C was well polymerised (T_g=144°C in Fig. 7, top), whereas the sample cured 2.5 h had a sensibly lower glass transition temperature (T_g=138°C in Fig. 7, bottom). This result was in agreement with the slight retention of volatile products deduced from the above mentioned mass changes.

According to DSC results, DMTA data, and the mass change measurements we were able to establish that the best curing conditions respecting the ‘shortest time’ rule, the fair polymerisation, and the high T_g value were 130°C for 3 h. With these new curing conditions preliminary tests on the microelectronics devices were carried out using the same adhesive Amicon C990J® and neither further inconvenience nor disadvantage were detected [11].

Conclusions

The present study aimed to study by DSC calorimetry and DMTA analysis the best curing conditions for the silver-filled one component epoxy adhesive called Amicon C990J® in order to overcome some disadvantages arising during the use of such adhesive as sealing paste in building up microelectronics devices. Both DSC and DMTA measurements showed that the curing conditions suggested for standard applications (150°C 1 h) gave origin to poor polymerisation degree with low T_g values and retention of volatile products. We attributed the bad technological performances of the epoxy adhesive in microelectronics to this poor polymerisation degree due to the inappropriate curing conditions. In particular, volatile products present in the not well polymerised adhesive would have contaminated some parts – capacitors near the polycells – of the electronic devices during the thermal annealing at 110°C jeopardising the electronics working.

DSC measurements performed in both isotherm and dynamic modes indicated that the best coupling curing temperature and time was 130°C and >3 h. In these conditions polymerisation was practically complete without any retention of volatile products. DMTA data established that the polymer obtained with this curing presented T_g values above 140°C confirming the formation of a high performance polymer.

The adoption of these curing conditions enabled to build up the microelectronics devices for the manufacture of the γ-rays sensor called ISGRI that will be placed in Integral satellite of the European Space Agency (ESA).

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References

1 Feldman and A. Barbalata, Synthetic Polymers: Technology, Properties and Applications, Chapman–Hall, New York 1996.
2 Y. C. Boey and W. Qiang, Polymer, 41 (2000) 2081.
3 W. R. Ashcroft, Chemistry and Technology of Epoxy Resins, Chapman–Hall, New York 1993.
4 S. K. Ooi, W. D. Cook, G. P. Simon and C. H. Such, Polymer, 41 (2000) 3639.
5 M. J. Richardson, Pure Appl. Chem., 64 (1992) 1789.
6 M. J. Richardson, in Calorimetry and Thermal Analysis of Polymers, V. B. V. Mathot Ed., Hanser, New York 1993, p. 91.
7 B. G. Min and Z. H. Stachurski, Polymer, 34 (1993) 4488.
8 E. M. Woo and J. C. Sefferis, J. Appl. Polym. Sci., 40 (1990) 1237.
9 P. V. Tiagarajan, P. V. Reddy, S. Sridhar and M. C. Ratra, J. Thermal Anal., 36 (1990) 277.
10 C. Montserrat, C. Flaqué, P. Pagés and J. Màlek, Thermochim. Acta, 269–270 (1995) 213.
11 F. Guasti, unpublished results.
12 W. W. Wendlandt, Thermal Methods of Analysis, 2nd Ed., John Wiley & Sons, New York 1974.
13 N. A. Allsop, M. R. Bowditch, N. F. C. Glass, A. E. Harris and P. M. O'Gara, Thermochim. Acta, 315 (1998) 67.
14 J. Vogt, J. Adhesion, 22 (1987) 139.
15 M. S. Heise and G. C. Martin, J. Appl. Polym. Sci., 39 (1990) 721.
16 M. S. Heise and G. C. Martin, Macromolecules, 22 (1989) 99.
17 J. K. Gillham and J. B. Enns, Trends Polym. Sci., 2 (1994) 406 and references therein.