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Humidity effects on adhesion strength between solder ball and epoxy underfills

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The curing behaviour and the development of physical properties of three commercial, silica filled epoxy/anhydride resins that are used in solder 'flip-chip' technology were investigated by differential scanning calorimetry, dynamic mechanical analysis (d.m.a.) and Fourier transform infra-red (*FT*i.r.) spectroscopy. In particular it was found that if the uncured resins were aged in the presence of moisture at 23°C and then cured, the resulting properties such as glass transition temperature and rubbery modulus were significantly lower than the ultimate properties which developed if the resins were stored in the absence of water and then reacted. Also, under elevated temperatures and in the presence of high humidities or steam the hydrolysis of fully cured resins which had been previously stored in a dry state was detected by *FT*i.r. and d.m.a. measurements. The adhesion strength between solder balls and these epoxy underfill materials was found to deteriorate when aged under humid conditions. © 1997 Elsevier Science Ltd.

(Keywords: epoxy underfill; adhesion strength; humidity)

INTRODUCTION

Solder 'flip-chip' technology is increasingly viewed as an attractive alternative for packaging/interconnection of integrated circuits in a broad range of microelectronic applications. The flip-chip solder interconnection is typically packaged with the underfill method. However, during temperature cycling the mismatch in thermal expansion between the silicon chip and the substrate material will result in mechanical fatigue of the solder joint, leading to early failure of the interconnection. In order to prevent this failure mode, a highly filled, low viscosity liquid epoxy resin is usually used to underfill the gap between the chip and the substrate. This epoxy underfill material mechanically couples the chip and the substrate and decreases the stress in the solder joints, thereby enhancing solder fatigue life. Many successful applications of underfill have been reported[1,2].

Good adhesion between the epoxy underfill material and the surface of the solder ball, silicon chip and substrate is necessary to minimize stress in a package. Use of this non-hermetic packing method does raise a potential concern, i.e. moisture induced interfacial delamination. The effect of moisture on epoxy moulding compounds has been an important issue in microelectronic packagings[3,4]. Typical epoxy underfill materials are hardened with anhydrides, which are very hygroscopic. The absorbed water can change the chemistry of epoxy underfills before or after curing, and the thermal and mechanical properties of cured epoxy underfills. In this study, the humidity effects on the adhesion strength between solder ball and epoxy underfill were investigated after exposing to moisture, and degradation mechanisms were also examined.

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EXPERIMENTAL

Materials

Three commercial epoxy underfill materials for flip-chip devices were tested, which were Hysol FP4510 and Hysol FP4511, manufactured by Dexter Corporation, and Shin-Etsu X-43-5235. Solder balls measuring 790 μm in diameter and manufactured by Aim Product, Inc. (Smithfield, RI) were used. The composition was 43% of tin, 43% of lead and 14% of bismuth. Prior work has shown that Hysol FP4511 had the best flow properties of these resins[5]. Thus, we focused on its behaviour in the remainder of this paper.

Adhesion test of solder and epoxy underfill interface

To measure the adhesion strength between solder ball and epoxy underfill materials, the underfill resins were spin-coated or doctor bladed on a glass slide measuring $75 \times 50 \times 1$ mm in size, and then solder balls were placed on the film. Under the effect of gravity the solder ball penetrated into the cast film so that the lower part of the ball penetrated the film. The epoxy resins were then cured at 150°C for 4 h. The thickness of epoxy underfill materials obtained by spin-coating at 5000 rev min^{-1} for 1 min ranged from 17.6 to 28.8 μm, which is about 1/30 of the height of the solder ball. Since Shin-Etsu X-43-5235 was too viscous, doctor blade coating was used to

obtain a thinner layer. The portion of the solder ball, just above the epoxy coating, was sheared in the direction parallel to the coated and cured film, and the force required to separate the solder ball from the epoxy underfill material was recorded using a bond tester manufactured by Keller Technology Corp.

Temperature–humidity (TH) test

The samples were placed in a chamber maintained at 85°C and 85% relative humidity (85°C/85% RH) for various lengths of time. They were then removed from the humidity chamber and were sheared within 30 min under ambient conditions.

Steam bomb test

The tensile test specimens, dynamic mechanical analysis (d.m.a.) specimens and Fourier transform infra-red (*FT* i.r.) samples cured at 150°C for 2 h were placed in a 120°C steam bomb for 24–120 h. The pressure of the steam bomb was 2 atm.

Thermal analysis

Values for the glass transition temperature (T_g), the onset temperature (temperature where reaction begins) and reaction exotherm were measured using power compensated differential scanning calorimetry (d.s.c.; Perkin-Elmer DSC-7)[6]. All d.s.c. scans were performed at a heating rate of 15 or 20°C min^{-1}. The T_g was measured from dynamically cured samples in a d.s.c. pan. To study the change of T_g in the 85°C/85% RH chamber, the samples were cured in a d.s.c. pan at 175°C in an oven for 60 min under a nitrogen atmosphere, and then placed in the 85°C/85% RH chamber after drilling off the caps of the d.s.c. pans. The T_g of samples cured at 150°C for 2 h was also measured after placing the specimens in the 120°C steam bomb for 24–96 h.

Linear thermal expansion measurements were carried out between −50 and 250°C on a Perkin-Elmer Thermo-mechanical Analyzer (TMA-7) for the samples cured at 150°C for 2 h.

Storage modulus and tangent δ were measured between −50 and 250°C at a heating and a cooling rate of 1°C min^{-1} using a Perkin-Elmer Dynamic Mechanical Analyzer (DMA-7) for the samples cured at 150°C for 2 h. The dimensions of the samples were 1 × 3 × 15 mm.

Mechanical properties of epoxy underfill material

Dog bone shape tensile test specimens (*Figure 1*) were placed in a 120°C steam bomb for 24–96 h. Tensile strength and Young's modulus were measured using an Instron after removing the samples from the steam bomb. The cross-head speed was 0.2 mm min^{-1} and the pneumatic grip was used.

FT *i.r. spectroscopy*

Hysol FP4511 was spin-coated on a ZnSe crystal at a rate of 5000 rev min^{-1}. The effects of water on the anhydride cured Hysol FP4511 were examined by *FT* i.r. (Nicolet Instrument Corp.) after placing the sample in the steam bomb for various lengths of time. The effects of water in the *FT* i.r. chamber were eliminated by subtracting the *FT* i.r. spectrum of a blank sample.

RESULTS AND DISCUSSION

A sample of uncured Hysol FP4511, which was stored in a syringe at −70°C, was warmed under a blanket of nitrogen (0% RH) to room temperature and then injected into a preweighed aluminium d.s.c. pan. After reweighing the sample and pan the container was hermetically sealed. The dry, unreacted epoxy was cooled to −70°C in the d.s.c. pan and then scanned at 15°C min^{-1} from −70 to 280°C. In *Figure 2*, the primary output of the d.s.c. instrument is scaled along the ordinate in heat flow units (W g^{-1}) which are proportional to the sample's specific heat (C_p). In this figure an endothermic response occurs upwards along the *y* axis and, conversely, exothermic events are plotted in the opposite direction. During the initial scan (solid line, *Figure 2*) an endothermic step increase in specific heat (ΔC_p) occurs between −49 and −43°C, which is associated with the glass transition temperature of the uncured Hysol FP4511. The mid-point (1/2 ΔC_p) of this glass transition (T_g) occurs at −45°C with the magnitude of the increase in C_p (ΔC_p) equal to 0.16 J g^{-1}°C^{-1}. The onset of the exothermic curing process begins near 60°C and reaches a maximum at 175°C. Termination of this curing process can be found by scanning the dynamically cured sample again and locating the temperature where the liquid C_ps of first and second scans match. In this instance it is near 250°C and amount of heat liberated (ΔH_{rxn}) by the epoxy during its first scan equals 107 J g^{-1}. Pyrolysis of Hysol FP4511 at 700°C in oxygen vaporized

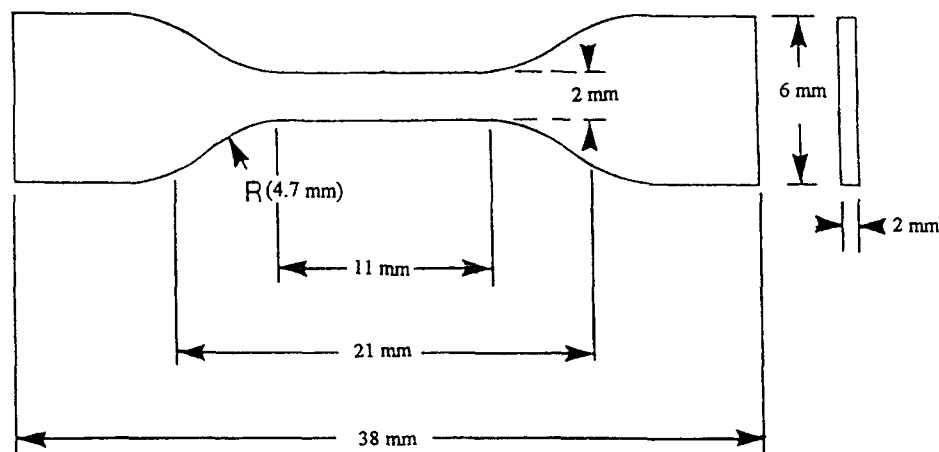

Figure 1 Geometry of tensile test specimen

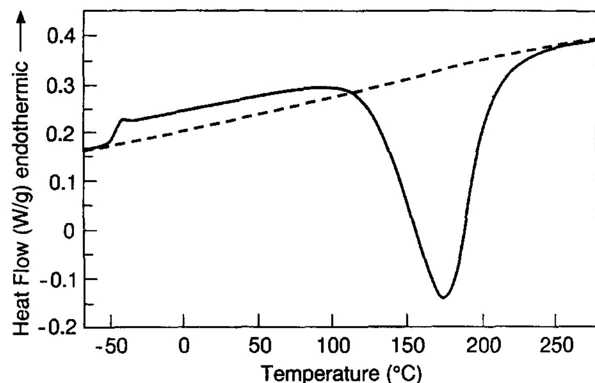

Figure 2 D.s.c. curves for Hysol FP4511: — first scan of uncured Hysol FP4511; --- second scan of cured Hysol FP4511

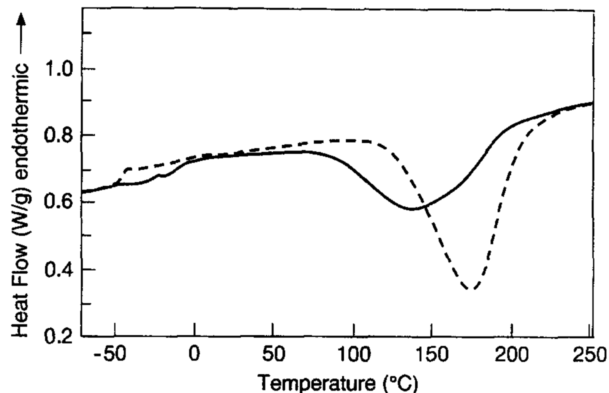

Figure 4 D.s.c. curves for uncured Hysol FP4511: — stored at 75% RH and 23°C at 2h; --- stored at 0% RH and 23°C for 20h

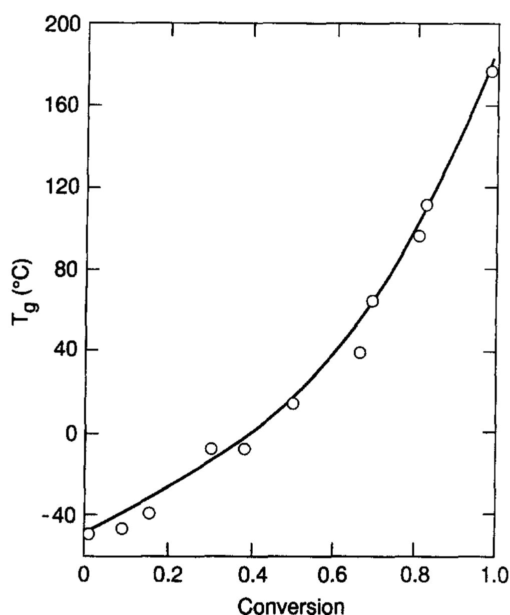

Figure 3 T_g as a function of extent of reaction for Hysol FP4511

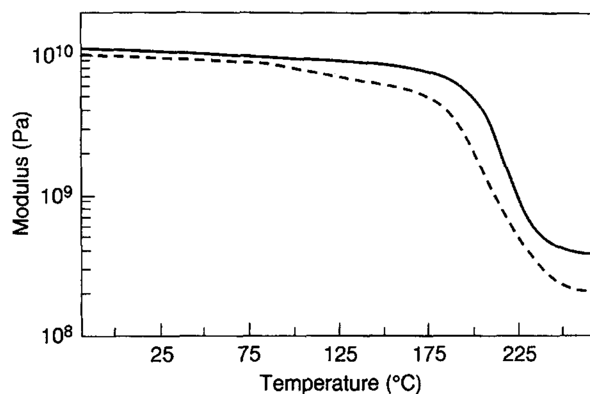

Figure 5 D.m.a. curves for cured Hysol FP4511: — stored at 0% RH and 23°C for 20h; --- stored at 78% RH and 23°C for 20h

30 wt% of the sample and left about a 70 wt% inorganic residue of silica.

The re-run of the cured Hysol FP4511 (broken line, *Figure 2*) shows the onset of T_g near 162°C and the end of this glass transition at 187°C with T_g at 176°C and ΔC_p equal to $0.063\,J\,g^{-1}{}^{\circ}C^{-1}$. Residual heats of cure of partially cured Hysol FP4511 were used to find the extent of reaction, and independent runs established the corresponding T_gs for these samples[7]. In *Figure 3*, the T_g is plotted against conversion for the epoxy/anhydride system cured in the dry state. Hysol FP4510 has similar curing behaviour and filler content as Hysol FP4511; however, the latter compound has silica particles smaller than those of Hysol FP4510, which should allow the epoxy with the smaller silica particles to have improved flow behaviour over the other Hysol resin.

Typically, these epoxy/anhydride products are stored in refrigerated syringes. However, if the syringes are allowed to warm in ambient conditions it is possible for moisture to sweep into the material via an imperfect syringe seal. Thus, we decided to check for the effect of moisture on the epoxy's curing behaviour.

A sample of uncured Hysol FP4511 was stored at 75% RH and 23°C for 20h and then placed in the d.s.c. instrument and scanned from −70 to 235°C at 15°C min^{-1} (solid line, *Figure 4*). The T_g occurred at −13 or 30°C higher than for a sample of Hysol FP4511 aged 20h at 23°C and 0% RH (broken line, *Figure 4*). In addition ΔH_{rxn} was $63\,J\,g^{-1}$ and the maximum was found at 141°C for the sample aged at 23°C and 75% RH as compared to values of $102\,J\,g^{-1}$ and 175°C for epoxy stored for 20h in a dry atmosphere. In addition, the storage modulus behaviour of these two samples is depicted in *Figure 5*. These data show that moduli of the sample aged for 20h at 23°C in 0% RH (solid line, *Figure 5*) is near 1.1×10^{10} Pa at 20°C and falls to 4×10^{8} Pa at 270°C, whereas Hysol FP4511 aged three days at 23°C and 78% RH (broken line, *Figure 5*) and then cured and dried has a storage modulus of about 1.0×10^{10} Pa at 20°C and 2×10^{8} Pa at 270°C. This 50% reduction in modulus at 270°C of the Hysol FP4511 aged at 78% RH as compared to the material stored and cured in a dry state indicates that the crosslink density of the former material is substantially lower than that of material which was kept dry and then cured. In addition, when Hysol FP4511 was aged wet and then cured its T_g was about 25°C lower than the T_g of the sample aged dry and then cured. In the *FT*i.r. study, anhydride peaks (1783 and $1857\,cm^{-1}$) disappeared and an acid peak ($1705\,cm^{-1}$) was formed with a sample of Hysol FP4511 aged for 20h at 23°C in 78% RH. These results and *FT*i.r. spectroscopy data indicate that the anhydride hardener absorbs and reacts with water to yield an acid which apparently alters its interaction with the epoxy to

Table 1 Thermal properties of epoxy underfill materials

Material designation	T_g (°C)	Extrapolated onset temperature (°C)	Peak exotherm ($J g^{-1}$)	CTE ($10^{-6} cm cm^{-1} °C^{-1}$)
Hysol FP4510	172	119	−111	21
Hysol FP4511	164	136	−108	23
Shin-Etsu X-43-5235	93	155	−103	27

Table 2 Adhesion strength between solder ball and epoxy underfill materials

Underfill materials	Underfill thickness (μm)	Interface area (cm^2)	Shear force (g)	Adhesion strength ($kg cm^{-2}$)
Hysol FP4510	23.9 ± 1.5	0.00275	479 ± 59	174 ± 21
Hysol FP4511	17.6 ± 2.8	0.00244	682 ± 56	280 ± 23
Shin-Etsu X-43-5235	28.8 ± 2.2	0.00463	792 ± 246	171 ± 53

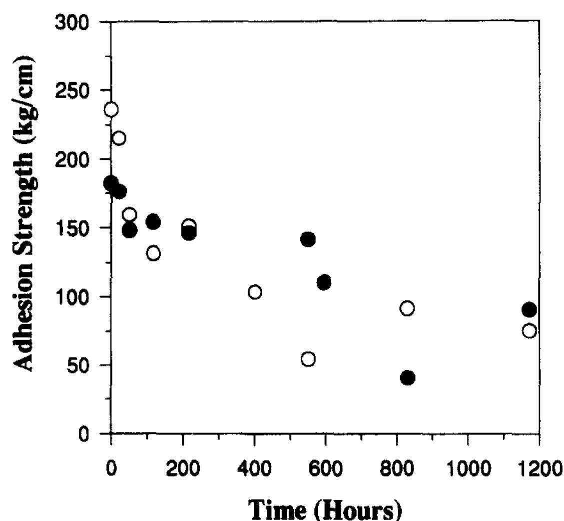

Figure 6 Decrease in adhesion strength between solder ball and epoxy underfills in 85°C/85% RH test. Epoxy underfills were cured at 150°C for 4 h: (○) Hysol FP4511; (●) Shin-Etsu X-43-5235

Figure 7 Scanning electron microscopy of the cross section of solder ball/Hysol FP4511 joint after exposure in 85°C/85% RH for 500 h (magnification ×1500)

yield a material with a lower crosslink density and T_g than when water is absent from this epoxy/anhydride system. Obviously it is important to keep these epoxy/anhydride resins dry during storage and cure in order that the materials can develop their ultimate properties. In the remainder of these studies, all materials were stored and cured in the absence of moisture.

The values of the T_g, the onset temperature and reaction exotherm obtained by the d.s.c. measurements are listed in *Table 1*. Included in *Table 1* are also the coefficient of expansion (CTE) data obtained using a thermomechanical analyser. From the data, it is evident that Shin-Etsu X-43-5235 has the lowest T_g, even though it exhibits the highest extrapolated onset temperature.

In *Table 2*, values of adhesion strength between solder ball and epoxy underfill materials calculated from the measured values of shear forces necessary to separate the solder ball from the cast epoxy film are listed. From the data, it is evident that Hysol FP4511 had the largest adhesion strength among the samples included in this study. The standard deviation of adhesion strength of Shin-Etsu X-43-5235 was large, probably due to the non-uniform thickness of epoxy film obtained by doctor blade coating. The surface of the solder ball is rendered rather rough during the curing operation. However, the debonded surface appears to be quite smooth. A closer examination of the debonded surface revealed that the locus of failure was either at the exact interface between the epoxy resin and the solder ball or in the epoxy resin layer near the interface.

In *Figure 6*, the values of adhesion strength are shown as a function of the time the samples have been aged at 85°C/85% RH for Hysol FP4511 and Shin-Etsu X-43-5235 formulations. In both cases, the adhesion strength decreased with increasing time of exposure to the humid environment. This is not surprising, since it is well known that the adhesion between polymers and other substrates is weakened when aged in the humid environments[8,9]. *Figure 7* shows the scanning electron micrograph of the cross-section of the solder ball and Hysol FP4511 joint placed in 85°C/85% RH for 500 h. The cracks in Hysol

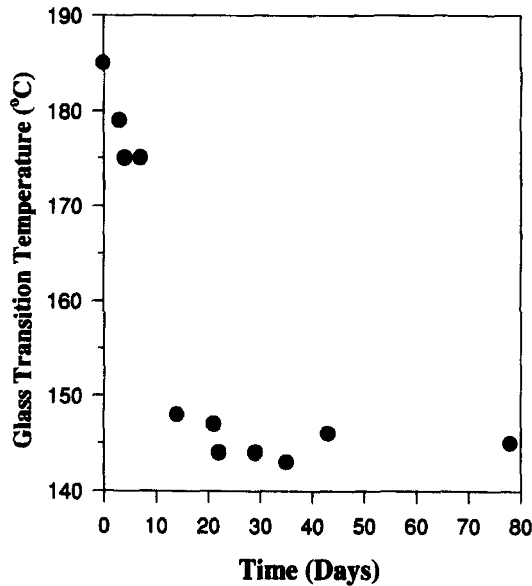

Figure 8 Decrease in T_g of cured Hysol FP4511 in 85°C/85% RH test. Hysol FP4511 in a d.s.c. pan was cured at 175°C for 60 min in an oven under nitrogen atmosphere

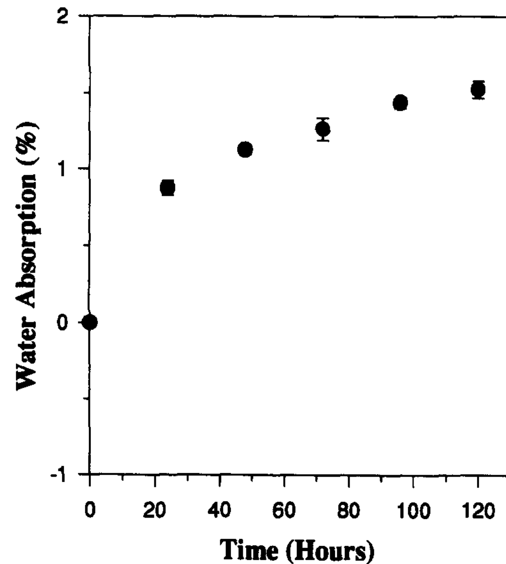

Figure 10 Water absorption of cured FP4511 at 150°C for 2 h in a steam bomb (120°C, 2 atm)

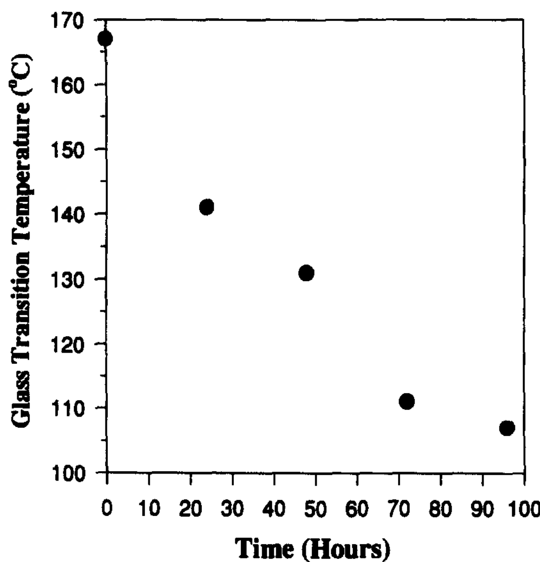

Figure 9 Decrease in T_g of cured Hysol FP4511 in a steam bomb (120°C, 2 atm). Hysol FP4511 in a d.s.c. pan was cured at 150°C for 2 h

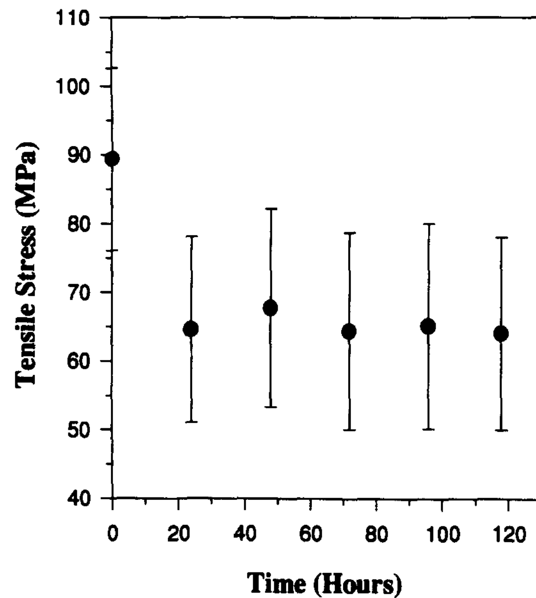

Figure 11 Decrease in tensile strength of Hysol FP4511 cured at 150°C for 2 h in a steam bomb (120°C, 2 atm)

FP4511 appear very close to the interface between the solder ball and the cured epoxy and indicates cohesive failure in the epoxy underfill. It implies that the humid environment could degrade the epoxy underfill and weaken the epoxy underfill layer. Even though the initial adhesion strength of Shin-Etsu X-43-5235 is lower than that of Hysol FP4511, the rate at which the adhesion strength decreases with exposure to the high humidity conditions is slower.

Figure 8 shows the decrease in T_g of cured Hysol FP4511 in 85°C/85% RH. Higher initial T_g (186°C) than that measured for dynamically cured samples in a d.s.c. pan (164°C) was observed, since the sample in the d.s.c. pan was cured at 175°C for 60 min in an oven under a nitrogen atmosphere. The decrease in T_g was very fast at the beginning and then was stabilized around 145°C after two weeks of ageing, which coincides with the decrease of adhesion strength in the 85°C/85% RH experiment. A greater decrease in T_g was observed in samples that were exposed to the steam bomb environment (120°C, 2 atm) (*Figure 9*). The T_g decreased to 107°C after 96 h in the steam bomb. The amount of water absorbed by Hysol FP4511 increased with increasing time in the steam bomb (*Figure 10*). Water absorption of Hysol FP4511 reached saturation at 1.5 wt% after 120 h in the steam bomb. It appears that the greater decrease of T_g in the steam bomb comes from more absorbed water as well as more permanent damage due to more severe conditions.

The tensile strength of Hysol FP4511 was decreased by placing the resin in a steam bomb, as shown in *Figure 11*. The tensile strength dropped to around 65 MPa from about 90 MPa after ageing in the steam bomb for 24 h, and then stayed at the same strength of about 70% of that of unaged sample even after ageing for 96 h. When the aged samples in the steam bomb were dried in a

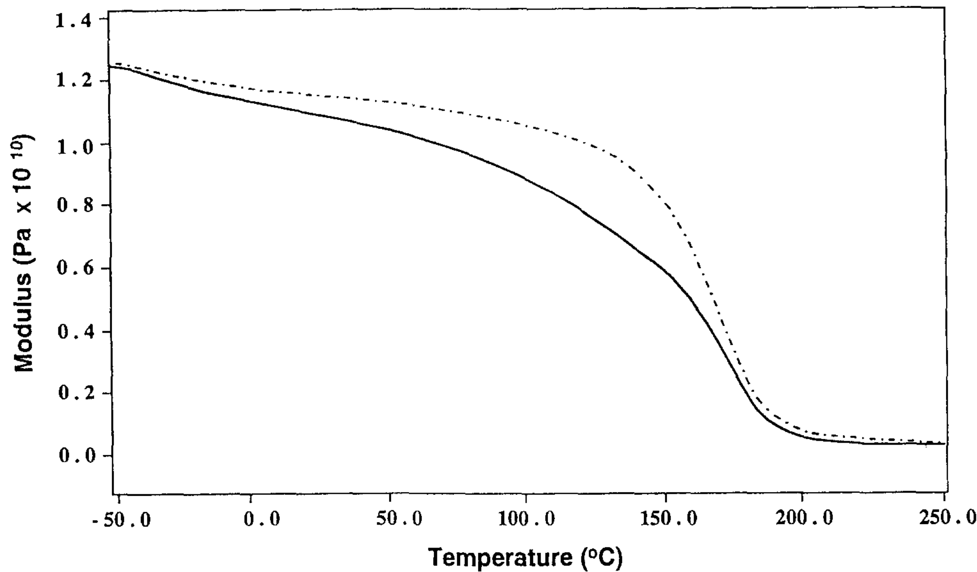

Figure 12 D.m.a. curves for Hysol FP4511 cured at 150°C for 2 h and aged in a steam bomb (120°C, 2 atm) for 24 h with heating and cooling rates of 1.0°C min: — heating; - - - cooling

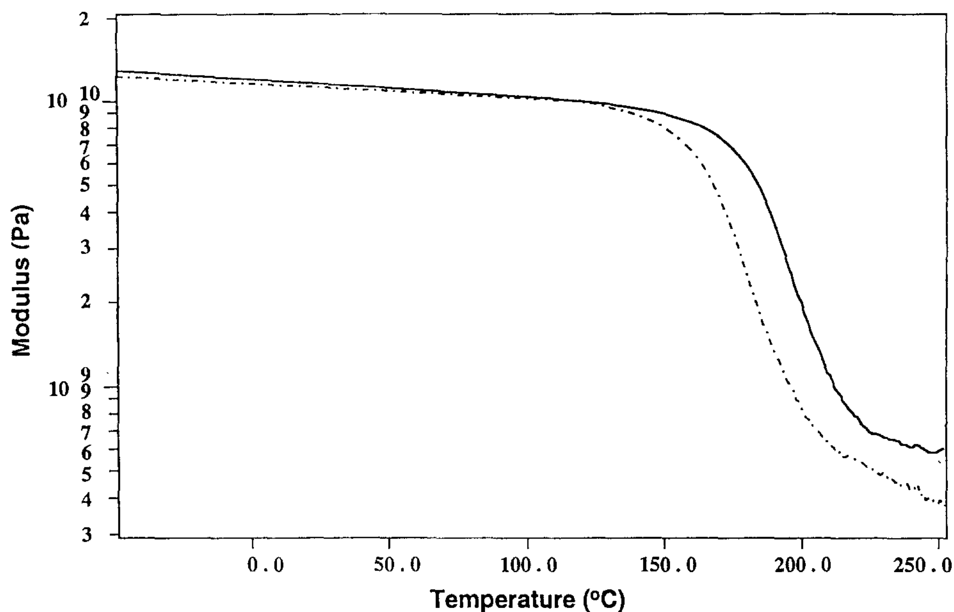

Figure 13 D.m.a. cooling curves for Hysol FP4511 cured at 150°C for 2 h with a cooling rate of 1.0°C min^{-1}: — not aged; - - - aged in steam bomb (120°C, 2 atm) for 24 h

120°C vacuum oven at 2.6 mmHg, the tensile strength did not recover at all although most of the absorbed water had evaporated, i.e. the absorbed water content decreased from 1.5 to 0.25 wt%. This irreversible phenomenon indicates that the absorbed water hydrolysed the structure of the epoxy underfill.

Figure 12 shows a d.m.a. diagram for 24 h in a steam bomb. Solid and dotted lines were obtained by heating and cooling, respectively, between −50 and 250°C at a rate of 1°C min^{-1}. Since the heating and cooling rate were low, the absorbed water evaporated during the process of heating up to 250°C and cooling down to 200°C. Therefore, a higher modulus was obtained with the cooling process than that with the heating process. The difference in these two d.m.a. curves comes from the plasticization of epoxy underfill with the absorbed water. After drying the d.m.a. samples in a 120°C vacuum oven for 24 h, the heating curve moved closely towards the cooling curve, which confirms that the absorbed water acts as a plasticizer to reduce the modulus.

In *Figure 13*, solid and dotted lines show storage modulus curves for FP4511 unaged and aged for 24 h at 120°C and 2 atm of steam and then cooled from 250 to −50°C. The rapid increase in modulus which accompanies cooling begins above 200°C for the unaged sample (solid line, *Figure 13*) and begins about 12°C lower for the specimen from the steam bomb (broken line, *Figure 13*). This behaviour indicates that the steam bomb sample's T_g is some 20°C below the epoxy sample's T_g. In addition, the rubbery modulus plateau of the sample aged in steam is only half of the value found for the unaged sample. Note that the lowering of T_g does not

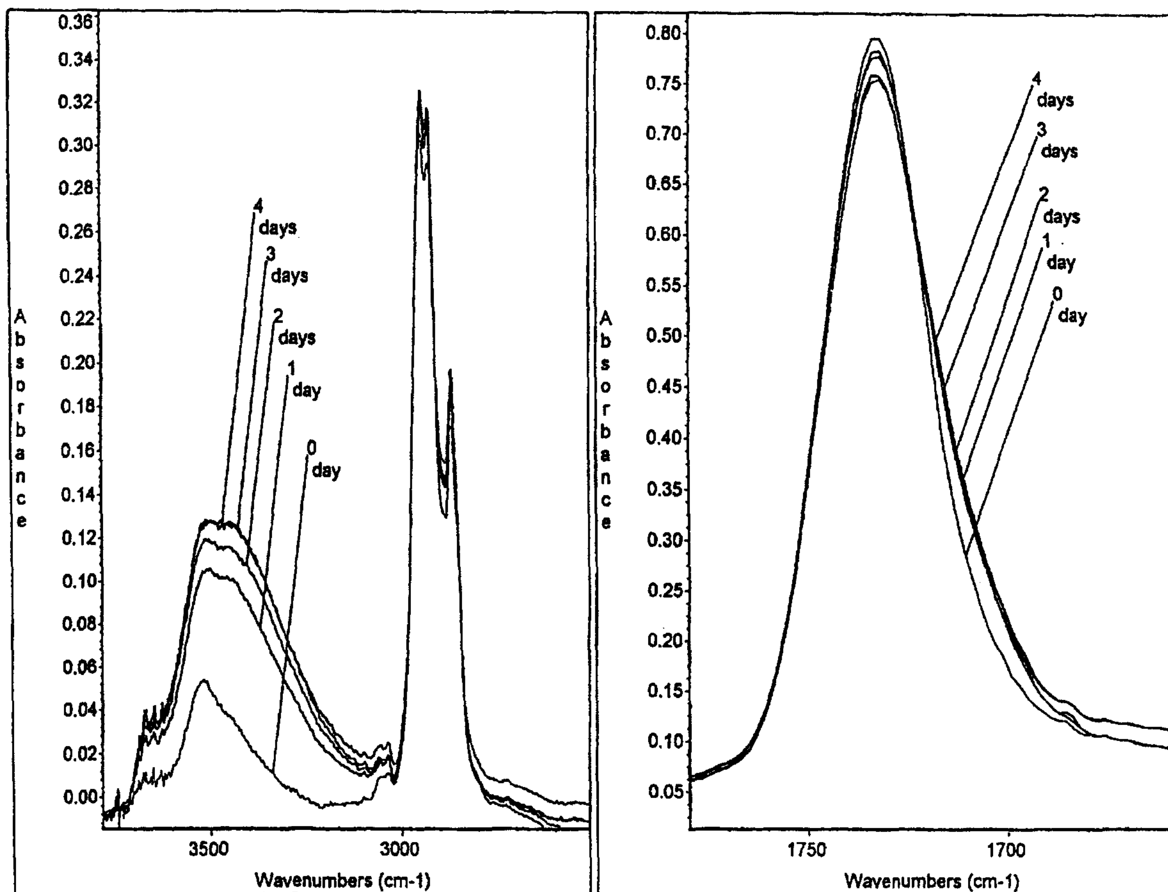

Figure 14 *FT*i.r. spectra of Hysol FP4511 cured at 150°C for 2 h and aged in a steam bomb (120°C, 2 atm) for various times

originate from plasticization of the epoxy resin by water since all the absorbed water was removed from the steam treated sample during heating to 250°C. After aging to 96 h under steam bomb conditions the T_g was lowered further to 107°C (*Figure 9*), indicating more hydrolysis occurred in this anhydride cured epoxy resin.

Evidence for the hydrolysis of the cured FP4511 is shown in the *FT*i.r. spectra of the steam bomb aged samples as compared with those of the unaged epoxy (*Figure 14*). An increase in the hydroxyl group at 3500 cm^{-1} and in the carboxylic acid at 1705 cm^{-1}, and a corresponding drop in the ester peak at 1735 cm^{-1} with increased ageing of the underfill epoxy in the steam bomb supports our contention that the material is undergoing chemical hydrolysis in the steam bomb. As shown in *Figure 14* the hydrolysis reaction was fastest in the first 24 h of ageing, slowed afterwards and stabilized after 72 h. This chemical degradation of the epoxy is accompanied by a decrease in adhesive strength and glass temperatures at 85°C and 85% RH, and a drop in tensile strength in the samples aged in the steam bomb.

CONCLUSIONS

Thermal mechanical measurements revealed that if the uncured epoxy/anhydride is stored in a humid environment and then cured, its ultimate properties will be significantly lower than those associated with the resin stored and cured without water present. The adhesion strength of the epoxy resin stored and cured in the dry state with solder balls embedded in this underfill material decreased with increasing time at 85°C and 85% RH. Initially, the adhesive strength between the underfill epoxy and solder balls decreased rapidly and then stabilized after two weeks of ageing at 85°C/85% RH. The T_g of the epoxy resin also decreased as the underfills' adhesive strength dropped at 85°C and 85% RH. The tensile strength of the epoxy underfill was lowered to about 70% of the original value after ageing for 24 h at 120°C and 2 atm of steam and then stabilized. Finally, the locus of failure was found in the epoxy underfill layer very close to the interface between the solder balls and epoxy.

Hydrolytic degradation of the epoxy underfill, which had been cured in the dry state but aged in steam at 120°C, was found in a *FT*i.r. study where hydroxyl and carboxyl groups increased and ester groups decreased with increased ageing in the steam environment. In addition, a reduction in the aged resin's crosslink density and glass temperature when stored under humid conditions supports the *FT*i.r. findings of chemical degradation. The combined thermal, mechanical and spectroscopic measurements indicate conclusively that the epoxy/anhydride underfill material can be hydrolytically degraded by water at 85°C and 85% RH as well as at 120°C in steam (2 atm).

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