

Thermal Aging of Laminate Materials and the Maximum Use Temperature of Organic Packages

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Abstract

The assessment of package reliability is often based on finite element models which typically use properties of materials that have undergone only a standard cure treatment which often amounts to exposure to elevated temperatures for a few hours. Today's applications however often require packaging materials to be exposed to use temperatures for thousands up to 100,000 power on hours (POH). Yet, the reliability of components for such applications is evaluated after exposure to use temperatures for only a few hundred to a few thousand hours. The change in material properties during prolonged exposure to power-on conditions is generally neglected. In this paper we discuss the changes in the mechanical behavior upon thermal aging of typical packaging materials such as solder masks and build up materials. We also describe methods that allow an assessment of the maximum continuing use temperature of packages containing such materials.

Key words: laminate materials, thermal stability, thermal aging, mechanical properties, long term reliability

Introduction

The power of models in predicting the reliability of an electronic package is limited by the quality of both the model and of the materials data that is being used in the model. Typically the materials data is obtained from manufacturers' data sheets. The state of the sample used to obtain this data, if it is described, is often closely related to the conditions the material will see during processing of a standard package. Thus the material properties are essentially the properties of the package at time zero.

This type of data might be sufficient to be used for reliability models of low power organic packages. However for high power applications in which the temperature in some parts of the package can exceed 100°C the properties measured after standard treatment and the properties after prolonged time at use temperature can be significantly different.

The first mention of significant temperature gradients in organic substrates was made by A. Hasan et al [1]. In this paper it was assumed that the substrate should not exceed a continuous use temperature of 120°C to allow a package lifetime of

60,000 POH. However it was not clear how this upper limit was arrived at. Thus we set out to establish test methods and criteria to measure the longevity of laminate material properties.

Experimental

Uncured materials for three different solder masks (referred to in this paper as SM-A, SM-B, and SM-C) and two different build up materials (referred to as BU-A and BU-B) were obtained from their manufacturers. Two of the solder masks were photoimageable and one (SM-B) was not. The build-up materials and solder mask SM-B were supplied as b-staged films which were laminated onto thin copper foil and cured according to the recommendations of the manufacturer. The build up materials were laminated on either one side or both sides with copper. The final film thicknesses (after removal of the copper) were $43 \pm 2 \mu\text{m}$ for BU-A, $41 \pm 2 \mu\text{m}$ for BU-B, and $35 \pm 2 \mu\text{m}$ for SM-B.

Solder masks SM-A and SM-C were supplied as multi-component liquids. These materials were prepared according to the

manufacturers recommendations and applied onto copper foil using doctor blading techniques. The films were cured according to the manufacturers' recommendations. The final film thicknesses (after removal of the copper) were $50 \pm 11 \mu\text{m}$ for SM-A, $49 \pm 10 \mu\text{m}$ for SM-C,

Films were subjected to additional thermal aging in air at temperatures from 75 to 200°C. Thermal aging treatments lasted from 1 to 1000 hours. After thermal treatments, the copper films were removed using FeCl_3/HCl based etching solutions.

The thermal stability of the films to decomposition was measured on a TA Instruments TGA Q500 thermo-gravimetric analyzer. The temperature was ramped from room temperature to at least 400°C at a rate of 10°C/min in a nitrogen atmosphere. The mechanical properties of freestanding films were measured using a TA Instruments DMA2980 dynamic mechanical analyzer. Single frequency temperature ramps at a rate of 3°C/min were used for measurements of modulus and tan delta, and controlled force measurements at a constant ambient temperature of 100°C were used for stress-strain evaluations.

UV – visible spectra were obtained on an Agilent Technologies ChemStation 8453. Samples were coated onto quartz discs and measured via transmission.

Results and Discussion

Solder Mask Materials

It is common practice in the electronic industry to characterize the thermal stability of an organic material by quoting the decomposition temperature which is the temperature at which a 5 % weight loss is recorded in a dynamic thermogravimetric analysis (TGA). While this number is rather easy to obtain, it is of very limited use. This is demonstrated by the two TGA plots of Figures 1 and 2 which show the weight loss behavior of a photo-sensitive solder mask material, SM-A.

In Figure 1 the behavior at a continuous heating rate of 10°C/min is shown. The onset of thermal degradation appears to be somewhat above 300°C which is interpreted as meaning that this material is thermally stable to that temperature. It is often assumed that processes below 300°C can be carried out without adverse impact to the material. This information, however, does not make any statement about the acceptable time of exposure at a given temperature below the degradation temperature or what happens when the material is exposed to an

oxygen containing environment at elevated temperatures.

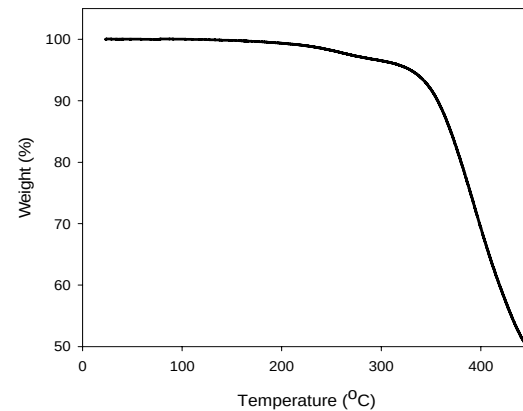


Figure 1. Thermogravimetric analysis of solder mask SM-A after standard cure.

A different picture emerges in Figure 2. Here a sample was kept at a set temperature in nitrogen for 2 hours before stepping up to the next temperature. This plot shows that measurable weight loss is observed at temperatures as low as 120°C, not far from the operating temperatures of many processor chips. Weight loss increases significantly when the solder mask is held at temperatures above 120°C.

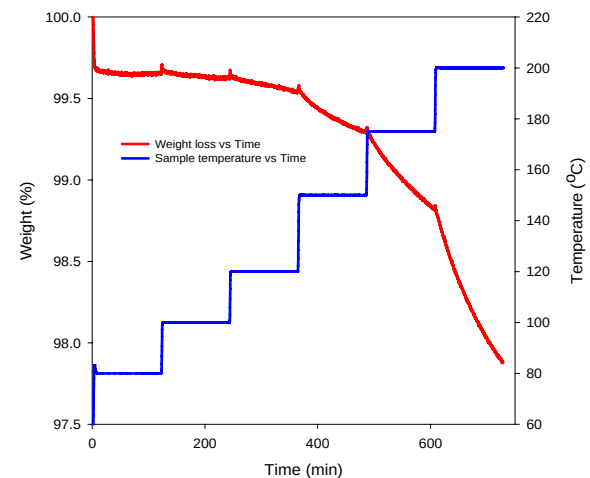


Figure 2. TGA analysis of SM-A with 2 hour isothermal soaks at 80, 100, 120, 150, 175, and 200 °C

Another sign that changes in the photo-mask material occur at relatively low temperatures was a darkening in color observed in test vehicles used to identify the limits of the power carrying capabilities of organic laminates. These color changes can be followed by UV-visible spectroscopy. Figure 3 shows the UV-vis spectrum of a fully cured

photosensitive solder mask and spectra taken after additional thermal aging at 200°C from 1 hour to over 12 hours. The spectra show a significant increase in absorbance over the range of 240-350 nm with thermal aging indicating a chemical change in the material after relatively short times at 200°C.

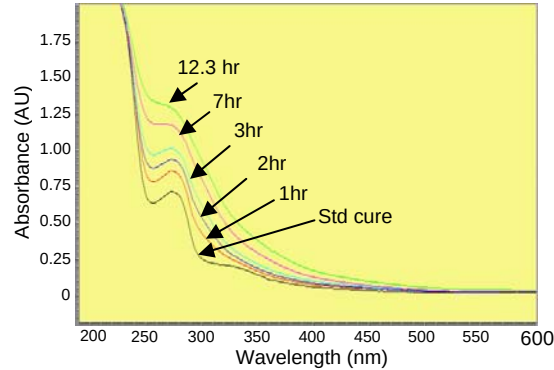


Figure 3. UV-visible spectra of SM-A after standard cure and additional aging at 200°C

This thermal aging experiment was repeated at 150°C and 100°C (Figure 4) which indicates that even at 100°C chemical changes slowly take place over time. The absorbance data of Figure 4 was converted to an Arrhenius plot (inset, Figure 4) which shows that the thermal aging reaction follows a simple Arrhenius relationship characterized by approximately a doubling of the reaction rate for every 10°C increase in temperature. This is rather typical for organic reactions.

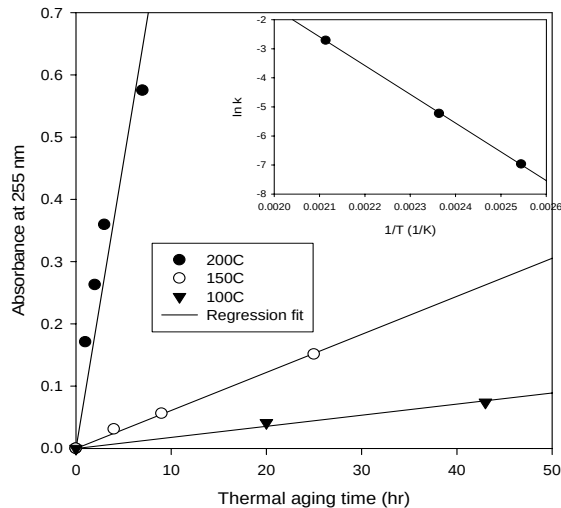


Figure 4. Plot of absorbance of SM-A films after thermal aging at 200°C, 150°C, and 100°C. Inset is Arrhenius plot of linear fits to absorbance data

To investigate if the observed visible and weight loss changes affect the mechanical properties, solder mask films were evaluated by dynamic-

mechanical analysis (DMA). Figure 5 demonstrates the changes in dynamic storage modulus and Figure 6 changes in tan delta obtained after thermal aging of the solder-mask at various temperatures and times.

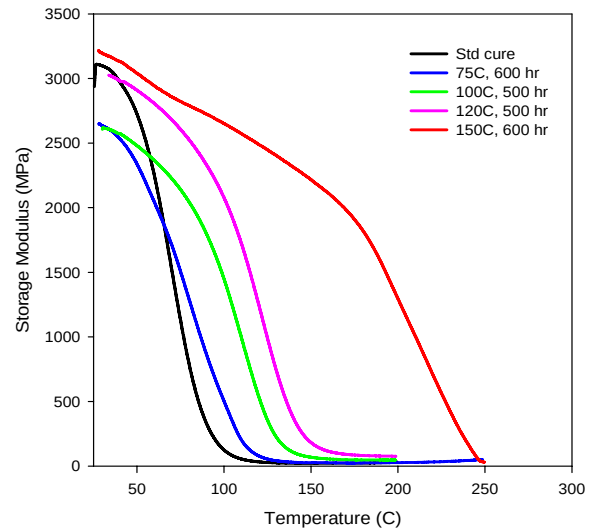


Figure 5. Storage modulus vs temperature of SM-A after thermal aging at various temperatures and times

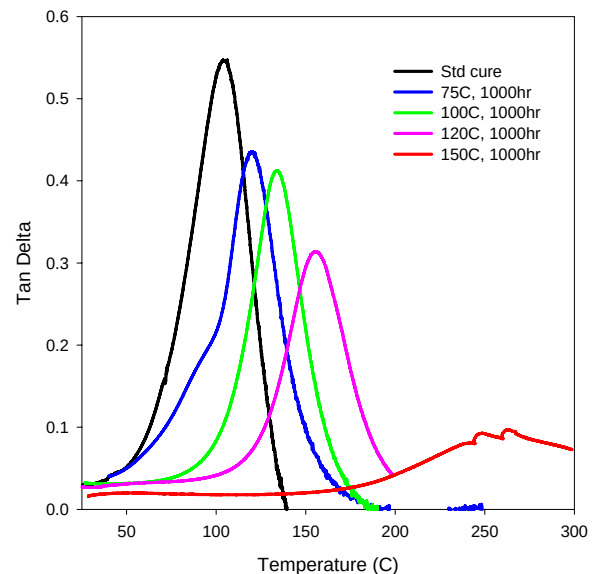


Figure 6. Tan delta vs temperature of SM-A after thermal aging at various temperatures for 1000 hr.

Significant changes are observed in both the storage modulus and tan delta. The tan delta peak is representative of the glass transition temperature (T_g) of the material [2,3]. After 1,000 hours at 150°C the peak was over 250°C – an increase of about 150°C compared to the standard cured sample. The modulus increased significantly with thermal aging as well. While some chemical changes might be expected at 150°C, both the modulus and tan delta

indicated that changes were occurring in the films after thermal treatments at temperatures as low as 75°C for relatively short times. The DMA data indicates that even after using standard curing protocol, the mechanical properties of this solder mask are likely to change with additional thermal aging, even at temperatures in the range of standard operating temperatures.

We applied the Arrhenius relationship obtained earlier to the shift in the tan delta peak and found that the reactions that leads to the tan delta shift and to the change in the UV-vis spectra follow similar reaction kinetics. This allows the use of the Arrhenius relationship to predict the mechanical property changes during thermal aging of this solder mask.

Not all solder masks tested had identical responses to thermal aging, however. We evaluated solder masks with and without photoinitiator compounds. Solder mask SM-C, which also contains a photoinitiator exhibited very similar initial mechanical properties as well as similar changes upon thermal aging to SM-A. The tan delta peak for SM-C increased by about 110°C after thermal aging at 150°C for 1000 hr, as opposed to the 150°C increase observed for SM-A.

A solder mask that is not photoactive - SM-B - however, exhibited significantly different performance, as is evident in Figures 7 and 8. Solder mask SM-B has much higher modulus and tan delta values after the initial standard cure. There are only

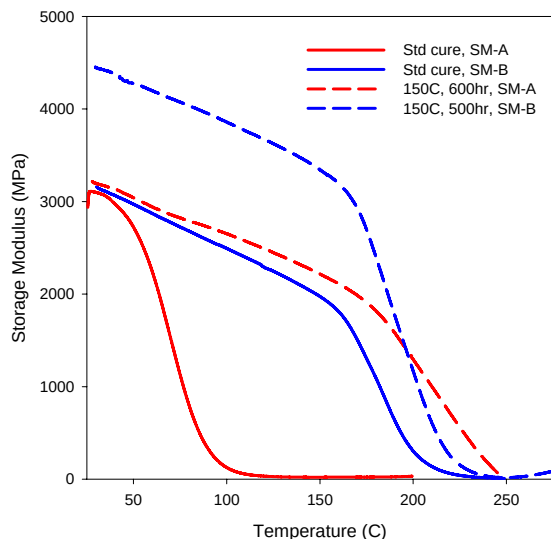


Figure 7. Storage modulus of SM-A and SM-B after standard cure and 1000 hr at 150°C

relatively small changes in these values after thermal aging – the tan delta peak, for example, only increased by a little over 20°C after 1000 hrs at 150°C. The mechanical properties after thermal aging

remained slightly below those for SM-A. The solder mask without a photoinitiator appears to be much more stable with regard to thermal aging than either of the photoimageable solder masks that we tested.

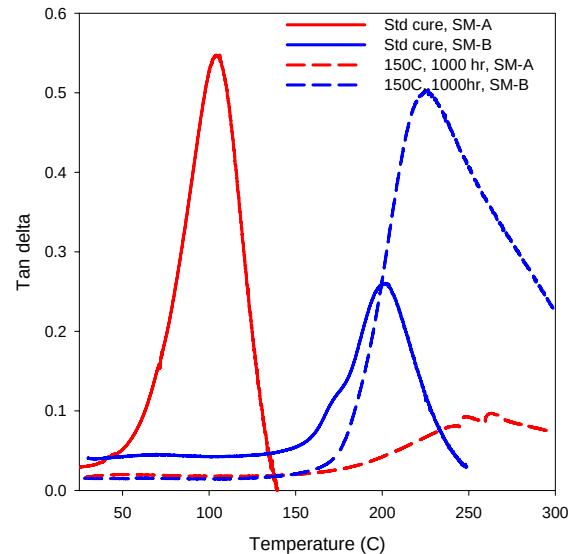


Figure 8. Tan delta of SM-A and SM-B after standard cure and 1000 hr at 150°C

The change in mechanical properties is also evident in stress – strain experiments (Figures 9 and 10) which show a dramatically reduced elongation at break. The solder masks were evaluated at an ambient temperature of 100°C, a possible operating

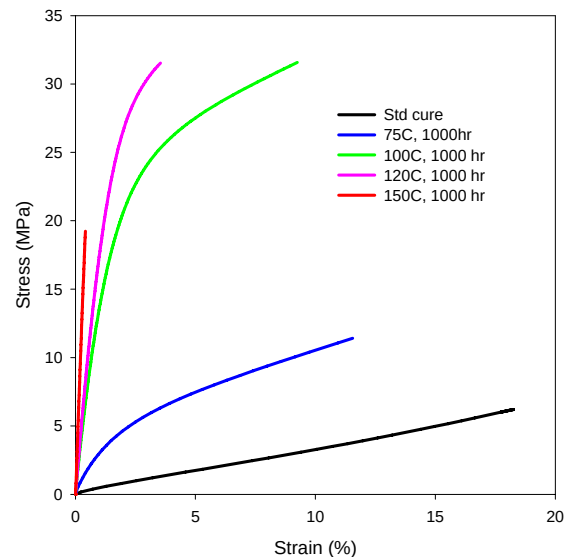


Figure 9. Stress-strain behavior of SM-A after standard cure and variable thermal aging. Measurements were taken at 100°C ambient.

temperature for organic packages. The elongation at break for SM-A decreased from about 18% for the standard cure to about 0.5% for samples thermally

aged at 150°C for 1000 hr, indicating a significant increase of the brittleness of the films. The change in Tg [2,3] with thermal aging is also apparent from the change in the stiffness of the films at 100°C. The tan delta peak for films with the standard cure is around 100°C, and it increases up to a maximum of 250°C after aging at 150°C.

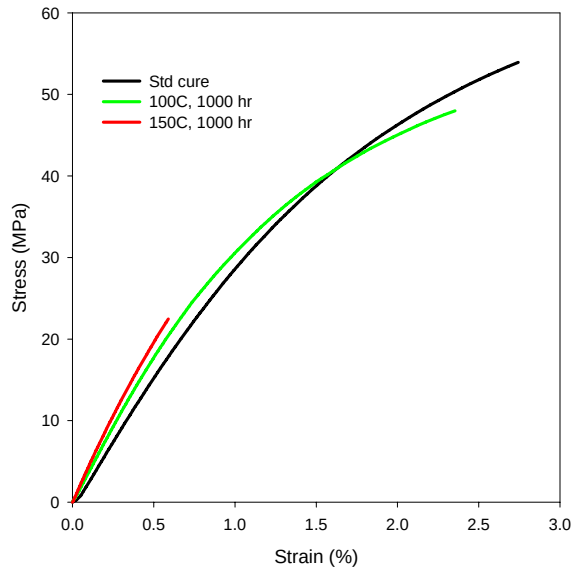


Figure 10. Stress-strain behavior of SM-B after standard cure and variable thermal aging. Measurements taken at 100°C ambient.

The performance of SM-B again showed less change as a result of thermal aging, especially at lower aging temperatures, but the strain at the break point still dropped from over 2.5% to about 0.5% after 1000 hr at 150C indicating that these films still become more brittle after aging at elevated temperatures.

Build-up Materials

Following the procedures outlined above several build-up materials were evaluated. Since build-up materials in a laminate can be coated by metal or the solder mask it is often not directly exposed to air. However, in some places, such as regions opened for surface contacts, oxygen might penetrate to the build-up material. Thus thermal aging was performed in air (with one side protected by a copper foil) and without air (both sides protected by copper foil).

To begin with, the optical appearance in thermally aged samples in the presence of air changes from whitish to brown, dark brown and finally black (similar to the solder mask), while in the absence of oxygen the color remains nearly unchanged. Similarly the shift in the tan delta peak in the

presence and absence of air shows a pronounced difference (Figures 11 and 12). In the presence of air the studied build-up materials still show a marked shift to higher temperatures in the tan delta peak (by roughly 50°C) but it is not as pronounced as in the solder masks after comparable aging conditions. In the absence of oxygen the variation in tan delta is much smaller, on the order of only 5 to 20°C, and the peak does not shift to higher temperatures.

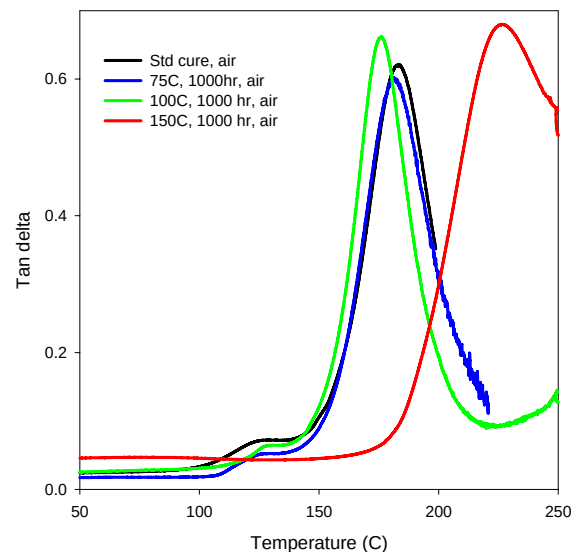


Figure 11. Tan delta of BU-A laminated with copper on one side, so film is exposed to air during curing and thermal aging.

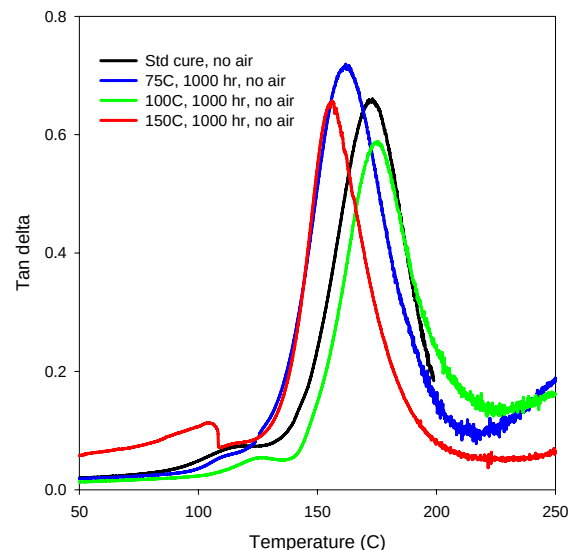


Figure 12. Tan delta of BU-A laminated with copper on both sides, eliminating exposure of film to air during curing and thermal aging.

The stress-strain data echoes the difference between samples exposed and un-exposed to oxygen

(Figure 13). There was an increase in the overall stress for a given elongation for samples that were exposed to air, indicating that there is some reaction with oxygen that affects the mechanical properties of the films. There is also an increase in brittleness reflected in the reduction in elongation at break upon thermal aging – for the samples exposed to air it is up to 80%. While the elongation at break of unexposed samples varies, there is no consistent trend with thermal aging.

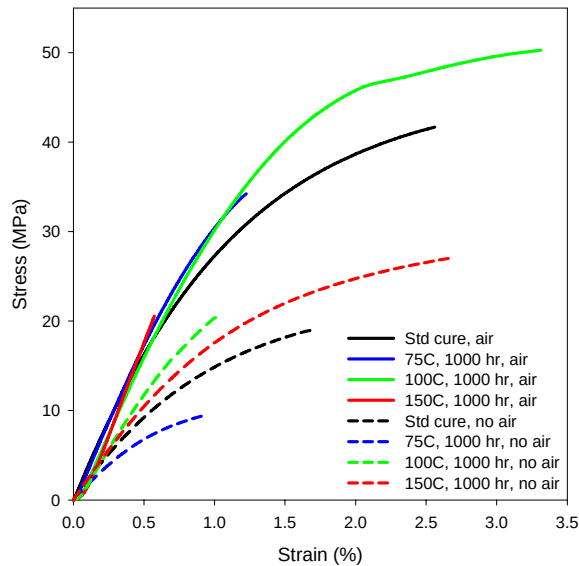


Figure 13. Stress-strain behavior of BU-A after thermal aging. Solid lines indicate samples laminated to copper on one side, dashed lines indicate both sides were laminated to copper.

Both of the build up materials tested exhibited very similar mechanical properties and response to exposure to air during thermal aging. BU-B had about a 10°C larger change in tan delta from a sample receiving a standard cure to one that was aged at 150°C for 1000 hr, but there were few other noticeable differences in their performance relative to thermal aging in the presence or absence of air.

Maximum Continuing Use Temperature

As we have shown, thermal aging at even moderate temperatures can change the material properties of today's laminate materials significantly. Since applications often require package reliability to 100,000 power on hours (POH) [4,5], the question arises what continuing maximum use temperature will guarantee such reliability.

To answer this question we define the maximum use temperature of a laminate as the maximum temperature at which a minimum required

residual reliability can be maintained for the thermally weakest material in the structurally highest stressed area over the expected package lifetime. This definition makes several assumptions. First it assumes that we know what the structurally highest stressed area is, what the weakest material, and what the minimum required residual properties are before package failure will occur. While we can obtain a fair knowledge of where the highest structural stress in a package will be through finite element modeling, and we have a fair idea what the weakest material is - the solder mask - we have much less information on what material property degradation could be tolerated before package failure is imminent.

There are several approaches to answering these questions. First we investigated failures in packages that had been exposed to elevated temperatures for long periods of time (e.g., 3,000 hours at 150°C). While that data is limited we did find that fails in the solder mask can indeed translate into fails of the package. Figure 14 shows the thermal degradation of the solder mask has led to adhesion loss which subsequently initiated a crack through the build-up material weakened by thermal aging. This crack caused an open in a copper line.

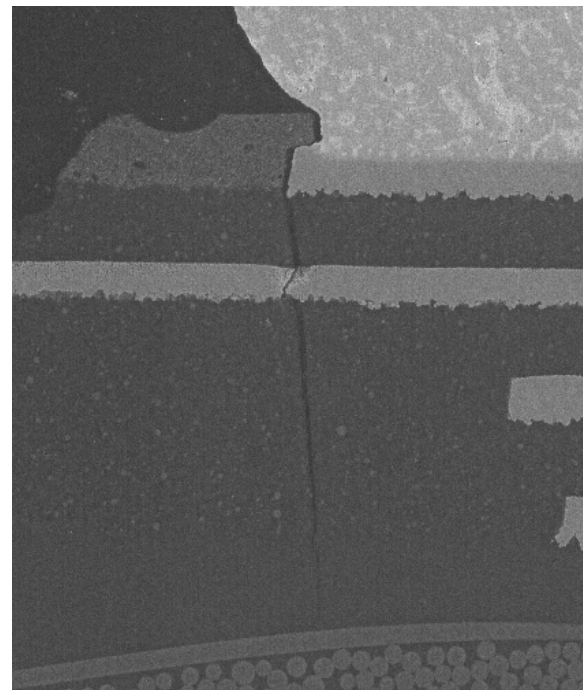


Figure 14. Crack through a BU material caused by delamination of a solder mask at the BGA side of a laminate. Substrate aged at 3,000 h at 150°C.

Figure 15 shows further how ingress of oxygen can affect the build-up material in localized areas.

Lacking a better criterion at present, we have chosen the mechanical properties reached after

exposure to 150°C for 1,000 hours as minimum required residual properties. Using the Arrhenius relationship described above we can predict a maximum continuous use temperature. For a laminate consisting of a current material set we conclude that the maximum continuing use temperature will be around 105°C.

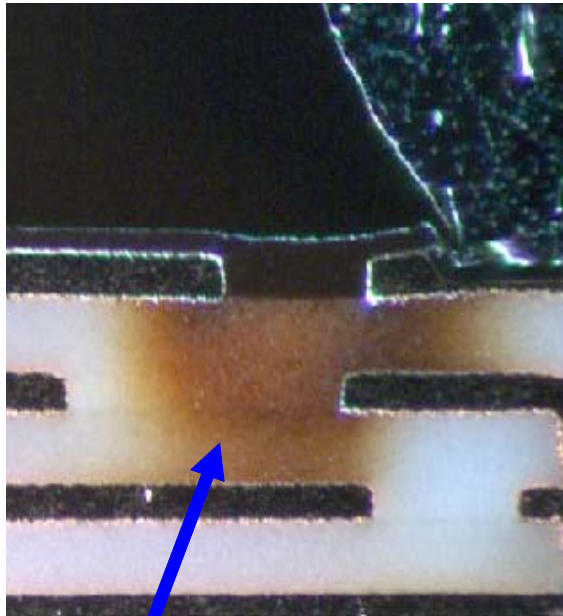


Figure 15. Discoloration observed in BU layers that are exposed to oxygen during thermal aging at 150°C after 1,000 hr. Oxygen penetrates through the solder mask but not the copper lines.

Conclusions

We have shown that properties of organic materials that have seen standard cure conditions often vary considerably from the properties these materials attain after thermal aging. Assessment of the reliability of organic packages therefore requires material property data as a function of thermal aging time and temperature. To identify the maximum continuing use temperature of an organic package further requires the knowledge of the minimum required residual reliability, the thermally weakest

material, and the structurally highest stressed area. Much work remains to obtain complete information.

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