Chapter 3

Environmental Aging Effects on Thermal and Mechanical Properties of Electrically Conductive Adhesives

Abstract

This paper investigates environmental aging effects on thermal and mechanical properties of three model electrically conductive adhesives (ECAs). A combination of several experimental techniques including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and stress-strain dogbone testing has been utilized throughout this study. Samples were aged at 85°C, 100% RH for periods of up to 50 days and some of the samples were dried at 150°C after aging. Results obtained on aged samples with and without drying suggest that the conductive adhesive may have experienced both reversible and irreversible effects during environmental aging. Both plasticization that is reversible and further crosslinking and thermal degradation, which are irreversible, are indicated upon exposure of ECAs to the hot/wet environment.

Keywords: Electrically conductive adhesives; environmental aging; thermal properties; mechanical properties; reversible effect; irreversible effect.

3.1 Introduction

Environmental concerns have created an increasing need for user-friendly alternatives to environmentally harmful solders in electronic applications. As emerging alternatives to lead based solder materials, electrically conductive adhesives (ECAs) are gaining great interest in the electronics industry for electrical interconnections. ECAs consist of a polymer binder that provides mechanical strength and conductive fillers, which offer electrical conduction. The binder materials that are commonly used in the electronics industry are epoxies due to their many superior properties, such as low shrinkage, good adhesion, and good resistance to moisture and chemical attacks [1]. On the other hand, silver particles are commonly selected as conductive fillers because of their high electrical conductivity, good chemical stability, and lower cost compared with gold [2]. Numerous studies have shown that electrically conductive adhesive joining possesses many advantages over conventional solder

interconnection technology such as improved environmental performance, finer pitch printing, lower temperature processing, and more flexible and simpler processing. Nonetheless, the replacement of solder by this technology has not been widely adopted by the electronics industry owing to several drawbacks which are mainly seen in the reliability aspect of the adhesive joining, such as limited impact resistance [3-4] and the long-term mechanical and electrical reliability concerns [4-5]. Adhesive type [6-7], filler size and shape [8-9], degree of curing [10], and damping properties of the ECAs [3,11] are among the factors that play important roles in determining the reliability performance of electrically conductive adhesives.

Electrically conductive adhesives may be exposed to various environmental conditions during their service life. Moisture is commonly encountered in the service environment, and must be considered a critical factor in determining the long-term reliability of adhesively bonded joints. As has been shown in many polymeric systems, warm, moist environments can considerably alter the performance of the adhesives. Moisture absorbed in a polymer matrix can lead to a wide range of effects, both reversible and irreversible, including plasticization by weakening the intermolecular interactions among the functional groups of the chains [12-13], debonding at filler-matrix interfaces [14-16], leaching of unreacted functional groups [21], structural damage such as microcavities or crazes [17-18], further crosslinking [19-20], and chemical degradation of the matrix due to hydrolysis and oxidation during long-term exposure to water [21]. In response to the effects of water in polymers, the thermal properties such as the glass transition temperature and damping properties [12], and mechanical properties including tensile strength, moduli, and the failure strain [15,22-23] and fracture toughness [23-24] can be significantly affected.

The kinetics of water diffusion in adhesives has been described by many researchers using different models. In many cases, the kinetics of water diffusion is assumed to follow the one-dimensional Fick's second law, which considers that the driving force of diffusion is the water concentration gradient. Some other models have also been applied to describe more complex diffusion processes. Jacobs and Jones [25-26] have extended Fick's law to consider the existence of a two-phase epoxy material with different densities. A two-phase model has been utilized by Bonniau and Bunsell [27] to interpret the Langmuir diffusion process, in which the absorbed water is divided into a free phase and a strongly bound phase. Lefebvre

et al [28, 29] have proposed a diffusion model to incorporate temperature and strain, as well as penetrant concentration terms in the equation of the diffusion coefficient. This model is based on free volume theories and assumes that the transport kinetics is governed by the constant redistribution of the free volume that is temperature, strain, and penetrant concentration dependent. Diamant *et al.* [18] have demonstrated that four factors play key roles in the coefficient of moisture diffusion into the epoxy resin: the polymer network structure, the polymer polarity, the physical morphology of the polymer, and the creation of microdamage in the material.

Water absorbed in the polymer is generally divided into free water and bound water [18,30]. Water molecules, which are contained in the free volume of the polymer and are relatively free to travel through the microvoids and holes, are identified as free water, while water molecules that are dispersed in the polymer matrix and attached to the polar groups of the polymer are designated as bound water. Research in references [30-31] further suggested that bound water within the polymer network can be recognized as loosely bound water, which can be released easily upon heating, and strongly bound water that is "frozen" in the network and difficult to be removed from the polymer. Antoon *et al.* [32] have found that water absorbed in an epoxy resin usually interacts with the polar groups by hydrogen bonding and the epoxy-water interactions are completely reversible. However, Woo and Piggot [33] have suggested that water in certain epoxy systems is not bonded to any polar groups or hydrogen-bonding sites. Clearly, the interactions between absorbed water and epoxy resins are different for different epoxy systems and further investigation is needed for specific epoxy systems.

In this study, thermal and mechanical properties of three electrically conductive adhesives were first characterized and compared. Numerous studies have shown that the reliability of conductive adhesive joints can be significantly degraded greatly by exposure to hot/wet environments. However, the mechanism of water adsorption into ECAs and subsequent effects of water on the properties of bulk conductive adhesives are not readily found in the literature. Therefore, a great part of this work is aimed to investigate the effects of absorbed water on thermal and mechanical properties of the three conductive adhesives and explore mechanisms underlying these effects. A combination of experimental techniques including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC),

dynamic mechanical analysis (DMA), and stress-strain dogbone testing was utilized throughout this study.

3.2 Experimental

3.2.1 Materials and Environmental Aging

Three silver-filled epoxy-based adhesive systems, which were designated as ECA1, ECA2 and ECA3, were supplied by Emerson & Cuming for this research. These are not commercial products, but rather are model systems formulated for the purpose of this study. According to the data sheets provided by the supplier, the silver loading in each adhesive is around 70%-90% by weight, while the epoxy resin, thermoplastic epoxy copolymer, curing agents, and other additives account for the rest of the adhesive formations (See Appendix A). Figure 3.1 is a scanning electron micrograph of a conductive adhesive with silver flakes distributed in the epoxy matrix. As can be seen from the figure, the silver flakes embedded in the matrix have different shapes and sizes. This wide size distribution is believed to offer improved conductance over a narrow size distribution [1, 34].

Samples for different tests were conditioned in a water bath for periods of up to 50 days. The water bath was maintained at 85°C and was tightly closed except when samples were removed for testing. Samples were placed on a rack above the water to avoid immersion in liquid water. As a result, the relative humidity in the water bath was nearly 100%. Selected samples were periodically removed from the water bath and tested.

3.2.2 Differential Scanning Calorimetry Analysis of ECAs

Differential scanning calorimetry (DSC) experiments were performed on the three adhesives using a TA Instruments 2920 modulated DSC. The DSC sample size was in the range of 10-20 mg. To investigate the cure information of the ECA formulations, isothermal scans on uncured resins were first conducted at 150°C, at which all the ECA samples were cured. DSC scans were also performed on as-cured samples between -10°C and 150°C at a constant heating rate of 5°C/min to investigate the glass transition temperatures of the three conductive adhesives. Two scans were run on each DSC sample and the T_g of each conductive adhesive was determined from the second scan.

3.2.3 Moisture Uptake Measurements

Moisture uptake tests were performed on bulk ECA1, ECA2 and ECA3 samples. Five samples of each adhesive having dimensions of 6 x 4 x 0.9 mm were conditioned at 85°C, 100% RH and periodically removed from the water bath, weighed and returned to the rack in the water bath. Weight measurements were taken using an electronic analytical balance from Mettler Inc. Each data point reported in the results is an average value from five samples weighed separately.

3.2.4 Thermogravimetric Analysis of ECAs

A TA 2950 Instruments thermogravimetric analyzer (TGA) was used to investigate the thermal stability of the three conductive adhesives, both prior to and after environmental aging. The TGA sample size was in the range of 10-20 mg. Samples were ramped between room temperature and 900°C at a heating rate of 10°C/min. Dry nitrogen gas was introduced into the test furnace at a rate of 45 mL/min as the test environment. The change in sample weight during the thermal scan is calculated as follows:

$$\frac{W_T - W_i}{W_i} \times 100\%$$

where W_T is the weight at a certain temperature during the scan and W_i is the initial weight before the TGA test.

3.2.5 Dynamic Mechanical Analysis of ECAs

To obtain the thermal transition characteristics of the three conductive adhesives, both prior to and after environmental aging, DMA experiments were performed using a TA Instruments 2980 dynamic mechanical analyzer (DMA) in single cantilever beam mode as shown in Figure 3.2 [35]. To prepare neat DMA samples from uncured adhesives, a DMA mold was first made by cutting three rectangular slots with a length of 37.0 mm and a width of 6.5 mm through a Teflon sheet with a thickness of 1.2 mm. This was then placed on top of a Teflon sheet. After pouring the uncured adhesive in the Teflon mold, another clean Teflon sheet was placed on the top of the mold and appropriate pressure was then applied on the top Teflon sheet by pushing a ruler blade back and forth along the sample length direction to make the adhesive surface smooth and the DMA sample thickness uniform. The whole

assembly was finally placed in an oven and cured at 150°C for 1h. Before DMA tests were conducted, the sides of each DMA sample were polished to make them smooth. In the DMA studies, the DMA samples were tested at a heating rate of 1°C/min from -80°C to 160°C with a single oscillation frequency of 1Hz.

3.2.6 Tensile Stress-Strain Testing

Tensile dogbone stress-strain specimens of the three conductive adhesives were prepared from uncured adhesives in accordance with ASTM D638-01 [36] Type V. The dogbone samples had an overall length of 24 mm, a nominal gage length of 9.5 mm and a width of 3 mm. All tensile tests were conducted on a 4505 Instron machine at a crosshead displacement rate of 1 mm/min at ambient conditions. Samples were clamped with flat-faced, pneumatic grips. To prevent slipping during testing, abrasive cloth tabs were used to increase the friction on the grip faces. The engineering stress, which is defined as the load divided by the initial cross-sectional area, was calculated and used in this study.

A non-contact laser extensometer manufactured by Fiedler Optoelektronik GmbH, Germany was utilized to acquire strain data. The laser extensometer consists of a scanner and a receiver, and is controlled by the extensometer software provided with the laser extensometer. During testing, a rotating mirror in the scanner continually swept a laser beam between two white marks establishing the gage section of each dogbone sample. The reflected light from the sample was collected by the receiver and the deformation between the two marks on the test sample was then calculated by the extensometer software.

3.3 Results and Discussion

3.3.1 Properties of As-Cured Conductive Adhesives

3.3.1.1 DSC Results

Cure behavior of the conductive adhesives was investigated using isothermal DSC scans at 150°C and the results are shown in Figure 3.3. As can be seen from the figure, the isothermal cure curves of the conductive adhesives level off after 15 min at 150°C. To ensure a complete cure, all the ECA samples were cured at 150°C for an hour.

Dynamic DSC scans were also conducted on as-cured conductive adhesives to obtain the glass transition temperatures of the conductive adhesives. The DSC traces of the second

scan for the three adhesives are shown in Figure 3.4, Figure 3.5, and Figure 3.6, respectively. In all cases, the T_g values were taken as the y-axis value halfway between the onset and the end of the step transition region. From these DSC traces, the glass transition temperatures of as-cured ECA1, ECA2 and ECA3 specimens are found to be around 106°C, 61°C and 30°C, respectively.

3.3.1.2 TGA Results

TGA results obtained on as-cured ECA1, ECA2 and ECA3 adhesive samples are summarized in Figure 3.7. The ECAs started decomposing at around 350ºC. Below the decomposing temperature, the materials were thermally stable and no evident weight loss was observed on the as-cured adhesives. Energy dispersive X-ray analysis (EDX) was performed on the residues following TGA testing, revealing that the remaining residue was silver. The TGA results demonstrate that the weight percent silver fillers in ECA1, ECA2, and ECA3 adhesives are approximately 83%, 82% and 86%, respectively.

3.3.1.3 DMA Results

During assembly and handling, and throughout the life, electronic devicess may experience mechanical shocks [4]. Therefore, impact strength should be a critical parameter for electrically conductive adhesives technology. The impact resistance of a material has been shown to be closely related to the loss factor or tan δ [3,11,37-38]. To investigate the damping behavior of the three conductive adhesives, DMA tests were conducted.

Figure 3.8 shows the change of tan δ as a function of temperature at a single frequency of 1Hz. As can be seen from the figure, these three adhesives exhibit very different damping behavior. ECA3 shows high tan δ values over a lower and broader temperature range, reaching a peak value around 50°C. On the other hand, ECA1 and ECA2 have higher tan δ peaks that are centered near 80°C and 125°C, respectively.

3.3.1.4 Tensile Test Results

To characterize the mechanical behavior of the three conductive adhesives evaluated in this study, stress-strain tensile tests were performed on the as-cured samples. Figure 3.9 shows typical stress-strain curves obtained on ECA1, ECA2 and ECA3. Note that the conductive adhesives exhibit very different stress-strain behavior. ECA1 and ECA2 exhibit much higher tensile strengths and much lower failure strains than ECA3. These differences

can be mainly attributed to the viscoelastic nature of the materials. As noted earlier, the glass transition temperature of ECA3 is around room temperature, which means that the polymer chains in the material have greater mobility under mechanical deformation and as a result, the material as a whole shows large tensile elongations. On the other hand, ECA1 and ECA2 both show glass transitions at temperatures well above room temperature. Therefore, at room temperature, the chains in both materials have less mobility and as a result, the materials show stiffer behavior, as can be observed in Figure 3.9.

Figure 3.10 shows the energies required to beak the dogbone samples of the three conductive adhesives. The energy values were obtained by integrating the area under each stress-stain curve as shown in Figure 3.9. As can be observed from the figure, ECA3 samples exhibit the greatest toughness among the three conductive adhesives, while ECA1 samples show the smallest toughness, compared to ECA2 and ECA3 samples.

3.3.2 Effects of Environmental Aging on ECAs

3.3.2.1 Moisture uptake results

Figure 3.11 summaries the moisture uptake results obtained on ECA1, ECA2 and ECA3 samples aged at 85°C, 100% RH. All three adhesives exhibit rapid uptake of increase in the initial aging days and then tend to reach an equilibrium with increasing aging time up to 20 days aging. However, as aging continues, there appears to be a second stage of moisture uptake in ECA1 and ECA2 samples, though no second stage of moisture sorption is observed in ECA3 samples. These moisture uptake results suggest that both concentration-gradient-controlled diffusion and relaxation-controlled diffusion may have occurred in the moisture sorption of ECA samples. For ECA1 and ECA2, which have relatively high glass transition temperatures, the rapid first stage of moisture uptake may be mainly attributed to concentration-gradient-controlled Fickian diffusion, which involves the diffusion of water moplecules into pre-existing free volume in the materials. On the other hand, the second stage of moisture uptake at the longer aging time is indicative of non-Fickian diffusion and may be a consequence of a relaxation process in the materials, or chemical interaction between the polymer and absorbed water molecules [39]. For ECA3 samples, as the material is purely rubbery-like under the aging condition (85°C, 100 RH%), the rates of different

diffusion modes may be quite similar, and therefore, the initial observed moisture sorption behavior may reflect a superposition of different diffusion processes.

3.3.2.2 Effects of Environmental Aging on Thermal Stability of ECAs

The thermal stability of the three conductive adhesives, both prior to and after environmental aging, was investigated by thermogravimetric analysis. The TGA curves of derivative weight vs. temperature for the three conductive adhesives are shown in Figure 3.12, Figure 3.13, and Figure 3.14, respectively. To capture the phenomena of thermal changes at lower temperatures, close-up TGA curves from 25°C to 350°C are presented in the main figures, with the TGA scans throughout the whole temperature range inserted in the figures. The inserted figures reveal that great loss in weight took place in the temperature range of 365°C-465°C for all three conductive adhesives, both prior to and after environmental aging, due to chemical decomposition of the conductive adhesives. The close-up TGA curves clearly show that the aged samples of ECA1, ECA2 and ECA3 all exhibited a significant weight decrease in the temperature range of 50°C-200°C, in contrast to the as-cured conductive adhesives samples. Furthermore, it is interesting to note that some of the aged ECA samples, especially for ECA2 and ECA3 samples aged for longer time, displayed greater weight loss in the temperature range of 200°C-300°C, compared to as-cured samples. Previous studies have revealed that absorbed water may exist in a polymer as free water or loosely bound water, which can escape out of the adhesive easily upon heating, and tightly bound water, which is strongly confined in the polymer network and requires additional energy for removal from the polymer. Weight loss occurring on TGA curves shown in Figures 3.12-14 suggests that absorbed water in the conductive adhesives may have existed in a state of free water or loosely bound water, which may have evaporated at 50°C-200°C, as well as in a state of bound water, which was not released from the adhesives until the adhesives were further heated at 200°C-300°C.

Further observations on the TGA curves demonstrate that weight loss profiles in the temperature range of 200°C-300°C are different for different conductive adhesive systems. For ECA1, the aged samples did not show much difference in the weight loss profile, compared to as-cured samples in this temperature region. However, for ECA2 and especially for ECA3, it is obvious from the figures that the aged samples exhibited greater weight loss at 200°C-300°C, compared with the as-cured samples of each adhesive, and greater weight loss

was observed for samples aged for longer time. These phenomena suggest that the absorbed water in ECA1 may have existed mainly in a state of free or loosely bound water, while the absorbed water in ECA2 and ECA3 may have partly interacted with functional groups of the polymers and strongly attached through hydrogen bonding to the functional groups. According to the water sorption mode proposed by Adamson [40], the transport of water below T_g is a three-phase process in which the absorbed water first fill the free volume, then is bound to network site, and finally enters the densely crosslinked region. Gupta and Drzal [41] have suggested that at higher temperature, water readily enters the material through gaps created by segmental motion of the polymer chains. As ECA1 shows a glass transition at 106°C (based on DSC), which is above the aging temperature (85°C), it is reasonably expected that ECA1 exhibits relatively low diffusivity for water to enter. Therefore, the water molecules absorbed into the material may mainly exist as free water and the samples may have not been aged long enough for many absorbed water molecules to travel to the network site and strongly combine with functional groups of the adhesive, as suggested by the TGA results. On the other hand, as the glass transition temperatures of ECA2 and especially ECA3 are below the aging temperature, it is easier for water molecules to travel through the polymer chains in ECA2 and ECA3. As a result, absorbed water in ECA2 and ECA3 may have partly distributed into the free volume as free water and partly traveled to the network site and attached to polymer chains as bound water.

3.3.2.3 Effects of Environmental Aging on Damping Behavior of ECAs

The changes in the loss factor with aging time for ECA1 are shown in Figure 3.15. It should be remembered that the DMA tests involved a dynamic heating process and water evaporated from the test samples continually throughout the heating, though the results should still be comparable for the same material aged at different times. In general, Figure 3.15 reveals that the peak of the loss factor, tan δ, slightly shifts to lower temperatures with increasing aging time due to the plasticizing effects of water. Close inspection of the DMA traces further reveals that the loss factor of the aged samples exhibits a shoulder in the temperature range of 80°C-100°C, whereas the as-cured sample shows a smooth curve with no shoulder detected during scanning. Apparently, the changes of the loss factor curves are due to the water absorbed in the sample during aging. To further investigate the effect of water on the loss factor of the conductive adhesive, curves obtained by subtracting the

normalized loss factor curves of aged samples from the normalized loss factor curve of the as-cured sample are plotted in Figure 3.16, along with the corresponding normalized loss factor curves of aged samples and as-cured samples. From the figure, one can observe that the peak of the subtraction curves is precisely located at 100°C, which is the boiling point of water. This finding further confirms that water, which was absorbed in the ECA1 and played a significant effect on the loss factor of the material, mainly exists in its free or loosely bound state and can escape out of the material easily. And the shoulder, which occurred in the curves of the aged samples, may suggest the phase separation in the material as a result of water ingress. For ECA2 and ECA 3 samples, no evident shoulder or other types of transitions were detected from the loss factor curves.

Figures 3.17-3.19 show the traces of the loss factor obtained on aged and then re-dried samples of ECA1, ECA2 and ECA3, along with the traces of the loss factor of as-cured samples for comparison. The dried samples were heated at 150°C for 2 hours after 50 days aging to remove the water absorbed during aging. From the figures, one can observe that the peak of the loss factor, tan δ, tends to shift to lower temperatures upon exposure to aging in the early aging period, due to plasticizing effects of water. As aging continued, however, the peak of the loss factor has the tendency to shift back to higher temperatures for all the three conductive adhesives, though the magnitude of the shift is different for different adhesives. ECA1 exhibits a slight change in the position of the loss factor peak for sample aged up to 50 days aging, while the loss factor peaks of both ECA2 and ECA3 show a significant shift back to higher temperatures after 50 days aging. Upon drying the samples aged for 50 days, the loss factor shifts to higher temperature than for samples aged for 50 days without drying, but never goes back to the values obtained on as-cured samples. One possible explanation for the shift of the loss factor of the conductive adhesives and the irreversible effect after water de-sorption may be attributed to further crosslinking in the water-plasticized conductive adhesives. The FT-IR results of Liu et al [19] brought evidence that further curing in the conductive adhesive can be observed on exposure of the cured adhesives to an 85°C and 85%RH condition. As water sorption and crosslinking of a polymer may play opposite effects on the T_g (referred here to the temperature of the loss factor peak) of the material, with crosslinking enhancing the T_g of the material and water depressing the T_g, the net result would depend upon the balance of these two mechanisms. The DMA results suggest that ECA1

exhibits relatively a stable viscoelastic transition upon exposure to environmental aging, while the viscoelastic behavior of ECA2 and ECA3 is greatly affected by water ingress. The different reactions of the three adhesives to water attack may be explained by different formulations of the three conductive adhesives. For example, the amount of base epoxy resin and other additives may greatly affect the rate of water diffusion into the adhesive and water interaction with the chains.

3.3.2.4 Effects of Environmental Aging on the Tensile Properties of ECAs

Figures 3.20-3.21 summarize the tensile strength and failure strain results obtained on ECA1, ECA2 and ECA3 samples aged at 85°C, 100% RH for periods up to 50 days. Curve fits have been drawn through the mean strength and failure strains for convenience, but are not meant to imply actual trends. The error bars in the figures are one standard deviation and obtained from at least four specimens. The overall trend is that the tensile strength and failure strain exhibit significant changes in the initial 1 or 2 days aging with the tensile strength going down and the failure strain going up, as compared to the values obtained on as-produced samples. Then the tensile strength and failure strain values tend to level out with increasing aging time up to 20 days. As the aging continues up to 50 days, however, there is a tendency for both tensile strength and failure strain to decrease, as will be seen in Figures 3.22-3.24. Careful observation of the tensile strength results further reveals that the tensile strength exhibited slight recovery for all three conductive adhesives after the great drop in the initial 1 or 2 days aging and before it finally leveled out. Reduction in the tensile strength and increase in the failure strain upon exposure of the adhesives to hot/wet environment can be attributed to the plasticization of the adhesive materials caused by moisture adsorption, while the slight recovery in the tensile strength implies that further crosslinking or other mechanisms, which can enhance the material strength, may have occurred during aging. Comparisons made among the three ECAs suggest that ECA1 shows relatively stable tensile strength throughout the aging period, while ECA2 and ECA3 exhibit evident changes in the tensile strength. This phenomenon may be explained from the point of kinetics of water diffusion. As the glass transition temperatures of ECA2 and ECA3 are well below the aging temperature (85°C), water could readily diffuse into the adhesives and plasticize the materials during aging. On the other hand, ECA1 exhibits a relatively high glass transition temperature and at the aging temperature, the material remains glassy. Therefore, the rate of water

diffusion into ECA1 may be greatly lowered with its tightly packed chemical structure, in contrast to that of water diffusion into ECA3, as well as ECA2. As a result, the tensile strength and strain of ECA1 are less affected by water ingress compared with ECA2 and ECA3 aged for the same period of time.

Figures 3.22-3.24 show characteristic stress-strain curves of aged and re-dried samples of ECA1, ECA2, and ECA3 conductive adhesives, respectively. These curves are typical of the behavior exhibited by multiple samples tested at the same condition. In general, the aged samples for all three adhesives show a reduction in tensile strengths and tensile moduli, and an increase in the failure strains. This effect can be attributed to the plasticization of the adhesive materials caused by moisture adsorption. On the other hand, reductions in both tensile stress and failure strain can be observed on samples aged for 50 days in contrast to samples aged for 20 days for all the three adhesives, though the moduli are very similar for samples aged at 20 days and 50 days for each adhesive. Previous studies [14-16] have suggested that the loss of strength in epoxy-filler systems by exposure to moisture could result from both matrix plasticization and debonding at filler-epoxy interfaces. It has been confirmed that plasticization can lower the tensile strength and modulus and increase the strain at failure. Thus, reduction in the failure strain, as well as the tensile strength, after 50 days aging may be due to degradation of the interfaces between the matrix and silver particles distributed in the matrix. The other possible reason for the reduction of the tensile strength and failure strain of the conductive adheisves after 50 days aging may be attributed to material degradation such as hydrolysis or oxidation when exposed to the hot/wet environment.

Some samples aged for 50 days were dried at 150°C for 2 hours to drive out the water absorbed in the samples. Results obtained on the dried samples are shown in Figures 3.22-24. The stress-strain curve of the dried sample of the ECA1 material resembles that for the as-produced specimen of ECA1. On the other hand, the samples of both ECA2 and ECA3 materials after drying show increased modulus (initial slope of the stress-strain curve) and tensile strength and decreased strain-to-failure value in contrast to as-produced samples and also the samples aged for 50 days without drying. These stress-strain dogbone results, along with the TGA and DMA results discussed in the above sections, suggest that water ingress in the conductive adhesives have altered the adhesive properties in both reversible and irreversible ways. The reversible effect such as plastization can be erased upon drying, and as

a result, the adhesive properties altered by the reversible process can be recovered. On the other hand, the irreversible effects such as further crosslinking and degradation may have chemically changed the materials and resulted in the permanent change in the adhesive properties. The full recovery of stress and strain behavior of ECA1 upon drying demonstrates that ECA1 might have mainly experienced the reversible effect of water and the chemical effect in the material is minimal throughout the aging time. On the other hand, ECA2 and ECA3 have undergone both reversible and irreversible effects during aging.

3.4 Summary and Conclusions

This study was performed to characterize the thermal and mechanical properties of three model electrically conductive adhesives, and investigate the effects of hydrothermal aging on the properties of the three conductive adhesives, which were designated as ECA1, ECA2, and ECA3, respectively. Conducted on as-cured adhesives, the study reveals that the three conductive adhesives exhibit very different properties in the glass temperature transition, the damping behavior, the tensile strength, and the strain to failure. DSC scans reveal that the T_gs of as-cured ECA1, ECA2 and ECA3 are around 106°C, 61°C, and 30°C, respectively. Water uptake measurements suggest that the conductive adhesives, when exposed to 85°C and 100% RH environmental condition, may have experienced both Fickian diffusion process and other diffusion processes that may be related to viscoelastic relaxation in the materials, or chemical interaction between the polymer and absorbed water molecule. Furthermore, it is shown that the properties of the adhesives are altered to some extent, upon exposure to the hydrothermal aging condition. ECA2 and especially ECA3 are greatly affected by water ingress in that both the damping property and the mechanical strength are changed considerably after aging. On the other hand, ECA1 exhibits relatively stable mechanical and thermal behavior. These differences in the thermal and mechanical properties of the three conductive adhesives, upon exposure to aging, may be attributed to the different diffusivity of water into the materials, as well as the state of water molecules (Free water or bound water) existing in the adhesives.

TGA, DMA and stress-strain results obtained on aged and re-dried samples suggest that water ingress in the conductive adhesives have altered the adhesive properties in both reversible and irreversible ways. Plasticization, which is a reversible effect, has been

observed on the aged samples of the three conductive adhesives. On the other hand, irreversible effects such as further crosslinking and degradation may also have occurred during aging, permanently changing the properties of the adhesives. The full recovery of the stress and strain behavior of ECA1 upon drying demonstrates that ECA1 might have mainly experienced the reversible effect of water and the chemical effect in the material is minimal throughout the 50-day aging time. On the other hand, the results obtained on ECA2 and ECA3 reveals that both adhesives have exhibited both reversible and irreversible effects during aging.

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