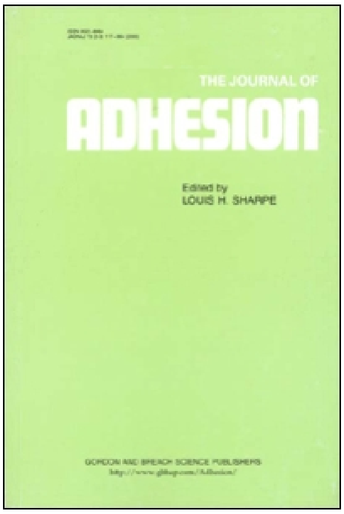

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Environmental aging effects on thermal and mechanical properties of electrically conductive adhesives

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ENVIRONMENTAL AGING EFFECTS ON THERMAL AND MECHANICAL PROPERTIES OF ELECTRICALLY CONDUCTIVE ADHESIVES

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This article 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), water uptake measurements, dynamic mechanical analysis (DMA), and stress-strain dogbone testing has been utilized throughout this study. Samples were aged at 85°C and 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 adhesives may have experienced both reversible and irreversible effects during environmental aging. Both plasticization, which 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

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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, which provides mechanical strength, and conductive fillers, which offer electrical conduction. Epoxy binder materials are commonly used in the electronics industry due to their many superior properties, such as low shrinkage, good adhesion, and good resistance to moisture and chemical attack [1]. Silver particles are commonly selected as conductive fillers because of their high electrical conductivity, good chemical stability, and lower cost compared with gold [1]. 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 electrically conductive adhesives has not been widely adopted by the electronics industry owing to several concerns, including limited impact resistance [2, 3] and long-term mechanical and electrical reliability concerns [3, 4]. Adhesive type [5, 6], filler size and shape [7, 8], degree of curing [9], and damping properties of the ECAs [2, 10] 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 studies, warm, moist environments can significantly alter the performance of polymers and adhesively bonded joints. Moisture absorbed in a polymer matrix can lead to a wide range of both reversible and irreversible effects, including plasticization by weakening the intermolecular interactions among the functional groups of the chains [11, 12], debonding at filler-matrix interfaces [13–15], leaching of unreacted functional groups [20], structural damage such as microcavities or crazes [16, 17], further crosslinking [18, 19], and chemical degradation of the matrix due to hydrolysis and oxidation during long-term exposure to water [20]. In response to the effects of water in polymers, properties such as the glass transition temperature, damping [11], tensile strength, moduli, failure strain [14, 21, 22] and fracture toughness [22, 23] 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 are 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 [24, 25] 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 [26] 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.* [27, 28] have proposed a diffusion model to incorporate the effects of 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 are governed by the constant redistribution of the free volume that is temperature, strain, and penetrant concentration dependent. Diamant *et al.* [17] 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 [17, 26, 29]. 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. It was 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 remove from the polymer [30]. Antoon *et al.* [31] have found that water absorbed in an epoxy resin usually interacts with the polar groups by hydrogen bonding and that epoxy-water interactions are completely reversible. However, Woo and Piggot [32] have suggested that water in certain epoxy systems is not bound to any polar groups or hydrogen-bonding sites. Clearly, the interactions between absorbed water and epoxy resins vary and are different 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 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 to explore mechanisms underlying these effects. A combination of experimental techniques including thermogravimetric analysis (TGA), moisture uptake measurements, dynamic mechanical analysis (DMA), and stress-strain dogbone testing was utilized throughout this study.

EXPERIMENTAL

Materials and Environmental Aging

Three silver-filled epoxy-based adhesive systems, which are designated as ECA1, ECA2, and ECA3, were supplied by Emerson & Cuming (Billerica, MA, USA) for this research. These are not commercial products, but rather are model systems specifically formulated for the purpose of this study. According to the material safety data sheet (MSDS) provided by the supplier (see Table 1), the silver loading in each adhesive ranges from 70% to 90% by weight, while the epoxy resin, thermoplastic epoxy copolymer, curing agents, and other additives account for the rest of the adhesive formations. The formulations of these three adhesives were varied by mainly adjusting the amounts of epoxy resin as well as fatty acid diglycidyl ester in the materials, with ECA1 containing much more epoxy resin than ECA2 and ECA3. ECA3 and ECA2 contained around 5–10% and 2–5% fatty acid diglycidyl ester, respectively, while ECA1 contained no ester-based linkages. These differences in composition among these conductive adhesives would obviously affect the properties of the final products, such as the glass transition temperatures and the resistance to moisture attack of the materials, as will be found in this study.

TABLE 1 Ingredients of ECA1, ECA2, and ECA3 Electrically Conductive Adhesives

Components	ECA1 % by weight	ECA2 % by weight	ECA % by weight
Modifiers and curing agents	< 4	< 4	< 4
Silver	70–90	70–90	70–90
Epoxy resin	10–15	5–10	1–5
Thermoplastic epoxy copolymer	5–10	5–10	3–5
1,4 butanediol glycidyl ether	2–5	2–5	1–5
Fatty acid diglycidyl ester	—	2–5	5–10

All the specimens tested in this study were cured at 150°C for 1 h, cooled to room temperature, and then stored in a desiccator prior to testing or aging. Figure 1 is a scanning electron micrograph of a typical cured adhesive sample with silver flakes distributed in the epoxy matrix. As can be seen from the photograph, the silver flakes embedded in the matrix have different shapes and sizes. The wide size distribution of the conductive filler particles is believed to offer improved conductance over a narrow size distribution [1, 33]. In addition, some voids can also be observed in the cured adhesive samples, as is also shown in the image. The size and amount of the voids in the adhesive samples no doubt would affect the water uptake level of the materials. By running differential scanning calorimetry (DSC) scans with a heating rate of 5°C/min on the three conductive adhesives, the glass transition temperatures of the adhesives were found to be: ECA1, 106°C; ECA2, 61°C; and ECA3, 30°C. The T_g values were taken as the temperature assoiciated with a point halfway vertically between the onset and the end of the step transition region.

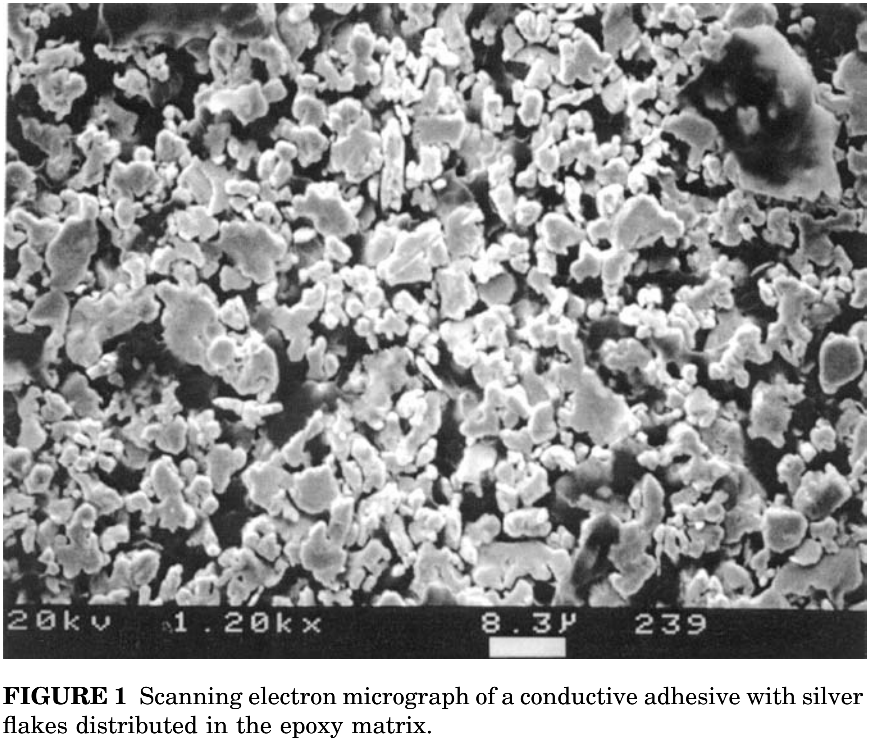

FIGURE 1 Scanning electron micrograph of a conductive adhesive with silver flakes distributed in the epoxy matrix.

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.

Moisture Uptake Measurements

Moisture uptake tests were performed on bulk ECA1, ECA2, and ECA3 samples. Five samples of each adhesive having dimensions of $6 \times 4 \times 0.9\,\text{mm}$ 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 Brinkmann Instruments Co., Westbury, New York, USA. Each data point reported in the results is an average value from five samples weighed separately.

Thermogravimetric Analysis of ECAs

A TA Instuments 2950 thermogravimetric analyzer (TGA) (TA Instruments, Inc., New Castle, DE, USA) 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 600°C at a heating rate of 10°C/min. Dry air 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.

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. To prepare neat DMA samples from uncured adhesives, a DMA mold was first made by cutting three rectangular slots with a length of 37 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 another Teflon sheet. After pouring the uncured adhesive into 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 1 h. Before DMA tests were conducted, the sides of each DMA sample were sanded 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 1 Hz.

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 [34] 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 (Instron Inc., Canton, MA, USA) 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 noncontact laser extensometer manufactured by Fiedler Optoelektronik GmbH, Luetzen, 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.

RESULTS AND DISCUSSION

Properties of As-Cured Conductive Adhesives

TGA Results

TGA results obtained on as-cured ECA1, ECA2, and ECA3 adhesive samples are summarized in Figure 2. The ECAs started decomposing

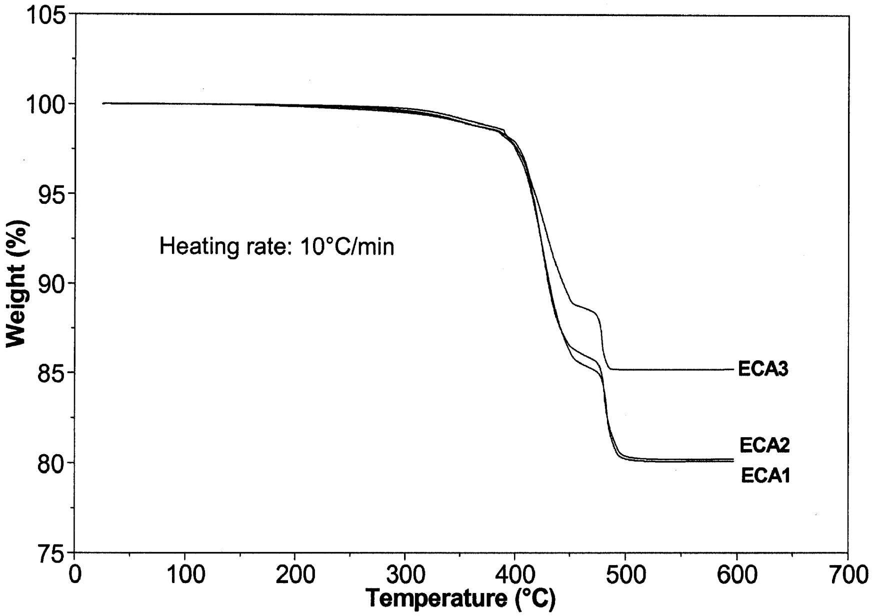

FIGURE 2 TGA plots of as-cured electrically conductive adhesive samples.

at around 350°C. 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 predominantly silver. The TGA results demonstrate that the weight percent silver fillers in ECA1, ECA2, and ECA3 adhesives are approximately 80%, 80%, and 85%, respectively, with ECA3 containing around 5% more silver than ECA1 and ECA2.

DMA Results

During assembly and handling, and throughout their service life, electronic devices may experience mechanical shocks [3]. Therefore, impact strength is of critical importance for electrically conductive adhesive technology. The impact resistance of a material has been shown to be closely related to the loss factor or tan δ [2, 10, 35, 36]. To investigate the damping behavior of the three conductive adhesives, DMA tests were conducted.

Figure 3 shows a plot of tan δ as a function of temperature at a single frequency of 1 Hz. 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

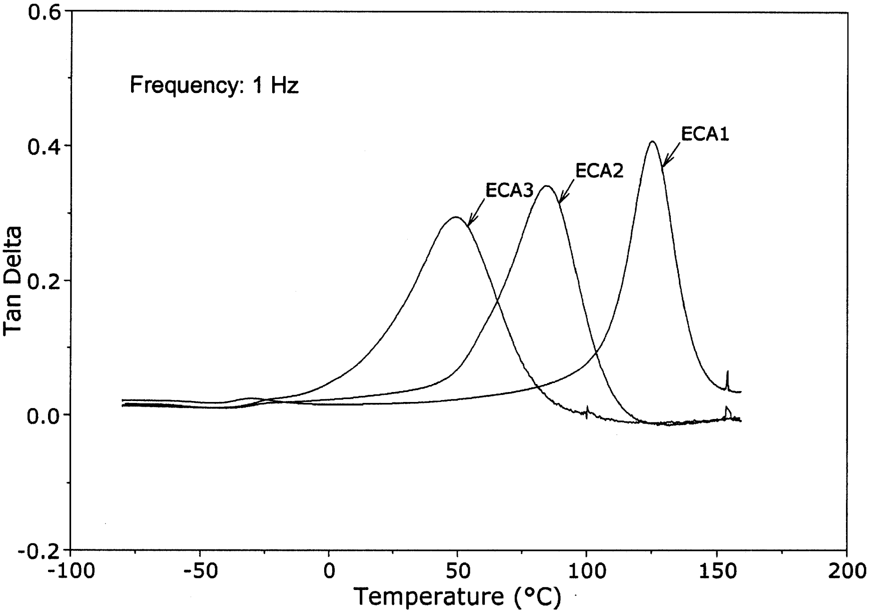

FIGURE 3 Plots of tan δ of as-cured conductive adhesives obtained from DMA scans conducted at 1°C/min.

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.

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 4 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 4.

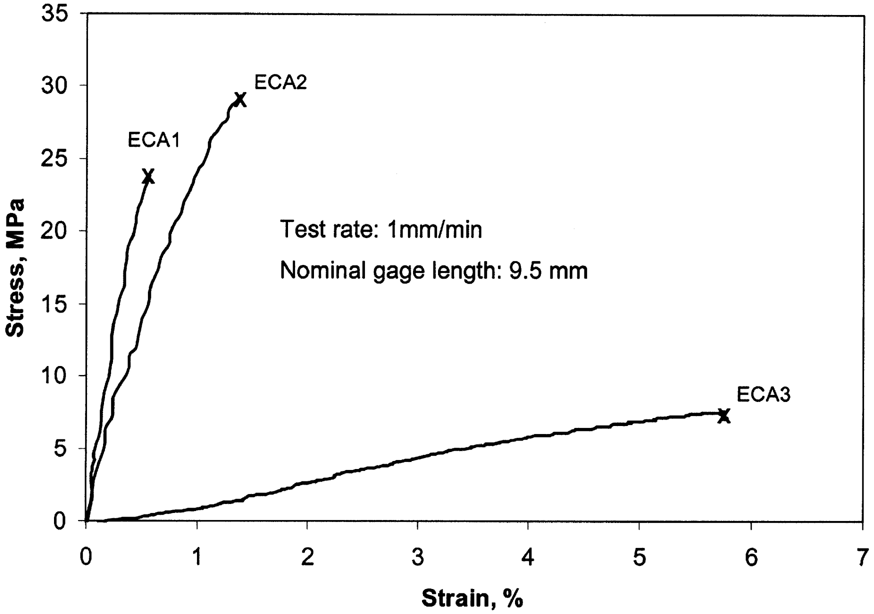

FIGURE 4 Typical stress-strain behavior of as-received ECA1, ECA2, and ECA3 samples tested at room temperature.

Effects of Environmental Aging on ECAs

Moisture Uptake Results

Figure 5 summarizes the moisture uptake results obtained on ECA1, ECA2, and ECA3 samples aged at 85°C and 100% RH. The curves were normalized to the weight fraction of epoxy resin present in the samples. The error resulting from the measurement is about ± 0.15% for each data point. As can be observed from the figure, the moisture absorption levels in the ECAs can reach 4–7% of the matrix weight, which is especially high for a typical epoxy. The high levels of moisture absorption in these ECA samples may be attributed to existing voids in the samples, which can increase the moisture uptake level, or further microcracking and voiding at silver/matrix interfaces during aging, as is commonly seen in many epoxy-filler systems.

From Figure 5, one can see that all three adhesives exhibit rapid moisture uptake in the few days of the exposure process 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

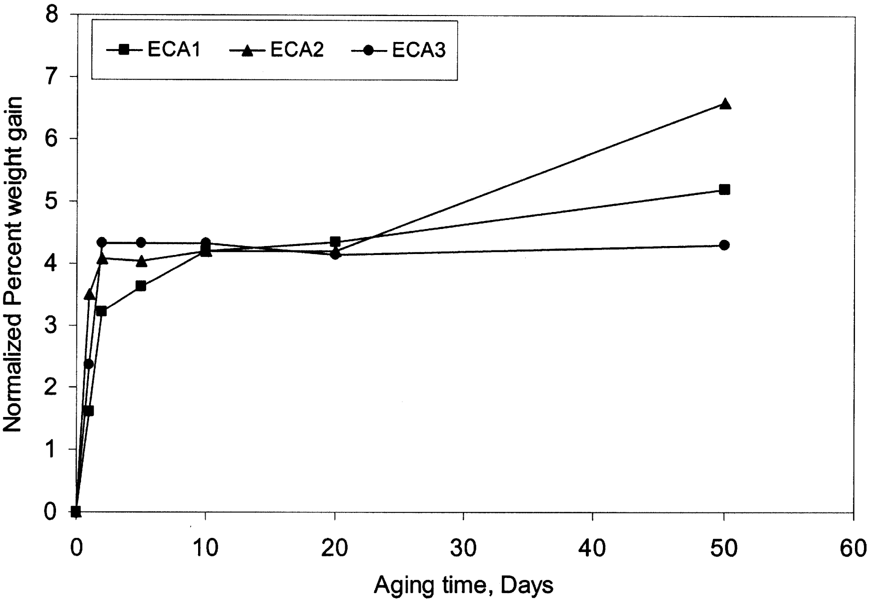

FIGURE 5 Weight gain in ECA samples as a function of aging time, when exposed to 85°C and 100% RH.

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 attributed mainly to concentration-gradient-controlled Fickian diffusion, which involves the diffusion of water molecules 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 [37], or an indication of microcracking and voiding at silver/matrix interfaces. For ECA3 samples, as the material is rubber-like at 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.

Effects of Environmental Aging on Thermal Stability 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 Figures 6, 7, and 8, 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 appearing as insets within the figures. The inset figures reveal that great loss in weight took place in the temperature range of 365–465°C for all three conductive adhesives, both prior to and after environmental aging, due to chemical decomposition of the polymer. 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 50–200°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 times, displayed greater weight loss in the temperature range of 200–300°C, compared with as-cured samples. The water uptake results shown also suggest that during aging, moisture absorbed in the adhesives has resided in the free volume or pre-existing voids, and has also traveled to the polymer networks and probably chemically interacted with the polymer chains. The

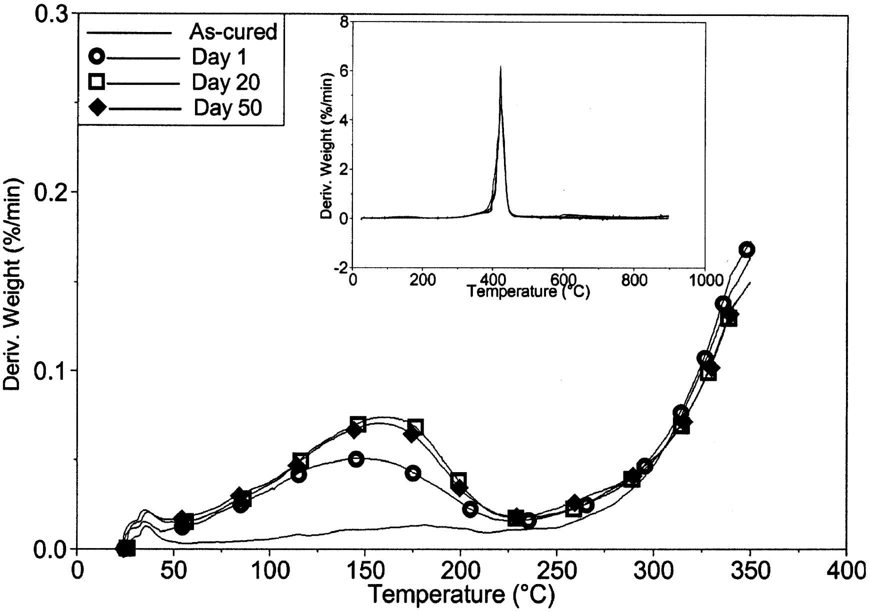

FIGURE 6 Differential thermogravimetric thermograms of as-cured and aged ECA1 samples heated at 10°C/min in nitrogen.

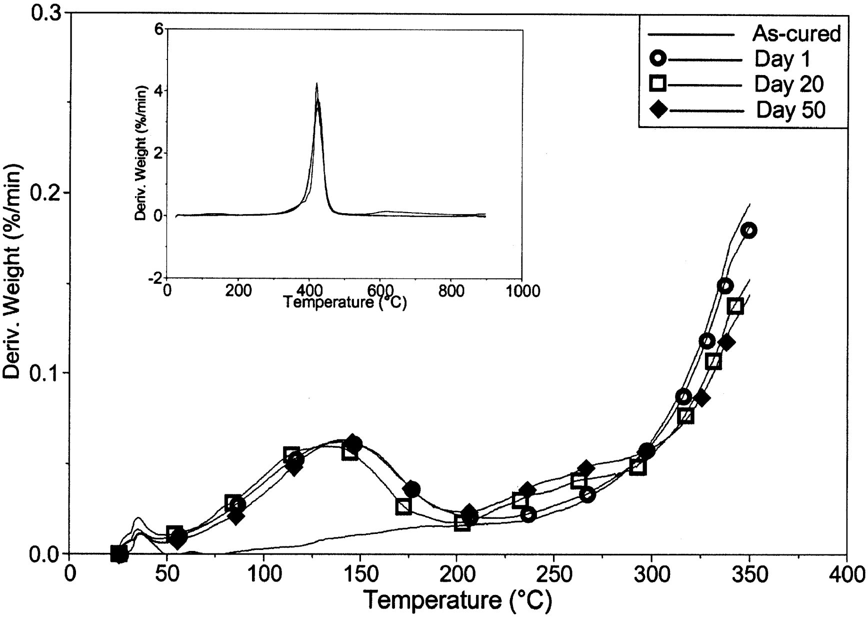

FIGURE 7 Differential thermogravimetric thermograms of as-cured and aged ECA2 samples heated at 10°C/min in nitrogen.

increased weight loss of the aged samples at 50–200°C shown in Figures 6–8 may be related to the evaporation of moisture trapped in the free volume or preexisting voids, while the greater weight loss on the aged ECA samples at 200–300°C in contrast to as-cured samples may correspond to the release of bound water from the polymer chains, as well as of other relatively small molecules produced due to chemical interactions between the adhesives and water molecules, due to degradation such as hydrolysis.

Further observation of the TGA curves demonstrate that weight loss profiles in the temperature range of 200–300°C are different for different conductive adhesive systems. For ECA1, the aged samples did not show much difference in the weight loss profile, as compared with 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 200–300°C, compared with the as-cured samples of each adhesive. Furthermore, greater weight loss was observed for samples aged for longer times. These phenomena may be explained by considering the chemical composition variations in the three ECAs and the viscoelastic properties of adhesives. As shown

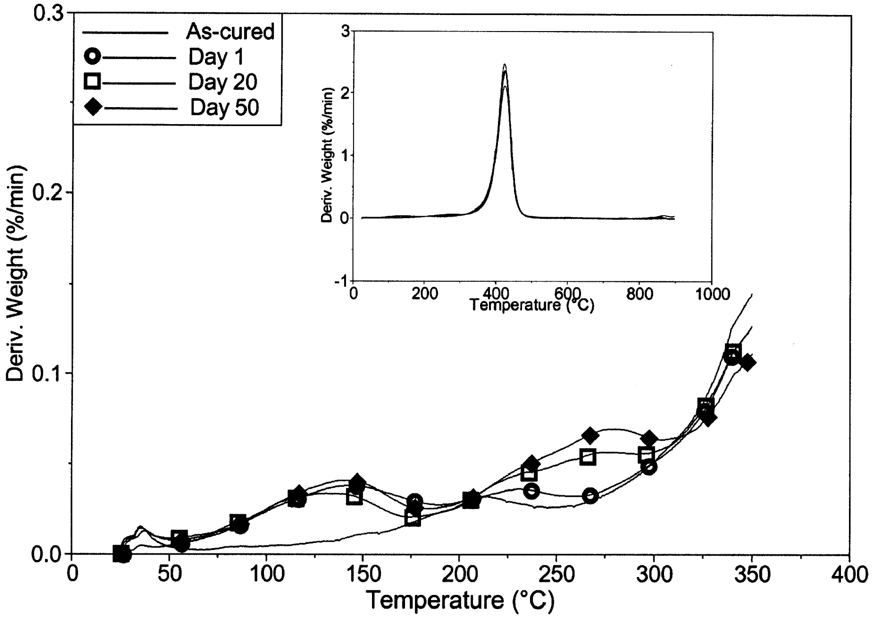

FIGURE 8 Differential thermogravimetric thermograms of as-cured and aged ECA3 samples heated at 10°C/min in nitrogen.

earlier, ECA1 contains more epoxy resin and exhibits a higher glass transition temperature (106°C) than ECA2 and ECA3. Therefore, ECA1 is expected to exhibit a relatively low diffusivity, due to its densely packed structure, and may have better resistance to water attack. On the other hand, because the glass transition temperatures of ECA2, and especially ECA3, are below the aging temperature, water molecules may more easily permeate into these polymers and interact with the polymer chains. Because ECA2, and especially ECA3, contain a considerable amount of ester-based linkages which are hydrolytically unstable [38], it is very likely that water hydrolysis might have occurred and caused chain scission in these two adhesive systems during the environmental aging. The small molecules resulting from degradation can also be released from the materials during heating after aging, and may contribute to the greater weight loss of aged samples at 200–300°C as compared with the as-cured ECA samples.

3.2.3 Effects of Environmental Aging on Damping Behavior of ECAs

Figures 9–11 show the traces of the loss factor obtained on aged and then redried samples of ECA1, ECA2, and ECA3, along with the traces

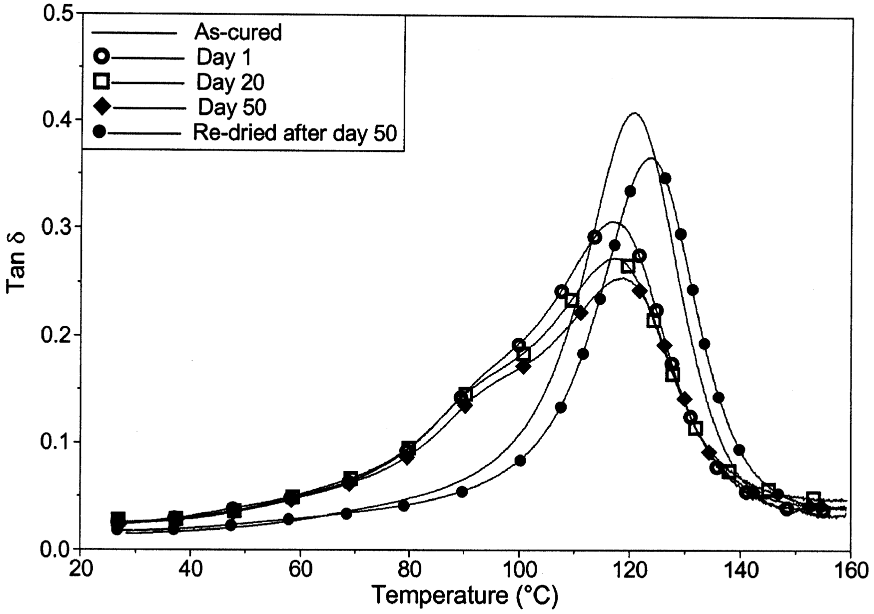

FIGURE 9 The loss factor of aged and dried ECA1 samples, as measured by DMA at 1Hz and 1°C/min.

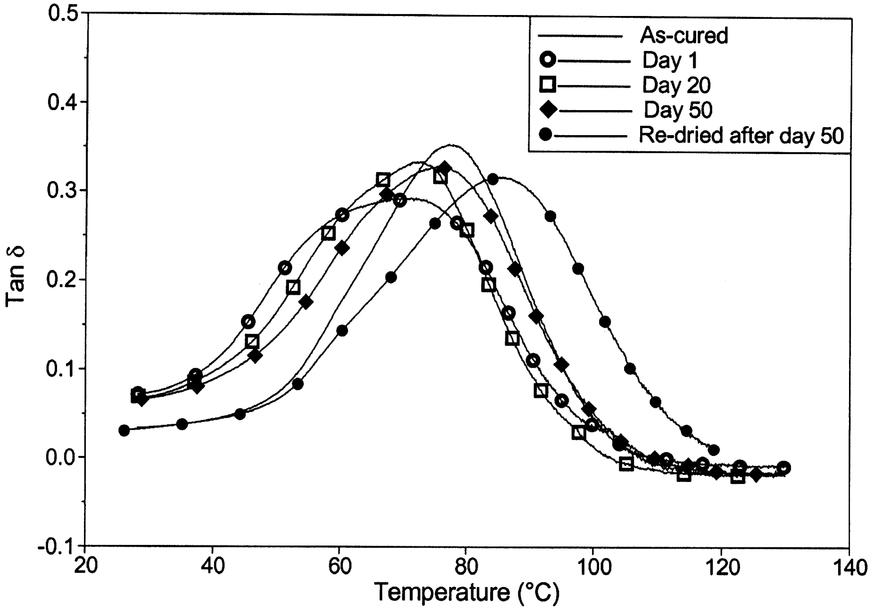

FIGURE 10 The loss factor of aged and dried ECA2 samples, as measured by DMA at 1Hz and 1°C/min.

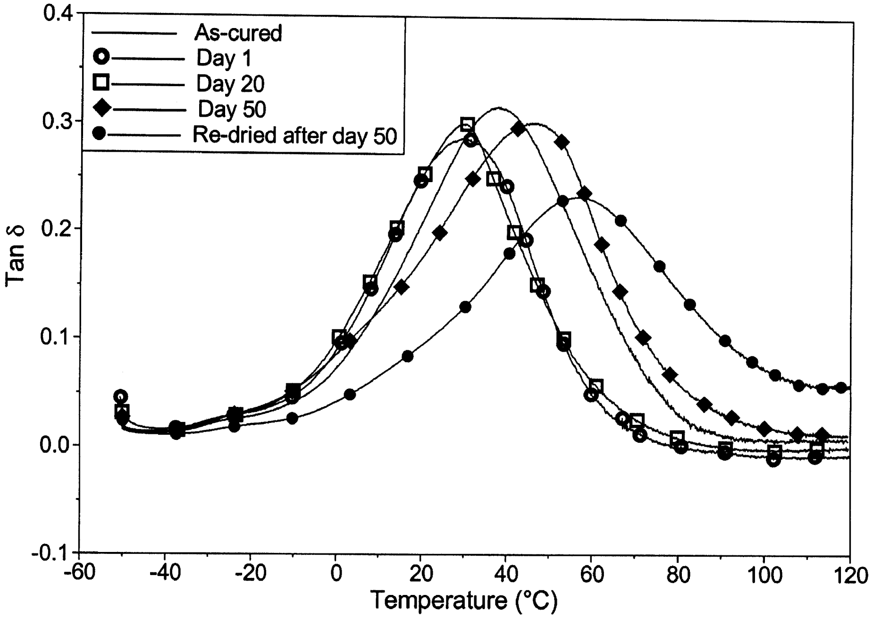

FIGURE 11 The loss factor of aged and dried ECA3 samples, as measured by DMA at 1Hz and 1°C/min.

of the loss factor of as-cured samples for comparison. The redried samples were heated to 150°C for 2 h following aging for 50 days to remove the water absorbed during aging. Because the DMA tests involve a dynamic heating process, water may have continued to evaporate from aged samples (that were not redried) during the temperature sweep. This complicates direct analysis, though the results should still be comparable for the same material aged at different times. 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 a tendency to shift back to higher temperatures for all the three conductive adhesives, though the magnitude of the shift is different for each adhesive. ECA1 exhibits a slight change in the position of the loss factor peak for samples aged up to 50 days, 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 desorption may be attributed to further crosslinking in the water-plasticized conductive adhesives. As water sorption and crosslinking of a polymer may have opposite effects on the T_g (referring 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 a relatively stable viscoelastic transition upon exposure to environmental aging, while the viscoelastic behavior of ECA2 and ECA3 is greatly affected by water ingression. The different reactions of the three adhesives to water attack may be explained by the 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.

Close inspection of the DMA traces for ECA1 (See Figure 9) further reveals that the loss factor curve of the aged ECA1 samples exhibits a shoulder in the temperature range of 80–100°C, whereas the as-cured and redried samples show smooth curves 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 investigate further 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 12, 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 located at 100°C, which is the boiling point of water. This finding further confirms that water, which was absorbed in the ECA1 and had 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 a 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.

Effects of Environmental Aging on the Tensile Properties of ECAs

Figures 13 and 14 summarize the tensile strength and failure strain results obtained on ECA1, ECA2, and ECA3 samples aged at 85° and 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

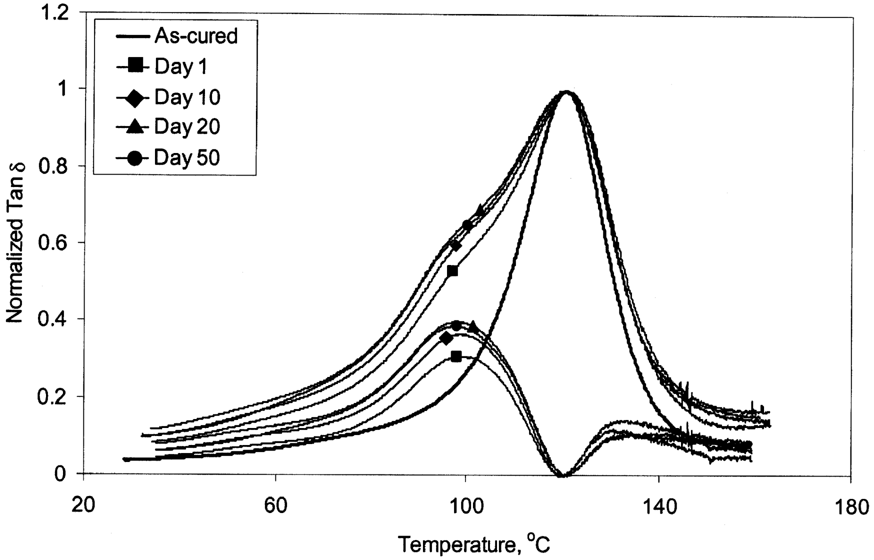

FIGURE 12 Effects of moisture on the damping properties of ECA1, as measured by DMA at 1Hz and 1°C/min.

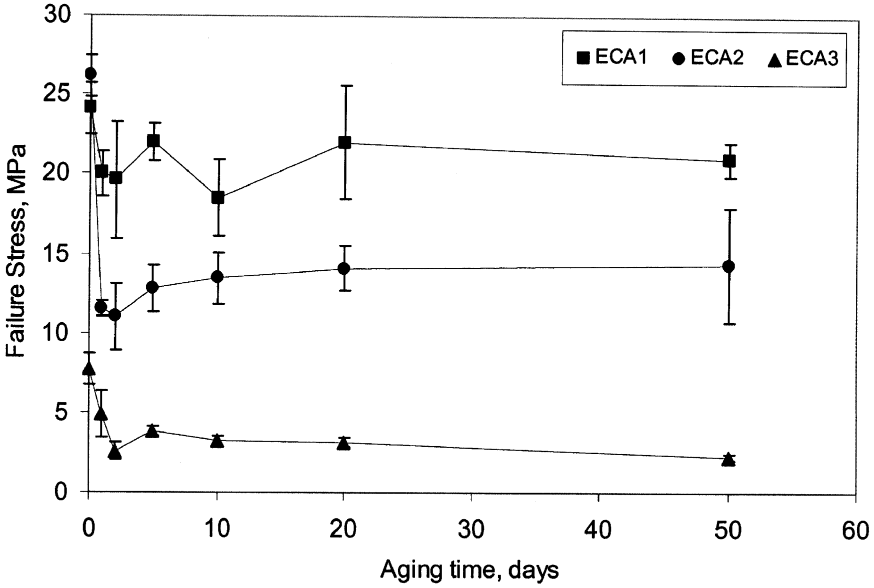

FIGURE 13 Failure stress of ECAs as a function of aging time.

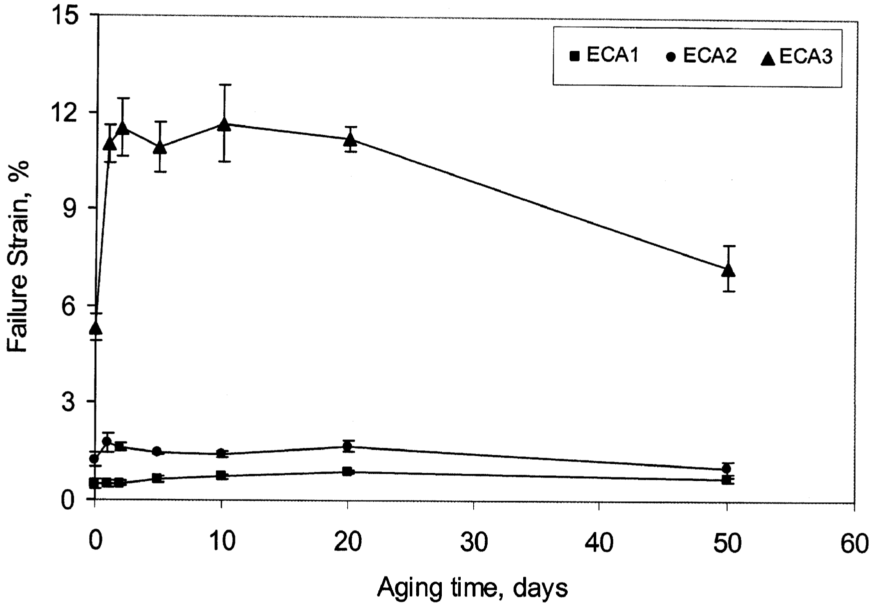

FIGURE 14 Failure strain of ECAs as a function of aging time.

meant to imply actual trends. The error bars in the figures are one standard deviation and are obtained from at least four specimens per condition. The overall trend is that the tensile strength and failure strain exhibit significant changes in the initial day or two of aging, with the tensile strength going down and the failure strain going up, as compared with 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 15–17. Careful observation of the tensile strength results further reveals that the tensile strength exhibited slight recovery for all three conductive adhesives after the significant drop during the initial 1 or 2 days of aging and before plateauing. The reduction in the tensile strength and increase in failure strain upon exposure of the adhesives to the hot/wet environment can be attributed to the plasticization of the adhesive materials caused by moisture absorption, 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

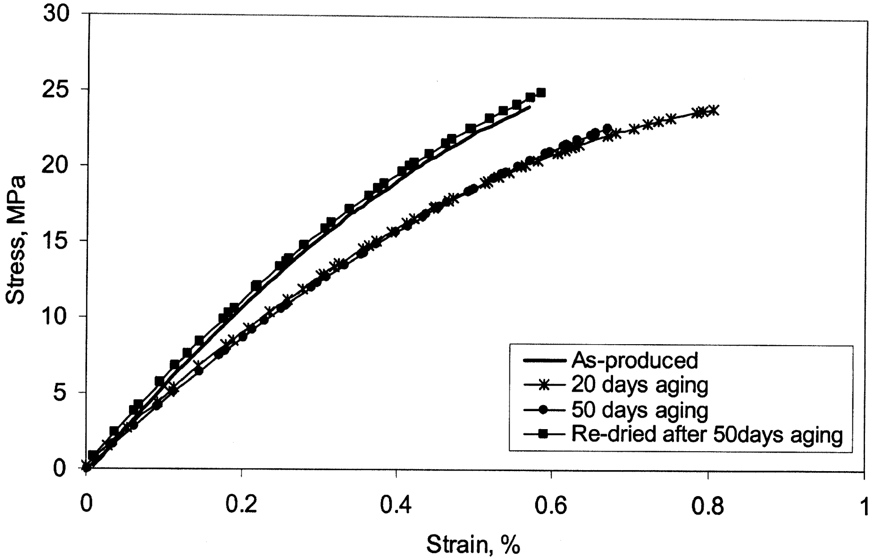

FIGURE 15 Typical stress-strain curves from aged and dried ECA1 samples.

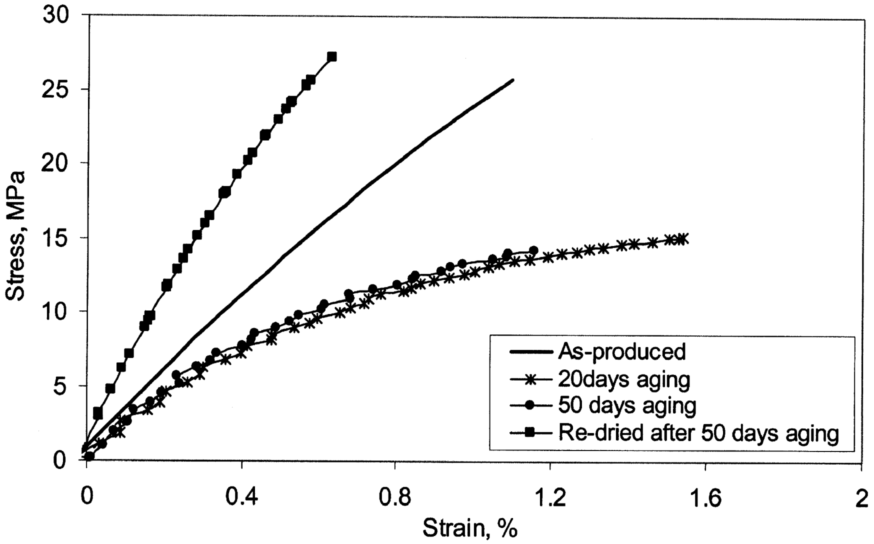

FIGURE 16 Typical stress-strain curves from aged and dried ECA2 samples.

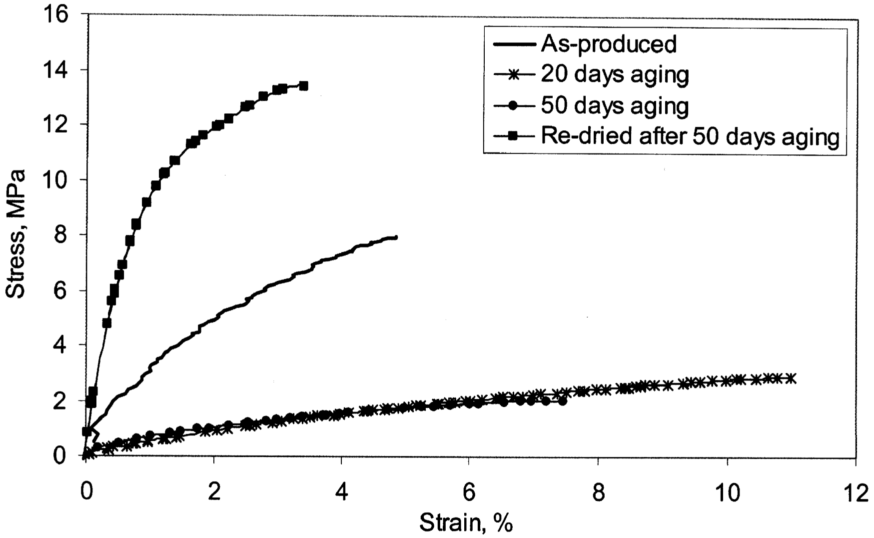

FIGURE 17 Typical stress-strain curves from aged and dried ECA3 samples.

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 significantly less within this 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 ingression compared with ECA2 and ECA3 aged for the same period of time.

Figures 15–17 show characteristic stress-strain curves of aged and redried 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 absorption. 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 [13–15] 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 adhesives after 50 days aging may be due to material degradation such as hydrolysis or oxidation when exposed to the hot/wet environment.

Some samples aged for 50 days were redried at 150°C for 2 h to drive out the water absorbed in the samples. Results obtained on the redried samples are also shown in Figures 15–17. The stress-strain curve of the redried 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 a 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 ingression in the conductive adhesives have altered the mechanical properties in both reversible and irreversible ways. Plasticization, a reversible effect, can be erased upon drying and, as a result, the adhesive properties altered by the reversible process can be recovered. On the other hand, irreversible effects, such as further crosslinking and polymer chain degradation, may have chemically changed the materials and resulted in permanent changes in the adhesive properties. The full recovery of stress and strain behavior of ECA1 upon redrying 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. As ECA1 contains more epoxy resin than ECA2 and ECA3, and no ester-based linkages, ECA1 may be expected to exhibit better resistance to water attack and better hydrolytic stability than ECA2 and ECA3.

CONCLUSIONS

This study was performed to characterize the thermal and mechanical properties of three model electrically conductive adhesives and to investigate the effects of hydrothermal aging on the properties of the three conductive adhesives, which were designated as ECA1, ECA2, and ECA3, respectively. As-cured adhesives exhibit significant differences in glass transition temperature, damping behavior, tensile strength, and 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 an 85°C and 100% RH environmental condition, may have experienced both a 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 molecules. 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 ingression in that both the damping properties and the mechanical strengths 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 chemical compositions of the three adhesives which subsequently result in different diffusivity of water into the materials, as well as chemical stability.

TGA, DMA, and stress-strain results obtained on aged and redried samples suggest that water ingression in the conductive adhesives has 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 mechanical properties of the adhesives. The full recovery of the stress and strain behavior of ECA1 upon redrying demonstrates that ECA1 might have mainly experienced the reversible effect of water and that 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 reveal that both adhesives have exhibited both reversible and irreversible effects during aging.

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