

Study on Mobility of Water and Polymer Chain in Epoxy and Its Influence on Adhesion

SHIJIAN LUO,¹ JOHANNES LEISEN,² C. P. WONG¹

¹ Packaging Research Center, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

² Georgia Tech NMR Center, Georgia Institute of Technology, Atlanta, Georgia 30332

Received 19 July 2001; accepted 9 September 2001

ABSTRACT: This paper presents a study on the mobility of water and polymer chains in epoxy materials and its influence on the rate of adhesion degradation in a humid environment. Solid state nuclear magnetic resonance (NMR) techniques (both ¹H NMR and ²H NMR) were used to study the binding states of water within two epoxy formulations along with the possible plasticizing effects of moisture affecting the mobility of polymer chains. Absorbed water reduces the glass transition temperature of polymeric materials. However, the presence of moisture has no significant effect on the polymer chain mobility at temperatures below the reduced glass transition temperature. Water in an epoxy in its rubbery state above the glass transition has a much higher mobility than in a polymer in its glassy state. The mobility of water absorbed by a polymer in its rubbery state is similar to that of pure water. The translational mobility of water within epoxies was studied by measuring the diffusion coefficient of water in epoxies through the water uptake. Higher rotational mobilities of water and polymer chains in the rubbery state lead to a significant increase of the water diffusion coefficient in the rubbery state polymer matrix as compared to a polymer in its glassy state. The higher mobility of absorbed water and the higher mobility of polymer chains in epoxy lead to faster adhesion degradation during aging in a humid environment. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1–8, 2002

Key words: water absorption; solid state nuclear magnetic resonance; epoxy; mobility; water diffusion; adhesion degradation; aging

INTRODUCTION

Epoxy has excellent properties such as a good adhesion to many substrates due to the presence of highly polar hydroxyl and ether groups. In the

microelectronics industry, epoxy is widely used as molding compound, underfill encapsulant, and coating for the protection of integrated circuits. However, unlike metals and ceramics, epoxy cannot provide a hermetic encapsulation. The permeability of moisture in organic materials such as epoxy is orders of magnitude higher than in metals or ceramics. Absorbed moisture affects the thermomechanical properties of epoxy materials, reducing the glass transition temperature (T_g), the modulus, and the strength, especially at high

Correspondence to: C. P. Wong (cp.wong@mse.gatech.edu).
Contract grant sponsor: National Institute of Standards and Technology

Journal of Applied Polymer Science, Vol. 85, 1–8 (2002)
© 2002 Wiley Periodicals, Inc.

temperatures. Moisture diffusion through epoxy is the major cause of corrosion of metals in electronic packaging. The adhesion of an epoxy to a substrate may be affected when moisture is absorbed by the epoxy. Moisture may also be absorbed by uncured epoxy, thus affecting the curing properties of epoxy and the thermomechanical properties of the cured material.¹

Moisture diffusion in epoxy can be monitored gravimetrically *in situ*. Another method to monitor moisture diffusion in epoxy uses a dielectric analyzer (DEA), which is based on the principle that absorbed moisture increases the dielectric constant of epoxy materials.²

The mechanism of moisture diffusion in epoxy has been extensively studied.^{4–6} Moisture transport in polymers is related to molecular-sized holes (nanovoids) within the polymer matrix and to the polymer matrix–water affinity. There are two states of water in the water-absorbed epoxy system. The unbonded free water, filling the nanovoids, does not cause swelling. Hydrogen-bonded water, on the other hand, causes swelling of the polymer. The amount of volume change due to moisture-induced swelling is significantly less than the volume of moisture absorbed, indicating that a large portion of absorbed water resides in the nanovoids.⁷ Although amino and hydroxyl groups in epoxies have a strong affinity to water, not every of these polar groups attracts a water molecule. This is due to the formation of hydrogen bonds between these polar groups on polymer chains. It is well accepted that the polarity of polymers affects the diffusion of water. However, it has not been established to what extent the topology has a significant effect on the moisture diffusion. The traditional theory suggests that the free volume affects the moisture absorption. However, studies have found no correlation between the topology (nanovoid size and total volume of nanovoids) and the moisture transport.⁵ Only when a series of resins with similar polarities were compared was the topology found to affect the moisture uptake. But the size and volume of nanovoids measured by positron annihilation lifetime spectroscopy (PALS) is not correlated with the kinetics of moisture transport.⁸ Additionally, it was found that the diffusion coefficient of moisture at low temperatures (5°C) is significantly greater in resins containing no amines than in amine-containing resins.⁸ At high temperatures (90°C), however, there is no significant difference between these epoxies.⁸ It was proposed that the

nanoporous structure, the polarity, and molecular motions of epoxy act in concert to control the moisture transport in epoxy materials.⁵ The dynamics of local-scale motions of a sub- T_g relaxation process appears to be the rate-limiting factor for moisture transport. Polar sites act as the bottleneck for transport through nanopores; the rate of formation and breakage of internal hydrogen bonds dictates the rate of the moisture transport. Furthermore, water in the nanopores may form hydrogen bonds with polymer chains, and thus the nanopores become blocked and water transport is reduced.⁵

Although the water diffusion mechanism in epoxy resins has been extensively studied, and the effect of water on the thermomechanical property of epoxy resin is generally understood, there is some concern regarding the understanding of binding states of water absorbed in epoxies. So far, the mobility of water in a polymer matrix and how absorbed water affects the mobility of polymer chains at temperatures below and above T_g are not well known. The objective of this study was to investigate the mobility of water and polymer chains in water-soaked epoxy formulations with solid state nuclear magnetic resonance (NMR) techniques. The translational mobility of water within epoxies was studied by measuring the diffusion coefficient of water in epoxies through the water uptake. The mobility of absorbed water and polymer chains was correlated to the rate of adhesion degradation in humid environments.

EXPERIMENTAL

Materials

Two epoxy systems with different glass transition temperatures were used in this study. Formulation A consists of 1 equivalent cycloaliphatic epoxy resin ERL4221 (7-oxabicyclo[4,1,0]heptane-3-carboxylic acid 7-oxabicyclo[4,1,0]hept-3-ylmethyl ester) from Union Carbide, 0.8 equivalent of hardener 4-methylhexahydrophthalic anhydride (MHHPA) from Aldrich Chemicals, and cobalt (II) acetylacetonate (0.4% of total weight of epoxy resin and hardener) from Aldrich as catalyst. The formulation A was cured in an oven at 250°C for 30 min. Formulation B consists of 1 equivalent of epoxy resin 1,4-butanediol diglycidyl ether from Aldrich, 0.8 equivalent of hardener MHHPA, and

catalyst 2E4MZ-CN (1-cyanoethyl-2-ethyl-4-methylimidazole, 1% of total weight of epoxy resin and hardener). Formulation B was cured at 175°C for 30 min.

Measurement of Glass Transition Temperature

The glass transition temperatures of all materials were measured using a modulated differential scanning calorimeter (TA Instruments, DSC 2920) with a heating rate of 5°C/min. The cured epoxy formulation A had a T_g of 190°C. T_g was found to drop to 130°C after the cured formulation A had been stored in a humid environment with 85% relative humidity (RH) at 85°C (85/85 chamber) for an extended period of time (500 h). For formulation B the T_g was 65°C for the dry sample and 45°C after storage in the 85/85 chamber for an extended period of time (500 h).

NMR Study

^1H NMR experiments of sample A were performed on a Bruker DSX-400 NMR spectrometer operating at a magnetic field strength of 9.4 Tesla corresponding to an excitation frequency of 400 MHz for ^1H . Spectra were recorded using a simple single pulse excitation sequence. In order to minimize the dead time between the radiofrequency (rf) pulse and the detection period a pulse length of 1 μs (corresponding to a pulse angle of about 20°) was used. The repetition delay between scans was 4 s. Between 4 and 32 scans were accumulated for each spectrum.

^2H NMR experiments of sample A were recorded on a Bruker DSX-300 NMR spectrometer operating at a magnetic field strength of 7 Tesla and an excitation frequency of 46 MHz for ^2H . Data were recorded using the quadrupolar echo sequence,⁹ which is based on two rf pulses. The length of these pulses was 3 μs and the spacing between the pulses was set to 30 μs . The repetition delay between scans was chosen to 500 ms and 8000 scans were accumulated for each spectrum.

Sample A was investigated using the optimum conditions available for ^1H and ^2H experiments, so that two different NMR spectrometers were used. Therefore, different sample preparations had to be investigated for the ^1H and ^2H experiments. In order to observe ^1H and ^2H NMR spectra of one single sample, sample B was investigated on the DSX-300 using a two-channel probe,

with one channel tuned to the frequency of ^1H (300 MHz) and the other channel tuned to ^2H (46 MHz). This way it was possible to record subsequent ^1H and ^2H experiments without changing samples or hardware settings. The experimental parameters used to characterize sample B are otherwise identical to those used for sample A.

Study on Moisture Diffusion Kinetics

The epoxy formulations were cured into circular disks with a diameter of 50 mm. The cured samples were polished until a uniform thickness was achieved. Then they were dried in a vacuum oven to remove any moisture absorbed during the polishing process. The dried samples were weighed and then placed in an 85°C/85% RH (85/85) chamber. The specimens were taken out of the chamber at different intervals and weighed. The saturated moisture pickup for formulation A after 85/85 aging is 2.7%, and the saturated moisture uptake for formulation B after 85/85 aging is 2.0%. The glass transition temperature after the moisture absorption is 130°C for formulation A, 45°C for formulation B.

Die Shear Sample Preparation and Die Shear Test

Silicon nitride passivated silicon dies (2 × 2 mm and 20 × 20 mm) were cleaned according to the standard procedure mentioned in Ref. 10. The steps were as follows: 5 min soak in terpene; 5 min soak in terpene during ultrasonic cleaning; 5 min soak in isopropyl alcohol; 5 min soak in isopropyl alcohol during ultrasonic cleaning; 3 rinses in deionized water; drying in oven at 120 °C for 30 min under vacuum. Glass beads (0.5% weight of underfill), with a diameter of 75 μm , were used as spacers to control the gap between the top and bottom dies. The smaller dies were dipped into a thin liquid film of the underfill to coat a uniform thin layer, and then placed on the larger die (20 × 20 mm). The die shear samples with different formulations were then cured according to their individual prescribed curing schedules. The die shear samples were aged in an environmental chamber at 85°C with 85% relative humidity. Die shear tests were performed on a die bond tester (Model 550-100K, Royce Instruments) for samples aged for different times. The adhesion strength is reported in MPa.

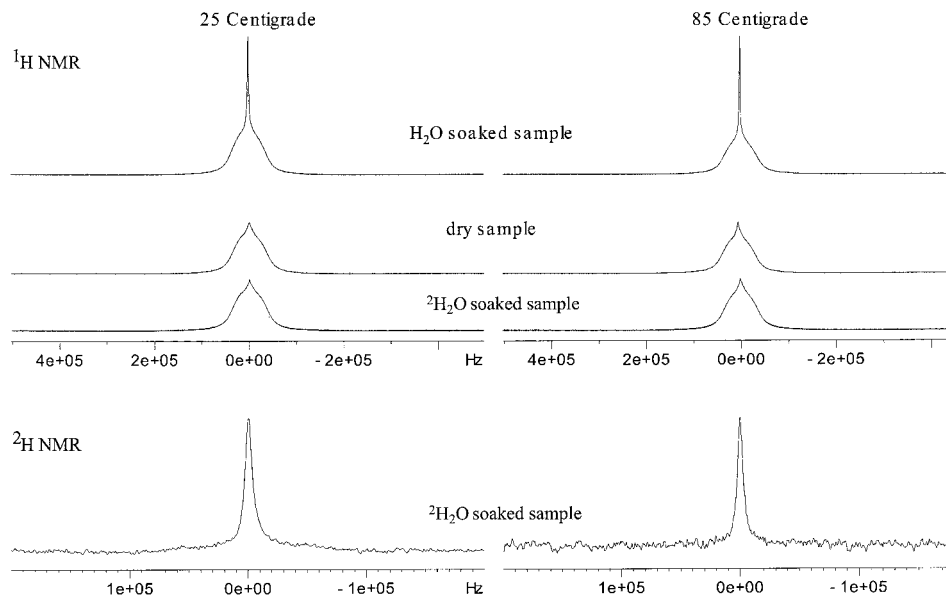


Figure 1 Solid state NMR spectra of formulation A at 25°C (left side ones) and at 85°C (right side ones) before and after water soaking.

RESULTS AND DISCUSSION

NMR Study on Formulation A

Samples in this study were investigated using ^1H and ^2H NMR mainly with the purpose of using isotope labels in order to achieve a spectroscopic distinction between water and the polymer matrix. While both techniques measure different nuclei, the interpretation of ^1H and ^2H solid state spectra is the same with the respect that the peak width of the spectrum is directly related to the mobility of the ^1H or ^2H environment. Broad lines correspond to moieties with no motion or motion occurring as small amplitude fluctuations with rates exceeding hundreds of kHz (librations). While narrow lines indicate large angle rotational motions with frequencies exceeding again hundreds of kHz. Note that solid state NMR experiments allow the determination of diffusion constants describing the rotational motion of molecules. Consequently, our qualitative discussion of NMR lineshapes is concerned with the extent and frequency of rotational motions experienced by either water molecules or the polymer matrix.

Both ^1H NMR and ^2H NMR, are based on different physical interactions. The ^1H NMR line width is given by dipolar interactions between individual ^1H nuclei. For the case of a rigid proton rich system, where no motion occurs, commonly

lineshapes resembling a Gaussian bell shape are observed. The width at half height of these spectra is 50 kHz and larger. The lineshape in ^2H solid state spectra is due to the interaction of the quadrupole moment of the ^2H nucleus with the electric field gradient tensor experienced by individual ^2H nuclei. This interaction is often better defined than the dipolar interaction experienced between several ^1H nuclei. ^2H NMR is therefore ideally suited to characterize molecular motions in great detail. For the context of this paper, it is only important to mention that characteristic “Pake Patterns” with a splitting of around 128 kHz will be observed for completely rigid, non-mobile molecules containing ^2H nuclei.¹¹

Figure 1 shows ^1H and ^2H solid state NMR spectra of formulation A at 25 and 85°C before and after soaking with regular water (H_2O) and deuterated water ($^2\text{H}_2\text{O}$ or D_2O). Note that the ^1H spectrum recorded for the samples soaked in H_2O contains clearly two components: a narrow component (width at half height of 2–3 kHz) corresponding to water and a broad component corresponding to the epoxy matrix (width at half height of ca. 70 kHz). ^1H NMR spectra of the dry sample and of the sample soaked in D_2O validate the accuracy of this interpretation. Isotopically pure D_2O will not give any ^1H NMR signal and deuterated water can be considered to be chemi-

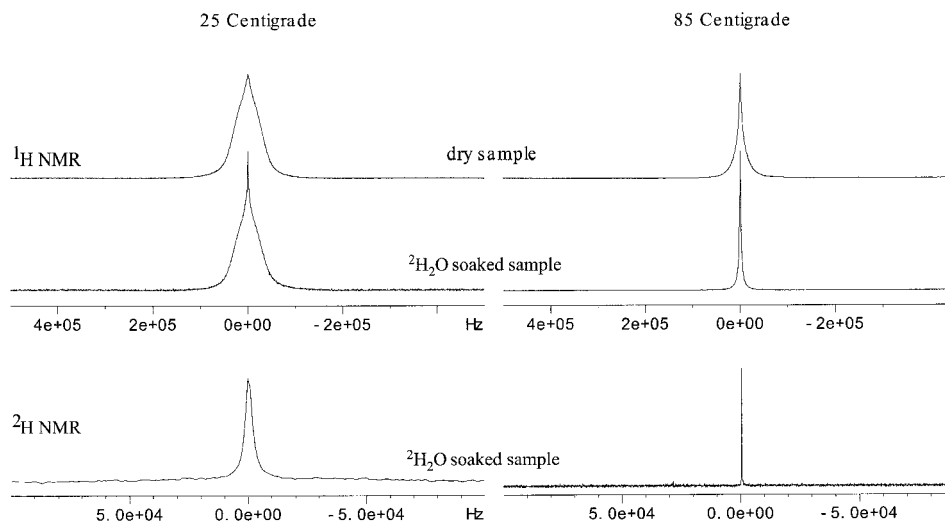


Figure 2 Solid state NMR spectra of formulation B at 25°C (left side ones) and at 85°C (right side ones) before and after water soaking.

cally almost identical to regular water. Therefore, the sample soaked in deuterated water will yield a NMR signal, which is entirely due to the protons of the polymer chains, while at the same time a wet sample is being investigated. For the dry sample and the sample soaked in D_2O virtually identical lineshapes are found, which are due to the rigid polymer components below the glass transition. Hence, the polymer chain mobility of formulation A is not significantly affected by absorbed water either at 25 or at 85°C, which are both temperatures significantly below the glass transition of formulation A. While water does not appear to have an effect on the chain mobility, a thorough analysis of NMR spectra of the dry samples reveals that the temperature increase from 25 to 85°C leads to a slight decrease in the peak width of the dry sample, indicating that the polymer chain becomes slightly more mobile at higher temperatures. This difference becomes most obvious when comparing directly NMR data as recorded in the time domain (data not shown here). Since this is a rather small effect, it is most likely that this increase in mobility is due to an increase in small angle fluctuations.

The mobility of water in the epoxy is best assessed from the 2H NMR spectra measuring the mobility of deuterated water within the epoxy matrix. The peak width observed here is in the range of 7.5 kHz, which is significantly broader than the width observed for free water (30 Hz, given by instrumental limitations). It is especially

noteworthy, that a broad component with a width at half height of around 120 kHz is clearly visible at 25°C. Epoxy A does not contain any free hydroxyl or amino groups, which could undergo a chemical exchange with the deuterium found in D_2O . Hence, the broad component is likely due to water, which is almost completely immobilized by binding to the epoxy matrix. The absence of a characteristic “Pake Pattern,” as observed for immobile molecules containing deuterium, leads to the conclusion that a distribution of mobilities and binding states exists. Increasing the temperature to 85°C leads to a slight decrease in the width of the narrow peak and hence an increased water mobility. Additionally, the broad component in the spectrum due to strongly bound water is significantly reduced in intensity.

NMR Study on Formulation B

Due to the high glass transition temperature of sample A, it was only possible to investigate sample A at temperatures far below the glass transition. Formulation B was prepared in order to study the state of absorbed water in epoxies both below and above T_g . Figure 2 shows the solid state NMR spectra of the dry and D_2O soaked formulation B at 25 and 85°C. The peak width observed for the dry sample at 85°C (above its T_g) is much narrower than that at 25°C (below its T_g). The polymer chain mobility as investigated by 1H NMR differs greatly below and above the glass

transition temperature. This is expected, since the glass transition is known to be ongoing with large amplitude motions of the polymer chain.¹² The ^1H NMR spectrum of the D_2O soaked formulation B at 25°C shows a narrow component overlying broad peak. This is attributed to a small amount of ^1H within the D_2O due to proton exchange with moisture in air during the sample preparation. Only a slight effect of water on the mobility of polymer chains is found at 25°C , when this narrow peak is neglected and the broad parts of the ^1H NMR spectra of the dry formulation B and the D_2O soaked formulation B at 25°C are compared. However, clear differences between ^1H NMR spectra of the dry and D_2O soaked formulation B at 85°C are obvious. This is expected since measuring at 85°C means measuring 20°C above T_g for the dry sample and measuring 40°C above T_g for the water soaked sample. Comparing the chain mobilities within wet and dry epoxies at comparable temperatures above T_g will be part of our future studies.

Comparing the two ^2H NMR spectra in Figure 2 shows interesting results. The D_2O in this cured formulation B has a much higher mobility at 85°C (above the glass transition temperature of the polymer) than at 25°C (below the glass transition temperature). This indicates that the water mobility is totally different below and above the T_g of the polymer matrix. Water has a much higher mobility in the polymer in its rubbery state than in its glassy state. The mobility of water above T_g of the polymer appears to be close to that of free water. Hence, it does not appear to be affected by the rubbery state polymer matrix.

Study on Moisture Diffusion Kinetics

The moisture absorption by epoxy at $85^\circ\text{C}/85\%\text{RH}$ condition can generally be described by Fick's law:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) \quad (1)$$

where C is the concentration of water, t is time, D is water diffusion coefficient, and x is the axis along the concentration gradient.

For the large plane sheet sample, the initial stages of the moisture uptake and diffusion process may be described by the following equation¹³:

$$\frac{M_t}{M_\infty} = 4 \left[\frac{D}{\pi l^2} \right]^{1/2} t^{1/2} \quad (2)$$

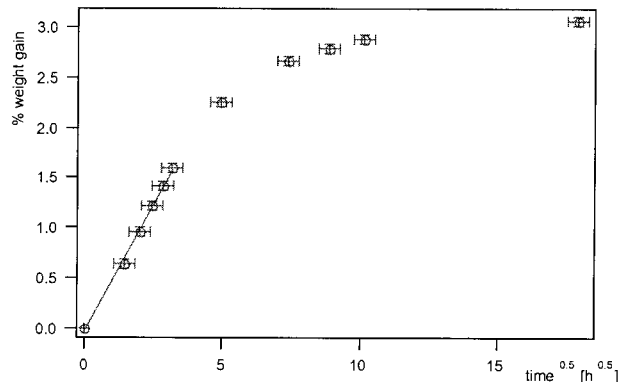


Figure 3 Moisture content in percent vs $t^{1/2}$ for epoxy formulation A with a thickness of 2.6 mm (85°C , 85% RH). Also indicated is the fit of the initial data to eq. (3).

where l is the half thickness of sample, and M_∞ is the mass of moisture contained in the epoxy at equilibrium. M_t is the moisture mass at time t .

The original weight of the dry sample (M_o) can be introduced into the equation above, and then eq. (2) can also be written as

$$\frac{M_t}{M_o} = 4 \frac{M_\infty}{M_o} \left[\frac{D}{\pi l^2} \right]^{1/2} t^{1/2} \quad (3)$$

The slope (k) of the initial linear region of the plot of the moisture content M_t/M_o vs $t^{1/2}$ would be

$$k = 4 \frac{M_\infty}{M_o} \left[\frac{D}{\pi l^2} \right]^{1/2} \quad (4)$$

Then the diffusion coefficient can be calculated:

$$D = \frac{k^2 \pi l^2}{\left(4 \frac{M_\infty}{M_o} \right)^2} \quad (5)$$

Several large disk samples with different thickness were prepared and their moisture absorption at 85°C and 85% relative humidity was recorded as a function of time. M_t/M_o was plotted vs $t^{1/2}$ in order to determine the slope k (Fig. 3). Several experiments using samples with different thickness were performed in order to determine the diffusion coefficients of $D = 0.011 \pm 0.001 \text{ mm}^2/\text{h}$ for the sample A. Cured formulation A at 85°C is in its glassy state, while sample B is in its rubbery state. At 85/85 conditions the diffusion coefficient for sample B was found to be 0.033 ± 0.003

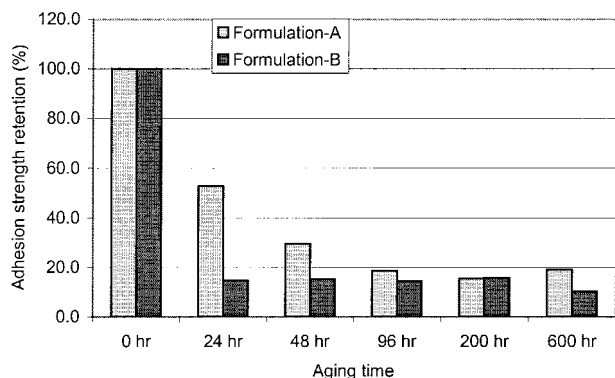


Figure 4 Adhesion strength retention of underfills during 85/85 aging (substrate: Si_3N_4).

mm^2/h , which is about three times as high as the diffusion coefficient found for moisture in the glassy state. Two interacting factors contribute to the higher moisture diffusion coefficient. One is the higher polymer chain mobility, and the other is the higher mobility of water within the rubber polymer matrix.

Influence of Component Mobility on Adhesion Degradation Rate

During aging at $85^\circ\text{C}/85\%$ relative humidity, moisture can saturate the epoxy materials with a cross section of 2 by 2 mm between the two substrates in less than 24 h.¹⁴ The adhesion strength of the two epoxy formulations to Si_3N_4 passivation for integrated circuit chip under $85^\circ\text{C}/85\%$ relative humidity aging was measured at various aging times. Adhesion strength decreased after 24 h of 85/85 aging for both formulation A and formulation B. However, a dramatic difference in the degradation rate of adhesion strength can be seen between formulation A and formulation B (Fig. 4). Half of adhesion strength was lost after 24 h of 85/85 aging for formulation A. Further aging in 85/85 condition further reduced the adhesion strength. This showed that the adhesion degradation is not complete as soon as the underfill is saturated with moisture. The adhesion strength reached an equilibrium value after 96 h of 85/85 aging.

The degradation of the adhesion of underfill formulation B with a relatively low glass transition temperature (T_g) was very fast. About 85% of original adhesion strength was lost after 24 h of 85/85 aging. Further aging for 48, 96, and 200 h seemed to have no additional effect on the adhe-

sion strength. It seems that the adhesion strength reached an equilibrium value after 24 h of 85/85 aging.

The difference in rate of adhesion degradation is related to the mobility of polymer chains of epoxy formulations and the activity of the absorbed water under 85/85 aging condition. The higher mobility of the absorbed water and polymer chain in formulation B leads to the faster adhesion degradation during 85/85 aging.

CONCLUSIONS

The absorbed moisture in epoxy materials can lead to a decrease of the glass transition temperature due to the plasticizing effect of water. However, solid state NMR studies showed that the absorbed moisture does not significantly increase the mobility of the polymer matrix below its reduced glass transition temperature. The chain mobility at temperatures above the glass transition temperature is greatly increased. A distribution of binding states from almost totally immobilized water to mobile water is likely in water-containing epoxies below the glass transition. However, it is evident that water within epoxies below its glass transition temperature is significantly less mobile with respect to rotational motions than free water. The mobility of water in an epoxy in its rubbery state is close to that of free water. The higher mobility of polymer chains and water contribute to the higher water diffusion coefficient in the rubbery polymer and faster adhesion degradation during humidity aging.

This work has been funded by the National Institute of Standards and Technology (NIST) through the Advanced Technology Program (ATP). The discussion with Dr. H.W. Beckham is highly appreciated.

REFERENCES

- Chian, K. S.; Lim, S. H.; Yi, S.; Chen, W. T. In Proceedings of the International Symposium on Electronic Materials and Packaging, Nov. 30–Dec 2, 2000, Hong Kong, p 289.
- Tong, W.; Teng, A. In Proceedings of International Symposium on Electronic Materials and Packaging, Nov. 30–Dec. 2, 2000, p 464.

3. Wong, T. C.; Broutman, L. J. *Polym Eng Sci* 1985, 25(9), 529.
4. Vanlandingham, M. R.; Eduljee, R. F.; Gillespie, J. W., Jr. *J Appl Polym Sci*, 1999, 71, 787–798.
5. Soles, C. L.; Yee, A. F. *J Polym Sci Part B Polym Phys* 2000, 38, 792–802.
6. Soles, C. L.; Chang, F. T.; Bolan, B. A.; Hristov, H. A.; Gidley, D. W.; Yee, A. F. *J Polym Sci Part B Polym Phys* 1998, 36, 3035.
7. Adamson, M. J. *J Mater Sci* 1980, 15, 1736.
8. Soles, C. L.; Chang, F. T.; Gidley, D. W.; Yee, A. F. *J Polym Sci Part B Polym Phys* 2000, 38, 776–791.
9. Davis, J. H., et al. *Chem Phys Lett* 1974, 42, 390.
10. Wong, C. P.; McBride, R. *IEEE Transactions on Components, Packaging, and Manufacturing Technology—Part A*, 1994, 17(4), 542–552.
11. Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 1994.
12. Leisen, J.; Schmidt Rohr, K.; Spiess, H.W. *J Non-Crystalline Solids* 1994, 172–174, 737.
13. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, 1975.
14. Luo, S.; Wong, C. P. In *Proceedings of the 51st Electronic Components & Technology Conference*, May 2001, Lake Buena Vista, FL, p. 155.