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WATER TRANSPORT IN EPOXY RESINS

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CONTENTS

1. THE STRUCTURE OF GRAPHITE/EPOXY COMPOSITES

1.1. *Epoxy resin matrix*

The resin matrix in fiber composites has two primary functions: (1) to enable the fibers to provide higher mechanical strength of the composite over neat resin; and (2) to hold the fibers together and distribute the stresses among them. Polymers used as matrices in composites are varied in properties. The main resins used in high performance fiber composites are thermosetting polymers that can be used at high temperature. Thermoplastic polymers are used to a lesser extent, because they are subject to changes in hardness with temperature, solvent resistance is often poor, and high melt viscosity makes fiber wetting and infiltration difficult. However, they are finding increased applications as composite matrices because of their low prices and low moisture absorption.

Among several kinds of thermosetting resins, epoxy resins are well known for their chemical resistance, toughness in some cases, and low shrinkage on curing. Although these materials are relatively expensive, their superior properties often make them the resins of choice in high performance fiber composites.

The main prepreg matrix resins used in graphite fibers for aircraft are the

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tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) epoxy resins. The heat resistance of these resins is outstanding. Their weaknesses include high moisture absorption, low fracture toughness, and an elongation at break of 3% or lower.[1] The diglycidyl ether of bisphenol A (DGEBA) is also commonly used. Epoxide resins are cured with crosslinking agents, of which amine crosslinking agents have at least two reactive amine groups that crosslink the epoxide resins. The mechanical properties of cured epoxy resins can be changed depending on the curing agent used, selection of the proper times and temperature of curing, and use of processing methods for minimizing the presence of voids in the composites. The curing agents generally used are diaminodiphenyl sulfone (DDS), triethylene tetramine (TETA), dicyandiamide (DICY), benzyldimethylamine (BDMA), and boron trifluoride monoethylamine (BF_3MEA).

1.2. *Graphite/epoxy composites*

Graphite/epoxy composites consist of graphite fibers embedded in an epoxy matrix. The graphite fibers provide stiffness and strength, while the epoxy matrix distributes the stress to and among the fibers and holds them together. Graphite/epoxy composites have higher tensile moduli, tensile strength, and (sometimes) toughness and much lower density than metals.

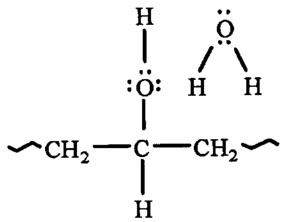
Graphite fibers are prepared chiefly from polyacrylonitrile (PAN), rayon or pitch.[2] These three types of precursors are heated in the presence of oxygen at temperatures of up to 400°C, then carbonized in an inert gas[3] at temperatures of up to 1500°C, and finally graphitized in the presence of an inert gas at temperatures of up to 2800°C. As the temperature of carbonization is increased, dehydrogenation occurs in the range of 400 to 600°C and denitrogenation at 600 to 1300°C. Graphite fibers have a more highly organized three-dimensional crystalline structure than non-graphitized carbon fibers. Therefore, graphite fibers have higher moduli and strength, and are better electrical and thermal conductors, than non-graphitized carbon.

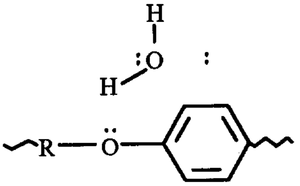
2. WATER EFFECTS ON GRAPHITE/EPOXY COMPOSITES

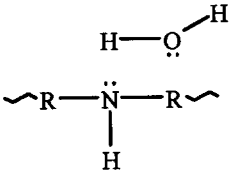
2.1. *Water–epoxy interactions*

Epoxy resins absorb moisture from humid environments. This moisture absorption can be attributed largely to the moisture affinity of specific functional groups of a highly polar nature in the cured epoxy resin. Water has been detected in neat epoxy resins[4] and epoxy composites[5] using NMR spectroscopy. Since the NMR line width decreases with increasing molecular mobility, the broadening of the water signal in epoxy resins indicates that the water is hydrogen-bonded to the resin; its mobility in epoxy resins is between the values in the solid and free water states. Using FTIR spectroscopy, Antoon *et al.*[6] showed that the frequency of the in-plane bending mode of sorbed water in epoxy resins lies between its frequencies in liquid and free (gaseous) water, another indication of hydrogen bonding.

Browning[7] proposed that absorbed water molecules can be combined with functional groups of a highly polar nature in cured epoxy resins as follows:







Karasz and collaborators[8,9] investigated the nature of the epoxy–water molecule interactions using quadrupole echo deuterium NMR spectroscopy. They revealed that: (1) the water in epoxy resin is impeded in its movement; (2) there is no free water; (3) there is no evidence for tightly bound water; and (4) it is unlikely that the water disrupts the hydrogen-bonded network in the epoxy resin. The water molecules migrate from site to site, but the jumping motion does not involve a specific hydrogen-exchange mechanism. Using dielectric experiments, Woo and Piggott[10] suggested that the water does not appear to be bound to polar groups in the resin or hydrogen bonding sites. They reported that there was only some clustering of water molecules in the polymer, rather than complete molecular separation.

2.2. *Mechanisms of water absorption*

Since moisture cannot penetrate fibers, the behavior of diffusing moisture in composites is usually affected by the resin properties. Apicella *et al.*[11,12] proposed that there are three modes of sorption: (1) bulk dissolution of water in the polymer network; (2) moisture absorption onto the surface of vacuoles which define the excess free volume of the glassy structure; and (3) hydrogen bonding between polymer hydrophilic groups and water. If the first two modes occur consecutively, a dual sorption behavior[13–15] can be detected.

Adamson[16] postulated that the transport of moisture below T_g is a three-stage process in which the absorbed water first occupies the free volume present in the form of voids. In the second stage, water becomes bound to network sites causing swelling. Finally, it enters the densely crosslinked regions. However, Barrie *et al.*[17] included the possibility of clustering of water molecules at high moisture content to explain the isotherm deviation from linearity at high activities. Mechanisms based on free volume neglect the existence of specific interactions between water and hydrophilic sites of the network. It has been proposed that the water equilibrium concentration is mainly governed by the available free volume[16,18,19] or that water molecules occupy essentially microvoids and other morphological defects.[12,20,21]

Johncock and Tudgey[19] found that water absorption depends on the amount of free volume in the polymer network. They showed that the contribution of polar groups in terms of their hydrogen bonding capabilities is reflected by the effect of *meta*-chloro, bromo, and methyl substituents on the water absorption of modified TGDDM epoxy resins cured with DDS hardener, while substituents in the *ortho* position adversely affect the hydrogen bonding capability of amine groups and limit the extent of reaction by steric interference. Also by using *O*-glycidyl resin systems cured with various amounts of DDS hardener, they proved that free volume plays an important part in determining the level of water absorption.

The interpretation based on interactions is the result of spectrophotometric observations[22,23] and suggests that water molecules are linked by strong hydrogen bonds to some hydrophilic groups, mainly hydroxyl[24] or amine[25] groups. The contributions of these groups could be interdependent.[26] Bellenger *et al.*[27] suggested that water absorption is essentially linked to the concentration of polar groups, but decreases with increasing extent of intramolecular hydrogen bonding.

Woo and Piggott[28] found that water does not appear to be bound to polar groups in the resin, or on hydrogen bonding sites, although dielectric tests indicate that it does not behave as free water, since its polarizability is much reduced. They also observed that the decrease of the effective dielectric constant of water is only about 55–77%, which indicates that there is some clustering of the water molecules in the polymer, rather than complete separation.

2.3. *Absorption kinetics in epoxy resins*

Brewis *et al.*[29] investigated the water sorption kinetics of the diglycidyl ether of bisphenol A cured with several kinds of hardener. They found that the water sorption behavior of all the samples followed a Fickian diffusion model in the temperature range from 25 to 100°C. Gupta *et al.*[12] found that the DGEBA resin cured with metaphenylenediamine showed Langmuir-type sorption behavior at room temperature, while, at higher temperatures, the Henry's law mode was more relevant.

Several workers have reported non-Fickian diffusion in tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) resins cured with DDS. Moy and Karasz[22] suggested that the non-Fickian diffusion observed in TGDDM-DDS samples could be due to diffusion coupled either to relaxation processes or to irreversible chemical reactions. They proposed that the water was interacting with the polymer by hydrogen bonding, as verified by differential scanning calorimetry, and they proved it by showing the presence of residual water, which could only be removed from the resin by exposing it to a dry atmosphere heated above 100°C. Wong and Broutman[30] concluded that the non-Fickian process observed during a first sorption cycle may be due to insufficient crosslinking. Additional crosslinking could potentially occur during this sorption process. They observed Fickian behavior for subsequent sorption cycles. Sahlin and Peppas[31] found that TGDDM-DDS resins exposed to water at 25°C showed non-Fickian behavior. They explained that this behavior can be exhibited when the relaxation phenomena are of the same order of magnitude of time scale as diffusion. The non-Fickian behavior observed in the water uptake curves at low sorption times for samples exposed to water at 25°C disappeared as the sorption temperature increased.

Whitney and Browning[32] observed a two-stage diffusion process in Hercules 3501-5 neat resin at 71°C. They suggested time-dependent matrix cracking as the mechanism associated with the two-stage diffusion process.

2.4. *Absorption kinetics in epoxy composites*

Moisture absorption or cyclic absorption and desorption at high temperatures and relative humidities can cause voids and/or microcracks in the epoxy resin. If these effects are extensive, conditions for non-Fickian transport can be induced. Thus, we can expect non-Fickian as well as Fickian transport, according to the resin properties and environmental conditions.

Studies over the last twenty years have revealed that the moisture transport in composites can be described by a Fickian diffusion model with a constant diffusion coefficient,[33–36] a concentration-dependent diffusion coefficient,[37] or a stress-dependent diffusion coefficient.[38]

Shen and Springer[33] developed a model with direction-dependent diffusion coefficients in a unidirectional fiber composite. Several workers[34,35,39] showed a two-staged sorption behavior. Shirrell[37] found that the non-Fickian absorption anomalies for both postcured and non-postcured T300/5208 composites exposed in moisture at 82°C, and the equilibrium moisture solubility of non-postcured specimens, are independent of testing temperature, while there is a definite trend toward lower equilibrium moisture content with increasing test temperature for postcured specimens. Carter and Kibler[15] suggested a Langmuir-type model to predict two-stage sorption behavior for composite resins. The model could fit anomalous moisture uptake curves for 5208 resin exposed to several relative humidities. From the fact that the same parameters give equally good fits to the data at all humidities, they suggested that the absorption anomaly does not result from non-linear effects (e.g. concentration-dependent diffusivity).

When an epoxy resin absorbs water, the local degree of swelling depends on the local water concentration. As a result, the more swollen regions experience a compressive force, whereas less swollen regions experience tensile forces. The tensile stress can enhance the water transport rate. Such a self-induced stress can cause a non-Fickian behavior. Farrar and Ashbee[40] found that the water transport rate under this self-induced stress is an order of magnitude greater than the rate without stress.

Mathematical description of the water transport in such composites is available, although the models proposed and tested up to now have been somewhat simplistic. For example, a model utilizing Fick's law (eq. (1)) has been used to describe the moisture transport in slabs:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{1}$$

Here, c is the water concentration, x is position and D is a concentration-independent water diffusion coefficient in the matrix of the composite.

In all cases discussed in the literature up to now, the stress associated with such a transport process has been expressed by eq. (2):

$$\sigma_1(x,t) = C_{ij}(\epsilon_j^0 - \beta_j M(x,t)). \tag{2}$$

Here, $\sigma_i(x,t)$ are the components of the local time-dependent stress, C_{ij} are the stress coefficients, ϵ_j^0 are the components of the total average strains, β_j are water-induced swelling expansion coefficients, and $M(x,t)$ is the weight fraction of the local time-dependent amount of water in the composite.

Equation (1) can be solved for constant concentration boundary conditions, so that we can express the local water weight fraction and the total average strain by eqs (3) and (4), respectively, where $2x_0$ is the thickness of the panel.

$$M(x,t) = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{4x_0^2}\right)\cos\left(\frac{(2n+1)\pi x}{2x_0}\right) \tag{3}$$

$$\epsilon_j^0 = \beta_i\left(1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(\frac{-(2n+1)^2\pi^2 Dt}{4x_0^2}\right)\right). \tag{4}$$

Several studies have been carried out to investigate the distributions of moisture-induced stresses in composite laminates using Fick's diffusion equation. Pipes *et al.*,[41] Hahn and Kim[42] and Lee and Peppas[43] described the distribution of hygrothermally-induced stresses. Recently, we have proposed[43] several other water transport models based on various non-Fickian mechanisms and have tested them for a variety of environmental conditions and composites.

2.5. *Experimental methods for the absorbed water distribution in composites*

Grayson[44] investigated the absorbed water distribution in graphite/epoxy composite samples by precision abrasion mass spectrometry. This technique applies abrasion of the polymeric material at a constant rate. Therefore, any volatile compounds trapped in the sample are desorbed, and the amount of a compound detected by the mass spectrometer reflects its concentration in the sample. For this experiment, he used a time-of-flight mass spectrometer (TOFMS) and found that the concentration distribution was Fickian.

Whiteside *et al.*[45] employed a reaction analysis to measure moisture distribution through the piles of specimens that had been exposed to hygrothermal cycling, dried, and reconditioned under constant temperature and heavy water vapor fraction. The absorbed D_2O could be quantitatively measured through the specimen thickness using a nuclear probe for deuterium. Sandorff and Tajima[46] determined the moisture distribution using microtomes. They split the graphite/epoxy sample into thin slabs of uniform thickness parallel to the face. They then weighed the slabs immediately and placed them in a drying environment and monitored the weight loss. The data were fitted well by Fick's second law.

3. EFFECTS OF ABSORBED WATER ON GRAPHITE/EPOXY COMPOSITES

Epoxy–graphite composites have been increasingly utilized for structural applications where their long-term properties are of primary importance. During their service lifetime, epoxy–graphite composites absorb water from their surroundings. In the early 1970s, it was realized that such water absorption had detrimental effects upon their high temperature properties. These effects, especially at higher temperatures, have been associated with moisture-induced micromechanical damages in the epoxy resin and/or at the epoxy–fiber interface as well as internal stresses, relaxation of mechanical properties and plasticization. Among these phenomena, micromechanical damage is not reversible.

3.1. *Swelling by absorbed water*

Swelling describes volumetric changes due to moisture content alone, independent of thermal expansion. Since water is polar, it is capable of forming hydrogen bonds with hydroxyl groups. Therefore, interchain hydrogen bonds can be disrupted to increase the intersegmental hydrogen bond length.[47] Rehage and Borchard[48] showed that water can combine with polymers in the glassy state, establishing an equilibrium between the liquid and glassy states.

The swelling volume increase of epoxy resins is lower than the volume of water absorbed. Adamson[16] explained that when water is absorbed by an epoxy material, the comparatively small water molecules must either occupy the free volume of the epoxy or swell the epoxy. In other words, absorbed water that does not occupy the free volume of the epoxy must increase the specific volume of the epoxy by an amount equivalent to the specific volume of the water. Kong and Adamson[49] also showed experimentally the decrease in partial volume of the water. Hahn[50] showed that the absorbed water produces relatively little swelling until a critical amount of water is absorbed, and then the resin sample volume increases proportionally to the additional water content. Moisture absorption in the fiber is negligible. Therefore, Hahn suggested that the transverse swelling strain of the composite could be calculated using eq. (5):

$$\epsilon_T = \frac{1+\nu_m}{3} d(M - M_0)H(M - M_0) \tag{5}$$

where

$$M_0 = \frac{V_0}{d} = \frac{V_m d_m M_{m0}}{d}. \tag{6}$$

Here, ϵ_T is the swelling strain in the transverse direction, ν_m is the matrix Poisson ratio, M is the moisture concentration (weight of absorbed moisture/weight of solid resin), M_0 is the minimum value of M at which swelling is observed, V_0 is the volume fraction of voids, d is the total specific gravity, d_m is the matrix specific gravity and H is the Heaviside step function.

Hahn[50] defined the transverse swelling coefficient α_T as

$$\epsilon_T = \alpha_T(M - M_0)H(M - M_0). \tag{7}$$

Halpin and collaborators[51,52] suggested the following moisture-induced swelling equation in epoxy resins:

$$\epsilon = \tfrac{1}{3}\rho_m m \bar{V}_w. \tag{8}$$

Here, ρ_m is the matrix density, m is the absorbed moisture weight and $\bar{V}_w$ is the specific volume of water. For the Hercules 3501-6 epoxy resin, Halpin also found that the volume change can be represented by the following equation:

$$\Delta V = 1.265M^{1.18}. \tag{9}$$

Cairns and Adams[53] showed that the moisture-induced linear strain of such an epoxy resin exhibits a linear relation with the amount of absorbed moisture,

$$\epsilon = 3.2 \times 10^{-3}M. \tag{10}$$

The coefficient of moisture expansion is 0.0032% at 66°C for Hercules 3501-6 epoxy resin.[54,55] Gazit showed that the weight increase of moisture was proportional to the linear dimensional change, and was the same for all samples having the same reinforcements at all levels of ambient humidity.

3.2. *Residual stresses due to absorbed water*

When composite materials absorb water, the local water concentration varies until equilibrium is reached. Therefore, swelling due to water absorption is not uniform throughout the material and residual stresses are caused by this inhomogeneous local swelling. In composite laminates, the residual stresses result from the incompatibility between the matrix and fiber, even with a uniform distribution of water. The residual stresses thus induced may lead to the creation of microcracks, especially under transient conditions, and cause further decrease of the strength of the composite.

Hahn[50] considered only longitudinal residual stresses, assuming orthotropic symmetry of the material. The composite stress can then be calculated from the following equations:

$$\sigma_{\mathrm{mL}} = \frac{V_{\mathrm{f}} E_{\mathrm{fL}} E_{\mathrm{mL}} (e_{\mathrm{fL}} - e_{\mathrm{mL}})}{(V_{\mathrm{m}} E_{\mathrm{mL}} + V_{\mathrm{f}} E_{\mathrm{fL}})} \tag{11}$$

and

$$\sigma_{\mathrm{fL}} = -V_{\mathrm{m}} \sigma_{\mathrm{mL}} / V_{\mathrm{f}}. \tag{12}$$

Here, σ is the stress, V is the volume fraction, E is the Young's modulus, e is the strain and subscripts m, f, L represent matrix, fiber and longitudinal direction, respectively. Hahn also concluded that only about 0.4–0.5% of absorbed water can completely remove the internal stress developed during the cooling process after curing.

Pipes and coworkers[41] suggested that the dynamic residual stresses, $\sigma_i(x, t)$, induced by changes in temperature and water concentration can be calculated as follows:

$$\sigma_i(x, t) = Q_{ij}[\epsilon_j - \alpha_j T(x, t) - \beta_j M(x, t)]. \tag{13}$$

Here, Q_{ij} is the plane stress stiffness matrix, α_j are the coefficients of thermal expansion, β_j are coefficients of hygroscopic expansion and x is the position measured from the medium center.

Using micromechanical analysis, Adams and Miller[57] calculated the stress of a single fiber subjected to the combined influence of water absorption, temperature change and external forces. They assumed that a fiber is elastic and transversely isotropic, while the matrix material is inelastic and isotropic, and assumed that temperature and water profiles are uniform in the sample.

Crossman and Wang[58] solved a two-dimensional diffusion equation to describe the water concentration profiles and the elastic stress field induced by water swelling. Farley and Herakovich[59] also reported that elevated temperature and humidity can be significant factors in the determination of interlaminar stresses in the boundary layer region of composite laminates. Browning[60] predicted stress distributions according to the water distribution in epoxy resin matrices. He found that, when the surface concentration is M_∞ and the core is nearly dry early in the diffusion process, the compressive stresses are greater at the surface and the balanced tensile stresses are greater in the center of the material.

Ashbee *et al.*[61] determined the local stresses using photoelastic analysis at the interface between the graphite fiber and the epoxy resin after long immersion in water. They hypothesized that the presence of water-soluble solutes in the "water-pocket" caused an osmotic pressure, and they calculated the overall pressure as a function of pocket volume.

3.3. *Plasticizing effects*

It is known that the glass transition temperature of a polymer is lowered if a compatible liquid is dissolved into the polymer. The susceptibility of epoxy resins to substantial changes in properties on exposure to humid environments is manifested in particular by a seemingly large depression in the measured glass transition temperature, T_g. Based on the free volume concept of polymeric materials, Bueche and Kelley[62] derived the following expression for the T_g of a plasticized system:

$$T_g = \frac{\alpha_p v_p T_{gp} + \alpha_d (1 - v_p) T_{gd}}{\alpha_p v_p + \alpha_d (1 - v_p)}. \tag{14}$$

Here, α is the expansion coefficient, v is the volume fraction, and subscripts p and d represent polymer and diluent, respectively. Several investigators[53,62,63] applied this equation to epoxy resin–water systems, and explained the dependence of T_g on water content.

Couchman and Karasz[64] extended the classical thermodynamic treatment of composition-dependent T_g originally proposed by Gordon *et al.*[65] Karasz and coworkers[66,67] modified this equation to apply it successfully to epoxy resin–water systems.

$$T_{g12} = \frac{x_1 \Delta C_{p1} T_{g1} + x_2 \Delta C_{p2} T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}}. \tag{15}$$

Here 1 and 2 refer to epoxy and water, respectively, x refers to the weight or mole fraction and ΔC_{p1} is the incremental change in specific heat at T_{g1}.

Mijovic and Weinstein[68] found that the depression of the glass transition temperature in a graphite–epoxy composite after water absorption is strongly dependent on the temperature of the environment during water absorption. At the same absorbed water content, the T_g depression after water absorption was greater at higher prior moisture absorption temperature. They explained that, at lower temperatures, the temperature dependence comes from the water that exists predominantly in the defects, at the interface and, to some extent, in the lower crosslink density matrix, while, at a higher temperature, it comes from water penetrating into the highly crosslinked regions within the resin. Other experimental data[69,70] have shown that the glass transition temperature of epoxy resins or graphite–epoxy composites generally decreases as the water content increases.

3.4. *Changes of mechanical properties*

Water absorption causes resin plasticization concurrently with swelling and lowering of its glass transition temperature. These effects usually accompany modulus changes of the composite material (such as shifting of the relaxation modulus to shorter times).[50] Modulus changes due to water can be accelerated with increasing temperature.

Shen and Springer[71] summarized the previous tensile modulus data of composites and concluded that, for 0° and $\pi/4$ laminates, there appears to be very little change in the buckling moduli over the entire spectrum of water contents from dry to fully saturated in the temperature range of 200 to 450 K, whereas, for 90° laminates, the elastic moduli decreased considerably with increase in both the water content and temperature.

Using the stress–strain data of various water-treated samples of neat resin and composites, Browning *et al.*[63] concluded that, as water absorption increased and/or as temperature increased, the tensile modulus of the resin matrix and the transverse modulus of the composite decreased. Crossman *et al.*[72] determined the tensile relaxation modulus after exposure to equilibrium moisture levels. They found drastic reductions in modulus and an enhanced rate of relaxation at higher temperatures and moisture contents.

The damping properties give information about the molecular weight, heat treatment, copolymer composition, degree of crosslinking and polymer degree of crystallinity. The damping peak almost always coincides with the point of inflection of the modulus. Around the damping peak, partial loosening of the polymer structure occurs so that groups and small-chain segments can move.

The damping peak at a frequency of 1 Hz is observed at a temperature which is 5 to 15°C above the glass transition temperature.[73,74] The damping is low below T_g because the chain segments are not free to move. In the rubbery region, the damping is also low because molecular segments are free to move and in the transition region only a portion of the segments is free to move.

Dynamic mechanical tests of epoxy resins have been used to investigate the change of molecular structure for various epoxy resin curing agent systems[75–78] and to study hygrothermal effects on their molecular structure.[75–77,79] Also, they have been applied to reinforced epoxy composites to investigate the effects of reinforcement[80,81] and hygrothermal effects.[81,82]

Kuzenko *et al.*[75] investigated the dynamic material properties of TGDDM epoxy resins cured with DDS curing agent and boron trifluoride catalyst. They observed an α-transition around 234°C; the width of the α-transition peak was proportional to the cyclic "viscosity" of the sample. They also observed that a sample containing 6.5 wt% water exhibited a significant plasticizing effect in the dynamic shear modulus vs. temperature curve. They also showed a shift towards lower values and a broadened peak of the α-transition.

Mikols *et al.*[76] observed that samples containing absorbed moisture showed an ω-transition around 30°C for DGEBA-TETA samples and around 50°C for TGDDM-Novolac-DDS samples. They suggested that the ω-transition was the result of structural or molecular rearrangements within the network as a result of moisture absorption. Chu and Seferis[77] observed that the α-transition peak could be split into two peaks, α_1 and α_2, in a TGDDM-Novolac-DDS epoxy system before postcuring. After postcuring, the α_1 peak disappeared. They also found that the ω-transition was between 50 and 100°C in the $\tan\delta$ vs. temperature curve of the sample containing absorbed moisture. Apicella *et al.*[78] observed that the shear modulus of moisture-saturated DGEBA-TETA decreased over a larger temperature range than that of the dry material.

In carbon fiber/epoxy resin composites, Yoshida[79] found that the dynamic modulus was related to the carbon fiber content. The dynamic modulus was not affected by temperature if the fiber direction was parallel to the stress direction, whereas the modulus was affected if the fiber direction was perpendicular to the stress direction. The tan δ values of the sample containing fibers perpendicular to the stress were much higher than those of the sample with fibers parallel to the stress. Mikols and Seferis[80] reported the observation of β, ω, and α transitions in 15, 30 and 45° oriented carbon fiber–epoxy resin composites. They suggested that the ω-transition is linked to unreacted molecular segments and/or inhomogeneities arising from dissimilar cross-link densities. They also observed plasticizing effects on the composites containing absorbed water.

Lee *et al.*[81] performed a hygrothermoelastodynamic test on a Hercules AS4/3501-6 composite and found that the specimens were characterized by decreased moduli at higher temperatures. This degradation was accelerated and the damping increased with increasing moisture content above 60°C. Using dynamic damping experiments, it was found that wet-aged conditions caused significant glass transition temperature depression in Fiberite 934/T300 and Narmco 5208/T300 composites[82] and in cured Epon 828 epoxy resin. Bouadi and Sun[83] concluded that increase in either temperature or moisture content resulted in a decrease of the storage modulus. Maymon *et al.*[84] reported that the damping characteristics were altered substantially in both fiber and matrix-controlled modes of deformation due to hygrothermal conditioning, while the dynamic modulus was reversibly altered in matrix-controlled modes of deformation.

The nature of the interface region between matrix and fiber in a composite influences its mechanical properties. Spathis *et al.*[85] prepared an epoxy matrix/fiber specimen and an epoxy matrix/silane-coated fiber specimen and compared the response of their dynamic mechanical properties. They found that the specimen having weaker interfacial bonding showed lower values of storage and loss moduli and higher values of damping factor. Chua[86] characterized the quality of the interfacial adhesion by the value of the damping factor at the glass transition temperature. He observed that the tan δ at the glass transition temperature of the glass fiber-reinforced polyester resin increased with increasing amount of unreacted organosilane at the interface. Banerjee *et al.*[87] reported that the poor interfacial bonding in the untreated fiber specimens led to a larger viscous dissipation at the carbon–epoxy interface and that the glass transition temperature of the untreated fiber specimen was slightly lower than that of the surface-treated fiber specimen because of a weak interface.

3.5. *Hygrothermal degradation in graphite/epoxy composites*

Degradation of composite materials in structural applications may be caused not only by mechanical loading but also by environmental exposure. Most of the environmental degradation in composites is due to their exposure to increased temperature and humidity. The absorbed moisture not only plasticizes the matrix resin, but also is able to change the state of residual stresses to cause microvoids and/or microcracks in the resin.[39,69,88,89]

Some researchers[90,91] observed hygrothermally induced cracks in the epoxy resin regions of glass fiber/DGEBA epoxy composites as well as at the interface of the glass fiber and the DGEBA epoxy resin. Browning[60] reported that one significant mechanism for the loss of elevated temperature properties in a moisture-rich environment is the formation and growth of cracks in the material where the crack growth process is aided by localized chemical chain scission at the crack tip. He also found that microcracking increases the equilibrium moisture absorption level.

Shirrell *et al.*[92] exposed T300/5208 composite samples to several different hygrothermal environments, and examined the hygrothermally induced microcracks by scanning electron microscopy (SEM). They found that severe microcracks were observed at 82°C; the severity and frequency of these microcracks increased with relative humidity. They also found that postcured specimens generally formed more severe microcracks than identically exposed non-postcured specimens.

Morgan and Mones[93] concluded that sorbed moisture enhances the craze cavitation and propagation processes in amine-cured epoxy resins, whereas the initial stages of failure enhance the accessibility of moisture to sorption sites within the epoxy to a greater extent than in the later stages of failure, which involve crack propagation alone.

When exposed to hygrothermal environments, composites undergo degradation[94] which manifests itself in terms of reduced structural performance and anomalous moisture diffusion behavior such as absorption–desorption hysteresis and two-step absorption. Hahn[94] explained that the hygrothermal degradation is the result of matrix plasticization, microvoid formation and microcracking. Apicella and Nicolais[95] also observed a Langmuir-type, two-step moisture diffusion in epoxy resins due to the moisture-induced microcavities. Halpin[52] observed that the rates of the apparent diffusion process and the magnitude of the equilibrium weight gain are accelerated by the presence of cracks and voids in a laminate.

Leung and Kaelble[96] predicted the possible microcracks and delaminations within the composite due to the stress gradient caused by moisture content gradient. Fedors[97] found that some inclusions in epoxy resin systems can be dissolved to form cavities when the diffused water reaches the surface of the inclusions. The difference in the chemical potential of the water in the pure state and in solution, which manifests itself as an osmotic pressure, tends to make the initially concentrated solution in the cavity more dilute. He suggested that this effect is the driving force for the growth of the cavity.

Besides causing cracks or microcracks, the hygrothermal conditions can also decrease the interlaminar shear strength[98] and the ultimate tensile strength[99] of various composites.

The above observations have contributed to our understanding of water interactions with epoxy composites, although several unanswered questions remain. Can non-Fickian transport be observed under normal operating conditions? Are the stresses developed during non-Fickian transport likely to cause cracking or damage of the composite? Can absorbed water be localized at the epoxy/fiber interface? These and other questions are presently being investigated in various laboratories using advanced spectroscopic and interferometric techniques.

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