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The effect of moisture on the physical and mechanical integrity of epoxies*

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The effect of specific combinations of moisture, heat, and stress on the physical structure, failure modes, and tensile mechanical properties of diaminodiphenyl sulphone (DDS)-cured tetraglycidyl 4,4'diaminodiphenyl methane (TGDDM) epoxies [TGDDM-DDS (27 wt% DDS)] are reported. Sorbed moisture plasticizes TGDDM-DDS epoxies and deteriorates their mechanical properties in the range 23 to 150° C. Studies of the initiation cavity and mirror regions of the fracture topographies of these epoxies indicate that sorbed moisture enhances the craze initiation and propagation processes. The effect of tensile stress-level, applied for 1 h on dry epoxies, on the subsequent moisture sorption characteristics of the epoxies was also investigated. Such studies indicate that the initial stages of failure that involve both dilatational craze propagation and subsequent crack propagation enhance the accessibility of moisture to sorption sites within the epoxy to a greater extent than in the latter stages of failure which involve crack propagation alone. The amount of moisture sorbed by TGDDM-DDS epoxies is enhanced by ~ 1.6 wt% after exposure to a 150° C thermal spike, as a result of moisture-induced free volume increases in the epoxies that involve rotational–isomeric population changes.

1. Introduction

The need to conserve energy has stimulated increased interest in the use and development of epoxies as adhesives and matrices for high-performance, light-weight, fibrous composites for the transportation industry, e.g., for use in aircraft, automobiles, and energy-storage systems such as flywheels. The durability of epoxies in many service environments is uncertain because of insufficient understanding of their structure–property relations.

Epoxy composites and adhesives sorb moisture which in both laboratory and field tests deteriorates the mechanical properties, particularly at high temperatures. The effect of sorbed moisture on the physical and mechanical integrity of epoxies and other thermosets utilized as adhesives and composite matrices in the aerospace industry has received considerable attention (references in [1].) Recently, we reviewed the pertinent basic physical phenomena that are induced and/or modified by sorbed moisture and that affect the durability of epoxies [1]. These phenomena included (1) lowering of T_g by sorbed moisture, (2) diffusion of sorbed moisture, (3) swelling stresses induced by sorbed moisture, (4) modification of the deformation and failure modes and the mechanical response by sorbed moisture, and (5) interaction of sorbed moisture with other environmental factors.

In this paper, we report our studies in three areas related to moisture induced physical and mechanical property modifications of diaminodiphenyl sulphone-cured tetraglycidyl 4,4'

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diaminodiphenyl methane epoxy (TGDDM-DDS). (This epoxy system is currently one of the most commonly utilized in the aerospace industry.)

(1) In any durability prediction of epoxies, it is vital to understand how sorbed moisture modifies the microscopic modes of deformation and failure and the mechanical response. There have been few studies on the modification of the modes of deformation and failure of thermosets by sorbed moisture [2–7]. Generally, such studies reported changes in fracture toughness induced by moisture with no attempt to explain such changes in terms of modification of the microscopic modes of deformation and failure.

In a previous investigation we studied the structure–property relations of TGDDM-DDS epoxies [8]. We monitored the tensile mechanical properties as a function of temperature and strain rate, and from fracture topography studies elucidated that these epoxies predominantly deform and fail by a crazing process.

In this study we monitored the mechanical properties of initially wet and dry TGDDM-DDS epoxies as a function of test temperature. The modification of the crazing process by sorbed moisture was determined from fracture topography studies. Scanning electron and optical microscopy were used to monitor the fracture topographies.

(2) The durability of epoxies directly depends on the deterioration of the mechanical properties caused by the plasticizing effect of sorbed moisture. The previous relative-humidity/time/temperature exposure of the epoxy component and the diffusion characteristics of moisture in this component determine the moisture profile and the resultant mechanical response of the material. Hence, the diffusion characteristics of moisture in an epoxy component are critical factors for predicting the mechanical response and durability in a given service environment.

Many diffusion processes can be adequately described by Fick's laws of diffusion [9]. A number of workers have successfully applied Fick's second law of diffusion to the sorption and desorption of moisture in epoxies and epoxy composites and have predicted the moisture profiles as a function of time for specific environmental conditions [10–30]. The utilization of Fickian diffusion as the controlling mechanism to predict the concentration and distribution of sorbed moisture and corresponding deterioration of the mechanical properties can lead to serious errors in the durability predictions of epoxies in many environments. Any damage induced in the epoxy or epoxy composite by applied stresses, fabrication procedures, and/or environmental conditions can cause deviations from Fickian diffusion and accelerate moisture sorption. Recently, Gillat and Broutman [29] have reported that applied external stress increases moisture diffusion in a graphite–epoxy composite which was submerged in water.

In this study we investigated the effect of increasing stress levels on the subsequent moisture diffusion and sorption characteristics of initially dry TGDDM-DDS epoxies. Our objective was to determine at what stress levels any stress-induced damage modified the macroscopically detectable moisture sorption characteristics of the epoxies.

(3) One of the more extreme environmental conditions experienced by an epoxy composite matrix on a fighter aircraft occurs during a supersonic dash. The aircraft dives from high altitude (outer surface temperature −20 to −55° C) into a supersonic, low-altitude run during which the surface temperature rises in minutes to between 100 and 150° C as a result of aerodynamic heating. On reduction of speed, the outer surface temperature drops rapidly at rates up to ~ 500° C min^{-1}, thus exposing the epoxy composite to a thermal spike. Simulation of such thermal spikes has been shown to increase the amount of moisture sorbed by the epoxy or epoxy composite [13, 14, 19, 28, 31–33]. However, after a certain number of consecutive thermal spikes, the amount of moisture sorbed ceases to increase. Browning [19] has reported that such increases result from microcracks caused by the moisture and temperature gradients present during the thermal spike. McKague [32] has recently noted that damage does not occur unless the thermal-spike maximum temperature exceeds the particular T_g of the moist epoxy. Indeed, for less severe thermal-spike conditions, Bergmann and Dill [34] and Bohlmann and Derby [22] report no evidence of damage in graphite–epoxy laminates.

In this study we investigated the effects of thermal spiking on the moisture sorption and surface damage characteristics of TGDDM-DDS epoxies. The epoxy surfaces were monitored by scanning electron microscopy for damaged regions. The objective of these studies was to elucidate the possible damage mechanisms caused by thermal spiking. Certainly the cessation of sorption of additional amounts moisture after a number of thermal spikes suggests that further microcrack propagation is inhibited.

In our previous studies on the structure–property relations of TGDDM-DDS epoxies [8] we found that annealing initially dry TGDDM-DDS epoxies from between 150 and 225° C enhances subsequent moisture sorption because of the elimination of unreacted, low-molecular-weight material. We therefore monitored the weight losses of initially wet and dry epoxies as a function of anneal temperature from 23 to 250° C to determine if significant low-molecular-weight material could be lost during a thermal spike and enhance subsequent moisture sorption.

2. Experimental details

2.1. Materials and sample preparation

The epoxy system studied was a diaminodiphenyl sulphone (Ciba Geigy, Eporal)-cured tetraglycidyl 4,4′ diaminodiphenyl methane (Ciba Geigy, MY720) epoxy (TGDDM-DDS). The TGDDM epoxide monomer is a liquid at room temperature, whereas the DDS is a crystalline powder with a melting point of 162° C.

For sample preparation, the fabrication techniques developed by Fanter [35] were utilized. A master batch of TGDDM was heated to 75° C, and the DDS was added slowly while the mixture was stirred. This mixture was then held at 75° C for 3 h, periodically stirred, and poured into vials and stored at −20° C. TGDDM-DDS mixtures were prepared containing 27 wt% DDS. (From our previous structure–property studies on TGDDM-DDS epoxies [8], the optimum mechanical properties and highest T_g values were obtained for epoxies prepared from TGDDM-DDS mixtures containing 25 to 30 wt% DDS.)

In order to prepare dogbone-shaped specimens suitable for tensile mechanical property studies, the TGDDM-DDS mixture was heated to 165° C. After 20 min at 165° C, the mixture was degassed in a vacuum chamber, reheated to 165° C, and then poured into dogbone-shaped silicone rubber moulds. The specimens were cured at 150° C for 1 h, followed by 5 h at 177° C, cooled to room temperature, and removed from the moulds. The specimens had a gauge length of 3.0 cm, a width of 0.4 cm within the gauge length, and a thickness of 0.6 mm.

Dogbone-shaped specimens, or machined and polished portions of these specimens, were used for the moisture sorption, thermal spike and annealing studies.

2.2. Experimental procedures

A table-model tensile tester (Instron TM-S-1130) was used to determine the tensile mechanical properties of the initially wet and dry TGDDM-DDS (27 wt% DDS) epoxies at a strain rate of 10^{-2} min^{-1} from 23 to 250° C. Wet specimens, containing 4 to 5 wt% moisture, were produced by exposing the specimens to steam for 3 h at 120° C in an autoclave.

A scanning reflection electron microscope (JEOL model JEM-100B) and optical microscope (Zeiss Ultraphot II) were used for fracture topography studies. For the scanning electron microscopy studies, the fracture surfaces were coated with gold while the sample was rotated in vacuum.

For the studies of the effect of stress on the subsequent moisture diffusion and sorption characteristics of epoxies, dry specimens were held at constant stress, from 0 to 60 MPa, at room temperature in the tensile tester for 1 h. These specimens were subsequently stored at room temperature in 100% relative humidity and periodically weighed to determine their moisture diffusion and sorption characteristics.

The following experimental sequence was followed for the thermal-spike studies: (1) After cure, all specimens were dried in a desiccator for 24 h and then weighed. (2) The epoxy specimens were then exposed to steam for 3 h at 105° C in an autoclave. The specimens were then removed from the autoclave, wiped dry, and weighed. (3a) Half of the specimens were exposed to a laboratory-simulated thermal spike. The actual thermal-spike characteristics that we attempted to simulate are similar to those utilized in previous studies [14, 16, 19, 32] and are depicted graphically in Fig. 1. This thermal spike was simulated by placing the wet specimens for 3.5 min in a helium atmosphere in a tube furnace which had been preheated to 150° C. These specimens were then quenched in ice water. (No attempt was made to cool these specimens to −20° C prior to introducing them into the oven.) The specimens were removed from the ice water, wiped dry, placed in a dessicator for 24 h, and reweighed. (3b) The other half of the specimens, which served as reference specimens, were not exposed to the thermal spike but otherwise were exposed to the same procedures as the thermal-

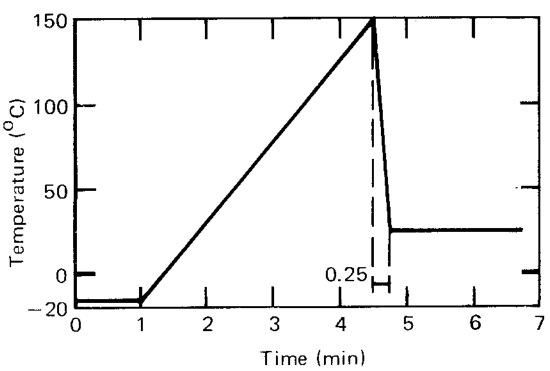

Figure 1 Thermal spike experienced by the surface of an epoxy component of a fighter aircraft as a result of a supersonic manoeuver.

spiked specimens. (4) For subsequent thermal-spike cycles, procedures (1) to (3) were repeated. (5) After each thermal-spike cycle, a spiked and nonspiked specimen were removed from the specimen batch for subsequent surface damage studies by scanning electron microscopy. Such specimens were coated with gold prior to these microscopy studies.

The experimental procedure for the studies of the weight losses of initially wet or dry epoxy specimens as a function of anneal temperature was as follows. The initially dry specimens were stored in a dessicator after cure, whereas 4 to 5 wt% moisture was introduced into the wet specimens in an autoclave at 105° C for 3 h. The wet and dry specimens were then annealed for 24 h in a He atmosphere in a tube furnace at a series of different temperatures from 23 to 250° C. After the 24 h anneal at each temperature, the initially wet and dry specimens were removed from the tube furnace and weighed. Previously unannealed, wet and dry specimens were used for each anneal temperature.

3. Results and discussion

3.1. Modification of the tensile mechanical properties and fracture topographies by sorbed moisture

In Fig. 2 the tensile strength, ultimate elongation, and Young's modulus of both initially wet and dry TGDDM-DDS epoxies are illustrated as a function of test temperature. The wet epoxies exhibit lower tensile strengths, ultimate elongations, and moduli than the dry epoxies from room temperature to 150° C. Plasticization of the epoxy, including a softening of the craze fibrils by the sorbed moisture, causes this deterioration in the mechanical properties. (Softer craze fibrils fracture at lower stresses and therefore enhance crack propagation and lower the tensile strength.) Above 150° C, the mechanical properties of both the initially wet and dry epoxies merge because significant amounts of moisture are eliminated from the wet glasses during the time of the test.

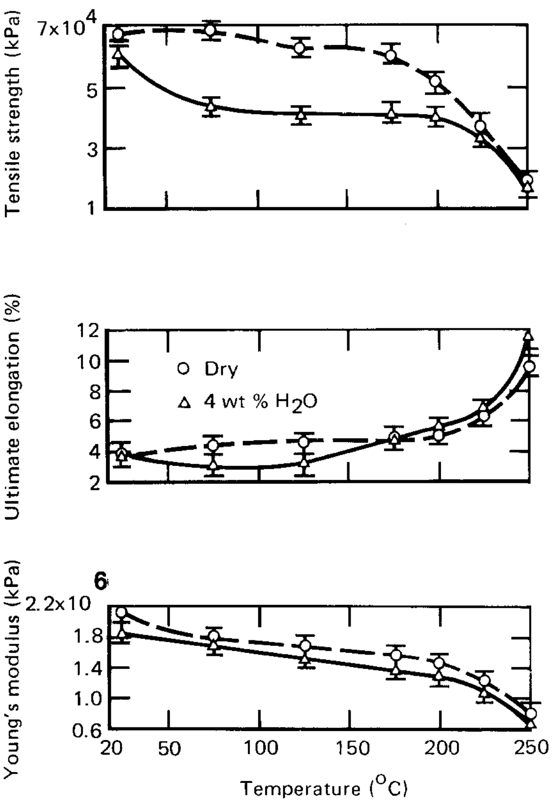

Figure 2 Tensile strength, ultimate elongation and Young's modulus of initially wet (~ 4 wt% sorbed moisture) and dry TGDDM-DDS (27 wt% DDS) epoxies as a function of test temperature (strain rate ~ 10^{-2} min^{-1}).

(TGDDM-DDS epoxies predominantly deform and fail by a crazing process. Scanning electron micrographs of the fracture topographies of these epoxies revealed cavities and fractured fibrils in the fracture topography initiation region which could only be explained by a crazing mechanism [8]. Although such features are not as pronounced as in non-cross-linked glasses, these observations are consistent with the observed glassy-state ductility (up to 17% ultimate elongation) of TGDDM-DDS epoxies. Recent infra-red studies of the cure processes of TGDDM-DDS epoxies indicate that the non-BF$_3$-catalysed systems do not form highly cross-linked networks during cure at 177° C, because of the steric and diffusional restrictions imposed on the cure reactions [36]. Indeed only ~ 65% of the epoxide groups reacted in a TGDDM-DDS (20 wt% DDS) epoxy system after 2.5 h at 177° C. The resultant lightly cross-linked TGDDM-DDS networks will be more susceptible to molecular flow and crazing than some of the more highly cross-linked epoxy systems.)

From room temperature to 150° C, the lower tensile strengths of the wet epoxies relative to those of the dry epoxies are equivalent to lowering the dry tensile strengths 100 to 125° C on the temperature scale. However, the T_g of a TGDDM-DDS epoxy is lowered only ~ 60° C by ~ 4 wt % sorbed moisture [1, 19]. These observations imply that the craze initiation and growth processes that involve simultaneous cavitation and flow processes are more susceptible to sorbed moisture than the main T_g. Hence, the magnitude that the T_g is lowered on the temperature scale by sorbed moisture cannot be utilized to predict any modification of the formation of permanent damage regions in these epoxies. The craze cavitation process would be more sensitive to sorbed moisture than the T_g for a heterogeneous distribution of moisture in the epoxy. High moisture concentrations in localized regions enhance cavitation by plasticization, which results in a lower local shear yield stress. (The surface energy for formation of a fresh surface when cavitation occurs is not enhanced by the presence of local concentrations of moisture because the surface tension of water (7.2 Pa) is greater than that of the epoxy (~ 4 to 5 Pa) [37]). The T_g of the epoxy, however, is generally measured on a macroscopic level and is not sensitive to high local moisture concentrations. Moisture was introduced into the TGDDM-DDS epoxy at 120° C in an autoclave, and the samples were then cooled to room temperature. The decrease in solubility of moisture in epoxies on lowering the temperature could result in local regions of high moisture concentrations [38–40]. These regions would be favourable sites for craze initiation and subsequent propagation.

Fracture topography studies also indicate that the craze deformation and failure modes in epoxies are modified by sorbed moisture. The optical micrographs in Fig. 3 compare the room-temperature fracture topography of a dry TGDDM-DDS epoxy with that of a sample containing ~ 4 wt % sorbed moisture. The smooth, mirror-like region in the wet epoxy is considerably larger than that in the dry epoxy. The mirror radii in the fracture topographies of the initially wet and dry epoxies are plotted versus test temperature in Fig. 4. Below 150° C the mirror radii of the wet epoxies are greater than those of the dry epoxies. The room-temperature fractured, wet epoxy that

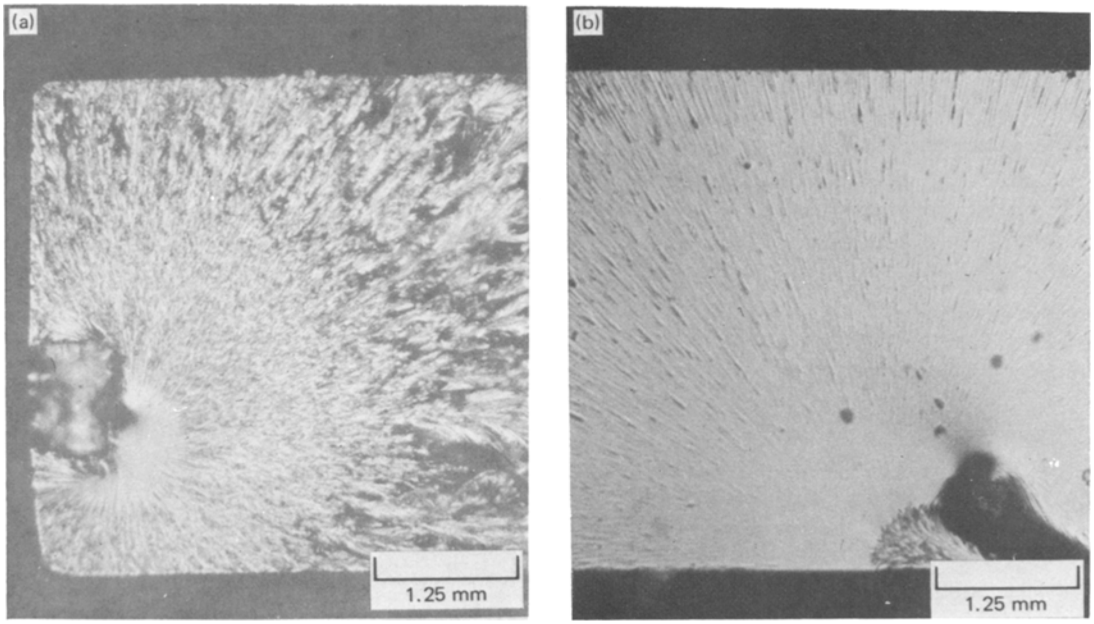

Figure 3 Optical micrographs of room-temperature fracture surfaces of (a) dry and (b) wet (~ 4 wt % sorbed moisture) TGDDM-DDS (27 wt % DDS) epoxy.

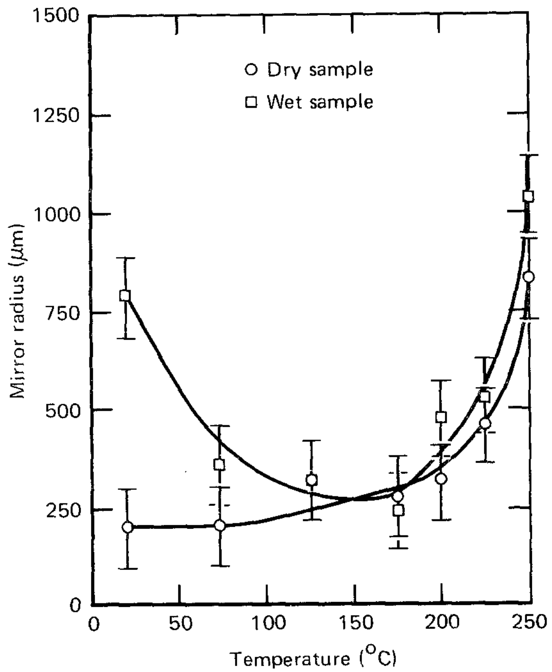

Figure 4 Mirror radius in the fracture topography of the initially wet and dry TGDDM-DDS (27 wt % DDS) epoxies versus fracture temperature.

contains the most moisture during fracture exhibits the largest mirror radius. The mirror radii of the wet epoxies approach those of the dry epoxies with increasing temperature because increasing quantities of moisture are lost during the test. At and above 150° C, the mirror radii of the initially wet and dry epoxies merge. The extent of the mirror-like region in epoxies is a measure of the area in which crack propagation occurs through a preformed craze [1, 8, 41, 42]. Hoare and Hull [43] suggested that in polystyrene, this area depends on the ease of craze growth, and crack nucleation and growth within the craze. Hence, the increases in the mirror radii of the wet epoxies indicate that sorbed moisture significantly enhances the craze–crack growth processes. (The mirror radii for all specimens increases with increasing temperature above 150° C because craze–crack growth is enhanced nearer the T_g. Furthermore, the increased mobility of the glass near T_g enhances relaxation of the topographical features, thus also favouring a smooth surface.)

Scanning electron micrographs of the fracture topography initiation regions in the wet TGDDM-

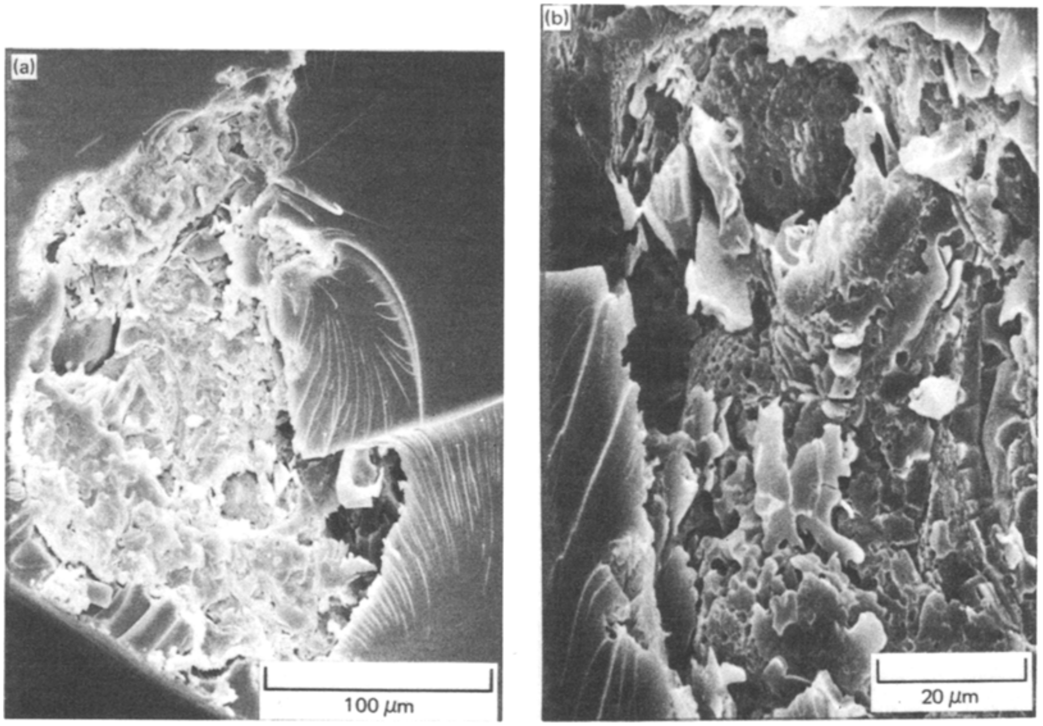

Figure 5 Scanning electron micrographs of cavities in the fracture topography initiation region of a wet TGDDM-DDS (27 wt % DDS) epoxy (~ 4 wt % sorbed moisture) that was fractured at room temperature at a strain rate of ~ 10^{-2} min^{-1}.

DDS epoxies reveal numerous cavities, as illustrated in Fig. 5. The cavities are more numerous than those observed in dry epoxy glasses fractured under similar conditions. This observation suggests that sorbed moisture enhances cavitation.

The enhancement of craze initiation and propagation in TGDDM-DDS epoxies by sorbed moisture directly affects the durability of these glasses in humid environments. The ease of diffusion of moisture through a porous craze structure and its accumulation near the craze tip where it enhances cavitation must be considered a significant mechanism for the growth of permanent damage regions in these glasses in humid environments.

3.2. Effect of applied stress on subsequent moisture sorption characteristics

Thirty dry TGDDM-DDS epoxy specimens were stressed under constant load for 1 h at room temperature from 0 to 60 MPa. Then the amounts of moisture sorbed by such specimens in 100% relative humidity (r.h.) at room temperature were monitored versus time. Typical plots of the wt% of moisture sorbed versus time for epoxies stressed at 5.6 and 61.6 MPa respectively are illustrated in Fig. 6. The epoxy subjected to the 61.6 MPa stress sorbs ~0.4 wt% more moisture than that epoxy subjected to the 5.6 MPa stress.

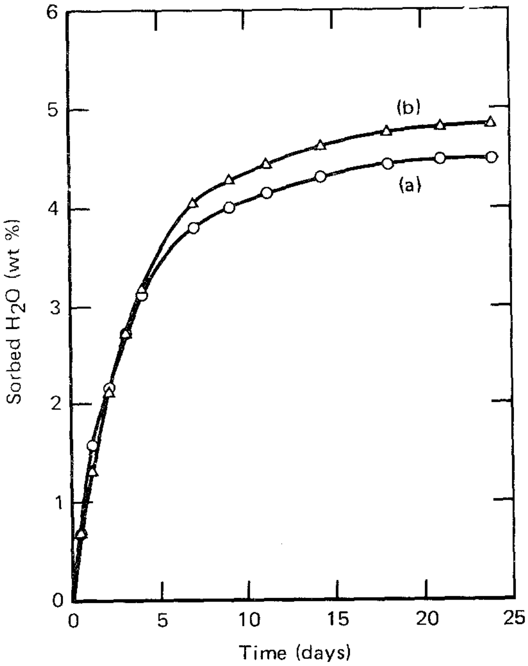

Figure 6 Weight percent of moisture sorbed at 23° C, 100% r.h. versus time for TGDDM-DDS (27 wt% DDS) epoxies prestressed under constant load at (a) 5.6 MPa and (b) 61.6 MPa for 1 h at 23° C.

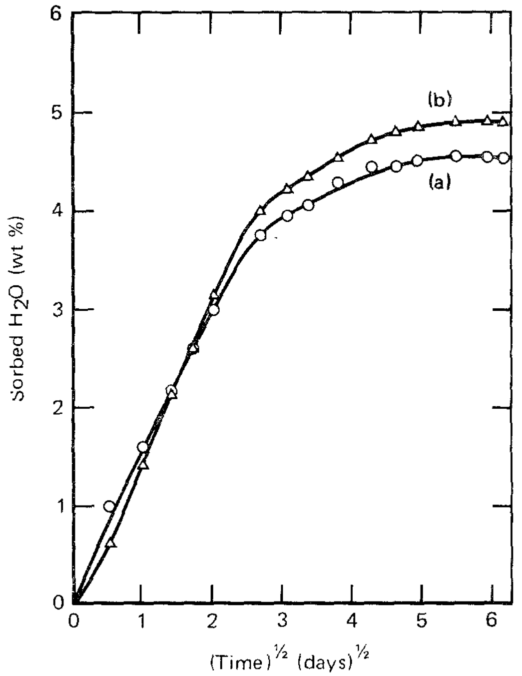

Figure 7 Weight per cent moisture sorbed at 23° C, 100% r.h. versus $(\mathrm{time})^{1/2}$ for TGDDM-DDS (27 wt% DDS) epoxies prestressed under constant load at (a) 5.6 MPa and (b) 61.6 MPa for 1 h at 23° C.

Previous studies have shown that Fick's second law of diffusion can be applied to the sorption and desorption of moisture in epoxies and epoxy composites [10–30]. Fick's second law for one-dimensional diffusion is given by

$$\frac{\mathrm{d}c}{\mathrm{d}t} = D\frac{\mathrm{d}^2c}{\mathrm{d}x^2}, \tag{1}$$

where c is concentration, D is the diffusion coefficient, and x is the distance the moisture has advanced from a given boundary. Equation 1 has been solved for the case of a flat sheet sorbing vapour at both faces under constant environmental conditions. The solution for the fraction of the equilibrium amount of moisture sorbed in time t is given by

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \tag{2}$$

where M_t is the amount of moisture sorbed after time t, M_∞ is the equilibrium amount of moisture sorbed, and L is the plate thickness [44]. Plots of the per cent of moisture sorbed (M_t) versus $(\mathrm{time})^{1/2}$ for the epoxies stressed at 5.6 and 61.6 MPa respectively are illustrated in Fig. 7.

These plots are linear, which is consistent with Fick's second law, below ~ 3 wt % sorbed moisture ($M_\infty \simeq 0.55$). Above ~3 wt% sorbed moisture, the epoxy specimens do not behave as semi-infinite plates as assumed in Fickian diffusion [44], and consequently M_t is no longer linear with the square root of time. The epoxies attain their equilibrium moisture content after ~ 30 days because no further moisture sorption was detectable in the 30 to 40 day time period.

The diffusion coefficients (D) of moisture in the prestressed TGDDM-DDS epoxies were calculated from Equation 2 using the slopes of the linear regions of M_t versus $t^{1/2}$ plots. The values of D were from $(0.95 \text{ to } 1.20) \times 10^{-9}$ cm^2 sec^{-1} and exhibited no detectable trend with previously applied stress. The diffusion coefficients of moisture in a variety of epoxies at room temperature from 75% to 100% r.h. have been reported to be from 10^{-8} to 10^{-11} cm^2 sec^{-1} [19, 30, 45, 46]. Our values of D at 100% r.h. are an order of magnitude higher than the values obtained by extrapolating Browning's data [19] to room temperature for a $BF_3:NH_2-C_2H_5$ catalysed TGDDM-DDS (24 wt% DDS) epoxy. However, the modifying influence of the catalyst on the final epoxy network structure and the moisture diffusion characteristics are unknown.

The equilibrium moisture sorption levels are more sensitive to the effect of the previously applied constant load than the diffusion coefficients. In Fig. 8, the equilibrium moisture sorption levels after ~ 40 days exposure to 100% r.h. at room temperature are plotted versus the stress levels that were applied to the epoxies prior to moisture sorption. All data points fall within the shaded areas. Stresses from 0 to 38 MPa had no detectable influence on the subsequent moisture sorption levels. However, moisture sorption increases sharply by up to ~ 11% from 38 to 43 MPa. At higher stress levels from 43 to 65 MPa, where a few specimens broke, there is only a slight trend towards higher moisture content with increasing stress.

The data in Fig. 8 indicate that the initial stages of craze/crack growth enhance the accessibility of moisture to sorption sites to a greater extent than in the later stages of growth. (The primary sorption sites within the TGDDM-DDS epoxy are the hydroxyl, sulphonyl, and primary and secondary amine groups all of which are capable of forming hydrogen bonds with water molecules.) TGDDM-DDS epoxy specimens that fractured under constant load were found to exhibit fracture topographies similar to previously studied specimens that fractured in shorter times in the 10^{-2} to 10^{1} min^{-1} strain rate region [8]. Such topographies have been interpreted in terms of a craze–crack growth process [8] with crazing, followed by crack propagation, predominating in the initial stages of failure and crack propagation alone predominating during the later stages of failure. The dilatational changes produced in the epoxy glass by the crazing process enhance the accessibility of moisture to sorption sites within the epoxy to a greater extent than crack propagation alone. Hence, the initial stages of failure in TGDDM-DDS epoxies enhance the accessibility of sorption sites to moisture to a greater extent than the later stages of failure.

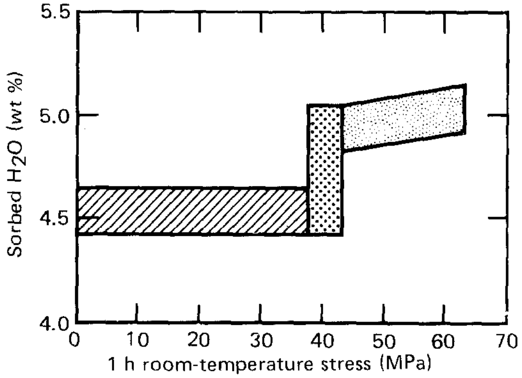

Figure 8 Equilibrium weight per cent moisture sorbed by TGDDM-DDS (27 wt% DDS) epoxies at 100% r.h. and 23° C versus 1 h constant stress levels that were applied prior to moisture exposure.

All epoxy specimens saturated with moisture that had not previously broken were fractured in tension at a strain rate of 10^{-2} min^{-1} at room temperature. However, the tensile strengths of these specimens exhibited no significant differences, within the experimental scatter of ± 10 MPa, as a function of previously-applied stress level. Also no differences in the fracture topographies of failed specimens were detected by scanning electron microscopy. The presence of sorbed moisture plasticizes the material at the tips of previously grown crazes or cracks which blunts their growth and minimizes differences in stress concentrations between specimens. Furthermore, the subsequent growth of crazes in these previously stressed specimens will propagate into fresh material in which the moisture concentration is similar for all specimens.

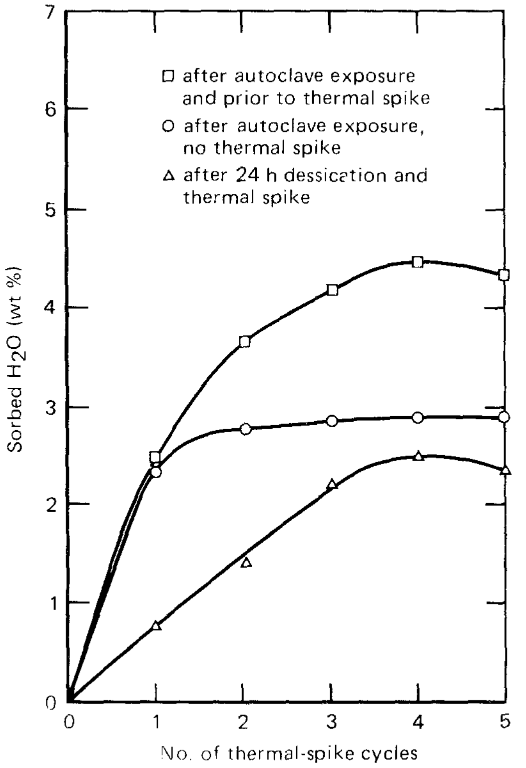

Figure 9 Weight per cent moisture sorbed by TGDDM-DDS (27 wt% DDS) epoxies versus number of thermal-spike cycles.

3.3. Effect of thermal spiking on physical structure

The effect of thermal spiking on the amount of moisture subsequently sorbed by TGDDM-DDS epoxies was determined by following the procedure outlined in the experimental section. In Fig. 9 the amount of moisture sorbed after autoclave exposure but prior to each thermal spike is plotted versus the number of thermal-spike cycles for the TGDDM-DDS epoxies. The amount of moisture sorbed by these specimens increases up to the fourth thermal-spike cycle and thereafter decreases slightly. In the same figure, the amounts of moisture sorbed immediately after autoclave exposure by both the reference and thermally-spiked specimens are compared. (The reference specimens were not exposed to the thermal spikes but otherwise were exposed to the same conditions within each thermal cycle as the thermally-spiked specimens.) The thermally-spiked epoxies sorb more moisture than the nonspiked epoxies, and by the fourth thermal cycle this difference attains a maximum of ~ 1.6 wt% moisture. Also, in Fig. 9 the amount of moisture sorbed by the thermally-spiked specimens immediately after 24h desiccation within each thermal cycle is plotted versus the number of thermal-spike cycles. Except for the lower moisture levels, this plot versus the number of thermal cycles follows the same trend as that for the thermally-spiked specimens that were weighed immediately after autoclave exposure. (Within each thermal cycle, the moisture sorption levels are lower for the specimens that have been weighed immediately after desiccation than for those specimens that have been weighed immediately after removal from the autoclave.)

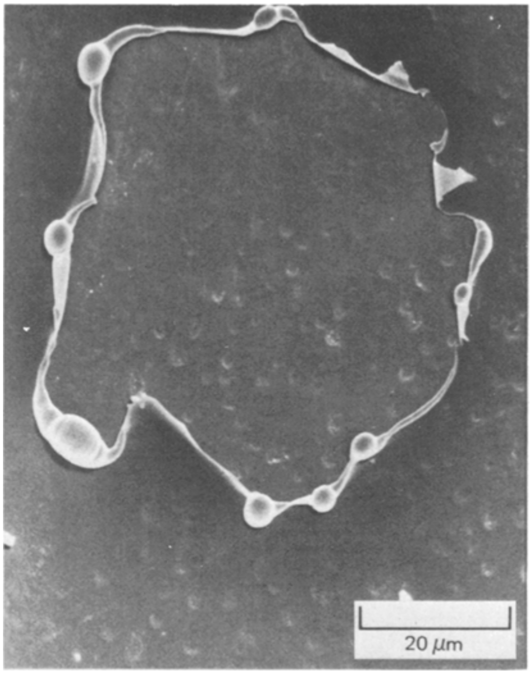

Figure 10 Scanning electron micrograph of surface blisters on a TGDDM-DDS (27 wt% DDS) epoxy after exposure to five thermal spikes.

The surfaces of the thermally-spiked and non-spiked TGDDM-DDS epoxies were examined by scanning electron microscopy for the presence of surface microcracks. No significant areas of microcracking were observed in any of the specimens when examined under magnifications of 30 000×, with the exception of a few, isolated fabrication markings. However, for thermally-spiked specimens that were exposed to more than three thermal spikes, evidence of surface blistering was observed. The scanning electron micrograph in Fig. 10 illustrates the remnants of a burst, ~ 50 μm blister. After bursting, the thin, apparently ductile surface layer of the blister relaxed and rolled-up at the outer boundary of the original blister. Smaller, 1 to 2 μm diameter protruding blisters also cover the surface in this micrograph.

The additional ~ 1.6 wt % moisture sorbed by epoxies after exposure to thermal spikes is not primarily caused by microcracking as suggested by Browning [19]. No surface microcracks were observed in thermally-spiked epoxies investigated in this study. Furthermore, in our studies of the effect of constant stress on subsequent moisture sorption by epoxies, the presence of fracture surfaces in specimens that fractured under constant stress did not enhance any detectable moisture sorption relative to specimens that had not fractured. We attributed the additional ~ 0.4 wt % moisture sorbed by the epoxies after stressing primarily to craze growth which occurs during the initial stages of failure. In the thermally-spiked specimens, however, no evidence of crazing was observed.

The primary mechanism by which thermally-spiked epoxies sorb additional moisture can be explained in terms of moisture-induced free-volume changes. The molecular mobility of the epoxy is enhanced as the T_g of the epoxy–moisture system is approached at the high temperatures experienced during the thermal spike. This molecular mobility is sufficient to enhance the dissociation of hydrogen bonds (H-bonds) between the water molecules and active sites within the epoxy. (H-bonds have small bond energies in the range 2 to 10 kcal/mol^{-1} and small activation energies are involved in their formation and rupture [47].) Although the ruptured H-bonds can reform at active sites, there is an overall decrease in the amount of H-bonding and a corresponding increase in the mobility of the water molecules. The more mobile, less H-bonded, water molecules require a greater free volume because H-bonding generally causes a volume decrease. (In organic compounds H-bonding is responsible for volume decreases from 1.5 to 9.0 cm^3 mol^{-1} [48]). The molecular mobility of the epoxy–moisture system during a thermal spike is sufficient to allow configurational changes to occur within the epoxy network that accommodates the greater free volume required by both the more-mobile water molecules and the normal moisture-induced swelling stresses imposed on the epoxy. These free-volume increases which involve permanent rotational-isomeric population changes within the epoxy network are fixed in the epoxy glass during the rapid cooling after the thermal spike. The additional free-volume allows water molecules access to previously unavailable active sites within the epoxy. However, many sites remain inaccessible to the water molecules because of steric effects associated with the permanent cross-links within the network. (In these studies < 4.5 wt % moisture was sorbed by the thermally-spiked specimens. However, for each hydroxyl, amine, and sulphonyl site within the TGDDM-DDS epoxy to be H-bonded with one water molecule would result in ~ 10 wt % moisture sorption. The exact number of active sites in the TGDDM-DDS epoxy is unknown at present because of the complexity of the cure reactions that produce this polymer [8].)

The experimental observations of a number of workers are consistent with moisture-induced free-volume changes being primarily responsible for the additional moisture sorbed by epoxies after exposure to thermal spikes.

Browning [19] found that thermally-spiked, wet TGDDM-DDS based epoxies exhibit a residual thickness increase of 1.75% on drying specimens to their original weight. However, no such dimensional changes were observed on drying wet, non-thermally-spiked specimens. These observations confirm that moisture, during a thermal spike, can induce configurational epoxy network changes which are permanently fixed in the glassy state. These changes are produced only if the T_g of the epoxy–moisture system is approached. Moisture-induced swelling stresses acting on a rigid epoxy network at lower temperatures do not produce permanent network changes. This mechanism is also consistent with DeIasi and Whiteside's [30] observations that initially wet TGDDM-DDS epoxies exhibit three-fold larger expansions as T_g is approached than do initially dry specimens.

Attenuated total-reflection Fourier-transform infra-red spectroscopy (ATR-FTIR) studies indicate that exposure to a combination of stress and sorbed moisture at 135° C in an autoclave produces a looser network structure in TGDDM-DDS epoxies than in specimens exposed to a similar stress in a dry environment at 135° C [49]. This looser network structure could be attributed to moisture-induced free-volume changes together with the rupture of some of the epoxy network cross-links. (The rupture of a few network cross-links occurs during thermal spiking and causes the enhanced surface ductility associated with the observed blister formation after three thermal-spike cycles.

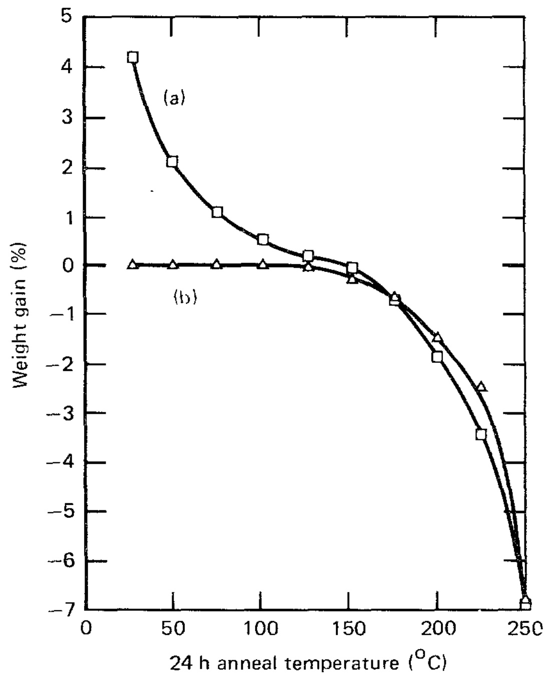

Figure 11 Weight changes of initially (a) wet (~ 4 wt% sorbed moisture) and (b) dry TGDDM-DDS (27 wt% DDS) epoxies as a function of 24 h anneal temperature.

A lower cross-link density network also lowers the constraints to rotational-isomeric configuration changes that occur in epoxy–moisture systems on exposure to high temperatures during a thermal spike.)

The failure to sorb additional amounts of moisture after four thermal spikes (Fig. 9) is also consistent with moisture-induced free-volume increases being primarily responsible for the enhanced moisture-sorption capabilities of the epoxies. This effect is caused by two factors. First, a finite number of active sites is available for moisture interaction within the epoxy. Second, the amount of free volume that can be generated under the conditions of a thermal spike is restricted, thus limiting the number of accessible active sites available for interaction with moisture.

The elimination of unreacted low-molecular-weight material from TGDDM-DDS epoxies during a thermal spike could leave vacant, active moisture sorption sites within the epoxy which would enhance subsequent moisture sorption. Previous studies on dry TGDDM-DDS (27 wt% DDS) epoxies show that annealing from 150 to 250° C causes $\overset{\sim}{<}$ 7 wt% loss of low-molecular weight material such as unreacted DDS [8]. The additional available moisture sorption sites produced by the elimination of this unreacted material enhance the amount of moisture subsequently sorbed in an autoclave by ~ 1.5 wt%. In Fig. 11, the weight losses of initially wet (~ 4 wt% sorbed moisture) and dry TGDDM-DDS epoxies are plotted as a function of 24 h anneal at 23 to 250° C. At 150° C, the maximum temperature of the thermal spike, there is negligible weight loss for either the initially wet or dry specimens. These observations therefore indicate that the loss of low-molecular-weight material is not a significant factor in enhancing subsequent moisture sorption in TGDDM-DDS epoxies after exposure to the thermal spike conditions utilized.

Hence, from the evidence available, moisture-induced free volume changes that are fixed in the epoxy glass are primarily responsible for the enhanced moisture sorption of thermally-spiked epoxies. To a lesser extent, the rupture of cross-links, crazing, and/or cracking and the loss of unreacted material can also contribute to enhanced moisture sorption after thermal-spike exposure.

Whether thermal-spike exposure will cause production of microcracks or crazes in epoxies depends on a number of phenomena. Browning [19] found that after exposure to thermal spikes, TGDDM-DDS based epoxies exhibited numerous microcracks. He suggested that such damage occurred during rapid cooling (~ 500° C min^{-1}) after the spike. The rapid cooling rate causes the exterior of the epoxy to be colder than the interior, which results in surface tensile stresses. In addition, moisture is volatilized from the exterior but not from the interior of the glass during the temperature-rise portion of the spike, which leads to a moisture gradient. The larger swelling stresses in the interior of the material relative to the less-swollen exterior results in surface tensile stresses which, together with those stresses that result from the temperature gradients and relaxation of fabrication stresses and strains, are sufficient large to cause growth of permanent damage regions. During the short duration of the thermal spike, some moisture remains in the epoxy surface region and lowers the craze cavitation stress, thereby enhancing the possibility of surface damage. This mechanism is a typical solvent-induced cracking and/or crazing phenomenon that occurs in polymeric materials [1].

The magnitude of the fabrication stresses and strains within the epoxy determines whether surface damage will occur after thermal-spike exposure. For example, Hopfenberg and co-workers [50–54] have shown that solvent crazing can be significantly enhanced by any orientation present in the polymer. Crazing has been shown to occur at the boundary between the outer swollen gel and the unpenetrated glassy core of the polymer when the combined orientation and swelling stresses are sufficiently large to cause craze cavitation and propagation. Subtle differences in polymer orientation can result in significant changes in the rate of solvent crazing. These workers also found that crazing can occur upon either sorption or desorption of the diluent from the glassy polymer depending on variations in the thermal and mechanical histories of the glass.

The fabrication stresses and strains should be less in the epoxy specimens used in this investigation than in those studied by Browning [19], which were five times thicker. (Larger temperature gradients and shrinkage stresses during cure are expected to cause larger fabrication stresses and strains in thicker epoxy specimens.) Hence, the former specimens should be less susceptible to crazing and/or cracking than those of Browning's after thermal-spike exposure. The thicker specimens studied by Browning [19] sorbed ~ 2 wt% more moisture after thermal spike exposure, whereas our thinner specimens only sorbed ~ 1.6 wt% more moisture. The larger enhancement of moisture sorption after thermal-spike exposure by the thicker specimens could be associated with the presence of surface crazes which allow moisture access to additional active sites.

4. Conclusions

(1) Sorbed moisture plasticizes TGDDM-DDS epoxies and lowers their tensile strengths, ultimate elongations, and moduli. The fracture topographies of the initiation cavity and mirror regions of these epoxies indicate that sorbed moisture enhances the craze initiation and propagation processes. The crazing process is more susceptible to sorbed moisture than T_g which can be explained in terms of local moisture concentrations enhancing the local cavitation and flow processes. Hence, modification of T_g by sorbed moisture cannot be utilized alone as a sensitive guide to predict deterioration in the mechanical response and, hence, the durability of epoxies.

(2) Constant tensile stresses > 38 MPa, applied for 1 h on initially dry TGDDM-DDS epoxies enhance subsequent moisture sorption by ~ 0.5 wt%. These studies when conducted as a function of stress-level indicate that the initial stages of failure that involve both dilatational craze propagation and subsequent crack propagation enhance the accessibility of moisture to sorption sites within the epoxy to a greater extent than in the later stages of failure which involves crack propagation alone.

(3) The amount of moisture sorbed by TGDDM-DDS epoxies is enhanced by ~ 1.6 wt% after exposure to a 150° C thermal spike. The moisture-induced swelling stresses together with the enhanced mobility of the water molecules within the epoxy–moisture system during a thermal spike produce free-volume increases that involve rotational-isomeric configurational changes within the epoxy network. Such changes are fixed in the epoxy during the rapid cooling after the thermal spike. This additional free-volume allows water molecules access to previously inaccessible active sites within the epoxy. To a lesser extent, the rupture of cross-links, crazing, and/or cracking and the loss of unreacted material can also contribute to enhanced moisture sorption after thermal-spike exposure.

(4) Thermal-spike exposure can cause surface crazing and/or cracking of epoxies if the moisture-induced swelling stresses together with those stresses that result from temperature gradients and relaxation of fabrication stresses exceed that of the craze initiation stress at the maximum thermal-spike temperature. Thicker epoxy specimens are more susceptible to the growth of permanent damage regions during thermal-spike exposure because they are exposed to larger temperature gradients and shrinkage stresses during cure, which produce larger fabrication stresses and strains.

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