Adhesion of Glass/Epoxy Composites Influenced by Thermal and Cryogenic Environments

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ABSTRACT: Little information regarding the effects of prior thermal and cryogenic conditionings on hydrothermal and mechanical behavior, for varied volume fractions of constituent phases in polymer matrix fiber composites, has been published to date. The present experimental investigation uses flexural test to assess the effects of thermal and cryogenic treatments, and concurrently followed hydrothermal aging on quality of adhesion of multilayered laminates for 55, 60, and 65 wt % of E-glass fiber-reinforced epoxy composites. The specimens were conditioned at 80°C and −80°C temperatures for different time durations, and thereafter they were immediately immersed in boiling water for an hour. Water absorption rates were evaluated for those conditioned specimens in such environment. Absorption study in hydrothermal aging showed a remarkable variation for the two cases of prior conditionings. The shear strength values were compared with the test value of as-cured samples. Degradation of mechanical property was found to be less prevalent during hydrothermal aging, with a prior conditioning at 80°C temperature compared to −80°C treated glass/epoxy composites. Improved shear strength for almost all conditions of thermal conditioning in the initial stages has highlighted better adhesion influenced by postcuring phenomena during thermal or cryogenic conditioning. It was also observed from water absorption data that high temperature conditioning contributed more strengthening effect and better adhesion at the interfaces. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1943–1949, 2006

Key words: composites; adhesion; ageing; absorption; mechanical properties

INTRODUCTION

The interphase is defined as a region that is manifested as a result of bonding and reactions between the fiber and the matrix. This region is the site of synergy in composite materials, and its influence to overall mechanical properties is significant.[1] It is generally recognized that the bond strength variation at the interface greatly affects the integrity of composite materials. The bond strength depends on the quality of interfacial adhesion. It can vary in epoxy resin composites on the kind of aging conditioning.[2] Environmental attack can degrade fiber/matrix interface mostly by mechanochemical principle. Thermal aging behavior of epoxy resins is of special interest, because of their expanding use for structural applications, where increased temperatures are common environmental conditions. Significant chemical and structural changes in epoxy networks take place during thermal and hydrothermal aging. Thermo-oxidative degradation and disintegration of short-range ordering are observed in epoxy network during thermal aging. It is concluded that these changes exert influence on the performance of epoxy matrix composites.[3,4] These alternations in bulk polymer matrix may affect the quality of adhesion at the interface. It is important to understand the aging mechanism of polymer composites for their use in wet and thermal environments. The mechanical behavior of composites depends on the ability of interface to transfer stress from the matrix to the reinforcement fiber. It is at the interface region where stress concentrations develop. FTIR imaging suggests that there is a chemical structural gradient in the epoxy matrix from glass fiber surface to the polymer bulk because of different conversions.[5]

Delamination and microcracking are some of the most frequently observed damage phenomena that may develop in polymer composites exposed to cryogenic temperatures.[6] Water in polymers, at room temperature and above, is considered to act as a softening agent, but at cryogenic temperatures, polymers become stiffer than do dry ones.[7] Research and development of polymeric materials for cryogenic applications have been intensified because of their specific usefulness in cryogenic environments. The physical properties of polymer materials depend decisively on frequencies of molecular excitation through the relaxation time, which depends on temperature.[8]

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The main objective of the present experiment is to assess the hydrothermal behavior at a high temperature for a certain time of thermally and cryogenically shocked glass fiber reinforced epoxy composites. Thermal and cryogenic conditionings were performed for different time periods. One of the major disadvantages of glass fibers is poor adhesion to matrix resins. Whereas epoxy resins have good adhesion characteristics and good resistance to heat distortion. The work was also extended for evaluating the effects of weight fraction of reinforcement fibers on water absorption kinetics, as well as mechanical behavior of the conditioned specimens. Fiber/matrix interfacial areas change with the variation of constituent phases, and thus the effects of high and low temperature loadings on bulk polymer matrix and interfaces appear to control the interfacial adhesion and performance of a composite. Experimental results on water absorption values reveal that the impact of thermal and cryogenic conditionings is statistically significant. The variation of matrix-dominated mechanical property also appears to be significant.

EXPERIMENTAL PROCEDURES

An unmodified epoxy resin, based on Bisphenol-A and aliphatic primary amine hardener, was used with woven fabric E-glass fibers, treated with a silane-based sizing system, to fabricate the laminated composites. Three fiber weight percentages, 55, 60, and 65%, were targeted in the laminate fabrication by hand lay up technique. They were cured for 48 h at room temperature. The laminates of multilayered structures were cut by diamond cutter into short beam shear (SBS) test specimens. These ASTM standard (D 2344-84) specimens were used for water absorption and interlaminar shear strength (ILSS) values. The fiber/matrix bond quality can be assessed from the gross mechanical properties, such as ILSS and transverse tensile strength.

The SBS test specimens were suddenly exposed to a 80°C temperature oven for 1, 4, 9, 16, and 25 h. Another batch of samples was similarly exposed to ultra-low deep freezer at −80°C temperature for the same time durations. One batch of specimens from thermal and cryogenic conditioning treatments, at each point of conditioning time, was tested in a three-point flexural mode at ambient temperature, to evaluate the ILSS values of the thermally as well as cryogenically aged samples. The other batches of conditioned samples from each time of conditioning treatment of thermal and cryogenic natures were further instantaneously immersed in a boiling water bath for an hour. Water absorption kinetics study was based on weight changes after hydrothermal treatment. Weights of thermally

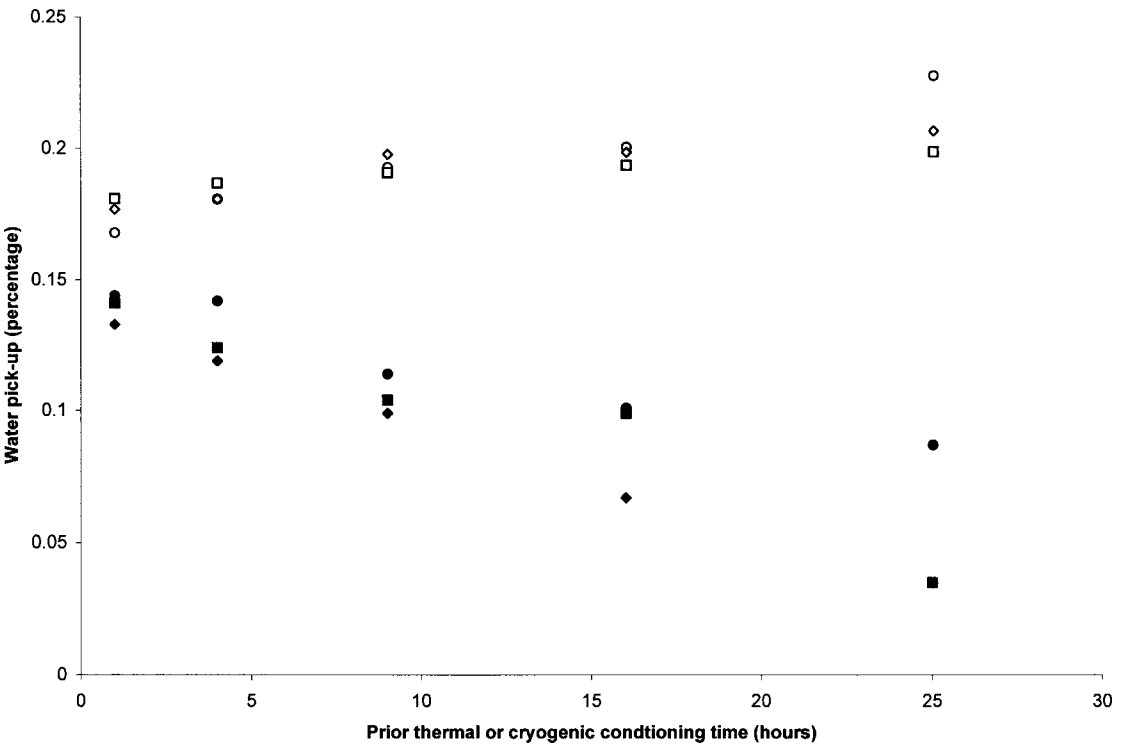

Figure 1 Water pickup percentage in boiling water for 1 h versus prior conditioning time, for 55 wt % glass fiber/epoxy (prior 80°C temperature (●) and −80°C temperature (○) conditioning), 60 wt % glass fiber/epoxy (prior 80°C temperature (■) and −80°C temperature (□) conditioning), and 65 wt % glass fiber/epoxy (prior 80°C temperature (◆) and −80°C temperature (◇) conditioning) composites.

and cryogenically shocked specimens were taken as an initial weight. The SBS tests were again performed at ambient temperature for those hydrothermally treated specimens, with a prior history of either thermal or cryogenic conditioning of different durations. Nearly, about 10 samples were tested at each point of experiment, and the average value was reported here.

The ILSS value was calculated as follows:

$$\text{ILSS} = 0.75P_b/wt$$

where P_b is the breaking load, w the width of specimen, and t the thickness of the specimen.

Water absorption percentage (W) was measured as follows:

$$W = (w_c - w_h)/w_c \times 100$$

where w_c is the weight of specimen after conditioning and w_h is the weight of specimen after hydrothermal aging.

Scanning electron microscope studies were performed on fractured surfaces of aged specimens, to assess the effect of thermal and cryogenic conditionings on interfacial adhesion of glass/epoxy composites.

RESULTS AND DISCUSION

Figure 1 shows the water pickup percentages for 1 h boiling water immersion treatment, with the conditioning time of prior thermal as well as cryogenic loadings for glass/epoxy composites of varied weight fraction fibers. It is observed that water absorption rate decreases with more conditioning time for the case of prior thermal conditioning at 80°C temperature of glass/epoxy laminates. The reverse trend was noticed in glass/epoxy laminated specimen for the prior cryogenically treated (−80°C temperature) specimen. These characteristics are found to be the same, irrespective of variation of weight percentages of fibers. Thermal conditioning at 80°C temperature might possibly improve adhesion level at the interfaces. Here, adhesion chemistry may be influenced by postcuring phenomena. This effect is supposed to increase with more conditioning time. Whereas low temperature conditioning might have introduced cracks and delaminated areas possibly by misfit strains at the interfaces, because of the differential coefficient of expansion between the fiber and polymer matrix. The diffusion coefficient of polymer chain has a strong power-law dependence on the degree of polymerization.[9]

Variations of ILSS values with the conditioning time for 55% glass fiber reinforced epoxy specimens, with only thermal and cryogenic treatments, and thereafter followed by hydrothermally aged specimens are shown in Figure 2. Experimental data show no statistically significant changes in ILSS values except for the less conditioning time. Figure 3 shows the changes of ILSS value with the prior thermal or

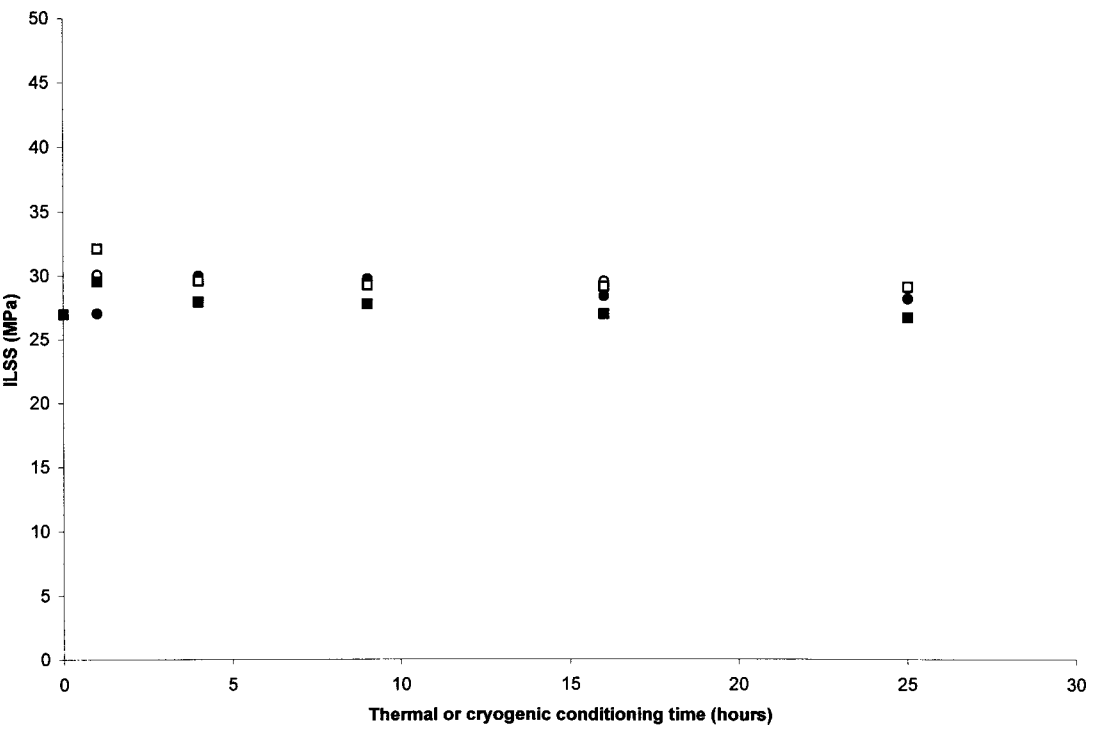

Figure 2 Variations of ILSS values with thermal or cryogenic conditioning time for glass/epoxy laminates (55% fibers) for only thermally (○) and further hydrothermally (●) conditioned specimens, as well as for only cryogenically (□) and further hydrothermally (■) conditioned specimens.

cryogenic conditioning time for 60% glass fiber/epoxy composites, with only thermal and cryogenic treatments, and for concurrently followed hydrothermally aged samples. Figure 4 shows the same variations of shear values for similar treatment in 65% glass fiber reinforced epoxy laminated composites.

A better fiber/matrix adhesion will impart better properties, such as ILSS and delamination resistance, to a polymeric composite.[10] The performance of fiber-reinforced polymer composite is often controlled by the adhesion chemistry at the fiber/matrix interface.[11] Thermal stresses caused by temperature gradient should be given critical attention in many application areas. The interactions between fiber and polymer matrix during thermal cycling are important phenomena. Environmental exposure generally results in reduced interfacial stress transmissibility.[12] A very large thermal expansion mismatch may nucleate fiber/matrix debonding or a possible matrix cracking during exposure to thermal and cryogenic environments. A number of properties of component performance are governed by the magnitude of strain fields around inhomogeneities, such as voids and cracks.[13]

The fiber/matrix interfacial behavior may be explained by the mechanical principle, with the assumptions made at the level of fiber/matrix adhesion and by surface chemistry approach.[14] Thermal conditioning prior to hydrothermal aging induces improved interfacial adhesion possibly by the surface chemistry phenomena. Cryogenic conditioning may contribute an incremental improvement of adhesion by mechanical keying factor only. The residual clamping stress acting normal to the fiber direction renders a synergistic benefit on top of the mechanical bonding. Thermal conditioning is likely to change the chemistry at the fiber/matrix interface either by forming an interpenetrating network[15] or by possible crosslinking in the epoxy network.[16] An established theory is that bonding through silane-treated glass fibers by other than simple chemical reactivity are possibly best explained by the interdiffusion and interpenetrating network formation at the fiber/matrix interface. A reasonable explanation for lesser improvement by cryogenic exposure is that crazing may possibly occur in lightly crosslinked thermoset resin but not in well-cured epoxy resins. It is generally believed that the reduction in shear strength is due to the partial debonding or the weakening of interfacial bond.[17] It is a three-point flexural test, which generally promotes failure by interlaminar shear, and the results of the test are useful for assessment of interfacial debonding and composite quality.

Figure 5 shows the adhesive failure between fiber and polymer in glass/epoxy composites for the unconditioned specimens. Figures 6 and 7 reveal a greater percentage of matrix/fiber coexistence of

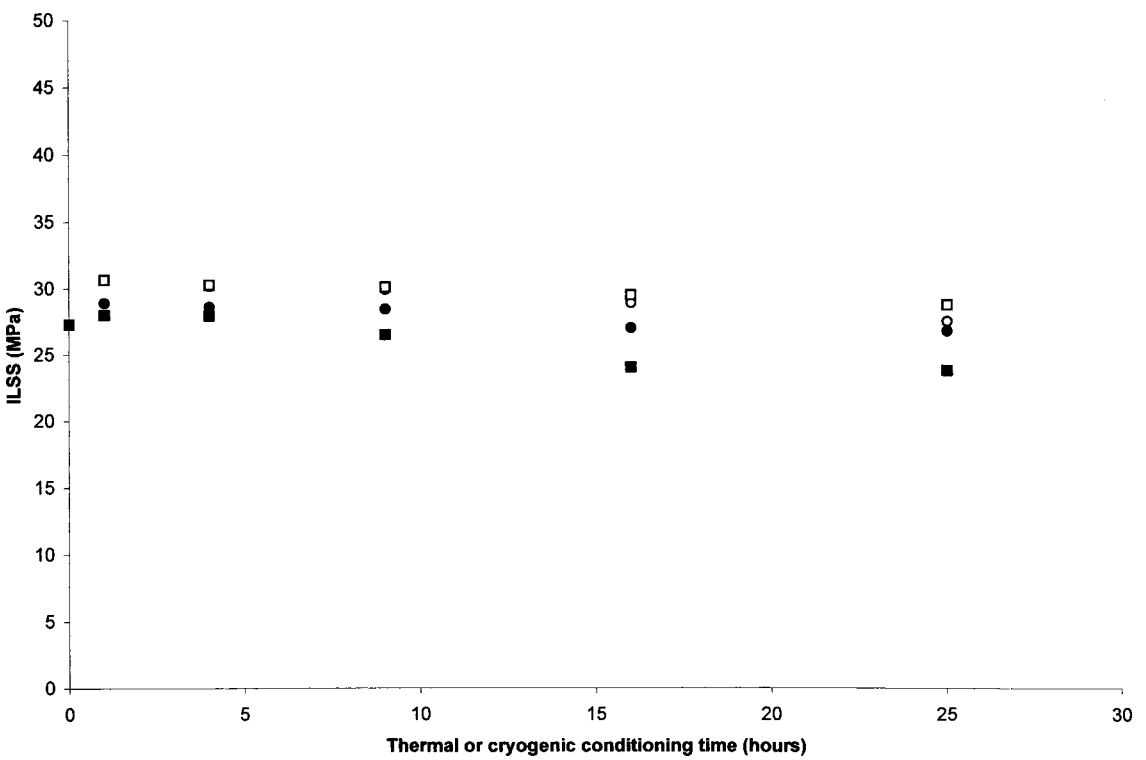

Figure 3 Variations of ILSS values with thermal or cryogenic conditioning time for glass/epoxy laminates (60% fibers) for only thermally (○) and further hydrothermally (●) conditioned specimens, as well as for only cryogenically (□) and further hydrothermally (■) conditioned specimens.

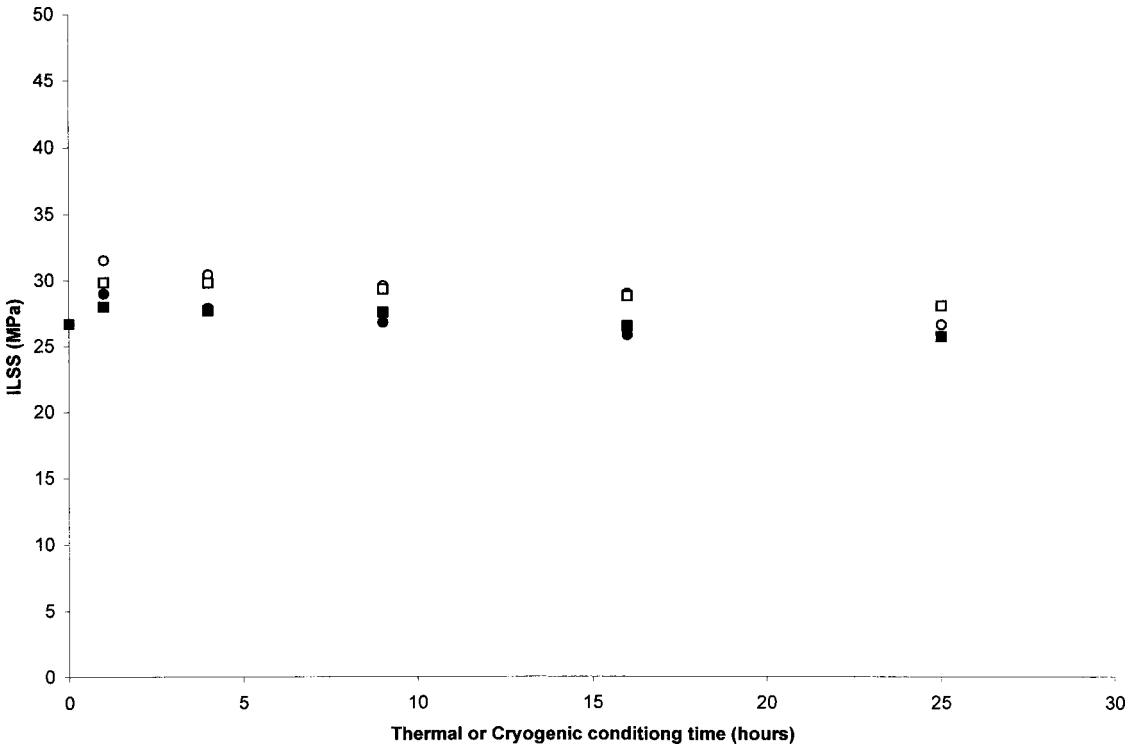

Figure 4 Variations of ILSS values with thermal or cryogenic conditioning time for glass/epoxy laminates (65% fibers) for only thermally (○) and further hydrothermally (●) conditioned specimens, as well as for only cryogenically (□) and further hydrothermally (■) conditioned specimens.

thermally aged specimen. A noticeable loss in interfacial integrity at the fiber/matrix areas is evident in cryogenically conditioned composite sample (Figs. 8 and 9). The mechanical performance of fiber-reinforced composites is strongly dependent upon the quality of fiber/matrix adhesion. Cryogenic hardening may modify the local threshold required for breaking of adhesion bondage at the fiber/matrix interface. Most polymers lose their ductile properties below their glass transition temperature. Cooperative chain motions involving main chain bond rotation become extremely restricted.[8] The transmissibility of stress, the stress build-up in broken fibers, and the redistribution of stresses in the neighboring intact fibers are all governed by the interfacial strength and integrity.[18] The deteriorated integrity can cause reduced strength properties.[19]

A very large thermal expansion mismatch between a fiber and polymer matrix can result in possible debonding and matrix/interfacial crackings in polymer composites because of misfit strains at the interface. Physical interactions between polymer and fibers are always present at the interface. These interactions may reasonably assumed to be dependent on temperature. The interfacial bond strengths in glass/epoxy composites may vary depending on parameters of aging conditioning.[2] The bond strength depends on the quality of interfacial adhesion. Further crosslinking in epoxy resin is highly probable during thermal conditioning, but not during cryogenic conditioning. The fiber/matrix adhesion has a direct impact on the formation of microcracks in a laminated composite in response to cryogenic cycling.[6] The first form of damage in laminates is commonly matrix microcracks and interlaminar cracks. The immediate effect of such cracks is to degrade the thermomechanical properties of a laminated composite, including Poisson ratios and thermal expansion coefficients. These microcracks can also induce delamination.

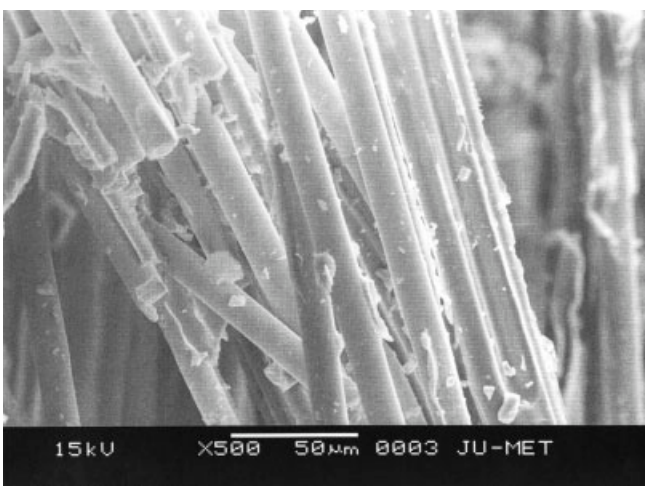

Figure 5 SEM micrograph shows deadherence of epoxy matrix with glass fibers for unaged specimens.

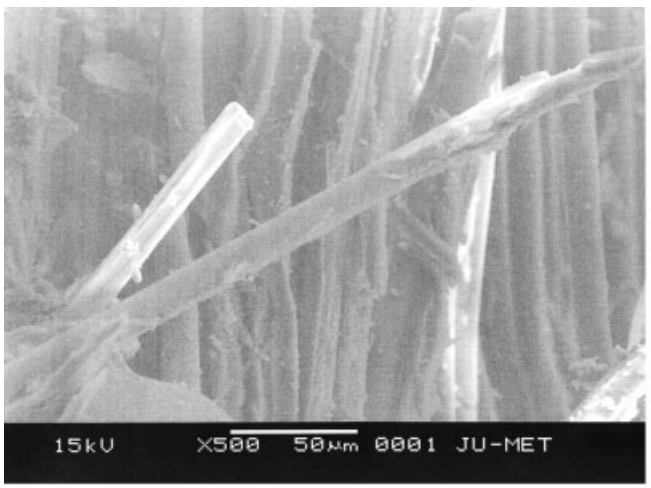

Fig. 6

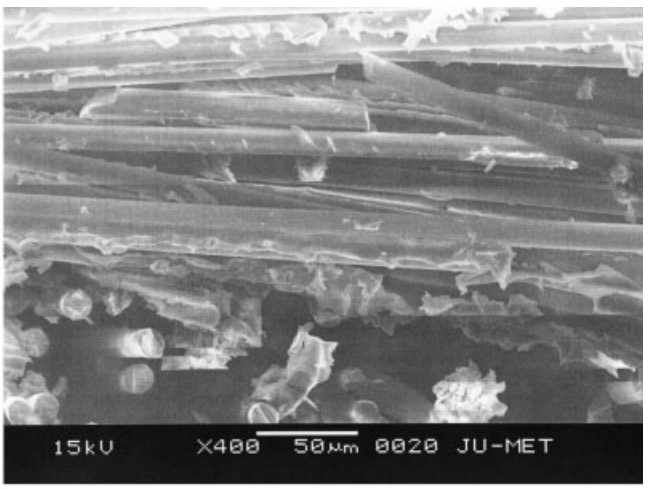

Fig. 7

Figures 6 and 7 SEM micrographs reveal the presence of better adhesion integrity at the fiber/polymer interface for thermally and concurrently followed hydrothermally aged glass/epoxy composites.

Thermal aging and subsequent hydrothermal exposure with a temperature gradient can promote irreversible effects of the epoxy resin matrix, especially in the vicinity of the substrate.[20] One of the key features of this material class is their damage initiation and propagation behavior, which is spatially distributed in nature, and comprises a variety of mutually interacting damage modes. The most common damage modes are matrix cracking, delamination growth, and fiber fracture.[21] A number of properties of amorphous materials, including fatigue, fracture, and component performance are governed by the magnitude of strain fields around inhomogeneities, such as voids and cracks.[13] Regardless of the application, once cracks have formed within polymeric materials, the integrity of structure is significantly compromised. Microcracking induced by environment is a long-standing problem in polymer composites. Cracking leads to mechanical degradation of fiber-reinforced polymer composites.[22]

Residual stresses are inherent in almost all fiber-reinforced polymer composites. They are often underestimated in both design and analytical modeling. This oversight can lead to misinterpretations of material characteristics and mechanical behavior. Residual stresses of thermal origin can be either micro- or macroresidual stresses. The microresidual stresses arise from the differential coefficient of thermal expansion (CTE) of the fiber and matrix resin and the temperature gradient. Whereas microresidual stresses are present within the individual ply of laminated composites. These arise from the difference between the

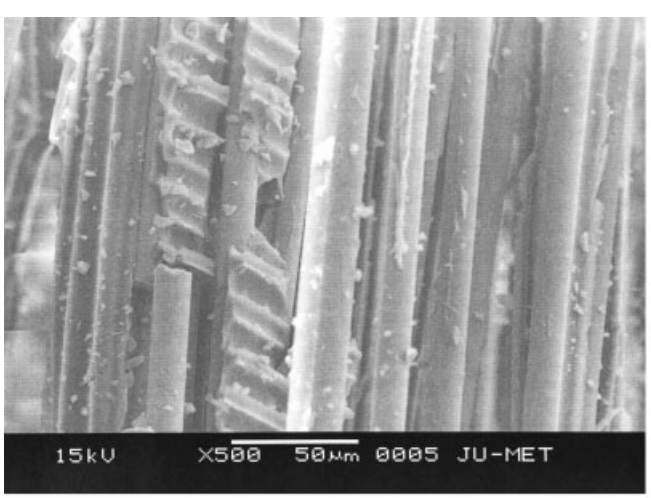

Fig. 8

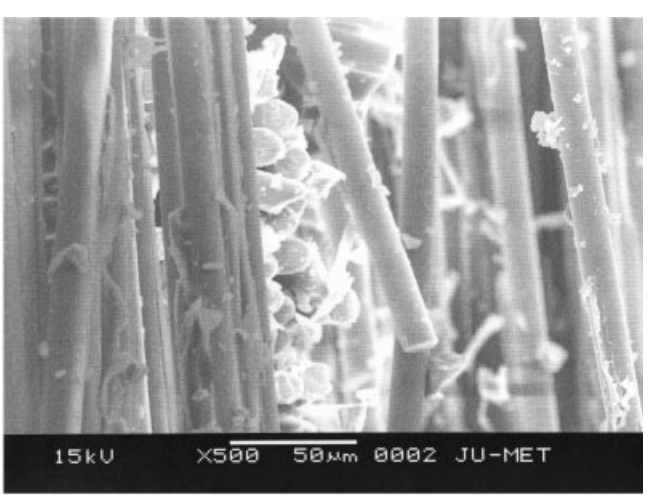

Fig. 9

Figures 8 and 9 SEM micrographs reveal a loss of adhesion integrity at the fiber/polymer interface for cryogenically and concurrently followed hydrothermally aged glass/epoxy composites.

ply CTEs, in the longitudinal and transverse directions. This so-called lamination residual stress promotes the onset of cracking and delamination.[23]

CONCLUSIONS

The present investigation leads to the following conclusions: water absorption rate decreases with more prior thermal conditioning time during hydrothermal aging. The reverse trend is noticed in prior cryogenic treatment for glass/epoxy composites in an hour of hydrothermal treatment. Cryogenic exposure might have introduced matrix cracking or interfacial debonding, which resulted in greater percentage of absorbed water in a shorter time.

Thermal conditioning imparts better adhesion and, thus, an improved ILSS value, especially at the less conditioning time. It is possibly attributed by surface chemistry principle at the fiber/polymer interface.

Low temperature conditioning effect is not so significant in improving the adhesion quality. Here strengthening phenomena are supposed to be introduced by mechanical keying factor only at the fiber/matrix interfaces.

Degradation of mechanical property is more prevalent in higher volume fraction reinforcement composites. Environmental damage is sensitive to fiber/polymer interfaces and quality of adhesion.

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