

Influence of KOH Solution on the Tensile Strength and Chemical Stability of Carbon Fiber-Reinforced Epoxy Resin Composites

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ABSTRACT: The effect of a relatively high concentration of KOH solution (4M) on the mechanical properties and chemical stability of carbon fiber-reinforced epoxy resin composites, prepared with different volume fractions of reinforcement, were investigated. Upon treatment of specimens of such composites with the KOH solution at different temperature and for different durations, their tensile strengths were adversely affected to varying degrees, depending on treatment conditions and volume percent of carbon fiber reinforcement used. Surfaces of treated specimens were examined for matrix stability, fiber disruption, and debonding. Optical microscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy

(XPS) were used to evaluate chemical and mechanical degradation of these composites. Results clearly showed that prolonged exposure of composite specimens to such aggressive environments markedly increased the degradation of their mechanical properties. On the other hand, these results also showed that increasing the volume fraction of the carbon fiber reinforcement reduced the severity of degradation of these composite and enhanced their mechanical stability. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1682–1690, 2005

Keywords: resins; reinforcement; composite; degradation; mechanical properties; ESCA/XPS

INTRODUCTION

Epoxy polymers are widely employed as the basic adhesive constituents and as matrix materials for composites containing glass, polyamide, and carbon fibers. When cured, epoxy resins produce highly crosslinked, amorphous thermoset polymers. The resulting structure of such polymers possesses many useful engineering properties. However, the greatest use of epoxies is being made in the aviation industry as adhesives and as matrix materials in fiber-reinforced composites for structural applications.¹

A major concern with these materials is the effect of their long-term exposure to severe environments on their physical and mechanical properties. Akay et al.² evaluated the effect of fiber type and exposure to a high temperature environment on the interlaminar-shear strength and impact performance of carbon fiber reinforced bismaleimide composites. Their result showed that the degradation of polymer and fiber-matrix interface with aging deteriorated progressively and the failure mode of the impact specimens changed from a brittle failure in the unaged state to a progressive delamination in the aged state. The effect of dis-

tilled water at 25°C on unidirectional glass fiber reinforced and glass-carbon fiber reinforced (glass to carbon fiber volume ratio 3 : 1) epoxy matrix composites was investigated by Shan and Liao.³ They found that the effect of water became apparent at low stress levels of 65 and 45% ultimate tensile strength (UTS). Thus, by incorporating an appropriate amount of carbon fibers in glass fiber composite, a much better performance in fatigue can be achieved. A study of changes in the microstructure, composition, and properties of glass, organic, and carbon fiber reinforced plastics was carried out by long-term exposure (up to 50 months) of specimens outside the Salute and Mir orbital stations by Deev and Nikishin.⁴ They revealed that the largest changes in the structure and composition were in the exterior surfaces of all specimens. They also reported that the depth of the structural change depended on exposure time and polymer matrix type. Kenny et al.⁵ focused in their thermogravimetric analysis study on the degradation of continuous carbon fiber reinforced composites with a polyether-ether ketone (PEEK) matrix. They confirmed that good thermal stability can be achieved by employing PEEK as a matrix for carbon reinforced composites. Degradation of filled epoxy resin surfaces by nitric acid fumes was investigated by Hepburn et al.⁶ They found that exposing resin samples to acid fumes for 50 h can produce changes that mimic changes in situations where synergetic reactions may have occurred.

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Recently, more attention has been given toward the chemical stability of polymeric materials. Kamo et al.⁷ discussed the reaction mechanism of polyvinyl chloride decomposition with *t*-decalin and tetralin solvents. The effect of ozone on the degradation of polypyrrole was reported by Cataldo and Omastová.⁸ The mechanism of Environmental Stress Cracking (ESC) of amorphous polycarbonate immersed in isopropyl alcohol, ethylene glycol monomethyl ether, and methanol were studied by Al-Saidi et al.⁹ They monitored the resistance of the polymer as a function of time at different given strain-values and different initial stresses. These researchers found that variation of stress with immersion time can be a very good indicator of how a polymer would behave in specific environments and strain conditions upon exposure to various chemicals.

Day et al.,^{10,11} Wazzan,¹² and other researchers (13–15) have focused on improving the mechanical properties of carbon fiber reinforced epoxy resin composite. Most of the reported work was concerned with the toughening of the polymer matrix¹⁰ and surface treatment of the carbon fiber as reinforcement.¹³ It was long believed that reinforced composites would not suffer corrosion or deterioration experienced by other conventional materials. However, it is now recognized that all engineering materials can be affected by environmental degradation within hours of exposure. There is, however, little knowledge available about the chemical stability of carbon fiber reinforced epoxy resin composites (CFRC).

The current research was initially motivated by the desire of one of the coauthors of this paper to investigate the possible utilization of reinforced epoxy resin composites as cell frame material for a pilot scale electrolysis cell employing 4M KOH aqueous solution as an alkaline electrolyte solution.¹⁶ The objective of this work was, therefore, to investigate the chemical and mechanical stability of a carbon fiber reinforced epoxy resin composite when exposed to aqueous alkaline solutions of relatively high concentrations.

Experimental investigations were therefore carried out using CFRC. Specimens prepared with different volume fraction of carbon fiber reinforcement were exposed to 4M KOH aqueous solutions at 50°C and 80°C, and for a duration of one and two weeks. These specimens were consequently subjected to tensile tests followed by morphological examinations using optical and scanning electron microscopy (SEM) and surface analysis using X-ray photoelectron spectroscopy (XPS) to quantitatively identify surface alkali residues.

Materials

Specimens of carbon fiber reinforced epoxy resin composites of this study were made using Shell Epon 828 epoxy resin with diamino-3, 5-diethyltoluene (Etha-

cure-100, Albemarle S.A.) as the hardener. These components were used in the ratio of 100 parts by weight resin to 23.91 parts by weight hardener, which gave a 1 : 1 stoichiometric ratio of epoxy : NH groups, based on functional group analysis by titration.¹² Work reported by others^{11,17} shows that this composition yields a highly-cross-linked resin with a glass transition at approximately 175°C.

The reinforcement used in this study was a high strength unidirectional carbon fiber fabric consisting of Tenax HTA 400 tex carbon fibers supported by a polyester scaffold. This fabric was manufactured by Heinsco and supplied by SP Systems. The as-received fibers had a proprietary epoxy-compatible surface treatment.

4M potassium hydroxide aqueous solution was prepared by dissolving 224.4 g of lab grade KOH granular solids in one liter of distilled water.

Preparation of the resin

To avoid the possible incorporation of air in the resin, a 1% by wt. of an air release additive, ByK-A 501 supplied by ByK Chemie GmbH, was added to the Epon 828 epoxy resin. The mixture was degassed under vacuum using a rotary film evaporator for 30 min. The hardener was then added and mixed carefully to minimize further entrainment of air. Finally, the mixture was degassed in a vacuum oven for 10 min before molding.

Resin-transfer molding

The composite specimens were made using a Plastech Hypaject resin-transfer molding machine linked to a composite tool with a cavity that is rectangular in shape and of dimensions 250 × 350 mm. Prior to molding, the tool was prepared by treatment with a release agent (Frekote 44-NC) and the faces of the mold were wiped with a silicone fluid based mold release agent. The edges of the mold were coated with high vacuum grease to aid ejection of the laminate. The mold was preheated to 100°C, which is the maximum temperature at which the tooling can be used. Once the mold was loaded with fiber, it was turned such that the plane of the cavity was vertical. In this way, entrainment of air during mold filling was minimized. The resin was injected from the bottom and the air vent was positioned at the top. The resin reservoir (commonly known as the homogenizer) was modified to allow it to be heated and maintained at a temperature of 70°C to reduce the viscosity of the resin. This allowed the use of lower injection pressures, thus minimizing fiber wash. Prior to injection, the resin was drawn into the homogenizer under vacuum and the vacuum was maintained until injection commenced so that degassing was possible. Injection

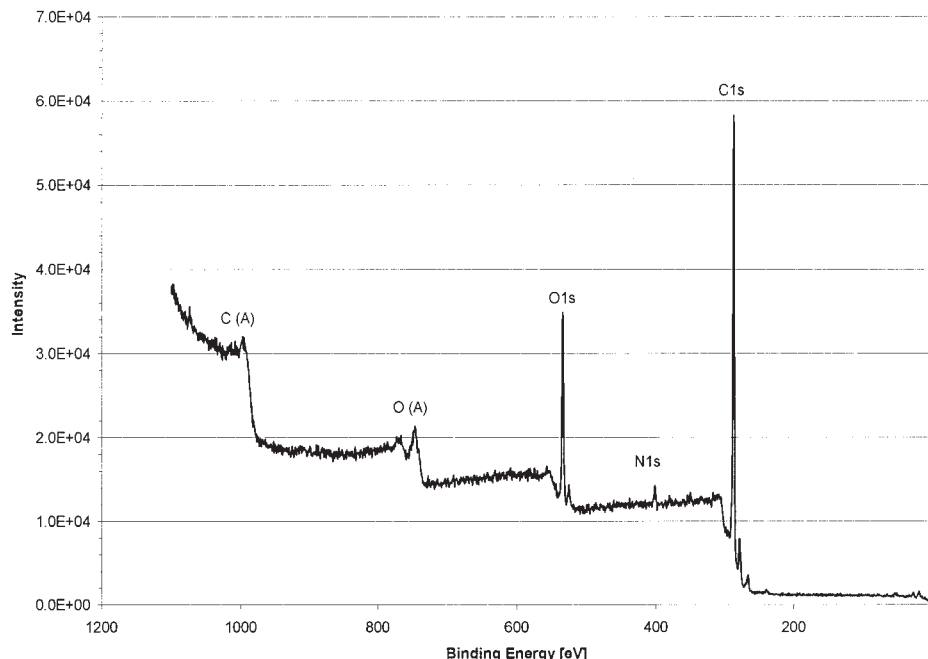


Figure 1 A typical XPS survey of untreated epoxy resin matrix prepared by resin transfer molding.

took place with an initial pressure of 0.5 bar, which was increased towards the end of mold filling to 4 bar. A commercial resin sensor (AGC supplied by Plastech T. T.) was built into the top of the mold. Arrival of the resin at this point was indicated by a voltage signal from the sensor, which then decreased when the resin gelled. Resin was observed at the vent soon after the sensor indicated the presence of the resin. The molding was left in the mold for 5 h at 110°C, after which it was removed and postcured in an oven under nitrogen at 185°C for 5 h. This procedure was necessary as a result of the relatively lower temperature limitation imposed by the composite tooling used. The scanning differential calorimetry experiments for a system similar to that used in this work showed these curing conditions to be satisfactory, as described elsewhere.¹⁰

Fiber volume fraction determination

In addition to preparation of the required number of un-reinforced epoxy resin specimens for this study, the required number of specimens of different carbon fiber reinforced epoxy resin composites was prepared as follows:

1. Unidirectional composites containing 4 layers of reinforcement: These specimens had a fiber-volume fraction of approximately 0.20.
2. Unidirectional composites containing 12 layers of reinforcement: These specimens had a fiber-volume fraction of approximately 0.50.

The fiber-volume fraction was determined using optical microscopy. Samples were taken from five different places in the laminate by cutting and then polishing cross-sectional surfaces perpendicular to fiber direction. An area containing 1000 to 1500 fibers was selected under an optical microscope with 500 × magnifications and fibers in the selected area were counted. Based on knowledge of the average fiber diameter and the actual size of the selected area, the area fraction of the fibers could be determined. This was then taken to be the same as the volume fraction of the fibers.

Tensile testing

Tensile testing was carried out using a computerized Instron 5568 universal testing machine. Rectangular samples of 20 mm width and 85 mm gauge length were cut of the cured laminates using a fine bandsaw and smoothed using P1200 waterproof abrasive paper. The unidirectional composites containing 4 layers of reinforcement were 1.5 mm thick, whereas those containing 12 layers of reinforcement were 3 mm thick. Clamping was achieved by wrapping a piece of emery cloth around the ends of the specimen. Measurements were carried out at $23 \pm 1^\circ\text{C}$ and with an extension rate of 0.5 mm min^{-1} . Results from samples that failed within the grips were excluded.

X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is proba-

bly the most widely adopted technique for surface analysis of polymers. This is mainly because of its high-surface sensitivity and low surface damage due to the low photon energy used for excitation. Ultra high vacuum environment (1×10^{-8} mbar or lower) is a basic requirement of XPS analysis to minimize the scatter of photoelectrons and contamination of the sample surface.

XPS is a useful tool to investigate surface chemical composition and the existence of chemical bonds. In fiber-reinforced composites, XPS is used to examine samples' surfaces before and after pretreatment for adhesive bonding.¹⁸ Carbon fibers are always given a surface treatment to improve their properties. XPS is used to analyze the carbon fibers after chemical modification¹⁹ and electrochemical modification.²⁰ To improve the impact resistance of carbon fiber-reinforced epoxy composites, XPS has been used to study the Ni-P coating on carbon fiber surfaces after treatment.²¹

In this study surface chemistry of both treated and untreated samples were investigated using XPS analysis. A MAX 200 multi-technique surface analysis system manufactured by LEYBOLD was used for this purpose. The sample magazine, which contains seven sample holders, was loaded with samples measuring 20 mm \times 20 mm each. All samples were investigated under the same conditions of ultra high vacuum in the order of 10^{-9} mbar and excited with Mg-K α radiation at 10 kV high voltage, 10 mA emission current, and acquired with a hemispherical analyzer at constant radiation mode. To avoid damaging the carbon signal, the carbon element was scanned first. This was followed by a general survey of the sample, and then the rest of the elements. A typical XPS general survey spectrum of the untreated epoxy is shown in Figure 1. XPS analysis is capable of detecting all basic elements except hydrogen. Thus, in addition to carbon, oxygen and nitrogen were scanned for as well as potassium in the treated samples. The area under each element peak was calculated by first subtracting the background signal and then integrating the area under the element peak. Sample surface composition in atomic and weight percentage was then calculated using the elements' relative cross-sectional area as supplied by the XPS manufacturer.

Scanning electron microscopy (SEM)

Tensile and impact fracture surfaces of the composite samples were coated with gold and then analyzed using a JSM SEM Model T300 scanning electron microscope operated at 15 keV.

RESULTS AND DISCUSSION

Tensile testing

Effects of treatment of different specimens of carbon fiber reinforced resin composites, of 0%, 20%, and

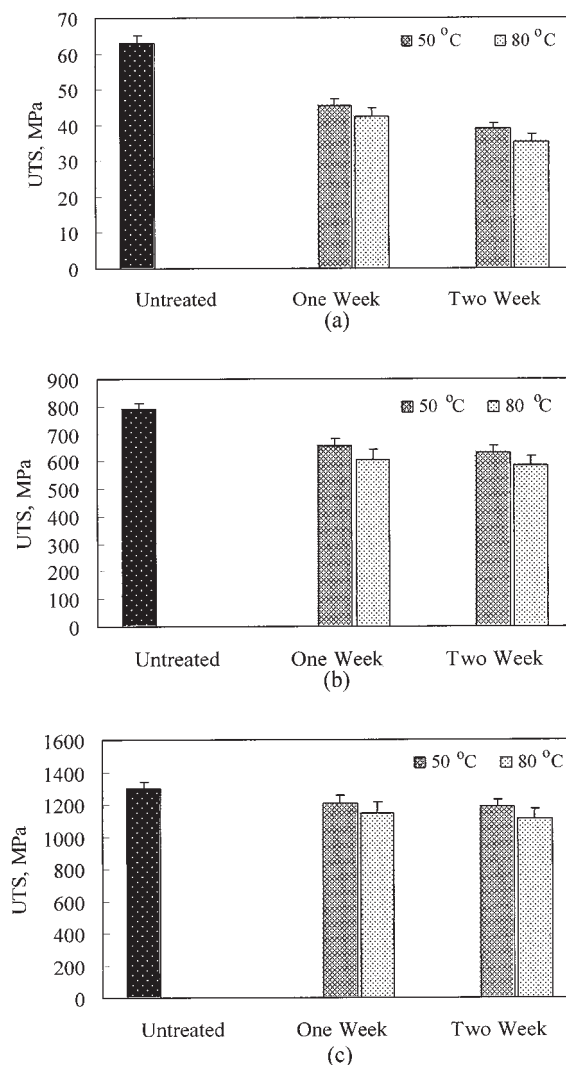


Figure 2 Effect of treatment with KOH solution on the ultimate tensile strength (UTS) of carbon fiber reinforced epoxy resin composites prepared by resin transfer molding: (a) an un-reinforced composite specimen; (b) a reinforced composite specimen containing 20% v/v unidirectional carbon fibers; (c) a reinforced composite specimen containing 50% v/v unidirectional carbon fibers.

50% v/v carbon fiber reinforcement, with 4M KOH aqueous solution at two temperatures, 50 and 80°C, and two duration of treatment, one and two weeks, are shown in Figures 2–4. Figure 2 depicts the effect of such treatment on the ultimate tensile strength (UTS) of these composite specimens. The data illustrate that the UTS of these specimens continued to decrease during their exposure to KOH solution. Furthermore, they also show that the percent decrease in the UTS of these specimens was higher at 80°C than at 50°C in all cases. This can be attributed to thermal and chemical degradation effects on these specimens. Chemical degradation can in turn be explained by alkaline solution attack on the surface of these specimens as revealed by surface mor-

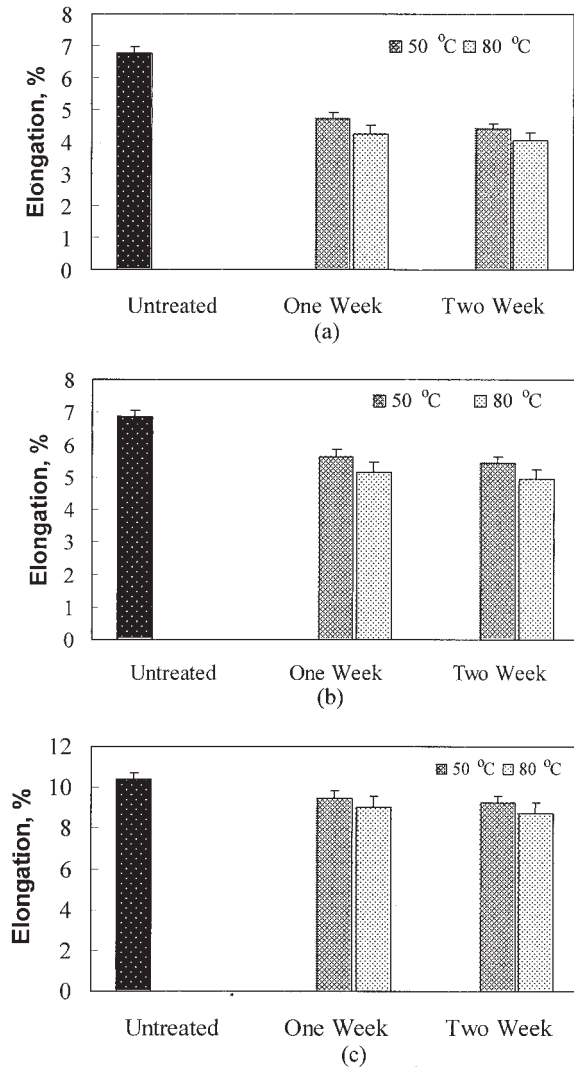


Figure 3 Effect of treatment with KOH solution on the ultimate elongation of carbon fiber reinforced epoxy resin composites prepared by resin transfer molding: (a) an unreinforced composite specimen; (b) a reinforced composite specimen containing 20% v/v unidirectional carbon fibers; (c) a reinforced composite specimen containing 50% v/v unidirectional carbon fibers.

phology and XPS analysis, which will be further discussed in the next section. Introducing the carbon fibers reinforcement, however, seemed to improve the thermal and chemical stability of these composite materials. This improvement was manifested by a much lower reduction in the tensile strength of fiber reinforced composites compared to what was observed in un-reinforced specimens subjected to similar treatment with KOH solution. For example, composite specimens reinforced with 50% volume fraction carbon fibers showed only a 7–15% reduction in their effective tensile strengths, depending on temperature and time of exposure to the alkaline solution, compared to 28–44% observed reduction in the UTS of un-reinforced epoxy resin subjected to similar treatments.

The ultimate elongation of the 0%, 20%, and 50% v/v carbon-fiber/epoxy composite specimens treated with 4M KOH solution at 50°C and 80°C for duration of one and two weeks are shown in Figure 3. These data reveal similar characteristic effects of KOH solution on these specimens' ultimate elongation as was observed for their UTS. Thus, the observed percent decrease in the ductility of these specimens was lower in the 50% volume fraction specimens than what was observed in the un-reinforced ones subjected to similar treatment. Percent reduction in ductility of these specimens subjected to similar treatments was in the order: 50% < 20% < 0% v/v carbon-fiber/epoxy composites.

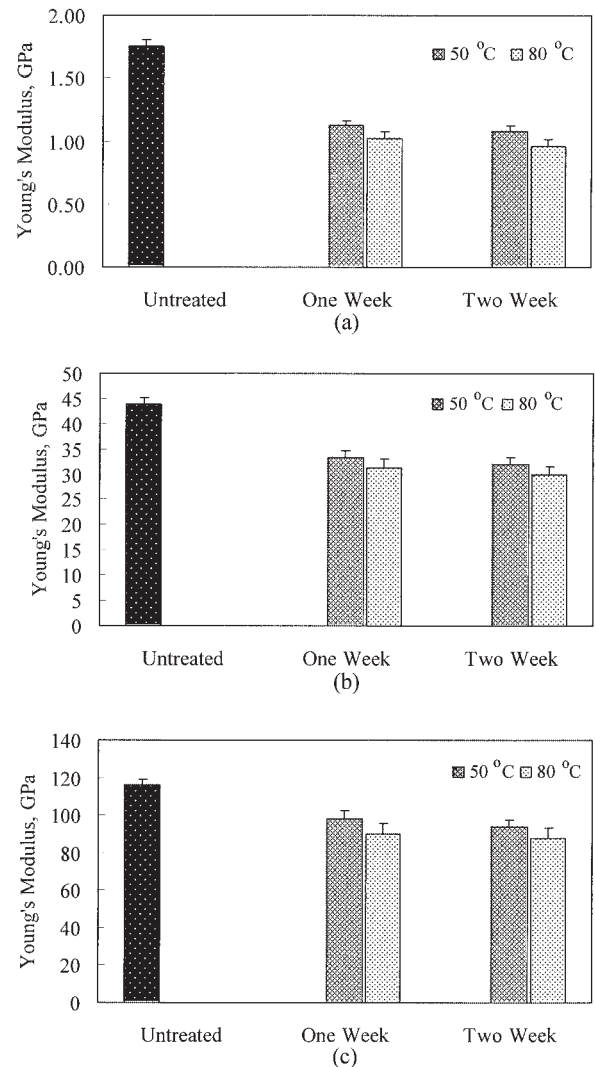


Figure 4 Effect of treatment with KOH solution on the Young's modulus of carbon fiber reinforced epoxy resin composites prepared by resin transfer molding: (a) an unreinforced composite specimen; (b) a reinforced composite specimen containing 20% v/v unidirectional carbon fibers; (c) a reinforced composite specimen containing 50% v/v unidirectional carbon fibers.

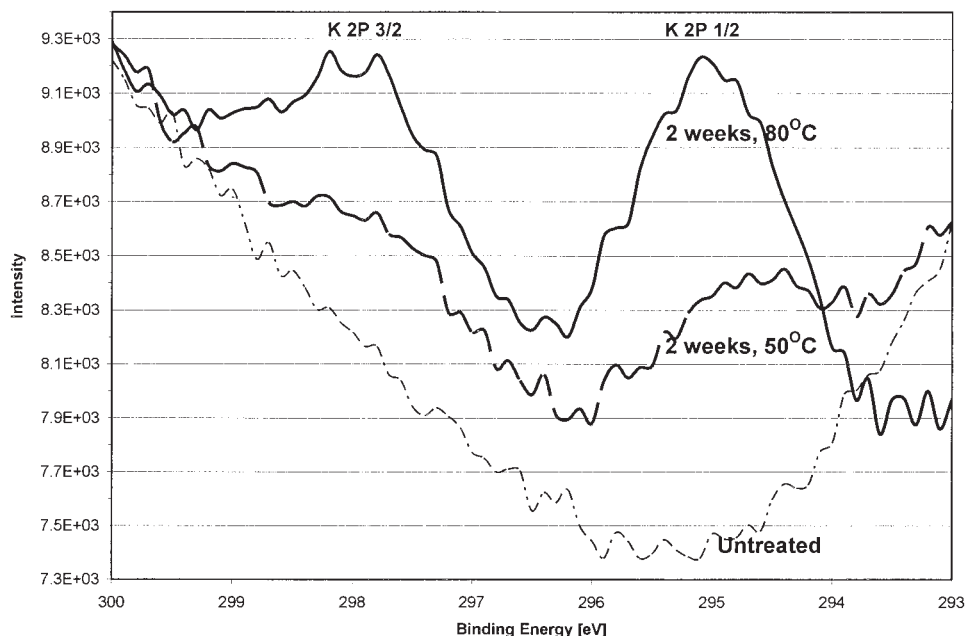


Figure 5 Typical potassium 2P peaks of an XPS analysis of untreated epoxy resin composite specimen prepared by resin transfer molding and those of similar specimens treated for two weeks with KOH solutions at 50°C and 80°C.

Figure 4 shows the effect of similar treatments of these specimens with 4M KOH solution on the Young's modulus of these specimens. The data reveal a similar effect of exposure to the alkaline solution on the specimens' Young's Modulus as was observed on their other two properties discussed above. Hence, reinforcement with 50% unidirectional carbon fibers produced the most effective toughening of these composite specimens and resulted in the least reduction in Young's modulus under similar treatment with the alkaline solution. These findings were in general agreement with the observations made by Al-Saidi et al.⁹ on the effect of exposing amorphous polycarbonate to three different organic liquids: isopropyl alcohol, ethylene glycol monomethyl ether, and methanol. These researchers found that exposure of polycarbonate samples to any of the above liquids would produce massive reductions in these specimens' tensile strength.

X-ray photoelectron spectroscopy (XPS)

Figure 5 shows a typical XPS analysis of an untreated epoxy resin composite specimen and specimens treated for two weeks with KOH solution at 50°C and 80°C. As expected, the untreated sample revealed no presence of potassium, whereas the treated samples showed potassium presence in their matrix but with different intensities reflecting the effect of the treatment temperature.

By integrating the area under each present element's peak, the weight percentage of each screened element was then calculated. The weight percent of potassium observed in un-reinforced epoxy resin composite specimens', 20% reinforced specimens', and 50% reinforced specimens' surfaces are shown in Figures 6a, b, and c, respectively. These data show that the potassium weight percentage found on the surface of these specimens increased with increasing exposure duration from one to two weeks and with increasing exposure temperature from 50 to 80°C. Furthermore, these data also show that for a given treatment duration and temperature, potassium weight percentage on the surface of these specimens increased with an increase in percentage of carbon fiber reinforcement in these specimens. This can be attributed to the more readily washed potassium residues from the surface of the un-reinforced samples, as shown in Figure 7a, compared to what was observed on surfaces of the 20% and 50% volume fraction carbon fiber reinforced specimens, as reflected by the morphology of the surfaces of these specimens shown in Figures 7b and 7c, respectively.

Fracture surface examination

Figures 8 and 9 show scanning electron micrographs of the tensile fracture surfaces of un-reinforced and reinforced carbon fiber-epoxy composite specimens, respectively. These specimens were pre-exposed to

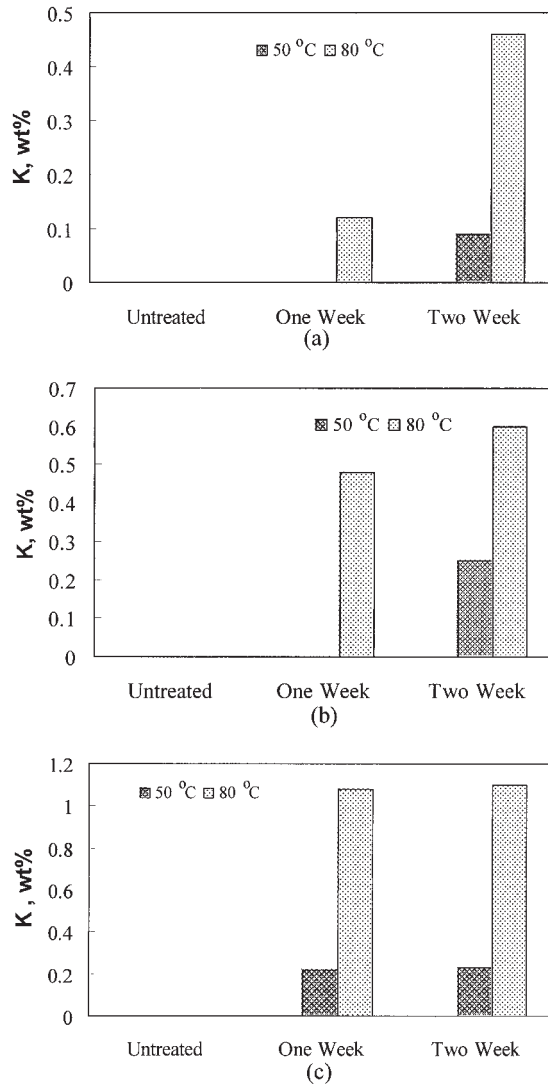
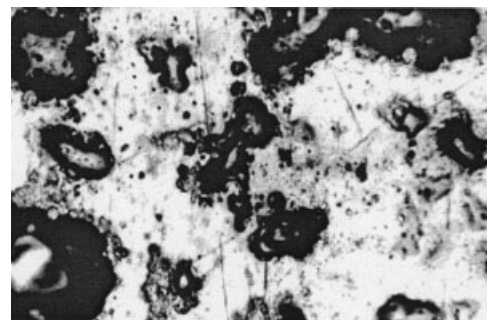


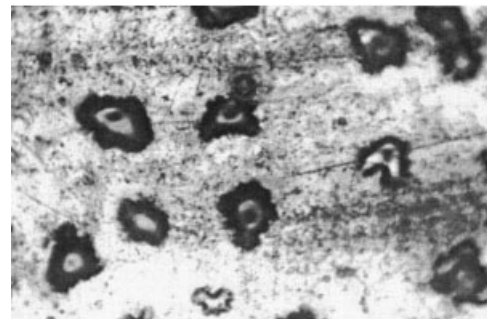
Figure 6 Effect of treatment with KOH solution on the potassium wt % uptake in carbon fiber reinforced epoxy resin composite surfaces as revealed by XPS analysis: (a) an un-reinforced composite specimen; (b) a reinforced composite specimen containing 20% v/v unidirectional carbon fibers; (c) a reinforced composite containing 50% v/v unidirectional carbon fibers.

KOH aqueous solution at 50°C or 80°C for one or two weeks duration. Figure 8 reveals that brittle fracture is the dominant mode of fracture witnessed by un-reinforced specimens whether or not subjected to KOH treatment. Figures 8b and c, however, clearly show the severe degradation of such specimens as a result of their exposure to KOH solution for a period of two weeks at 50°C and 80°C, respectively. The failure surface of specimens reinforced with 20 and 50% volume fraction carbon fibers are shown in the micrographs of Figure 9. These micrographs show that for both KOH treated and untreated specimens, fiber pullout and delamination are the major features of failure in such composites.

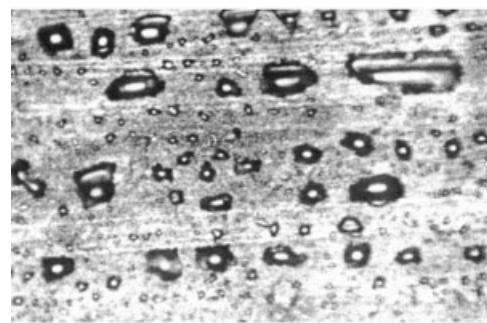
Similar observations were also reported by Akay et al.² A closer inspection of Figure 9c reveals, however, that there is little matrix degradation witnessed by the 50% volume fraction reinforced specimens subjected to two weeks treatment with KOH at 80°C compared to degradation witnessed by un-reinforced specimens subjected to similar treatments, as reflected in Figure 8c. This clearly reflects the added benefits to the stability of the epoxy resin composites subjected to harsh alkaline environments by introducing carbon fibers reinforcement in their matrix.



(a)



(b)



(c)

Figure 7 Optical micrographs of composite specimens prepared by resin transfer molding and treated with KOH solution for two weeks at 80°C: (a) an un-reinforced composite specimen; (b) a reinforced composite specimen containing 20% v/v unidirectional carbon fibers; (c) a reinforced composite specimen containing 50% v/v unidirectional carbon fibers $\times 200$.

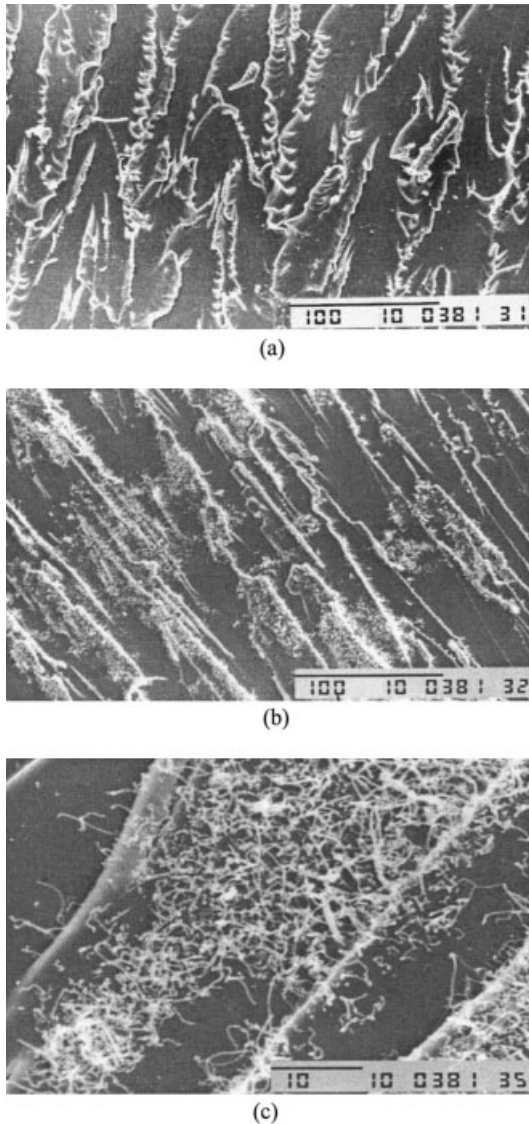


Figure 8 Scanning electron micrographs of tensile fracture surfaces of un-reinforced epoxy resin composite specimens prepared by resin transfer molding and subjected to different treatments with KOH solution: (a) an untreated specimen; (b) a specimen treated for two weeks at 50°C; (c) a specimen treated for two weeks at 80°C.

CONCLUSIONS

On the basis of the outcome of this research work, the following conclusions can be made:

1. The tensile properties of un-reinforced epoxy resin and reinforced with unidirectional carbon fiber composites were adversely affected by their treatment with 4M KOH solution to varying degrees, depending on treatment conditions and volume percent of carbon fiber reinforcement used.
2. Composite specimens utilizing 50% volume fraction of carbon fiber reinforcement demon-

strated a higher chemical and mechanical stability upon treatment with KOH solutions compared to un-reinforced specimens.

3. Investigations of fracture surface morphology using optical microscopy and XPS analyses clearly demonstrate that potassium deposited on surfaces of these composites upon treatment with KOH solution were more readily washable from the surface of un-reinforced specimens compared to reinforced composites.
4. Investigations of fracture surface morphology of carbon fiber reinforced epoxy resin compos-

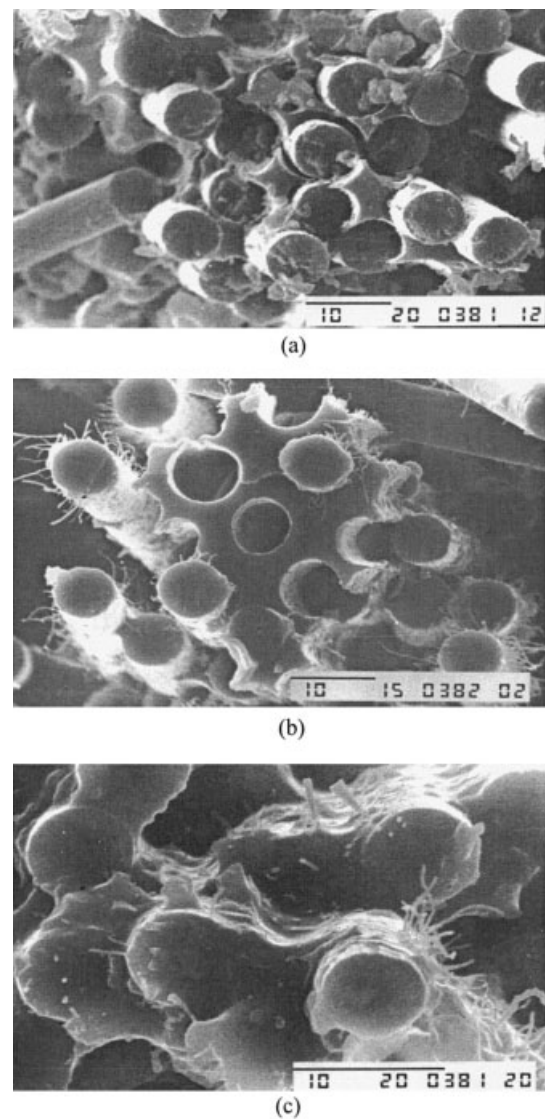


Figure 9 Scanning electron micrographs of tensile fracture surfaces of reinforced epoxy resin composite specimens prepared by resin transfer molding and subjected to different treatments with KOH solution: (a) an untreated specimen containing 20% v/v unidirectional carbon fibers; (b) a specimen containing 50% v/v unidirectional carbon fibers treated for two weeks at 80°C; (c) a higher magnification of micrograph (b).

ites using scanning electron microscopy show that fiber pullout and delamination are the major features of failure in such composites.

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