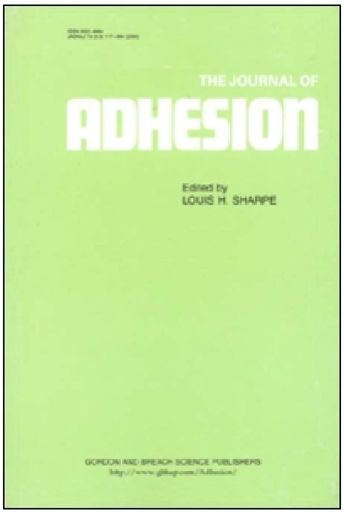

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An NMR Imaging Study of the Interface of Epoxy Resin-Glass Fiber Reinforced Composites*

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NMR imaging was used to analyze E-glass fiber/epoxy composites. The NMR images revealed specific interactions between the glass fiber and epoxy, as indicated by the different degree of curing in the proximity of the fiber. When as-received glass fibers were used, an accelerated degree of curing in the proximity of the fibers as compared with the bulk was observed, whereas when heat-treated glass fibers were used the above trend was substantially inhibited. Finally, when E-glass fibers treated with an aminosilane coupling agent (γ-APS) were used, no variation in the degree of curing in the proximity of the glass fiber was observed. The above results suggest that physisorbed or chemisorbed molecular water present in the surface of the glass fiber assists in the opening of the epoxy ring by hydrogen bonding effects.

KEY WORDS: NMR imaging; E-glass fiber; epoxy resin; interface; surface-accelerated cure; coupling agent interfacial interactions

INTRODUCTION

The performance of a fiber resin composite depends not only on the properties of its components but, to a large extent, also on the coupling between the fiber and the matrix. For this reason the interface is considered to be the heart of the composite material, a major factor affecting mechanical and various physical properties of fiber-reinforced composites.

Since glass fiber reinforced plastics (FRP) appeared industrially many years ago, fabrication techniques have been developed which yield high performance materials. Several methods have been proposed to improve the glass fiber-matrix adhesion, though the use of organofunctional silane coupling agents yields the greatest improvement in properties.[1] One of the most widely accepted theories for the interpretation of the mechanism of reinforcement suggests that the coupling agent forms covalent bonds to both the glass surface and the resin matrix.[2–4]

A large amount of research has been conducted on the detailed examination of the glass fiber-matrix interface and many modern surface techniques such as RAIR, ATR, SERS and XPS have been applied.[5–7] Nuclear Magnetic Resonance Imaging (NMRI)

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** Corresponding author.

originates from conventional NMR spectroscopy and allows the determination of the spatial distribution of molecular species and structures in a heterogeneous sample. Although NMRI has become popular in medical studies, it has also found many applications in the materials science field.[8–15] Using NMRI, it is possible, in a non-invasive way, to follow the curing of the epoxy matrix and to observe the interfacial region.[16]

In this study, NMR imaging was used to characterize the interface of epoxy/E-glass fiber composites in order to provide a better understanding of those engineering factors which influence the interface structure.

EXPERIMENTAL

The NMR images were obtained on a Bruker MSL FT-NMR spectrometer, operating at a proton frequency of 300 MHz. The spectrometer was equipped with a 15 mm microimaging insert. NMR images were collected on an ASPECT 3000 computer and transferred to a DecStation 5000/200 *via* ETHERNET for further data processing.

The experiment used a typical Carr-Purcell[17,18] spin echo pulse sequence with selective 90-degree and non-selective 180-degree pulses with CYCLOPS phase cycling (Fig. 1). Typical duration times for the 90-degree and the 180-degree pulses were 65 and 130 μs, respectively. Magnetic field gradients were 9–10 Gauss/cm in the in-plane space and 2–3 Gauss/cm in the z-direction. Four scans were accumulated to produce images with 256 × 256 pixels from a slice approximately 1 mm thick. Pixel resolution in the slice plane was 47 μm × 47 μm. A recycling delay of one second was used between pulse sequence repetitions, yielding an accumulation time of approximately 20 minutes for one image. The echo time used was 12 ms.

The NMRI experiments involved the imaging of the protons of the methyl unit in the gem dimethyl. This arises from the fact that in the epoxy-curing agent structure the rest

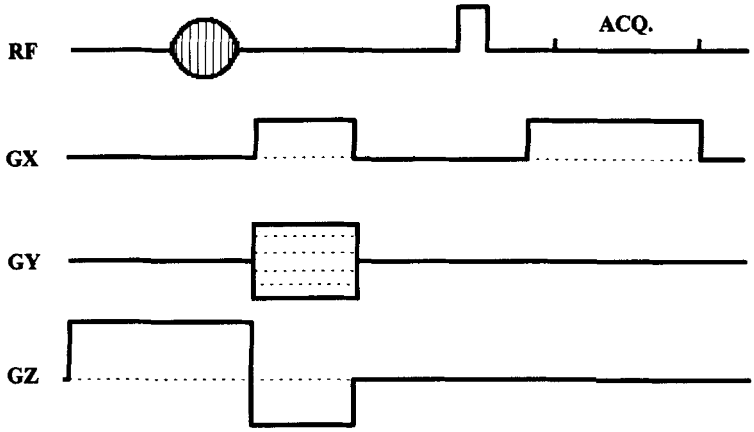
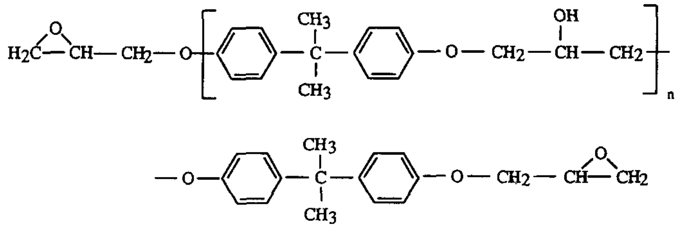


FIGURE 1 The spin echo pulse sequence used to obtain the images with a Gaussian selective 90° and a non-selective 180° pulse.

of the protons are too immobile, that is they have a relatively short T_2, and so their NMR signal decays in the time it takes to acquire the signal of the protons of the methyl unit in the gem dimethyl.

Glass fiber/epoxy composites were designed for the NMRI analysis. The reinforcing agent was E-glass from PPG industries Inc., whereas the epoxy resin was DER 331, a bisphenol-A-based liquid resin from Dow Chemical company, with an average epoxy equivalent of 189 (Scheme 1). The resin was mixed in stoichiometric proportions with an aliphatic polyamine curing agent, DEH 26 (tetraethylenepentamine) with an amine hydrogen equivalent weight of 27.0.



SCHEME 1 Chemical structure of the epoxy resin.

Two different sample arrangements were used in order to obtain the maximum possible information for the epoxy/glass fiber interface. In the first sample arrangement (A) (Fig. 2), glass fibers were threaded through a glass tube (13 mm ID × 45 mm long)

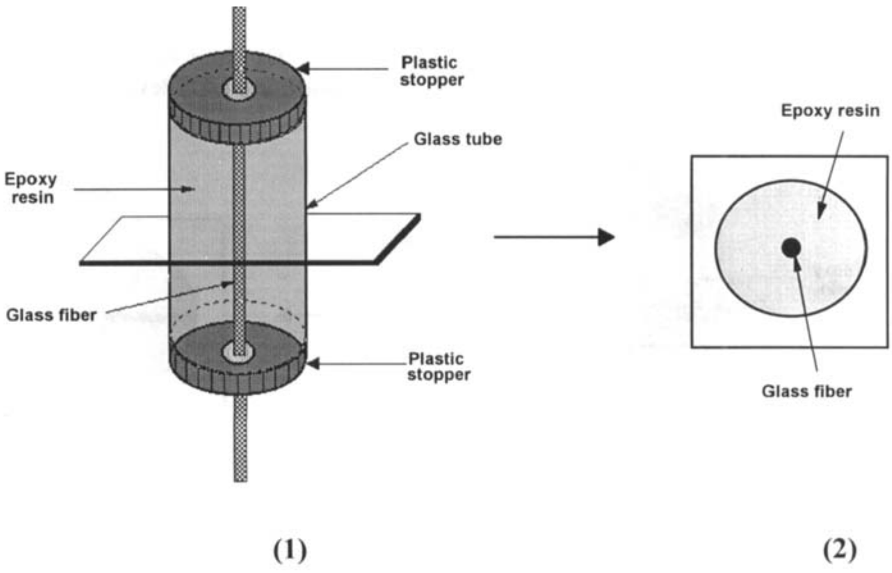


FIGURE 2 The sample arrangement A with a slice selection (1) and the resulting NMR image (2).

enclosed at both ends with plastic caps and stretched for alignment. In the second one (B), one glass fiber was threaded through a plastic tube (13 mm ID, 50 mm long) in a horizontal position (Fig. 3). Next, in both cases, the tubes were filled with uncured epoxy, after which NMR imaging was performed as a function of time.

Three different types of glass fiber were used in order for differences in the interfacial region to be imaged: a) as-received glass fibers, b) glass fibers heat-treated at 600°C for 24h and, c) E-glass fibers treated with an aminosilane coupling agent gamma-aminopropyl-triethoxysilane (γ-APS) from Petrarch Systems, Inc.

$$H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$$

SCHEME 2 The γ-APS coupling agent

In the last case, the silane was hydrolyzed in deionized water at pH = 3.5 for 2 hours. The concentration of the coupling agent was 2% by weight. The adsorption of silane on the E-glass was done by immersing the heat-cleaned glass fiber into the aqueous solution for 10 minutes. After filtration, the fiber was dried for 24 hours at room temperature.

RESULTS

The NMR images of the epoxy/glass fiber composites revealed specific inhomogeneities related to varying degrees of cure. Contrast in the images is due to spatial differences in T_2 originating from different degrees of cure. Thus, as the sample cures the T_2 values become smaller and the time and spatial variation of these values is characteristic of the epoxy curing behavior. The intensity at a given pixel reflects the cured state of the sample at that location. For each sample the acquisition of three images in a one-hour period of time was made possible.

In all images, red represents the highest intensity and dark blue the lowest, with the green, yellow and orange representing the intermediate intensity level in increasing

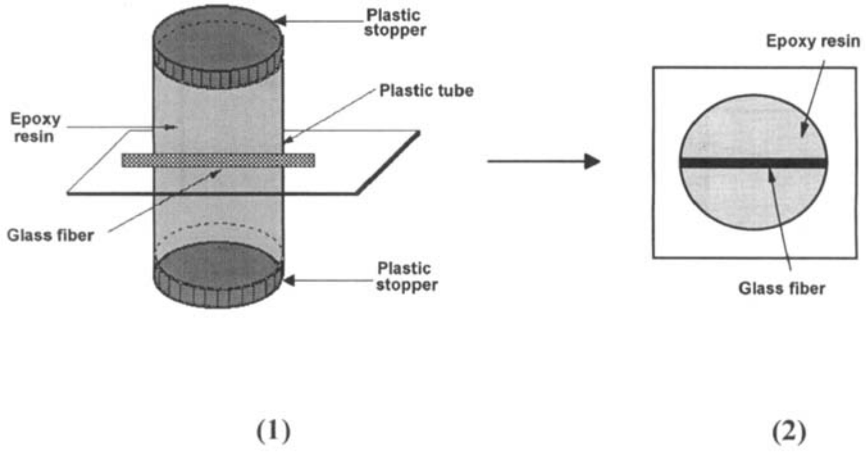


FIGURE 3 The sample arrangement B with a slice selection (1) and the resulting NMR image (2).

order. The intensity of the image illustrates levels of cure: red indicates areas of high mobility or uncured domains, while blue represents low mobility or cured domains.

Composites Prepared with As-received Glass Fibers

The images of composites prepared with as-received glass fibers are shown in Figures 4 and 5. Sample arrangement A was used in Figure 4 where images of four as-received glass fibers in epoxy were taken. Figure 5 represents an as-received glass fiber in epoxy with sample arrangement B.

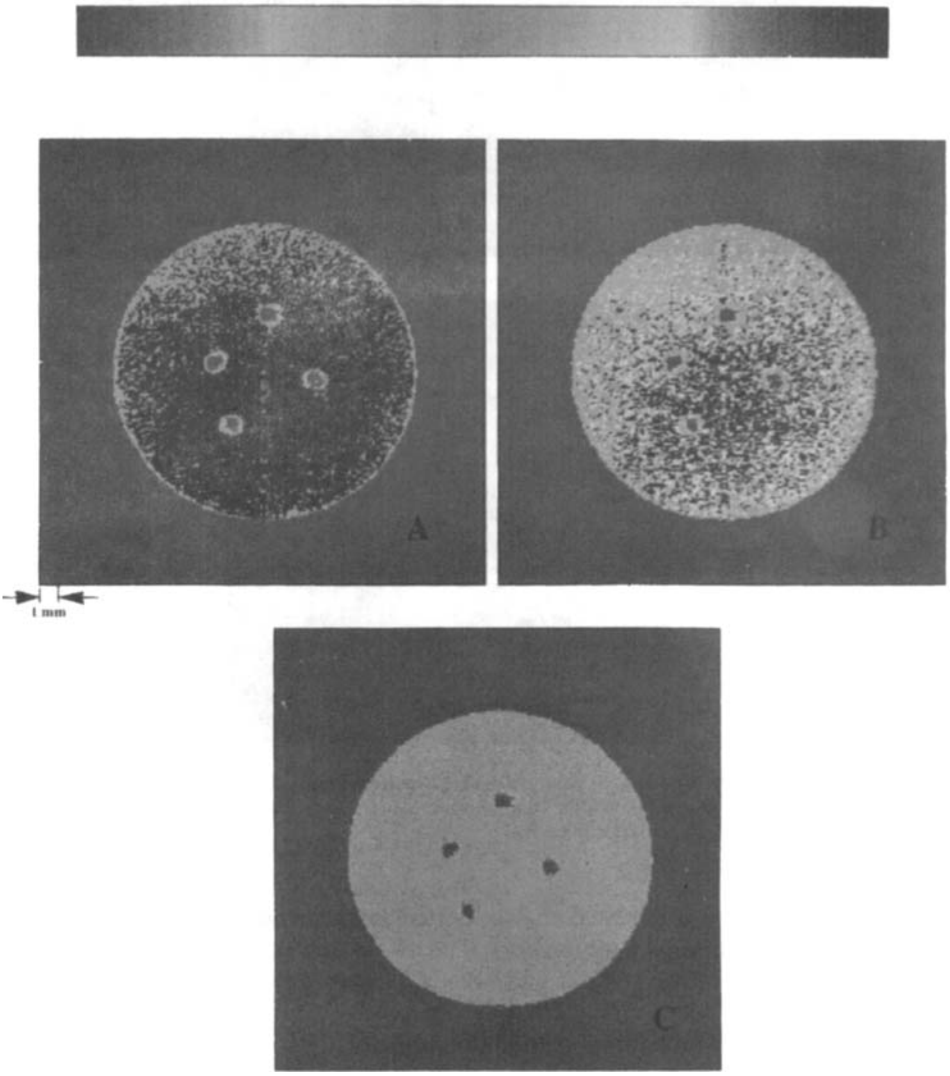


FIGURE 4 NMR image of four as received E-glass fibers in epoxy. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate I.

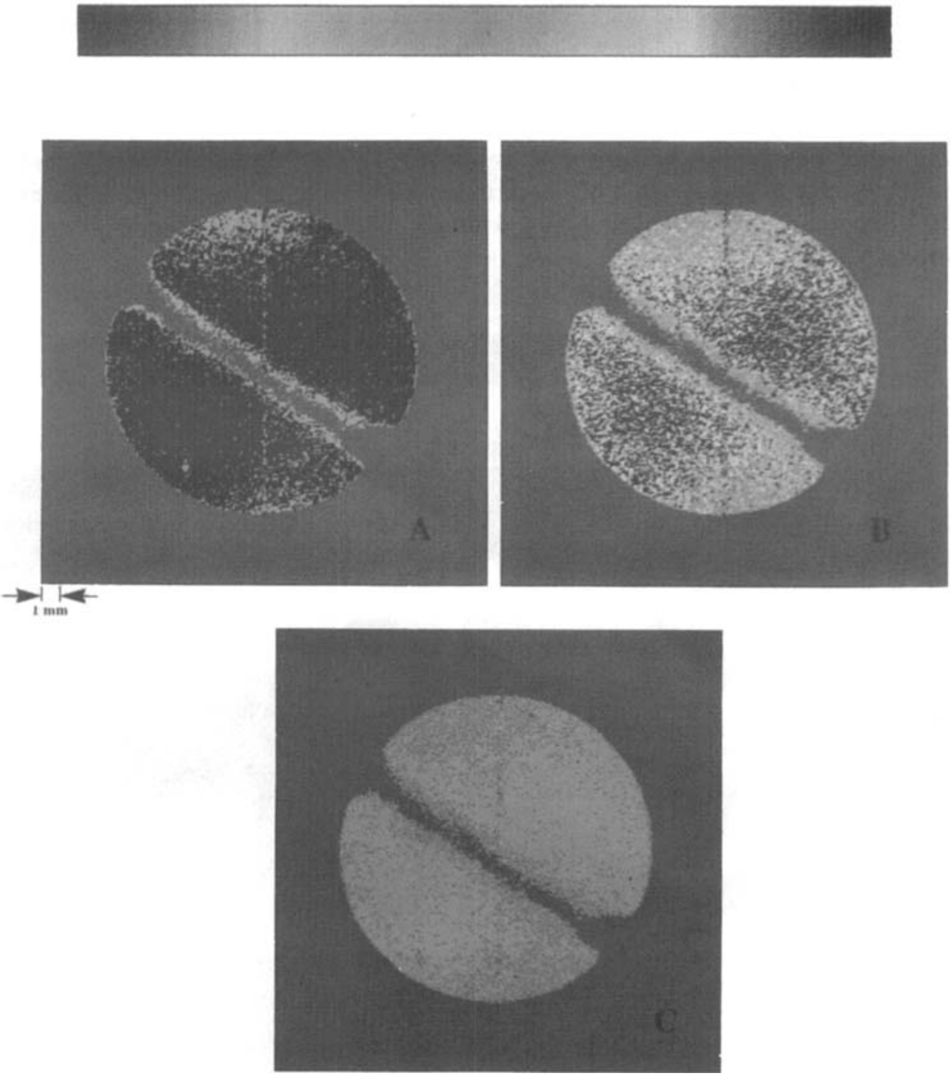


FIGURE 5 NMR images of one as received E-glass fiber in epoxy. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate II.

Both these sets of images reveal an accelerated degree of curing in the proximity of the glass fiber as compared with the bulk. The above observation is present from the start of the cure and after one hour when the last image was taken.

Composites Prepared with Heat-cleaned Glass Fibers

Again, two sets of images were acquired from this type of composite. Figure 6 illustrates images of four heat-cleaned glass fibers in epoxy with sample arrangement A, whereas

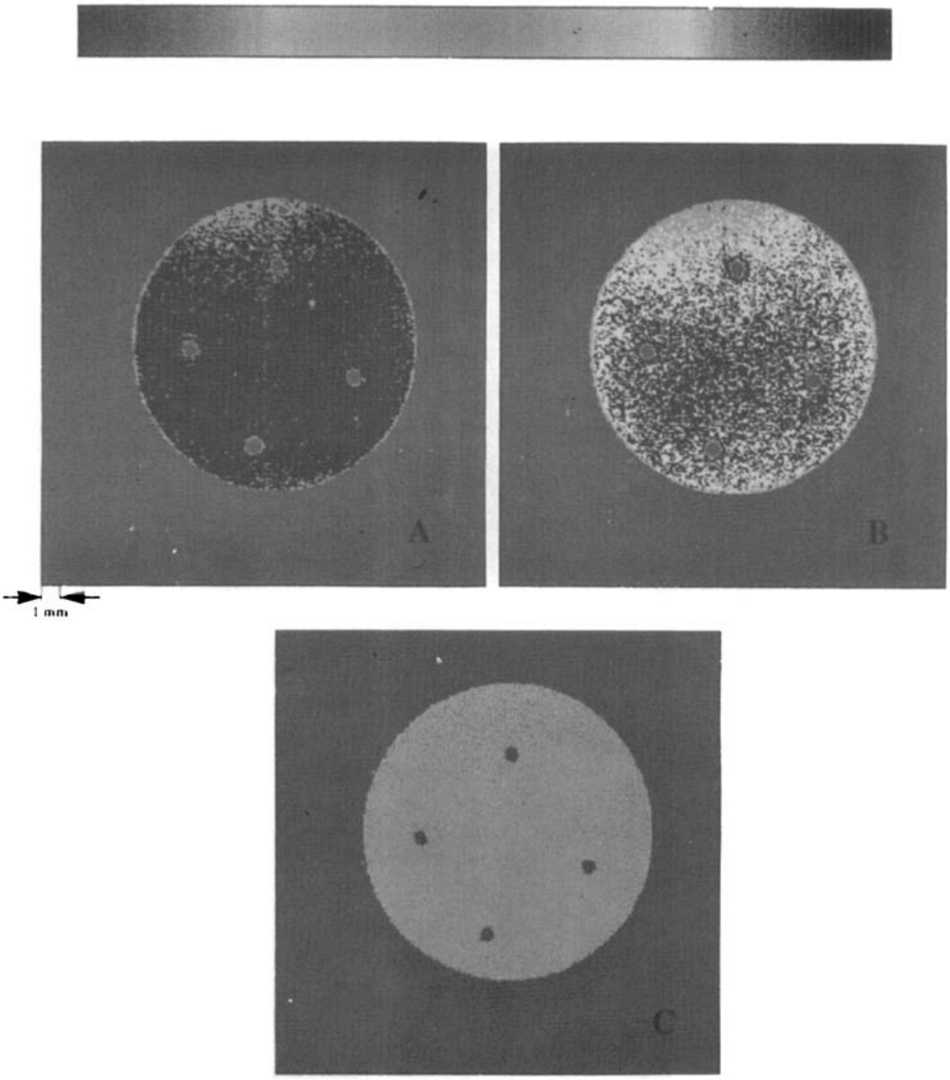


FIGURE 6 NMR images of four heat treated E-glass fibers in epoxy. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate III.

images of a heat-cleaned glass fiber in epoxy with sample arrangement B are shown in Figure 7.

Substantial inhibition of the trend noticed in composites containing as-received glass fibers is observed in composites prepared with heat-cleaned E-glass fibers. Images reveal a very small amount of accelerated curing in the interfacial region throughout the period in which NMR images were taken.

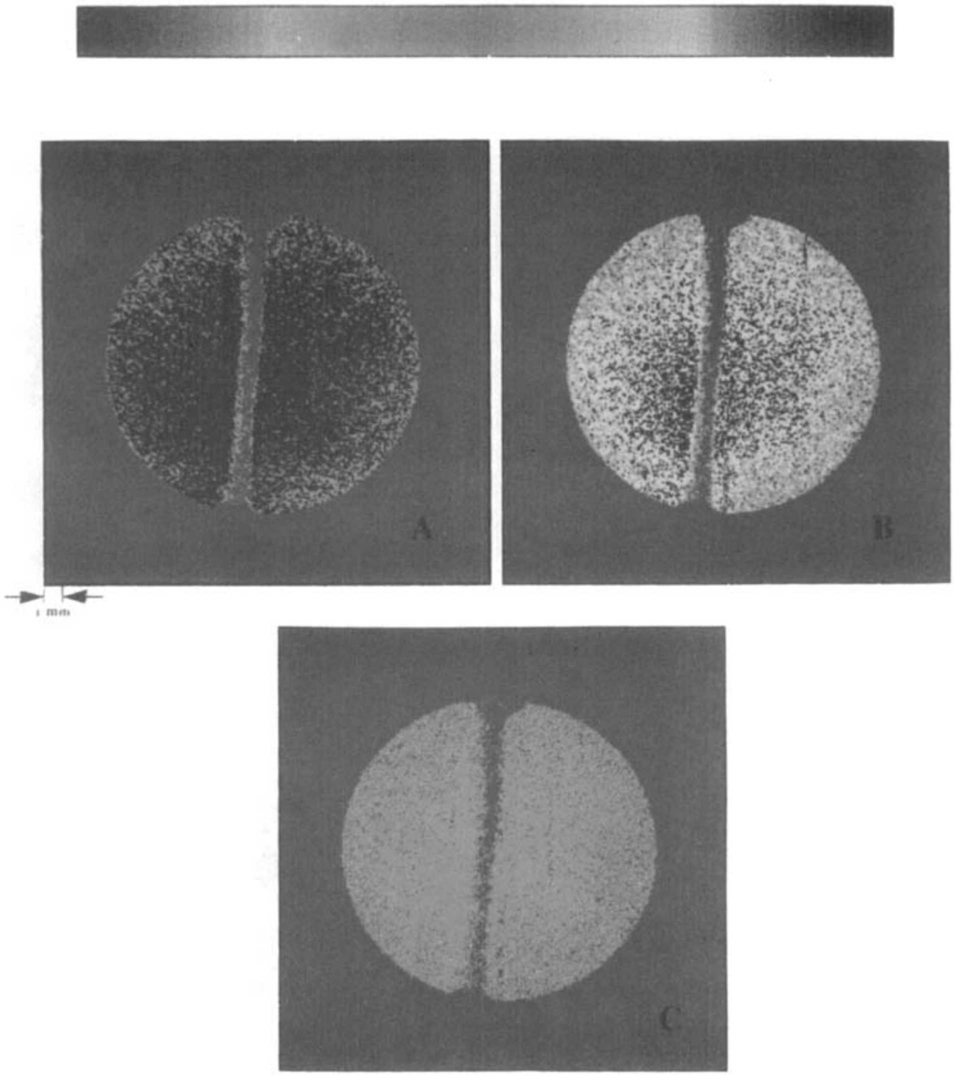


FIGURE 7 NMR images of one heat treated E-glass fiber in epoxy. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate IV.

Composites Prepared with Glass Fibers Treated with a Silane Coupling Agent

NMR images of this type of composite material are shown in Figures 8 and 9. Similarly to the previously mentioned materials, two sets of images were taken. Figure 8 illustrates images of four glass fibers treated with coupling agent in epoxy, using sample arrangement A. NMR images of Figure 9 were taken from a glass fiber treated with coupling agent in epoxy with sample arrangement B.

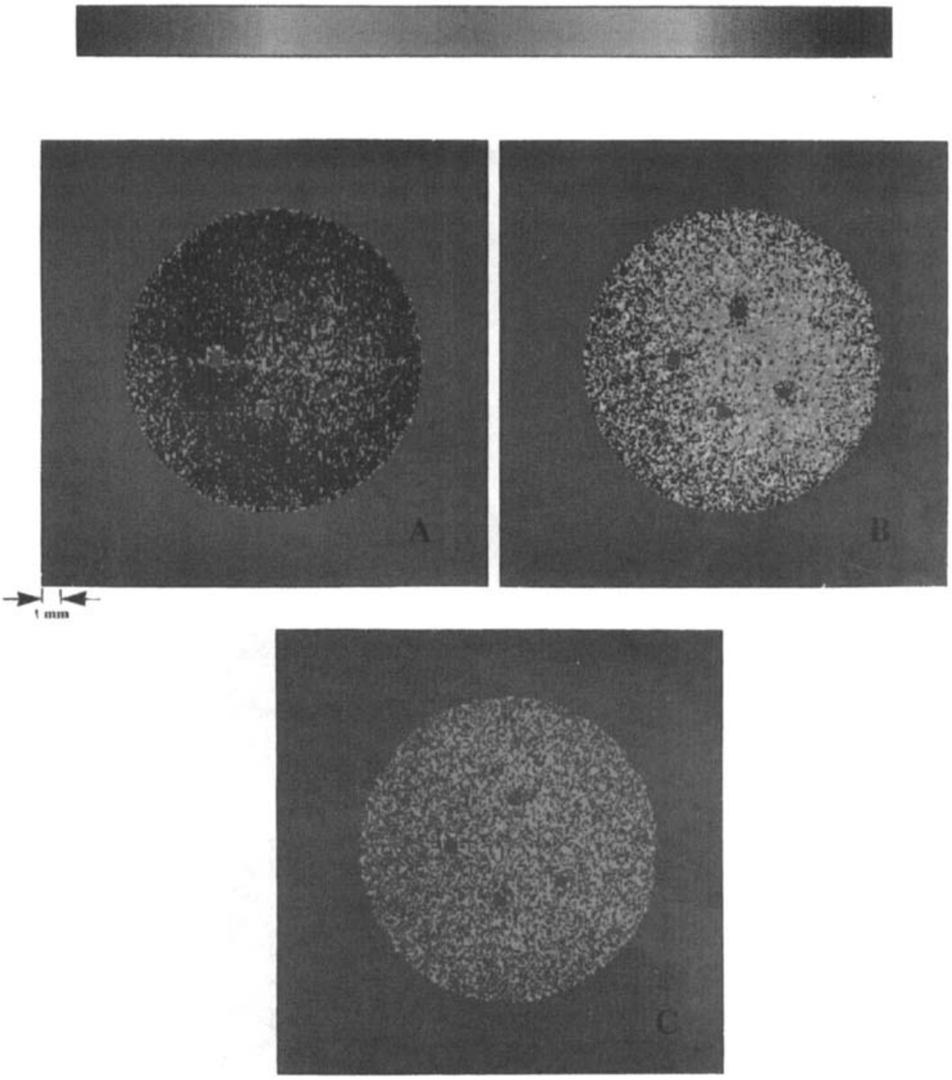


FIGURE 8 NMR images of four E-glass fibers treated with a silane coupling agent (γ-APS) in epoxy. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate V.

NMR images suggest that no variation in the degree of curing takes place in the proximity of the glass fiber in this type of material. The curing of the epoxy in the interfacial region seems to be uniform, revealing no effect of the glass fiber surface on the curing process of the epoxy.

Control Experiments

Due to the geometry of the samples, susceptibility mismatches are likely to occur at the fiber-resin interface. Control experiments were performed in order to prove the absence

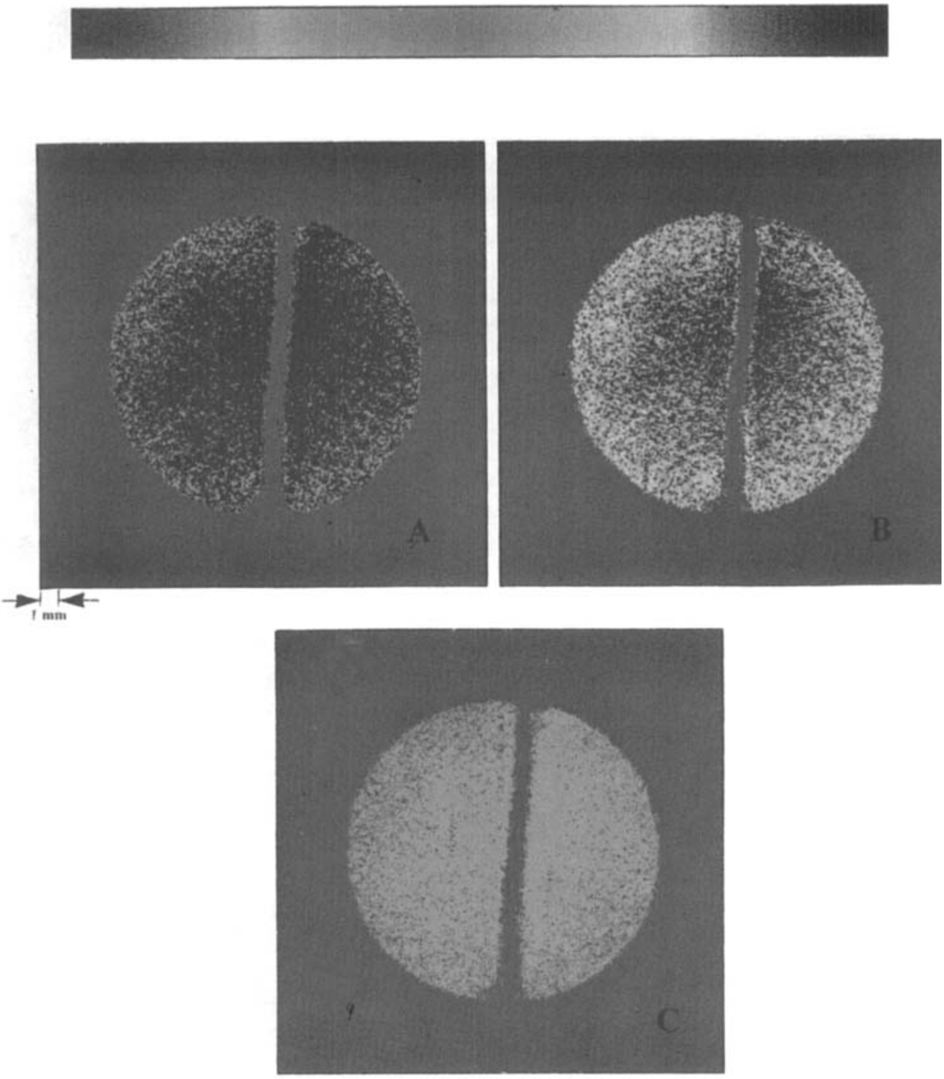


FIGURE 9 NMR images of one E-glass fiber treated with a silane coupling agent (γ-APS) in epoxy. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate VI.

of the susceptibility mismatches or artifacts in the above-presented NMR images. Figure 10 shows images of glass fibers in epoxy resin, which was not mixed with a curing agent. In image A sample arrangement A was used, whereas image B was taken using sample arrangement B. The absence of a color difference at the interfacial region indicates that the relatively low signals around the fibers shown in Figures 4,5,6 and 7 represent an accelerated curing of the epoxy resin, and are not due to susceptibility mismatches or artifacts.

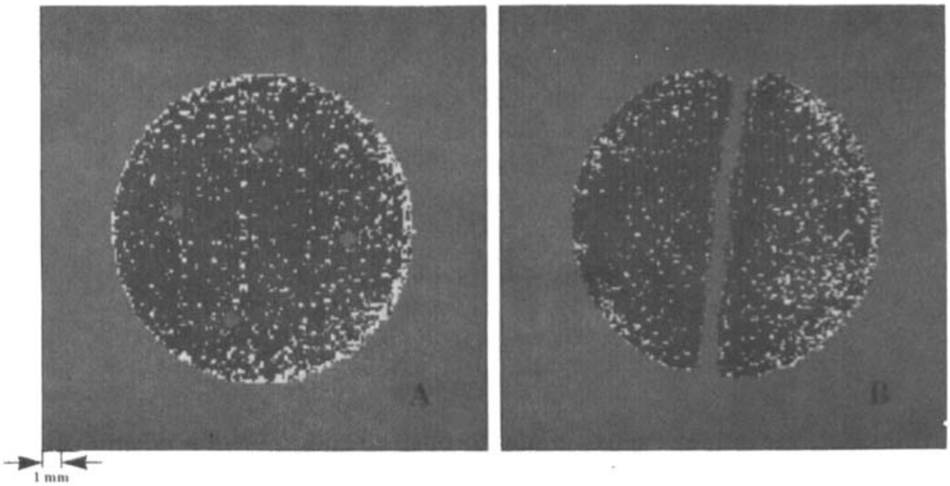
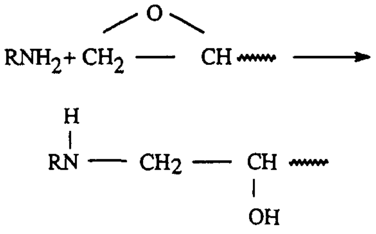


FIGURE 10 NMR images showing the control experiments, where no curing agent was added to the epoxy resin. Sample arrangement A was used in image A, while image B was taken using sample arrangement B. See color plate VII.

DISCUSSION

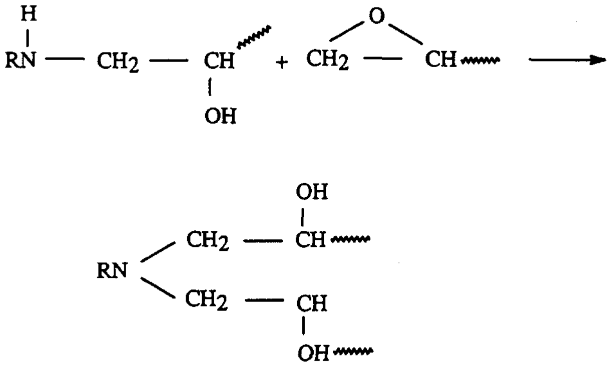
NMR images taken from epoxy composites containing three different types of glass fibers revealed significant differences in the degree of curing in the proximity of the fiber. When as-received glass fibers were used, an accelerated degree of curing in the interfacial region was observed. The above trend was substantially inhibited in the case of heat-cleaned glass fibers. Finally, when glass fibers treated with an aminosilane coupling agent (γ-APS) were used, no variation in the degree of curing occurred in the vicinity of the glass fiber. These results suggest that the surface properties of glass fibers exhibit substantial changes when heat-treated or treated with an aminosilane coupling agent.

The curing process of epoxy systems mainly involves reactions of epoxy groups and primary amines, to form secondary alcohols and tertiary amines. The amines react with the epoxy group through the active amine hydrogen. Each primary amine group is theoretically capable of reacting with one epoxide group. The reaction of a primary amine with an epoxy is seen as follows:



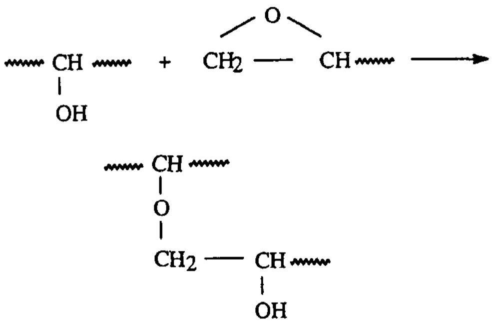
(1)

The secondary amine thus formed reacts further:



(2)

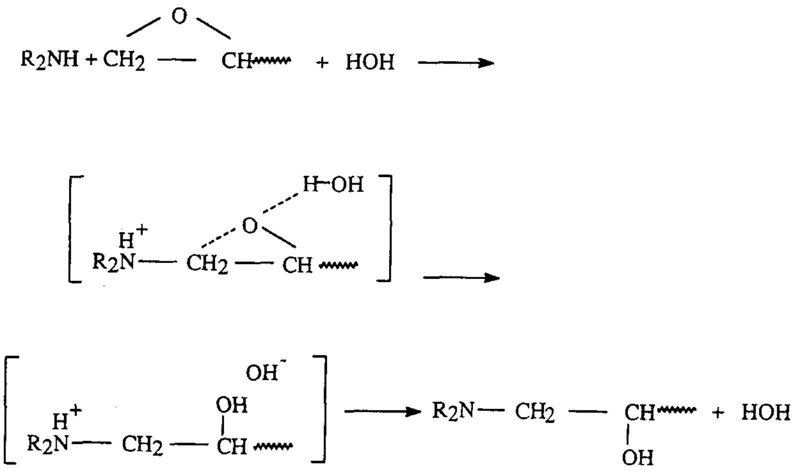
Homopolymerization of epoxy groups through etherification of pendant hydroxyl groups formed by reactions (1) and (2) is an important side reaction of the curing process:



This reaction is often catalyzed by tertiary amines. However, the presence of hydroxyls has an important function because they assist in opening the epoxide ring and, thus, accelerate the primary and secondary amine curing.[19]

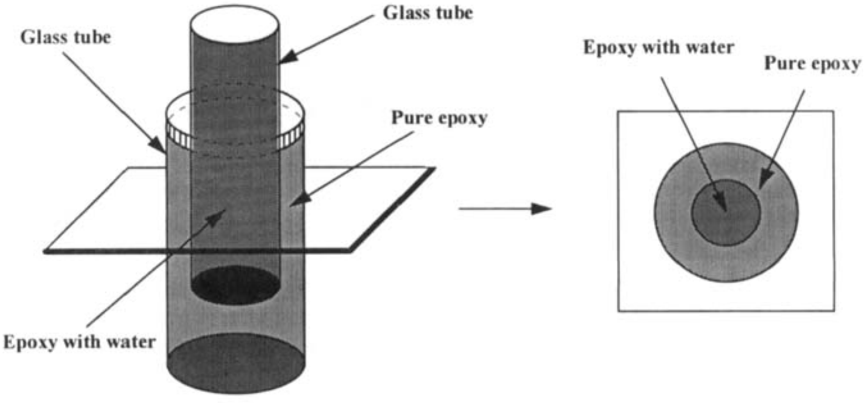
The chemical composition of the glass fiber surface is different from the bulk composition.[20] Since the glass surface is equilibrated with ambient air, water is present either in the physisorbed or chemisorbed state. This hydrated surface of glass is responsible for its reactivity. The cations present in the glass easily hydrate to provide a surface rich in hydroxyl groups. The ability of the hydroxylated surface to hydrogen bond with additional water molecules causes the formation of multilayers of water hydrogen-bonded to the surface.[21] However, thermal treatment at 600°C removes molecular water and most silanol groups condense to form siloxane bonds.[22]

Based on the above remarks, the accelerated degree of curing that occurs in the interfacial region of composites with as-received glass fibers can be explained as follows: Water present in the interfacial region is assisting in the opening of the epoxy ring. This acceleration is presumed to be caused by hydrogen bonding effects, and is represented by the following chemical reaction:[23,24]



To confirm the above explanation, the following system was designed for NMRI analysis: Two glass tubes (differing in the diameter size) were put one inside the other. The glass tube with the larger diameter was filled with pure epoxy resin while epoxy resin mixed with a very low proportion of water (0.1 w/w%) was put in the glass tube with the smaller diameter (Fig. 11). NMR imaging was then performed as a function of curing time, with the same parameters used in the images of the epoxy/E-glass systems.

The NMR images obtained (Fig. 12) indicate that the presence of water has a significant effect on the curing of the epoxy resin. Comparison of the color (which is



(1) (2)

FIGURE 11 Sample arrangement showing the effect of water on the curing of the epoxy, with a slice selection (1) and the resulting NMR image (2).

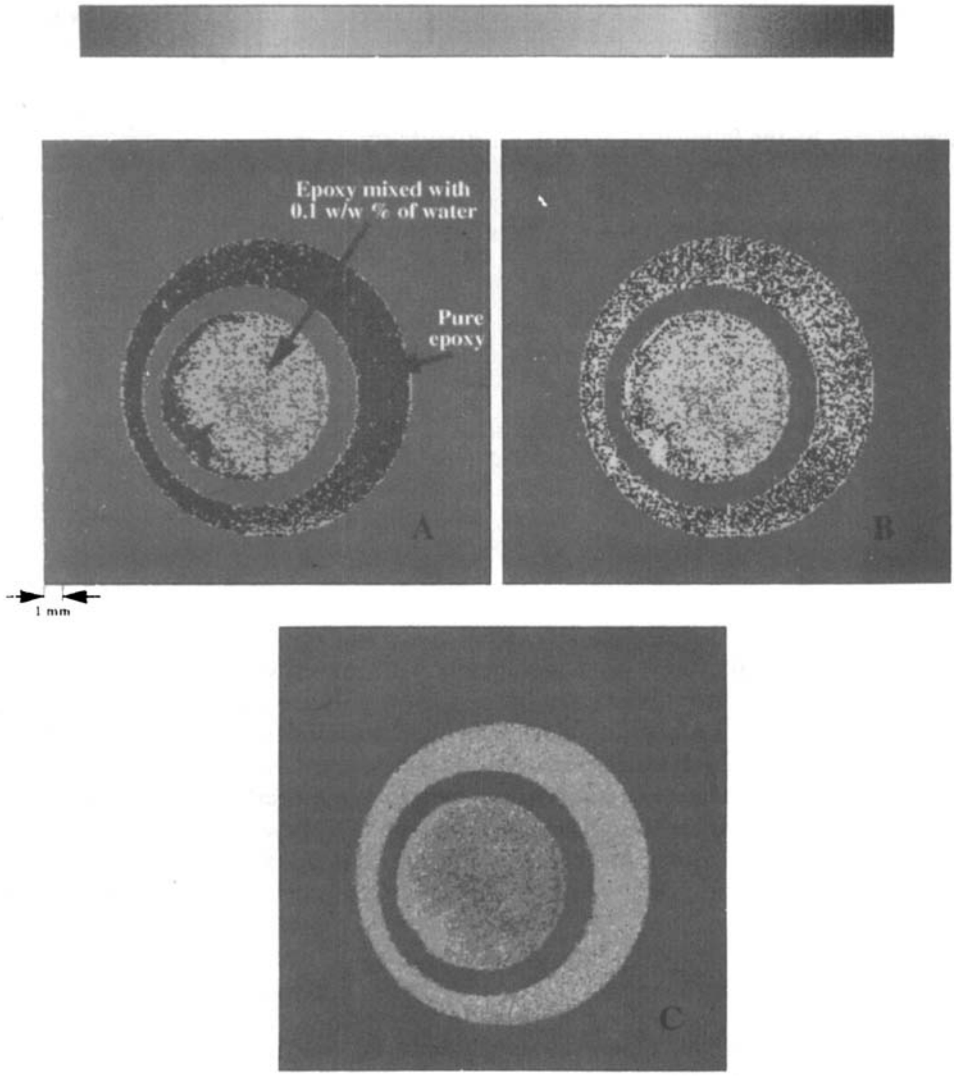


FIGURE 12 NMR image showing the effect of water in the curing process of the epoxy resin. Image A was taken after 20 minutes in the curing process. Image B was taken after 40 minutes in the curing process. Image C was taken after 60 minutes in the curing process. See color plate VIII.

indicative of the level of cure) inside and outside the internal glass tube implies a definite difference in the curing of the epoxy resin. Pure epoxy resin cures at a lower rate than if it is mixed with water, suggesting that water causes an accelerated curing of the epoxy resin.

NMR images of epoxy composites prepared with heat-treated glass fibers demonstrate that a significant inhibition of the accelerated degree of curing in the vicinity of the fiber is taking place. The most probable reason for the above-mentioned trend is, again, the presence of molecular water in the interfacial region.

Although heat treatment of glass fibers is believed to remove all molecular water, chemisorbed or physisorbed, over the glass surface, DRIFT spectroscopy has shown that traces of molecular water still exist.[22] This is most probably due to the presence of B_2O_3 on the glass surface. B_2O_3 is considered to be exceedingly reactive with water and this hydrolytic susceptibility leads to the creation of sites for water absorption. This can occur mainly during sample preparation.[24]

Application of silane coupling agents for surface modification of the substrate usually improves the adhesion.[25] An important contribution to adhesion is thought to be provided by the coupling agent *via* a chemical bonding mechanism. This chemical bonding theory requires the establishment of covalent bonds between the silane and both the glass surface and the organic matrix. A number of investigators have studied the reaction between silane and glass and have concluded that silanes can anchor themselves to the glass surface *via* Si–O–Si bonds[26] (Fig. 13). In addition to the hydrolyzable groups, the silane contains an organic nonhydrolyzable group which can potentially react with the matrix resin.[27] In the case of an epoxy resin, this functional group may be an amine or epoxy group. A schematic representation of the interfacial region in composites prepared with glass fibers treated with a silane coupling agent is shown on Figure 14.[4]

Silane treatment is considered to protect against attack by moisture in the interface region in composites.[28] It diminishes the physisorptive capacity of glass fiber substrates and, thus, promotes wet strength retention and enhances other composite properties that otherwise would degrade when moisture adsorbs at the fiber matrix interface.[29] Inhibition of moisture adsorption at the glass /resin interface can be ascribed to three concurrent phenomena:

1. Coupler molecules block glass surface silanols by selective adsorption, or eradicate them by condensation reaction, diminishing the adsorptive potential of the substrate for water.

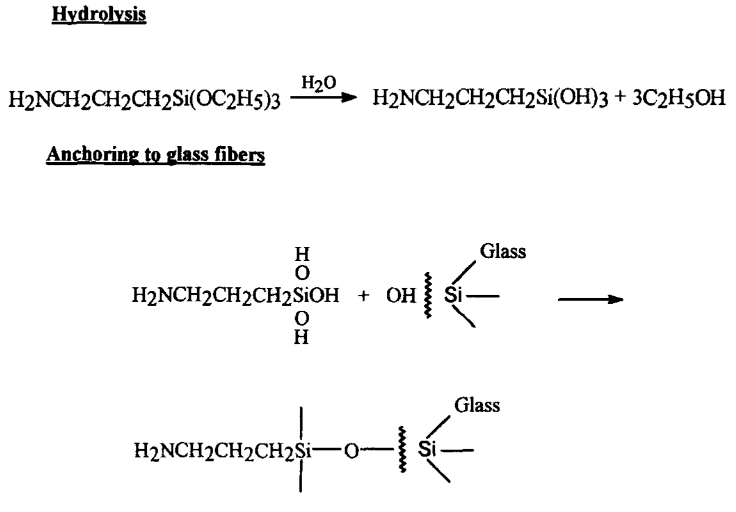


FIGURE 13 The anchoring mechanism of the silane coupling agent (γ-APS) to glass fibers.

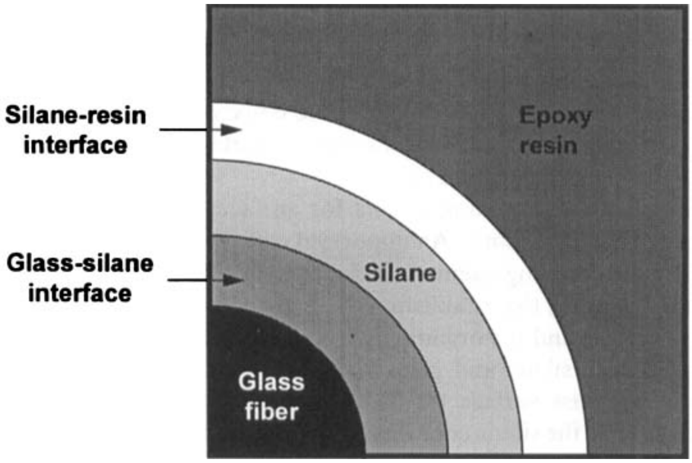


FIGURE 14 The interface of glass fiber (treated with a silane coupling agent)-epoxy composites.

2. Organic substituents in the coupler molecule cover the glass surface, rendering it hydrophobic.
3. Organosilanes bond resin to glass, promoting interfacial adhesion which prevents delamination by environmental moisture.[30]

Thus, silane coupling agents are normally coated onto glass fibers to reduce the moisture-induced degradation of composites.[31] A water-repellent film may be formed, which has been attributed to the hydrophobicity of the siloxane bonds formed by the coupling agent.[32,33] The fact that silanes impart a hydrophobic character to the fiber is most probably the reason for the absence of accelerated curing in the interfacial region of composites as observed in the NMR images.

CONCLUSIONS

NMRI was found to be an excellent tool for interfacial studies·of epoxy/glass fiber composites. NMR images revealed nonuniform cure of the matrix in these composites. An accelerated degree of curing in the vicinity of as-received glass fibers is observed, while the same trend, but to a substantially smaller extent, is present when the glass fibers were heat-treated. Finally, the treatment of glass fibers with an aminosilane coupling agent results in a uniform curing of the epoxy in the interfacial region.

The above observations are most probably due to the presence or absence of molecular water physisorbed or chemisorbed over the glass surface. The molecular water found at the interface of epoxy/glass fiber composites assists in the opening of the epoxy ring by hydrogen bonding effects and, thus, accelerates the degree of curing in the interfacial region.

Acknowledgements

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