Matrix–Size Interactions in Epoxy–Glass Fibers Composites in Relation to Mechanical Relaxations and Effects of Thermal Aging

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SYNOPSIS

A study was carried out to examine the effect of removing the size from the surface of glass fibers in order to determine its role with respect to thermoxidative aging. Dynamic mechanical relaxation data have revealed that mechanical losses were always greater than the calculated upper bound values. The effects of removing the size from the surface glass fibers for epoxy matrix composites were found to be completely different when a fluoroligomer was used to modify the resin. Contrary to the case of the conventional epoxy resin, the characteristics of the composites containing fluoroligomer-modified resin were found to be insensitive to the removal of the size from the glass fibers surface. The presence of the size on the surface of the fibers provides an interlayer that degrades through the formation of more lightly crosslinked products than the matrix, thereby providing a large increase in dynamic mechanical losses after thermal aging. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In previous work it has been shown that suitably modified functionalized perfluoroether oligomers can be used in small amounts to enhance the mechanical properties of epoxy resins, particularly toughness and ductility and the resistance to thermoxidative aging.[1-3] It has been found, however, that such improvements in properties could not be transferred to glass fiber composites when the fluoroligomer-modified resin was used as the matrix material.[4]

It was postulated that this may be due to the formation of a higher crosslinking density in the matrix as a result of reactions of the resin with species in the "size" (i.e., the fiber coating) and/or other reactants from the glass surface. It is easily envisaged, in fact, the possibility of hydrogen fluoride or fluorine anions being formed as a result of degradation reactions of fluoroligomer-modified epoxy resins, which would react with SiOH groups on the glass fiber surface or with the boron oxide component to produce BF_3, which would catalyze the crosslinking reactions and produce a higher crosslinking density in the bulk of the matrix.

The possibility of reactions occurring between epoxy resins and silane coupling agents or other components of the size covering the surface of glass fibers, on the other hand, has been confirmed by Al-Moussawi et al.[5] The results suggest that these reactions can produce a brittle interlayer between the fibers and matrix, which could accentuate the deterioration of mechanical properties brought about by degradation reactions within the matrix. At the same time the embrittlement of fiber–matrix interlayers could mask the improvements resulting from enhancements in the intrinsic toughness of the matrix. Di Benedetto et al.,[6] in fact, endorses the importance of interlayer brittleness by stipulating that fracture at the interphase of composites occurs under plane strain conditions within the interlayers rather than through interfacial shear failures. This would explain why the use of rubbery and ductile fiber coatings has been widely advocated as a criterion to enhance the toughness of composites.[7-14]

The work of Chang et al.[13] on the use of acrylate copolymers coatings of varying T_g's and different

coating thicknesses for carbon fiber–epoxy composites showed that the presence of an interlayer between fibers and matrix always decreased the interlaminar shear strength of the composite. The effect became increasingly more pronounced with increasing thickness of the interlayer while the impact strength showed a maximum for coating thicknesses in the region of 0.1 μm.

In the present work the authors examine the effects of removing the size and coupling agent from the surface of glass fibers in order to determine whether they have any effects on the degradation reactions occurring within the matrix and in the interphase regions of composites. In particular, the epoxy resins modified with fluoroligomers were examined in view of their much higher toughness and thermoxidative resistance than the equivalent unmodified resins when tested as castings.[4] Although it is normally assumed that the components of the size are dissolved by the resin during fiber impregnation, some residues will no doubt be left on the fibers' surface and produce an interfacial layer. The fluoroligomer-modified resin is expected to exhibit a lower degree of solubility with the size components of the fibers and, in view of its higher viscosity, it is anticipated that the amount of undissolved size remaining on the surface of the fibers will be greater than for the unmodified resin.
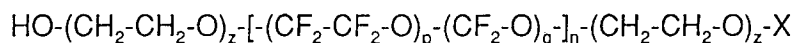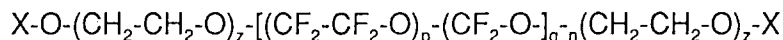
EXPERIMENTAL

Materials

The materials used were epoxy resin Rovepox 860, a standard bisphenol A epoxy resin (DGEBA) with an epoxy equivalent in the region of 230–270, supplied by Epoxital (now Dow Chemicals); hardener HY906, a methyl nadic anhydride curing agent (MNA), supplied by Robnorganic Systems; and catalyst BDMA; N,N'-dimethyl benzyl amine, obtained from Aldrich Chemical Company; carboxy terminated perfluoroether oligomer (CTMF), a modifier having the chemical structure shown in Figure 1 and produced according to the procedure described in previous publications,[1-3] starting from a hydroxy-terminated perfluoroether oligomer, Fomblin ZDOL-TX, supplied by Ausimont SpA; and glass fibers. These were in the form of untwisted rovings, coated with an epoxy compatible size and coupling agents, supplied by Fibreglass Ltd.

Resin Formulations

The two resin mixtures used were: (a) DGEBA + 80 phr MNA + 1 phr BDMA (control resin) and (b) DGEBA + 66 phr MNA + 40 phr CTMF + 1 phr BDMA (modified resin). The fluoroligomer content

$$HO\text{-}(CH_2\text{-}CH_2\text{-}O)_z\text{-}[\text{-}(CF_2\text{-}CF_2\text{-}O)_p\text{-}(CF_2\text{-}O)_q\text{-}]_n\text{-}(CH_2\text{-}CH_2\text{-}O)_z\text{-}X$$

and

$$X\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_z\text{-}[(CF_2\text{-}CF_2\text{-}O)_p\text{-}(CF_2\text{-}O\text{-}]_{q\text{-}n}(CH_2\text{-}CH_2\text{-}O)_z\text{-}X$$

where $z \sim 1.5$

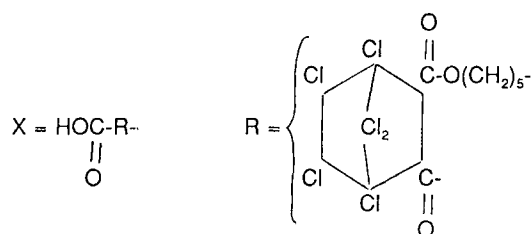p/q molar ratio $= 0.67$

$n \sim 10$

Figure 1   Chemical structure of carboxy-terminated perfluoroether oligomer (CTMF).

was deliberately chosen to be much greater than in previous work in order to magnify the effects of the interaction with the matrix and fiber–matrix interfacial components. The resin, hardener, and modifier were mixed at 80°C, cooled to room temperature, and then the catalyst was added. The catalyzed resin mixtures were then used to produce castings in open PTFE molds and to prepare composites. The thickness and curing conditions were the same in the two cases.

Fiber Desizing

Two methods were used to remove the size from the surface of glass fibers: (a) the fibers were wound on a steel frame, immersed for 5 min in MEK contained in an ultrasonic bath and allowed to dry at room temperature for one day; (b) the fibers were wound on a frame and heated in a furnace at 500°C for 2 h.

Production of Composites

A filament winding wet lay-up technique was used by which the fibers were wound on a steel frame to a total of five passes and impregnated with the epoxy resin in a leaky mold. To assist the penetration of the resin in the fibers interstices, the impregnated fibers were allowed to stand overnight in a vacuum oven at 50–60°C before being pressed in the leaky mold. Spacers 2 mm thick were used to control the thickness of the laminates (40 mm wide, 100 mm long). Two G-clamps were used to hold the composite under pressure while being cured in an oven at 120°C for 24 h. The composites were postcured freely for 3 h at 150°C and 1 h at 180°C and specimens 10 mm wide were cut out longitudinally and in the transverse direction to the fibers. A number of specimens were also thermally aged in an air oven at 200°C for 168 h. Overall the fiber content was found to vary between 59.2 and 63.1 by weight.

Dynamic Mechanical Spectra

Dynamic mechanical tests were carried out using a Polymer Laboratories DMTA apparatus, model MRII, using a cantilever bending mode at a frequency of 1 Hz and strain setting of 64 μm, scanning the temperature over the range from −120 to 250°C at a ramp temperature rise of 10°C/min. For the case of composites, measurements were made both in the longitudinal and transverse directions to the fibers alignment.

RESULTS AND DISCUSSION

Figure 2 shows the surface appearance of the fibers after removing the size coating by solvent washing and heat treatment, respectively. The absence of size material from the surface of the fibers is clearly ev-
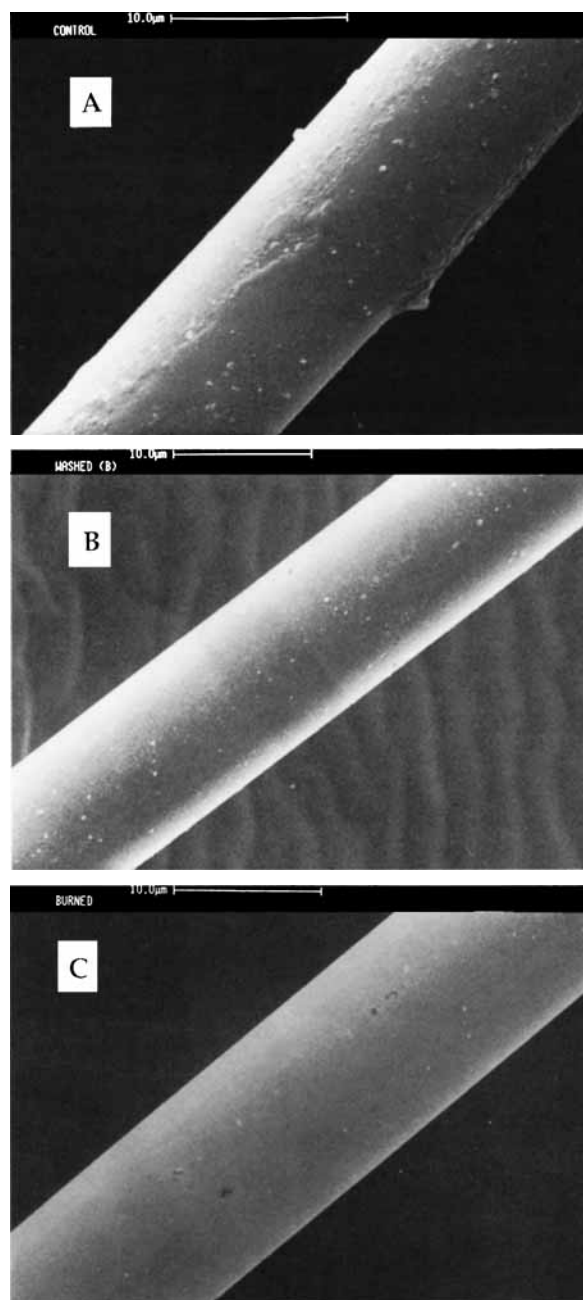

Figure 2   Appearance of glass fibers after removing the size (×400): (A) original fiber, (B) fiber after solvent extraction, and (C) fiber after heat treatment.

idenced by their much smoother appearance, particularly for fibers subjected to the heat treatment.

Figure 3 shows plots of the ratio of the complex modulus of the composite to that of the matrix (obtained from measurements on castings) as a function of temperature for systems based on the unmodified epoxy resin (control) tested in the longitudinal direction [Fig. 3(a)] and transverse direction to the fibers [Fig. 3(b)]. From an inspection of these graphs, the following features are revealed with respect to the effects on the composite–matrix modulus ratio:

1. A maximum occurs at around the glass transition temperature of the matrix.
2. It is higher for the longitudinal direction than for the transverse direction to the fibers (as expected).
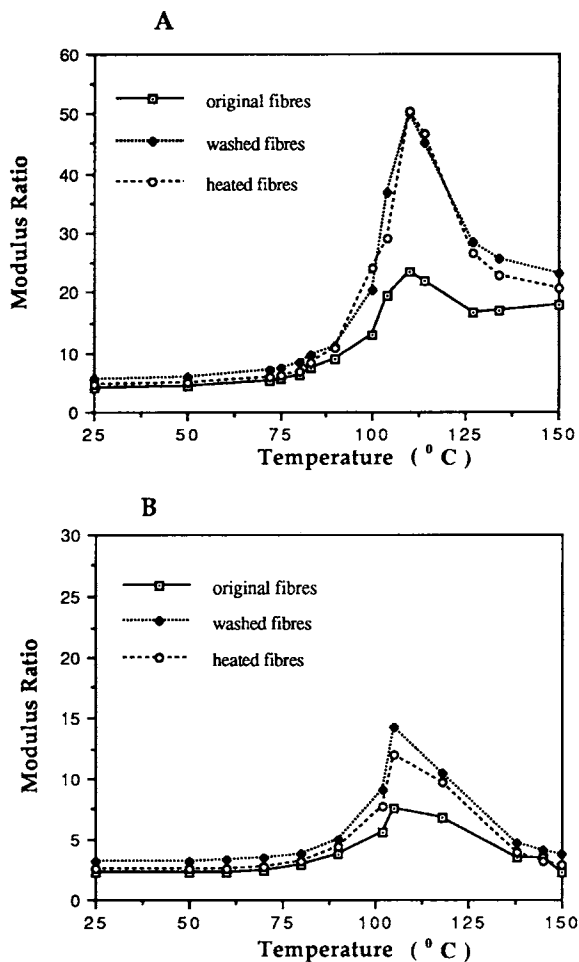

A

B

Figure 3 Composite–matrix dynamic modulus ratio for unidirectional glass fiber epoxy laminates with different fibers: (A) specimens tested in the longitudinal direction and (B) specimens tested in the transverse direction.
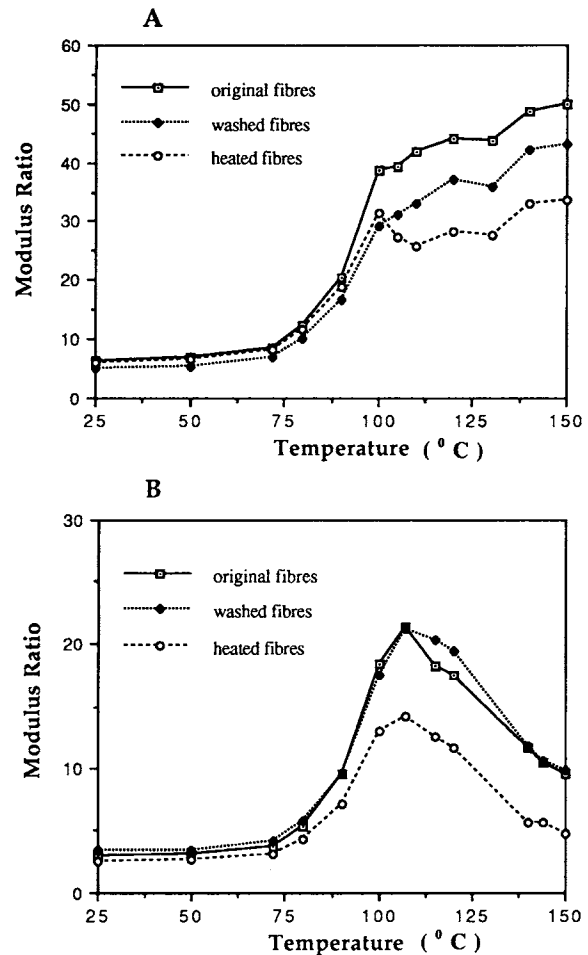
A

B

Figure 4 Composite–matrix dynamic modulus ratio for undirectional glass fiber laminates based on a CTMF-modified epoxy resin and different fibers: (A) specimens tested in the longitudinal direction and (B) specimens tested in the transverse direction.

3. It increases considerably when the size is removed from the surface of the fibers, the effect being approximately the same for the two treatments used.

For the case of composites based on the CTMF-modified resin (Fig. 4), the following observations are worth noting:

1. A very broad maximum occurs around the glass transition temperature of the matrix for tests in which the axial stresses act in the transverse direction to the fibers, but no clear maximum appears at temperatures up to 150°C for specimens tested in the longitudinal direction.

2. The effects of removing the size from the fibers for composites based on the CTMF-modified resin is the reverse of that observed for composites based on the unmodified resin. For CTMF-modified resin composites the original (untreated) fibers give the highest composite–modulus ratio while the heat treatment produces the lowest level of reinforcement.

3. At temperatures around the glass transition temperature of the matrix the composite–matrix modulus ratio is much higher for composites containing the CTMF-modified resin that those based on the unmodified resin.

The latter is likely to be related to the modulus of the matrix, which is much lower for the CTMF
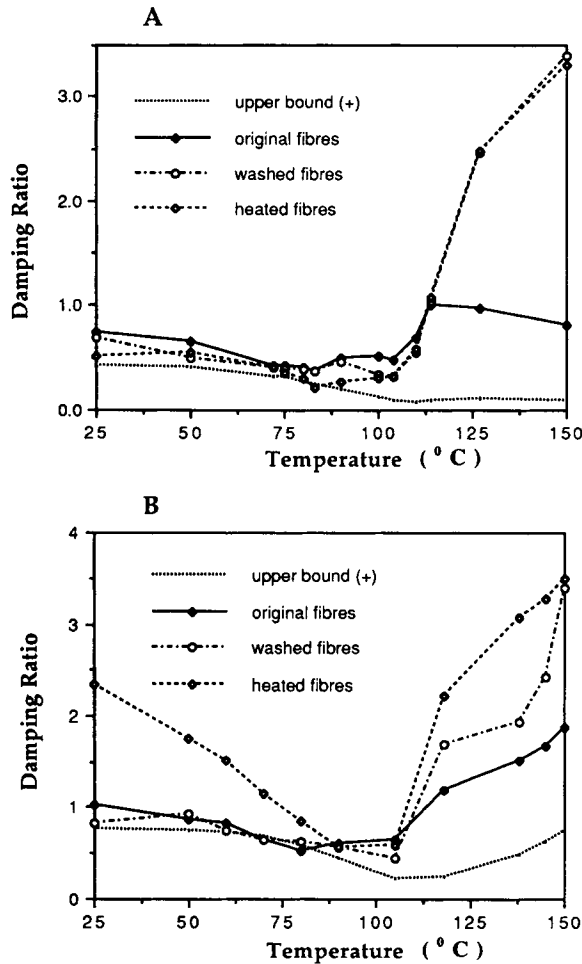

A

B

Figure 6 Composite–matrix damping ratio for unidirectional glass fiber laminates based on a CTMF-modified epoxy resin using different fibers: (A) specimens tested in the longitudinal direction and (B) specimens tested in the transverse directions.

A

B

Figure 5 Composite–matrix damping ratio for unidirectional glass fiber epoxy laminates with different fibers: (A) specimens tested in the longitudinal direction and (B) specimens tested in the transverse directions.
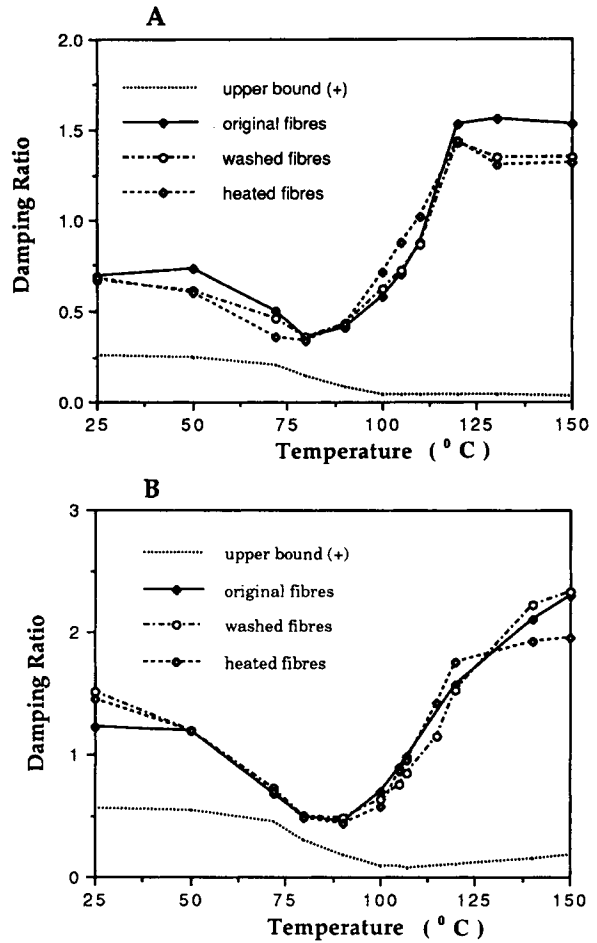
modified resin, owing to its much lower crosslinking density resulting from the incorporation of large quantities of perfluoroether oligomeric chains in the network.

The contrasting effect in removing the size from the surface of the fibers in the two cases, on the other hand, is a clear reflection of the difference in the nature of the interphase in the two situations (see later).

Plots of the composite–matrix damping ratio, i.e., the ratio $(\tan \delta)_{composite}/(\tan \delta)_{matrix}$ for the various composites tested in the longitudinal and transverse directions are shown in Figures 5 and 6. In these diagrams are included also the plots for the upper bound damping ratio (+) calculated on the assumption that there are no interfacial contributions to the overall damping dissipations in the composite and that the fibers are elastic, i.e.,

$$\left[\frac{(\tan \delta)_{\text{composite}}}{(\tan \delta)_{\text{matrix}}}\right]^{(+)} = \frac{(E_c)^{(+)}}{E_m} \simeq \frac{1}{\phi_m}\frac{E'_m}{E'_c}$$

where m and c denote matrix and composite, respectively, and ϕ_m is the volumetric fraction of matrix:

$$E_c^{(+)} = Im\left[\left(\frac{\phi_m}{E_m^*}\right)^{-1}\right]$$

where Im is the imaginary part and E_m^* is the complex modulus of the matrix.

The large positive deviations of the damping ratio from the calculated upper bound values clearly indicate that there are extensive interfacial losses. These increase even further when the size is removed from the fibers in the case of composites containing the unmodified resin (Fig. 5). For composites based on the CTMF-modified resin, on the other hand, the removal of the size from the fibers has no effect on the damping ratio.

It is worth noting that all three types of fiber used give rise to substantial levels of interfacial losses, particularly at temperatures above the T_g of the matrix. Furthermore the composite–matrix damping ratio shows a minimum at around the T_g of the matrix (Figs. 5 and 6). Since the composite–matrix modulus ratio exhibits a maximum in the same temperature region (Figs. 3 and 4), it can be inferred that the two phenomena are related to the stress transfer efficiency at the fiber–matrix interface. This behavior is, in fact, similar to the variation of coefficient of friction of glassy polymer with temperature.[15]

If the ratio of the loss modulus of the composites to that of the matrix is plotted against temperature, the only difference that emerges from the damping ratio curves is the appearance of a maximum at around the T_g of the matrix for specimens tested in the transverse direction. This does not effect, however, the inferences derived from discussion of the damping ratio data.

The plots in Figs. 7 and 8 show the effects of thermal aging on the damping characteristics of the composites, expressed as the ratio of tan δ value after aging to the original value for postcured samples. The removal of the size from the surface of the fibers reduces considerably the magnitude of the increase in α relaxations brought about by aging for the case of composites based on the control resin (Fig. 7), but it has hardly any effect on the behavior of the composites based on the CTMF-modified resin. There are two possible explanations for this behavior:
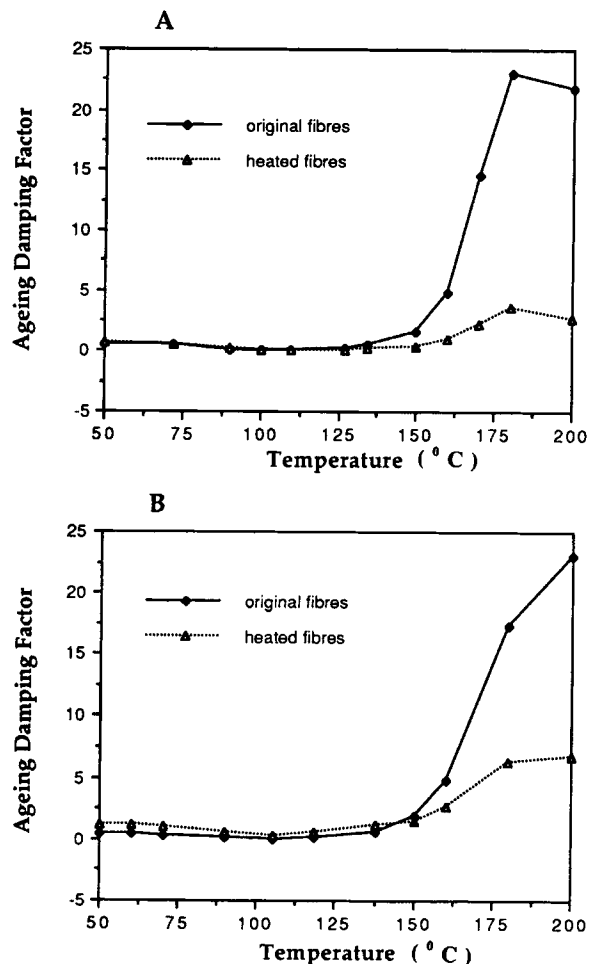

Figure 7 Plots of the ratio of tan δ values for composites subjected to thermal aging to tan δ values of postcured samples. Systems based on an unmodified epoxy resin: (A) specimens tested in the longitudinal direction and (B) specimens tested in the transverse directions.

1. The increase in losses for composites based on the control resin is due to degradation reactions of residual (undissolved) size from the surface of the fibers, whereas for composites based on the CTMF-modified resin the increase in losses results from degradation reactions within the matrix, i.e., the residual size may degrade much less in the latter systems.

2. For composites based on the control resin the size on the surface of the fibers prevents the densification of the network in the interphase regions, whereas for composites based on the CTMF-modified resin the degradation products of thermal aging treatment can increase the losses in both matrix and the interphase.
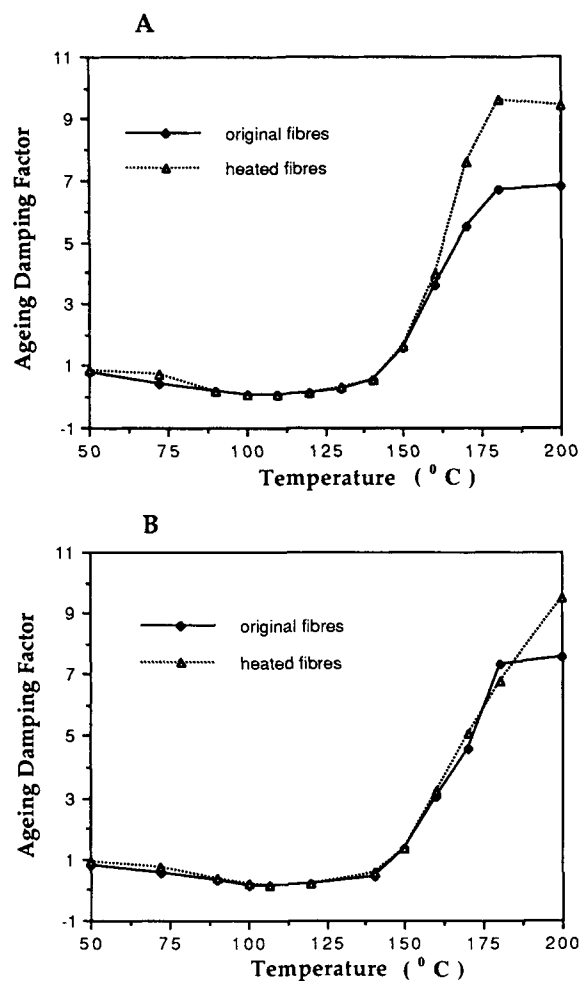
A

B

Figure 8 Plots of the ratio of tan δ values for composites subject to thermal aging to tan δ values of postcured samples (aging damping factor). Systems based on a CTMF-modified epoxy resin: (A) specimens tested in the longitudinal direction and (B) specimens tested in the transverse directions.

CONCLUSIONS

The main conclusions that can be drawn from this work are:

1. The reinforcing efficiency in fiber–matrix composites, expressed as the ratio of the modulus of the composite to that of the matrix, reaches a maximum at around the T_g of the matrix.

2. The CTMF-modified resin provides a greater reinforcement efficiency than an equivalent unmodified resin.

3. The removal of the size from the surface of glass fibers causes an increase in dynamic mechanical losses in the case of composites based on the unmodified resin and not in composites containing the CTMF-modified resin.

4. For composites based on a conventional anhydride-cured epoxy resin thermoxidative aging produces an increase in crosslinking density of the matrix. In the fiber–matrix interfacial regions, however, this occurs to a lesser extent when the size is present on the surface of the fibers.

5. For composites based on the CTMF-modified resin thermoxidative aging causes a very large increase in dynamic mechanical losses at temperatures above the T_g of the matrix, irrespective of whether the size is present or not on the surface of the fibers.

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