# Environmental Effects on Thermoplastic and Elastomer Toughened Cyanate Ester Composite Systems

ROMAN W. HILLERMEIER, JAMES C. SEFERIS

Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington, Seattle, Washington 98195-1750

**ABSTRACT:** The effects of temperature and moisture on thermal and mechanical properties of high-temperature cyanate ester composite materials were investigated. A resin transfer molding process was used to impregnate glass fiber fabrics with matrices that underwent thermoplastic or elastomeric toughness modifications. The elastomer-modified material obtained the highest mode I fracture toughness values primarily because the toughener did not phase separate. Extended exposure to 200°C, however, deteriorated initial toughness improvements regardless of the modifier utilized. Although the thermal stability was increased by using thermoplastic modifiers in comparison to the elastomer-modified material, the degradation was mainly governed by the cyanate ester network. Gaseous degradation products caused delaminations and therefore reduced strength when the materials were exposed to 200°C for 1000 h. Also, upon immersion in water at 95°C, the matrices absorbed up to 3.3 wt % more than previous values reported in the literature. Fiber/matrix interfacial phenomena were responsible for this behavior because fiber/matrix adhesion also was reduced drastically as shown by the strong reduction in flexural strength. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 556–567, 2000

**Key words:** cyanate ester; composites; degradation; water absorption; interlaminar fracture toughness

## INTRODUCTION

During the last decade, aromatic cyanate esters have emerged as a new class of thermosetting resins for composite matrices in both aerospace and electronic industries. Being derived from cyanation of hydroxyl-containing species, a variety of backbone structures have been studied.[1] These have in turn imparted varying chemical, thermal, mechanical, and dielectric properties. The dicyanate ester monomers cyclotrimerize via addition polymerization to form polycyanurates or triazines.[2] Compared to epoxies and bismaleimides (BMIs), cyanates are considerably more hydrophobic. Cured neat resin specimens only absorb up to 2.5 wt % water.[1,3,4] The cured network is responsible for high glass transition temperatures ($T_g$) that are between BMIs and epoxies.[5] Relatively low crosslink densities and high free volumes make cyanate esters inherently tougher than most high-temperature thermosets. In addition, balanced dipoles in the cured state and the absence of hydrogen bonding functionality are responsible for the low moisture absorption and the excellent dielectric properties.[5]

These unique features along with their excellent processing characteristics have made cyanate esters desirable for many aerospace applications including radomes, antennae, and low ob-

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servable structures. However, materials used for these types of applications, as well as others, typically require enhanced performance characteristics that the base resins alone do not possess. Common desires for these materials are increased fracture toughness and improved resistance to microcracking. Therefore, modifiers such as elastomers and thermoplastics are usually incorporated into the base resins to improve these characteristics.[6] These materials, however, must be selected so that they do not inhibit processing or reduce other characteristics such as thermal or mechanical performance. As a result, selection of a modifier for a specific material and application becomes increasingly difficult especially when considering long-term as well as hot-wet performance.

A variety of modifiers have previously been utilized to improve the toughness performance of cyanate esters. These include reactive and nonreactive elastomers as well as a variety of engineering thermoplastics.[7–13] Most studies, however, considered only neat resin properties which do not always translate directly into composite properties.[10,12,13] Little research has been done to investigate the effect of modified cyanate esters on the composite toughness performance[8,9,11] and the impact of environmental effects on such modified material systems.

The objective of this study was to investigate the effect of different toughening strategies, namely the inclusion of elastomers or thermoplastics, on the fracture toughness of a high-temperature cyanate ester composite system. The developed resin transfer molded glass fiber composites were analyzed further in relation to their flexural and thermal properties. Most importantly, the long-term durability of these materials was studied by considering the same performance characteristics after moisture absorption experiments and exposure to a high-temperature environment.

## EXPERIMENTAL

### Materials

The base cyanate resin formulation consisted of 50 wt % AroCy B-30 prepolymer, 30 wt % bisphenol A dicyanate monomer (AroCy B-10), and 20 wt % AroCy L-10 monomer supplied by Ciba Polymers. The catalyst for this system was a blend of 2.5 phr nonylphenol and 0.42 phr 2% chromium naphthanate, from OMG America, Inc. Hydroxy

functional butadiene acrylonitrile (HTBN) reactive rubber AT x 013 Type III (Echo Resins), polyetherimide (PEI; Ultem 1000), and polysulfone (PS; Udel P1800) were used in the amount of 10 wt % to toughen the base resin. The finely ground thermoplastics were dried in an vacuum oven for approximately 24 h at 130°C prior to use. The reinforcement for the laminates was a glass-fiber 8 harness satin fabric (Style 7781; Clark-Schwebel Inc.) finished in 4354CS-767 cyanate ester tailored sizing.

The base resin was formulated by mixing the cyanate ester monomers and prepolymers at 100°C in an oil bath. After degassing at 80°C, the catalyst was added under continuous stirring for 3 min, and the material was then quenched to room temperature. The HTBN-modified resin was formulated accordingly, except that the elastomer was heated separately before the preheated B-30, B-10, and L-10 resins were added, respectively. The PEI- and PS-modified resins were created by adding the dried finely ground thermoplastics to the B-10 and L-10 resin mixture under continuous stirring at 130°C for 3 h. After adding the B-30 and degassing at 110°C, the resins were cooled to 80°C followed by addition of the catalyst and quenching to room temperature.

### Laminate Processing

0°-symmetric 16-ply laminates with a target fiber volume content of 57% were fabricated using the bleed resin transfer molding (BRTM) process described elsewhere.[9,14] The materials were cured for 1 h at 178°C and 2 h at 240°C using heating/cooling rates of 3.3°C/min and a consolidation pressure of 1 MPa. During the heating to 178°C, two impregnation/consolidation steps (100°C and 115°C) were performed for 15 min each to optimize processing.

### Analysis

The neat resins were analyzed by differential scanning calorimetry (DSC) using a TA Instruments DSC 2910 interfaced to a Thermal Analyst 3100 controller. Dynamic DSC experiments were performed at a heating rate of 5°C/min to 350°C in a nitrogen atmosphere. The activation energy was determined using heating rates of 2.5°C, 5°C, 10°C, and 20°C. Cure cycle simulations were carried out using heating/cooling rates of 3.3°C/min. Residual cure analyses were performed by heating to 350°C at a rate of 5°C/min.

Rheology was investigated using a controlled stress rheometer CSL 100 from TA Instruments. The rheometer was run with parallel plates, a oscillation frequency of 6.28 rad/s and a heating rate of 2.8°C/min for dynamic experiments.

Cured laminates were cut into 12.7-mm-wide specimens for environmental conditioning and testing. All specimens were dried at 110°C for 48 h (24 h atmospheric pressure followed by 24 h vacuum) before they were tested or subjected to thermal aging or water absorption studies. Thermal aging was carried out at 200°C in an air circulation oven. Water conditioning was performed by placing the specimen in a bath that was heated to 95°C and filled with deionized water. The weight of the materials, which were subjected to thermal and water conditioning, was measured sequentially to monitor weight changes. One large specimen per material instead of many little specimens was used to monitor weight changes reducing edge effects. The coupon sizes were approximately $52 \times 12.7 \times 3.3$ mm (L $\times$ W $\times$ D) for the thermal aging specimens and $250 \times 12.7 \times 3.3$ (L $\times$ W $\times$ D) mm for the water absorption experiments.

Mode I interlaminar fracture toughness was measured using the double cantilever beam (DCB) method.[15–17] Specimens were approximately 300 mm long and 12.7 mm wide. A Kapton film crack initiator, 50.8 mm long, was placed into the midplane during the lay-up. The symmetric laminates were laid up such that the warp face of all fabric plies was facing the midplane. Therefore, the fiber tow geometry in the midplane was similar to the geometry obtained by unidirectional materials. Each sample was first precracked in a mechanical testing apparatus to provide a sharp crack tip before the test was performed. For all materials at least five specimens were tested. Samples were pulled apart at a rate of 25.4 mm/min until a final displacement of 63.5 mm was observed.

Mode II interlaminar fracture toughness was measured using the end-notch flexure (ENF) test.[16,17] The laminates were prepared in the same manner as the DCB specimens. A three-point bending apparatus with stationary posts set 76.2 mm apart was used to create shear fracture in the midplane of each specimen. The crack tip was set 19.05 mm from the stationary post, and the loading point was set 38.1 mm from this post. Specimens were precracked in the mechanical testing apparatus to provide a sharp crack tip before testing was performed. A displacement rate of 2.54 mm/min was used to load the specimen in flexure until the load decreased upon crack propagation.

Flexural properties were determined in a three-point test according to ASTM D790.[18] For each material, five specimens with a length of 60 mm and 12.7 mm width were tested. The support span was 48 mm and the crosshead speed was 1.2 mm/min.

To determine the temperature-dependent viscoelastic properties, dynamic mechanical analysis (DMA) was carried out on cured materials with a TA Instruments DMA 2980 using single cantilever clamps. A heating rate of 5°C/min in conjunction with a oscillation frequency of 1 Hz was used.

Morphology of the laminates was examined by optical microscopy of polished cross sections. The HTBN-modified material was stained with osmium tetroxide, while the PEI- and PS-modified materials were etched with methylene chloride and methyl ethyl ketorn, respectively.

Fracture surfaces were investigated using optical and scanning electron microscopy (SEM) using an accelerating voltage of 25 kV and a working distance of 20 mm.

## RESULTS AND DISCUSSION

### Resin Characteristics

The base model resin containing cyanate monomers and prepolymers was formulated such that RTM-sufficient characteristics were obtained. The bisphenol A dicyanate monomer (AroCy B-10) and prepolymer (AroCy B-30) were the main ingredients. The ratio used provided satisfactory rheological characteristics necessary for low-viscosity impregnations. However, these two resins tended to crystallize at ambient temperatures because of the symmetry of the bisphenol A dicyanate monomer (BADCy). Hence, liquid dicyanate monomer AroCy L-10 was incorporated into the formulation because it provided resistance against crystallization of the overall formulation due to its asymmetric molecular structure.[1,19] Although the formulation still tended to crystallize after relatively long times at ambient temperatures, it exhibited satisfactory characteristics. Rheometry showed that the four systems exhibited viscosities quite different from each other. The unmodified resin reached a minimum viscosity of approximately $2 \times 10^{-3}$ Pas · at 120°C, which is adequate for RTM processing.[20] The
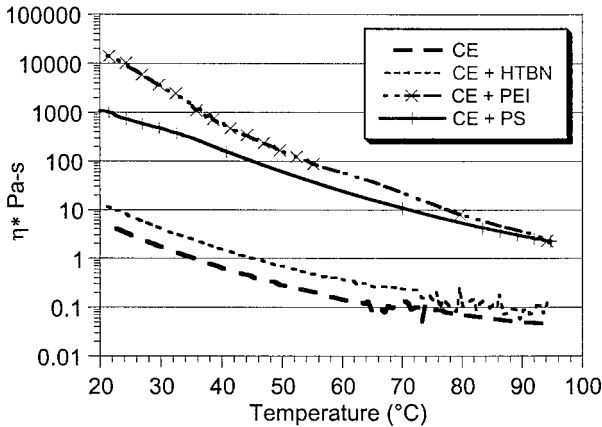
**Figure 1** Complex viscosities of four model cyanate ester (CE) resins containing different modifiers (heating rate: 2.8°C/min).

modification by HTBN increased the viscosity only a small degree because of the low molecular weight of the elastomer. Thus, it was also suitable for conventional RTM, as shown in Figure 1. However, the addition of PEI and PS to the cyanate ester formulation increased the viscosity significantly and resulted in resins that were too viscous for conventional RTM processing. Consequently, the bleed resin transfer molding technique was used, as it has been used previously for processing highly modified resin systems in an RTM-like manner.[8,9]

In RTM processing the selection of the catalyst is important because the resins typically need to maintain low-viscosity values for longer periods to provide enough time for impregnation. Catalysts that are latent but still result in high conversions must be used. Chromium naphthanate in conjunction with nonylphenol has been previously found to offer these features.[8,9] DSC revealed that the activation energy for the catalyzed formulation was 77.5 kJ/mol (determined using the method by Ozawa and Doyle[21,22]). The catalyst lowered the reaction onset of the uncatalyzed resin from approximately 200°C to 130°C. This provided enough latency for sufficient laminate impregnation for BRTM processing. Isothermal rheometer experiments at 100°C and 120°C confirmed that the viscosity did not change significantly over 30 min.

The heat of reaction for the modified resins were around 550 J/g, approximately 10% lower than the observed heat of reaction for the unmodified system. This corresponded to the weight fractions of modifiers in these three systems. The

measured peak temperatures were approximately 5°C higher for the systems containing PEI and HTBN, suggesting that these modifiers might have hindered to a small extent the trimerization reaction of the cyanate ester groups. The addition of polysulfone, however, increased the peak temperature slightly. This shows that this system may have reacted differently than the other two materials.

Through the DSC cure cycle experiments, the optimum processing conditions were defined. In this study it was desirable to obtain complete conversion for the following aging experiments. However, this has been a controversial issue, since optimum properties are sometimes obtained below 100% conversion.[7] Good results were obtained when the materials were cured for 2 h at 240°C, according to the cure cycle described previously. The conversion was <99%, and the associated glass transition temperatures were 266°C, which are in the range of the values reported in literature for similar cyanate ester systems.[1,3,23]

## Properties of Unconditioned Materials

The cured laminates had high surface qualities without any imperfections, as often found for laminates processed by conventional RTM.[24] The fiber volume content was 57% ± 1.5% for all materials and were determined by using the laminate thickness, material densities, and the assumption of void free laminates.

The mode I interlaminar fracture toughness was measured to investigate the effect of the modifiers on the damage resistance of the cured laminates. Mode I interlaminar fracture toughness was calculated as $G_{IC}$, the critical energy release rate, which was defined by the area method.[15,16] The developed composite systems reached toughness values higher than found for most toughened epoxy composite systems (Table I).[6,25] This was partly a function of the cyanate ester chemistries, which are known to reach toughness values greater than those obtained by most highly crosslinked matrices.[7] Another important factor for the relatively high toughness values was the glass fibers, which exhibit high strain-to-failure values (up to 5%). The $G_{IC}$ values were found to increase by approximately 20% when either the HTBN elastomer or the PEI was included in the base formulation (Table I). These were relatively small improvements compared to the values found in literature for neat resin properties.[10,26] However, resin properties often do not translate

**Table I   Properties of Unaged Glass Fiber Reinforced Cyanate Ester Composites**

|  | CE | CE + HTBN | CE + PEI | CE + PS |
|---|---|---|---|---|
| Interlam. Fract. Toughness $G_{IC}$ (J/m$^2$) | 557 ± 64 | 669 ± 12 | 653 ± 74 | 563 ± 36 |
| Flexural Modulus* (MPa) | 23100 ± 188 | 23530 ± 133 | 23183 ± 230 | 23594 ± 211 |
| Flexural Strength* (MPa) | 674 ± 14 | 661 ± 4 | 691 ± 15 | 667 ± 6 |
| Tg by Peak in E″ (°C) | 271 | 251 | 265 | 272 |

(± values correspond to standard deviations for at least four measurements, * flexural properties were linearly normalized to 57% fiber volume content)

directly into composite properties and greater improvements are commonly found using higher modifier concentrations.[26] In addition, the four matrices were developed primarily to serve as high-temperature materials, which were more stable because of the complete conversions.

The results of the mode II interlaminar fracture tests showed similar trends and were in the range between 1 and 1.3 kJ/m$^2$. However, the test results for each material are not reported here, because fiber bridging in the interlayer occurred to a large extent. Therefore, the measured values might represent fiber dominated situations and not the true interlaminar properties. SEM analysis of the fracture surfaces showed that fibers were pulled out of the matrix, as shown by the matrix grooves in Figure 2. As can be seen from the figure, the stresses applied in mode II caused the matrix to crack, which again caused the fibers to delaminate. The fibers probably possessed strain-to-failure values greater than the brittle
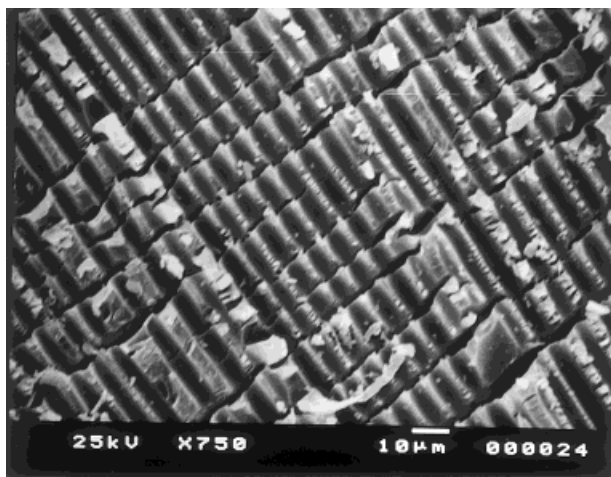


**Figure 2**   SEM micrograph showing mode II fracture surface of HTBN-modified cyanate ester composite material. Grooves caused by delaminated fibers and low strain-to-failure behavior of matrix (cracks).

matrix; therefore, they remained intact in some cases causing fiber bridging between the two fracture surfaces.

The high conversions found by DSC were confirmed by DMA experiments, which showed that the base material had a $T_g$ of 271°C, as defined by the peak in the loss modulus (Table I). The $T_g$ values decreased by 20°C for the HTBN and 5°C for the PEI-modified system. This suggested that the HTBN and PEI modifiers did not phase-separate to a great extent in the cured systems. The PS-modified system, however, maintained the $T_g$ of the unmodified system, indicating that a high degree of phase separation occurred. It is likely that for the same reason, the mode I interlaminar fracture toughness was not improved for the PS-modified system, which can be seen in Table I. As has been reported previously, highly crosslinked matrices with a tough second phase rarely lead to sufficient increases in mode I fracture toughness.[27–29]

Optical microscopy of polished crosssections revealed that all four materials were well impregnated and essentially void free. It was found that a second phase (dark areas) was formed in the PS-modified cyanate ester (Fig. 3) confirming the DMA findings. The observed domain sizes were between 2 and 20 $\mu$m. The HTBN-modified materials did not contain a second phase; however, the PEI-modified system showed phase separation to a small extent.

Although the mode I and mode II interlaminar fracture toughness results identified the toughness performance, the three-point bend tests characterized the flexural moduli and strengths of the developed composite systems. These are crucial to consider, as toughness improvements usually lead to sacrifices in the modulus of the material. The flexural moduli were calculated using the linear section between 25% and 75% (maximum load) of the load-displacement plot, the results of which are depicted in Table I. Surpris-
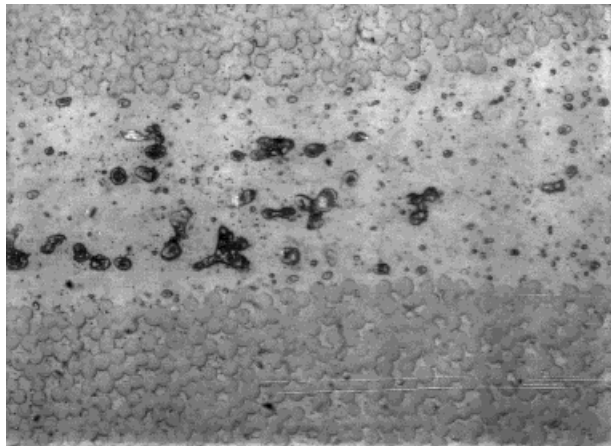
**Figure 3** Cross section of PS-modified cyanate ester material showing PS domains (dark areas) in resin-rich interlayer.

ingly, the flexural moduli were not affected significantly by the addition of the modifiers, although the HTBN and PEI materials must have plasticized the matrix to some extent. This was probably partially due to the fact that cyanate esters can reach their maximum modulus when the crosslink density is below the maximum value.[7] In addition, it is important to notice that these are the modulus values for the composite materials that are dominated by the reinforcing fibers. The measured flexural strengths followed the same trend as found for the moduli (Table I). All four systems were on a similar level, indicating that structural integrity was not affected by the addition of the modifiers.

### Effect of a High-Temperature Environment

In aerospace industries the maximum allowable usage temperature of polymeric composite materials is usually defined to be at least 50°C below the temperature where the storage modulus starts to decrease drastically. This occurred for the initial cured cyanate ester materials at approximately 250°C; therefore, 200°C was selected as the aging temperature to simulate realistic peak temperature aging conditions.

The results of the weight measurements are shown in Figure 4. As shown in the figure, all materials lost <0.5% weight during the 1200 h at 200°C. The majority of the gaseous products evolving from the four materials are believed to be based on degradation products of the cyanate ester. Shimp et al.[3,30] reported that at temperatures ≥200°C polycyanurates outgas notable

amounts of $CO_2$ from carbamates formed when residual cyanate functionality encounters moisture in air at temperatures producing segmental mobility. They observed a weight loss of 2% when dicyanate ester castings (BADCy) were exposed to 235°C for 500 h. Although the cyanate ester network was the major contributor to the measured weight loss, variations among the differently modified systems could be identified. The HTBN-modified material lost substantially more weight than the other three materials during this period, possibly a result of the degradation of the butadiene acrylonitrile rubber. Interestingly, the thermoplastic modified systems were the most stable, losing on average between 15% and 20% less than the control (Fig. 4). This was more than the weight fractions of the thermoplastics contained in the composites. It seemed likely that the thermoplastic portions of the matrices improved the thermal stability of these system, possibly because of entanglement between the crosslinked cyanate ester network.

The effect of toughness modifications on morphology and thermal and mechanical properties has been studied for a large variety of cyanate ester materials.[8–10,26] Nevertheless, the effect of high-temperature environmental exposure on the toughness properties has not been investigated for cyanate ester composites. Figure 5 compares the mode I interlaminar fracture toughness values obtained for the unaged materials and the same materials subjected to thermal aging at 200°C for 500 h. As can be seen from the figure, the exposure to high temperatures had detrimental effects on the toughness performance of all
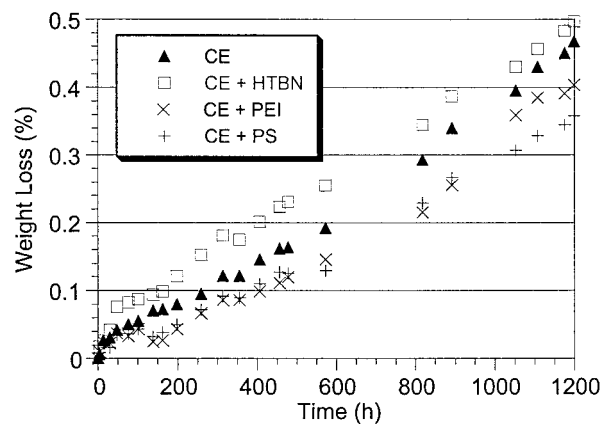


**Figure 4** Weight loss caused by thermal aging in air at 200°C of four model cyanate ester (CE) composite systems containing different modifiers.
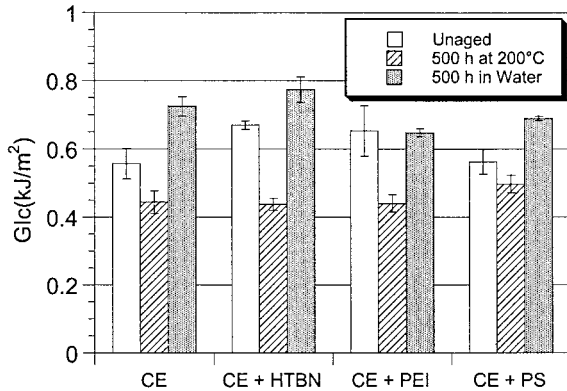
**Figure 5** Mode I interlaminar fracture toughness of unaged, thermally aged (in air at 200°C), and conditioned (in water at 95°C) cyanate ester composite materials.



**Figure 7** Flexural strength of unaged and aged cyanate ester composite materials (CE) containing different modifiers (aging at 200°C in air, by ASTM D790).

four materials. Degradation of the matrix as well as fiber/matrix interfacial degradation might have led to the decay of the material properties. Interestingly, the toughness improvement for the unaged materials obtained through the incorporation of the HTBN or PEI was completely deteriorated. These two materials, including the control, showed the same mode I value after the aging experiment. It appeared that the degradation of the toughness properties was governed by the degradation of the cyanate ester network. SEM analysis confirmed these findings. Figure 6 shows the fracture surface of the HTBN-modified material. As can be seen from the figure, inten-
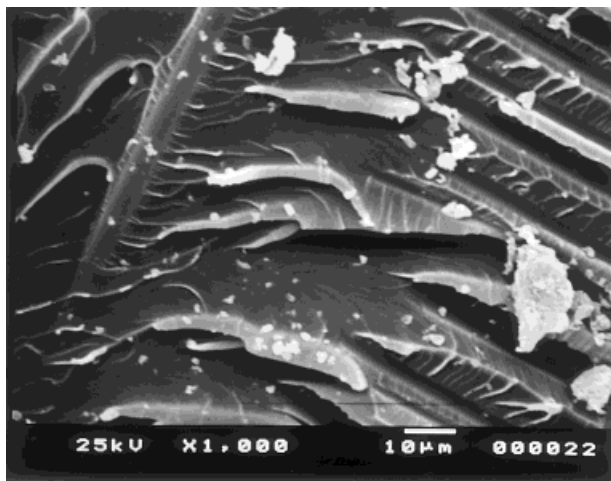


**Figure 6** Brittle failure of cyanate ester matrix during mode I interlaminar fracture testing (material: CE + 10 wt % HTBN aged in air at 200°C for 500 h, by SEM).
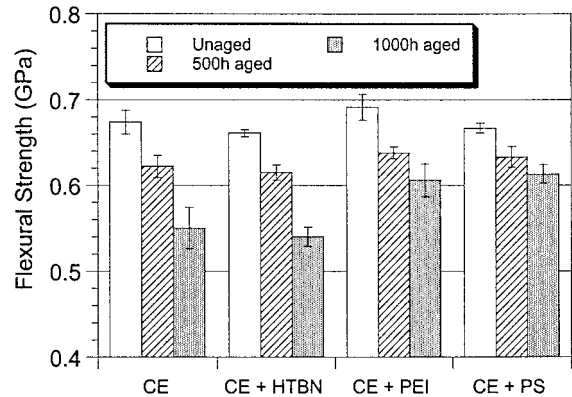
sive hackling took place in resin-rich areas, indicating relatively brittle fracture. These fracture characteristics were found for all materials. In addition, large areas of delaminated fibers were observed. The relatively small decrease in mode I toughness for the PS-modified system suggested that the second phase helped to retain the toughness when the continuous phase lost its ability to absorb stresses induced by the propagating crack tip.

The flexural properties were measured after 500 and 1000 h of thermal aging in air at 200°C. The flexural strength was found to decrease only by 5–7% when the materials were aged for 500 h (Fig. 7). Matrix embrittlement and possibly fiber/matrix interfacial phenomena may have caused the decay. A trend among the different materials was not observed, suggesting that weakening was caused mainly through aging of the cyanate ester network. Microscopy of the specimens demonstrated that the materials did not microcrack or delaminate. After 1000 h, however, the strength values were found to decay by approximately 20% for the unmodified and the HTBN-modified systems. As found by microscopy, the surface plies started to delamimate, probably because of formation of volatile products during the degradation of the matrix. This "swelling" phenomenon has been observed previously by other researchers and was believed to be the limiting degradation mechanism in long-term service at high temperatures.[30,31] It could be concluded that the majority of the strength decrease was caused by the swelling of the specimens. For the thermoplastic-modified systems, delamination of the surface plies occurred to a smaller extent if at all. This
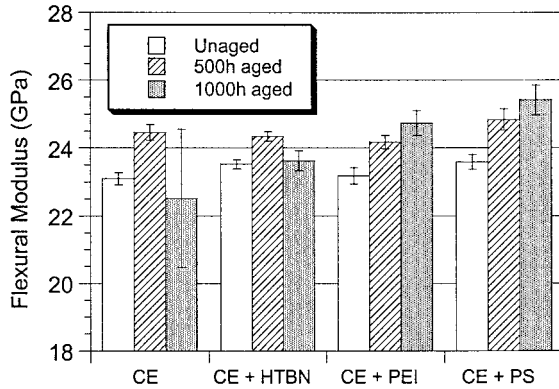
**Figure 8** Flexural moduli of unaged and aged cyanate ester composite materials (CE) containing different modifiers (aging at 200°C in air, by ASTM D790).



**Figure 9** Glass transition temperatures ($T_g$) of unaged and aged cyanate ester composite materials (CE) containing different modifiers (aging at 200°C in air, by E″ using DMA).

helped the thermoplastic-modified materials to retain approximately 90% of their initial flexural strength. The results of the weight analysis are in good agreement with these findings, as it was found that the thermoplastic-modified materials were the most thermally stable systems. Similar observations are represented in Figure 8, where flexural moduli for the different materials are depicted. After 500 h of aging time, the composite moduli increased by approximately 5% for all materials, possibly because of matrix embrittlement. After 1000 h, however, the materials behaved quite differently. The moduli declined for the unmodified and HTBN-modified material, mainly as a result of the delaminated surface plies. The moduli of the PEI- and PS-modified materials increased slightly, confirming that less areas were delaminated and additional matrix embrittlement took place.

Dynamic mechanical analysis of the aged specimens was carried out after 500 and 1200 h in the high-temperature environment. It was found that after thermal aging for 500 h, the glass transition temperatures remained in the same range for all materials except for the HTBN-modified cyanate ester (Fig. 9). This verified that the increase in stiffness of the cyanate ester laminates was not gained through postcure effects, but through embrittlement of the matrix. The HTBN-modified system, however, showed transitions at 199°C and 246°C, possibly a result of a partially degraded cyanate ester network. Also, the degradation of the HTBN, as found by the weight analysis (Fig. 3), might have been responsible for this phenomenon. The plot of the relative storage modulus E′ for the base and the HTBN-modified cy-
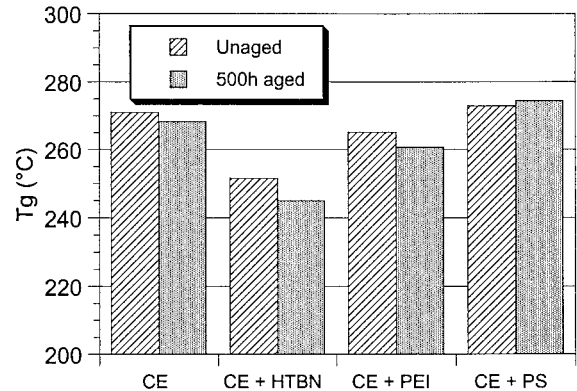
anate ester laminates in their initial and aged version reinforces this assumption (Fig. 10). As can be seen from the figure, the temperature dependence of the modulus increased substantially when the HTBN-modified material was exposed to thermal aging. It is evident that this particular material loses its high-temperature properties to a greater extent than the unmodified cyanate ester material after being exposed to high temperatures. The PEI- and PS-modified cyanate esters were found to retain the temperature-dependent storage modulus in a manner similar to the base system. Interestingly, the materials behaved quite differently after they were exposed to 200°C for 1200 h. Figure 11 depicts a plot of the relative loss moduli for the four materials. Unlike the
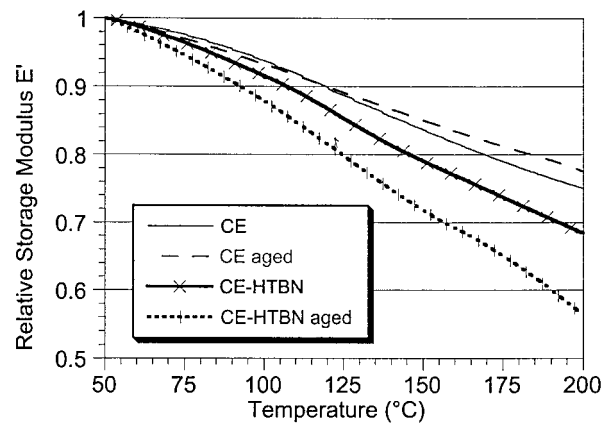


**Figure 10** Relative storage moduli (E′) of unaged and aged base cyanate ester (CE) and HTBN-modified cyanate ester composite material (aging for 500 h in air at 200°C, by DMA).
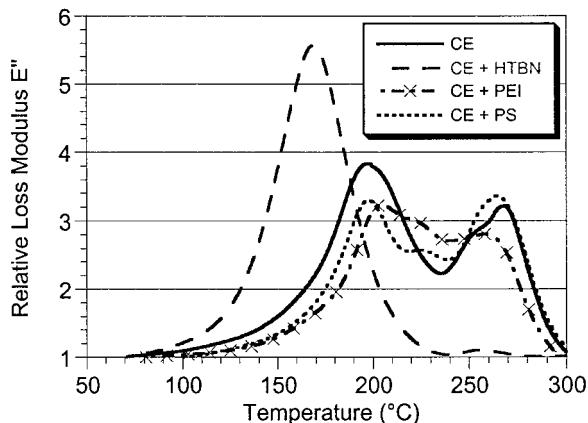
**Figure 11** Relative loss moduli (E″) of cyanate ester composite materials (CE) containing different modifiers after 1200 h aging in air at 200°C (by DMA). All materials exhibit two loss peaks after aging experiments: one close to the peak of unaged material and a second one between 70°C and 100°C below this initial value.

unaged materials, all four materials exhibited two transitions, indicated by the peaks in the loss moduli. The first transition was, except for the HTBN-modified system, at approximately 195°C. The second transition was in the range of the transitions of the unaged materials. This behavior suggested that localized degraded areas in the cyanate ester existed in the thermally aged material. Although a few studies have focused on the degradation of cyanate esters,[3,23,30] such behavior has not been reported in the literature. Nevertheless, the results are in agreement with the findings of the mechanical tests and the microscopy results. As shown before, changes in laminate structure due to outgassing led to a significant reduction in the mechanical performance between 500 and 1000 h of aging. Although it was assumed that the evolving gas was $CO_2$ (as shown by other researchers), this should not have led to chemical degradation of the cyanate ester network.[1,3] Therefore, it was believed that chain scission took place to a significant extent, such that localized degraded areas existed in the cyanate ester networks.

## Effect of Water

Cyanate esters are known to exhibit excellent hot–wet properties because they absorb less water at saturation than competing resins such as epoxies or BMIs. This is mainly a result of the cyanurate linkage, which is very resistant to hy-

drolysis.[23] The key aspect to success in avoiding the deleterious effects of moisture for cyanate esters and epoxies is complete conversion. The hydrolysis of a cyanate function leads to a carbamate, which can decompose above 190°C.[32] Shimp et al.,[33,34] however, found that hydrolysis takes place very slowly and suggested that moisture might be absorbed mainly through physical absorption.

The results of the water absorption experiments are shown in Figure 12. All composite materials exhibited similar behavior, and the total amount of water absorbed after 500 h in 95°C water was between 0.82 and 0.88 wt %. This approximately corresponded to the 3.3% weight gain of the cyanate ester matrix, assuming the water was only absorbed by the matrix and not by the fibers. Shimp et al., however, observed only 2% water absorption for a similar resin system after 500 h immersion in boiling water. It is believed that the fibers in the material contributed to the different behavior. The sizing material might have affected the matrix stoichiometry close to the matrix/fiber interface, leading to changes in hydrophobicity or interfacial phenomena such as wicking. Microscopy showed that no microcracking occurred in the matrix. Interestingly, the cross sections of these materials were more difficult to polish than the unconditioned specimen. Only cross-sectional areas with fibers in the transverse direction (the fibers pointing out of polishing plain) and resin-rich regions could be polished adequately. The areas with fibers aligned in the polishing plain, on the other hand, could not be polished sufficiently. The fibers here
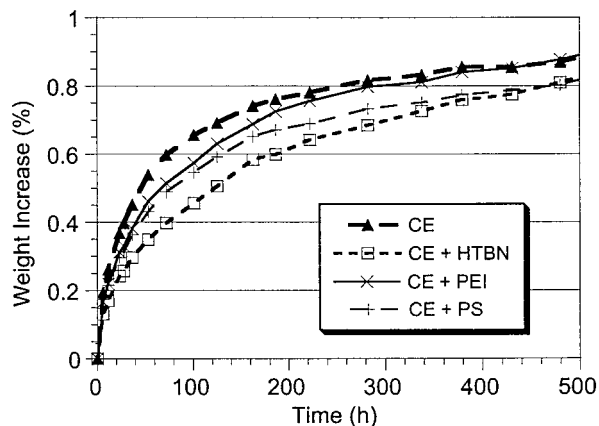


**Figure 12** Weight increase due to water absorption of cyanate ester composite materials (CE) containing different modifiers (immersion in 95°C water).
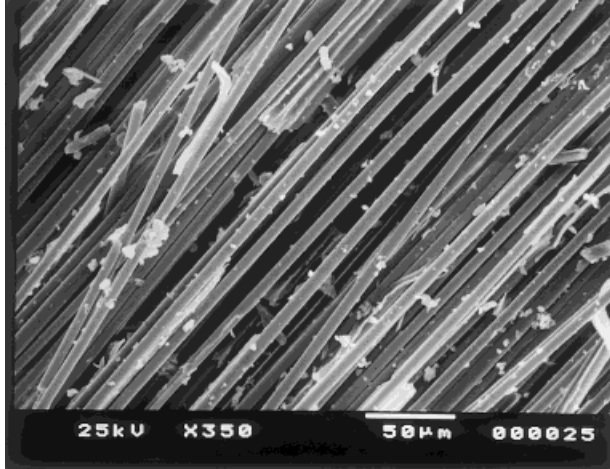
**Figure 13** Mode I fracture surface showing large areas of delaminated fibers. Lack of matrix residuals on fiber surfaces indicates poor interfacial adhesion (material: HTBN-modified CE, by SEM).



**Figure 14** Flexural moduli of unaged and water-conditioned cyanate ester materials containing different modifiers (immersion in 95°C water for 500 h, by ASTM D790).

were pulled out during the polishing procedure, indicating poor fiber/matrix adhesion. The small differences among the four materials were possibly a result of slightly different resin contents of the analyzed specimens.

Mode I interlaminar fracture toughness results for the water-conditioned specimens are shown together with the unconditioned and thermally aged specimens in Figure 5. As one can see from the figure, the wet mode I toughness performance increased slightly for most materials, partly because plasticization of the matrix occurred. SEM analysis, however, indicated that poor interfacial adhesion was apparent because many ruptured fiber bundles with no resin residues were found on the fracture surfaces (Fig. 13). Although no discrepancies were observed during mode I testing, the large amount of delaminated fibers might have caused fiber bridging during testing. This usually leads to increases in the interlaminar fracture toughness, as parts of the stresses in the interlaminar zone are carried by the fibers.[35,36] Hence, the observed values have to be read with caution.

The flexural properties were measured after immersion in water for 500 h. As expected, the flexural modulus decreased for all materials (Fig. 14). Matrix plasticization due to the water absorption can account for such behavior. Trends among the four materials were not obvious, suggesting that the materials were equally plasticized, as already indicated by the weight analysis. The modifier did not seem to have a great influ-
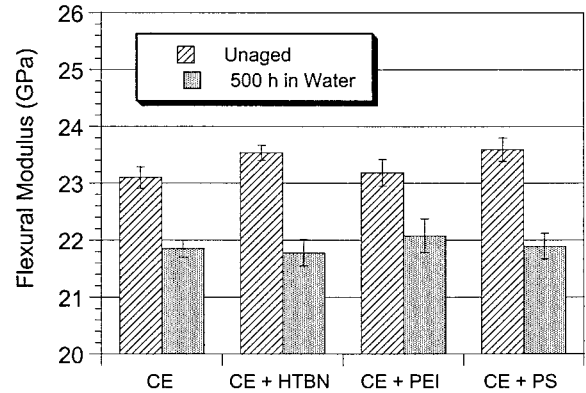
ence on absorption behavior, partly because of their small weight contributions to the overall formulations. Hence, the moduli were affected similarly. The flexural strength was more affected than the modulus for the four systems, as shown in Figure 15. After water immersion, these materials lost about 50% of their initial strength. This again indicated that poor interfacial adhesion was possibly the reason for the large decrease. The interfacial adhesion, commonly a function of the fiber sizing, has been shown by many researchers to effect flexural and interlaminar strength values.[37,38]

Dynamic mechanical analysis confirmed that large amounts of water were absorbed by all materials. The $T_g$s declined to approximately 160°C for all materials, as shown in Figure 16. This is in
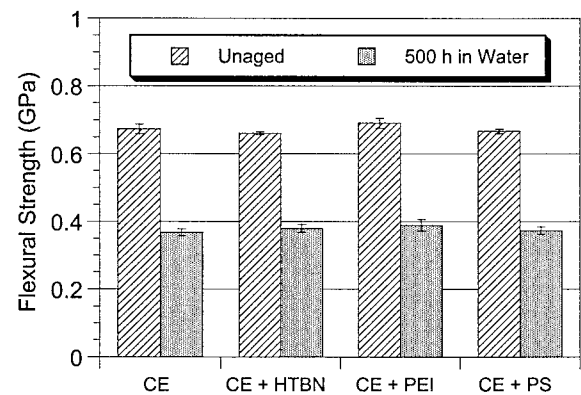


**Figure 15** Flexural strength of unaged and water-conditioned cyanate ester materials containing different modifiers (immersion in 95°C water for 500 h, by ASTM D790).
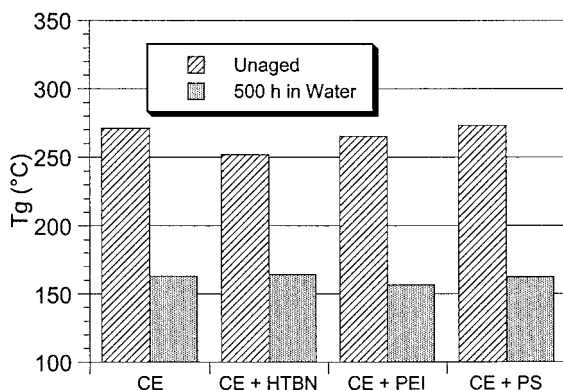
**Figure 16** Glass transition temperatures ($T_g$) of unaged and water-conditioned cyanate ester materials containing different modifiers (immersion in 95°C water for 500 h, by E″ using DMA).

good agreement with the findings of Shimp et al.[1] for a resin system containing only B-30. As the $T_g$s for the conditioned materials were in the same range, it could be concluded that the modifiers did change the hydrophobicity of the matrices, as already indicated by the weight analysis.

## CONCLUSIONS

In the present work, four high-temperature cyanate ester resins were developed, three of which were modified with 10 wt % of either an elastomer or a thermoplastic. After impregnation of these resins into glass fiber fabric using the BRTM process, the effects of the modifiers were characterized in relation to fracture toughness, flexural, and thermal properties. Essential to this work was further comparison of these properties to the properties after thermal aging at 200°C in air and conditioning at 95°C in water. It was initially found that by the incorporation of hydroxyl terminated butadiene acrylonitrile rubber or polyetherimide into the matrices, improvements in the mode I interlaminar fracture toughness were observed. Interestingly, these two materials were found to not phase-separate to a large extent. In contrast, polysulfone was found to phase-separate and not cause any improvements in the mode I fracture toughness.

After subjection to thermal aging for 500 h, the toughening effects deteriorated. Primarily matrix embrittlement of the cyanate ester network was responsible for these losses. Further thermal aging at 200°C caused reductions of up to 20% in

strength after 1000 h. Gaseous degradation products evolving from the matrices were assumed responsible for such behavior as they caused delamination. Dynamic mechanical analysis confirmed that the HTBN-modified material was most susceptible to degradation and indicated that localized degraded areas in the cyanate ester existed in all four materials.

The water absorption behavior of the four composite systems was not affected by the type of modifiers used. Thus, all materials responded similarly after immersion for 500 h at 95°C. Surprisingly, the four matrices absorbed more water than typically observed for neat resin specimens. This was believed to be due to fiber sizing and interfacial phenomena. Great reductions in flexural strength, up to 50%, after immersion in water for 500 h indicated that the fiber/matrix interface was affected. However, further investigations are necessary to confirm these findings. Matrix plasticization and increased fiber bridging led to slightly increased mode I fracture toughness values.

Collectively, this work identified the necessity of understanding the effects of modifiers on the long-term aging and hot–wet performance of cyanate ester resin composite systems.

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