

Exposure of Polycyanurate and Epoxy Matrix Composites to Hypergolic Rocket Fuel Components

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Polycyanurates are a new class of thermosetting polymers having properties superior to those of epoxies for spacecraft applications. These polymers are gaining wide acceptance due to their lower moisture uptake, reduced outgassing, high glass transition temperature, and excellent resistance to thermally induced microcracks. Polycyanurate composites are being used in current satellite programs and will likely see increased applications in satellite and launch vehicles. It is necessary to determine the compatibility of these composites with spacecraft propellants. The compatibility is examined between two hypergol rocket propellants (anhydrous hydrazine and nitrogen tetroxide) and polycyanurate composites composed of T-300 fibers and polycyanurate matrices derived from bisphenol-A. The mechanical performance of polycyanurate composites is compared to T-300/934 epoxy composites, a current state-of-the-art system for these applications. Fiber and neat resin specimens are tested in addition to the composite systems. The tensile strength of the polyacrylonitrile-based T-300 fibers is not affected by 24-h exposures in hydrazine and nitrogen tetroxide. The neat resin specimens are significantly affected by both fuel (anhydrous hydrazine) and oxidizer (nitrogen tetroxide), as witnessed by changes in mass, surface hardness, and tensile strength. Hydrazine dissolves the polycyanurate, but is absorbed by the epoxy. Nitrogen tetroxide attacks both resins, with degradation occurring twice as fast for the epoxy. Tensile strengths are determined for both exposed and unexposed specimens. Tensile strength decreases are observed to differing degrees for both of these composite systems as a function of propellant and exposure time. Scanning electron microscopy is also used to examine the fracture surfaces and microstructure of both systems before and after exposure.

Introduction

POLYCYANURATE composite systems, due to their improved performance, are being introduced as a replacement for epoxy composites in many structural and space applications. Composites utilizing a polycyanurate matrix are superior to those with epoxy matrices due to their increased toughness and dimensional stability, lower moisture absorption, and reduced outgassing.¹

The cyanate ester monomers used in this study are bisphenol-A derivatives containing cyanate (OCN) functional groups. On heating, they undergo cyclotrimerization to form networks with triazine rings as crosslinks linked by bisphenol units. Resin and polycyanurate properties can be varied by changing the bisphenol linkage or aromatic ring substituents. The low crosslink density of these polymers allows a high degree of rotational freedom around ring couplings, which produces a composite matrix of superior toughness. Because OH groups are also eliminated during monomer synthesis, the cured polymers exhibit low moisture absorption, approximately two to three times lower than typical epoxies, which contributes to high-dimensional stability.

Polycyanurate composites are currently used on several satellite programs and are proposed for use on numerous other spacecraft. Current programs include the military's MILSATCOM, NASA's AXAF-1, and Clementine, as well as other commercial satellites. Programs considering these composites for future applications include the next generation of military early-warnings satellites, space- and ground-based ballistic missile interceptors, Earth Observing System, Pluto Fast Flyby, and advanced bus and spacecraft structures under development by TRW, Inc., and The Boeing Company.

Common satellite components utilizing polycyanurate composites are primary bus structures, tubes and struts, solar-array panels, metering trusses, optical benches, backing material for mirrors, and phased-array antennas.^{2–5}

Although quickly gaining popularity, polycyanurates are relatively new materials with a limited database. Because they are already being incorporated into space vehicles, it is imperative that we have a thorough understanding of how they will react in this unique environment. Hypergol rocket propellants are toxic and highly reactive substances. The most common fuels are hydrazine (N_2H_4) and its derivatives, with nitrogen tetroxide (N_2O_4) used as an oxidizer. Leakage of these propellants threatens the safety of personnel and hardware. This threat increases if materials with poor resistance to these propellants become contaminated, especially loaded structures such as pressurant tanks.^{6,7} The objective of this study was to determine the effects of hypergol rocket propellants on the mechanical and physical properties of polycyanurate composites and to compare these effects with those of a current state-of-the-art epoxy system. This material compatibility study will help assess the use of fiber-reinforced polycyanurate composites on future spacecraft and launch vehicles.

Experimental

Materials and Processing

The two thermoset polymers selected for this study are Ciba Geigy's AroCy B cyanate ester resin and ICI Fiberite's 934 epoxy resin. The AroCy B resin is a bisphenol-A dicyanate, where the bisphenol linkage consists of an isopropyl group $[(CH_3)_2C]$ with single hydrogen atoms serving as aromatic ring substituents (Fig. 1). The published tensile strength and modulus for the polycyanurate are 12.0 ksi and 0.47 Msi, respectively.⁸ The associated values for the epoxy are 12.0 ksi and 0.60 Msi. The reinforcing material selected for use in the composite systems is the T-300 polyacrylonitrile-based carbon fiber produced by Amoco Performance Products, Inc. All fibers used in this study were shear treated and unsized, having a tensile strength of 530 ksi and tensile modulus of 33.5 Msi. Four types of test specimens were manufactured from these materials in

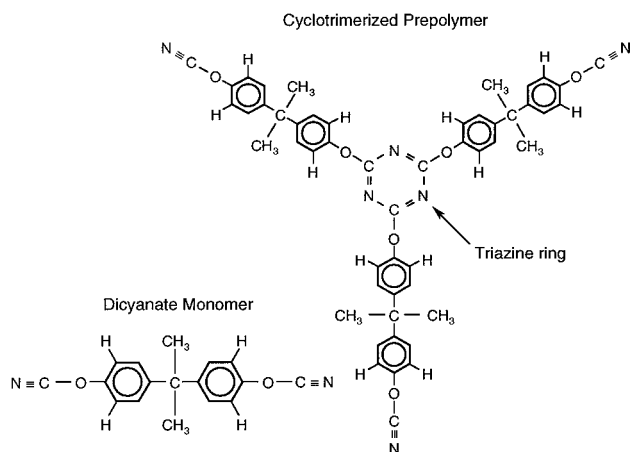
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Table 1 Test matrix of test specimens used for each exposure condition

Specimen type	Number of test specimens for each exposure condition										
	Control, 0 min	Hydrazine					Nitrogen tetroxide				
		2 min	5 min	30 min	1 h	24 h	30 min	1 h	2 h	5 h	24 h
Raw T-300 fiber	25	na	na	na	na	25	na	na	na	na	25
Polycyanurate resin coupons	10	5	5	5	5	na	5	5	5	5	na
Epoxy resin coupons	10	5	5	5	5	na	5	5	5	5	na
Polycyanurate composite tows	25	25	25	Not testable	na	na	na	25	25	na	na
Epoxy composite tows	25	25	25		25	na	na	na	25	25	na
Polycyanurate composite panels	10	5	5	na	na	na	na	na	5	5	na

**Fig. 1** Chemical structures of both the cyanate monomer and the cyclotrimerized prepolymer.

this study: neat resin coupons, raw fiber tow bundles, impregnated unidirectional tow composites, and multiple-ply composite panels. This allowed for the examination of propellant effects on each component as well as on the combined composite system. The test matrix is shown in Table 1.

Neat resin coupons were produced by melting and casting each resin into Teflon[®] molds designed according to American Society for Testing and Materials (ASTM) standard D 638, type IV. Two molecular weight oligamers of dicyanate monomers were blended by YLA, Inc. The catalyst used was a cobalt acetyl acetonate mixture, which accounted for 1.0 wt% of the total formulation. ICI Fiberite's 934 epoxy blend was supplied as a hot melt resin. A 15-wt% solution of the resin in acetone was necessary to facilitate processing. The cyanate ester resin was processed at 120°C (248°F) under a 30-in. (762-mm) Hg vacuum for 30 min to remove trapped air and volatiles. The epoxy resin was processed similarly, except that a total of 60 min was allowed for complete removal of the solvent. Both resins were cured in ambient air according to manufacturer's specifications. The AroCy B was cured at 177°C for 1 h with a final 2-h postcure at 232°C (449.6°F) (Ref. 9). The 934 epoxy was heated to 121°C for 4 h followed by a 2-h cure at 177°C. On cooling, the specimens were removed and machined to final dimensions. The resin dogbone gauge width and thickness measured 0.25 in. (0.635 cm) and 0.12 in. (0.30 cm), respectively.

Raw fiber bundles and unidirectional tow composites were fabricated from T-300 fibers (3000 filaments/tow). Those with the cyanate ester resin matrix were provided as 55% resin content prepreg from YLA, Inc., using the same formulation as the neat resin. This prepreg was wound on a rack and placed in an oven for curing. Composites made with epoxy resin were solution impregnated. The tow was first prepared by winding it on a rack and solution impregnating with a 30-wt% solution of resin in acetone. The solvent was then allowed to evaporate in a fume hood overnight. With the prepreg free of solvent, the rack was placed in an oven for curing. All tows were subjected to the same cure cycles as the neat resin specimens. On cooling, the tows were cut to 5-in. (12.7-cm) lengths and removed from the rack. To isolate the effects of the propellants on the bare fiber, raw fiber bundles were also

mounted and epoxy impregnated after undergoing exposure to the propellants.

Polycyanurate matrix composite panels were also fabricated. These panels consisted of eight, 0.010-in.-thick (0.0254-cm-thick) layers arranged in a 0/+45/-45/0 balanced, symmetric orientation. The prepreg tape used for these panels was supplied by YLA, Inc., with a resin content of 55% and the same formulation as the neat resin. After vacuum bag processing in a press at 50 psi and 177°C for 1 h, the panels were postcured at 232°C (449.6°F) for 5 h. Two panels were produced, and their fiber volumes were determined by optical microscopy to be 0.48 and 0.59. For purposes of mechanical data analysis, each fiber volume was normalized to 0.60. Specimens were cut from the panels and milled to the dimensions specified in ASTM D 3039 (see Ref. 10).

Propellants

Several types of hydrazine fuels are commonly used on spacecraft, four of which were examined in this program: anhydrous hydrazine or hydrazine (N₂H₄), monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), and Aerozine-50, a 50/50 by weight mixture of anhydrous hydrazine and UDMH. The most common spacecraft oxidizer, nitrogen tetroxide, was also selected. All propellants were used as supplied.

For purposes of this study, the most reactive of the four hydrazine fuels was selected for testing. A pathfinder test procedure, using mass and physical changes of exposed resin as selection criteria, was employed to make this determination. Specimens consisting of 100-mg cubes of each cured polymer were placed in vials and immersed in each of the four fuels. After exposure durations of 30 and 60 min, the specimens were rinsed with deionized water and allowed to dry in a fume hood for 72 h. The resin cubes were then reweighed, and mass and dimensional changes were measured. Physical changes were also noted.

Test specimens were exposed to the propellants in several ways. For the raw fiber bundles, tow material was wrapped on two aluminum frames, with one immersed in hydrazine and the other in nitrogen tetroxide. All unidirectional tow composites were completely immersed in graduated cylinders containing fuel or oxidizer. Because of the rapid degradation of polycyanurate in hydrazine, the ends of the tows were protected by Apiezon[®] sealing compound to enable later application of mechanical testing tabs. Teflon holders were used for neat resin coupons and composite panels to minimize the use of propellants and corresponding hazardous waste. The ends of both specimen types were preserved with adhesive-backed Teflon tape; however, the gauge section of each specimen remained completely immersed for the entire exposure duration. All specimens were rinsed with deionized water after exposure and allowed to dry in a fume hood for 48 h before further processing. Fuel exposures were conducted for up to 24 h; oxidizer exposures lasted as long as 72 h. The propellant exposure durations for each specimen type are indicated in Table 1.

Analysis

A mass loss or gain analysis was conducted on cured resin specimens exposed to the selected fuel and oxidizer. Polycyanurate and epoxy specimens were cut into 150-mg cubes and immersed in the propellants. After exposure, the specimens were rinsed with deionized water and allowed to dry in a fume hood. Each specimen was

reweighed after 24 h and again after 72 h in a fume hood. No further change in mass was detected for either polymer after the 72-h check.

Tensile testing was performed on neat resin coupons, unidirectional tows, and composite panels. The ends of both types of composites were bonded between tabs. The gauge lengths for the resin coupons, tow, and panels were 1.0, 2.0, and 6.0 in. (2.54, 5.08, and 15.24 cm), respectively. All samples were loaded to failure in a Universal Instron testing machine. The crosshead speed for the resin coupons and tows was 0.05 in./min (0.127 cm/min), whereas a speed of 0.10 in./min (0.254 cm/min) was used for the panels. The ultimate load was recorded for each sample and used to calculate tensile strength. A strain gauge was attached to the resin coupons and composite panels to record tensile strain data, which were then used to calculate tensile modulus. All testing was conducted as specified in ASTMs D 638, D 3039, and D 4018 for the resin coupons, composite panels, and unidirectional tows, respectively.^{10–12}

Cross sections of the resin coupons were subjected to hardness testing to further examine the effects of the propellant penetration on the polymers. Samples were cast in Epon 815 epoxy and polished in preparation for testing. Knoop hardness numbers were calculated for nine points evenly spaced across the width of the gauge sections. Scanning electron microscopy (SEM) was also used to analyze the microstructure and fracture surfaces of all specimens.

Results and Discussion

Pathfinder Results

An important indicator of chemical compatibility of a material is the change in mass that occurs as a result of exposure.^{13,14} For the polycyanurate, fuel exposures resulted in either no change or a considerable mass loss depending on the fuel, with a 42% mass loss after 60 min in anhydrous hydrazine being the most significant. However, epoxy specimens experienced either no change or a slight increase in mass due to absorption, with a 2% mass increase after 60 min in anhydrous hydrazine being the most significant (Fig. 2). Physical changes in the resins and fuels were also noted. The polycyanurate specimens that were affected appeared to dissolve partially in the fuels, turning the fuels yellow in color with white particulates settling out of solution. The surfaces of the affected epoxy specimens became discolored, but the specimens maintained their original dimensions, and the fuels remained clear. For both polymers, anhydrous hydrazine had the most significant effect, both in mass and physical changes, followed by Aerozine-50 and MMH. UDMH essentially did not affect the mass or appearance of either polymer. As a result of this selection process, anhydrous hydrazine, hereafter referred to as hydrazine, was the fuel chosen for testing.

Effects of Propellants on Carbon Fiber

Neither hydrazine nor nitrogen tetroxide affected the tensile strength of the T-300 fibers. The published strength of the fiber is 530 ksi (material information from Amoco Performance Products, Ciba-Geigy, ICI Fiberite, and YLA, Inc.). The calculated strength for control specimens was 490 ksi, or 92.5% of the published strength. For fibers exposed to fuel and oxidizer, strengths of 467 and 495 ksi, respectively, were achieved. Exposed fiber strengths

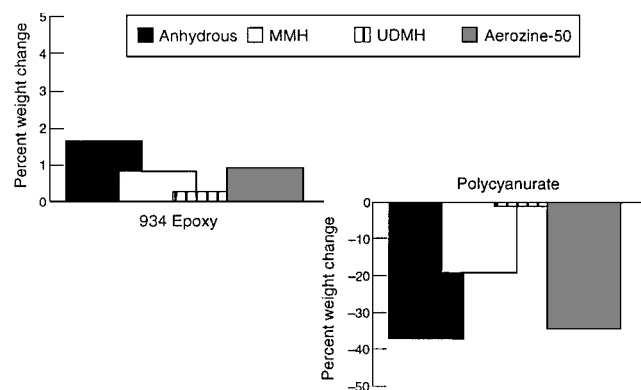


Fig. 2 Effect of various hydrazine fuel exposures on polycyanurate and epoxy resin mass changes (60-min exposure).

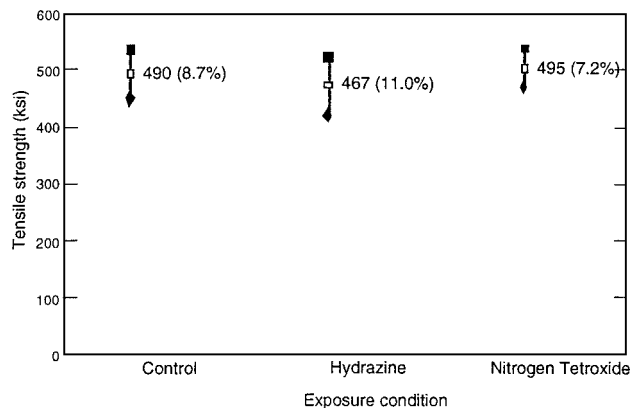


Fig. 3 Effect of 24-h exposure condition on the tensile strength of T-300 carbon fiber.

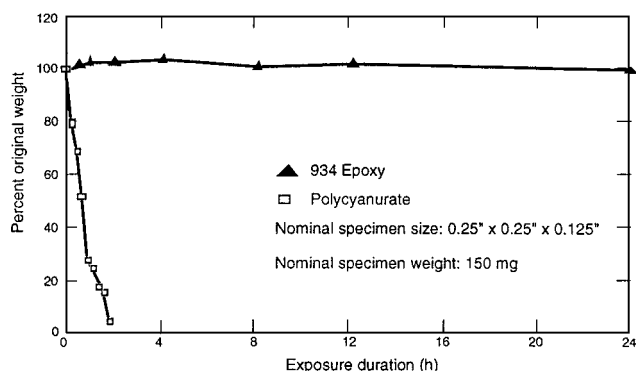


Fig. 4 Effect of hydrazine exposure on polycyanurate and epoxy resin mass changes.

differ less than 5.0% from the strength of the control specimens, as shown in Fig. 3. These calculations are based on the assumption of 100% fiber strength utilization.

Micrographs obtained from the SEM were compared for the exposed and unexposed cases. No observable changes in the surface of the fibers were detected as the result of exposure to either propellant. Fracture surfaces of composite tows fabricated from exposed fiber were also compared with those from the control group. Analysis revealed the same amount of fiber pullout for both types of composites for all three conditions (unexposed, oxidizer exposed, and fuel exposed).

Effects of Propellants on Neat Resin Coupons

The effect of fuel type and exposure time on mass gain or loss was determined for both resin systems. Figure 4 shows the effect of hydrazine on the mass as a function of exposure time for both resin systems. As shown, the cured polycyanurate resin sample shows 95% mass loss within the first 2 h of exposure. The epoxy, however, does not show any significant variation in mass loss over a 24-h exposure time. This variation in chemical resistance is believed to be due to the inherent differences in the chemical structure of both polymers.¹⁵ The single bond between the carbon and oxygen atoms of the cyanate (OCN) functional group of the polycyanurate resin is a site that is highly susceptible to hydrolysis by a strong base. Even after formation of the triazine ring, this ether linkage is susceptible to reactions with a strong base such as hydrazine. Because this linkage is at a crosslink site, severing it will cause degradation of the polymer structure. Bauer et al.¹⁶ have also recently reported the reaction kinetics of 2,4,6-triphenoxy-1,3,5-triazine with octylamine at various temperatures. The aim of the study was the determination of the rate constants for the three successive substitutions of the triazine ring and their activation energy using a monofunctional amine. Using high-pressure liquid chromatography, this investigation identified and exhibited the susceptibility and fragmentation of a very similar system at the oxygen linkage site to chain scission by the amine. This work corroborates the mechanism for the degradation of the polycyanurate resin system to hydrazine exposure. On the

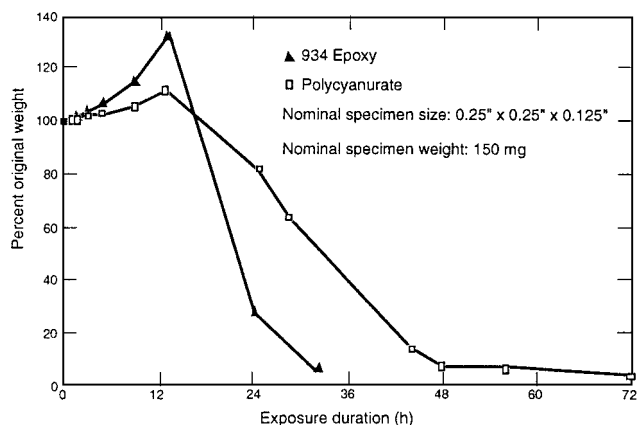


Fig. 5 Effect of nitrogen tetroxide exposure on polycyanurate and epoxy resin mass changes.

other hand, such a weak link does not exist in the epoxy structure, which may explain the negligible changes in resin mass loss.

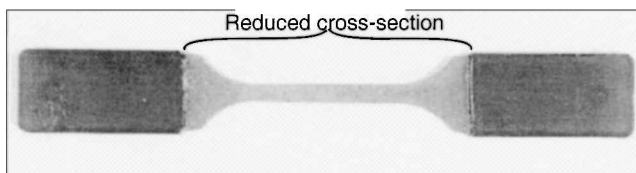
Figure 5 shows the effect of nitrogen tetroxide on the mass as a function of exposure time for both resin systems. As shown, both systems show an initial increase in mass after 12-h exposure, after which both resins are completely dissolved. During this initial 12 h of exposure, the rate and degree of weight gain is much greater in the epoxy system than that of the polycyanurate because the epoxy system is much more polar in nature compared to the polycyanurate resin, and, therefore, a much greater driving force exists for diffusion. Other research¹⁷ has shown this same type of behavior with a number of other solvents. In the case of hydrazine exposure, the small weight loss due to epoxy resin decomposition was countered by this fuel absorption, therefore exhibiting negligible weight change. The epoxy was the first to dissolve, with only 5% of its original mass left after 32 h of exposure, compared to 72 h required to consume the same quantity of polycyanurate. Nitrogen tetroxide is initially more easily absorbed by the epoxy network, initiating a mechanism by which the epoxy is more rapidly consumed than the polycyanurate resin. This variation in rate may also be due to the oxidation behavior of both of these polymer networks. The aliphatic groups formed by the opening of the epoxide rings are likely to oxidize readily when exposed to nitrogen tetroxide. The lack of similar aliphatic groups in the polycyanurate may explain the nearly double degradation rate, or mass loss, of the epoxy compared to that of the polycyanurate.

Following the mass analysis, exposed resin dogbones were subjected to tensile testing to observe variations in mechanical behavior. After a 1-h exposure to hydrazine, the strength of the polycyanurate was 10.2 ksi compared to 11.2 ksi for the control group. This accounts for only a 9% decrease in strength. However, in reality, there is a 75% reduction in the ultimate failure load. This variation between the ultimate failure stress and the ultimate failure load is entirely due to the significant mass loss of the resin after exposure, as observed from the reduced cross-sectional area in the dogbone specimens shown in Fig. 6b compared to the control sample in Fig. 6a. The hydrazine appears to etch chemically and remove the polycyanurate resin as a function of exposure time, without affecting unpenetrated areas. High-magnification, cross-sectional micrographs show little to no change in the microstructure or fracture behavior of the resultant specimens. Microhardness measurements were also performed across the cross-sectional area of the material to measure any physical changes. None were observed. This again is because the rate of diffusion of the hydrazine is equal to the rate of decomposition; therefore, any material that remains for analysis has not been exposed to the fuel.

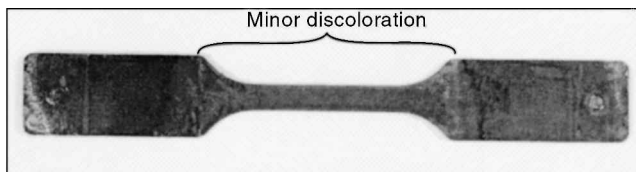
For the same exposure duration time, the strength of the epoxy was reduced by 54% to 5.2 ksi compared to 11.3 ksi for the control group. However, unlike the polycyanurate resin, the epoxy exhibited minimal mass loss, as shown in Fig. 7b, compared to the control sample in Fig. 7a. The strength decrease is believed to be due to the penetration of hydrazine into the polymer network. Figure 8b shows the cross-sectional fracture surface of an exposed epoxy dogbone.



a) Control polycyanurate sample



b) Hydrazine-exposed polycyanurate sample

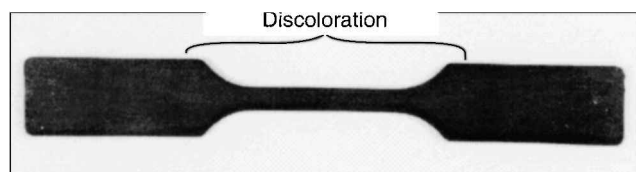


c) NTO-exposed polycyanurate sample

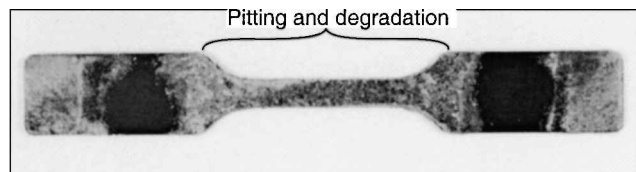
Fig. 6 Effect of nitrogen tetroxide and hydrazine exposure on polycyanurate dogbone specimens.



a) Control epoxy sample



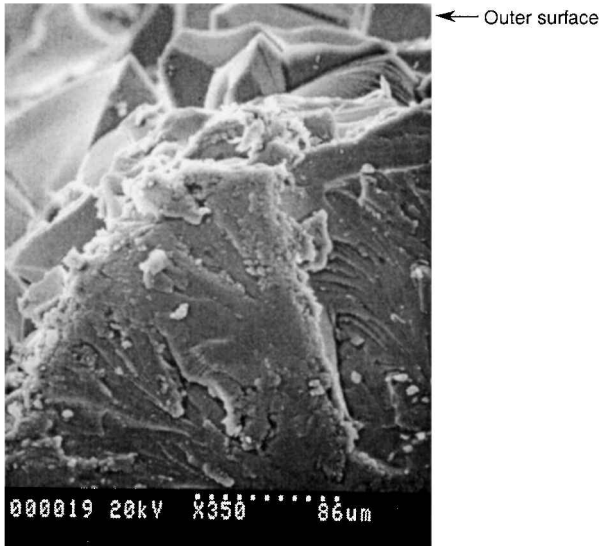
b) Hydrazine-exposed epoxy sample



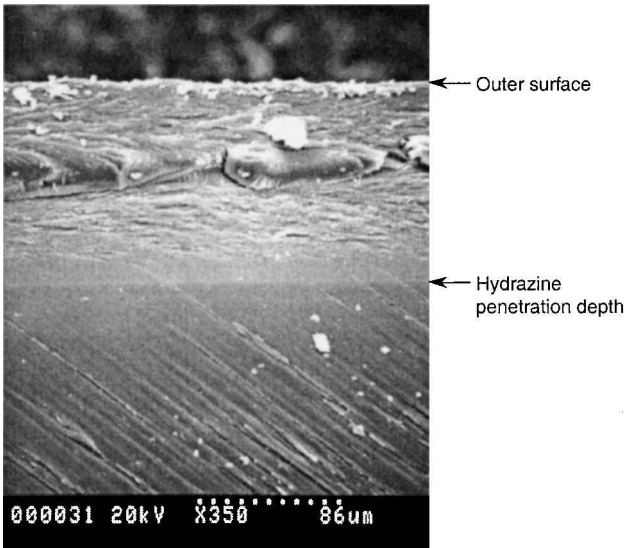
c) NTO-exposed epoxy sample

Fig. 7 Effect of nitrogen tetroxide and hydrazine exposure on 934 epoxy dogbone specimens.

The light-gray area indicates the more affected penetration depth of the resin by the hydrazine. The darker-gray inner portion indicates a less exposed but still affected region. A clear demarcation line can be seen between both regions. The outer more exposed region appears to have a finer fracture structure than the remaining inner portion. Hardness measurements across the cross-sectional area of this specimen indicate that a 38% decrease in outer surface hardness occurred as a result of a 1-h exposure in hydrazine. Unlike the exposed polycyanurate material, as the hydrazine diffuses into the epoxy sample, microstructural characteristics are affected; however, the bulk of the material appears to remain intact. Thus, the dimensions of the material do not vary from the control sample by much, but the penetrated regions have been deleteriously affected. Note that the inner region, though not as dramatically changed, also



a) NTO-exposed epoxy resin



b) Hydrazine exposed epoxy resin

Fig. 8 Scanning electron micrographs of fracture surfaces of nitrogen tetroxide and hydrazine-exposed epoxy dogbone specimens.

appears to be affected by hydrazine penetrations, as observed by its much less textured fracture surface.

As expected, both resins experienced a loss in strength due to exposure to nitrogen tetroxide. As shown after exposure to nitrogen tetroxide, the physical appearance of epoxy and polycyanurate resins are markedly different. Figures 6c and 7c show the effect of nitrogen tetroxide exposure on a polycyanurate and epoxy resin dogbone, respectively. The polycyanurate resin shows minimal observable evidence of degradation, whereas the epoxy sample exhibited a high degree of pitting, flaking, and discoloration. After 5-h exposures, the strengths of the polycyanurate and epoxy resin samples were reduced by 71% (3.2 ksi) and 41% (6.7 ksi), respectively. In all cases, tensile moduli of the resins were not affected, and, therefore, the reduced strain-to-failure observed for each condition was proportional to the reduction in tensile strength. A plot of ultimate load vs exposure duration for both propellants and resin systems is found in Figs. 9 and 10. However, the effect of exposure of these resins to nitrogen tetroxide has differing results with respect to their degradation behavior. As described earlier, the rate of mass loss is greater for the epoxy than the polycyanurate resin. This is again due to the differences between the relative ratios of the rate of diffusion of the oxidizer and the rate of decomposition for the two resins. Figure 11a shows the cross-sectional fracture surface of

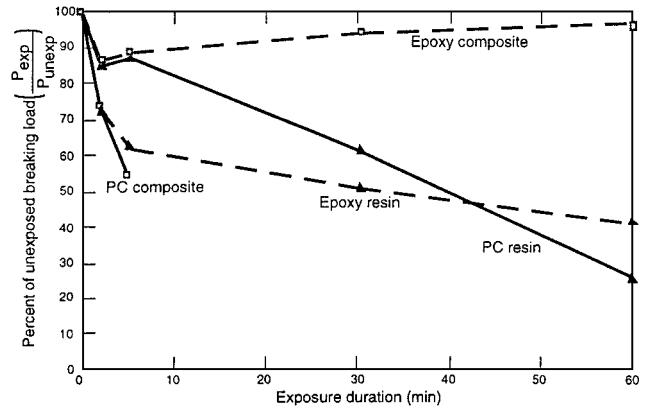


Fig. 9 Effect of hydrazine exposure on polycyanurate and epoxy resin and composite samples.

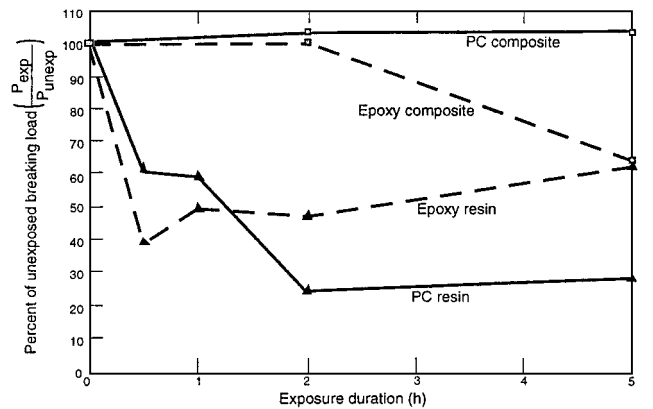
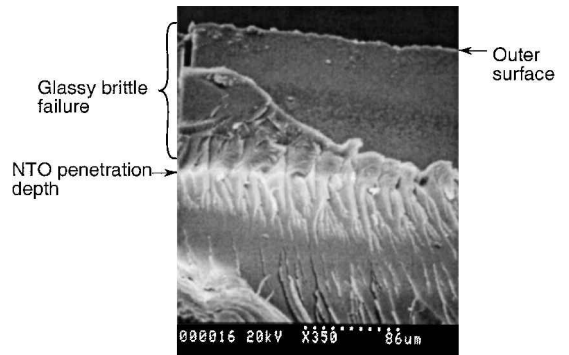
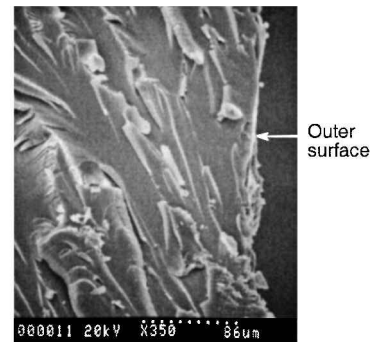


Fig. 10 Effect of nitrogen tetroxide exposure on polycyanurate and epoxy resin and composite samples.



a) NTO-exposed polycyanurate resin



b) Hydrazine-exposed polycyanurate resin

Fig. 11 Scanning electron micrographs of fracture surfaces of nitrogen tetroxide and hydrazine-exposed polycyanurate dogbone specimens.

a polycyanuratedogbone exposed to nitrogen tetroxide. The sample shown has been exposed for 5 h. The dark-gray area represents the penetrated portion of the specimen. Hardness measurements of this cross section exhibited a 24% increase in surface hardness compared to the hardness at the center. This zone of embrittlement at the outer surface caused by the nitrogen tetroxide corresponds well with the brittle planar fracture behavior of this region in comparison to the more granular ductile failure of the polycyanurate's inner cross section. On the other hand, the epoxy resin sample exposed to nitrogen tetroxide shows a rate of decomposition that is equal to the rate of diffusion and shows selective degradation as shown in Fig. 8a.

Effects of Propellants on Composite Systems

Unidirectional tow composites were also exposed to both propellants. Following exposure, these specimens were subjected to tensile testing. Figure 9 shows a plot of fiber strength utilization for the epoxy and polycyanurate composites upon hydrazine exposure. The strength utilization value is normalized relative to the fiber cross-sectional area. The T-300/polycyanurate composites could withstand exposures of hydrazine for up to 5 min, after which an insufficient amount of matrix remained intact to allow further testing. Specimens exposed for 5 min produced a strength of 276 ksi, compared to 506 ksi for control specimens, a 45% strength loss. Figures 12a and 12b show SEM micrographs of both unexposed and hydrazine-exposed unidirectional polycyanurate composites after tensile testing. As shown, the matrix material has been entirely consumed except for a small matrix core. The strength loss can, therefore, be attributed to the reduction of the stress transfer capabilities of the matrix material inasmuch as the fiber has been shown to be resistant to hydrazine exposure.

On the other hand, the T-300/epoxy composites were exposed for as long as 1 h. After this exposure duration, the composites yielded a strength of 472 ksi, which closely compares to the 490 ksi strength of the unexposed specimens. Figures 13a and 13b show

the fracture surfaces of unexposed and hydrazine-exposed epoxy composite. No observable matrix loss was evident, as verified by resin dogbone data. The microstructural changes observed earlier on the hydrazine-exposed epoxy resin dogbones appear to have a minimal effect on the mechanical behavior of the composite. Although microstructural changes in the matrix may have occurred, these changes do not appear to have affected the bonding behavior, and thus the stress transfer capabilities, of the matrix material. The fiber-dominated strength of the composite overshadows any direct load-carrying contributions of the matrix material.

Figure 10 shows the effect of nitrogen tetroxide exposure on the strength utilization of both polycyanurate and epoxy unidirectional composites. Both of the specimen types were exposed for 2 and 5 h. T-300/polycyanurate composites did not experience any loss in strength after either exposure. However, as revealed by the mass analysis of exposed neat resin, the matrix will eventually degrade to the degree where a loss in strength will occur. Figure 12c shows the fracture surface of a polycyanurate unidirectional composite after 5 h of nitrogen tetroxide exposure. Matrix degradation has occurred at the outer surfaces of the composite, but the comparable degree of fiber pullout with the unexposed specimen indicates that the fiber-matrix interface has remained intact. The embrittlement of the matrix material also appears to have minimal effect on the composite properties. This degradation was more readily apparent with the T-300/epoxy composites, which suffered a 36% strength reduction after 5 h of exposure. Again, this occurred from mass loss of the matrix as shown in Fig. 13c. The resultant strength is comparable to that of a dry fiber bundle.

Composite panels were fabricated with a polycyanurate matrix to study propellant effects with respect to composite size. The composite panels were affected in the same manner as the unidirectional tows; however, the rate of degradation was reduced due to the decreased surface area-to-volume ratio. The 5-min hydrazine exposures yielded strength reductions of 9 and 45% for the panels



Fig. 12 Scanning electron micrographs of T-300/polycyanurate composite fracture surface as a function of exposure.

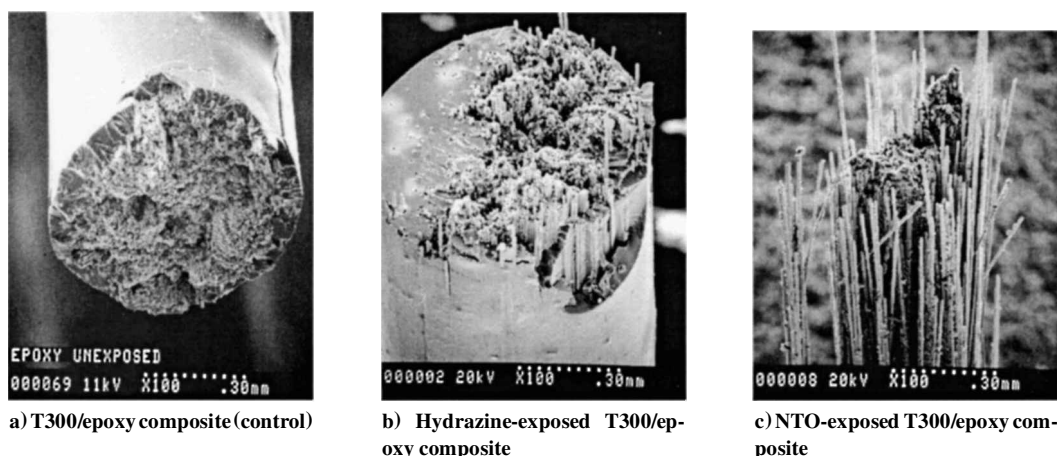


Fig. 13 Scanning electron micrographs of T-300/epoxy composite fracture surface as a function of exposure.

and tows, respectively. The 5-h exposures to nitrogen tetroxide did not affect either composite type.

Conclusions

The T-300 PAN-based carbon fiber was unaffected by exposures to anhydrous hydrazine and nitrogen tetroxide. Tensile testing revealed no change in tensile strength as a result of the exposures. Neither propellant altered the surface of the fiber nor affected the bonding within the polymer matrices.

Both propellants have a pronounced effect on the two unreinforced resin systems. Hydrazine exposures resulted in strength reductions for both materials. The differences were related to the ratio of the diffusion rate of propellant penetration into the matrix to the rate of resin degradation. The polycyanurate resin exhibited equal rates of resin degradation and propellant diffusion. The polycyanurate resin was, therefore, dissolved as rapidly as the fuel diffused into the system, resulting in a small strength loss but a significant reduction in ultimate load. The epoxy reacted differently because the rate of penetration was greater than the rate of degradation. The defects resulting from degradation caused a reduction in strength. Both materials were degraded by nitrogen tetroxide. The oxidizer attacked the surface of the resins, was absorbed, and eventually consumed them. The degradation introduced flaws into the materials, which led to premature failure of the resin specimens.

Composite specimens fabricated using each resin system retained the majority of their load-carrying capability until mass loss of the matrix was experienced. A significant mass loss was observed for polycyanurate matrices exposed to anhydrous hydrazine and epoxy matrices exposed to nitrogen tetroxide. This reduction in the stress transfer capability did not allow the composite to utilize fully the strength of the reinforcing fibers. Conversely, polycyanurate matrices were less susceptible to degradation by the oxidizer, as were epoxy matrices when exposed to the fuel. As a result, the integrity and stress transfer capability of the matrices were maintained, allowing the composites to maintain properties near those of the unexposed specimens. Any flaws introduced into the resins by reaction with the propellants were mitigated by the reinforcing fibers, which served to disrupt crack propagation.

Polycyanurates appear very promising for spacecraft structural applications and offer numerous benefits over current state-of-the-art epoxies. Although extended exposure of these two types of composite systems to hypergol propellants is not recommended, it is clear from this study that epoxy composites offer better resistance to anhydrous hydrazine, and polycyanurate composites afford more protection against nitrogen tetroxide.

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