

Chemical Resistance of Carbon Fiber-Reinforced Poly(ether ether ketone) and Poly(phenylene sulfide) Composites

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Studies have been conducted to investigate the aircraft fluid and chemical solvent resistance of the carbon fiber-reinforced poly(phenylene sulfide) (PPS) and poly(ether ether ketone) (PEEK) composites. The solvents and aircraft fluids utilized in this work include hydraulic fluid, paint stripper, JP-4 jet fuel, methyl ethyl ketone, and methylene chloride. The weight gain of the composites as a function of time is measured. Tensile and flexural strength, thermal behavior, and dynamic mechanical properties of the composites are examined. The alteration of crystallinity change of the composites is investigated by X-ray diffraction. It is found that paint stripper degraded the mechanical properties of the composites significantly. Furthermore, crystallization enhancement of the low crystallinity composites in the presence of solvents and aircraft fluids is also observed.

INTRODUCTION

Continuous carbon fiber-reinforced high performance thermoplastic composites have been widely developed and evaluated in the past few years (1, 2). High performance carbon fiber-reinforced thermoplastic composites offer a number of potential advantages, which include toughness enhancement, damage tolerance, repairability, postformability, and ease of processing. From the application point of view, the ability to resist hostile environments is a major consideration for material selection. The susceptibility of the carbon fiber/epoxy composites to the attack of chemicals and aircraft fluids commonly encountered in aircraft usage has been studied (1-3).

Chemical and aircraft fluid resistance of polymer composites depend significantly on the inertness of the resin matrix; furthermore, the fiber/matrix interface is also susceptible to chemical attack. Resin matrix may absorb chemical solvents and aircraft fluids; this may cause swelling, plasticization, and degradation of the composites and may induce crystallization in composite materials. The chemical and aircraft fluid resistance of the poly(ether ether ketone) (PEEK) and the poly(phenylene sulfide) (PPS) matrix

and their composites has been studied and evaluated by several researchers (4-10). Stober, *et al.* (4), reported that methylene chloride can be absorbed to a high extent in PEEK material, thus causing two significant effects: plasticization and additional crystallization for incompletely crystallized films. Johnson and Ryan (5) pointed out that the amorphous PPS is susceptible to solvent-induced crystallization by methylene chloride. Hay and Kemmish (6) reported that the diffusion rate of the low-molecular weight substances in PEEK decreases with increasing molecular weight. Seferis, *et al.* (7-10), reported that the initial crystallinity shows a pronounced effect on both the kinetic and equilibrium sorption of methylene chloride in PEEK.

The objective of this research is to investigate the effect of the absorption of chemicals on the properties of carbon fiber reinforced PEEK and PPS composites. Environmental effects on the water absorption and mechanical properties of carbon fiber reinforced PEEK and PPS composites were reported previously (13, 14). In this study, sorption behavior, thermal properties, solvent-induced crystallization, static and dynamic mechanical properties, and chemical resistance of PEEK/C.F.(woven), PEEK/unidirectional C.F.(APC-2), and PPS/C.F. composites are investigated.

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EXPERIMENTAL

Materials and Test Specimens

A 0.075 mm (3 mils) thick PEEK film and a 0.125 mm (5 mils) thick carbon fiber-reinforced PEEK prepreg tape (APC-2) used in this study were supplied by Imperial Chemical Industries, U.K. The 0.125 mm (5 mils) thick PPS film used is a commercial product under the trade name Ryton® Poly(phenylene sulfide) from the Phillips Petroleum Co., Bartlesville, Okla. The carbon fiber woven cloth (3K, #3101) with a weight of 200 g/m² is a product of the Toho Co., Japan.

The test specimens were compression molded with a picture frame mold by interlaying film and carbon fiber cloth. Samples were preheated at 390°C for 20 min, and then compressed at 7.90×10^4 N/m² (200 psi) for 20 min, and finally transferred to a cold press. APC-2 was processed by compression molding with the processing conditions recommended by the manufacturer.

Chemicals and Aircraft Fluids

The chemical solvents and aircraft fluids used for specimen immersion included methylene chloride, methyl ethyl ketone, MIL-T-5624 JP-4 jet fuel, MIL-H-5606 hydraulic fluid, and MIL-R-83936 paint stripper (T-5351, a product manufactured by Techcon System Inc.). All specimens were immersed in individual, closed containers at room temperature. Weight gain of the specimens was measured with a Mettler AE 100 semimicrobalance.

Thermal Properties

A Perkin-Elmer DSC-4 Differential Scanning Calorimeter (DSC) was utilized to investigate the thermal properties of the PEEK and the PPS film as received and after exposure to chemicals. Samples of 3 to 5 mg were heated at a rate of 20°C/min from room temperature to above the melting temperature.

Dynamic Mechanical Properties

The dynamic mechanical properties of the specimens were measured using a Rheometrics Mechanical Spectrometer (Model RMS-605). Samples were subjected to rectangular forced torsion at 0.1% strain. The equipment was operated in a temperature sweep mode at a rate of 6.28 rad/sec.

X-Ray Diffraction

Wide-angle X-ray (WAXR) diffraction measurements were made with a Shimadzu X-ray diffractometer (Model XD-5 with a CuK_α radiation). The degree of crystallinity of APC-2 was calculated using the ratio of the height of h110/hc from the diffraction spectrum, as described by Blundell, *et al.* (11).

Mechanical Properties

The flexural and tensile strength tests were conducted using an Instron testing machine Model 1123.

Specimen dimensions and test procedures followed the specification of ASTM D790 and ASTM D3039, respectively.

RESULTS AND DISCUSSION

Sorption Behavior

It is observed that the chemical solvents and aircraft fluids are absorbed by both the PEEK/C.F. and the PPS/C.F. composites. Sorption of various fluids in those composites is illustrated in Figs. 1 through 3. The weight gain due to the penetration of fluid in composites is plotted against the reduced time ((h)^{0.5}/mm). It can be seen that methylene chloride is absorbed to the greatest extent and shows the greatest weight gain for each of the three composites studied. Hydraulic fluid has the least weight gain in the PEEK/C.F. composites.

As observed in Figs. 1 through 3, the sorption curves possess a steeper slope at the beginning stage, and then tend to plateau after 108 days immersion. Sorption of fluids in composites is similar to the Fickian diffusion behavior; however, the diffusion of methylene chloride in these composites demonstrate a case II behavior, as discussed in the previous paper (14). Table 1 illustrates the equilibrium weight gain of a variety of fluids in composites. JP-4 jet fuel and hydraulic fluid show a relative small weight gain as compared to methylene chloride and MEK. In addition, the PEEK/C.F. composites show more weight gain than the PPS/C.F. composites in methylene chloride, but show less weight gain in MEK.

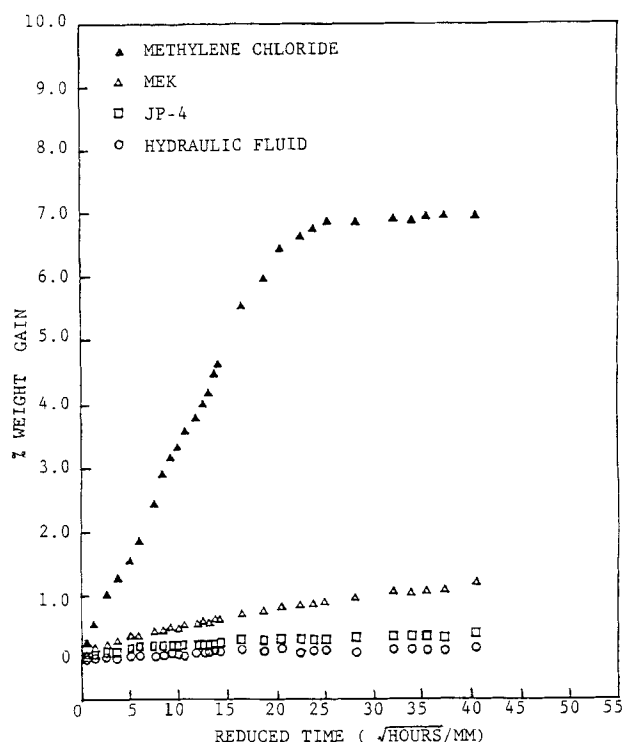


Fig. 1. Sorption of various fluids in PEEK/C.F. composites as a function of reduced time.

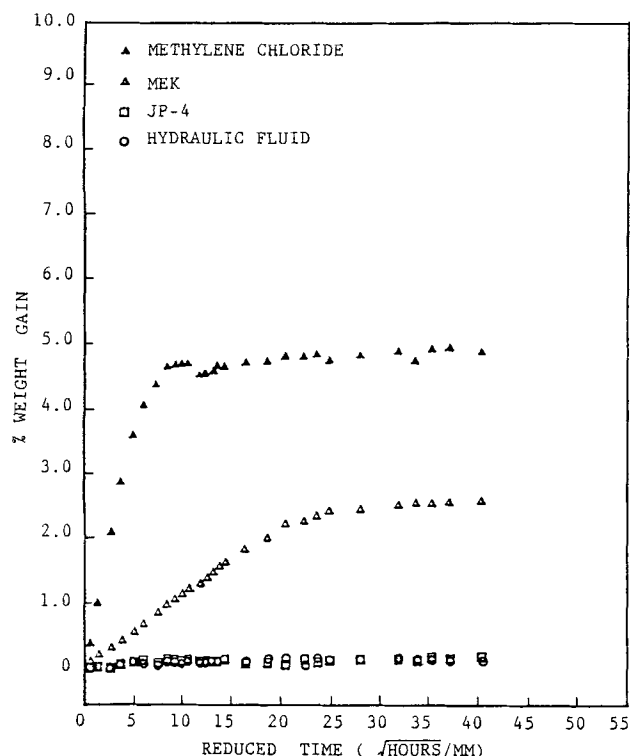


Fig. 2. Sorption of various fluids in PPS/C.F. composites as a function of reduced time.

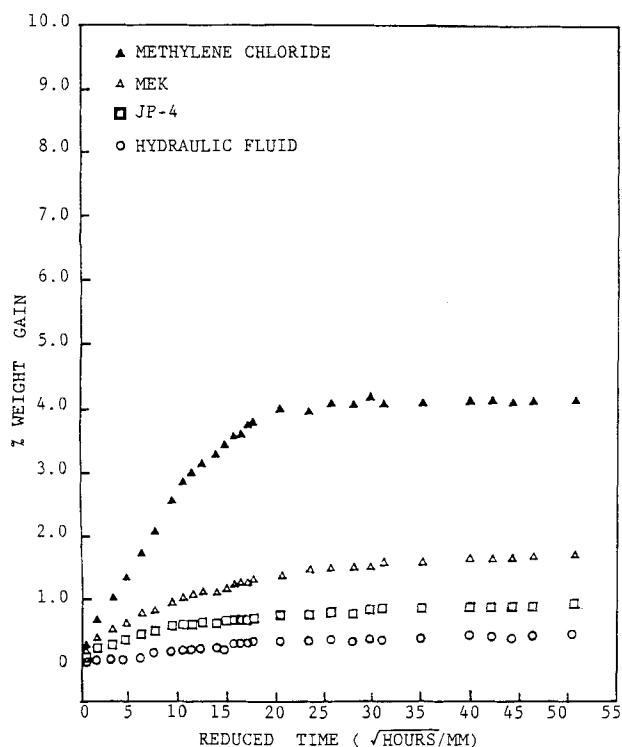


Fig. 3. Sorption of various fluids in APC-2 composites as a function of reduced time.

Thermal Properties

Figures 4 and 5 illustrate the DSC thermograms of the PPS and the PEEK film after exposure to various chemicals and fluids. As can be seen in Fig. 4, there is a shoulder (small endothermic peak) associated with an endothermic melting peak in each curve. Furthermore, the temperature of the melting peak increases slightly when the films are exposed in the chemicals and fluids. For the PEEK film, as shown in Fig. 5, the sample exposed to paint stripper shows a

Table 1. The Apparent Equilibrium Weight Gain for Carbon Fiber-Reinforced Composites.

Exposure	% Weight Gain		
	PEEK/C.F. (woven)	PPS/C.F.	APC-2 PEEK/C.F. (U.D.)
JP-4 jet fuel	0.37	0.12	0.93
Hydraulic fluid	0.18	0.15	0.46
MEK	1.17	2.57	1.67
Methylene chloride	6.95	4.90	4.13

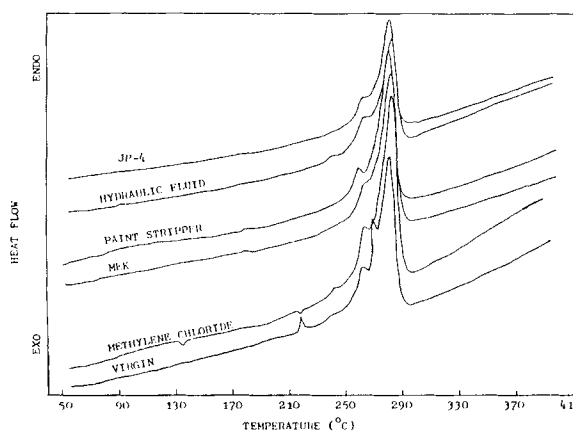


Fig. 4. DSC thermograms of PPS film after exposure to various solvents for 69 days.

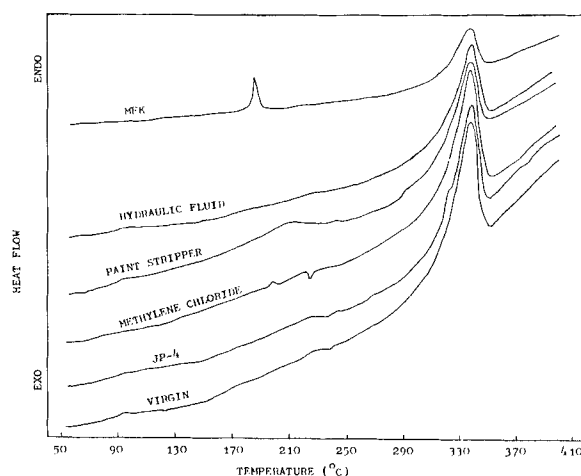


Fig. 5. DSC thermograms of PEEK film after exposure to various solvents for 69 days.

broad endothermic peak just above the glass transition temperature, while the sample exposed to MEK shows a sharp endothermic peak around 180°C due to the chemical aging.

Dynamic Mechanical Properties

In Fig. 6, the loss tangent ($\tan \delta$) of the aged PPS/C.F. composites is plotted against temperature. It can be seen that the glass transition temperature ($\tan \delta$ peak temperature) shifts toward lower temperature for specimens exposed to paint stripper, MEK, and methylene chloride; this is due to the plasticization of the composites by fluids (12). Furthermore, the specimens exposed to the aforementioned fluids show only one damping peak. It is believed that the additional crystallization has been induced other than plasticization in the PPS/C.F. composites because of exposure to paint stripper, MEK, and methylene chloride. Dynamic mechanical properties of the fluid-aged

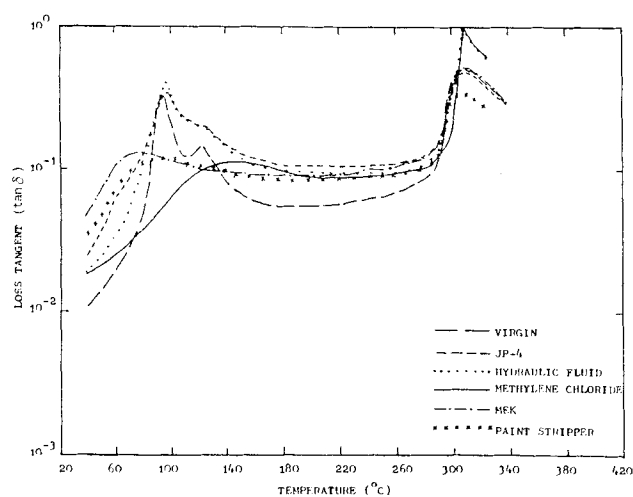


Fig. 6. Loss tangent of PPS/C.F. composites after aging in various solvents for 49 days.

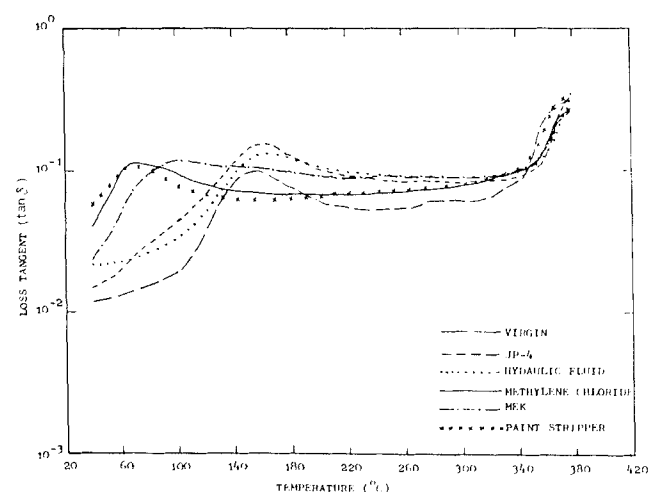


Fig. 7. Loss tangent of PEEK/C.F. composites after aging in various solvents for 49 days.

PEEK/C.F. composites are shown in Fig. 7. The glass transition temperature of the composites shifts to a lower temperature; this is probably due to the plasticization of the composites by paint stripper, MEK, and methylene chloride. However, owing to the low absorption of the fluids by composites, the glass transition temperature of the specimens exposed to JP-4 and hydraulic fluid is not affected.

X-Ray Diffraction

Figure 8 depicts the X-ray diffractograms of the PPS/C.F. composites subjected to a variety of chemicals and fluids. There is a relatively sharp peak at $2\theta = 20.5^\circ$. This is due to the crystalline component superimposed upon a broad peak centered around $2\theta = 19^\circ$ corresponding to the amorphous component in the specimens exposed to paint stripper, MEK, and methylene chloride. It is believed that the additional crystallization has been induced during exposure to fluids. The additional broad peak at $2\theta = 25.1^\circ$ is due to the amorphous component of the carbon fiber. Table 2 summarizes the crystallinity of the chemical aged APC-2 composites. It shows that methylene

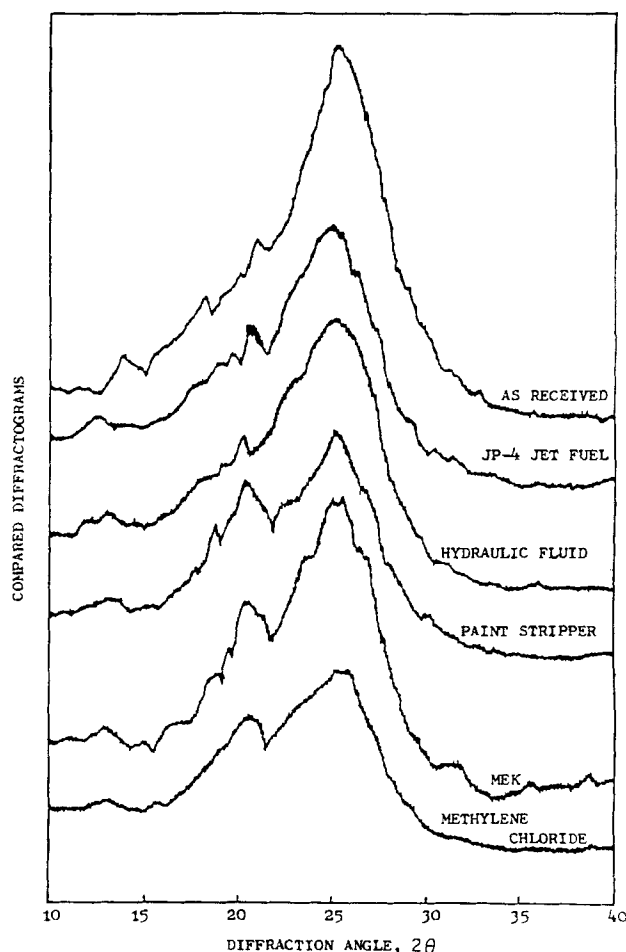


Fig. 8. X-ray diffractograms of PPS/C.F. composites exposed to various solvents for 70 days.

chloride induces significant additional crystallization in APC-2 composites. So does the MEK.

Mechanical Properties.

Figure 9 illustrates the effects of chemical aging on the mechanical properties of the PEEK/C.F. composites. It is found that JP-4 jet fuel has an insignificant effect on the mechanical properties of the PEEK/C.F. composites. It is also found that the PEEK/C.F. composites retain 90% tensile strength after exposure to the other four chemicals and fluids, except JP-4 fuel, for 108 days. Owing to the swelling of the composites, a slight increase in flexural strength of the composites was observed after exposure to the JP-4 fuel. However, a drastic decrease in flexural strength was found for the specimen exposure to paint stripper for 108 days. The retention of the mechanical properties of the PPS/C.F. composites after immersion in fluids for 108 days is shown in Fig. 10. It can be seen that the effects of chemicals and fluids on the mechanical properties of the PPS/C.F. composites are much more significant than on those of the PEEK/C.F. composites. Hydraulic fluid shows almost no effect on the

Table 2. The Effect of Various Fluids on the Crystallinity of APC-2, From X-ray Diffraction (112 Days Exposure).

Exposure	Crystallinity (wt %)
As received	24.5
JP-4 jet fuel	25.6
Hydraulic fluid	25.4
MEK	34.8
Methylene chloride	37.0
Paint stripper	28.6

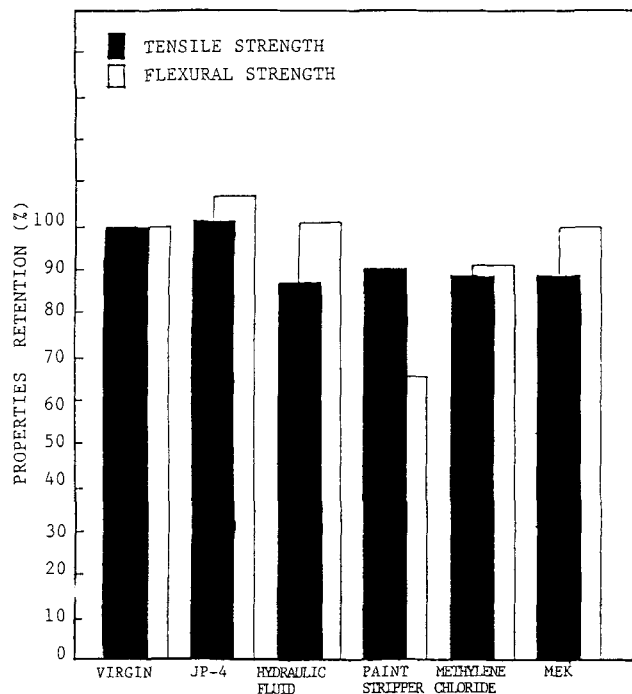


Fig. 9. Effect of fluids on the mechanical properties of the PEEK/C.F. composites after 108 days exposure.

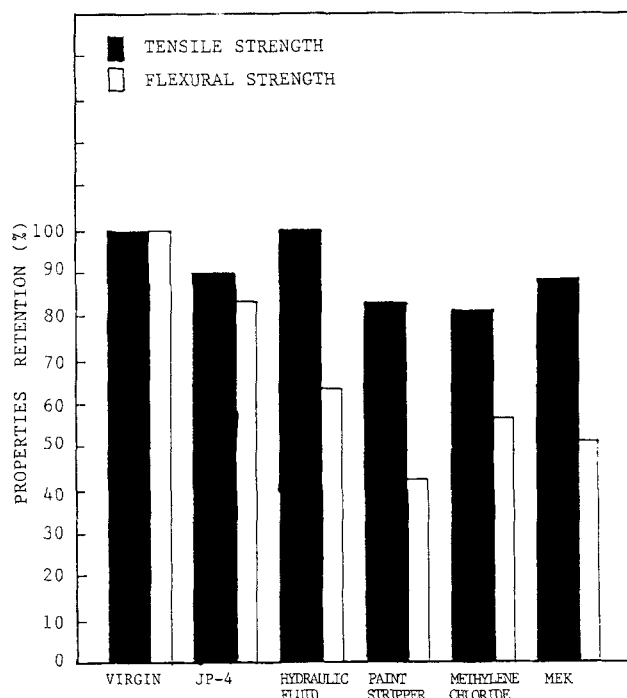


Fig. 10. Effect of fluids on the mechanical properties of the PPS/C.F. composites after 108 days exposure.

tensile strength of the PPS/C.F. composites. Furthermore, the other five cases offer a tensile strength retention above 80%. However, chemicals and fluids have greater effect on the flexural strength of the PPS/C.F. composites, while paint stripper appears to be the most harmful to the composites.

CONCLUSIONS

From this study, one may conclude that the continuous carbon fiber-reinforced PEEK and PPS composites demonstrate good resistance to chemical solvents and aircraft fluids such as methylene chloride, MEK, JP-4 jet fuel, and hydraulic fluid but not to paint stripper.

Both the PEEK and the PPS composites absorb methylene chloride to the greatest extent among the five chemicals and fluids after 108 days exposure. Paint stripper, methylene chloride, and MEK are found to be able to induce additional crystallization in carbon fiber-reinforced PEEK and PPS composites; consequently, they lower the mechanical properties of the composites.

The absorption of fluids in the PEEK/C.F. and the PPS/C.F. composites has significantly lowered the glass transition temperature of the materials, with the exception of JP-4 and hydraulic fluid. In addition, paint stripper shows a significant effect on the flexural strength of both composites.

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