Flexural Fatigue Behavior of Injection-Molded Composites Based on Poly(phenylene ether ketone)

JIANG ZHOU, GANG LI, BINYAO LI, TIANBAI HE

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 18 October 1996; accepted 16 January 1997

ABSTRACT: Flexural fatigue tests were conducted on injection-molded short fiber composites, carbon fiber/poly(phenylene ether ketone) (PEK-C) and glass fiber/PEK-C (with addition of polyphenylene sulfide for improving adhesion between matrix and fibers), using four-point bending at stress ratio of 0.1. The fatigue behavior of these materials was presented. By comparing the *S–N* curves and analyzing the fracture surfaces of the two materials, the similarity and difference of the failure mechanisms in the two materials were discussed. It is shown that the flexural fatigue failure of the studied materials is governed by their respective tensile properties. The matrix yielding is main failure mechanism at high stress, while at lower stress the fatigue properties appear fiber and interface dominated. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1857–1864, 1997

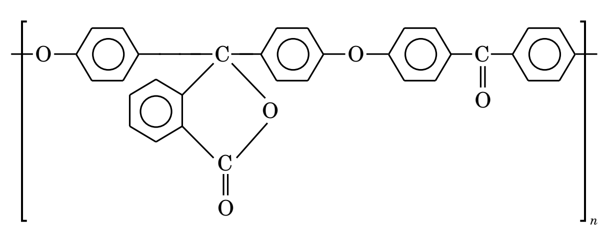
Key words: injection-molded composites; flexural fatigue; poly(phenylene ether ketone); *S–N* curves; fatigue damage

INTRODUCTION

A large amount of fatigue data has been obtained in the past decades on many types of materials. However, there is not much data available comparing injection-molded composites with continuous fiber-reinforced composites and chopped-strand composites, even though a recent book lists some of these data.[1] Because injection-molded composites not only have some special advantages (such as they can be molded into complex-shaped parts and can be processed at high production rates) but also have attractive mechanical properties, these types of composites are being used more often for applications where considerable and repeated loading is involved. Therefore, it is important to acquire a better understanding of the fatigue performance and failure mechanisms of these materials under conditions of cyclic loading. This is an essential prerequisite for them to be used reliably, safely, and efficiently in service applications.

For injection-molded composites, some important systems have undergone significant study under fatigue conditions.[2,3] The results indicate that injection-molded composites may show different responses to fatigue loading, depending on matrix ductility and fiber/matrix bond quality. Even for a given set of systems, the loading parameters also affect the fatigue behavior of injection-molded composites.[4] These studies are undoubtedly useful and necessary for material selection and component design.

Poly(phenylene ether ketone) (PEK-C) is a relatively new material.[5]



Correspondence to: J. Zhou.

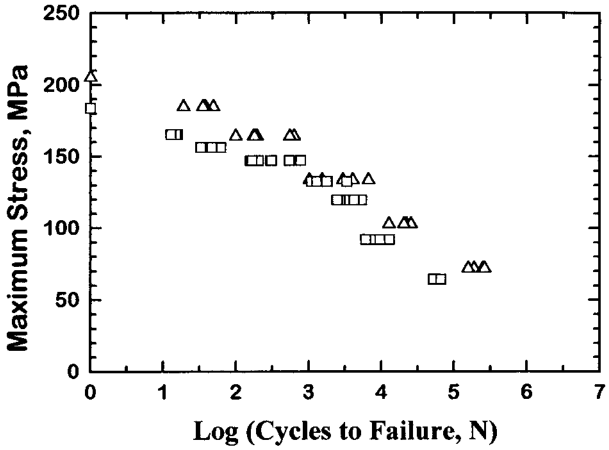


Figure 1 *S–N* data for injection-molded PEK-C-based composites: (△) CF/PEK-C, (□) GF/PEK-C.

Its high performance and good processability make it and its blends potential matrices for injection-molded composites. The primary purpose of this work is to extend the data available on injection-molded composites based on PEK-C to include fatigue testing, and to obtain a deeper understanding of the effects of matrix and interface properties on the fatigue performance by comparing the fatigue behavior of composites with different reinforcement fibers and interface conditions.

EXPERIMENTAL

Materials and Specimen

The materials used in this study were injection-molded carbon fiber (CF)-reinforced PEK-C (CF/PEK-C) and glass fiber (GF)-reinforced PEK-C (GF/PEK-C). In order to improve the adhesion between the PEK-C and glass fiber, poly(phenylene sulfide) (PPS) was added to this latter system,[6] (i.e., in the GF/PEK-C, the matrix is a mixture of 85% PEK-C and 15% PPS). The PEK-C was offered by Xuzhou Engineering Plastic Co., Xuzhou, China. Its reduced viscosity in chloroform at a temperature of 25°C is 0.5 dL/g. The PPS was supplied by Zigong Chemical Reagent Factory, Zigong, China; its grade was SZPPS-3P1. Carbon fiber and glass fiber were supplied by Jilin Carbon Fiber Co. (Jilin, China) and Nanjing Institute of Glass Fiber (Nanjing, China), respectively.

The powder of matrix resin (for GF/PEK-C system, the PEK-C and PPS were mechanically mixed at room temperature first) and fiber were fed to a SHJ-30 twin-screw extruder, extruded at 330°C, then pelletized. The weight percent of the fiber is estimated to be 20 wt % in CF/PEK-C and 25 wt % in GF/PEK-C. The test specimens, which were injection-molded using a JSW-17SA injection-molding machine, were end-gated, rectangular bars, 80 mm long, 16.35 mm wide, and 4.25 mm thick. No attempt was made to smooth the edges and surfaces of the specimens.

Test Method

The tests were carried out under ambient conditions in a laboratory atmosphere using a four-point bending fixture. The ratio of support span to load span was 3 and the ratio of support span to specimen thickness was 16. An Instron 8501 servohydraulic testing system was used to perform both static and fatigue tests.

Static strength was measured using a crosshead speed of 100 mm/min. Ten specimens were tested to determine the average ultimate flexural strength (UFS). The UFS was calculated by the formula

$$\mathrm{UFS} = 3P(L - s)/2Wh^2 \tag{1}$$

where P is the breaking load (N), L the distance between supports (mm); s the distance between loading (mm); W the specimen width (mm); and h the specimen thickness (mm).

Fatigue tests were carried out under load control with a sinusoidal waveform. A range of frequencies (0.89–2.29 Hz), which is low enough to avoid significant hysteresis heating, was used in

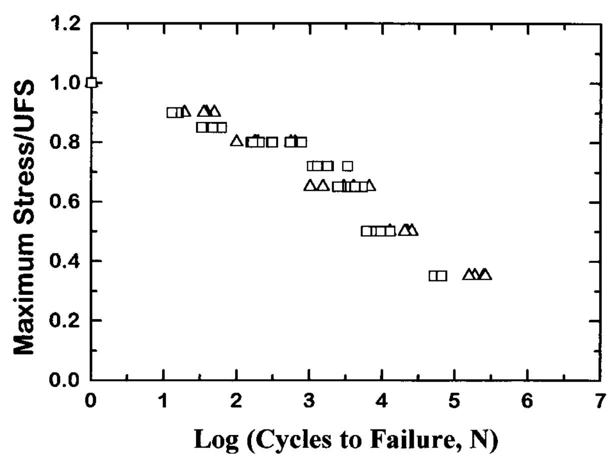


Figure 2 Normalized *S–N* curves for injection-molded PEK-C-based composites: (△) CF/PEK-C, (□) GF/PEK-C.

generating S–N curves. The frequency was varied as function of the maximum stress to maintain a constant load rate. A series of cyclic stresses was applied to the specimens by changing the maximum stress and fixing the stress ratio, R, at 0.1. The maximum stress levels, calculated on the basis of measured specimen dimensions relative to the determined UFS, were selected between 0.35 and 0.9 UFS. The actual fatigue stress applied during a cycle may vary a few percent. Tests were continued until the specimens broke.

The fracture surfaces after fatigue test at different stress levels were inspected using a Hitachi S-570 scanning electron microscope (SEM) to identify the failure mechanisms. All samples were sputter-coated with a thin layer of gold to improve sample conductivity.

RESULTS AND DISCUSSION

S–*N* Curves

The S–N semilogarithmic plots, the maximum of the cyclic stress S against the number N of cycles to failure, are shown in Figure 1. The UFS was plotted at one cycle. Despite the inevitable scatter, the shape of the S–N curves appears to be similar for two materials, which is nearly linear, but the shape becomes more steep at long lifetime. It is believed that CF systems are generally fatigue-resistant as long as either the matrix or interface is fatigue resistant. Glass systems usually degrade more rapidly in fatigue. From Figure 1, it can be seen that the GF/PEK-C system is more sensitive to fatigue than the CF/PEK-C system at lower stress levels, while at higher stress levels they have no significant difference.

In order to eliminate the differences in fiber strength and composite volume fraction, Figure 2 gives a representation of the data in Figure 1, with the stress coordinate normalized by the UFS. It is shown that the curves are close to identical for two systems at high stress levels, but they deviate from each other with decreasing of the stress level. This result suggests that the fatigue sensitivity of this group of injection-molded PEK-C-based composites is determined by the matrix at high stress levels and by reinforcement fibers at low stress levels.

In general, it is thought that a shift in the slope of the S–N curve is a clear indication of a transition in failure mechanism.[1] However, since the fatigue failure mechanisms are too complex, most of the fatigue models for composites reported in the literature are empirical, considering the static strength, material constants, cyclic stress, and some measure of the fatigue life as its fundamental parameters. This is exemplified by eq. (2), which expresses the empirical observation that the S–N curves of composite materials can often be represented by a straight line:

$$S_{\max}/S_{\mathrm{UFS}} = a - b \log N \qquad (2)$$

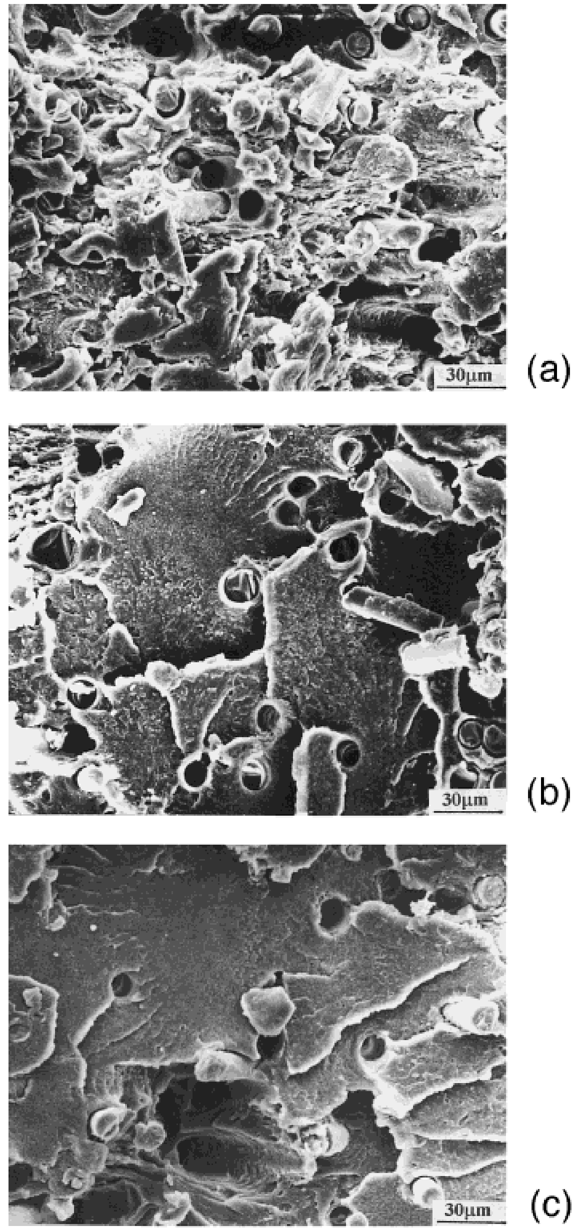


Figure 3 SEM micrographs of the tensile failure areas of the fatigue fracture surfaces for the GF/PEK-C system: (a) $S_{\max}$ = 0.9 UFS, (b) $S_{\max}$ = 0.72 UFS, and (c) $S_{\max}$ = 0.35 UFS.

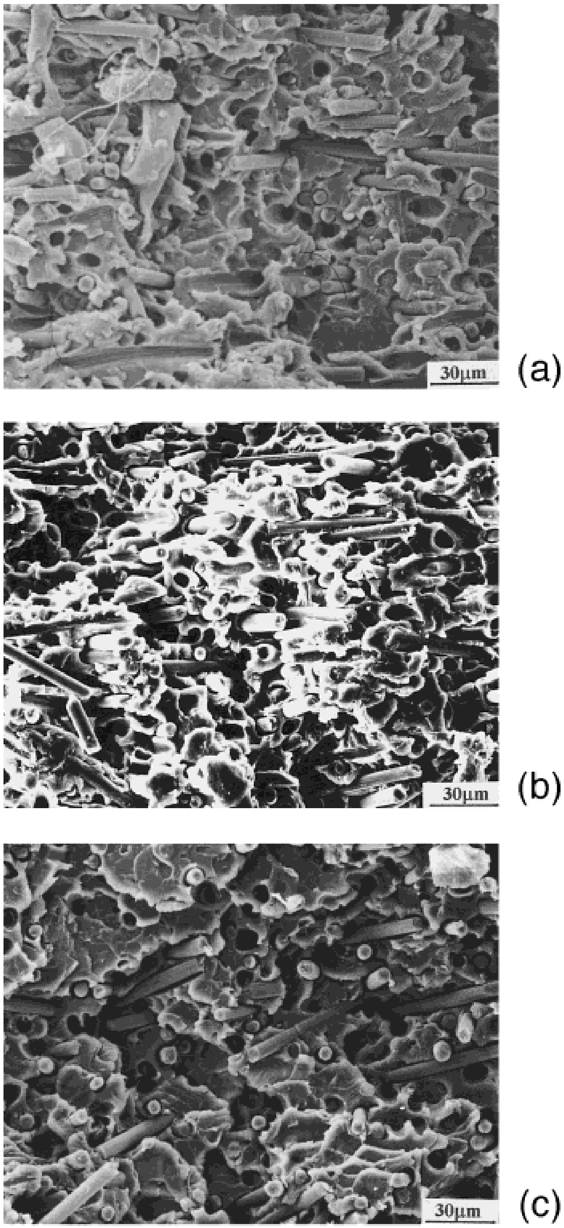


Figure 4 SEM micrographs of the tensile failure areas of the fatigue fracture surfaces for the CF/PEK-C system: (a) $S_{max} = 0.9$ UFS, (b) $S_{max} = 0.65$ UFS, and (c) $S_{max} = 0.35$ UFS.

where S_{UFS} is the ultimate flexural strength, and a and b are material constants. The slopes, b, of the normalized curves represent the fatigue sensitivity of materials. Since both S–N curves for the two systems obviously shift their trends at long lifetime, it is impossible to obtain the fatigue parameters by using eq. (2) through linear regression analysis for all the data. Therefore, it is difficult to assess the fatigue properties of the two systems by comparing the fatigue parameters. However, from S–N curves presented in Figures 1 and 2, it can be seen that the fatigue performance of the CF/PEK-C system still differs slightly from that of GF/PEK-C, even if the shape of S–N curves is generally similar for the two materials. As the static strength of the GF/PEK-C system is smaller than that of the CF/PEK-C system, the S–N curve of the former falls below that of the latter. The slope of S–N curve for GF/

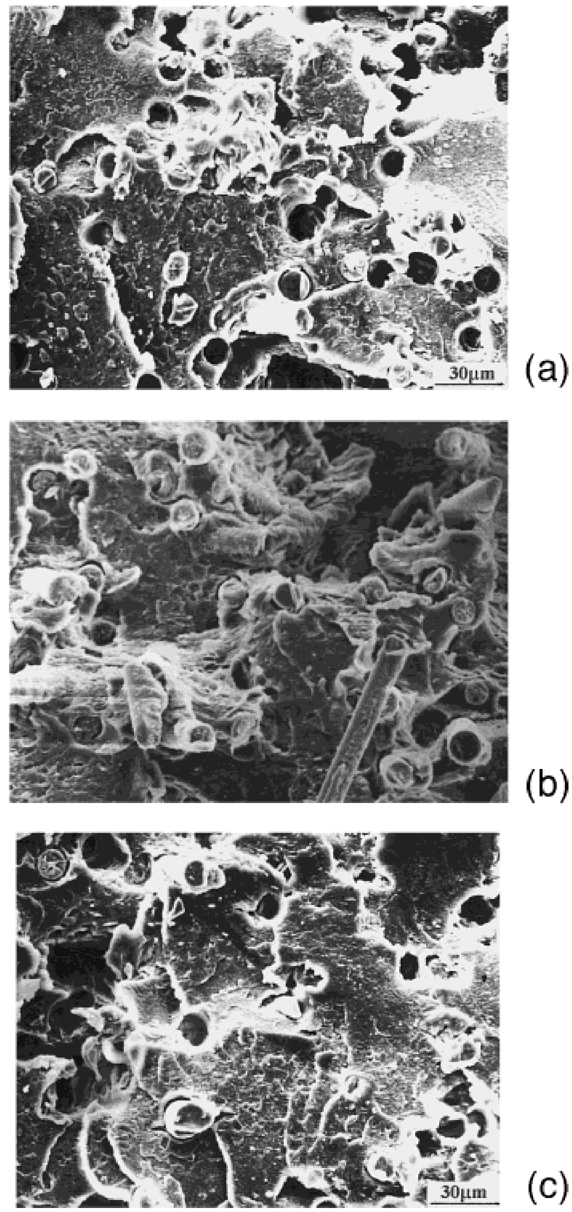


Figure 5 SEM micrographs of the compressive failure areas of the fatigue fracture surfaces for the GF/PEK-C system: (a) $S_{max} = 0.9$ UFS, (b) $S_{max} = 0.72$ UFS, and (c) $S_{max} = 0.35$ UFS.

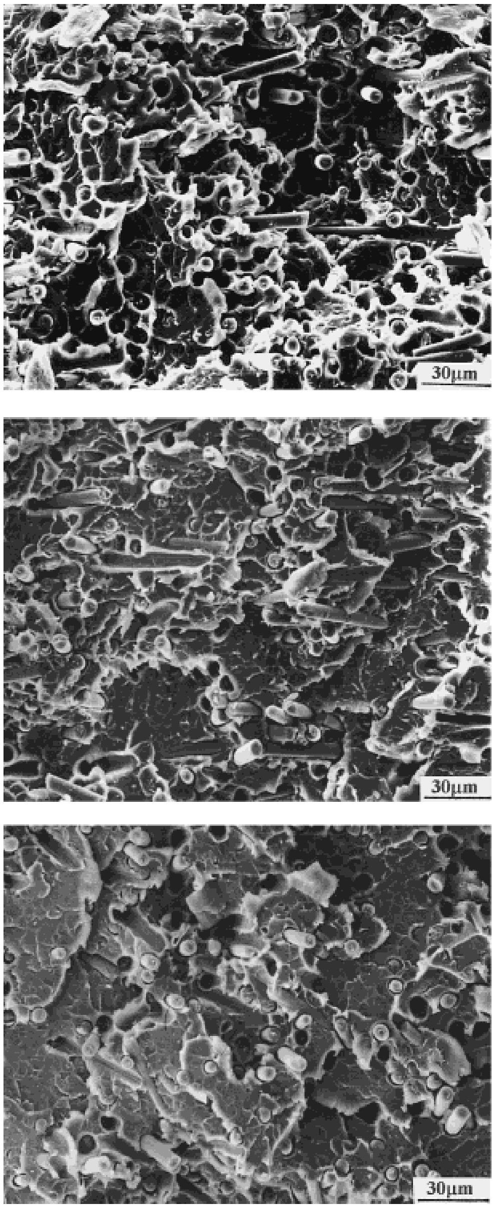


Figure 6 SEM micrographs of the compressive failure areas of the fatigue fracture surfaces for the CF/PEK-C system: (a) S_{max} = 0.9 UFS, (b) S_{max} = 0.65 UFS, and (c) S_{max} = 0.35 UFS.

PEK-C is steeper, especially in the portion of lower stress levels. The stress level at which the S–N curve shifts its trend for GF/PEK-C is lower than that of CF/PEK-C.

Fatigue Failure Behavior

In flexural testing, one side of the specimen is always subjected to tension and the other is always subjected to compression; therefore, flexural fatigue produces simultaneous tension–tension and compression–compression cycling. Although no damage-monitoring techniques were employed during the fatigue tests, it can be observed that there were many microcracks oriented at 90 degrees to the length direction of the GF/PEK-C specimen on the tensile surface, while no incipient damage was found on the compressive surface. It was also noted that the crack density on the tensile surface of specimens tested at high stress lev-

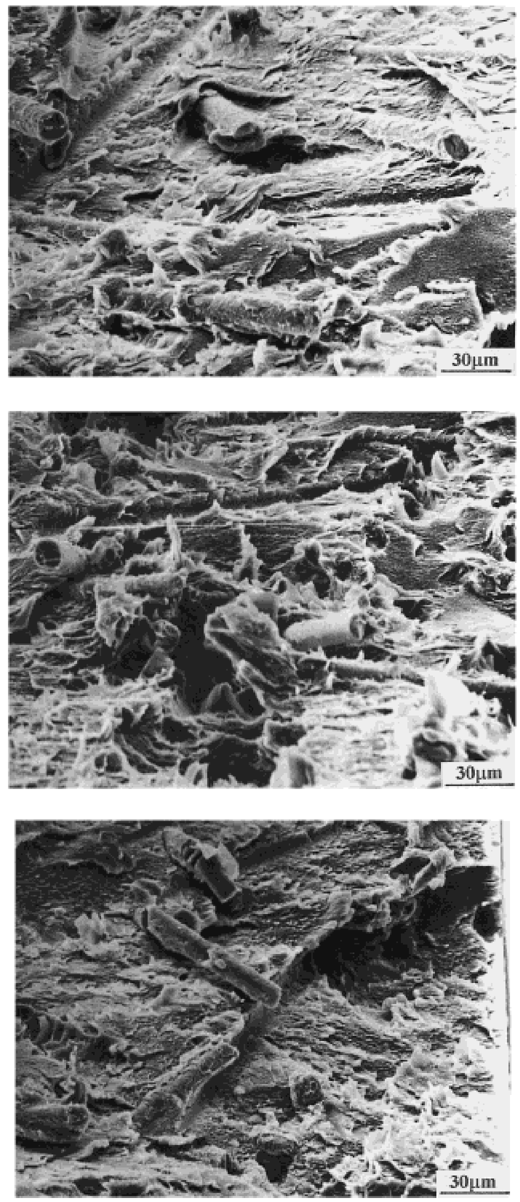


Figure 7 SEM micrographs of the changeover areas of the fatigue fracture surfaces for the GF/PEK-C system: (a) S_{max} = 0.9 UFS, (b) S_{max} = 0.72 UFS, and (c) S_{max} = 0.35 UFS.

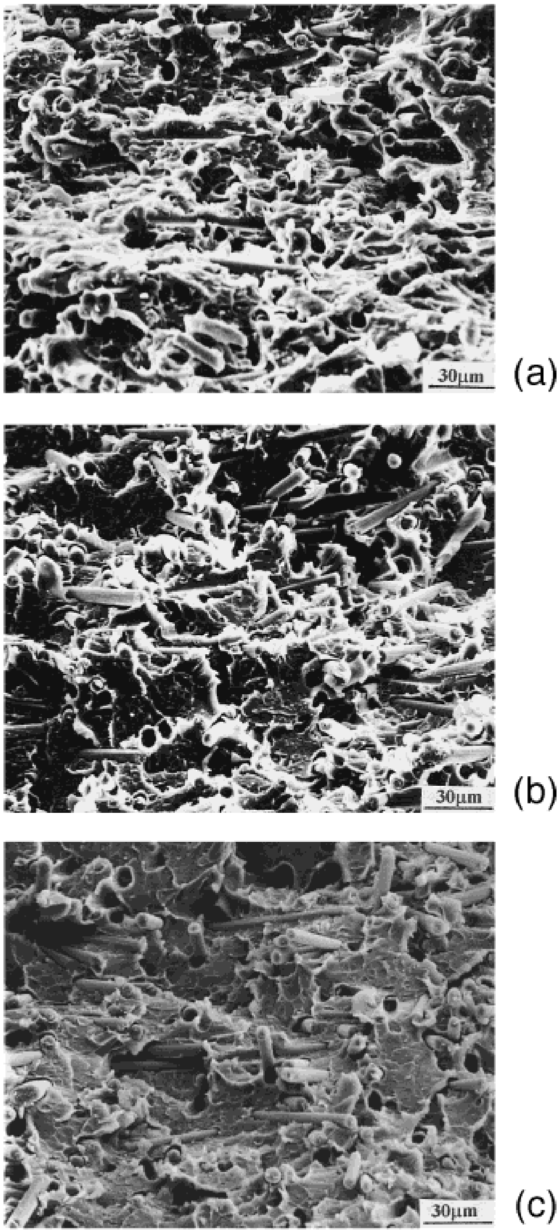


Figure 8 SEM micrographs of the changeover areas of the fatigue fracture surfaces for the CF/PEK-C system: (a) S_{max} = 0.9 UFS, (b) S_{max} = 0.65 UFS, and (c) S_{max} = 0.35 UFS.

els was larger than that on the surface of specimens tested at low stress levels. These microcracks on the tensile surface appear to be related to the maximum cyclic stress, thus, may be crazes as a result of matrix yielding. For CF/PEK-C specimens, few microcracks can be found by the naked eye on both surfaces, even at high stress levels.

In order to determine the similarities and differences of the failure mechanisms for the two systems, it is necessary to examine the fracture surfaces of the specimens tested at various stress levels. The fracture surfaces generated in flexural fatigue tests can be divided into tensile-dominated failure and compressive failure. The changeover is visible as an almost perfectly straight line parallel to the neutral axis. The tensile failure area is about 80–90% of the area of the rectangular cross section for both systems at all the stress levels. It has been established that the relative areas of tensile and compressive failure on flexural fracture surfaces can give an indication of the initiation mechanism.[7] Our observation suggests that the flexural fatigue failure in these injection-molded PEK-C-based composites is governed by the tensile properties of the composite.

Figures 3 and 4 show the SEM micrographs of the tensile failure areas of fatigue fracture surfaces for the two systems at different stress levels. Comparing these fractographs, the following features can be found. First, for both systems, the degree of deformation of matrices and roughness of the fracture surfaces were unlike at different stress levels. For the specimens tested at high stress level, the matrix on the fracture surface is drawn and yielded, and shows more signs of ductility [Figs. 3(a) and 4(a)]. For the specimens subjected to lower fatigue loading, however, there are many small plateau zones around the fiber tips and holes on the fracture surfaces, and the whole fracture surface appears to be the incorporation of these plateau zones [Figs. 3(c) and 4(c)]. It has been concluded that these plateau zones are created by the growth of fatigue cracks which are nucleated at fiber tips and debonding interface.[8] These observations suggest that the fatigue failure of these injection-molded composites appears to have been induced by matrix yielding at high stress levels and crack growth at low stress levels. Second, the GF/PEK-C system showed a few pull-out fibers and holes on the fracture surfaces, and the fiber surfaces show considerable matrix bonded to them, which is usually taken as an indication of a well-bonded material. For the CF/PEK-C system, however, there were more bare fibers well-separated from the matrix on the fracture surfaces, which indicates a poorly bonded system. It is known that the glass/PPS system is well bonded.[1] Therefore, the addition of PPS could improve the adhesion between matrix and fibers in the GF/PEK-C system.

Figures 5 and 6 give the SEM micrographs of the compressive failure areas of fatigue fracture surfaces for the two systems at different stress levels. In contrast with the tensile failure areas, the roughness of fracture surfaces appear independent on the applied stress levels. It is generally thought that the postfailure abrasion will make the compressive failure surfaces more complex. However, there are no obvious abrasion traces noted on the compressive failure surfaces, so a presumptive cause is that the compressive cracks initiate and propagate unstably at the last cycle, just like the failure in the static bending test with high crosshead rate. Though the actual loading rates may have small differences at various stress levels, it is impossible to observe from the smoothness of the fracture surfaces the differences among the degrees of brittle or ductile fracture that occurred at different stress levels.

Figures 7 and 8 give the SEM micrographs of the changeover areas of fatigue fracture surfaces for the two systems. In GF/PEK-C, the changeover areas at various stress levels show evident signs of shear, whereas the changeover areas for the CF/PEK-C were relatively smooth on a large measure with the matrix showing few signs of shear. The changeover areas were produced at the instant before the tensile failure and compressive failure were encountered; the results in Figures 7 and 8 indicate that the matrix in GF/PEK-C was softer than that in CF/PEK-C due to the addition of PPS.

From the examinations of failure surfaces and analysis of fatigue data, the following possible fatigue failure mechanisms of the materials studied are proposed.

At higher stress levels, many microcracks are formed on the tensile surface of the specimen as the result of matrix yielding and creep; they grow as yielding-type cracks and merge until large enough to cause unstable fracture at the load level used. Therefore, the mechanism of cumulative damage at high stress is creep–rupture of the matrix. As mentioned above, since PPS was added to the matrix of GF/PEK-C, the yield strength of its matrix was decreased compared with that of CF/PEK-C. This is why the portions of the normalized S–N curves at high stress level for the two systems are not exactly identical, and the curve for GF/PEK-C is slightly below that of CF/PEK-C.

At lower stress levels, the microcracks or crazes are too few or too small to form a fatigue crack. The fatigue cracks are more likely to nucleate at some spots where there are high stress concentrations (such as fiber ends or defects at edges and corners of specimens) and weakness (such as interface debonding). Though the initiation of these cracks possibly differed, they grow in a stable fashion as fatigue-type cracks first, and finally result in fracture due to unstable crack growth or coalescence of isolated cracks. So the failure mechanism at low stress is crack growth fracture. However, the difference in the resistance of fibers, matrices, and interfaces makes the CF/PEK-C system more fatigue-resistant.

Figure 2 shows that the stress levels at which the S–N curves shifted their trend were different for the two systems. The presence of PPS decreased the yield strength of the matrix in GF/PEK-C, also making the matrix-yielding mechanism dominant at lower stress levels in the GF/PEK-C system. On the other hand, the poor matrix/fiber bonding in the CF/PEK-C system makes it easy for the fatigue cracks to originate at interfaces. This may be another reason that the CF/PEK-C system changes into crack growth mechanism earlier than the GF/PEK-C system. It is noted that the scatter degree of fatigue data at the stress level corresponding to the failure mechanism transition was larger compared with that at other stress levels. This may be a reflection of the competition between the two failure mechanisms, matrix-yielding and crack growth.

CONCLUSIONS

The flexural fatigue failure of injection-molded CF/PEK-C and GF/PEK-C composites is governed by the tensile properties of composites. The fatigue behavior of the two materials is generally similar.

The matrix has a main influence on the fatigue behavior at high stress. But at lower stresses, fatigue properties appear fiber- and interface-dominated.

The stress level at which the failure mechanism transition occurred depended on the yielding strength of matrix and the bonding quality of interface.

One of the authors (J.Z.) expresses his appreciation to the National Natural Science Foundation of China for their financial support. Another author (T.H.) is greatly indebted to the support of the National Outstanding Young Scientist Fund from the Natural Science Foundation of China.

REFERENCES

1. J. F. Mandell, in *Fatigue of Composite Materials,* Vol. 4, Composite Materials Series, K. L. Reifsnider, Ed., Elsevier, Amsterdam, 1990, Chap. 7.
2. J. F. Mandell, D. D. Huang, and F. J. McGarry, *Polym. Compos.,* **2,** 137 (1981).
3. J. F. Mandell, F. J. McGarry, D. D. Huang, and C. G. Li, *Polym. Compos.,* **4,** 32 (1983).
4. J. Zhou, A. D'Amore, and L. Nicolais, *Sci. Eng. Compos. Mater.,* **4,** 17 (1995).
5. H. C. Zhang, T. L. Chen, and Y. G. Yuan, Chinese Patent 85108751.5 (1985).
6. Y. M. Yang, B. Y. Li, and L. S. Dong, *J. Appl. Polym. Sci.,* **56,** 531 (1996).
7. G. Dillon and M. Buggy, *Composites,* **26,** 335 (1995).
8. J. Zhou, B. Y. Li, and T. B. He, *Compos. Sci. Technol.,* to appear.