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The mechanical properties of insert-molded poly (ether imide) (PEI)/C fiber poly (ether ether ketone) (PEEK) composites

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The mechanical properties of insert-molded poly(ether imide) (PEI)/carbon fiber poly(etheretherketone) (CF PEEK) have been examined. Bimaterial composite specimens were constructed by injecting CF PEEK into a mold containing one-half of a PEI tensile specimen. These PEI/CF PEEK composites retained much of their strength and dimensional integrity at temperatures as high as 200°C. Variations in test speed had little affect on breaking strains or stiffness. For two grades of PEI examined, properties were independent of the molecular weight of the PEI. Ultimate properties and fracture surfaces suggested good adhesion between the PEI and CF PEEK, possibly aided by miscibility between the two materials. The PEI/CF PEEK bimaterial composites behaved similarly to PC/CF PEEK specimens, but exhibited higher breaking stresses and moduli, both at room and elevated temperatures. © *2001 Kluwer Academic Publishers*

1. Introduction

Insert molding often involves molding a higher performance polymer, such as poly(etheretherketone) (PEEK), on to a less expensive one. This approach marries the best features of both materials and provides an economical method of producing higher performance products at a reduced cost [1, 2]. In some cases, it is a good alternative to polymer blends.

Recently, insert-molding has been employed in the construction of poly(carbonate) (PC)/carbon fiber polyetheretherketone (CF PEEK) containers for the transportation and storage of silicon wafers [3–7]. Poly(etherimide) (PEI), like PC, is a rigid, amorphous polymer. However, it has several advantages over PC, such as greater stiffness, better chemical resistance, a higher glass-rubber transition temperature [8–10], and better flame retardancy. Also, PEI is miscible with PEEK [11–15], which potentially could lead to improved adhesion. These properties make PEI an attractive alternative to PC where higher performance is required.

In this study, the mechanical properties of PEI/CF PEEK composites were examined. Composite tensile specimens were constructed by injecting CF PEEK into a mold containing one-half of a PEI dogbone. The hot, molten CF PEEK melts the PEI interface. As the interface solidifies, a thermophysical bond is formed. The resulting composite specimens were tested in tension to determine the influence of polymer molecular weight, test speed, and temperature.

2. Analysis

2.1. Thermal properties

The crystalline fraction, X_c, for CF PEEK was calculated as [16]

$$X_c = (\Delta H/H_f)/(1 - X_f), \tag{1}$$

where X_f is filler fraction, ΔH is the melting enthalpy, and H_f is the enthalpy for melting of 100% crystalline, unfilled PEEK, $H_f = 130$ J/g [17].

2.2. General mechanics

Apparent tensile stresses, σ, of monolithic and composite samples were calculated using the elongation force, F, divided by its initial or undeformed cross-sectional area, A [18–20],

$$\sigma = F/A. \tag{2}$$

Apparent tensile strains, ε, were determined from sample elongation, ΔL, and its initial length, L,

$$\varepsilon = \Delta L/L. \tag{3}$$

Apparent tensile moduli, E, were computed as stress over strain, where strains were small and the materials were linearly elastic ($\varepsilon < 0.01$),

$$E = \sigma/\varepsilon. \tag{4}$$

Velocity of elongation (crosshead speed), v, and initial sample length were used to estimate strain rate, ε',

$$\varepsilon' = v/L. \tag{5}$$

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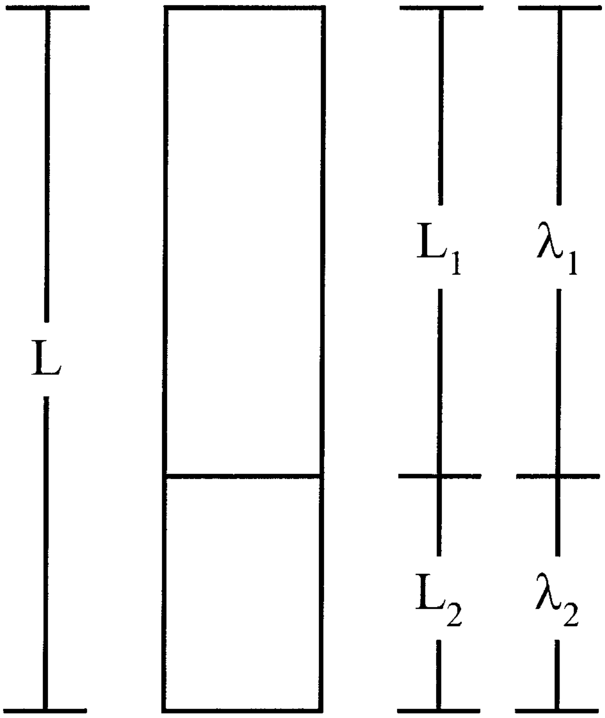

Figure 1 The central portion of a series composite specimen comprised of two materials with different tensile moduli, E_1 and E_2, where $E_1 \leq E_2$.

2.3. Mechanics of the composite specimens

Fig. 1 shows the central portion of a bimaterial composite tensile specimen. The specimen is comprised of two materials in series with tensile moduli of E_1 and E_2, where $E_1 = E_2$. Both segments have the same cross-sectional area, A, but the relative length of each component, L_1 and L_2, can vary [4, 7, 20–27]. When load is applied, the bimaterial composite deforms with the same average stress in each component, independent of fractional length,

$$\sigma = \sigma_1 = \sigma_2. \tag{6}$$

However, if the materials of construction differ in their stiffness, the individual components will not deform to the same extent. The stiffer material deforms less while the softer material deforms more. The apparent strain, ε, in the composite sample is the sum of the strain in each of the components,

$$\varepsilon = \Delta L/L = \lambda_1\varepsilon_1 + (1 - \lambda_1)\varepsilon_2, \tag{7}$$

where

$$\lambda_1 = L_1/L, \tag{8}$$

$$\lambda_2 = L_2/L, \tag{9}$$

$$\varepsilon_1 = \Delta L_1/L_1, \tag{10}$$

$$\varepsilon_2 = \Delta L_2/L_2, \tag{11}$$

and

$$\lambda_1 + \lambda_2 = 1. \tag{12}$$

Thus, the apparent stress generated within a bimaterial composite specimen depends on the applied apparent strain, component moduli, and component fractional lengths,

$$\sigma = E_1E_2/[\lambda_1E_2 + (1 - \lambda_1)E_1]\varepsilon. \tag{13}$$

Accordingly, the apparent tensile modulus, E, of the bimaterial composites is

$$E = E_1E_2/[\lambda_1E_2 + (1 - \lambda_1)E_1]. \tag{14}$$

3. Experimental

3.1. Materials

Two grades of poly(ether imide) (PEI) and one grade of C fiber poly(ether ether ketone) (CF PEEK) were used to mold monolithic and bimaterial composite specimens. The PEI grades were unfilled and differed only in their number-average molecular weight, M. For PEI1, $M \approx 1.2 \times 10^4$ g/mol; for PEI2, $M \approx 1.1 \times 10^4$ g/mol. Both had a polydispersity, Z, of 1.9. The CF PEEK compound contained <20% short C fiber ($M \approx 3.1 \times 10^4$ g/mol with $Z \approx 2.4$).

3.2. Sample preparation

Monolithic specimens (ASTM D638 Type 1) were made by injection molding of PEI1, PEI2, and CF PEEK. Bimaterial composites were fabricated by cutting monolithic PEI specimens in half with a bandsaw, inserting a half-piece back into the mold, and then injecting CF PEEK.

3.3. Materials characterization

3.3.1. Melt flow rate

Melt flow rate (MFR) was determined using a Kayeness Galaxy I melt flow indexer with a 1.048 mm orifice. Triplicate samples were cut from tensile specimens and dried four hours at 150°C. Approximately six grams of material were loaded into the instrument. Barrel temperatures were 337°C for PEI and 385°C for CF PEEK. After preheating for 6 minutes, a 6.6 kg load was applied to the PEI and 5.0 kg load to CF PEEK (ASTM D1238-98).

3.3.2. Differential scanning calorimetry

Glass transition temperatures, T_g, and melting temperatures, T_m, were determined using a Perkin-Elmer DSC7 differential scanning calorimeter, DSC. Three (3) samples, with masses of 4 mg to 7 mg, were taken from tensile bars and scanned at a rate of 10°C/min. For PEI, samples were heated from 20°C to 300°C, cooled to 20°C, and then heated a second time to 300°C. For CF PEEK, samples were heated to 400°C, cooled to 20°C, and then heated again to 400°C. Analysis was performed using the software resident in the DSC7. T_g values were taken from inflection point of the second heating run. Melting properties of CF PEEK were taken from the peak of the first heating run to better reflect its cystallinity after molding.

3.4. Mechanical testing

Specimens were tested in tension using an Instron® 5582 test machine equipped with a 100 kN static load cell (ASTM D638). Gage length (distance between the clamps) was set at 115 mm. Most specimens were tested at 2 mm/min ($\varepsilon' = 3 \times 10^{-4}$ s^{-1}). Alternatively, some samples were tested at other rates, from 0.1 mm/min to 500 mm/min ($\varepsilon' = 1 \times 10^{-5}$ s^{-1} to 7×10^{-2} s^{-1}). A convection oven was used to test at temperatures, T, up to 220°C. Samples were heated in the oven for 20 minutes to achieve thermal equilibrium prior to testing. An extensometer was used to measure strains at temperatures ≤200°C (the upper operating limit of the extensometer). Five samples were tested at each rate and temperature. Stress versus strain curves were plotted and used to determine yield stresses and strains, breaking stresses and strains, and moduli.

4. Results and discussion

4.1. Materials characterization

4.1.1. Flow properties

Table I shows the flow characteristics of the materials used in both the monolithic specimens and the composites. Melt flow rates, MFR, from the molded specimens of the CF PEEK and two grades of PEI fell within manufacturers' specifications and were unchanged compared to values measured for the resin, suggesting that no degradation occurred during molding.

4.1.2. Thermal properties

Thermal properties of the various monolithic and bimaterial specimens, also listed in Table I, were in general agreement with literature values [12–16]. PEI had a glass transition temperature, T_g, of about 220°C. CF PEEK had a glass transition temperature, T_g, around 145°C and a melt temperature, T_m, of 348°C. The crystalline fraction, X_f, in the CF PEEK was approximately 35%, which is the maximum attainable crystallinity for PEEK under typical injection molding conditions.

4.2. Mechanical properties

4.2.1. Stress-strain behavior

Fig. 2 shows the stress-strain behavior of a typical PEI1/CF PEEK bimaterial composite ($\lambda_1 = 0.5$) at room temperature along with a curve for monolithic CF PEEK and the initial portion of a PEI1 curve. PEI1 specimens yielded after elongating 7% and then broke at 80% elongation with a stress of 100 MPa. CF PEEK broke at 1.8% strain without yielding. PEI1/CF PEEK composites also broke without yielding at strains that were only slightly less than those from the monolithic CF PEEK specimens, but their breaking stresses were much lower.

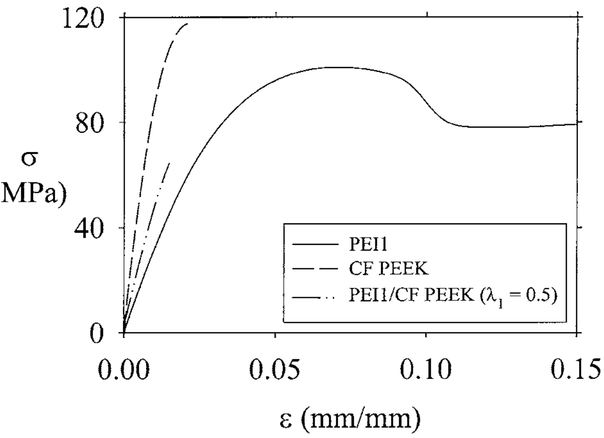

Figure 2 Stress, σ, versus strain, ε, for PEI1, CF PEEK, and a PEI1/CF PEEK bimaterial composite ($\lambda_1 = 0.5$) at 25°C.

Table II summarizes the mechanical properties at room temperature. Data for PC and the PC/CF PEEK composites are included for comparison [4, 7]. Properties for the monolithic specimens are in general agreement with literature values [8, 9, 12, 28–30]. The CF PEEK specimens were approximately four times stiffer than the PEI specimens. No difference was observed in the mechanical properties of the two grades of PEI. For rigid thermoplastic polymers moderate changes in molecular weight usually do not affect the short-term mechanical performance.

The nearly identical mechanical properties of the PEI/CF PEEK bimaterial composites from two grades of PEI were curious. As PEI and PEEK are miscible [11–15], some extent of interdiffusion should have occurred. If PEI and PEEK chains did mingle at the interface, one might have expected the lower viscosity PEI2 (shorter chains) to diffuse into the CF PEEK faster and to a greater depth than the PEI1 [31], possibly leading to better adhesion and higher breaking strains [32–34]. However, there was no difference between the two grades of PEI. Either little molecular mixing occurred before solidification, or more likely, mixing was sufficient to reach the maximum attainable adhesion for the given processing conditions. It has been shown for a number of glassy [35, 36] and partially crystalline polymers [37] that toughness of a bimaterial interface

TABLE I Summary of materials characterization[a]

Material(s)	MFR (dg/min)	T_g (°C)	T_m (°C)	ΔH (J/g)	X_c (%)
PEI1	8.8 ± 0.3	219 ± 1	–	0	0
PEI2	19.0 ± 1.2	217 ± 1	–	0	0
CF PEEK	39.8 ± 0.6	149 ± 3	346 ± 1	40.9 ± 2.7	38 ± 3
PEI1 from PEI/CF PEEK	10.9 ± 0.2	220 ± 1	–	0	0
PEI2 from PEI/CF PEEK	20.7 ± 1.4	216 ± 1	–	0	0
CF PEEK from PEI1/CF PEEK	42.6 ± 0.7	146 ± 1	345 ± 1	35.6 ± 1.9	33 ± 2
CF PEEK from PEI2/CF PEEK	45.5 ± 0.5	137 ± 2	344 ± 1	33.5 ± 0.4	31 ± 1

[a] MFR is melt flow rate. T_g is glass transition temperature, T_m is melt temperature, ΔH is melt enthalpy, and X_c is crystalline fraction, determined from Equation 1.

TABLE II Tensile properties of the various materials of construction and bimaterial composites ($\lambda_1 = 0.5$) at $T = 25°C$ and $v = 2$ mm/min[a]

Material(s)	σ_y (MPa)	ε_y (m/m)	σ_b (MPa)	ε_b (m/m)	E (GPa)
PEI1	103 ± 1	0.071 ± 0.001	101 ± 2	0.78 ± 0.07	3.2 ± 0.1
PEI2	105 ± 1	0.070 ± 0.001	101 ± 6	0.81 ± 0.12	3.2 ± 0.1
CF PEEK	NY	NY	129 ± 1	0.018 ± 0.001	12.0 ± 0.4
PEI1/CF PEEK	NY	NY	60 ± 5	0.014 ± 0.001	4.9 ± 0.2
PEI2/CF PEEK	NY	NY	60 ± 5	0.013 ± 0.002	5.1 ± 0.1
PC	61 ± 1	0.060 ± 0.001	66 ± 1	1.04 ± 0.01	2.4 ± 0.1
PC/CF PEEK	NY	NY	36 ± 1	0.011 ± 0.004	3.9 ± 0.1

[a] Yield stress, σ_y; yield strain, ε_y; break stress, σ_b; break strain, ε_b; modulus, E; no yield, NY.

'stitched' together by polymer chains is independent of molecular weight. In this case, the adhesive strength is dictated by the number of polymer chains that cross the interface [38].

Crack propagation was initiated in the immediate vicinity of the interface due to high associated stresses [21–25]. Examination of the fracture surfaces suggested that PEI/CF PEEK produced a strong bond. Fracture of the PEI/CF PEEK composites left a very thin layer of CF PEEK on the PEI. Turned on end, the fracture surfaces of the PEI and CF PEEK segments were indistinguishable—both resembled CF PEEK. This cohesive failure implies that the bond between the PEI and CF PEEK was stronger than the cohesive strength of the CF PEEK. The combination of the carbon fibers acting as stress initiators and the lower yield stress of PEEK matrix [29] compared to PEI probably led to failure through the CF PEEK. In contrast, PC/CF PEEK composites showed fracture surfaces with a mixture of PC and CF PEEK [4].

The PEI/CF PEEK composites were stiffer and stronger than their PC/CF PEEK counterparts. While yield and breaking strains of PEI and PC were similar, PEI yielded with stresses that were 40% greater than PC. PEI also was 33% stiffer. The greater strength and stiffness of the PEI manifested itself in the composites. The PEI/CF PEEK composites ($\lambda_1 = 0.5$) were 67% stronger than their PC/CF PEEK counterparts and 25% stiffer.

4.2.2. Influence of PEI fraction

By changing extensometer position, it was possible to test composites with a wide range of effective compositions. Fig. 3 shows breaking stresses, σ_b, for PEI1/CF PEEK composites with different fraction lengths of PEI, λ_1. The points represent experimental data. Even though the relative length of PEI varies, as expected, stresses were constant, as per Equation 6. The solid line represents an average value (59 MPa). Composites made with PEI2 behaved similarly.

Fig. 4 shows breaking strain, ε_b, versus fractional length of PEI1, λ_1, for PEI/CF PEEK composites. Points are experimental data. The solid line represents linear regression. As the modulus of the CF PEEK was much greater than the modulus of PEI, strains were not uniform throughout the specimens—the softer PEI deformed more than its stiffer counterpart. Consequently, shifting extensometer position to increase the relative proportion of PEI ($\lambda_1 \longrightarrow 1$) increased the breaking strain. As expected from Equation 7, changes in apparent breaking strain were linear with relative component length.

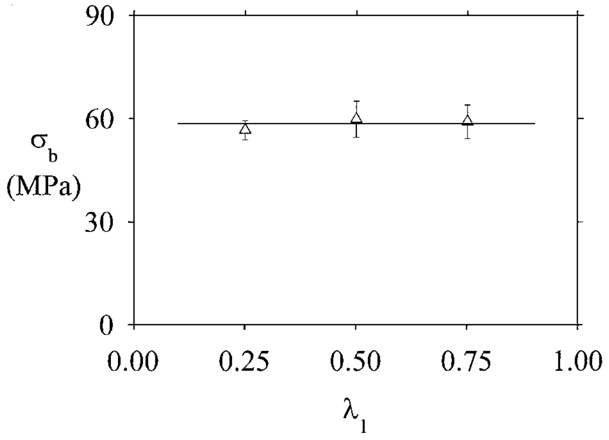

Figure 3 Breaking stress, σ_b, versus fractional length, λ_1, of PEI for PEI1/CF PEEK bimaterial composites (25°C and $v = 2$ mm/min).

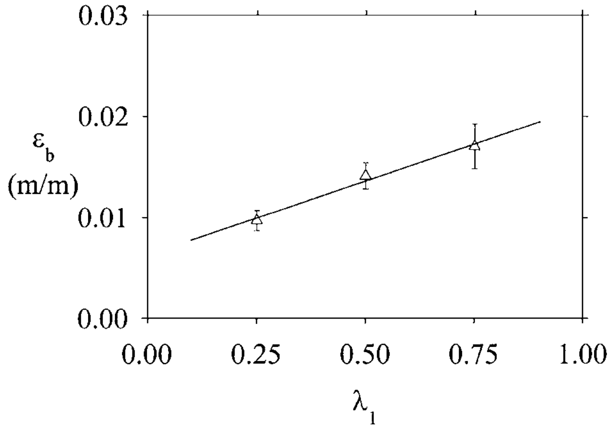

Figure 4 Breaking strain, ε_b, versus fractional length, λ_1, of PEI for PEI1/CF PEEK bimaterial composites (25°C and $v = 2$ mm/min).

Fig. 5 shows the apparent moduli, E, for PEI1/CF PEEK composites where the fractional length of the PEI, λ_1, was varied. The points are experimental data. Points at $\lambda_1 = 0$ represent monolithic CF PEEK; points at $\lambda_1 = 1$ are for monolithic PEI. The moduli of the composites were intermediate to the moduli of the individual components, decreasing with PEI fraction. The solid line was calculated according to Equation 14. Agreement between measured and predicted values was excellent.

Values of λ_1 also were varied by changing the clamp position, rather than extensometer position. Apparent

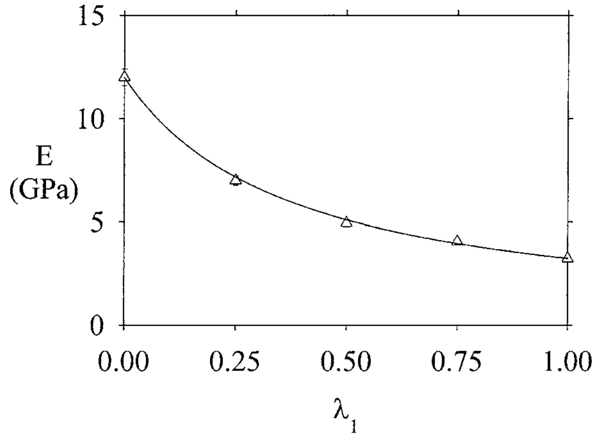

Figure 5 Modulus, E, versus fractional length, λ_1, of PEI for PEI1/CF PEEK bimaterial composites (25°C and $v = 2$ mm/min). The solid line was calculated according to Equation 14.

modulus was not affected by changes in clamp position. However, changes in clamp position altered specimen compliance and consequently, influenced breaking stresses and breaking strains. (Ultimate properties depend upon specimen compliance and flaw size [39]).

4.2.3. Rate dependence

Monolithic and composite specimens were pulled at different rates to uncover any strain rate effects. With the exception of modest increases (=20%) in yield and breaking stresses, the mechanical properties were rate invariant. Similar findings have been reported by other investigators [29, 30, 40].

4.2.4. Temperature dependence

Fig. 6 shows the breaking stress, σ_b, versus temperature, T, for CF PEEK and the PEI1/CF PEEK composites ($\lambda_1 = 0.5$). Breaking stresses for both materials tended toward zero as temperature increased. The decline in breaking stress for CF PEEK was more pronounced above the T_g of PEEK, 145°C. Breaking properties of monolithic PEI were not measured at elevated temperatures due to travel limitations of the mechanical test equipment, but its yield properties can be found in the Appendix.

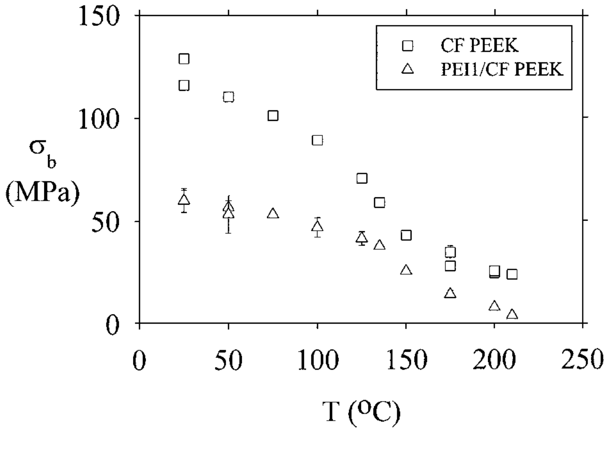

Figure 6 Breaking stress, σ_b, versus temperature, T, for CF PEEK and PEI1/CF PEEK bimaterial composites ($\lambda_1 = 0.5$).

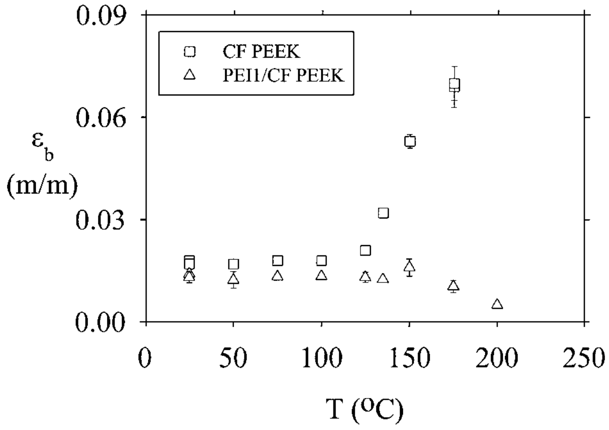

Figure 7 Breaking strain, ε_b, versus temperature, T, for CF PEEK and PEI1/CF PEEK bimaterial composites ($\lambda_1 = 0.5$).

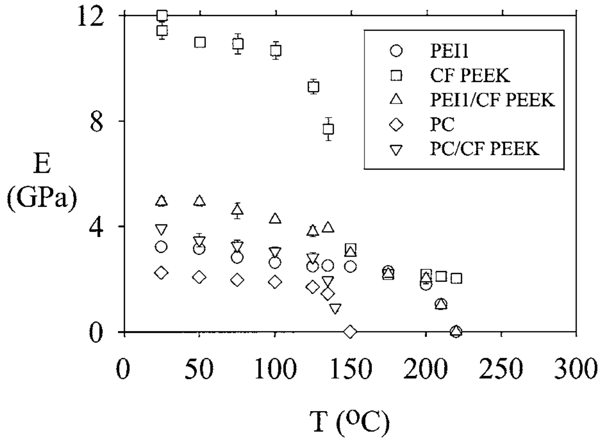

Figure 8 Modulus, E, versus temperature, T, for PEI1, CF PEEK, and PEI1/CF PEEK bimaterial composites ($\lambda_1 = 0.5$). Data for PC and a PC/CF PEEK bimaterial composite ($\lambda_1 = 0.5$) data are included for reference.

Breaking strain, ε_b, versus temperature, T, for CF PEEK and the PEI1/CF PEEK composites ($\lambda_1 = 0.5$) are shown in Fig. 7. Breaking stains were steady up to the T_g of PEEK. As temperature was increased further, breaking strains of the monolithic CF PEEK specimens increased, while breaking strains of the PEI/CF PEEK composites declined.

Fig. 8 shows the relation between tensile modulus, E, and temperature, T, for monolithic PEI1, monolithic CF PEEK, and the PEI1/CF PEEK bimaterial composites ($\lambda_1 = 0.5$). There was little change in stiffness of the materials of construction until temperatures reached their respective glass transition temperatures, $T_g = 220$°C for PEI and $T_g = 145$°C for PEEK. However, there was a slight dip in the moduli of both PEI and CF PEEK due to secondary thermal transitions in the vicinity of 50–75°C for PEI and 25–50°C for CF PEEK [29]. Above 220°C, the amorphous PEI was a viscous liquid, completely void of structural integrity. On the other hand, the partially-crystalline CF PEEK maintained some of its rigidity up to its melting temperature, $T_m = 345$°C.

The stiffness of the PEI/CF PEEK composites was determined to a large degree by the thermal characteristics of the PEI. The stiffness of the PEI/CF PEEK composites declined only slightly with increasing

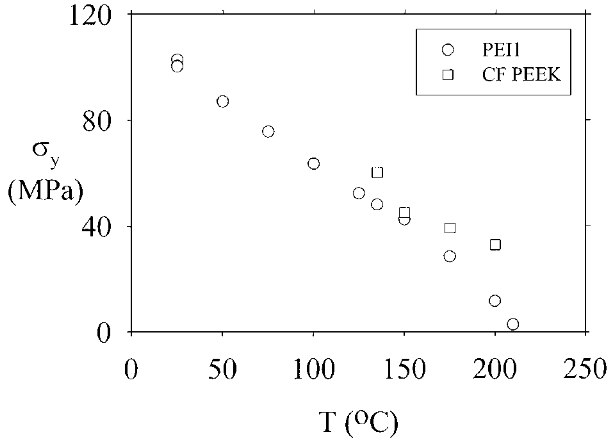

Figure 9 Yield stress, σ_y, versus temperature, T, for monolithic PEI1 and CF PEEK.

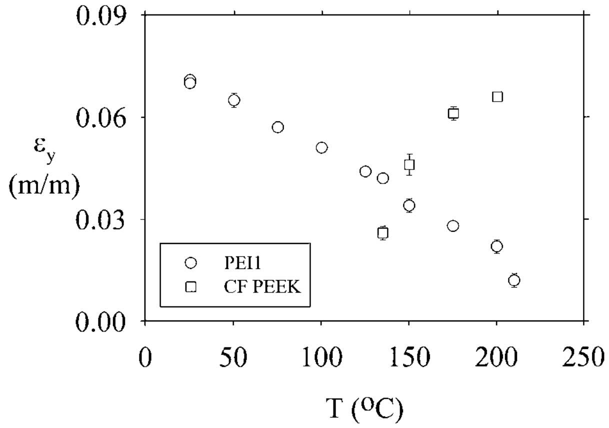

Figure 10 Yield strain, ε_y, versus temperature, T, for monolithic PEI1 and CF PEEK.

temperature up to the T_g of PEEK. Above 145°C, the PEEK matrix softened and the stiffness of PEI and CF PEEK were nearly identical. With further increases in temperature, the PEI/CF PEEK composites follow the path of PEI. Composites constructed with PEI2 gave the same results.

Data for PC and the PC/CF PEEK bimaterial composites ($\lambda_1 = 0.5$) are included for comparison [6]. The PC/CF PEEK composites failed above 150°C as the PC began to flow. Moduli calculated from Equation 14 agreed well with measured values for all composites.

5. Conclusions

PEI and CF PEEK can be used to create insert-molded bimaterial composites. These PEI/CF PEEK composites retained much of their strength and dimensional integrity at temperatures up to 200°C. Variations in test speed had little affect on breaking strains or stiffness. Ultimate properties and fracture surfaces suggested good adhesion between the PEI and CF PEEK, possibly aided by miscibility between them. For two grades of PEI examined, properties were independent of viscosity (molecular weight) of the PEI. The PEI/CF PEEK composites were stronger and stiffer at room temperature than analogous PC/CF PEEK composites and retained their mechanical integrity at much higher temperatures. Therefore, insert-molded composites of PEI/CF PEEK should have better dimensional stability and a higher continuous-use temperature (by 50–70°C) than PC/CF PEEK.

Appendix

Figs 9 and 10 show the yield stress, σ_y, and yield strain, ε_y, versus temperature, T, for monolithic PEI1 and CF PEEK. For PEI, both stresses and strains decreased linearly with increasing temperature up to the onset of the glass transition temperature, T_g. This linear decline in the yield properties has been noted by other investigators [29, 30, 40] and often is described using an Eyring rate activated process. At temperatures well below the T_g of PEEK, CF PEEK failed at low strains without yielding. However, at temperatures near or above its T_g, CF PEEK yielded. σ_y values of CF PEEK increased with temperature, while ε_y decreased.

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References

1. H. H. KAUSCH, “Advanced Thermoplastic Composites” (Hanser, New York, 1993).
2. J. DE GASPARI, *Plast. Technol.* **44** (1998) 44.
3. S. BHATT, *Micro* **17**(5) (1999) 37.
4. C. W. EXTRAND and S. BHATT, *J. Appl. Polym. Sci.* **76** (2000) 1777.
5. *Idem.*, *J. Adhesion* **72** (2000) 219.
6. *Idem.*, *J. Mater. Sci.* **35** (2000) 5427.
7. *Idem.*, *J. Appl. Polym. Sci.* **78** (2000) 173.
8. H. SAECHTLING, “Plastics Handbook,” 2nd ed. (Oxford University Press, New York, 1992).
9. “International Plastics Selector” 17th ed., Vol. 2 (D.A.T.A. Business Publishing, Englewood, CO, 1996).
10. J. BRANDRUP, E. H. IMMERGUT and E. A. GRULKE (eds.), “Polymer Handbook,” 4th ed. (Wiley, New York, 1999).
11. J. E. HARRIS and L. M. ROBESON, *J. Polym. Sci. B* **25** (1987) 311.
12. *Idem.*, *J. Appl. Polym. Sci.* **35** (1988) 1877.
13. G. CREVECOEUR and G. GROENICKX, *Macromolecules* **24** (1991) 1190.
14. H.-L. CHEN and R. S. PORTER, *Polym. Eng. Sci.* **32** (1992) 1870.
15. B. S. HSIAO and B. B. SAUER, *J. Polym. Sci. B* **31** (1993) 901.
16. J. P. RUNT, in “Encyclopedia of Polymer Science and Engineering,” 2nd ed., Vol. 4, edited by H. F. Mark and J. I. Kroschwitz (Wiley, New York, 1986).
17. D. J. BLUNDELL and B. N. OSBORN, *Polymer* **24** (1983) 953.
18. I. M. WARD, “Mechanical Properties of Solid Polymers,” 2nd ed. (Wiley, New York, 1983).
19. J. M. GERE and S. P. TIMOSHENKO, “Mechanics of Materials,” 2nd ed. (PWS-Kent Publishing, Boston, 1984).
20. L. E. NIELSEN and R. F. LANDEL, “Mechanical Properties of Polymers and Composites,” 2nd ed. (Marcel Dekker, New York, 1994).
21. M. L. WILLIAMS, *Bull. Seism. Soc. Am.* **49** (1959) 199.
22. G. C. SIH and J. R. RICE, *J. Appl. Mech.* **31** (1964) 477.
23. F. ERDOGAN, *J. Appl. Mech.* **32** (1965) 403.
24. J. R. RICE and G. C. SIH, *ibid.* **32** (1965) 418.
25. V. L. HEIN and F. ERDOGAN, *Int. J. Fracture Mech.* **7** (1971) 317.
26. G. P. ANDERSON, S. J. BENNETT and K. L. DEVRIES, “Analysis and Testing of Adhesive Bonds” (Academic Press, New York, 1977).

27. S. WU, "Polymer Interface and Adhesion" (Marcel Dekker, New York, 1982).
28. P. CEBE, S. Y. CHUNG and S.-D. HONG, *J. Appl. Polym. Sci.* **33** (1987) 487.
29. R. GENSLER, PH. BÉGUELIN, C. J. G. PLUMMER, H.-H. KAUSCH and H. MUNSTEDT, *Polym. Bull.* **37** (1996) 111.
30. N. D. ALBÉROLA, P. MÉLÉ and C. BAS, *J. Appl. Polym. Sci.* **64** (1997) 1053.
31. P. G. DE GENNES, "Scaling Concepts in Polymer Physics" (Cornell University Press, Ithaca, NY, 1979).
32. Y. H. KIM and R. P. WOOL, *Macromolecules* **16** (1983) 1115.
33. D. ADOLF, M. TIRRELL and S. PRAGER, *J. Polym. Sci. B* **23** (1985) 413.
34. D. Y. HUANG and R. S. CHEN, *Polym. Eng. Sci.* **39** (1999) 2159.
35. C. CRETON, E.J. KRAMER, C.-Y. HUI and H. R. BROWN, *Macromolecules* **25** (1992) 3075.
36. K. CHAR, H. R. BROWN and V. R. DELINE, *ibid.* **26** (1993) 4164.
37. E. BOUCHER, J. P. FOLKERS, H. HERVET, L. LÉGER and C. CRETON, *ibid.* **29** (1996) 774.
38. H. R. BROWN, *ibid.* **24** (1991) 2752.
39. J. G. WILLIAMS, "Fracture Mechanics of Polymers" (Wiley, New York, 1987).
40. PH. BÉGUELIN, M. BARBEZAT and H.-H. KAUSCH, *J.Phys. III France* **1** (1991) 1867.

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