

The Chemical Compatibility of Insert-Molded Bimaterial Composites of Polycarbonate and Carbon Fiber Polyetheretherketone

C. W. EXTRAND, S. BHATT

Entegris, 3500 Lyman Blvd., Chaska, Minnesota 55318, USA

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ABSTRACT: Chemical compatibility of a bimaterial composite composed of polycarbonate (PC) and C fiber polyetheretherketone (PEEK) was examined. Series composite specimens were constructed by injecting C fiber PEEK into a mold containing one half of a PC dogbone. Specimens were exposed for 2 weeks at room temperature to various cleaning chemicals that are commonly used in semiconductor fabrication facilities: deionized water, 0.1% aqueous Triton CL10 surfactant, 0.1% aqueous Alifonic 610-3.5 surfactant, and isopropyl alcohol. To increase the severity of the test, some samples were strained and/or notched before immersion. After exposure, specimens were tested in tension and results were compared to their corresponding pre-exposure values. None of the chemicals affected the strength of the unstrained, unnotched PC/C fiber PEEK composite. However, isopropyl alcohol and the surfactant solutions caused the strained specimens to fail (both unnotched and notched) during chemical exposure. The strains used during exposure were near the respective breaking points of the unnotched and notched composite. Consequently, only a slight reduction in strength from chemical exposure was needed to cause failure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 173–178, 2000

Key words: insert-mold; bimaterial; composite; chemical compatibility

INTRODUCTION

Insert molding involves injecting a polymer over another material.^{1,2} This approach marries the best features of different materials and provides an economical method for producing higher performance products at a reduced cost. In some cases, it is a good alternative to polymer blends. The mechanical properties and the performance of the resulting adhesive bond are important considerations for many insert-molded products. However, little work has been published in this area,¹ particularly for rigid thermoplastics.

Recently, insert-molding has been used in the construction of polycarbonate (PC)/C fiber polyetheretherketone (PEEK) containers for the transportation and storage of silicon wafers.³ Earlier work on these bimaterial composites examined the mechanical performance⁴ and fracture properties.⁵ Although the strength of the bimaterial composite and its thermophysical bond were deemed adequate for the intended application, there were concerns that exposure to cleaning chemicals may weaken or destroy the bond.

Thus, the chemical compatibility of a PC/C fiber PEEK bimaterial composite and the adhesive strength of its interface have been examined. Series specimens were constructed by injecting C fiber PEEK into a mold containing a fraction of a PC dogbone to create a thermophysical bond. The

Correspondence to: C. Extrand (chuck_extrand@entegris.com).

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materials of construction and their corresponding bimaterial composite were exposed to various chemicals that might be used to periodically clean silicon wafer containers in a semiconductor fabrication facility. Strength and toughness of the exposed specimens were compared with values for their unexposed counterparts. Possible mechanisms for loss of adhesion are discussed, such as environmental stress cracking⁶ of the polymers or attack of the interface itself.⁷

ANALYSIS

Tensile Stresses and Strains

Tensile stress or tensile strength σ was calculated using the elongation force F divided by its initial or undeformed cross-sectional area A ⁸⁻¹⁰:

$$\sigma = F/A. \quad (1)$$

From elongation ΔL of the specimen and its initial length L , apparent tensile strain ϵ was computed as:

$$\epsilon = \Delta L/L. \quad (2)$$

Tensile modulus E was calculated as stress over strain:

$$E = \sigma/\epsilon, \quad (3)$$

where strains were small and the materials were linearly elastic ($\epsilon \leq 0.01$).

Fracture Mechanics

The adhesive strength of the interface and the component materials were calculated using fracture mechanics. Fracture energy or fracture toughness G was calculated from the notch length a and mechanical response of notched specimens as^{11,12}:

$$G = 2.5\pi aU, \quad (4)$$

where U is the strain energy density to break (or area under the stress-strain curve), computed by integrating the stress-strain curve up to the breaking point:

$$U = \sigma(\epsilon)d\epsilon. \quad (5)$$

Table I Materials Properties^a

Material	δ (MPa ^{1/2})	γ (mN/m)	T_g (°C)	T_m (°C)
PEEK	20–22	42	144	335
PC	19–20	43	150	—
H ₂ O	48	73	—	—
0.1% Triton	17	31	—	—
0.1% Alfonic	19	26	—	—
IPA	23	22	—	—

^a Solubility parameters δ were estimated for the neat surfactants using the Small method¹³; others were taken from the literature.¹³⁻¹⁵ Surface tension γ values came from the literature^{13,16,17} or the surfactant manufacturers.¹⁸ T_g and T_m are rubber-glass transition temperature and melting temperature, respectively.^{13,19}

Retention of Properties

The retention of properties was quantified using ratios of breaking strength:

$$\sigma_{b,f}/\sigma_{b,i} \quad (6)$$

and fracture toughness:

$$G_f/G_i \quad (7)$$

where subscripts i and f represent unexposed and exposed specimens, respectively.

MATERIALS AND PROCEDURE

Materials

Monolithic specimens and bimaterial composites were constructed using PC and a C fiber PEEK. The C fiber PEEK compound contained <20% short C fiber. The chemicals used for compatibility testing were deionized (DI) water, 0.1% aqueous surfactant solutions of Triton CF10 (a non-ionic benzyl ether of octylphenylpolyoxylate; Union Carbide) and Alfonic 610-3.5 (a nonionic mixture of hexanol, octanol, and decanol that has been ethoxylated with 3.5 mols of CH₂CH₂O; Condea Vista), as well as isopropyl alcohol (IPA). Properties of the various materials (solubility parameter, surface tension, glass-transition and melt temperatures) are listed in Table I.¹³⁻¹⁹

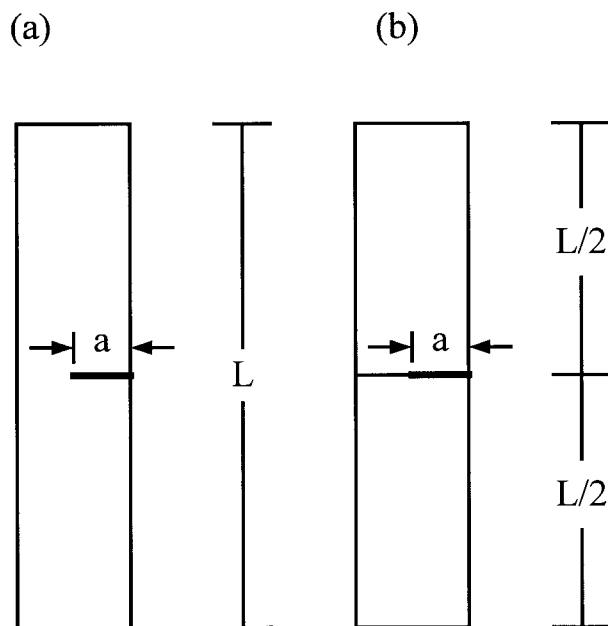


Figure 1 The central portion of tensile specimens (ASTM D638 Type I dogbone) with a single edge notch of length a . (a) monolithic specimen, (b) bimaterial composite composed of PC and C fiber PEEK.

Sample Preparation

Figure 1 shows the central portion of monolithic and series composite tensile specimens. Bimaterial composites were made by first molding PC tensile dogbones (ASTM D638 Type 1), cutting them with a bandsaw, inserting a premolded piece back into the mold, and then injecting C fiber PEEK. Dogbones were notched at their midpoint. For the composite specimens, this corresponded to notching at the interface. Single edge notches of length $a = 1$ mm were made by cutting the first 0.5 mm with a scroll saw (0.025" blade). Then, a utility blade was mounted in a test machine (Instron, model 5582) and the final 0.5 mm was cut by pushing the blade into the notch at 2 mm/min.

Contact Angle Measurements

Contact angles were used to measure the wettability of the various cleaning solvents/solutions on the materials of construction. PC and C fiber PEEK dogbones were cleaned by rinsing with IPA, methanol, and DI water. After drying for 24 h, 3- μ L drops were deposited on the dogbones with a microsyringe (Hamilton Co., Reno, NV), then an additional microliter was injected in to each sessile drop to advance its contact line. Ad-

vancing contact angles θ were measured from both sides of each drop using a goniometer (Ramé-Hart, model 100-00-115). Average values and standard deviations were calculated from six measurements.

Chemical Exposure

Some unnotched specimens were placed directly into the chemicals, whereas other unnotched and notched specimens were immersed after clamping in a three-point bending fixture. The desired strain, $\phi = 1\%$, was achieved with a deflection of $\delta = 6.5$ mm for a bending length of $L = 105$ mm and a sample thickness of $D = 3.2$ mm¹⁰:

$$\phi = 6\delta D/L^2. \quad (8)$$

After 14 days of exposure at room temperature, specimens were removed from the various chemicals, rinsed with DI water, and allowed to dry at least 24 h before testing.

Tensile Testing

Five samples of each type were pulled at 2 mm/min and 23°C using a tensile test machine (Instron, model 5582) equipped with a 100 kN static load cell and rigid clamps.¹² Gage length was 115 mm. Most samples were elongated using an extensometer; alternately, the ultimate properties of monolithic PC were measured without an extensometer.

RESULTS

Contact Angles

Advancing contact angles of the various cleaning solvents/solutions on PC and C fiber PEEK are shown in Table II. Water did not wet either ma-

Table II Advancing Contact Angles θ of the Various Solvents/Solutions on PC and C Fiber PEEK

Solvent/Solution	θ on PC (°)	θ on C Fiber PEEK (°)
H ₂ O	81 ± 2	75 ± 2
0.1% Triton	27 ± 2	12 ± 3
0.1% Alifonic	7 ± 2	≈0
IPA	≈0	≈0

Table III Tensile and Fracture Properties of the Materials of Construction and the Bimaterial Composite

Material	σ_y (MPa)	ϵ_y (mm/mm)	σ_b (MPa)	ϵ_b (mm/mm)	E (GPa)	G (kJ/m ²)
Unstrained						
C fiber PEEK	NY	NY	129 ± 1	0.018 ± 0.001	12.0 ± 0.4	9.2 ± 0.8
PC	59 ± 1	0.061 ± 0.001	59 ± 3	0.87 ± 0.09	2.3 ± 0.1	2.7 ± 0.2
PC/C fiber PEEK	NY	NY	47 ± 8	0.013 ± 0.004	3.9 ± 0.1	1.6 ± 0.3
After two weeks of bending strain ($\phi = 1\%$)						
C fiber PEEK	NY	NY	120 ± 2	0.017 ± 0.000	10.1 ± 0.3	9.9 ± 1.0
PC	57 ± 1	0.061 ± 0.001	58 ± 2	0.853 ± 0.093	2.2 ± 0.1	2.9 ± 0.5
PC/C fiber PEEK	NY	NY	36 ± 10	0.011 ± 0.004	3.4 ± 0.2	2.0 ± 0.7

NY, no yield.

terial. Values agreed with previously published results.^{16,20} The surfactants greatly improved wetting. IPA and 0.1% Alionic solution completely wet both materials ($\theta < 10^\circ$).

Mechanical Properties before Exposure

A summary of the mechanical and fracture properties before exposure is given in Table III. Mechanical properties for PC and C fiber PEEK agreed well with literature values.^{21,22} Unnotched PC elongated approximately 6% before yielding with considerable necking; failure occurred at 90% elongation with a breaking stress of 66 MPa. On the other hand, unnotched C fiber PEEK elongated less than 1.3% before breaking at 110 MPa without yielding. The PC/C fiber PEEK composite failed at slightly smaller strains than the monolithic C fiber PEEK. Its modulus was intermediate to the moduli of the individual components.⁴

Fracture energies for PC and C fiber PEEK are in general agreement with values reported by other investigators.^{23,26} PC is a material known for its toughness. Consequently, it exhibited a large fracture energy. The fracture behavior of the PC/C fiber PEEK composite was similar to the monolithic C fiber PEEK, but its fracture toughness was lower.

Strain ($\phi = 1\%$) alone was of little or no consequence. Yield and breaking properties of strained specimens were nearly identical to their unstrained counterparts. Moduli of the strain samples were slightly lower due the permanent set.

Retention of Mechanical Properties after Exposure

All strained (unnotched and notched) PC/C fiber PEEK composite specimens failed after 14 days of

exposure to the surfactant solutions or IPA. Specimens still intact after chemical exposure were tested. Table IV shows their retention of tensile strength and fracture toughness. Ratios of $\sigma_{b,f}/\sigma_{b,i}$ and G_f/G_i ratios exhibited the same general trend. In a few cases, G_f/G_i was considerably less than $\sigma_{b,f}/\sigma_{b,i}$.

C fiber PEEK was unaffected by exposure.²⁷ For PC and the composite, the added severity of a strain and/or a notch reduced both strength and toughness. Loss of strength was more pronounced in the composite. IPA and both surfactant solutions caused the strained (unnotched and notched) specimens to fail during immersion. Even DI water affected the composite. Because the bending strain used during chemical exposure ($\phi = 1\%$) was near the breaking limit ($\phi_b = 1.3\%$) of the composite (Table V) the chemical interaction required to cause failure was minimal.

DISCUSSION

There are two relevant explanations for the observed strength reduction of the composite: wetting of the interface by the solvents/solutions⁷ or an environmental stress mechanism.⁶ The first postulates that certain chemicals, having low surface tensions, can spread into a polymer–polymer interface and reduce the surface energy for crack formation.⁷ The second (environmental stress cracking or crazing) requires a stress in addition to the presence of a swelling liquid. Small flaws or other stress raisers (such as an interface) increase local swelling.²⁸ The swelling agent then acts as a plasticizer, lowering T_g of the polymer and allowing the formation of small cracks or crazes that weaken the polymer and initiate failure.

Table IV Retention of Tensile Strength ($\sigma_{b,f}/\sigma_{b,i}$) and Fracture Toughness (G_f/G_i) after 2 Weeks of Chemical Exposure

Chemical	$\sigma_{b,f}/\sigma_{b,i}$ (%)		G_f/G_i (%)	
	Unstrained and Unnotched	Strained and Unnotched	Strained and Notched	Strained and Notched
C fiber PEEK				
None	100 ± 1	100 ± 3	100 ± 3	100 ± 35
H ₂ O	96 ± 1	99 ± 4	104 ± 7	125 ± 61
0.1% Triton	92 ± 1	96 ± 3	103 ± 5	113 ± 37
0.1% Alfonic	89 ± 2	98 ± 4	99 ± 5	101 ± 28
IPA	94 ± 3	101 ± 4	101 ± 4	103 ± 30
PC				
None	100 ± 1	100 ± 3	100 ± 4	100 ± 20
H ₂ O	97 ± 1	101 ± 2	103 ± 3	87 ± 21
0.1% Triton	99 ± 1	102 ± 2	103 ± 4	77 ± 14
0.1% Alfonic	88 ± 11	99 ± 2	56 ± 7	10 ± 2
IPA	98 ± 1	101 ± 2	48 ± 7	10 ± 1
PC/C fiber PEEK				
None	100 ± 33	100 ± 4	100 ± 24	100 ± 65
H ₂ O	82 ± 34	93 ± 30	68 ± 16	48 ± 14
0.1% Triton	95 ± 19	0	0	0
0.1% Alfonic	103 ± 24	0	0	0
IPA	98 ± 20	0	0	0

As the wetting liquids (the surfactant solutions and IPA) were no more detrimental toward the strength and toughness of the unstrained composite than nonwetting water (Table IV) and strain was required to weaken the composite, the likely cause seems to be an environmental stress mechanism.

The solubility parameter δ is an excellent indicator of the potential for a solvent to swell a polymer and reduce its T_g . If a solvent and a polymer have similar solubility parameters, the solvent can cause swelling. Both PC and PEEK

have solubility parameters similar to the surfactants and IPA (Table I), but PEEK is partially crystalline and therefore should be less susceptible to environmental stress attack.⁶

PC, on the other hand, is an amorphous polymer known for its susceptibility to attack by environmental agents. The reported critical strain of PC for crack or craze formation in the presence of IPA is $\phi \cong 1.5\%$.¹⁴ The strain used here ($\phi = 1.0\%$) did not cause failure in monolithic PC (Table IV), but the addition of a notch undoubtedly raised the stress²⁹ beyond the threshold for crack or craze formation in PC, and consequently, led to failure. The Triton surfactant seemed to be less detrimental toward the monolithic PC. It has a much higher molecular weight than Alfonic, which may have hindered (or slowed) penetration into the stressed regions of PC.

Considering the similarity in the solubility parameters of PC, the surfactants, and IPA, stress near the interface of the composite seems to be a necessary and sufficient condition to cause localized swelling in the PC and thereby failure. The composite specimen immersed in water, which has a much larger solubility parameter than the polymers, experienced a modest loss of strength and toughness.

Table V Bending Breaking Strains (ϕ_b) of Unnotched and Notched Specimens^a

Material	ϕ_b (mm/mm)	
	Unnotched	Notched
C fiber PEEK	0.025 ± 0.001	0.018 ± 0.003
PC	>0.16	>0.16
PC/C fiber PEEK	0.013 ± 0.003	0.013 ± 0.003

^a $v = 2$ mm/min, $L = 105$ mm, and $D = 3.2$ mm. Notches were 1 mm in length.

Breaking strains were calculated according to Eq. (8).

CONCLUSIONS

Chemical exposure had no effect on the tensile strength or fracture toughness of C fiber PEEK, even with the added severity of strains and/or notches. A notch, strain, and 14-day exposure at room temperature to IPA or aqueous Alifonic surfactant reduced the strength and toughness of PC and the PC/C fiber PEEK composite. The loss in strength and toughness was attributed to an environmental stress mechanism.

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