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Interfacial Adsorption And Crystallization Of
Polycarbonate In Carbon Fiber Composites

by

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INTERFACIAL ADSORPTION AND CRYSTALLIZATION
OF POLYCARBONATE IN CARBON FIBER COMPOSITES

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ABSTRACT

A polycarbonate (PC)/carbon fiber (CF) composite system has been examined with regard to interfacial adsorption and crystallization by altering times and temperatures of annealing. Times up to 180 min and temperatures of 245, 275, and 300°C have been investigated. Transverse tensile, transverse toughness, and scanning electron microscopy results on unidirectional, continuous-fiber composites indicate improved fiber/matrix adhesion at longer times and higher temperatures of annealing. Improvements in transverse toughness and transverse tensile strength of a factor of two is achieved. The data indicate that primarily adsorption rather than secondary interfacial crystallization is the likely mechanism for increased adhesion. Isothermal transverse toughness values have been found to fit well to a Langmuir-type expression. The temperature dependence of adsorption as measured by transverse toughness is described well by an Arrhenius equation. The dependence of transverse toughness on PC molecular weights from $M_w=26,600$ to 39,800 was found to be large, with higher molecular weights adsorbing more effectively.



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INTRODUCTION

The use of thermoplastics instead of thermosets as matrices in fiber-reinforced composites introduces the added complexity of slow matrix adsorption onto the fibers and possible matrix crystallization. The fibers can alter the normal matrix crystallization by acting as a nucleating agent. Nucleation of crystals close together along the fiber and subsequent radial growth lead to the formation of transcrystallinity. Transcrystallinity has been reported for a variety of fiber/matrix combinations¹⁻¹⁵, including some crystal-type growth of bisphenol A polycarbonate (PC) on carbon fibers (CF)¹⁻³. A transcrystalline interphase with modulus intermediate between that of fiber and matrix is favorable for stress transfer¹⁻³ and could also possibly improve fiber/matrix adhesion and fiber compression characteristics.

Kardos et.al.¹⁻³ processed PC/chopped CF composites for 10 min at 275°C (above the PC melting point of 260-265°C) and found increased strength and modulus by annealing the composites at 245°C for 3 hours. The increase was attributed to generation of a crystalline layer adjacent to the fibers, as observed by electron diffraction. Scanning electron microscopy of the fracture surfaces showed increased fiber/matrix adhesion. Studies on other systems have given disparate observations concerning the role of interfacial structure on properties¹⁶⁻¹⁷.

The present study examines the PC/CF system further with particular interest in the role of interfacial adsorption and crystallization on

fiber/matrix adhesion and composite properties. The PC/CF system is particularly amenable to a study of interfacial crystallization because PC's sluggish bulk crystallization means that crystallization occurs only at the interface. Various processing times and temperatures as well as different PC molecular weights were examined in order to gain further insight into this composite system and related ones.

EXPERIMENTAL

Three different molecular weight PC's ($T_g=150^{\circ}\text{C}$) were obtained from General Electric: (1) PC film, 0.13mm thick, $M_w=34,200$, designated PCB, (2) PC powder, $M_w=26,600$, designated PCA, and (3) PC powder, $M_w=39,300$, designated PCC. All PC's were dried overnight in a vacuum oven at 100°C before use. Films of PCA and PCC were made by compression molding the powders for 10 min at 275°C . Unsized T500 3k PAN-based carbon fiber yarn was obtained from Amoco and used without pretreatment. PC/CF continuous-fiber, unidirectional composites were fabricated by alternately placing PC film on a Teflon-covered aluminum plate, and wrapping carbon fiber yarn around the plate in aligned fashion. The aluminum plate's edges were rounded in order to prevent fiber breakage. Typically 4 layers of film and 3 layers of fiber yarn were used. The layers were then consolidated at 275°C in a Carver press by holding them for 5 min with low pressure, pressing 10 min at 0.8 MPa, then either (1) cooling the composite to room temperature in the press cooling cycle (less than 5 min), or (2) releasing the pressure and holding the composite for a longer time at either 245, 275, or 300°C before cooling

to room temperature. Cooling from 275 to 245°C or heating from 275 to 300°C required only 3 min. These conditions thus produced composites which varied only in annealing time and temperature. Annealing here refers to heat treatment above as well as below the melting point. Composite plates were typically 0.45mm thick and had fiber weight fractions of 0.45, 0.36±0.01 (volume fraction = 0.28), and 0.32 for PCA/CF, PCB/CF, and PCC/CF respectively. Weight fractions were found by dissolving out the PC with methylene chloride. Samples were cut with a paper cutter and the edges sanded with fine sandpaper.

Transverse toughness tests were performed on a buckled plate (BP) specimen with a Model 4202 Instron testing machine. Complete details of the BP test for composites can be found elsewhere¹³. Small, rectangular composite specimens, typically 2.5cm long, 0.9cm wide, and 0.045cm thick, with fibers oriented perpendicular to the testing direction, were buckled in compression at room temperature at 2 cm/min. Compression continued until fracture occurred by propagation of a central precrack. A chart recorded the load/deflection curve. Average and standard deviation were obtained by testing 4-8 specimens of each kind.

Transverse tensile tests were also performed with a Model 4202 Instron testing machine, interfaced with a computer. Composites samples were typically 0.5cm wide and 0.045cm thick, with 2.5 cm between grips. Manilla tabs were superglued to the composite to prevent breaking in the grips. (Epoxy tabs did not bond well to the composites.) All tests were performed at room temperature at a crosshead speed of 1mm/min. Four to six specimens of each type were tested.

The fracture toughness of pure PC film of similar thickness (0.48mm) to the composites was found using a single edge notch (SEN) specimen and the J-integral method¹⁹. Specimens were 1cm wide, with 4cm between grips. Crack lengths of 3 to 7mm were examined. Energies were found by integrating the stress/strain curves up to the peak (crack propagation point).

Composite fracture surfaces were examined in a JEOL 35CF scanning electron microscope after coating with a thin layer of gold in a Polaron E5100 SEM sputtering unit. Differential scanning calorimetry was performed on a Perkin Elmer DSC-4 equipped with data station.

Gel permeation chromatography (GPC) was performed with Polymer Laboratories PLgel columns (10^4 , 10^3 , 10^2 angstrom), a Knauer 98 refractive index detector, and interfaced computer. The mobile phase was methylene chloride at 25°C. A universal calibration procedure was used with polystyrene (PS) standards. The Mark-Houwink coefficients used were $K=6.1 \times 10^{-3}$, $a=0.74$ for PS and $K=11.9 \times 10^{-3}$, $a=0.80$ for PC²⁰.

RESULTS AND DISCUSSION

Experimental Data for PCB/CF

Table I and Figures 1-4 show the results for transverse tensile strength, toughness, strain at break, and energy at break (area under the stress/strain curve) for the PCB/CF composites annealed at different times and temperatures. Error bars (standard deviation) are not included on the figures for clarity, but are generally less than $\pm 20\%$ for all quantities except energy at break, for which the error is

slightly larger. Transverse composite modulus values were found not to change significantly with processing conditions and were 3.49 ± 0.16 GPa for the BP test and 2.7 GPa for transverse tensile tests. The difference between these is likely due to gripping difficulties in the tensile test, as discussed in a previous paper¹⁸. All quantities shown here indicate a general trend of higher values with longer annealing time and higher temperature.

Figures 1 and 2 show the similarity in trends of transverse tensile strength and toughness as measures of the interfacial adhesion. At temperatures of 275-300°C, annealing times above 30-45 min can give problems with degradation (see below) and thus were not examined fully. Transverse tensile strength in Figure 1 increases with annealing time and approaches the same maximum of about 65 MPa for all temperatures. The trends are similar in Figure 2 for transverse toughness, but the increases are more gradual. There is also some question as to the final maxima, but all are well below a pure PC value of about 30 kJ/m². This value was found here by the J-integral method (pure PC does not fracture in a BP test) and is close to the plane stress value of 25 kJ/m² found by Fraser and Ward²¹. Transverse toughness, because it can see differences where transverse tensile strength cannot, is seen to be a more sensitive measure of the interface. This is because PC begins to yield near 65 MPa, so transverse tensile strength loses its sensitivity near this point. In fact at some of the longer times and higher temperatures, yielding as seen by a downturn in the stress/strain curve occurred just before fracture. (See Figure 5.)

Figures 3 and 4 for transverse strain and energy at break, respectively, do not level off as much as strength because they are sensitive even at yielding. The interesting thing to note in these figures is the crossover of the 275 and 300°C curves at longer times. This is due to the beginning of significant degradation, with tensile strength values not sensing this yet. GPC data shows no molecular weight degradation after annealing 45 min at 275°C, but M_w decreased from 34,200 to 28,000 after 45 min at 300°C. Data for transverse toughness at 300°C for 45 min was scattered and is not included here due to degradation.

Scanning electron micrographs of fracture surfaces (Figure 6) confirm better fiber/matrix adhesion with longer times and higher temperatures of annealing. In Figure 6(a) the fibers can be seen to pull out cleanly from the matrix for the unannealed composite, whereas some PC can be seen adhering to the fibers in the composite annealed 45 min at 275°C (Figure 6(b)).

Differential scanning calorimetry curves of PCB/CF composites in Figure 7 show T_g at the expected PC value of 150°C and no significant crystallization or T_g shift even after annealing 3 hr at 245°C. This indicates that any crystallization is small and confined to the interface as found by Kardos et.al.¹⁻³. Crystallization cannot occur at 275°C and above because this is above the normal PC melting point of 260-265°C²².

Adsorption and Crystallization

The experimental data lend some insight into the mechanism of mechanical property increase in the PC/CF system. Since similar mechanical property increases can be obtained by annealing at higher temperatures where crystallization cannot occur, interfacial crystallization is likely not the primary cause of the increases. The faster rates of increase at higher temperatures and the leveling off of the curves are consistent with better adsorption as the mechanism of improvement. Interfacial crystallization below T_m could then occur as a consequence of how a polymer chain adsorbs onto the fiber surface. When several adjacent segments of a polymer chain interact with the fiber, a small region of order occurs and can lead to nucleation of crystallization²³. One could envision a process in which there are adsorption or interaction sites on the fiber surface which continually are filled. Adsorption and desorption may occur until an equilibrium is approached as indicated by a slowing fiber/matrix adhesion increase (as in transverse toughness) which approaches a maximum. The kinetics of approach is naturally higher at higher temperatures just as normal chemical kinetics. It is difficult to extrapolate the data to very long times or get long time data because of degradation, but for an exothermic interaction like adsorption, the equilibrium extent of interaction would be expected to be lower at higher temperatures. The transverse toughness data here only indicate a similar maximum. There is further discussion of equilibrium in the Data Fitting section below.

This concept of adsorption would also explain other work. For example, Kardos et.al.¹⁻³ processed his PC/chopped CF composites for 10 min at 275°C before annealing. They were therefore operating at the low end of the time scale, leaving plenty of room for increases with annealing. Increases were seen in modulus as well as strength in that work because of the random rather than unidirectional (transverse) orientation of the fibers. Work on PEEK/CF by Lee and Porter¹⁵ noted an increase in transverse tensile strength with increased time above the melting point. Increases attributed to transcrystallinity are more appropriately explained by better adsorption. Indeed adsorption must occur before transcrystallinity and therefore is of primary importance in the PC/CF and other fiber/matrix systems.

Data Fitting

The data in Figures 1 and 2 and the concept of adsorption suggest the use of a Langmuir-type equation (isotherm)²⁴ to fit the data at each temperature. It should be noted that the Langmuir-type equation as used here is purely a mathematical description of the data. Transverse toughness rather than transverse strength was used because it was the more sensitive measure of the interfacial adhesion, as discussed earlier. The equation used was

$$\Delta G_c / \Delta G_{ceq} = kt / (1 + kt) \quad , \quad \Delta G_c = G_c - G_{c0} \quad (1)$$

where G_c = transverse toughness of composite

G_{c0} = transverse toughness before annealing

ΔG_c = change in toughness with annealing

ΔG_{ceq} = equilibrium change in toughness ($t \rightarrow \infty$)

t = annealing time

k = kinetic parameter.

This is apparently the first time that an equation of this form has been used to describe composite mechanical data. Equation (1) can be rearranged to

$$t/\Delta G_c = 1/k\Delta G_{ceq} + 1/\Delta G_{ceq} \quad (2)$$

Plotting $t/\Delta G_c$ versus t then gives a line with slope $=1/\Delta G_{ceq}$ and intercept $=1/k\Delta G_{ceq}$. Table II shows the parameters found for each temperature upon fitting the experimental data. Figure 2 shows the fit curves. It can be seen that equation (1) describes the data well. The limited data and their variance, however, limit the conclusions that can be drawn. It can be said that the k values, which indicate the speed of approach to equilibrium, increase with temperature as expected. Equilibrium or maximum values, ΔG_{ceq} , are nearly the same but slightly higher at lower temperatures. Again this is as expected for an exothermic interaction like adsorption. The fact that the ΔG_{eq} values are nearly the same indicates a small heat of interaction. This is anticipated for a PC/CF system, which has limited possibilities for actual chemical reaction. Indeed, GPC data indicate no change in M_w even after annealing 45 min at 275°C, supporting the idea of no chemical reaction.

The data has also been examined with regard to temperature dependence. k indicates kinetics at the different temperatures, and was found to fit well to an Arrhenius equation, $k=A \exp(-E_a/RT)$, as seen in Table III. This is as anticipated for a rate parameter.

Molecular Weight Dependence

Transverse toughness results, which are independent of fiber volume fraction¹⁸, are shown in Figure 8 for the three different molecular weight PC's in PC composites. It is evident that matrix molecular weight has a dramatic effect on adsorption and resulting toughness, with better adsorption at higher molecular weights. Fitting the upper two curves to equation (1) gives $G_{ceq} = 11.0 \text{ kJ/m}^2$ for $M_w = 34,200$ and $G_{ceq} = 13.3 \text{ kJ/m}^2$ for $M_w = 39,300$, while $G_{ceq} = 4 \text{ kJ/m}^2$ for $M_w = 26,600$.

These results are not explainable by chain mobility, as the temperature dependence might have been. Here the effective adsorption is best for the least mobile (highest molecular weight) chains. Mobility or diffusion is thus not the controlling factor here. The results can also not be explained by the matrix properties. Pure PC toughness, as measured by an SEN test, was found to be essentially the same at the three molecular weights studied.

The molecular weight dependence of adsorption and transverse toughness is consistent with other work. Lipatov²⁵, in one of the few experimental works on adsorption from the melt, found that high molecular weight fractions of PS adsorb preferentially onto the surface of glass. This was explained by the molecular weight dependence of polymer surface tension and the minimization of interphase energy. Scaling arguments for a single chain on a surface show that the fraction of adsorbed chain segments depends on the strength of interaction but is independent of molecular weight²⁶. This means that the actual number of interactions per chain scales with molecular weight. Furthermore,

interactions with a longer chain can be more effective than with a shorter chain because there is more possibility of entanglement formation between the remainder of the chain and the bulk matrix. The molecular weight dependence of mechanical properties is thus amplified. This helps explain the data. Although all the molecular weights here are well above the critical length for entanglement, $M_c^{27,28}$, and the molecular weight where mechanical properties are constant²⁹, adsorption reduces the effective molecular weight. This reduction in effective molecular weight especially hinders lower M_w 's in forming entanglements with the bulk matrix. Adsorptions are thus much less effectively translated into good interfacial properties at lower matrix molecular weights, as the data here indicates.

CONCLUSIONS

Examination of a PC/CF composite system was done at processing conditions which alter only time and temperature of annealing. Transverse tensile and fracture toughness data show improved interfacial adhesion at longer times and higher temperatures of annealing, short of PC degradation. Scanning electron microscopy of fracture surfaces confirm better fiber/matrix adhesion at these conditions. Since mechanical property improvements occur on annealing above as well as below the melting point, interfacial crystallization is not the primary mechanism of improvement. Better adsorption is the likely primary mechanism. Interfacial crystallization can occur secondarily below the melting point as a consequence of how a polymer chain adsorbs on the fiber surface. This idea of adsorption also explains related data on

PC/CF and data on PEEK/CF. Data for transverse toughness has been found to fit well to a Langmuir-form equation. The temperature dependence of the toughness data is described well by the Arrhenius equation. The dependence of PC molecular weight on adsorption and transverse toughness was found to be large, with higher molecular weights adsorbing more effectively.

The data has practical implications for processing thermoplastic matrix composites. First, the time and temperature processing history of the composites is important in determining interfacial and thus composite properties. The processing history must be controlled and understood. Development of equilibrium adsorption can require long times and high temperatures. Second, matrix molecular weight is also important in developing composite properties. More effective adsorption occurs with higher molecular weights. Efforts to improve processability by lowering molecular weight must therefore be carefully considered with respect to composite properties.

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Table 1 - Experimental Data for PCB/CF Composites

Annealing Temperature, °C	Annealing Time, min	Transverse Toughness, kJ/m ²	Transverse Tensile Strength, MPa	Transverse Strain at Break, %	Transverse Energy at Break, 10 ⁶ J/m ³
245	15	5.1+0.9	47+4	2.06+0.22	0.55+0.12
245	45	6.0+1.7	57+3	2.8+0.3	0.92+0.14
245	90	8.2+1.2	63.7+1.5	3.7+0.3	1.53+0.16
245	180	9.0+1.3	66.0+1.0	5.1+0.5	2.4+0.4
275	0	4.0+0.5	33+3	1.32+0.23	0.25+0.06
275	15	6.0+1.0	56+5	2.8+0.4	0.9+0.3
275	30	7.2+1.4	63+4	3.6+0.4	1.4+0.3
275	45	7.8+1.4	65+5	4.5+0.8	2.0+0.5
300	15	7.5+1.5	65.0+2.1	3.5+0.6	1.5+0.3
300	30	8.7+1.0	64.8+1.2	3.8+0.4	1.6+0.3
300	45	*	67.5+1.4	3.9+0.7	1.8+0.4

* Data scattered.

Table II - Fitting Parameters for Time Dependence of PCB/CF Transverse Toughness, Equations (1) and (2)

Annealing Temperature, °C	$\Delta G_{eq}, \text{kJ/m}^2$	$G_{eq}, \text{kJ/m}^2$	k, min^{-1}	Correlation Coefficient
245	8.50	12.51	0.0084	0.947
275	7.03	11.04	0.027	0.996
300	6.98	10.99	0.067	1*

* Fit for only 2 points

Table III - Temperature Dependence of k: Arrhenius Fit

<u>Parameter</u>	<u>Intercept</u>	<u>Slope</u>	<u>E_a, kJ/mole</u>	Correlation
				<u>Coefficient</u>
k	16.81	-1.12×10^4	93.0	0.999

FIGURE CAPTIONS

- Figure 1 - Transverse tensile strength versus annealing time at 245, 275, and 300°C for PCB/CF composites previously consolidated 15 min at 275°C.
- Figure 2 - Transverse toughness versus annealing time at 245, 275, and 300°C for PCB/CF composites previously consolidated 15 min at 275°C. Dashed lines are best fit to equation (1).
- Figure 3 - Transverse strain at break versus annealing time at 245, 275, and 300°C for PCB/CF composites previously consolidated 15 min at 275°C.
- Figure 4 - Transverse energy at break versus annealing time at 245, 275, and 300°C for PCB/CF composites previously consolidated 15 min at 275°C.
- Figure 5 - Example stress/strain curves for PCB/CF composites annealed for 0, 15, 30, and 45 min at 275°C after being consolidated 15 min at 275°C.
- Figure 6 - Scanning electron micrographs of transverse tensile fracture surfaces for PCB/CF composites (a) unannealed, and (b) annealed 45 min at 275°C.
- Figure 7 - Differential scanning calorimetry first heats at 40°C/min for PCB/CF composites (a) unannealed, and (b) annealed 3 hr at 245°C.
- Figure 8 - Transverse toughness versus annealing time at 275°C for PCA/CF, PCB/CF, and PCC/CF composites previously consolidated

15 min at 275°C. PC molecular weights, M_w , are labeled for each curve. Dashed lines are best fit to equation (1).















