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Composites Reinforced With Thermotropic
Liquid Crystal Copolyester Fibers

by

Roger S. Porter

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COMPOSITES REINFORCED WITH THERMOTROPIC
LIQUID CRYSTAL COPOLYESTER FIBERS

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ABSTRACT

Composites reinforced with thermotropic liquid crystal copolyester fibers (Celanese Vectran) have been studied with regard to fiber properties and fiber/matrix adhesion. As-spun (AS) and heat-treated (HT) fibers have been characterized. Heat treatment increases the crystal-to-nematic melting point by 40°C , and increases modulus 18% while doubling strength. Composites made with Vectran fibers (HT) should be processed at or below 275°C , because fiber properties are significantly reduced on processing above this temperature, which corresponds to the AS melting point. Composites made with Vectran fibers are found to have low transverse properties, regardless of thermoplastic matrix. Specific fiber surface treatment, such as oxidation with ozone, increases transverse properties, but values remain low compared to the bulk matrix. Scanning electron microscopy of transverse fracture surfaces indicates that fiber splitting occurs, especially for surface treated fibers. Poor fiber transverse properties (low interchain interaction) rather than fiber/matrix adhesion thus appear to be limiting composite transverse properties, especially in composites with surface treated fibers.



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INTRODUCTION

In an earlier paper¹ we have discussed interfacial adsorption and crystallization in polycarbonate (CF)/carbon fiber (CF) composites. In this paper, our study of the interface in fiber-reinforced thermoplastic-matrix composites is extended to composites reinforced with the relatively new thermotropic liquid crystal copolyester fibers. The focus is moved from interfacial crystallization of the matrix to the general subject of adhesion to the fibers. The fibers under study are Celanese Vectran, based on hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA). Results are given first on fiber characterization and the effect of composite processing temperature on fiber properties. Adhesion to several thermoplastic matrices as well as the effect of fiber surface treatment have been studied by transverse composite tests and scanning electron microscopy of fracture surfaces.

Background

Celanese Vectra, or Vectran when referring to fibers, is a random copolymer with structure shown in Figure 1. (See Calundann and Jaffe² for an overview.) This copolyester forms a nematic liquid crystal on heating, with the crystal-to-nematic melting point dependent on the HBA/HNA ratio. Fibers with high orientation and good mechanical properties are formed by spinning from the liquid crystalline melt. HBA/HNA has been studied rather extensively in film and fiber form, but the literature on adhesion in blends and composites with HBA/HNA has been more limited, and will be reviewed briefly here.

Blends with HBA/HNA have been reported for polytetrafluoroethylene³, aromatic polyethers⁴, polyimide⁵, polyesters^{6,7}, polyester-amide⁸, PEEK and polyarylate^{9,10}, epoxy¹¹, nylon 12¹², amorphous polyamide¹³, polyetherimide¹⁴, and polycarbonate^{15,16}. Laminates with HBA/HNA have been reported for itself¹⁷ and polycarbonate¹⁸. In all cases the blends are immiscible, with in situ fiber formation occurring in some systems¹²⁻¹⁶. The only reports on interfacial adhesion indicate poor adhesion with polyetherimide, and good with amorphous polyamide. Blends with polycarbonate have been reported to show both good (modulus comparison with composite theory)¹⁵ and poor (fracture surfaces)¹⁶ interfacial interaction. While blend results can give some indication of interaction between phases, adhesion in composites is generally more difficult because the matrix must interact with the HBA/HNA fiber while the fiber is in the solid rather than liquid crystal state.

Several reports of HBA/HNA fiber use in composites have considered conditions where the fibers are melted out to form the matrix with carbon fiber reinforcement^{5,19}. Only one patent deals with intact fibers²⁰, for use as tire cord with a pentaerythritol monobasic acid ester finish.

In summary, virtually no information is available in the literature on composites reinforced with HBA/HNA fibers other than those formed in situ. The only information on interaction with HBA/HNA can be obtained from related work on blends. The present study, therefore, is necessary and important for the understanding of fiber properties and adhesion in these composites.

EXPERIMENTAL

Celanese Vectran fibers (VF) with an HBA/HNA molar ratio of 73/27, were obtained in both as-spun (AS) and heat-treated (HT) form. The 20-25 μ m diameter fibers had no finish, and came with 300 fibers per bundle. Vectra (V) pellets, with an HBA/HNA molar ratio of 58/42, were also obtained from Celanese. Polycarbonate (PC) film, 0.13mm thick, $M_w = 34,200$, was obtained from General Electric. The PC and V were dried overnight in a vacuum oven at 100°C before use. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-4 equipped with a data station. Single fiber samples were prepared by gluing the fibers onto manilla tabs with epoxy. Tensile properties were measured at room temperature in an Instron machine with a 2kg load cell at a crosshead speed of 0.1 cm/min. A chart recorded the load/deflection curve. Fiber lengths from 1-3 cm, with 4-5 fibers at each length, were examined in order to make compliance corrections^{21,22}.

Continuous-fiber, unidirectional composites were made by alternately placing previously molded films on a Teflon-covered aluminum plate, and wrapping VF yarn around the plate in aligned fashion. Typically 4 layers of film and 3 layers of fiber yarn were used. The layers were consolidated under vacuum in a Carver press by holding them for 5 min with low pressure, pressing 10 min at 0.8 MPa, then either (a) cooling the composite to room temperature in the press cooling cycle, or (b) releasing the pressure and holding the composite for a longer time before cooling. Composites were typically 0.45mm thick and had fiber volume fractions of 0.40 for PC/VF and 0.45 for V/VF. Volume fraction

fiber for PC-matrix composites was found by dissolving out the PC with methylene chloride after testing. Fraction of fiber in V/VF composites was determined from wrapping a known weight of fiber per composite plate area, and weighing the composite plate after fabrication. Composite cutting was done with either a scissors or razor blade, and edges were sanded with fine sandpaper.

Buckled plate tests, for measuring transverse toughness as an indication of fiber/matrix adhesion, were performed in an Instron machine as described in detail in a previous paper²³. Composite specimens, typically 2.5cm long, 0.9cm wide, and 0.045cm thick, were buckled in compression at room temperature at 2 cm/min. Average and standard deviation were obtained by testing 4-6 specimens of each kind.

Transverse tensile tests were performed with a Model 4202 Instron testing machine, interfaced with computer. Samples were typically 0.6-0.7cm wide and 0.045cm thick, with 2.0 or 2.5 cm between grips. All tests were done at room temperature at a crosshead speed of 1 mm/min. Four specimens of each type were tested.

For surface modification, ozonation of VF(HT) fibers was carried out at 20°C in a Welsbach model T-408 Ozonator. The ozone concentration was 5.0 weight % in oxygen, as determined by iodometric-thiosulfate titration. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin Elmer-Physical Electronics 5100 with MgK α excitation. An angle of 75° between the sample and detector was used. Scanning electron microscopy of fracture surfaces was done on a JEOL 35CF SEM after

coating with a thin layer of gold in a Polaron E5100 SEM sputtering unit.

RESULTS AND DISCUSSION

Fiber Properties

Figure 2 shows the first-heat DSC curves for V, VF(AS), and VF(HT). V 58/42 is the minimum melting HBA/HNA composition², and has a crystal-to-nematic transition, T_m , of 247°C. VF(AS) with composition 73/27 has a peak melting point of 284°C. Heat treatment, which is normally annealing about 30°C below T_m for long times², raises the T_m to 328°C. A small remnant can still be seen, however, in the AS melting region. Heat treatment reportedly increases crystal size and perfection as well as increasing molecular weight by solid state reaction².

Average single fiber modulus, strength, and strain to break are shown in Table I. Heat treatment increases modulus by 18 % while more than doubling strength. This increase can again be associated with increased crystal size and perfection, and higher molecular weight. VF(HT) has strength about equal to Kevlar 49, whereas its modulus of 84 GPa is well below the 125 GPa reported for Kevlar²⁴.

The effect of composite processing temperatures on fiber properties was examined by subjecting the HT fibers to various temperatures for 60 min. (See also Table I.) Room temperature fiber properties after 60 min at 275°C remained nearly the same. After 60 min at 285°C, however, a significant reduction occurred in fiber strength and strain to break. After 60 min at 300°C, modulus and strength are only about 50% of their original values. This indicates that composites must be processed at

275°C or less in order to avoid fiber property reduction. It appears that the AS melting point controls fiber properties, even for HT fibers. Figure 3 shows the DSC for original HT fibers and HT fibers held for 60 min at 275, 285, and 300°C. After 60 min at 285°C, the transition broadens and moves slightly to lower temperatures, while after 60 min at 300°C, the transition essentially disappears. This confirms that significant structural changes take place in the fibers below the HT melting point.

Adhesion in Composites

Table II shows transverse tensile strength and transverse toughness (buckled plate test) results for V/VF(HT) and PC/VF(HT) composites. Adhesion as measured by transverse properties is low in all cases when comparing to matrix strength or the transverse toughness of 4-10 kJ/m² found previously for PC/CF composites¹. Increased processing time leads to some improvement in V/VF(HT) composites. Small trial pieces on other matrices including nylon 66, amorphous polyamide (DuPont J2), polysulfone, polyarylate, poly(butylene terephthalate), polyethylene (PE), and PE/acrylic acid copolymer also indicate low transverse properties judged by apparent fiber pullout and easy crack formation on bending or cutting. Note that an amorphous polyamide had been found previously to give good adhesion to HBA/HNA in blends¹³. The result of low transverse properties independent of thermoplastic matrix composition seemed to indicate poor interaction with the fiber surface and led us to attempts at fiber surface treatment.

Fiber Surface Treatment

Treatments which break the ester linkages such as strong acid or base treatment were found to give a weak, yellow powdery surface layer, unfavorable for bonding. Vectran has an oriented layer structure, so it is especially susceptible to this problem. Efforts at fiber surface treatment, therefore, focused on possible treatments which could attack the aromatic rings rather than the ester linkages. Several attempts at Friedel-Crafts reaction on the rings proved unsuccessful as judged by XPS. Reactive gas treatment was the other major attempt at surface treatment. Recent work by Kaplan et.al.²⁵ indicated that oxygen or ammonia gas plasma treatment of Vectra film improved adhesion with epoxies and urethanes. After plasma treatment, failure changed from adhesive failure to cohesive failure of the Vectra. A related gas treatment, with ozone, was thus tried with Vectran fibers.

Ozone is a highly reactive gas which attacks carbon-carbon double bonds, including aromatic rings²⁶. Razumovski et.al.²⁷ found ozone reacts with polymers mainly on the surface, and the mechanism and kinetics of reaction varies with chemical structure. Polynaphthalene was found to react readily, as well as polyesters. Oxidation of the surface can lead to both chain scission and crosslinking. Peeling et.al.²⁸ used XPS effectively to study the surface oxidation of polystyrene by ozone.

The oxidation of VF was studied by using V 58/42 film as a model. Films were ozonated at 20°C for various times. XPS results in Table III indicate that ozonation increases surface oxygen content by 50%, and most of the reaction is complete after 10 min. With this information as

a guide, VF(HT) for use in composites was ozonated for 1 hr at 20°C. No changes in DSC or fiber tensile properties were noted for the ozonated fibers, even after 60 min at 275°C. Heating slightly darkened the fiber surface.

The ozonated fibers were used to make a composite with PC. Table IV shows the resulting transverse properties. A 50% increase in transverse tensile strength and a 35% increase in transverse toughness occurred upon ozone treatment of the fibers. Transverse properties, however, are still not high.

Fracture Surfaces

The reason for poor transverse properties, regardless of matrix or surface treatment, can be found by looking at transverse tensile fracture surfaces of the PC/VF(HT) composites, Figure 4. Some fiber splitting occurs in composites with untreated fibers, Figure 4(a), whereas fiber splitting is particularly evident in composites with surface-treated fibers, Figure 4(b). There is apparently a transition from mixed interfacial and fiber failure in (a) to largely fiber failure in (b). Transverse properties are therefore being limited by weakness in the fibers rather than by poor fiber/matrix adhesion, especially in composites with surface-treated fibers. Low transverse strength and fiber splitting in surface treated systems has also been reported for Kevlar composites²⁴.

Poor transverse properties of the Vectran fibers are related to poor shear and compressive properties because all these properties are largely determined by interchain interaction. DeTeresa et.al.²⁹ found a

linear correlation between fiber compressive strength and shear modulus for high performance fibers including nematic thermotropic polyester (VF), Kevlar, and graphite. VF had the lowest compressive strength and shear modulus, while Kevlar was intermediate and graphite the highest. This explains the poor transverse strength and fiber splitting for VF composites. With Kevlar, intermolecular hydrogen bonding can occur, so the tendency for compressive failure and fiber splitting may not be as great as for VF. In conclusion, further efforts at improving transverse properties in Vectran composites should likely focus on altering the fiber itself to increase interchain interaction.

Conclusions

Our studies of the interface in fiber-reinforced thermoplastic-matrix composites have been extended to composites reinforced with Celanese Vectran fibers. As-spun and heat-treated fibers have been characterized. Heat treatment raises the melting point by 40°C, and increases modulus slightly, while doubling strength. Composites made with Vectran fibers (HT) must be processed at or below 275°C, because fiber properties are significantly reduced on processing above this temperature, which corresponds to the as-spun melting point. Composites made with Vectran are found to have low transverse properties, regardless of thermoplastic matrix. Specific fiber surface treatment, such as oxidation, increases transverse properties, but values remain low compared to the bulk matrix. The SEM of fracture surfaces indicates that fiber splitting occurs, especially for surface-treated fibers. Poor fiber transverse properties rather than fiber/matrix adhesion thus

appear to be limiting composite transverse properties, particularly in composites with surface treated fibers.

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Table I - Vectran fiber tensile properties, room temperature.

<u>Fiber</u>	<u>Modulus, GPa</u>	<u>Strength, GPa</u>	<u>Strain to Break, %</u>
Vectran(VF) As Spun(AS)	71±9	1.34±0.16	1.83±0.14
Vectran(VF) Heat Treated(HT)	84±12	2.96±0.28	2.48±0.32
VF/HT after 60 min at 275°C	83±12	2.81±0.15	2.22±0.02
VF/HT after 60 min at 285°C	80±3	1.81±0.56	1.8 ±0.3
VF/HT after 60 min at 300°C	39±10	1.51±0.23	2.7 ±0.4

Table II - V/VF(HT) and PC/VF(HT) transverse properties, room temperature.

<u>Composite, Processing</u>	<u>Transverse Tensile Strength, MPa</u>	<u>Transverse Toughness, kJ/m²</u>
V/VF*, 15 min at 275°C	13.0±2.2	1.6±0.4
V/VF*, 75 min at 275°C	15.5±0.9	2.3±0.6
PC/VF ⁺ , 15 min at 275°C	13.3±1.3	1.4±0.5
PC/VF ⁺ , 60 min at 275°C	no change	

* Vectra 58/42 (V) matrix strength = 40-50 MPa (unoriented).

+ PC matrix strength = 65 MPa.

Table III - Ozone treatment time effect on the surface atomic carbon/oxygen ratio and surface oxygen content of Vectra (V) film, XPS results.

<u>Treatment Time, min</u>	<u>Atomic Carbon/Oxygen Ratio</u>	<u>Oxygen Mole %</u>
0	4.00 *	19.9
10	2.65	27.2
30	2.51	28.3
60	2.22	30.8

* The theoretical stoichiometric atomic carbon/oxygen ratio for V 58/42 is 4.34.

Table IV - Ozone treatment of VF(HT) effect on PC/VF(HT) transverse properties.

<u>Composite</u>	<u>Transverse Tensile Strength, MPa</u>	<u>Transverse Toughness, kJ/m²</u>
PC/VF* (untreated)	13.3±1.3	1.4±0.5
PC/VF* (ozonated 1hr at 20°C)	20 ± 4	1.9±0.4

* Processing time = 15 min at 275°C.

FIGURE CAPTIONS

- 5.1 Chemical structure of Vectra.
- 5.2 First-heat DSC curves at $40^{\circ}\text{C}/\text{min}$ for V, VF(AS), and VF(HT).
- 5.3 DSC heating curves at $40^{\circ}\text{C}/\text{min}$ for separate VF(HT) samples after being held 0 min at 275°C , 60 min at 275°C , 60 min at 285°C , and 60 min at 300°C .
- 5.4 Scanning electron micrographs of transverse tensile fracture surfaces for PC/VF(HT) composites processed 15 min at 275° ; composite made with (a) untreated VF(HT), and (b) VF(HT) ozonated 1 hr at 20°C .

VECTRA







