Evaluation of Interfacial Adhesion in Sheath/Core Composite Fibers

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SYNOPSIS

Rayon/nylon sheath/core composite fibers were produced using a wire coating-type process. Fumaric acid (FA) was chosen as an adhesion promoter to pretreat the nylon core fiber before rayon coating to improve the adhesion between skin and core. Different FA pretreatment concentrations and times were used and the effects of the pretreatment conditions on the adhesion were evaluated. A fiber pull adhesion test technique was developed to determine the interfacial shear strength of the composite fibers. The results indicated that the interfacial adhesion in the rayon/nylon composite fibers was significantly improved for specific sets of FA application conditions. Adhesion results were confirmed with electron microscopy. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

An experimental sheath/core composite fiber with a synthetic core and a rayon skin has been produced by a coating process in which the core fiber is passed through a fiber coating die where it is contacted by viscose rayon.[1] The rayon coating is then regenerated in a sulfuric acid bath. The core fiber dominates the mechanical properties and the rayon skin dominates the surface properties.[1-4]

Adhesion between the core fiber and the rayon skin is a critical aspect of this internally reinforced rayon composite fiber. Several coupling agents have been tried to enhance the adhesion; however, the improvement was not sufficient.[3,5] Maleic anhydride has been shown to be an effective coupling agent for wood fiber-filled polystyrene composites.[6] The mechanical properties were improved with increased concentrations of maleic anhydride up to a certain limit (about 5%) and then leveled off at higher concentrations. This study selected fumaric acid (FA) as an adhesion promoter to pretreat the nylon core fiber before rayon coating to improve the interfacial adhesion. FA has the difunctionality and steric hin-

derance necessary to form covalent bonds with both layers.[7]

A simple and reliable adhesion test method is needed to determine the interfacial adhesion level of these composite fibers under different pretreatment conditions. Several adhesion test methods have been developed to test the interfacial adhesion between a polymer matrix and its reinforcing fibers.[8-19] In one technique, the single filament critical length method, a single fiber is embedded in a polymer tensile bar.[8,9] The specimen is then subjected to tensile loading until the fiber breaks into fragments inside the polymer matrix. The fiber fragment lengths are determined by the microscope directly. The interfacial shear strength, τ, is then calculated by the following equation:

$$\tau = \sigma_f d/2l \tag{1}$$

where σ_f is the fiber tensile strength; d, the fiber diameter; and l, the fiber fragment length. The polymer matrix should have a failure strain and strength larger than that of the fiber so that the fiber breakage cannot cause the polymer failure.[14]

Another technique is the single-fiber pullout test. The single-fiber pullout test has been used extensively to determine the adhesion on model composite materials.[11-15] In this technique, a single fiber is embedded a short distance in a polymer matrix. A

tensile load is then applied to the fiber until pullout occurs. The adhesion strength, τ, is determined by

$$\tau = F/\pi d l \qquad (2)$$

where F is the force required for pullout; d, the fiber diameter; and l, the embedded length.

There are certain limitations with the single-fiber pullout test. First, the scatter of the data is of some significance.[13] Second, the force required to pull out the fiber varies with the embedded length in the matrix,[19] but this is not a linear relationship.[15] The embedding is also a very difficult step. Very short embedded lengths are needed so that the fiber does not break before it pulls free.[10,11,14,17,18]

Because of the problems associated with the pullout method, a microbond technique was later developed.[17,18] This method uses only a very small amount of resin for each test in the form of a droplet deposited on the fiber. The fiber specimen is pulled out of the microdroplets and the force is recorded. The test is conducted on a Instron tensile tester, with one end of a fiber specimen glued to a metal tab that is connected to a load cell and shearing blades used to shear the cured microdroplet off. This is a rapid, simple technique and there is a linear trend of debonding force vs. embedded length.[19] However, the scatter in the data and nonuniform shear stress distributed along the interface and localized mainly at the top of the droplet are still inherent in this type of test.[17,18]

It should be noticed that all these adhesion tests mentioned above used model composite materials instead of actual composite materials. In this paper, the adhesion strength between the core fiber and skin coating was investigated using the actual composite textile fibers. The method developed, a fiber pull adhesion test, determines the bonding strength of the skin/core composite fibers.

EXPERIMENTAL

Materials and Sample Production

This research used 9 tex nylon 66 supplied by Shakespeare Monofilament Division of Anthony Industries as the core fiber and viscose rayon supplied by International Paper Company as the skin coating. FA was chosen to pretreat the nylon 66 core fibers for enhancing adhesion between skin and core. The structure of FA is presented in Figure 1. Ethanol was used to dissolve FA since the solubility in water was very low (less than 0.5%).
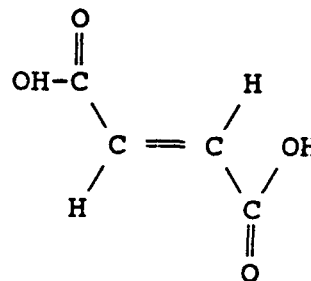

Figure 1 Structure of FA.

Table I presents the experimental design for the application conditions of FA. An incomplete randomized factorial experiment was used to determine the effects of concentration, the pretreatment time, and the interaction (concentration × time) on the adhesion in rayon/nylon composite fibers. One-half percent, 9 s, and 2%, 36 s, pretreatment conditions were excluded since a low concentration (0.5%) at the shortest pretreatment time (9 s) and a high concentration (2.0%) at the longest pretreatment time (36 s) were not expected to promote adhesion according to trial run results. After removal of the spin finish by 1 h water washing,[3] the nylon 66 fibers were pretreated with FA at the selected pretreatment concentrations and times and then were passed through a coating die where they were coated by viscose rayon flowing from a 10 kPa feed gauge pressure reservoir. The coated fiber then passed through a commercial strength rayon coagulation bath containing 9 wt % sulfuric acid and 13 wt % sodium sulfate, where the cellulose was regenerated from the viscose, forming a white solid rayon coating. The coated fiber was dried in a countercurrent flow drying tube (80–90°C), wound on a take-up device, and then washed with water after holding for 15 min.

Fiber Pull Adhesion Test

After the composite fibers were produced, a fiber pull adhesion test method was developed to test the interfacial adhesion of the composite fibers. In this technique, two Taber Calibrase CS-10 wheels (which are used to test abrasion resistance of fabrics in ASTM Method D3884-80[20]) were adapted and mounted as shown in Figure 2. A coated fiber was pulled through these nonrotating wheels at a speed of 5.2 m/min to abrade away the rayon skin coating from the core fiber. The distance between the wheel centers, which determines the compressive force levels, is adjustable. During the tests, the wheels were compressed at the following different com-

Table I   Application Conditions for FA

Fiber	Fumaric Acid Concentration (%)	Pretreatment Time (s)
1	0.5	18
2	0.5	27
3	0.5	36
4	1.0	9
5	1.0	18
6	1.0	27
7	1.0	36
8	1.5	9
9	1.5	18
10	1.5	27
11	1.5	36
12	2.0	9
13	2.0	18
14	2.0	27

pressive force levels and the fibers were pulled through the wheels, testing for coating failure:

1. At the impingement point.
2. 0.05 mm past the impingement point.
3. 0.10 mm past the impingement point.
4. 0.15 mm past the impingement point.
5. 0.20 mm past the impingement point.
6. 0.25 mm past the impingement point.
7. 0.45 mm past the impingement point.
8. 0.50 mm past the impingement point.

The applied interfacial shear stress τ was determined using the following formula modified from Ref. 17:

$$\tau = \frac{P\mu}{\pi d_f 1} \tag{3}$$

where P is the applied compressive force; μ, the frictional coefficient between the wheel and the composite fiber = 0.6; d_f, the fiber diameter = 0.102 mm; and 1, the embedment length:

$$1 = 2[R^2 - (R - Y)^2]^{1/2} \tag{4}$$

as shown in Figure 2. The applied compressive force P was determined by[21]

$$P = \frac{YbE}{x[1.788x^2 + 3.091 - 0.637/(1 + 12x^2)]} \tag{5}$$

where Y is the wheel deflection caused by the compressive load as shown in Figure 2 = distance past

the impingement point/2; b, the wheel length = 13 mm; x, the ratio of mean radius to wheel thickness = $[(R + r)/2]/(R - r)$ = 1.4; and E, the wheel modulus of elasticity = 11 MPa. From eq. (5), the compressive force in Newtons is

$$P = 0.0155 \times 10^6 \times Y \tag{6}$$

The frictional coefficient was determined by measuring the minimum angle at which the Calibrase CS-10 wheels would slide down an incline. The flat-end surface of the wheels, which is constructed of the same material as the rolling surfaces, was placed in contact with the coated fibers wrapped on the incline (Fig. 3). The angle was increased by changing the positions of a fine-threaded bolt until the wheel slid. This angle, α, was measured using a digital levelmeter. The coefficient of friction μ = tan α. Ten measurements were performed, giving an average α value = 30.7° and, therefore, μ = 0.6. A similar result was obtained by mounting the fabric knitted from the composite fibers on the incline.

From eq. (3),

$$\tau = 1873P/1 \ (\text{Pa}) \tag{7}$$

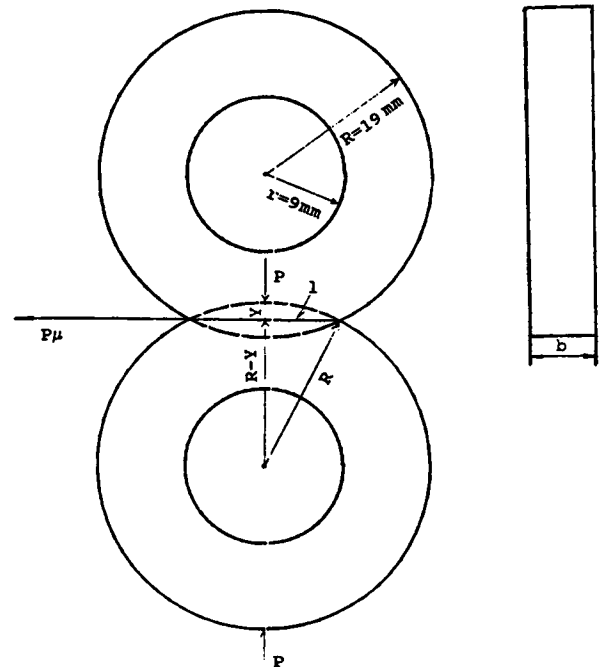A high interfacial shear stress value indicates good adhesion.
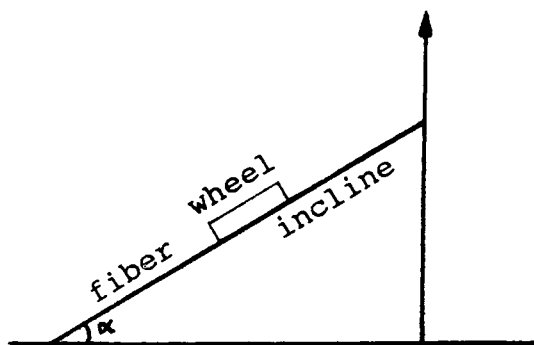

Figure 2   Fiber pull adhesion test.

Figure 3　Measurement of coefficient of friction.

Scanning Electron Microscope (SEM) Observation

The longitudinal surface and cross section of the coated unabraded and abraded fibers were observed using a scanning electron microscope. The purpose of SEM observation was to compare the surfaces of the coated fibers before and after the adhesion test in order to confirm the adhesion test results.

The fibers were cut with a razor blade to 5–10 mm lengths to enable mounting on 13 mm diameter stubs. The fibers were then mounted on the stubs with Spot-O-glue and air-dried. An Edwards S150 sputter coater was used to coat the specimens, which were examined with a Cambridge S-260 scanning electron microscope.

RESULTS AND DISCUSSION

FA has carboxyl end functional groups and has the *trans* configuration of this difunctional acid as opposed to the *cis* configuration of maleic acid. The double bond between the second and the third carbon atoms restricts rotation from the *trans* to the *cis* configuration, inhibiting reaction of these two functional groups to one surface only. Hydrogen bonds can form between cellulose and polyamide molecules and between FA and both cellulose and polyamide. With the existence of a mineral acid catalyst and elevated temperature, the carboxyl groups of FA can react with the amine end group of nylon, forming a stable amide linkage similar to those formed during polymerization of nylon 66. Because of steric hinderance, the other carboxyl ends of FA should react with the hydroxyl groups of rayon, forming stable ester bonds.[7] Because of the formation of these bonds, the adhesion between the skin and the core was improved.

The effectiveness of the FA pretreatment was determined by the fiber pull adhesion test. Since discrete positions were used, this is a discrete test. At the position of 0.05 mm past the impingement point, no coating was abraded away for any of these composite fibers. When the wheels were moved to 0.10 mm past the impingement point, the coating of the composite fibers with pretreatment conditions, 1.0% FA, 9 s; 0.5% FA, 18 s; 0.5% FA, 27 s; and 0.5% FA, 36 s, was abraded away. When the wheels were moved to 0.15 and 0.20 mm past the impingement point, the results were the same as at the position of 0.10 mm past this point. At 0.25 mm past the impingement point, only the coating of the fibers with pretreatment conditions of 1.0% FA, 36 s; 1.5% FA, 18 s; and 2.0% FA, 9 s, totally remained on the core fibers and completely survived. The coating of the composite fibers with pretreatment conditions of 1.0% FA, 18 s; 1.0% FA, 27 s; 1.5% FA, 9 s; 1.5% FA, 27 s; 1.5% FA, 36 s; 2.0% FA, 18 s; and 2.0% FA, 27 s, did not completely survive. When the wheels were moved to 0.45 mm past the impinge-

Table II　Interfacial Shear Strength of the Composite Fiber

| Pretreatment Condition	Distance Past Impingement (mm)		Compressive Force (N)		Interfacial Shear Strength (MPa)	
	Survive	Fail	Survive	Fail	Survive	Fail
All 0.5% FA treatment and 1.0% 9 s	0.05	0.10	0.39	0.78	0.37	0.53
1.0% FA 18 and 27 s; 1.5% FA 9, 27, 36 s; 2.0% FA 18 and 27 s	0.20	0.25	1.55	1.94	0.75	0.83
1.0% FA 36 s; 1.5% FA 18 s; 2.0% FA 9 s	0.45	Fiber breakage 0.50	3.49	Fiber breakage prior to debonding	1.12	Fiber breakage prior to debonding

(a)

(b)

(c)
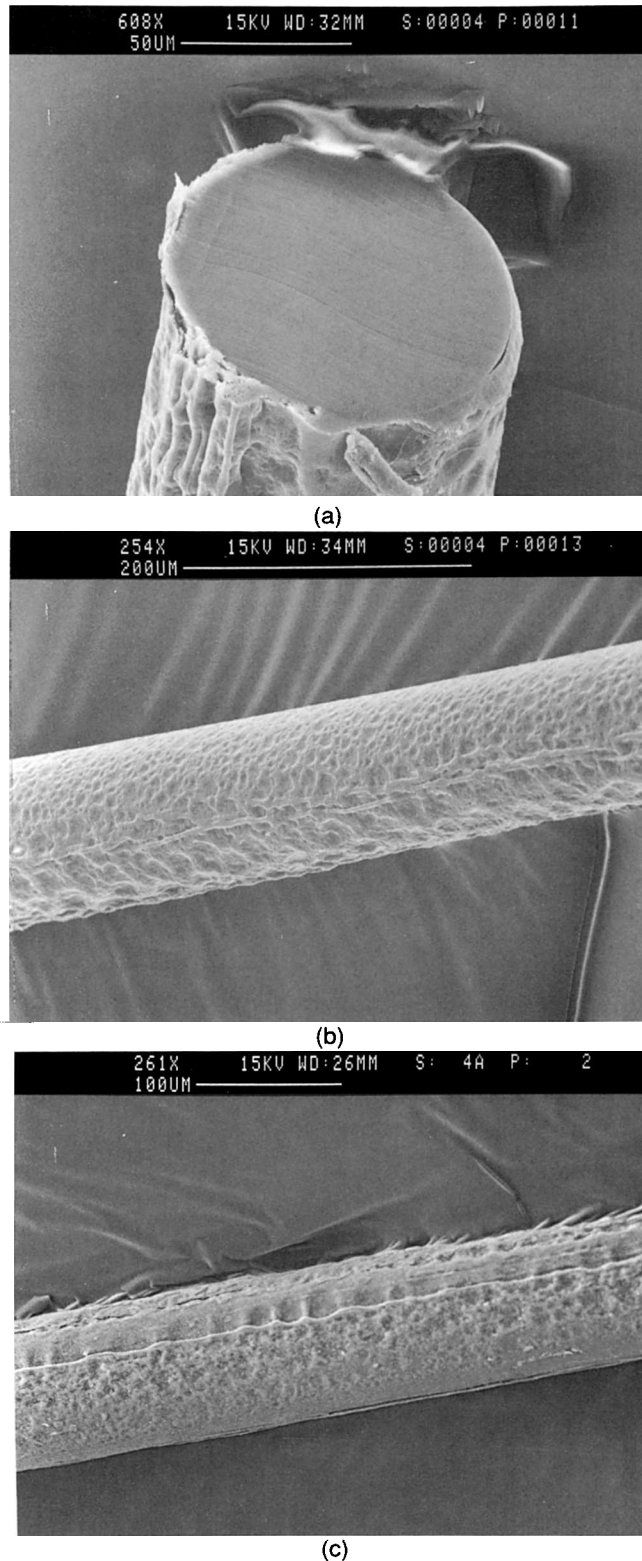
Figure 4   Good adhesion between skin and core with 1.0% FA 36 second pretreatment:
(a) cross section; (b) unabraded; (c) abraded.

ment point, the coating of the previous three sur-
viving sets still survived, but at the next position,
0.50 mm past the impingement point, the composite

fibers could not be pulled through the wheels since
the compressive force was too high, causing tensile
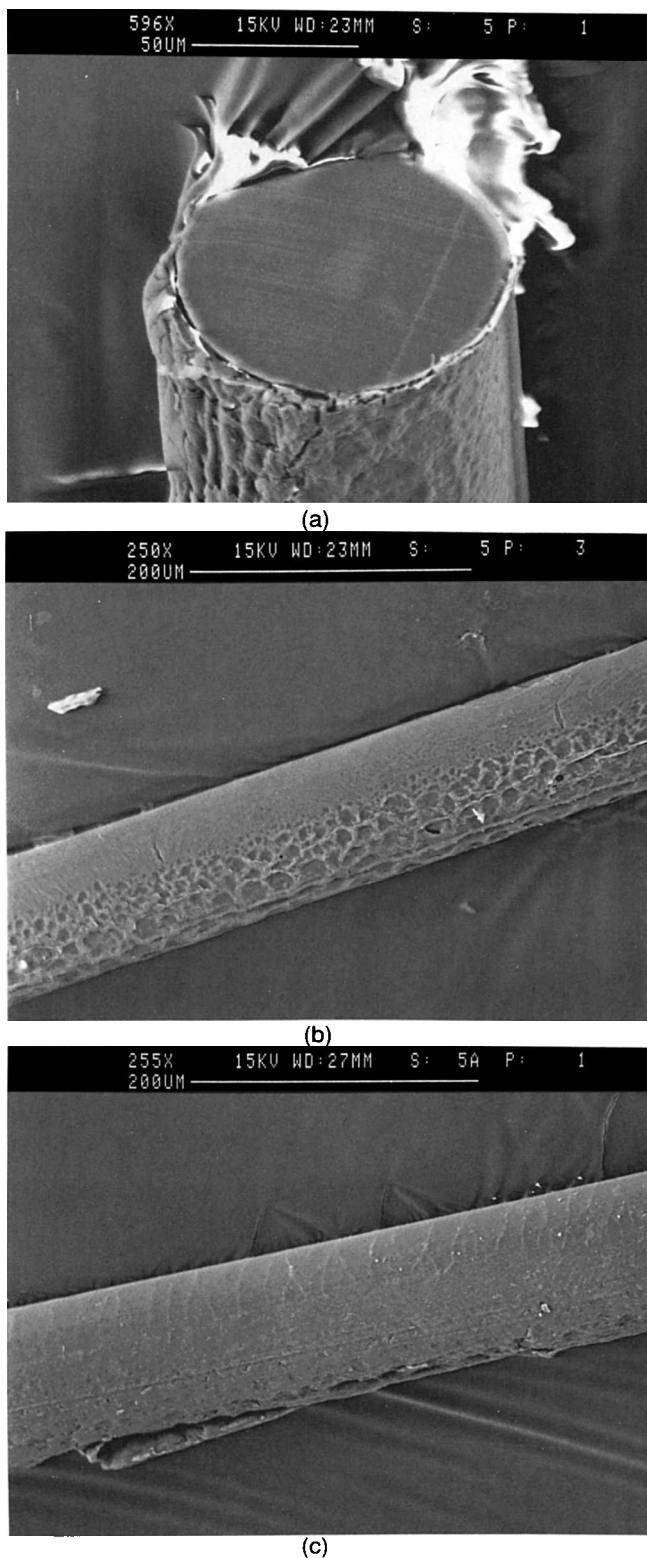failure of the core fibers. Therefore, the position of

Figure 5 Fair adhesion between skin and core with 1.0% FA 27 second pretreatment:
(a) cross section; (b) unabraded; (c) abraded.

0.45 mm past the impingement point was the tightest position that could be set to test the interfacial adhesion of the composite fibers.

Table II shows the calculated values of the applied interfacial shear stress using eq. (7). It is seen from Table II that both pretreatment concentration and
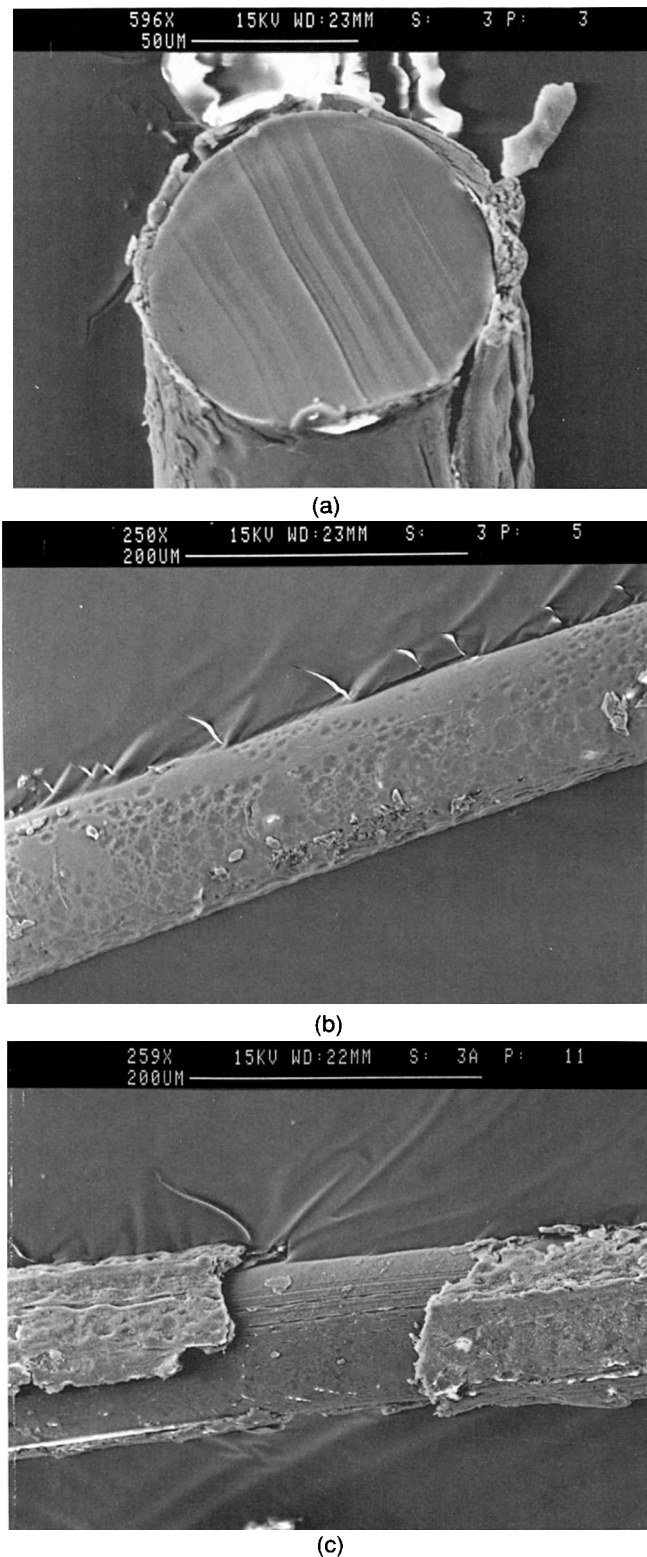
(a)

(b)

(c)

Figure 6   Poor adhesion between skin and core with 0.5% FA 18 second pretreatment: (a) cross section; (b) unabraded; (c) abraded.

time affected the adhesion; however, the interaction, pretreatment concentration multiplied by pretreatment time, is more significant. The three combi-

nations (1.0% FA concentration with 36 s pretreatment time, 1.5% FA concentration with 18 s pretreatment time, and 2.0% FA concentration with 9

s pretreatment time) gave the highest interfacial adhesion. The interfacial shear strength of the bond of the poor adhesion fibers was at least 0.37 MPa, that of the fair adhesion fibers was at least 0.75 MPa, and that of the good adhesion fibers was at least 1.12 MPa.

Scanning electron micrographs showing the cross section and longitudinal surface of the coated fibers before and after the fiber pull adhesion test are illustrated in Figures 4–6. The nylon core fibers are completely surrounded by the rayon skin coating with some pretreatment conditions showing good adhesion and others showing poor adhesion. At 1.0% pretreatment concentration with 36 s pretreatment time, a condition that gave the highest interfacial adhesion strength value, the coating adheres to the core and all the coating remains on the core fiber after the adhesion test (Fig. 4). At 1.0% FA concentration with 27 s pretreatment time, a condition that gave the intermediate interfacial adhesion strength value, localized debonding starts to occur (Fig. 5), whereas at 0.5% with 18 s, a condition that gave the lowest interfacial shear strength value, the coating is not totally adhered to the core fiber and general debonding occurred after the adhesion test (Fig. 6). It is also seen from these figures that the major failure mode is interfacial debonding. These SEM micrographs confirmed the fiber pull adhesion test results.

CONCLUSIONS

A new technique, the fiber pull adhesion test, was developed to test the interface-related shear strength using the actual composite material. The interfacial shear strengths of rayon/nylon sheath/core composite textile fibers under different FA pretreatment conditions were determined directly using the actual composite fiber. This method is simple and rapid, and no model sample preparation is needed. The test indicated that FA is an effective adhesion promoter to improve the interfacial adhesion in the rayon/nylon bicomponent fiber and there are interactions between the pretreatment concentration and time. A low concentration with a long pretreatment time and a high concentration with a short pretreatment time exhibit the best results. The test results were confirmed with SEM observation.

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