ESTIMATION OF FIBER-MATRIX INTERFACIAL SHEAR STRENGTHS IN LIGNOCELLULOSIC-THERMOPLASTIC COMPOSITES

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ABSTRACT

The interaction and adhesion between fibers and the matrix in composite materials have a significant influence on the properties of the fiber composite. It is, therefore, of utmost importance to be able to evaluate the properties of the interface/ interphase of the fiber-matrix for optimization of the properties of the composites. Techniques that are currently used to evaluate the properties of this region will be discussed with special attention to lignocellulosic-thermoplastic composites. Sample preparation, applicability, problems and advantages of each technique will be highlighted. Results obtained at our laboratory for wood-low molecular weight polyethylene systems using the pull-out test will be discussed.

INTRODUCTION

The fiber-matrix interface and interphase in a composite material determines the ability of the matrix to transfer stress to the fibers. (The interphase is a volume element with properties differing from the bulk properties of the fiber and the matrix, Fig. 1). This stress transfer efficiency plays a dominant role in determining the properties of the composite, and this is particularly so with short-fiber composites. Furthermore, an improvement in the fiber-matrix interaction results in enhanced off-axis properties, fatigue behavior, environmental resistance, compression behavior and creep properties of the composite. However, an improvement in the interfacial shear strength (IFSS) can result in a loss in composite toughness [1,2]. It is therefore important to "tailor" the interphasial region for optimized composite properties.

The fiber-matrix interphase

The properties of the interphase depends on the chemical nature of the fiber and the matrix and also on the type of interaction between the two bulk phases. The properties depend not only on the chemical interaction between the fiber surface and the matrix polymer, but also on molecular parameters and physical composition of the polymer adjacent to the fiber surface. It is important to remember that the properties of the polymer adjacent to the fiber surface can be quite different

from the polymer properties in the bulk form [3,4,5]. A solid surface can restrict the mobility of the macromolecules by curtailing bond rotation.

The performance of the composite is governed by the physico-chemical nature of the interphase [6] and several other important factors. The presence of defects (voids, etc.) [7], the fiber modulus (E_f), matrix modulus (E_m) and the interphasial modulus (E_i) are important considerations in studying the performance of the composite [5,8]. Stress concentrations around the interphase are due to the presence of a strain mismatch near the fiber- matrix interface and depends on E_f, E_m and E_i [5]. The following summarizes the factors that govern the properties and the performance of the interphase:

Properties:

---physico-chemical effects:

Chemical composition:
--functional groups and primary interactions such as covalent bonding, etc.
--surface effects-secondary interactions eg. acid-base interactions, etc.

Molecular parameters:
--branching, molecular wt. distribution of polymer adjacent to fiber, etc.

Physical composition:
--interpenetrating networks, crystallinity, thermodynamic segregation of polymer alloys, etc.

Performance:

---voids and surface defects.

---topography of fiber.

---interphase properties (as listed above).

---composite effects:

--stress distribution around interphase.
--strain mismatches between fiber, interphase and matrix.

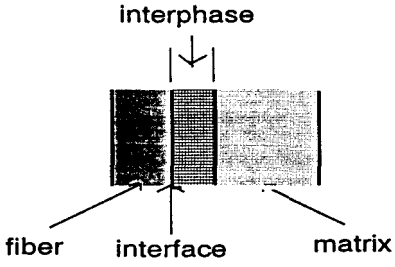

Figure 1. Schematic of the three phases of a composite: the fiber, the matrix and the interphase. The interface is a physical boundary between the fiber and matrix.

Interphase test techniques

In order to *"tailor"* the interphase for optimized composite properties, a reliable technique to evaluate the properties of the interphase is essential. Composite properties will reflect changes in the quality of the interphase, but factors such as fiber orientations and fiber length distribution can mask the real effect of interphase modification. The test used for interphasial evaluation should compare modifications reliably and also be useful in determining the mode of failure. The difference between adhesive stress transfer and frictional stress transfer is important and is one of the reasons that different fiber-matrix interface tests using the same fiber-matrix-interphase combinations show discrepancies [9].

Four methods are frequently used in estimating interphase properties and have recently been reviewed by a number of workers [9,10,11]. The fiber fragmentation test (Fig. 2A) involves embedding a single fiber in a polymer dog-bone shaped specimen and stressing the polymer in the direction of the fiber longitudinal axis. The fiber breaks into fragments until all the fragments are below the fiber critical length. The relationship between the IFSS and fragment lengths involves the ultimate fiber tensile strength, σ_u, and it is important to know the fiber strengths at lengths equal to the fragment lengths. The matrix and fiber Poisson's ratios (ν_m and ν_f, respectively) that contribute to shrinkage stresses are balanced [9,10]. However, the test is limited to systems where the matrix ultimate strain is at least three times that of the fiber [10]. Debonding is likely to precede ultimate fragmentation, and care needs to be taken to account for this. Studies using this test in comparing lignocellulosic-thermoplastic interphases have been conducted [12,13] and the test appears promising.

The fiber push-out test (Fig. 2B) is realistic as it utilizes a cross-section of the actual composite and invilves pushing a single fiber out of the composite using a nano-indentor. However, the disadvantage is that the Poisson's expansion of the fiber can result in high interfacial pressures and fiber crushing can occur near the indentor tip. This test, though useful for many sustems, is unlikely to be useful in case of organic fiber-organic matrix interphases where fiber crushing and buckling will occur prior to any push-out.

The pull-out test (Fig. 2C) and the micro-debonding test (Fig. 2D) are similar. The former involves a cylindrical button of matrix while the latter uses a small ellipsoidal bubble of the polymer around the fiber, It is difficult to obtain a consistent shape and size of the polymer bubble in the micro-debond test which can cause variations in the stress distribution during testing. This inconsistency does not occur in the pull-out test. Poisson's shrinkage of the fiber results in lower interfacial pressures for both the tests: external pressure can be applied to compensate for this in the pull-out test, though this can be inconvenient when testing a large number of samples.

The pull-out test

The selection of a test should accomplish two primary goals: (i) to effectively compare the IFSS of different fiber-matrix interphasial systems and (b) to determine the failure mode of the interphase. It is also important to use a test to simulate, as closely as possible the stress distribution in a real situation.

During the pull-out test, three possible modes of failure have been studied;

(i) the interphase yields, resulting in a uniform shear stress distribution along the fiber length. This results in a linear relation between the debonding force, F, and the embedded length, L:

$$F=2\pi rL\tau_{iy} \tag{1}$$

where r is the fiber radius and τ_{iy} is the yield stress of the interphase. This behavior has been observed with tungsten in copper **[14].**

(ii) Failure occurs when the stress reaches the interphase maximum stress , τ_{iu}, then the debonding force, F, is related to the embedded length by [15,16];

$$F=\frac{2\pi r^2\tau_{iu}\tanh(nL/r)}{n} \tag{2}$$

here, n is constant and is equal to;

$$n^2=\frac{E_m}{E_f(1+\nu_m)\ln(R/r)} \tag{3}$$

(iii) The third scenario is failure due to brittle fracture. Penn and Lee [17] considered the energy release of propagation of a crack and developed the relationship between F and L to be:

$$F=2\pi r^2(E_fG_i/r)^{1/2}\tanh(nL/r) \tag{4}$$

where G_i is the work of fracture of the interphase. There is, of course, a fourth case of mixed mode failure which is complex and difficult to analyze.

Comparing equations 2 and 4, an equivalent interfacial debonding shear strength , τ_d, for the fracture process can be obtained [9]:

$$\tau_d=n\sqrt{E_fG_i/r} \tag{5}$$

At low embedded lengths where $nL/r\leq 0.2$,

$$F \approx 2\pi r \tau_d L \quad (6)$$

and at higher lengths where $nL/r > 3$,

$$F \approx 2\pi r^2 \tau_d / n \quad (7)$$

In equation 7, F is independent of L and an asymptote of F is reached. Penn and Lee [17] have observed this dual type behavior of increasing F at lower L, followed by a constant F at larger L. If τ_d is known, then the work of fracture can be evaluated [9].

The pull-out test can also be used to estimate the interfacial pressure on the fibers and the coefficient of friction at the interface during sliding of the fibers. These factors are important contributors to toughness of composites, particularly in the energy absorption mechanism of crack propagation.

EXPERIMENTAL METHODS

Materials and treatments

Hardwood birch dowels (E_f=230 MPa, diameter (d)≈ 2.14 mm) were rinsed in distilled water and dried at 80°C. For consistency all the dowels were carefully polished in the same manner with a fine crocus cloth.

A low molecular weight polyethylene and a low molecular weight ethylene-acrylic copolymer were used as the matrix. Anionic emulsions of maleic anhydride-grafted polypropylene (E43) and maleic anhydride-grafted polyethylene (E15) were used to modify the fiber surface; both E43 and E15 have been used as compatibilizers in cellulosic fiber-thermoplastic composites systems. An emulsion of alkyl ketene dimer (AKD), a polyethenimine modified with epichlorohydrin (PEI) and an emulsion of a copolymer of ethylene and acrylic acid (EPA) were also used to modify the fiber surface. Details of the matrix polymers and the surface modifiers are listed below:

Matrix:

PE: Polyethylene (Scientific Polymer Prod., USA), MW_n =6500, 6000 centipoise at 140°C.

EAA: Ethylene Acrylic Acid copolymer (Scientific Polymer Products., USA), 5% acrylic acid content, acid number 40mg KOH/g, 500 cp at 140°C.

Coatings:

E43: Anionic Emulsion (Eastman Kodak Co.) of maleic anhydride-modified PP. MW_n-4500. (a) 3.5% solid content of MAPP in the emulsion and (b) 0.2% solid content in the emulsion.

E15: Anionic emulsion (Eastman Kodak Co.) of maleic anhydride-modified PE. 10 ml emulsion with distilled water to make 500 ml.

PEI: Polyethylenimine (PEI), epichlorohydrin-modified (17% solid in water) (Scientific Polymer Prod., USA). 10 ml mixed with 10 ml distilled water.

AKD: Alkyl Ketene Dimer (AKD). 0.2 % AKD in an anionic emulsion.

EAA: Emulsion of ethylene acrylic acid copolymer (EAP). %20 acrylic acid content- 2 % solid content of the copolymer.

Surface modification was carried out by dipping the dowels in the emulsions/ solutions for 15 min and drying the dowels at 105°C for 1 hour. This was followed by storing the dowels in an oven at 80°C until use.

Specimen preparation and testing

Pull-out specimens (Fig. 2D) were prepared using 12.5 mm inner diameter teflon tubes which were about 12.5 mm long. One end of the tube was sealed off using teflon sealing tape. The polymer in powder/pellet form was then inserted into the tube. The tubes were then placed in a special jig designed so that the thin wooden dowels could be inserted and held vertically in the center of the tube. Up to 20 specimen were fitted into the jig in one run, and the jig was placed in an oven, set at 170°C, which melted the plastic around the dowels. After 15 minutes the oven door was opened and the dowels were pushed lightly to ensure that they were totally embedded. The specimens were cooled in the oven after it was switched off.

Comparison of surface treatments was conducted by recording the debonded stress of at least 20 samples with embedded lengths varying between 2.0 mm and 21 mm. Higher lengths invariably resulted in matrix cracking when the specimen was removed from the holder. All samples with the dowels off center and with any cracks in the matrix were rejected. On average, about 15 to 18 specimens out of 20 were suitable for testing.

Testing was conducted using a Universal Tensile Tester at 2.5 cm per min, using a jig designed to shear the dowel from the matrix. The force needed to totally debond the dowel from the plastic, F, was recorded using a X-Y recorder. The rod diameter and embedded lengths were measured using a vernier calipers (average of five readings for each dowel) for every test performed.

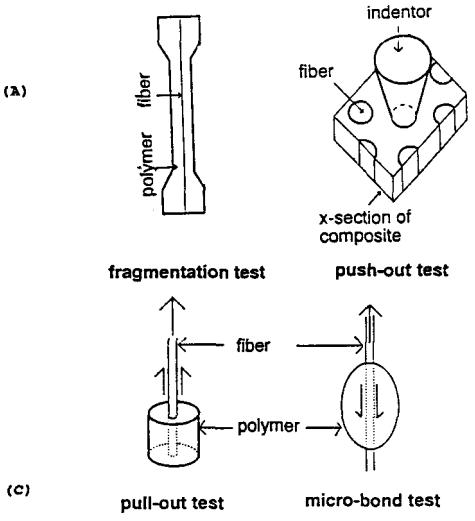

Figure 2. (A) the fragmentation test, (B) the push-out test, (C) the pull-out test, and (D) the micro-bond test.

RESULTS AND DISCUSSION

Length-Debonding Force Relationship.

Figure 3 shows a typical pull-out curve for unmodified and untreated wood dowels in polyethylene. The force increases until total debonding has occurred. In all the samples tested there appeared to be some nonlinearity near the point of total debonding. Some interphase yielding may be occurring, but any conclusions related to interphase failure through yielding may be misleading, as will be discussed later. At F there is sudden drop in force indicating that the dowel has debonded totally from the matrix. Frictional stresses are then generated at the interface and the dowels start retracting from the plastic button.

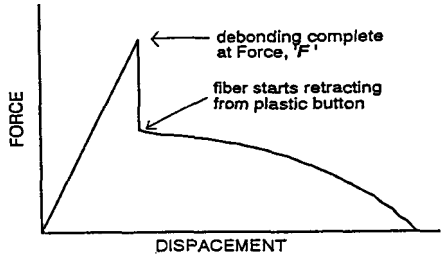

Figure 3. Typical force versus displacement curve during pull-out. F is the point of complete debonding of the dowel.

Figure 4 shows the plot between the debonded force, F, and the embedded length of E-43 treated (deposited from a 3.5% solid content emulsion) dowels in the PE matrix that were predried and polished. At low lengths there appears to be a linear increase in force, followed by a region where the force appears to be leveling off. This behavior, also observed by Penn and Lee [17] and Piggott [9,18], suggests that the debonding process is not constant over the length of embedment. A linear behavior suggests uniform stress distribution along the length of the fiber and that failure was due to interface yielding. A nonlinear region, as seen at higher embedded lengths in Fig. 4, suggest a complex mechanism that may involve a brittle type interface failure. To obtain meaningful comparative data in cases where fracture occurs at the interface it is necessary to evaluate a large distribution of embedded lengths.

The plot of debonding force versus the square root of the embedded length of untreated dowels in the PE matrix shows a more linear relationship (Fig. 5). Similar data scatter has been observed by others [9]. In all our tests performed with different surface-treated wood dowels, the F versus $L^{1/2}$ plot followed was linear. The interfacial shear strength versus the length or the aspect ratio (the aspect ratio is the ratio of the length to the dowel diameter) showed an asymptotically decreasing relationship consistent with earlier work [19]. An example of this can be seen in Fig. 6, where untreated dowels were pulled out from ethylene-acrylic acid copolymer.

Comparison of surface treatments

Penn and Lee [15] also suggest that a comparison should be made throughout the different regions of the debonding force-embedded length plot. Piggott [9] has suggested the use of results from short embedded lengths to avoid the complications arising due to the frictional contribution to the recorded debonding stress and thereby obtain a maximum interfacial strength. Pithkethly and Doble [19] also stress the importance of using the maximum interfacial shear strength since it is a key parameter in optimizing composite properties. A maximum interfacial shear strength can be obtained from the slope of the initial linear region of the force versus length plot. In our systems, the plateau regions were not apparent in the F vs. L plots; it is likely that the flattening of the curve occurs at higher embedded lengths. In our experiments, we were unable to obtain L more than 21 mm due to cracks forming in the plastic button while removing the samples. To minimize any contribution of the frictional stress of partially debonded dowels to the IFSS measurements the estimation of shear strengths were conducted at low embedded lengths.

Two methods were used to estimate the IFSS. The first was by drawing a linear line from the origin through the initial points resulting in a line with the apparent maximum slope (eg. the dotted line in Fig. 4). The second was by drawing a line, using linear regression, for all points below lengths equal to 3.0 mm. Table I shows data obtained using the different surface coatings. As expected, the untreated dowels showed the least

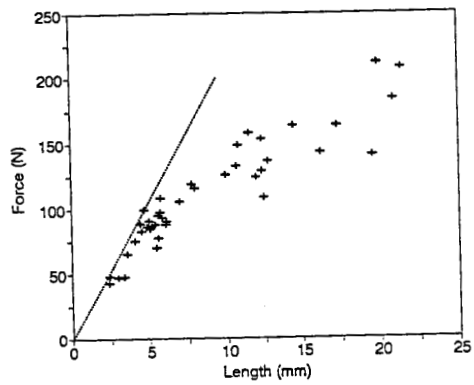

Figure 4. Debonding force versus length plot of the pull-out of E43 coated dowels-PE- dotted line is the apparent maximum slope through the origin.

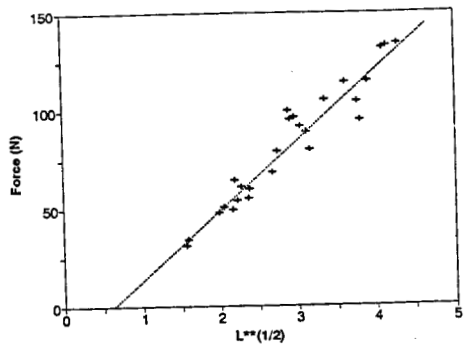

Figure 5. Plot of the debonding force versus the $L^{(1/2)}$ for untreated dowels in the polyethylene matrix.

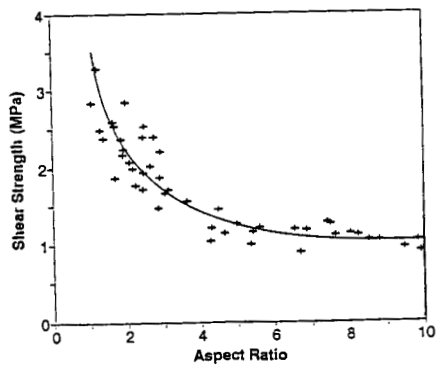

Figure 6. Plot of the shear strength of untreated dowels-ethylene-acrylic acid copolymer. (Aspect ratio is the ratio of the length by diameter.) Line shows visual trend.

IFSS for both methods of estimation. E-43 coated dowels the highest IFSS when PE was used as the matrix. Both PEI and AKD coated dowels had nearly equal shear strengths, an improvement over the untreated dowels but lower than the E43 coated samples. The improvement in IFSS over the untreated dowels are also shown in Table I. Both techniques showed similar differences. The ethylene-acrylic copolymer gave the highest shear strength and this is mainly due to enhanced secondary interaction between the polar component of the polymer, acrylic acid, (which is nonexistent in the PE matrix) and the highly polar cellulosic surface. Here, acid base interactions can enhance the properties of the interphase. It is also important to note that any change in the surface characteristics of the dowel will change the orientation of the polymer molecules adjacent to the surface: this factor will also contribute to any differences in the IFSS observed.

Since the F versus L was nonlinear, a brittle fracture is the likely failure mode. Estimation of the work of fracture, G_i, (from eqn. 5) is shown in Table 2. In this case E_f is known, n can be estimated (eqn. 3) and τ_d (from maximum slope) is given in Table 2. The improvement in G_i when using surface treatments is apparent. However, the work of fractures are very low. The low values could be attributed to the low molecular weight of the polymer and also to the formation of an interphase with properties different from that of the bulk matrix. The interphase region contains polymer molecules with restricted bond rotation capability due to hindrance from the solid surface. Molecular weight segregation and morphological changes in the interphase are also factors that are important.

The stabilization of fibers against moisture sorption is important to develop improved lignocellulosic-thermoplastic composites for outdoor application. Environmentally induced sorption can result in fatigue cycling at the interface that may be very destructive to interphase properties. Acetylation [20] is a well known method to decrease swelling in lignocellulosics through the stabilization of the cell wall and has potential to improve the environmental stability of the interphase and the properties of these organic fiber-organic matrix composites.

CONCLUSIONS

The pull-out technique developed in this study of the evaluation of interface bond strengths in cellulosic-thermoplastic systems appears to be quite reproducible. Differences in the maximum interfacial shear strengths were observed when changing the interaction potential between the two phases. We feel that for systems that have low interfacial shear strengths, the best gauge of the change in interface properties is obtained through an estimate of the maximum interfacial shear strength, which was obtained graphically from the initial linear region of the debonding force versus the embedded lengths. The low interphasial work of fracture obtained for our systems is likely due to the surface interaction between the fiber and the polymer causing changes in the morphology and molecular weight distributions of the polymer adjacent to the fiber-matrix interface.

TABLE I-Comparison of surface treatments.

pull-out system	Shear Strength -from maximum slope.		Shear Strength -from Linear Regression	
	IFSS- (MPa)	% of control	IFSS- (MPa)	% of control
untreated-PE	2.0	100	1.72	100
E43(3.5%)coated -PE	3.1	155	2.75	160
EAA coated-PE	2.6	130	2.41	140
AKD coated-PE	2.4	120	2.03	120
PEI coated-PE	2.4	120	2.10	120
E15 coated-PE	2.7	135	2.42	140
E43(.2%) coated-PE	2.8	135	---	---
untreated-EAA matrix	3.3	165	2.65	155

TABLE 11-Estimated work of fracture (eqn. 5) of selected interphases.

pull-out system PE matrix	Work of fracture Gi(J/m2)	% change
untreated	151	0
E43(3.5) coated	363	240
EAA coated	255	169
AKD coated	217	144

ACKNOWLEDGEMENTS:

The work reported here was supported by Dr. Helena Chum and the National Renewable Energy Laboratory (formerly Solar Energy Research Institute), Golden, Colorado (Grant Number 144 AD 34). The authors would also like to acknowledge the comments of G. E. Myers during the course of this work.

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In: Rowell, Roger M.; Lautenberg, Theodore L.; Rowell, Judith K., eds. Materials interactions relevant to recycling of wood-based materials: Proceedings of Materials Research Society symposium; 1992 April 27-29; San Francico, CA. Pittsburg, PA: Materials Research Society; 1992:

MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS VOLUME 266

Materials Interactions Relevant to Recycling of Wood-Based Materials

Symposium held April 27-29, 1992, San Francisco, California, U.S.A.

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MATERIALS RESEARCH SOCIETY
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CODEN: MRSPDH

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Published by:

Materials Research Society
9800 McKnight Road
Pittsburgh, Pennsylvania 15237
Telephone (412) 367-3003
Fax (412) 367-4373

Library of Congress Cataloging in Publication Data

Materials interactions relevant to recycling of wood-based materials/editors, Roger M. Rowell, Theodore L. Laufenberg, Judith K. Rowell.
p. cm. -- (Materials Research Society symposium proceedings,
ISSN 0272-9172; v. 266)
Includes bibliographical references and indexes.
ISBN 1-55899-161-1
1. Waste paper--Recycling--Congresses. 2. Composite materials--Congresses.
I. Rowell, Roger M. II. Laufenberg, Theodore L. III. Rowell, Judith K. IV. Series: Materials Research Society symposium proceedings; v. 266.
TS1120.5.M38 1992 92-26330
676'.142--dc20 CIP

Manufactured in the United States of America