

Effect of Fiber Treatments on Mechanical Properties of Coir or Oil Palm Fiber Reinforced Polyester Composites

C. A. S. HILL,¹ H. P. S. ABDUL KHALIL²

¹ School of Agricultural and Forest Sciences, University of Wales Bangor, Gwynedd, LL57 2UW, United Kingdom

² School of Industrial Technology, Wood, Paper, and Coatings Division, Universiti Sains Malaysia, 11800 Penang, Malaysia

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ABSTRACT: The use of plant fibers as a reinforcement in polyester matrices requires the issue of compatibility between the two phases to be addressed. Because plant fibers present hydrophilic surfaces and polyesters are generally hydrophobic, poor fiber–matrix dispersion and wetting of the fibers by the matrix may result. As a consequence, the mechanical properties of the composite are severely reduced. This study considers the effect of fiber treatment by chemical modification of the fibers (acetylation) or the use of silane or titanate coupling agents on the mechanical properties of coir or oil palm reinforced polyester composites. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1685–1697, 2000

Key words: natural fibers; composite; coupling agents; acetylation; mechanical properties

INTRODUCTION

The use of long vegetable fibers as replacements for glass for reinforcement in composites is currently generating much interest in the research community. Plant fibers offer a number of advantages over glass in such applications. Because plant fibers sequester CO₂ from the atmosphere, their use represents a net positive contribution to the global carbon budget. The ultimate disposal of composites is an important issue; plant fiber based composites may be combusted or composted at the end of their product life cycle, an option not possible with glass fiber reinforced equivalents.¹ Cost benefits may also be realized by the use of plant fibers as a replacement for glass.² Within a European context, the overproduction of certain agricultural commodities has resulted in great

interest in the production of alternative crops on set-aside land.³ Tropical fibers such as coir⁴ or oil palm⁵ are produced in millions of tons per annum; new applications are urgently required for these materials.

The use of plant fibers in composites are the subject of a number of reviews.^{6–8} Although such fibers are generally considered to be viable for use in composites, the problem of compatibility of the fiber with the matrix is an area that must be considered. Plant fibers are hydrophobic in nature because of an abundance of hydroxyl groups, so they are not compatible with hydrophobic matrices such as polyester. This incompatibility leads to a low fiber–matrix interfacial bond strength, poor wetting of the fibers by the matrix resin, and a reduction in mechanical performance when the composite is exposed to moisture.^{9,10} For this reason a number of studies looked at the effectiveness of coupling agents such as silanes with sisal/epoxy,¹¹ jute/epoxy,¹² jute/polyester,¹³ and banana fiber/polyester.¹⁴ Titanate coupling

Correspondence to: C. A. S. Hill (c.a.s.hill@bangor.ac.uk).

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agents were also investigated with jute/polyester composites.¹⁵ An alternative approach is to alter the surface chemistry of the fibers by chemical modification. Of the various reactions possible, acetylation with acetic anhydride appears to be the most viable, both technically and commercially.¹⁶ The effect of acetylation upon the interfacial shear strength (ISS) properties between modified wood fiber and polystyrene was reported,¹⁷ and an increase in the ISS was observed when acetylated fibers were used.

The purpose of the study reported herein was to determine whether acetylation of plant reinforcing fibers would lead to any improvement in the mechanical properties of composites formed therefrom. We anticipated that an enhancement in properties such as the tensile strength (TS) and modulus (TM) would result, because a reduction in the hydrophilic nature of the fiber improves resin–fiber compatibility. Furthermore, Hill et al. established that an improvement in the mechanical properties of coir and oil palm empty fruit bunch fibers (op-efb) occurs as a result of acetylation, provided that the reaction temperature does not exceed 100°C.¹⁸ Improvements in the mechanical properties, if observed, would probably be due to a combination of the above effects. The tensile, flexural, and impact properties of coir and op-efb polyester matrix composites were determined for unmodified and acetylated fibers in a range of fiber contents. A comparison study was also made with fibers treated with silane or titanate coupling agents at a fiber content of 45% (by weight). Although throughout this article reference is made to coir or op-efb fibers, it should be noted that these were fiber bundles rather than ultimates.

EXPERIMENTAL

Fiber Preparation

The op-efb was supplied by Sabutek Ltd. (Malaysia); coir fibers were supplied by the BioComposites Centre (U.K.). Nonwoven plant fiber mats were prepared on a Dilo model UC-11/30-1973 needleloom machine by JB Plant Fibers Ltd. (Holyhead, Anglesey, U.K.). Mats were cut to dimensions of 25 × 30 cm. Several mats were coiled together and tied with string and then placed in a Soxhlet apparatus. Solvent extraction was performed with a mixture of toluene/acetone/methanol (4:1:1, by volume) for 5 h. After extraction the

mats were uncoiled and dried in an oven at 105°C overnight. After drying, the mats were allowed to cool in a desiccator over silica gel before weighing. The fiber mats were then used without further treatment, chemically modified by acetylation, or treated with a silane or titanate coupling agent.

Fiber Treatment

For acetylation the oven-dried fiber mats were placed in a 3-L reaction flask, and sufficient reagent grade acetic anhydride was added to the flask to ensure that the mats were covered. The flask and contents were placed in an oil bath set at 100°C, a reflux condenser was fitted, and heating was continued for 30 min. At the end of this time the flask was removed from the oil bath, and the mats were withdrawn from the flask and placed in another flask containing acetone. The reacted mats were then refluxed for 3 h to remove unreacted reagent and by-product. The modified and extracted mats were then dried in an oven at 105°C overnight. This method resulted in a weight gain of 8–10%, which was due to modification.

For silane treatment the fiber mats were vacuum impregnated with a 5% solution (by weight) of γ -methacryloxypropyltrimethoxy silane [Aldrich; Fig. 1(b)]. The fiber mats were vacuum impregnated with a 5% solution (by weight) of the silane in methanol for 30 min, then they were allowed to soak in the solution at room temperature for 24 h. The mats were then removed from the solution and the solvent allowed to evaporate in an air stream at room temperature. Following this the treated mats were heat cured in an oven at 100°C for 5 h. The weight gain due to such treatment was in the range of 5–6%.

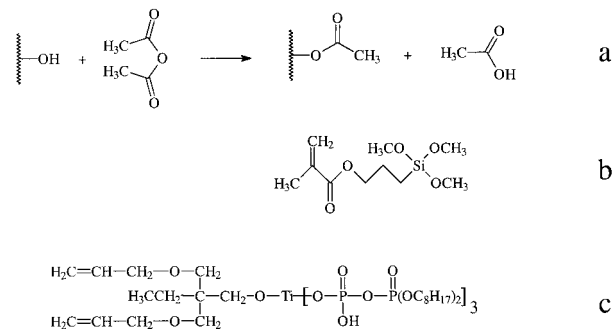


Figure 1 (a) The reaction scheme for acetylation and the molecular structures of (b) γ -methacryloxypropyltrimethoxy silane and (c) neopentyl(diallyl)oxytri(dioctyl)pyrophosphate titanate.

For titanate treatment the mats were vacuum impregnated with a 5% solution of neopentyl(diallyl)oxytri(diethyl)pyrophosphate titanate [Lica 38, Kenrich Petrochemicals Inc.; Fig. 1(c)] in toluene for 30 min, followed by soaking for 24 h at room temperature. The mats were removed from solution and the solvent allowed to evaporate in an air stream at room temperature. Treated mats were heat cured in an oven at 75°C overnight. This treatment method resulted in weight gains of 5–8%.

ISS Determination

In order to determine the effect of acetylation on the interfacial properties, determination of the ISS between unmodified or acetylated fibers and the matrix was performed. Perspex specimen holders were prepared. Their dimensions are shown in Figure 2. Fibers were acetylated to low (below 10 wt %) and high (approximately 18 wt %) weight percent gains by heating for 30 min or 3 h accordingly. Fibers were placed in the center of the specimen holders and resin (Crystic 471 PALV, Scott Bader) was added using a 0.1-mm diameter pipette, such that the embedded length of the fibers was about 10 mm. The resin was allowed to cure at 20°C overnight. In addition to testing the ISS between the fiber and resin, a series of tests was performed using styrene as the matrix. In this case, styrene was mixed with azobisisobutyronitrile as a catalyst in a ratio of 100 : 0.2 (v/w). After the resin and fiber were added to the holder, the samples were partially cured at 20°C for 4 h and then placed in an oven at 70°C to

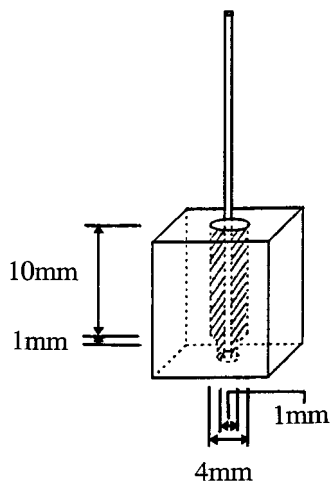


Figure 2 A schematic of a sample holder used for the interfacial shear strength tests.

cure overnight. Prior to the fiber pull-out tests, samples were conditioned at 65% relative humidity and 25°C for 1 week. Testing was conducted using an Instron universal testing machine (model 4301) at a crosshead speed of 0.5 cm/s. The force required to totally debond the fiber from the matrix was recorded. The embedded length of the fiber was determined using a Vernier calliper, and the fiber diameter was determined using a traveling microscope. Thirty-five replicates were used for each fiber treatment or resin type. The maximum of the ISS was estimated using the following equation:

$$\tau_{\max} = F_{\max} / \pi DL \quad (1)$$

where τ_{\max} is the maximum ISS, F_{\max} is the maximum force required to debond the fiber, D is the mean fiber diameter, and L is the embedded length of the fiber.

Composite Manufacture

A commercially available polyester (Crystic 471 PALV, Scott Bader) was used as the matrix phase. The formulation consisted of 100 parts resin/1.5 parts (by weight) catalyst (methyl ethyl ketone peroxide, Scott Bader). The resin was prepared by thoroughly mixing the resin plus hardener and then subjecting it to a vacuum to remove trapped air. A high density polyethylene liner was used for fiber mat impregnation. The liner was closed in the middle with clips, one-half was filled with resin, and the end was sealed with tape. The fiber mat was placed in the other half of the liner, which was then connected to a vacuum pump. A vacuum was applied to the liner containing the fiber mat; then the clips in the center were removed, thus allowing the resin to flow into the mat. The process of resin impregnation was aided by the application of a hand roller to the exterior of the liner. Once impregnation of the mat was complete, the vacuum connection was removed and the liner cut open. The resin impregnated mats were transferred to an 8 mm thick perspex sheet, which was placed in a cold press. Spacers of 6-mm thickness were placed around the mat, and the mat was compressed until the top platen of the press closed onto the spacers, squeezing out excess resin in the process. The press was left closed at room temperature overnight to allow partial cure of the resin. The press was then released, the plate dismantled, and the composite

placed in an oven at 40°C for 18 h to postcure the resin.

Density Determinations

The density of the coir and op-efb powder was determined based on the 1987 ISO pyknometer method for high precision measurements at all ranges of polymer dispersions; a glass pyknometer (Gay–Lussac type) was used. The composite densities were determined by weighing a sample of known volume on a four figure balance. The volume was determined by measuring the dimensions of the sample using a Vernier calliper. Samples were oven dried at 50°C for 24 h prior to measurement.

Mechanical Testing

All mechanical tests were performed following conditioning of the specimens at 22°C and 65% relative humidity for 1 week in accordance with BS2782.

Tensile tests of the composites were performed on an Instron model 4301 according to BS2782. The tests were performed using a load cell of 500 N with a gauge length of 50 mm and crosshead speed of 2 mm/min. For each test batch, 10 dumb-bell-shaped specimens were cut from a composite sheet using a Beaver NC5 router connected to a Crusader II computer control system. A tungsten spindle was used to cut the specimens. Samples were carefully edge sanded to remove any small cracks. The TS to failure (σ), TM (E), and strain to failure (ϵ) were determined.

The flexural properties were determined according to BS2782. Samples of 12 × 1.5 × 0.6 cm (length × width × thickness) dimensions were cut using a radial arm saw equipped with a diamond cutter (Herber Arnold 72/300). The sample edges were carefully sanded to remove small cracks. The support span for the flexural tests was 10 cm and the diameter of the loading nose was 1 cm. Tests were conducted using a crosshead speed of 2 mm/min on an Instron model 1195. Because the modulus is determined from small initial deflections, a low force load cell (500 N) was used to ensure accuracy. The load deflection curve was recorded until sample failure. The means of 12 results were used for calculating the flexural strength (FS) and flexural modulus (FM). The FS (σ_f) was calculated from the equation

$$\sigma_f = (3FL)/(2bh^2) \quad (2)$$

where F is the force (N), L is the distance between the supports (mm), b is the specimen width (mm), and h is the specimen thickness (mm).

The FM (E_f) was calculated according to

$$E_f = [L^3/(4bh^3)][\Delta F/\Delta d] \quad (3)$$

where ΔF is the change in force of the initial linear part of the load deflection curve (N) and Δd is the corresponding change in deflection.

Impact tests were performed according to BS2782. Test specimens (10 replicates, 6.5 × 1.5 × 0.6 cm) were tested on a Zwick model 5101 impact pendulum tester at a velocity of impact of 3.8 m/s and a 160° swing angle using a 15-J hammer. The Charpy impact strength was calculated according to

$$(A/xy) \times 10^3 \quad (4)$$

where A is the impact energy (J), x is the specimen width (mm), and y is the specimen thickness (mm).

Scanning Electron Microscopy (SEM)

Samples were mounted onto holders using double-sided electrically conducting carbon adhesive tabs. Specimens were coated with gold to a thickness of 20 nm using a Polaron Equipment Limited model E500 coater at a voltage of 1.2 kV (10 mA) in a vacuum of 20 Pa for 10 min. Samples were observed with a Hitachi S-520 SE microscope.

RESULTS AND DISCUSSION

ISS

Table I shows the variation in ISS with low and high degrees of acetylation with styrene or polyester matrices. Acetylation of fibers increases the ISS in all cases compared to the unmodified fibers. The effectiveness of the fiber–matrix bond depends upon the compatibility of the two phases and the mechanical “keying” between the fiber and the matrix.¹⁹ The results of an ANOVA test showed that there was no significant difference in the ISS between coir and op-efb fibers, but there was between modified and unmodified fibers ($p \leq 0.05$). There was no significant difference between fibers modified to low or high weight percent gains. These results indicate that acetylation of the fibers improved the compatibility between

Table I Mean Values of Maximum Interfacial Shear Strength (MPa) for Unmodified and Acetylated Fibers with Polyester or Polystyrene Matrices

Matrix	Oil Palm (efb)			Coir		
	Unmod.	Low wpg	High wpg	Unmod.	Low wpg	High wpg
Polystyrene	1.62 (0.71)	2.39 (0.74)	2.74 (0.99)	1.35 (0.67)	2.29 (0.66)	1.96 (0.78)
Polyester	1.39 (0.37)	1.97 (0.43)	1.83 (0.53)	1.48 (0.32)	1.92 (0.37)	1.98 (0.43)

The standard deviations are in parentheses. wpg, weight percent gain.

the fibers and matrix in both cases. This was due to such modification rendering the fiber surface more hydrophobic.

SEM Studies of Fiber Surfaces

The effect of different treatments upon the fiber surface morphology is shown in Figure 3. Figure

3(a) illustrates the surface of an op-efb fiber. It exhibits a corrugated topography with the presence of numerous pits containing silica bodies about 3 μm in diameter (identified using SEM and energy-dispersive X-ray analysis). Acetylation [Fig. 3(b)] removes these silica bodies, although the undulating surface appearance remains. Following silane treatment [Fig. 3(c)] both

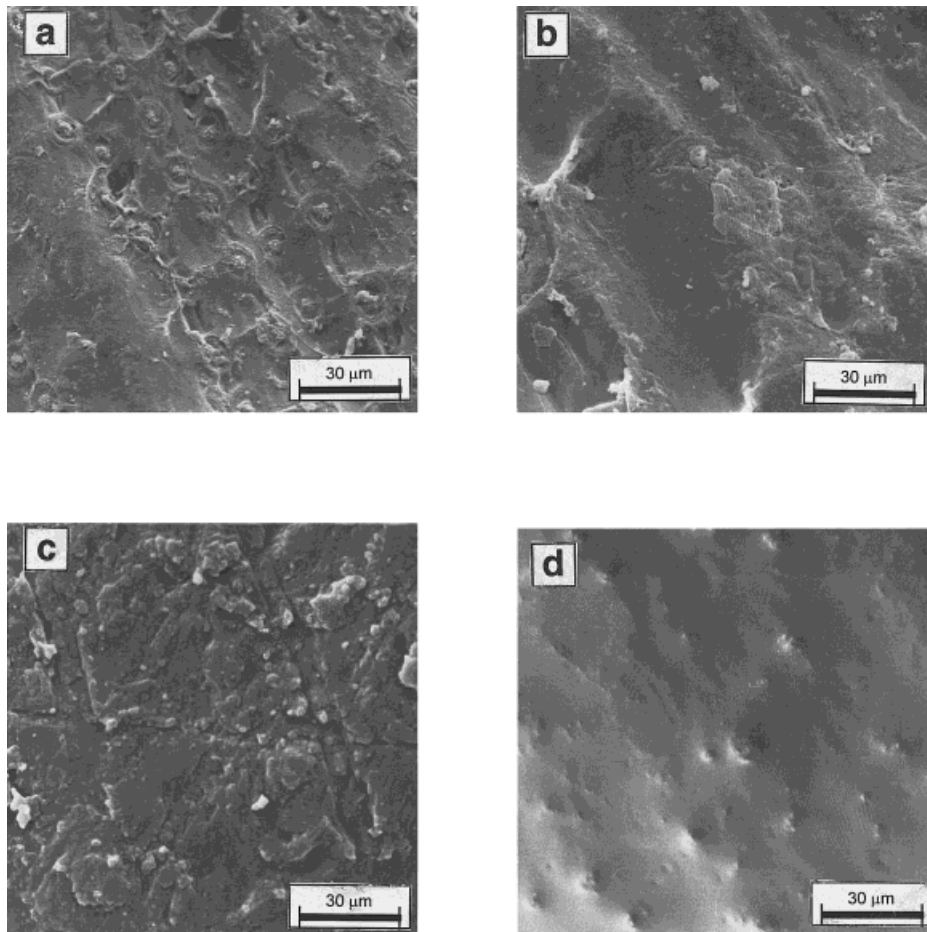


Figure 3 SEM micrographs illustrating the surface topography of (a) untreated, (b) acetylated, (c) silane treated, and (d) titanate treated op-efb fibers.

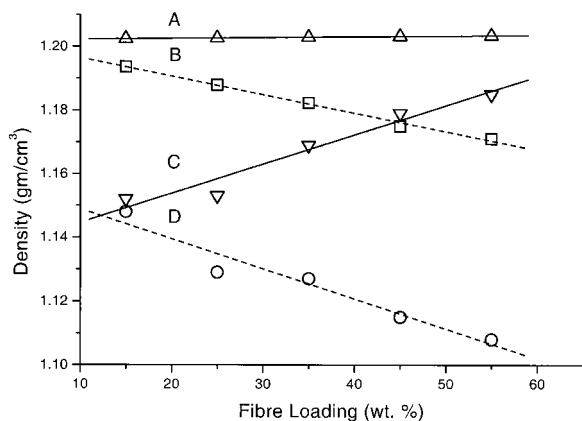


Figure 4 The effect of increasing fiber loading upon the theoretical composite density for (Δ , line A) coir and (\square , line B) op-efb compared with experimentally determined values for (∇ , line C) coir and (\circ , line D) op-efb reinforced polyester matrix composites.

these features are absent. Instead, a rough irregular surface is present. Titanate treatment produces a very smooth coating [Fig. 3(d)], although a number of silica bodies are clearly protruding through this.

Density Determinations

Figure 4 shows the effect of varying the fiber weight fraction upon the composite density compared with the theoretical value calculated from the measured density of the plant cell wall material and the polyester matrix. The density of the op-efb and coir powder was found to be 1.138 and 1.205 g/mL, respectively, and the density of the matrix was 1.202 g/mL. It is apparent from Figure 4 that the density of the op-efb reinforced composites decreased as the fiber content increased. This was anticipated, because the density of the op-efb cell wall material was less than that of the matrix. The measured density of the composites was lower than calculated. Furthermore, the rate of density decrease with fiber loading was greater than that theoretically predicted. With coir reinforced composites the behavior was different. The density of the composites increased proportionally with fiber loading.

Again, this observation is predictable because the density of the coir cell wall material is higher than that of the matrix. The measured density was again lower than that theoretically predicted, but this difference became smaller as the fiber content increased. The difference between the theoretical and experimentally determined densi-

ties was assumed to be due to the presence of voids in the composite. These voids may occur in the matrix, at the fiber–matrix interface, or within the fiber lumens. In the op-efb reinforced composites the void content increased with fiber loading, but with coir the void content decreased as the fiber loading increased. This may be due to the higher lignin content of the coir fibers, which renders them more hydrophobic and hence allows for better wetting by the resin. Unfortunately, it was not possible to determine the density of the cell wall material of acetylated fibers using the pycnometer method, because effective wetting by water was not possible because of entrapped air bubbles.

Tensile Properties

The effect of fiber acetylation upon the tensile properties of composites was determined for a range of fiber contents from 0 to 55% (by weight). The results for the TS are illustrated in Figure 5 for efb and coir. The surfaces of the cellulosic fibers are rendered more hydrophobic by acetylation, and it would be expected that enhanced compatibility between fiber and matrix would occur as a consequence. This would lead to improved wetting of the fiber by the polyester resin and a stronger interfacial bond. It would therefore be anticipated that more efficient stress transfer would occur between the fibers as a load is applied. In addition, it was shown that modified fibers exhibited higher TS and TM values when acetylated, which was due to a lower equilibrium

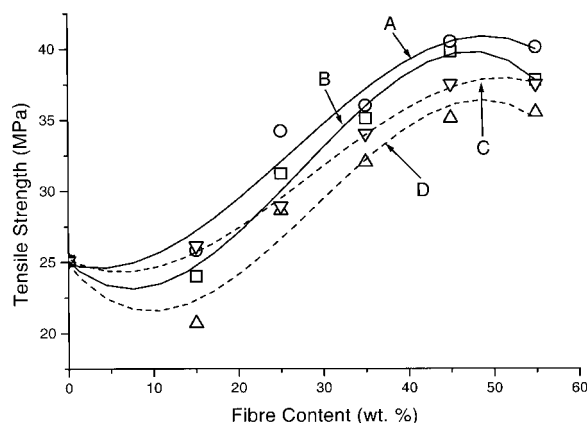


Figure 5 The variation of the tensile strength with fiber loading for polyester matrix composites reinforced with (\circ , line A) acetylated coir, (\square , line B) unmodified coir, (∇ , line C) acetylated op-efb, and (Δ , line D) unmodified op-efb.

Table II Fiber Properties of Unmodified and Acetylated Coir and Oil Palm Empty Fruit Bunch (efb) Fibers

Property	Oil Palm (efb)		Coir	
	Unmodified	Acetylated ^a	Unmodified	Acetylated ^a
Diameter (mm)	0.408 (0.081)		0.336 (0.094)	
Cellulose ^b (%)	48		47	
Hemicellulose ^b (%)	22		15	
Lignin ^b (%)	25		31	
Length (m)	0.130 (0.044)		0.113 (0.035)	
σ (MPa)	130 (34)	136 (25)	144 (34)	152 (32)
E (GPa)	3.58 (0.56)	3.88 (0.66)	4.69 (0.75)	5.12 (0.96)
ε (%)	9.70 (2.09)	8.80 (2.81)	14.21 (3.36)	13.30 (3.07)

The standard deviations are in parentheses.

^a There is a 9 wt % gain.

^b See Hill et al.¹⁸

moisture content associated with the modified fiber (Table II).¹⁸ A higher value for the TS of the composite would thus be expected for reinforcement with acetylated compared to unmodified fibers. The results presented in Figure 5 do show that higher TS values were obtained when using acetylated fibers, although the improvements realized were only marginal. Furthermore, it is apparent that the small improvement in the TS due to the use of acetylated fibers is lessened as the fiber content of the composite is increased. The relationship between the TS and fiber loading is of interest. At a fiber weight fraction of 15%, the TS values do not increase beyond that recorded for the unreinforced resin; indeed, with the unmodified fibers a fall in the TS is seen. Thereafter, the TS increases proportionally to the fiber loading, except at the highest weight fraction where a decrease in the TS occurs. This behavior was reported previously for randomly oriented natural fiber reinforced composites.^{14,20} With unidirectional fiber reinforced composites a linear relationship between the TS and fiber content was observed,¹⁹ although there was a tendency for the TS to fall off at high fiber contents.²¹ The decrease in TS at the highest fiber loading is associated with the greater likelihood of fiber–fiber contact occurring, resulting in inefficient stress transfer between fibers.⁵ Resin starved areas were also noted at very high fiber loadings.²² At the lowest fiber content it is possible that the presence of voids at the resin–fiber interface may be responsible for this reduction in the TS. The resin penetration into a nonwoven or random fiber mat may not be completely homogeneous; thus, the

regions where the resin flows around the fiber intersections may lead to the presence of voids in the matrix. The behavior of the flow of the resin is affected by the surface properties of the fiber, so better contact between the resin and the fiber surface occurs if the fiber is more hydrophobic. Thus, the decrease in TS at the lowest fiber content is lower with acetylated fibers and with coir compared to op-efb fibers. In the latter case, the explanation may be the higher lignin content of the coir (31%) compared with op-efb (25%), resulting in a more hydrophobic surface.²³ This is consistent with our earlier explanation given for the observed changes in density in the ISS with fiber loading. However, no difference was noted in the ISS between coir and op-efb fibers when embedded in a polystyrene or polyester matrix. In this case it is likely that the effects of mechanical keying obscure those due to differing lignin contents. The decrease in TS at low fiber loadings is observed in composites where the matrix phase has a higher strain to failure than the fiber phase.²⁴ With the composites investigated in this study, the fibers had much higher strains to failure than the resin; hence, this form of behavior would not be predicted. However, because the fibers are not aligned along the tensile axis of the specimen, this simple interpretation may not be viable. If some account is taken of the essentially random 3-dimensional orientation of the fibers in the matrix, then it may be more reasonable to take an average value of one-third of the fiber elongation to break for the value in the composite. If this is done, then the values for op-efb, acetylated op-efb, coir, and acetylated coir become 3.2,

Table III Comparison of Fiber Acetylation with Coupling Agent Treatment on Composite Tensile Properties at Fiber Weight Fraction of 45%

	Oil Palm (efb)			Coir		
	σ (MPa)	E (GPa)	ε (%)	σ (MPa)	E (GPa)	ε (%)
Unmodified	35.1 (2.3)	3.29 (0.5)	3.75 (0.22)	39.8 (3.0)	3.60 (0.19)	5.20 (0.45)
Acetylated	37.5 (4.7)	3.70 (0.45)	3.48 (0.52)	40.5 (3.4)	4.01 (0.39)	4.54 (0.52)
Silane	36.8 (2.3)	3.60 (0.25)	3.60 (0.25)	36.6 (1.7)	4.17 (0.17)	4.50 (0.2)
Titanate	34.5 (1.5)	3.33 (0.23)	3.65 (1.10)	38.4 (3.1)	3.59 (0.18)	4.74 (0.38)

The standard deviations are in parentheses.

2.9, 4.7, and 4.4%, respectively. Thus, the effective values for elongation at break of the op-efb fibers are on the order of the value for the unreinforced resin (3.0%). However, the values for coir are still larger. Hence, it would appear that this behavior is more likely to be due to the presence of voids in the composite (in particular at the fiber-matrix interface). As a consequence of this, inefficient transfer of loads between the fiber and matrix occurs. Thus, at low fiber loading this has a negative effect upon the TS; but as loading increases, the higher TS of the reinforcement becomes dominant. This is only a tentative conjecture, because the interpretation of such data for a composite with such a complex fiber orientation is not simple. However, it is apparent that fiber orientation does affect the relationship between TS and fiber loading. The TS properties of acetylated, silane treated, or titanate treated natural fiber reinforced composites at a fiber weight fraction of 45% are compared in Table III. The properties for unreinforced resin and glass fiber reinforced resin (fiber weight fraction 45%) are also given in Table IV. It is apparent that silane treat-

ment of coir fibers results in a small increase in the TS over that obtained when untreated fibers are used as the reinforcement whereas titanate treatment results in a small decrease. With op-efb, a small decrease in the TS is observed with both treatments. Of all the fiber treatments studied, it is apparent that acetylation affords the highest increase in TS. However, the observed increases are not significant, particularly when the results are compared with glass reinforced polyester. The TS values obtained for the glass fiber are considerably higher than those obtained with either natural fiber with any of the treatments considered in this study. This is to be expected, because glass fibers typically exhibit TS in excess of 1 GPa²⁵ whereas the two fiber types in this study exhibit tensile strengths in the order of 10% of this value.

The effect of fiber loading on the TM properties for coir and op-efb are illustrated in Figure 6. The

Table IV Comparison of Properties of Unreinforced and Glass Reinforced (CSM, Weight Fraction 45%) Resin

Property	Resin	Glass Reinforced Resin
σ (MPa)	25.1 (3.3)	94.0 (4.6)
E (GPa)	2.59 (0.44)	5.76 (0.24)
ε (%)	2.98 (0.44)	2.10 (0.13)
σ_f (MPa)	50.9 (3.3)	180.0 (18.1)
E_f (GPa)	3.23 (0.26)	6.11 (0.36)
IS (kJ/m ²)	6.9 (0.4)	68.1 (3.5)

The standard deviations are in parentheses.

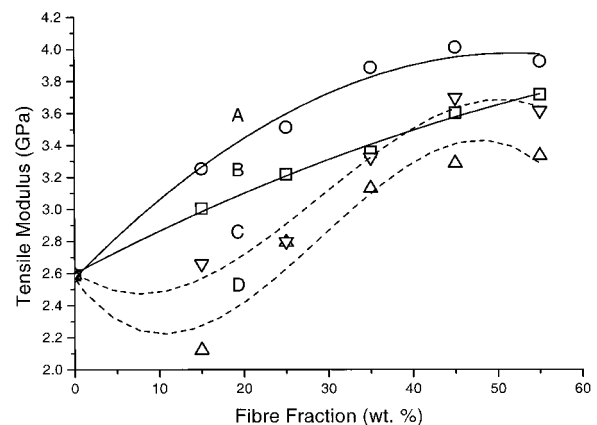


Figure 6 The variation of the tensile modulus with fiber loading for polyester matrix composites reinforced with (○, line A) acetylated coir, (□, line B) unmodified coir, (▽, line C) acetylated op-efb, and (△, line D) unmodified op-efb.

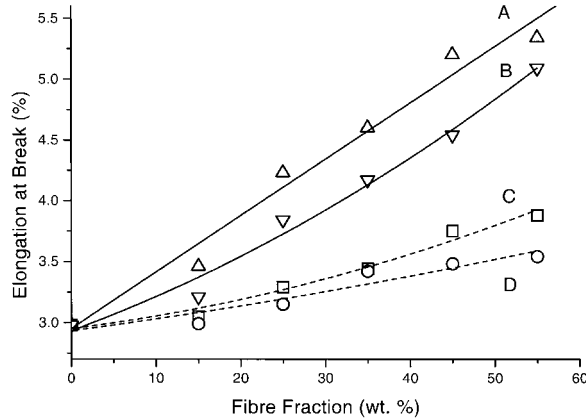


Figure 7 The variation in the elongation at break with fiber loading for composites reinforced with (Δ , line A) unmodified coir, (∇ , line B) acetylated coir, (\square , line C) unmodified op-efb, and (\circ , line D) acetylated op-efb.

difference in the behavior between the two fiber types is apparent. Although the op-efb reinforced composite exhibits a decrease in the TM at low and high fiber content, this does not occur with coir, except at the highest fiber loading with acetylated coir. This difference in behavior may be attributable to the higher tensile moduli of the unmodified and acetylated coir fibers. Again the decrease observed with op-efb may be due to void formation at the fiber–matrix interface. However, such an explanation seems less likely in view of the fact that the unmodified coir fibers do not display the initial decrease in TM at low fiber contents whereas such behavior is observed with unmodified and acetylated op-efb fibers. This suggests that fiber–matrix compatibility does not influence this property. It is also unlikely that the fiber mat geometry is responsible for this difference, because both coir and op-efb reinforcements had the same geometry. In a study of composites made from the fibers of *Yucca carnerosana* that were randomly oriented in a polyester matrix, a linear relationship between the TM and fiber loading was reported, which was seen with coir in this study.²⁰ The increase in TM with silane treated fiber reinforced composites is comparable to that observed with acetylated fibers whereas the TM due to titanate treatment is no different than that observed with untreated fibers. Again, the increase in TM with natural fiber reinforcement is lower than that observed with glass fibers (Table IV), which is due to glass fibers exhibiting moduli in the region of 10–20 times that measured with the natural fibers in this study.²⁵

The relationship between the elongation at break and fiber content of composites is shown in Figure 7. The elongation at break of the composites increases with fiber loading. In this case, an essentially linear relationship pertains with no decrease at low or high fiber loading. The elongation at break of coir reinforced composites is higher than with op-efb, which is due to the higher values exhibited by the fibers themselves. Acetylation has the effect of reducing this property of the fibers and composites formed therefrom. A decrease in elongation at break is also seen with composites reinforced with fibers treated with coupling agents. Because such a treatment does not affect the fiber properties,²⁶ we concluded that in this case improved wetting of the treated fibers by the matrix is responsible.

Flexural Properties

The variation of the FS with fiber loading is shown in Figure 8. A large decrease in FS is observed when fibers are present in the matrix. This fall in the FS is particularly severe at the lowest fiber loading, but it shows a moderate increase with fiber content thereafter. At the highest fiber loading, a small decrease in the FS occurs. There is no fiber loading at which the FS exceeds that of the unreinforced resin. Acetylation of the fibers has little effect upon this property, although a slightly higher FS is seen with acetylated op-efb fibers. Thus, the fibers are not acting as a reinforcement in this case but are apparently serving to separate regions of the resin, and there is little effective transfer of stress

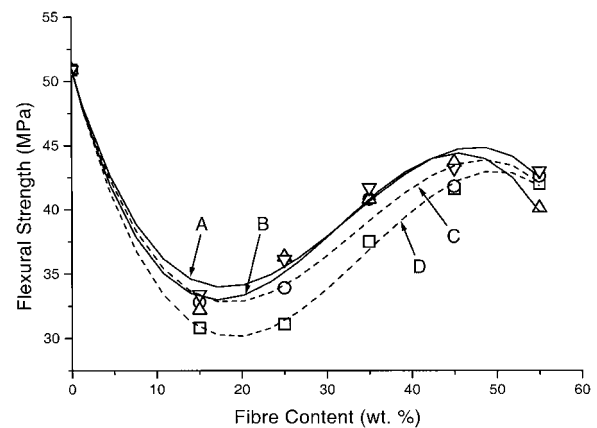


Figure 8 The variation in the flexural strength with fiber loading for composites reinforced with (Δ , line A) unmodified coir, (∇ , line B) acetylated coir, (\circ , line C) acetylated op-efb, and (\square , line D) op-efb.

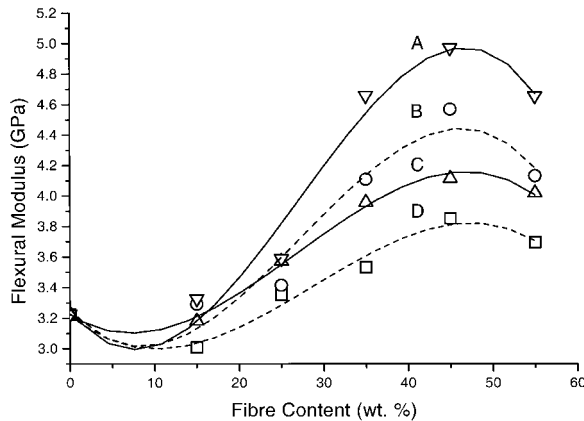


Figure 9 The variation in the flexural modulus with fiber loading for composites reinforced with (∇ , line A) acetylated coir, (\circ , line B) acetylated op-efb, (\triangle , line C) unmodified coir, and (\square , line D) unmodified op-efb.

between these regions. Studies of unidirectional composites formed of sisal/epoxy¹¹ or jute/polyester²² showed that there is a linear relationship between the FS and fiber loading, and the composite FS always exceeds that of the resin. However, randomly oriented coir fibers in a polyester matrix were shown to exhibit an FS lower than that of the resin at all fiber loadings.²³ This was also found for banana fiber reinforced polyester (random).¹⁴ In a study of op-efb fibers randomly oriented in a phenol-formaldehyde matrix, the FS increased linearly up to a maximum at 38% fiber loading. In this case, the FS of the resin was only 11 MPa⁵ compared with 50 MPa for the polyester in the present study. The FS of the natural fiber reinforced composites was again considerably lower than that determined for the glass fiber reinforced equivalents. Neither silane nor titanate treatment of the natural fibers had any significant effect on this property.

The relationship between the FM and fiber loading shows the same behavior (Fig. 9); but the FM of the plant fiber reinforced composites exceeds that of the resin, except at a loading of 15%, where little improvement occurs. Acetylation of the fibers leads to large increases in the FM (at a fiber weight content of 45%), and there is a significant difference in the FM between coir and op-efb reinforced composites. Again, with glass fibers the FM of the test pieces is higher than with coir or op-efb composites, but the difference is not so great as observed with TM. Silane or titanate treatment of the fibers results in FM values that fall between those of unmodified and acetylated fibers (Table V).

Impact Properties

The relationship between fiber loading and impact strength exhibits the commonly observed relationship, in that at low fiber loading no increase is seen and there is an approximately linear increase thereafter, followed by a decrease at the highest fiber loading (Fig. 10). Sanadi et al. reported that the impact resistance of unidirectional sunhemp/polyester composites shows a linear increase with fiber loading.¹⁹ Acetylation results in a moderate increase in the impact strength between fiber loadings of 25–45%. At a fiber loading of 55% the op-efb reinforced composites exhibit higher impact strengths than coir reinforced ones, but no difference is observed with acetylated compared with unmodified fibers. Titanate or silane treatment does not result in any significant difference in this property, when compared to the untreated fibers, except perhaps with titanate treated op-efb fibers, where a small increase in impact strength is observed. The impact strength of a composite is influenced by many factors including the toughness properties of the

Table V Comparison of Acetylation with Coupling Agent Treatment on Composite Flexural Properties at Fiber Weight Fraction of 45%

Fiber Content (wt %)	Oil Palm (efb)		Coir	
	σ_f (MPa)	E_f (GPa)	σ_f (MPa)	E_f (GPa)
Unmodified	41.6 (3.5)	3.85 (0.36)	43.7 (6.5)	4.11 (0.61)
Acetylated	41.8 (3.9)	4.57 (0.31)	43.2 (3.8)	4.97 (0.33)
Silane	38.8 (2.5)	4.46 (0.15)	40.5 (2.3)	4.62 (0.24)
Titanate	38.3 (2.2)	4.04 (0.22)	42.0 (2.7)	4.12 (0.32)

The standard deviations are in parentheses.

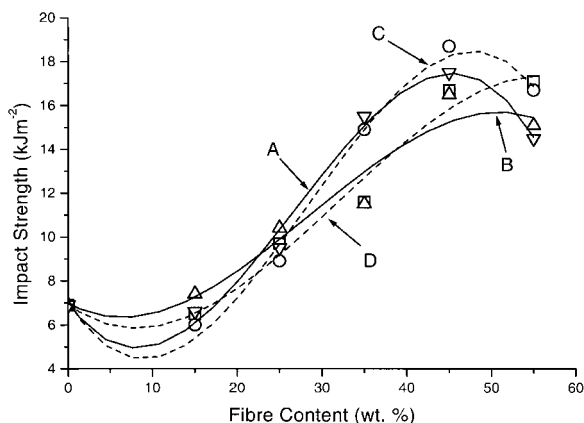


Figure 10 The variation in the impact strength with fiber loading for composites reinforced with (Δ , line A) acetylated coir, (∇ , line B) unmodified coir, (\circ , line C) acetylated op-efb, and (\square , line D) unmodified op-efb.

reinforcement, the nature of the interfacial region, and the frictional work involved in pulling the fibers from the matrix.²⁷ With glass fiber reinforced composites, frictional losses as the fiber is pulled out of the matrix are a major contributor to the observed toughness of the composites. This is facilitated by the surface smoothness and regular cross section of these fibers. With the natural fibers in this study such a mechanism is not favored because of mechanical keying between the fibers and the matrix.¹⁹ As a consequence, limited fiber pull-out is observed. Any enhancement in toughness due to the presence of these natural fibers must then rely upon the nature of the fiber matrix bond or the inherent toughness of the fibers themselves. In the well known Cook–Gordon theory the presence of a weak fiber–matrix interface is able to account for a tough composite that is itself formed from two brittle phases. The opening up of a new surface at the interface results in the absorption of energy, diversion of cracks, and so forth.²⁸ The nature of the interphase region is thus of extreme importance in determining the toughness of the composite. If the fiber–matrix interfacial strength is too low, then poor stress transfer occurs and a weak composite results. Conversely, a strong interfacial bond allows for very efficient stress transfer but produces a composite exhibiting poor toughness properties.²⁹ Fiber acetylation results in a small but significant increase in the toughness of the composite. Because acetylation also results in an increase in the interfacial bond strength, it is most unlikely therefore that the increase in toughness is due to any changes at the interface. It is known, how-

ever, that small increases in the toughness of wood can occur as a result of acetylation.³⁰ Furthermore, coupling agent treatment of the fibers does not generally result in any toughness enhancement (Table VI). The use of coupling agents should increase the strength of the interfacial bond but not increase the toughness of the fibers; hence, there is no enhancement of composite toughness. Titanate treated op-efb is an exception to this, but further data are required to verify whether this difference is significant. The explanation in this case may be related to the smoother fiber surface due to the treatment, which may reduce the effect of mechanical keying. Toughness enhancements may also occur because of the presence of plant fibers, because they are composites themselves and are capable of displaying additional energy absorbing mechanisms such as defibrillation. SEM micrographs of the fracture surfaces of op-efb reinforced composites at a fiber volume fraction of 45% are illustrated in Figure 11. An example of poor fiber–matrix bonding of an unmodified fiber is shown in Figure 11(a). In Figure 11(b) a fracture surface of a silane treated reinforced composite is shown. A number of features are discernible. In some cases, the fiber–matrix bond appears to be intact, but there is clear evidence of decoupling in most cases. A number of sockets are visible where fibers have pulled out of the matrix. However, where fiber pull-out has occurred, the fiber lengths are very short, particularly when such features are compared with glass-fiber reinforced composites. Furthermore, fiber failure is brittle in nature, and there is no evidence of defibrillation of the fiber bundles. Such a typical transverse brittle failure is shown in Figure 11(c) for a titanate treated fiber, which also shows clear evidence of fiber–

Table VI Comparison of Effect of Acetylation Compared with Coupling Agent Treatment of Fibers on Impact Properties of Composites at Fiber Weight Fraction of 45%

	Impact Strength (kJ/m ²)	
	Oil Palm (efb)	Coir
Unmodified	16.7 (1.6)	16.5 (1.8)
Acetylated	18.7 (0.8)	17.5 (1.3)
Silane	17.1 (0.9)	16.4 (0.5)
Titanate	16.5 (0.8)	17.7 (0.9)

The standard deviations are in parentheses.

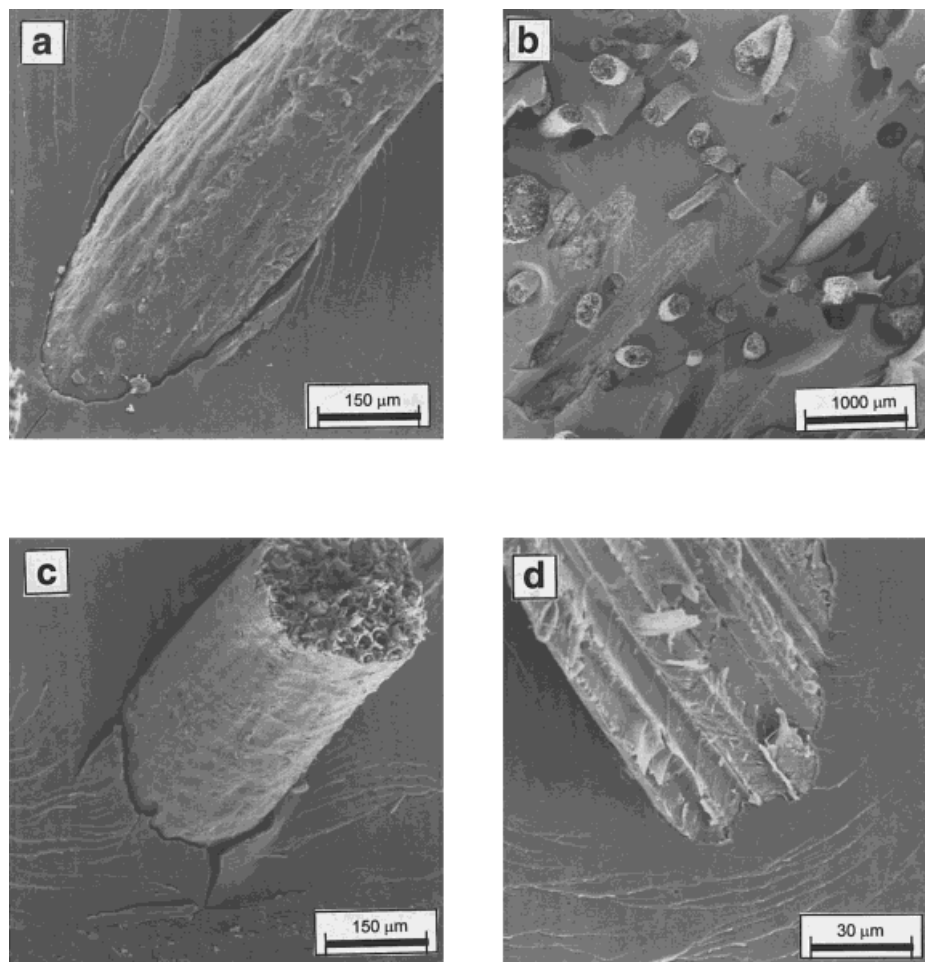


Figure 11 SEM micrographs showing impact fracture surfaces of composites reinforced with (a) unmodified, (b) silane treated, (c) titanate treated, and (d) acetylated op-efb fibers.

matrix decoupling. The weak fiber–matrix bonding explains the poor mechanical properties in composites reinforced with titanate treated fibers. However, this may allow for more effective fiber pull-out, leading to toughness enhancements. By contrast, a proportion of acetylated fibers exhibit evidence of good fiber–matrix bonding along with longitudinal failure of the fiber [Fig. 11(d)]. The existence of transverse brittle failure of natural fibers was previously reported for jute/polyester composites.^{21,22} The SEM studies showed that, although some changes in the failure mode were observed with various treatments, this was not universal, in that only a proportion of the fibers exhibited different behavior. This is a problem that is typical of natural fibers, and it means that prediction of performance is very difficult because of such inherent variability.

CONCLUSIONS

Acetylation of coir or op-efb fibers results in increases in the ISS between the fiber and matrix (polyester or styrene). In addition, slight increases in the TS, TM, and impact strength of composites reinforced with modified fibers are noted. Conversely, the TM, elongation at break, and FM are all reduced when compared with composites reinforced with unmodified coir or op-efb fibers. These changes are due to a combination of a change in the mechanical properties of the modified fibers and the increased hydrophobicity of the surface allowing for improved wetting of the fiber by the resin. Treatment of fibers with silane or titanate coupling agents does not result in significant changes in the mechanical properties of the composites formed therefrom. In all cases,

although changes in mechanical properties do occur, they are not large. When compared with a glass reinforced composite, they compare unfavorably.

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