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Evaluation of wood–thermoplastic-interphase shear strengths

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A macroscopic pull-out technique has been developed to determine the interphase properties in wood/low-molecular-weight-thermoplastic systems. Experimental variables affecting the shear properties of these types of composites were first identified so that the test could be used to compare the effect of different surface treatments on the interfacial properties. The relationship between the debonded force, F, and embedded length, L, was not linear, suggesting a failure mechanism that was different from interfacial yielding. Low embedded lengths provide useful comparative data on the maximum interfacial-shear strength of the system. The test is also useful for evaluating the quality of the fibre–matrix bond after exposure to water, since dimensional stability is an important consideration for wood–fibre–based composites. The test can be used to screen the effects of modifications on the lignocellulosic and/or the thermoplastic matrix on adhesive bonding for the development of composites. The use of lignocellulosic fibres (recycled wood fibres and natural fibres such as jute) in combination with recycled plastics could find applications in the automotive, furniture and building-materials industry.

1. Introduction

A great deal of interest has been generated in wood–fibre/plastic composites for various high volume, cost-sensitive products [1, 2, 3]. A variety of bio-based materials can be used in these composites; for example, enormous quantities of agro-wastes have been incorporated as fillers in thermosetting resins [4]. Wells *et al.* [5] and White and Ansell [6] suggested that lignocellulosic fibres will reduce the costs of composites for specific applications. Coutts *et al.* [7] have conducted considerable research on the replacement of asbestos fibres with wood-based fibres in cement roofing sheets. Thomas *et al.* [8] have suggested that wood-pulp-reinforced, high-density polyethylene (HDPE) has an equivalent stiffness, at equal weight, to glass-reinforced HDPE, but at half the material cost. According to Thomas *et al.* wood fibres with high aspect ratios and low densities are potentially outstanding non-abrasive reinforcing fillers for thermoplastics. The use of recycled lignocellulosic fibres (from recycled newspaper and demolition wood) in combination with recycled plastics could find applications in the automotive, furniture and building-material industry.

The main restrictions to the wide-scale use of bio-based fibres in thermoplastics [9] have been the poor compatibility between the fibres and the matrix and the inherently high moisture sorption which causes dimensional changes in the fibres. The efficiency of a fibre-reinforced composite depends a great deal on the fibre–matrix interface and the ability to transfer stress from the matrix to the fibre. This stress-transfer efficiency plays a dominant role in determining the mechanical properties of the composite and also in the material's ability to withstand environmentally severe conditions. The inherent polar nature of lignocellulosic fibres is responsible for their hydrophilic properties and sorption phenomenon. This is critical, and it needs to be considered in the improvement of the wet-strength properties of bio-based composites.

Adhesive properties and, therefore, the fibre–matrix interface and *interphase* are complex subjects whose characteristics are governed by numerous factors such as chemical, physical and mechanical properties, and processing techniques [10]. (The *interphase* is a volume of material between the fibre and the matrix with properties different from the two main phases.) Furthermore, the deposition of long-chain macromolecules onto a surface can result in the properties of the interphasial region being quite different from the bulk phases [11].

Methods to *directly* characterize the interface in reinforced composites have recently been developed and evaluated; they include the fibre-pull-out test, the single-fibre-fragmentation test, the microdebonding-tension test, and the microdebonding-push-out test. Although none of these techniques has been standardized, the pull-out test has received considerable attention [12–15], because of the possibility of obtaining important information about the interface (or interphase) and the ability to distinguish between failure modes. This test can provide useful comparative data on different surface-modification techniques. Considerable information can be obtained from the

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test including the debonding energies, the average and maximum shear strengths, and the frictional shear components of the fibre–matrix under study.

The pull-out test measures the force required to pull a fibre out of a button of solid matrix. An average debonding shear strength, τ_d, of the interface can be estimated using the following equation:

$$\tau_d = \frac{F}{\pi d L} \quad (1)$$

where F is the debonding force, d is the fibre diameter, and L is the embedded length. This linear relationship between the embedded length and debonding force is due to uniform yielding of the interphase all along the embedded length. On the other hand, the shear stress can change with the length of fibre embedded in the matrix and a plot of the debonding force against the embedded length may not be linear [12, 14, 15]. For example, in certain cases a dual behaviour can be exhibited, as described by Penn and Lee [14]: an increasing force at low embedded lengths, followed by a constant force at higher length. Careful control and analysis of experiments are needed to use the test effectively [12, 14].

Tai *et al.* [16] and Felix and Gatenholm [17] have used the single-fibre-fragmentation test to evaluate the fibre–matrix shear strength in lignocellulosic–thermoplastic systems. It should be pointed out that if the single-fibre test is used then the fibre length–strength relation is needed, and the presence of turns and twists in the wood fibre complicates analysis.

The purpose of this study is to develop and standardize a pull-out test for comparison of the interfacial properties of wood modified with different surface treatments in a thermoplastic resin. The test can then be used as a method of screening different interfacial treatments for a more rigorous study involving actual composite testing. We have used wood dowels instead of wood fibres for this study since it is difficult to analyse data for the fibres due to their non-uniform and complex shape which twists and turns. Furthermore, sample preparation and testing of pull-out specimens from wood fibres is very difficult. Care was taken to polish the wood dowels so that the surface topography was comparable between specimens. Low-molecular-weight polymers were selected because of their easy specimen preparation.

2. Experimental methods

2.1. Materials

Hardwood birch dowels (diameter about 2 mm) were rinsed in distilled water and dried at 80 °C; they had an elastic modulus of about 230 MPa. Acetylation of the wood dowels was conducted as described by Rowell [18] and the average weight gain due to this treatment was 18%.

Low-molecular-weight polyethylene (PE) and a copolymer of ethylene and acrylic acid (EAA) were used as the matrix. Details of the matrix polymers are: (a) PE, from Scientific Polymer Products USA, $MW_n = 6500\ g\ mol^{-1}$, the viscosity was 6000 cp (6 Pa s) at 140 °C, elastic modulus, 60 MPa; and (b) EAA From Scientific Polymer Products, USA, 5% acrylic-acid content, 40 mg KOH g^{-1} acid number, the viscosity was 500 cp (0.5 Pa s) at 140 °C.

An anionic emulsion of maleic-anhydride-grafted polypropylene (MAPP) and an emulsion of a copolymer of ethylene and acrylic acid (EPA) were used for the modification of the fibre surface. Details of the emulsions used are: (a) MAPP, From Eastman Kodak, USA, $MW_n = 4500$, 3.5% solid content in emulsion; (b) EPA, From Michelman Chemicals, 20% acrylic acid content in polymer, 2% solid content in emulsion. Surface modification of the dowels was carried out by dipping the dowels in the emulsions for 15 min and subsequently drying them at 105 °C for 1 h. The dowels were kept in an oven at 80 °C until they were used.

2.2. Specimen preparation and testing

Pull-out specimens (Fig. 1) were prepared with 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 dowels could be inserted and held vertically in the centre of the tube. Up to 20 specimens 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 min the oven door was opened and the dowels were pushed lightly to ensure that they were totally embedded.

Initial experimentation was conducted to standardize the specimen-preparation technique. Ten pull-out specimens were tested with embedded lengths varying from 2.5 to 10 mm, and an average value of

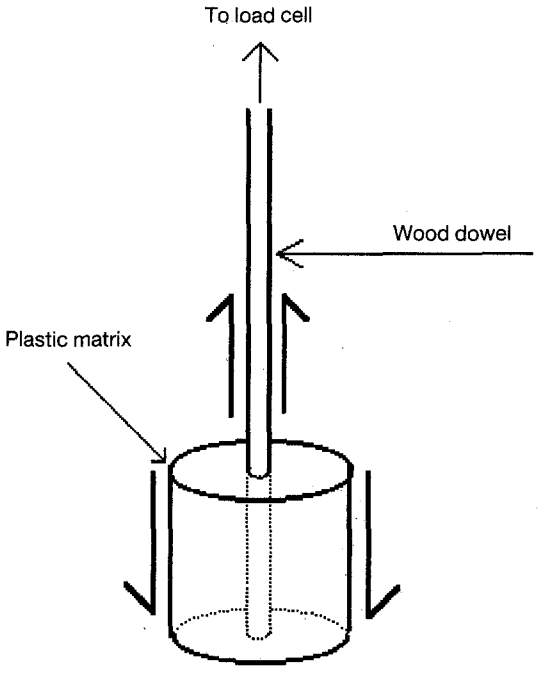

Figure 1 Schematic representation of a pull-out specimen.

the debonded stress was recorded; care was taken to have an equal representation of different lengths for all comparisons. This preliminary testing involved cooling the whole jig in air.

The results obtained from preliminary work for specimen preparation led to a change in the cooling procedure because of excessive matrix cracking; this involved switching off the oven and letting the samples cool in the oven. The chemical modifications of the wood (acetylation) changed the surface topography; for consistency all the dowels were carefully polished in the same manner with a fine crocus (abrasive) cloth. Final comparison of surface modifications and data on the length–strength relationships involved dowel polishing and oven cooling, unless otherwise specified. Further details of the reasons for the selection of this method of specimen preparation are given in the next section.

A comparison of the surface treatments was conducted by recording the debonded stress of at least 20 samples with embedded lengths varying between 2.5 and 21 mm. Higher lengths invariably resulted in matrix cracking when the specimen was removed from the holder. All samples with the dowels off-centre or with any cracks in the matrix were rejected. On average, about 15 to 18 specimens out of 20 were suitable for testing. Care was taken to ensure the reproducibility of processing and testing conditions.

Testing was conducted on a universal tensile tester at a crosshead speed of 2.5 cm min^{-1}, with 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 an x–y-recorder. The rod diameter and embedded lengths were measured with vernier calipers (an average of five readings were taken for each dowel) for each test specimen. The water resistance of the fibre–matrix bond was evaluated immediately after immersing the pull-out specimen in water for 1 h at 80 °C.

3. Results and discussion

3.1. Preliminary results

Table I shows data from preliminary tests conducted to standardize the testing procedure. Predrying of the dowels, at 105 °C for 1 h and storing in an oven at 80 °C, resulted in a significant increase in the debonded stress. This was mainly due to the reduced formation of voids from the evaporation of moisture present in the dowels. Acetylation resulted in an increase in the surface area of the dowels and in an increase in the debonding force. No significant differences are expected between the interphasial interactions with the polymer matrix of acetylated wood and the untreated dowels. Polishing was, therefore, considered to be a critical step to ensure that the surface area of the dowel was consistent. This is particularly important when comparing chemically modified wood. Cracking of the matrix during air cooling of the pull-out specimen, due to high thermal and solidification stresses, resulted in the rejection of a large number of specimens. Oven cooling decreased this problem dramatically and was thus chosen for the comparative evaluation of surface treatments.

3.2 Length–debonding-force relationship

Fig. 2 shows a typical pull-out curve for unmodified and untreated wood dowels in the low-molecular-weight polyethylene. The force increases until total debonding has occurred. In all the samples tested there appeared to be some non-linearity near the point of total debonding. Some interphase yielding may have occurred, but any conclusions related to interphase failure through yielding may be misleading, as discussed later. At F, there is sudden drop in force indicating that the dowel has debonded totally from the matrix and frictional stresses are then generated at the interface.

Fig. 3 shows a typical plot relating the debonded force, F, to the embedded length of MAPP-coated dowels which were predried and polished. A uniform yielding of the interphase should result in a linear relationship (through the origin) between the debonded force and the embedded length; this behaviour was not observed in any of the systems studied. In all our evaluations the force increases with the embedded length; at higher lengths the relative increase in force with an increase in length appears to decrease, suggesting the possibility of a region of constant force at

TABLE I Interfacial debonding shear stress using the pull-out test for the low-molecular-weight-polyethylene matrix

Predried dowel	Polished dowel	Specimen cooling	Dowel treatment	Debonding stress (MPa) (standard deviation)
				Average
No	No	Air	None	0.42 (0.22)
Yes	No	Air	None	0.81 (0.16)
Yes	No	Oven	Acetylated	1.10 (0.41)
Yes	Yes	Oven	None	1.60 (0.28)
Yes	Yes	Oven	Acetylated	1.92 (0.13)

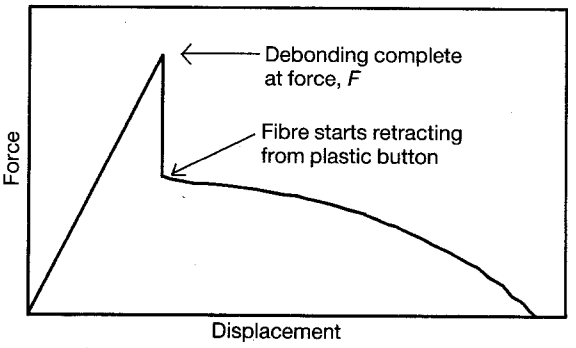

Figure 2 Typical force versus displacement curve during pull-out of the dowel from the plastic button.

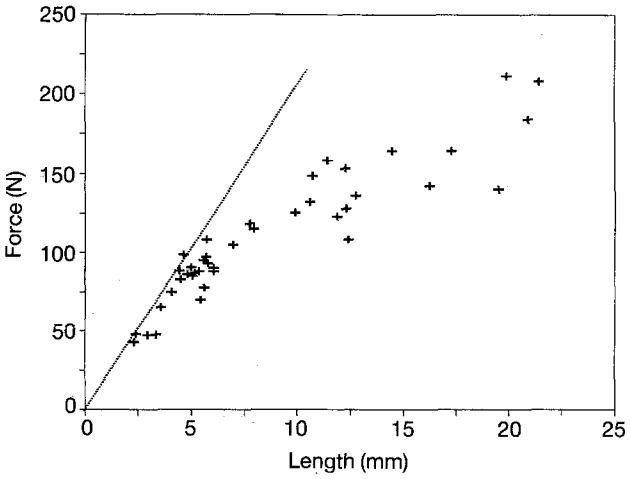

Figure 3 Debonding force versus embedded length of the pull-out of MAPP-coated dowels from the polyethylene (PE) matrix. The dotted line is the apparent maximum slope through the origin.

higher lengths. Due to experimental limitations we were unable to prepare samples of embedded lengths greater than about 21 mm and therefore did not observe the plateau region of the F versus L relationship observed by others [14]. However, a non-linear relationship between the debonded force and the embedded length suggests a failure mechanism that may involve a brittle-type interface failure [12, 14].

If failure is due to brittle fracture the crack is initiated at the region where the dowel enters the matrix. Penn and Lee [14] considered the energy release during the propagation of a crack and developed the following relationship:

$$F = 2\pi r^2 \left(\frac{E_f G_i}{r}\right)^{1/2} \tanh\left(\frac{nL}{r}\right) \quad (2)$$

where E_f is the fibre elastic modulus, G_i is the work of fracture of the interphase and r is the fibre radius. The constant n can be estimated by the following relationship [12, 14]:

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

where E_m is the matrix elastic modulus, R is the radius of the matrix button around the fibre, ν_m is the Poisson's ratio of the matrix. Piggott [12] extracted a relationship between the debonding shear stress and the work of fracture of the interphase for the brittle-failure process.

$$\tau_d = n(E_f G_i/r)^{1/2} \quad (4)$$

Comparison of the different surface modifications by the estimation of the debonding stresses and estimated work of fractures are explained in the next section.

A graph of the interfacial shear strength versus the length (Fig. 4) showed an asymptotically decreasing relationship consistent with earlier work [15, 19].

3.3. Comparison of surface treatments

Penn and Lee [14] suggest that a comparison should be made throughout the different regions of the debonding-force-versus-embedded-length plot. However, as explained earlier data at higher embedded lengths was unobtainable, i.e. at lengths greater than about 21 mm. Piggott [12] has suggested the use of results from short embedded lengths to avoid the complications arising from the frictional contribution to the debonding stress. 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.

Two methods were used to estimate the IFSS from the length-versus-debonded-force plots. The first was by drawing a linear line from the origin through the initial points resulting in a line with the apparent maximum slope (for example the dotted line in Fig. 3). The second was by drawing a line through the origin, using linear regression, for all points below lengths of 3.0 mm. Table II shows debonded-stress data using the different surface coatings. The percentage changes in the IFSS and the untreated dowels are also shown in Table II. Both techniques showed similar differ-

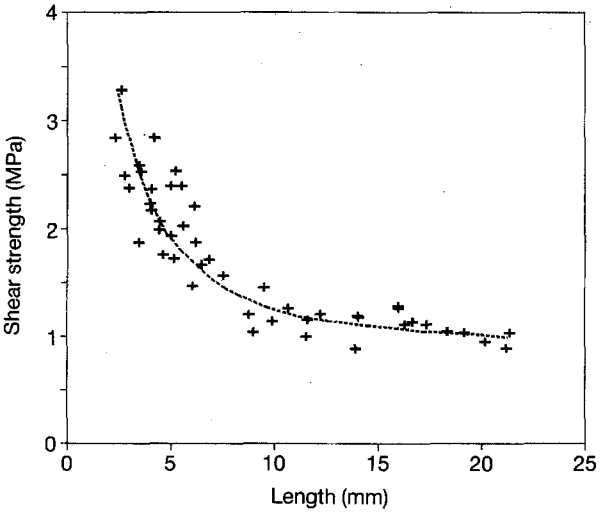

Figure 4 Plot of the interfacial shear strength versus embedded length for untreated dowels in the copoly(ethylene–acrylic acid) copolymer (EAA) matrix.

TABLE II Comparison of the interfacial shear strengths (IFSSs) for the different interphase systems

Pull-out system	Shear strength from maximum slope		Shear strength from linear regression	
	IFSS (MPa)	Control (%)	IFSS (MPa)	Control (%)
Untreated dowel/ polyethylene matrix (control)	2.0	100	1.72	100
MAPP-coated dowel/polyethylene matrix	3.1	155	2.75	160
EPA-coated dowel/polyethylene matrix	2.6	130	2.41	140
Untreated dowel/ ethylene–acrylic-matrix	3.3	165	2.65	155

ences, compared to the untreated dowels as the control; however, as expected, the maximum values were higher than those from the method of linear regression. Any difference between the two methods is due to statistical variability in estimating the maximum IFSS and the contribution of friction in the analysis.

As expected, the untreated dowels showed the lowest IFSS. The interaction between the highly polar wood and the non-polar polyethylene is limited to dispersive interaction. (Some polar interaction can occur due to oxidation of the matrix during processing in air, but this is about the same for all the systems). MAPP-coated dowels exhibited the highest IFSS when polyethylene was used as the matrix. EPA-coated dowels showed an improvement over the untreated dowels, but had lower values than the MAPP-coated samples. MAPP has been used by many workers [16, 20, 21] to improve wood fibre/thermoplastic composite properties; the anhydride in MAPP has the potential to covalently bond with the hydroxyl groups in wood. The ethylene–acrylic copolymer matrix resulted in the highest shear strength; this is primarily 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.

Since the relationship between F and L was non-linear, a brittle fracture is a possible failure mode. The work of fracture, G_i, can be estimated from Equation 4. In this case E_f is known, n can be estimated from Equation 3 and τ_d (maximum value) is given in Table II. The improvement in G_i, Table III, when using surface treatments is apparent. However, the works of fracture are very low. The low values could be attributed to the low molecular weight of the polymer and also the formation of an interphase with properties different from those of the bulk matrix; this region contains polymer molecules with a restricted bond-rotation capability due to the hindrance from the solid surface. Brittle behaviour of the fibre–matrix bond has also been observed with higher-molecular-weight polyethylene (more ductile than the polyethylene we have used) with both glass and Kevlar fibres [15].

The effect of water on the interfacial strength of the wood–polyethylene bond is particularly interesting. There is little difference in the IFSS of untreated and acetylated dowels in polyethylene. The behaviour of the system after soaking in hot water is however very different. Water soaking (1 h at 80 °C) of untreated-dowel pull-out specimens resulted in total failure of the polymer button, resulting in matrix cracking and debonding prior to testing. This is due to the high level of dowel swelling from water absorption, and no data on the interfacial shear strength could be obtained. However, the acetylated-dowel pull-out specimen showed no signs of cracking after water soaking and the maximum shear strength (2.01 MPa) was about the same as in the dry state (1.92 MPa). Acetylation is well known to dimensionally stabilize wood, and swelling in the presence of water is very small (less than 10%) compared to unacetylated wood [18]. This stabilization is very important when considering the use of wood-fibre composites in outdoor applications. Furthermore, environmentally induced sorption can result in fatigue at the interphase, which could be very destructive to composite properties.

Initial pull-out experiments using a nitrogen atmosphere for specimen preparation, and the use of commercial polyethylene and polypropylene as the matrix polymers, indicate the test will be invaluable in the initial phase of the selection of interphase systems to optimize lignocellulosic–thermoplastic composite properties.

TABLE III Estimated works of fracture of selected interphases in the polyethylene matrix

Interphase system	Work of fracture G_i(J m^{-2})	Control (%)
Untreated (control)	151	100
MAPP coated	363	240
EPA coated	255	169

4. Conclusion

The pull-out technique developed in this study for the evaluation of interface bond strengths in cellulosic–thermoplastic systems provides reproducible data that can be a useful screening test for interphase modification for the development of lignocellulosic–thermoplastic composites. 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 by an estimate of the interfacial shear strength at low embedded lengths. The test is also valuable for the determination of the effects of moisture and other types of environmental conditions on the interphase properties. Future work will involve the use of lignocellulosic fibres such as jute as the reinforcing material, and the use of high-molecular-weight polymers (both virgin and recycled plastics) as the matrix system.

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