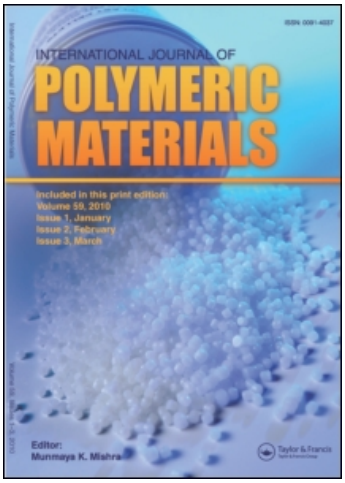

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The Effect of Surface Treatment on the Strength and Adhesion Characteristics of Phoenix dactylifera-L (Date Palm) Fibers

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There is a growing interest in the use of natural/bio-fibers as reinforcing components for thermoplastics and thermosets. However, they do suffer from a few limitations, such as lower compatibility with relatively hydrophobic polymer matrixes. Thus, improvement of the interface and interphase interactions in natural fiber–polyester composites is essential. In this research date palm (Phoenix dactylifera-L) fibers were modified by surface treatment using chemical method in order to improve their adhesion to polyester matrixes. Alkaline treatment, as an example of dissolution and treatment with silane coupling agents were performed. Furthermore, a combination treatment of alkaline and silane coupling agents was also carried out. Fiber modifications were monitored by Scanning Electron Microscopy (SEM). In addition to that, the improvement of adhesion and strength between date palm–modified fibers and polyester matrix was investigated by single filament pull-out test as well as tensile tests. It was found, from interfacial shear strength values, that substantial improvements in fiber-matrix compatibility have been achieved. According to single filament pull-out test results, interfacial shear strength increased for all treated fibers as compared to non-treated fibers. Particularly, combination of alkaline and silane coupling agents resulted in substantial adhesion improvement to the polyester matrix in comparison to the untreated fibers and fibers treated by alkaline and silane methods only.

Keywords: natural fiber, date palm fiber, surface treatment, polyester resin, single filament pull-out test, SEM

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INTRODUCTION

Natural fibers are now increasingly used for the reinforcement of plastics along with traditional fibers. It has been reported that, in the building community, there is growing demand for high-performance, low-maintenance, and low-cost building components [1]. Compared with the traditional reinforcements, for example, glass and carbon fibers, lignocellulosic fibers impart the composite certain benefits such as lower density and result in a highly reduced wear of the processing equipment while working with plastic composites. Moreover, they are readily available from natural sources at a low price.

Over the years it has been well established that the strength and toughness of fiber-reinforced materials are determined to a great extent by the interface between the reinforcing fibers and the matrix. Extensive research has been carried out in order to understand the nature of the interfacial bond and to characterize its properties. A strong interface creates a material that displays exemplary strength and stiffness but that is very brittle in nature with easy crack propagation through the matrix and fiber. A weaker interface reduces the efficiency of stress transfer from the matrix to the fiber and consequently the strength and stiffness are not as high [2]. Given the significance of the interfacial properties, it is not surprising that a large amount of research work has been carried out in the past twenty years on the characterization of the fiber–matrix interface. All of the approaches formulated have identified the so-called interfacial shear strength as the key parameter, which has been linked directly with the interfacial bond. There are four mainstream techniques for assessing the interfacial strength through single fiber testing; the single fiber pull-out test, the microdebond test, the single fiber fragmentation test, and the microindentation test. A detailed description of these four testing techniques may be found in the literature [3,4]. The single fiber pull-out test shown schematically in Figure 1 has received considerable attention in recent years as a method of measuring the interfacial shear strength (IFSS) [5–8]. There are several advantages of this test. First, it is a direct measure of the quality of the adhesive

FIGURE 1 Schematic illustration of pull-out micromechanical test method.

bond between the fiber and matrix. Second, it requires only a small amount of fiber and matrix. Third, the pull-out test is not generally limited by the properties of the fiber and matrix. This should be compared with fragmentation test [9] where the failure strain of the matrix needs to be more than three or four times the failure strain of the fibers to meet the needs of achieving a saturated fragmentation state. The pull-out test can be carried out successfully with both brittle and ductile matrix system. Therefore, in the present study the single fiber pull-out test was used.

There are several reports concerning the natural fiber–matrix interfacial bonding and strength of composites. Brahmakumar et al. [10] studied the effect of natural waxy surface layer of the coconut fiber on fiber–matrix interfacial bonding and composite properties by single fiber pullout test. They reported that the waxy layer provided good fiber–matrix bond such that removal of the layer resulted in drastic decrease of the fiber pull-out stress, increase of the critical fiber length, and corresponding decrease in tensile strength and modulus of the composites. Thielemans and wool [11] reported the improvement in the interface between the unsaturated thermosetting resin (mixture of acrylated epoxidized soybean oil and styrene) and reinforcing flax fibers by butyrated kraft lignin. The SEM images illustrated a clear improvement in the adhesion of the resin to the fibers by showing the fibers fracturing together with the resin, without fiber pullout. They also reported that flexural strength increased by 40% for a composite containing 5% butyrated lignin. The effect of surface treatment of hemp fiber on the properties of the resulting bio-fiber reinforced unsaturated polyester resin composites was studied [12]. The authors revealed that bio-composites made from acrylonitrile-treated hemp fiber showed enhanced mechanical and thermal properties. They [12] also reported that low percent acrylonitrile treatment was quite effective to improve fiber–matrix adhesion. Several researchers [13–16] reported in their reviews the work on natural fiber–reinforced composites with special reference to the type of fibers, matrix polymers, treatment of fibers, and fiber–matrix interface. They also reported that one of the most important factors that determine the final performance of the composite materials is the quality of the fiber–matrix interface. A sufficient degree of adhesion between the surface of hydrophilic lignocellulosic natural fibers and the polymer matrix resin is usually desired to achieve optimum performance of the biocomposite. Dewaxing, alkali treatment, isocyanate treatment, peroxide treatment, vinyl grafting, bleaching, acetylation, and treatment with coupling agents are useful ways to improve fiber–matrix adhesion in natural fiber composites.

Date palm farming and agriculture has experienced a considerable boom in recent years. Thus, enormous quantities of date palm biomass are produced annually through seasonal pruning as an essentially regular agricultural practice. Trimming of the date palm trees is curried out annually. From each individual tree 10 to 15 branches are cut down. Thus, on average, 35 kg of palm residues are obtained per tree. Kandeel et al. [17] estimate the palm biomass produced in this way to amount to 500,000 metric tons per annum in Saudi Arabia only. This truly huge amount of national wealth is too precious to be wasted year after year.

Recently, published researches by the author and others have focused on the utilization of date palm fiber with both thermoset [18–21] and thermoplastic [22] matrices. The work so far has been concentrated on the effect of fiber orientation and chemical treatment on the mechanical properties and fracture characteristics of date palm fiber–reinforced composites. There is, however, little knowledge about the effect of chemical treatment on the strength and adhesion characteristics of date palm fiber.

In the present study three interface modifiers, an aqueous alkaline solution, silane coupling agent, and a combination of an aqueous alkaline solution and a silane coupling agent are investigated through single fiber pull-out tests, for use in date palm fiber (Phoenix dactylifera-L) composites. The compatibility of the fibers is considered for low and high viscosity polyester resin.

MATERIALS AND METHODS

Materials

Date palm fibers manufactured and supplied from a local market were used throughout this study. In order to improve the strength of the fiber and the adhesion between the fiber and the matrix, the fibers employed in this study were subjected to one or more of the following surface treatments (see Table 1), which are described hereafter.

- Alkaline treatment to influence the fiber strength: the alkaline treatment was done by treating the date palm fibers with a NaOH at 2% w/v aqueous solution, for 1 h at 25°C, then, they were washed with distilled water until the water used to wash the fibers no longer indicated any alkalinity reaction. Subsequently, the fibers were dried at 60°C for 24 h.
- Silane treatment to influence the fiber–matrix adhesion in unsaturated polyester composites: to improve the fiber–matrix adhesion

TABLE 1 Different Fiber Treatments Applied to Date Palm Fibers

Keyword	Surface treatment
W1	No treatment (as received)
W2	Treated with an aqueous alkaline solution
W3	Treated with a silane coupling agent
W4	Treated first with an aqueous alkaline solution and then with a silane coupling agent

in unsaturated polyester based composites, a fiber modification with silane was applied. This modification was carried out with an aqueous silane solution [1.0% w/w silane and 0.5% w/w dicumyl peroxide, dissolved for their hydrolysis in a mixture of methanol-water (90/10 w/w)]. The pH of the solution was adjusted to 3.5 with acetic acid and stirred continuously for 10 min. Then the fibers were immersed in the solution and left for 1 h with agitation. At last, the fibers were dried at 60°C for 24 h.

Two grades of polyester resin were used as matrix materials in this study, with Methyl Ethyl Ketone Peroxide (MEKP) as the hardener: SIROPOL 8340 and SIROPOL 8340-TP, which are low and high viscosity polyester resins supplied by Saudi Industrial Resins LTD, Jeddah, Saudi Arabia. The manufacturer specifications of the resins supplied are shown in Table 2. The components were used in the ratio 100 parts by weight of resin to 1.0 part by weight of hardener, according to the specification set by the manufacturer.

Testing Methods

Single fibers test specimens were subjected to tensile tests as well as pull-out test, which are described here in detail.

TABLE 2 Specifications of SIROPOL 8340 and SIROPOL 8340-TP as Provided by the Manufacturer

Type	Viscosity (cps)	Percent solid (%)	Acid number	Gelling time (min)	Appearance
SIROPOL 8340	500	62	25–30	25	Clear yellowish
SIROPOL 8340-TP	1200	59	20–25	25	Pink

Single Fiber Tensile Tests

Specimen preparation. Single fibers were carefully separated from the bundles manually and both fiber ends were bonded to window-frame paper cards for handling purposes, using a slow-setting epoxy adhesive (Araldite, Ciba Speciality Chemicals), taking care to ensure that a minimum of 10 mm of fiber was embedded in the resin at each fiber end. The length of the window in the paper card defined the gauge length to be tested. Specimens were left for at least 3 days before testing in order to ensure full curing of the resin. During mounting, the specimens were handled only by paper tabs and the working zone of the fiber was not touched. This procedure made the handling of the fibers easier and damage less likely.

Test set-up. The tests were carried out on an Instron 3300 tensile machine. The load was measured by the 5 N standard load cell and displacement was registered by an electronic unit of the tensile stage. During the experiment, the data were transferred to the PC. Pneumatic grips made by Instron were used to clamp the fiber. The distance between the grips was fixed to 10, 20, 30, or 60 mm, depending on fiber length. The upper end of the fiber was clamped first (right below the paper tab). In order to allow the fiber to self-align, under the weight of lower paper tab, approximately 1–2 min pause was made before the lower end of the fiber was clamped. Lower end of the fiber was clamped just above the lower paper tab. Clamping pads of the grips were covered with PVC tape in order to prevent fiber damage in the clamping area. During the clamping pressure in the grips is reduced to minimal level and after both grips were closed, pressure was raised to the working level (20–30% lower than maximum allowed for these particular grips). Both edges of the frame were cut before the testing. All tests were displacement controlled with the loading rate of 0.5 mm/min. Because the fiber was not pre-stretched before the test, there was excessive initial displacement before load was actually applied on the fiber. The amount of this displacement was defined as an interval from the beginning of the test until the point at which load increase is observed. It was discounted later on during data processing. A minimum of 10 samples per gauge length were tested.

Single Fiber Pull-Out Tests

Specimen preparation. It is known that the work done in separating the fiber–matrix interface surfaces makes a major contribution to the total energy of fracture. The most common method is to dip one end of a fiber into a pot of uncured resin and hold it in position until

the curing finished. Specimens were prepared by embedding one end of a single date palm fiber in a block of uncured low and high viscosity polyester resin matrixes over the critical length. The fiber was held in correct position during the specimen curing process. The embedded lengths of the specimen were between 80 and 180 μm (a longer embedded length led to fiber failure instead of fiber pull-out).

In order to measure the fiber diameter, digital pictures of the fibers were made before the loading. Images were made by the computer control digital camera (CCD) attached to the microscope and then transferred to the PC for further processing. Fiber diameter was evaluated from analysis of digital images as the average of five apparent diameter measurements taken along the fiber.

Test set-up. After the resin had solidified, the mold was placed in an Instron 3300 tensile machine with special arrangement for the test. The fiber end is gripped and an increasing load is applied and measured by the 5 N standard load cell and displacement was registered by an electronic unit of the tensile stage as the fiber is pulled out of the matrix, the load and displacement are transferred to the PC. The pull-out tests were conducted at crosshead speed of $0.05\ \text{mm min}^{-1}$. The maximum load, F, measured before detachment of the fiber from the matrix is related to the average value of fiber–matrix shear strength, τ, through the equation.

$$F = \tau \pi l d \tag{1}$$

where πd is the fiber circumference and l is the embedded length.

RESULTS AND DISCUSSION

Single Fiber Tensile Tests

The UTS of the fibers as a function of surface treatment and gauge length are shown in Figure 2. Extrapolation of the data of untreated fibers gives a failure stress of approximately 1426 MPa at the critical length. As was expected, surface modification has caused a shift of the critical length to higher UTS values in comparison with the untreated date palm fibers. This shift is an indication of a higher stress transfer at the interface, and indirectly of a stronger interface. The date palm fiber treated first with an aqueous alkaline solution and then with a silane coupling agent (W4) was found to be the fiber with the strongest interface, with a failure stress of 2164 MPa at the critical length. The differences with the other two treatments (W2 and W3) were better than the untreated fibers with a failure stress at the critical length of 1702 and 1975 MPa, respectively. The obtained

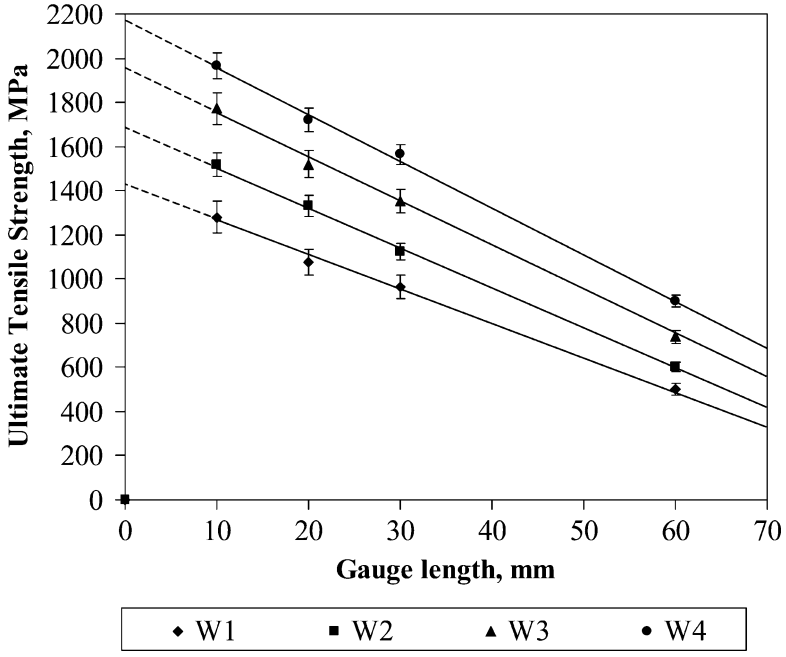

FIGURE 2 Ultimate tensile strength of date palm fibers with different surface treatment as a function of gauge length.

results compares well with 1834 ± 900 MPa reported for hand decorticated fibers and 1522 ± 400 MPa for standard decorticated fibers at 3 mm gauge length [23].

Single Fiber Pull-Out Tests

Figures 3 and 4 show the variation of the debonding force, F, with embedded length, l, at different chemical treatment of date palm fiber for the two resin matrix systems, respectively. It can be seen that the data are rather scattered but both sets of data fall on straight lines, as predicted by Eq. (1) (the error bars have been omitted for clarity). It should be pointed out, however, that the data extrapolate to finite values of debonding force for zero embedded length—a point also noted by Piggott [24]. Varying the surface treatment of the date palm fiber from only NaOH aqueous solution treatment-to-only silane coupling agent-to-treatment first with an aqueous alkaline solution and then with a silane coupling agent, leads to a continuous increase in the debonding force. The order of increase in debonding force is high as

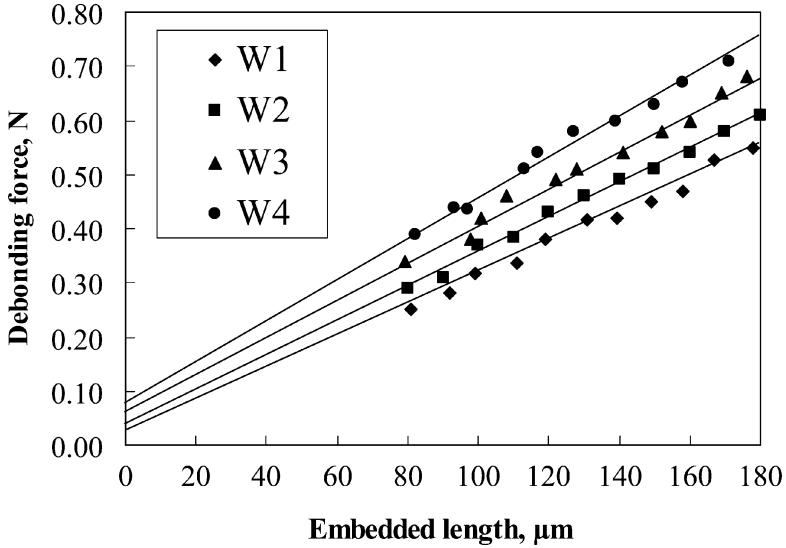

FIGURE 3 Variation of debonding force with date palm fiber length at different chemical treatment with low viscosity polyester resin for pull-out tests.

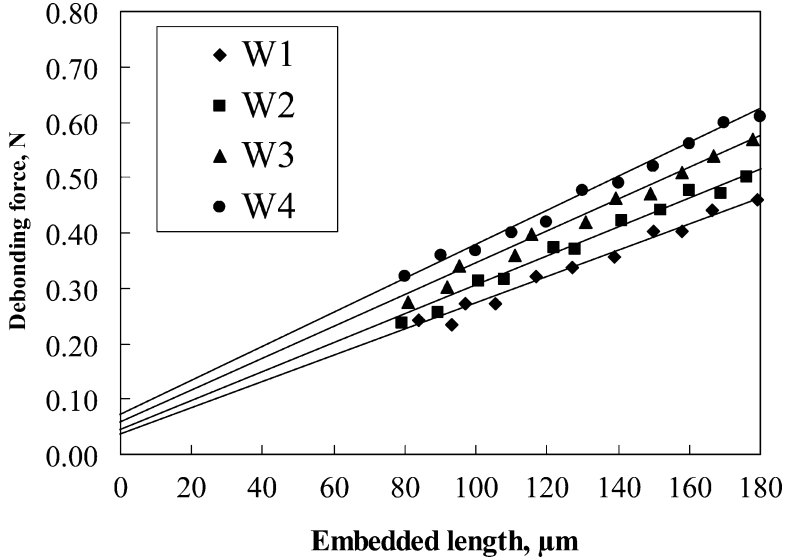

FIGURE 4 Variation of debonding force with date palm fiber length at differet chemical treatment with high viscosity polyester resin for pull-out tests.

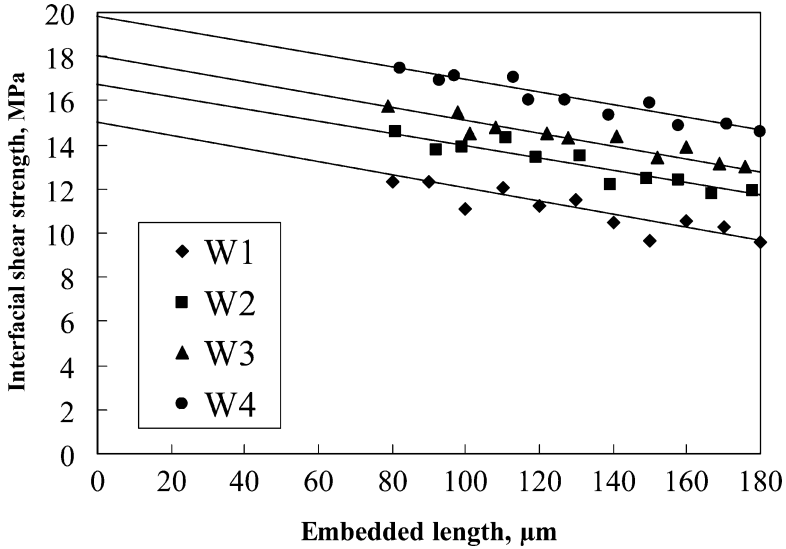

FIGURE 5 Variation of interfacial shear strength (IFSS), calculated using Eq. (1), with embedded fiber length at different chemical treatment with low viscosity polyester resin for pull-out tests.

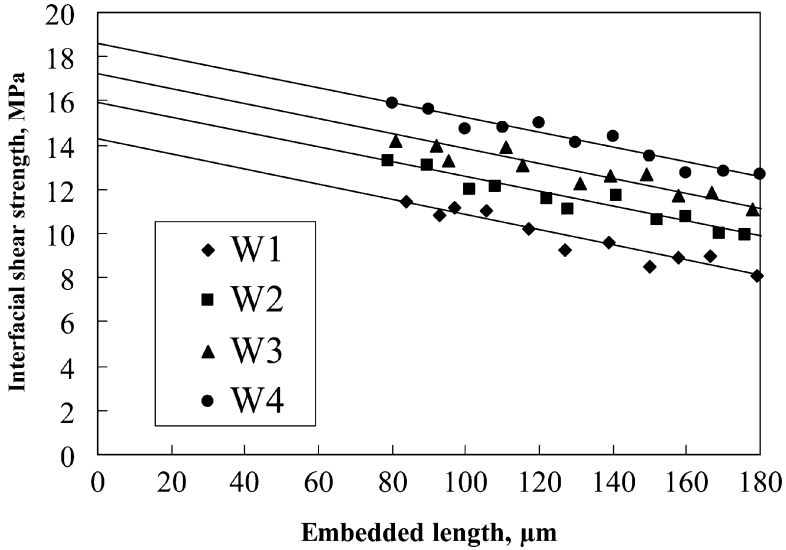

FIGURE 6 Variation of interfacial shear strength (IFSS), calculated using Eq. (1), with embedded fiber length at different chemical treatment with high viscosity polyester resin for pull-out tests.

was observed for low viscosity matrix specimens. This is developed in Figures 5 and 6, which shows a variation of IFSS with embedded length for the two systems at different chemical treatment of date palm fiber. It can be seen that, for both systems, the apparent interfacial shear strength increases as the embedded length decreases. According to Eq. (1), there should be a linear increase of debonding force, F, with embedded length, l.

The results of fiber pull-out tests are in good agreement with the results obtained for the interfacial bond from the Single fiber tensile tests. Furthermore, the low viscosity polyester resin (SIROPOL 8340) shows higher shear strength compared to the high viscosity resin (SIROPOL 8340-TP). The results illustrate that the fiber treated with only the NaOH aqueous solution seem to improve the fiber–matrix shear strength of the composite material. The alkali treatment can give up to 18% increase to the shear strength, due to the removal of pectins. Higher shear strength is obtained when using the fibers treated with the silane coupling agent as compared with the fibers with no surface treatment. The best effect however is reached with a combination of both treatments (W4), which increases the average value of fiber–matrix shear strength by more than 40% with respect to the composite made with untreated fibers (W1). Comparable findings were reported by Thielemans and Wool [11], they report 40% improvement in the interface strength for a composite containing 5% butyrated lignin.

It is also revealed from the data of Figures 5 and 6 that untreated and treated composites prepared with high viscosity polyester resin follow the same inclination observed with respect to the effect of surface treatment on the average value of fiber–matrix shear strength, except with a lower value compared to the low viscosity polyester resin composites. In this case, it is suggested that less-viscous resin can fill the microgaps and flow in fiber interphase, which is beneficial for the impregnation afterward. Similar observation was reported by Van de Weyenberg et al. [25] in there studies on the influence of processing and chemical treatment of flax fibers on the composites. Further light is shed on this behavior in the scanning electron microscopy study described next.

Fracture Surface Examination

Scanning electron micrographs of the fracture surfaces for untreated and treated date palm fiber–polyester composites prepared by single fiber pull-out test are shown in Figures 7 and 8. Some characteristics that result from the fiber surface treatment can be pointed out. As can

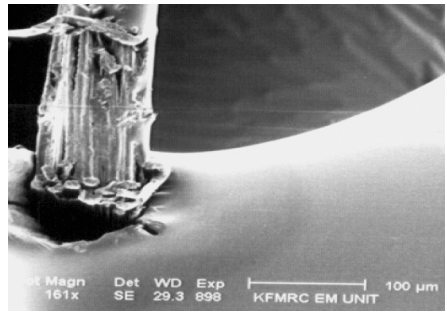

FIGURE 7 SEM micrograph showing the fracture surface of the untreated date palm fiber polyester composite.

be seen in Figure 7, for the untreated specimen (W1), The fiber pulls out smoothly from the resin matrix with cylindrical cavity left behind. A stronger interaction between the fiber and the matrix was observed during the fiber pull-out off the matrix, with the fiber surface treatment first with an aqueous alkaline solution and then with a silane coupling agent composite (W4) (Figure 8). This is suggested due to the removal of pectins, as a result of the alkali treatment and the increase in surface roughness, and the effect of silane coupling agent.

Figures 9 and 10 show micrographs examination of specimens prepared with low and high viscosity polyester resin matrixes, respectively. Figure 9 shows an area at the interphase site of a low viscosity polyester resin specimen. There is no evidence whatsoever of microgaps at the interphase between the fiber and the resin matrix.

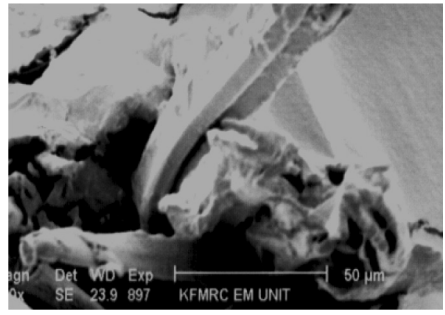

FIGURE 8 SEM micrograph showing the fracture surface of the treated first with an aqueous alkaline solution and then with a silane coupling agent date palm fiber polyester composite.

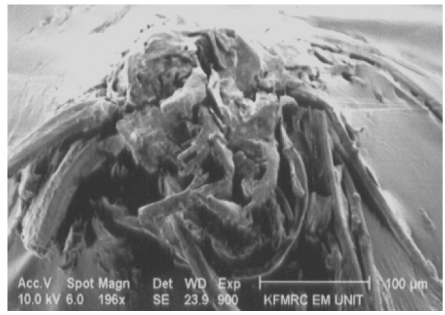

FIGURE 9 SEM micrograph showing date palm fiber embedded in low viscosity polyester composite.

FIGURE 10 SEM micrograph showing date palm fiber embedded in high viscosity polyester composite.

Figure 10 shows areas of microgaps at the fiber–matrix interface of a specimen prepared with high viscosity polyester resin matrix. These microgaps are evidence of the poor impregnation of the resin throughout the interphase.

These observations confirmed the conclusion stated earlier by the single fiber pull-out test, namely that the failure mode of the specimens changed with treatment from fiber pull-out smoothly in the untreated specimen, to a rough failure with the fibers fracture for the treated date palm polyester resin composites.

CONCLUSION

A study of the interface in treated and untreated date palm fiber–polyester resin composites was conducted by means of single fiber pull-out

test. It was found that fiber treated with a combination of both alkaline solution and silane coupling agent, improved the stress transfer efficiency at the interface by more than 40% compared to that of the untreated fibers. It is also concluded from fiber pull-out test that, the fiber–matrix shear strength of specimens prepared with low viscosity polyester resin has a higher value comparing to the high viscosity polyester resin composites. This is attributed to the fact that the low-viscous resin can fill the microgaps and flow into the fiber interphase, which is beneficial for the impregnation afterward. The UTS of the treated date palm fibers at the critical length was also determined. Single fiber tensile strength of untreated fibers gives a failure stress of 1426 MPa at the critical length, whereas, the fiber treated first with an aqueous alkaline solution and then with a silane coupling agent was found to be the fiber with the strongest interface with a failure stress of 2164 MPa at the critical length. It is suggested that this shift in failure stress is an indication of a higher stress transfer at the interface, and indirectly of a stronger interface. Investigations of fracture surface morphology using scanning electron microscopy verify that the fiber–matrix interphase is much stronger when the fiber surface topography is combined with the alkali treatment of the fiber surface and with a silane coupling agent. It can also be concluded from the present study as well as the previous studies by the author [18,19] that these findings are promising and further research is necessary to establish the use of treated date palm fiber with its enhanced properties.

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