SILANATED AGRICULTURAL WASTE BAGASSE FOR WOODEN-POLYESTER COMPOSITE

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Summary: This work aims to introduce agricultural waste fibers, specifically Bagasse, as filler of unsaturated polyester resin for making wooden-polyester composites. Bagasse fibers were firstly treated using 5% Sodium Hydroxide (NaOH) and then with methyl-trichloro silane coupling agent (CPL). Bagasse-UP (B-UP) composites were then prepared by addition of untreated (B), alkali-treated (ATB) and silanated (STB) Bagasse fibers as (5, 10 and 15%) by weight of UP. The B-UP composite mix was subsequently cross-linked at room temperature using methyl ethyl ketone peroxide then exposed to elevated temperature to achieve full crosslinking. The flexural behaviour of the B-UP composite was studied using standard flexural tests. In addition, water absorption at room and high temperatures was also examined. Young's modulus and flexural strength apparently improved with STB-UP composites. ATB-UP composites had higher water absorption compared with B-UP composites, but STB-UP composites had the least water absorption. To quantify the effect of water on the mechanical characteristics of the B-UP composite, dynamic mechanical analysis (DMA) tests were performed. DMA results show that silane treatment of Bagasse fibers significantly improved the storage modulus of the composite. While water exposure slightly reduced the storage modulus of B-UP and ATB-UP composites, silane treated composites STB-UP showed the least reduction of storage modulus after water exposure. TEM, FTIR, and XRD measurements were performed to explain the improvement of silane treatment of the Bagasse fibers over other treatment methods.

1. INRTODUCTION

In Egypt, agriculture waste makes a very critical environmental challenge requiring the disposal of thousands of tons of natural fibers annually. Farmers tend to burn large amounts of agricultural waste fibers in air resulting in recently what is known as "*Black Cloud*". The potential use of these agriculture waste fibers as filler of polymers is examined to achieve a

group of goals represented in maintaining a clean environment and production of advanced polymeric composites with acceptable mechanical properties for construction applications.

Agriculture waste such as Bagasse and rice straw is relatively cheap, easily available and sustainable material. Therefore, natural fibers-polymers composites are typically less expensive than composites with synthetic fillers such as carbon and glass fibers [1]. Generally, natural fibers have special advantages such as low cost, good aspect ratio and low energy consumption thus low carbon foot print. The use of natural fibers to make low cost composites is a subject of worldwide interest [2]. It is well-known that natural fibers consist of cellulose, hemicelluloses and lignin in addition to small concentrations of pectin and waxes. The undesired non-cellulosic components can lead to formation of ineffective fiber-matrix interface affecting the composite characteristics. To improve its interfacial bond with polymers, fiber were chemically treated via NaOH solution to remove these impurities [3]. One of the most available agricultural waste is Bagasse shown in Figure 1. Bagasse is the fibrous residue leftover after milling of Cane with 45-50% moisture content.



Figure 1: (a) Bagasse and (b) treated Bagasse.

Unsaturated polyester (UP) is obtained by condensation of both saturated and unsaturated acids such as phthalic anhydride and maleic anhydride, respectively with a diol such as propylene glycol or diethylene glycol. UP is dissolved in vinyl monomers such as styrene for reducing its viscosity. The unsaturation in the backbone provides sites for reaction with styrene monomer using free-radical initiator leading to formation of 3D-network. The solution of UP and styrene is known as UP resin that capable of producing very strong bond with other materials [4,5]. Unlike the compatible interaction between hydrophilic UP and hydrophilic fibers; UP might form weak interfacial adhesion with hydrophilic fibers [6]. Coupling agents were used in small quantities to treat the fiber surface to overcome this challenge [7]. Various studies on the use of different natural fibers, as fillers for polyester matrix, have been reported; polyester-jute composite [8], polyester-sisal composite [9], polyester-coir composite [10], polyester-rice straw composite [11], polyester-pineapple leaf composite [12], polyester-cotton-kapok composite [13] and polyester-short bamboo composite [14]. In this work; we prepared Bagasse-unsaturated polyester composites incorporating different Bagasse loadings with untreated, alkali-treated, and silvlated Bagasse fibers. The physical and mechanical properties of Bagasse-UP composites were studied. The flexural behaviour was examined using three point bending test. Water absorption test was performed for Bagasse-UP composites. The results enable identifying the preferred chemical treatment estimating the optimal fiber content needed to manufacture of green construction composites.

2. METHODS

2.1. Materials and Procedure

Bagasse fibers obtained from local plants with aspect ratio of 10. UP resin is Crystic-126 with 38% styrene content and 400 cps viscosity. MEKP and cobalt octoate were used as catalyst and accelerator; respectively. Methyltrichlorosilane was used as coupling agent (CPL). All ingredients and chemicals were applied without further purification except some Bagasse that underwent chemical treatment. Alkali treatment of Bagasse fibers was performed by soaking part of Bagasse within 5% NaOH solution for 60 minutes at room temperature followed by washing by distilled water. The washed fibers were then heated to 70°C for 4 hours to remove all moisture. To incorporate the CPL into Bagasse, fibers were suspended in distilled water as 0.5 wt.%, sonicated for 5 minutes and stirred for 24 hours. This aqueous suspension was solvent exchanged respectively with ethanol and acetone then methyl trichlorosilane was added as 5.0 wt.%. The suspension of silvlated Bagasse was stirred for 24 hours and dried at room temperature for 24 hours then at 70°C for 2 hours. Bagasse (B), Alkali-treated Bagasse (AB) and silvlated Bagasse (SAB) were used as fillers as 5, 10 and 15% by weight of UP resin. Curing reaction was performed by addition of 2 wt% of MEKP and 0.5 wt.% of cobalt octoate. All components were well mixed together and poured into moulds. Before demoulding, samples were cured for 24 hours at room temperature followed by post-curing for three hours at 85°C to insure complete crosslinking. Finally, all specimens of B-UP, AB-UP and SAB-UP composites were cooled to room temperature.

2.2. Mechanical Testing

Flexural behaviour of composites was examined using three point bending test according to ASTM D 790-03 [15]. Flexural tests were conducted on 140 mm length, 35 mm width and 9 mm thickness specimens using 10 kN servo hydraulic testing machine under displacement control mode of 2 mm/min. The flexural strength and Young's modulus of elasticity of the composites were calculated using Equation (1).

$$\sigma_{\max} = \frac{3P_{\max}L}{2bh^2} \qquad \& \qquad E = \frac{L^3}{4bh^3} \left(\frac{P}{\Delta}\right) \tag{1}$$

where σ_{max} is flexural strength, *E* is Young's modulus of elasticity, P_{max} is the maximum load, *L* is specimen span, *b* is specimen width, *h* is specimen thickness and (P/Δ) is the slope of the linear region of the load-deformation relationship observed in testing.

Water absorption (W_A) test was performed according to ASTM D 570-98 [16]. Specimens in the form of disks with 50.8 mm diameter and 3.2 mm thickness were weighted and results were calculated as an average value of three samples. For 24 hours immersion; the conditioned specimens were placed in distilled water at room temperature and then removed after 24 hours. After the surface was wiped off, the wet specimens were weighted immediately. For two hours immersion; the conditioned specimens were placed in distilled water at room temperature and then removed after 15 minutes. Specimens were weighted immediately after surface drying. Water absorption (ΔW %) was calculated using Equation (2).

$$\Delta W\% = \frac{W_{wet} - W_{conditiond}}{W_{conditiond}}\%$$
(2)

where W_{wet} and $W_{conditioned}$ are weights after and before immersion, respectively.

2.3. Microstructural Investigation

To help explain the observations of the mechanical testing, a group of microstructural investigations were conducted. The morphological features of treated and untreated fibers were investigated by transmission electron microscope (TEM) using JEOL-2100F microscope at 200 kV. Fourier transform infrared (FTIR) spectra were recorded using Nicolet IS-10 FTIR spectrophotometer-Thermo Fisher Scientific within 400-4000 cm⁻¹ wave number. The crystallinity of untreated and treated fibers was examined using wide-angle X-ray diffraction (XRD) within radiation λ =1.54Å, voltage of 40 kV and filament current of 40 mA. All samples were scanned in 20 from 5 to 70° at a rate of 1°/min.

3. RESULTS AND DISCUSSION

3.1. Mechanical Characterization

Figure 2 showing the stress-strain curve (a) for B-UP, (b) for AB-UP and (c) for SAB-UP composites. It is observed from Figure 2(a) that increasing Bagasse content resulted in reducing the flexural strength. Similar trend was also observed with AB-UP composites in Figure 2(b). However, strength increased gradually with increasing AB content showing that at 5% AB the flexural strength of AB-UP composite approximately equal to the neat UP. Figure 2(c) shows that silane treatment of Bagasse fibers enhanced the flexural strength in all SAB contents by values that exceed UP. The highest improvement is achieved by 10% SAB.



Figure 2: Strength-strain curve (a) for B-UP, (b) for AB-UP and (c) for SAB-UP composite.

For a detailed study of each mechanical characteristic, Figure 3 and Figure 4 respectively represent flexural strength and Young's modulus of elasticity for different B-UP, AB-UP and SAB-UP composites. Young's modulus increased after alkaline treatment recording 4.5 GPa for 5% AB-UP composites compared with 3.5 GPa of UP. After silane treatment, Young's modulus increased in all percentages. Moreover, 10 and 15% SAB-UP composites recorded Young's modulus at 5.8 and 4.8 GPa. Consequently, filling of UP with SAB improved Young's modulus of elasticity and flexural strength at almost all SAB contents higher than that achieved by AB. This enhancement is attributed to strong interfacial adhesion between UP matrix and SAB fibers compared with AB fibers.







Figure 4: Young's modulus of Elasticity for B-UP, AB-UP and SAB-UP composites.

In Figure 5(a), a representation for polyester-treated fibers interface is shown schematically. It is suggested that the polyester matrix is bonded with fibers via hydrogen bonding. Figure 5(b) illustrates the polyester-CPL-treated fibers interface, the strong interfacial adhesion is created by CPL through bonding silane with hydroxyl groups in cellulose. Meanwhile, methyl group is bonded with the polymeric matrix through Van der Waals forces. This behaviour of CPL allows it to work as a bridge that combines Bagasse fibers and polyester matrix together.



Figure 5: Schematic representations (a) for polyester-fiber interface and (b) for polyestersilane-fiber interface.

3.2. Water Absorption

Figure 6 illustrates water absorption of B-UP, AB-UP and SAB-UP specimens through immersion in water at room temperature and boiling water. It is apparent that increasing of Bagasse fiber content resulted in increasing the water absorption of the composite within room temperature and boiling water immersion conditions. In addition, water absorption of AB-UP composites is higher than B-UP composites. This observation is attributed to the alkali-treatment effect on the surface of Bagasse fibers. While this treatment is important to remove non-cellulosic materials, it exposes higher surface area of Bagasse fibers to hydroxyl groups resulting in higher water absorption compared with untreated fibers. The maximum water absorption after alkaline treatment was 0.023% and 0.041% for 15% AB-UP in cold and boiling water immersion.



Figure 6: Water absorption (WA) % for B-UP, AB-UP and SAB-UP composites with cold and boiling water.

The alkali treatment seems to have two contradicting effects; first is to enable strong bond with the polymer matrix and second to enable high surface area of the fibers making it prone to water absorption. Water absorption of SAB-UP composites was significantly decreased compared with B-UP and AB-UP composites. With CPL treatment, the silane interacts with hydroxyl groups at the cellulosic surface bonding them with the polymer via strong bonds. This process yields fewer sites at cellulose surface free to absorb water. The maximum water absorption after silane treatment was 0.006% and 0.011% for 15% SAB-UP in cold and boiling water immersions. These values are acceptable compared with 0.6% water absorption that was reported in previous study [17].

3.3. Microstructural Characterization

TEM images of B, AB and SAB are illustrated in Figure 7 (a, b and c). The images indicate that high aspect ratio of AB and SAB was successfully obtained. In addition, AB was obtained as nanocrystals in the form of significant rod-like nanoparticles with different dimensions that ranged from 100 to 500 nm in length and from 20 to 50 nm in diameter. It is apparent that B has highly agglomerated morphology than AB and SAB. It is observed that separated needle cellulosic particles were generated after treatment of Bagasse fibers.



Figure 7: TEM (a) for Bagasse, (b) for alkali-treated Bagasse and (c) for silvlated Bagasse.

For FTIR in Figure 8 (a), the characteristic cellulosic hydroxyl O–H stretching at 3300-3500 cm⁻¹, C–H stretching at 2850-2950 cm⁻¹, C–H bending at 1350-1480 cm⁻¹ and C–O stretching at 1000-1150 cm⁻¹. The peak around 1640 cm⁻¹ is corresponding to the O–H bending in water. In the spectrum of B, the peak at 3390 cm⁻¹ is attributed to the presence of free and hydrogen bonded OH groups, the peak observed in the region of 1700-1800 cm⁻¹ is ascribed to C=O stretching in acetyl and ester groups in hemicellulose and also to the C=O stretching in carboxylic acid groups in lignin. The weak peak around 1450 cm⁻¹ is for the aromatic C=C stretching in lignin. In the spectrum of AB, most of the characteristic peaks for B were observed after alkaline treatment but with an enhancing amount of OH stretching peak and with absence of others. This is evidence that the bonded OH groups of the untreated Bagasse became un-bonded due to the removal of the matrix materials (hemicelluloses and lignin). In addition, the lack of peaks of 1700-1800 cm⁻¹ is another evidence for the progressive removal of hemicellulose and lignin through this treatment.



Figure 8: FTIR (a) for Bagaase (B), alkali-treated Bagasse (AB) and silvlated Bagasse (SAB) and (b) for polyester (UP) and (SAB-UP) composite.

A typical spectrum of surface silvlated cellulose SAB is also shown in Figure 8 (a). This spectrum shows the characteristic peaks for the silvlated cellulose at the same regions

discussed above. The silylation process of Bagasse was assured by the increase in the relative intensity of the peak at 1050 cm⁻¹, which might be attributed to the Si–O–Si group stretching. In addition, the existence of silylated cellulose is further confirmed by the broad band around 700-780 cm⁻¹ which might be attributed to Si-CH₂ group [18] and at 450-650 cm⁻¹ which might be attributed to SiCl₃ symmetric and antisymmetric stretch [19].

Generally, treatment of AB with silane is assured by the presence of characteristic peak at around 1050 cm⁻¹ which is attributed to the stretching vibration of –Si–O–Cellulose [20]. In Figure 8 (b), the spectrum of UP contains the characteristic peaks of polyester; C–H stretching at 2940 cm⁻¹, C=O stretching of the ester carbonyl group at 1770 cm⁻¹, C–H bending at 1450 cm⁻¹ and C–O stretching near 1050 cm⁻¹. On the other hand, the spectrum of SAB-UP composite confirms the chemical bond between the UP matrix and cellulose fibers; Si–CH₃ at 700-750 and 1200-1270 cm⁻¹, Si–O–Si and C–O stretching at 1770 cm⁻¹, C–H bending near 1450 cm⁻¹, C=O stretching in ester group at 1770 cm⁻¹, C–H stretching at 2900 cm⁻¹ and hydroxyl/silanole O–H stretching at 3500 cm⁻¹. These peaks provide evidence for coating the fiber surface with silane. FTIR spectra also confirm that cellulose fibers and polyester matrix were chemically bonded and the cellulosic component in B, AB and SAB fibers was maintained during the chemical treatment after disposal of non-cellulosic materials.

The crystallinity of untreated and treated Bagasse fibers was examined using XRD technique. XRD patterns of Bagasse fiber (B) in addition to its modified forms (AB) and (SAB) are shown in Figure 9. It can be observed that the diffraction peak at $(2\theta=22)$ is wide and round for untreated fibers; however, the peak at $(2\theta=22)$ for the treated fibers is sharper and narrower than untreated fibers. A shoulder peak at $(2\theta=15)$ and a weak peak at $(2\theta=35)$ appear after treatment, which are assigned to the cellulose phase. This reveals the removal of most of lignin and hemicellulose from the fibers. The hydrogen bonds between cellulose molecules result in an ordered system. Based on previous research individual fibrillar units consist of long periods of ordered regions interrupted by completely disordered regions. Treatments affect the crystallinity of the cellulosic fibers where the sharper diffraction peak at $(2\theta=22)$ indicates higher crystallinity degree in the treated fibers [21].

In all cases, the portion of crystalline cellulose was found to be higher for treated cellulose fibers than for untreated fibers due to partial removal of the lignin and hemicelluloses by treatment. As a result, higher crystallinity in the treated fibers will be associated with improving fiber strength. The crystallinity of treated Bagasse fibers explains the improvement of mechanical properties of composite incorporating AB and SAB compared with B. Furthermore, XRD diffractogram of SAB fibers shows decreased crystallinity compared with AB fibers represented by the absence of the sharp peaks. It is therefore evident that the addition of coupling agent decreases the crystallinity. This might be attributed to the fact that after silylation process, the new functional groups attached to the fiber surface decrease its crystallization. As a result, this indicates that cellulose whiskers were generated upon chemical treatment without the destruction of cellulosic units.



Figure 9: XRD for Bagaase (B), alkali-treated Bagasse (AB) and silvlated Bagasse (SAB).

4. CONCLUSIONS

Bagasse-unsaturated polyester composites were prepared by addition of Bagasse fibers (5, 10 and 15%) by weight to unsaturated polyester resin. Bagasse fibers were also used as filler after treatment with 5% NaOH solution and methyltrichlorosilane coupling agent. The effect of untreated, alkali-treated and silane-treated Bagasse fibers with different contents was investigated using flexural test. Results indicated that increasing the Bagasse content adversely affected the mechanical properties. Addition of 5 and 10% alkali-treated Bagasse to polyester matrix began to retain Young's modulus of elasticity and flexural strength to values near the blank. Filling of polyester with silvlated Bagasse significantly improved both of Young's modulus and flexural strength with all concentrations compared with Bagasse or alkali-traded Bagasse. Similarly, water absorption was increased by addition of more Bagasse fibers to the polyester especially after alkaline treatment. After silane treatment, water absorption sharply decreased. The effect of chemical treatment of Bagasse on the mechanical and physical properties of Bagasse-polyester composites was approved using microstructural tests. TEM indicated that chemical treatment leaded to formation of rod-like cellulosic fibrils after removal of non-cellulosic materials such as hemicelluloses and lignin. This regenerated cellulose can chemically interact with polyester matrix through stronger interface. FTIR confirmed that treated-Bagasse fibers were chemically bonded with polyester matrix while the molecular structure of cellulose was remained unchanged. Moreover, XRD proved that treatment of Bagasse regenerated more crystalline cellulosic particles.

After silane treatment, the new silvlated cellulose interacted with the polyester resin with more compatibility resulting in improvements in the physical and mechanical properties of Bagasse-polyester composites. Consequently, silvlated Bagasse fibers can be applied as cost-effective filler till 15% to the polyester resin with enhanced mechanical and physical properties compared with neat polyester. This cheap composite can be applied in manufacture of articles bearing high loads such as constructions, car accessories, building and other many advanced industrial applications.

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