Sisal Fibers Coated with Conducting Polyaniline: Property and Structural Studies[1]

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Abstract—Sisal (*Agave sisalana*) fiber was extracted by manual process. These fibers were subjected to surface coating with conducting polyaniline, through in situ oxidative polymerization. The polyaniline modified sisal fibers were characterized by thermal, spectroscopic and microscopic techniques. It was shown that the fiber was coated with polyaniline through in situ oxidative polymerization and the latter had a smoothing effect on the surface as compared to uncoated sisal fiber. Besides, it was confirmed that polyaniline was deposited in conductive form of emeraldine salt. This in turn verified the introduction of active functionalities to the system, which is helpful to tune up surface chemistry of polyaniline for water treatment applications.

INTRODUCTION

Conductive polymers such as polypyrrole, polyaniline (PAni) and polythiophene become a top priority area for both academia and industry as a result of their unique electrical, optical and ion-exchange characteristics [1, 2]. These polymers and polymer composites have different functionalities, like amine, imine and thiol, which are responsible for various modifications and applications [3]. PAni is one of the most exciting conductive polymers due to its low cost, ease of polymerization, flexibility and environmental stability. However, engineering applications of such polymer are restricted as a result of poor processability in common solvents and low mechanical properties [4]. Besides, different research outputs have been proved that PAni could be coated on different substrates, like fibers, organic, and inorganic compounds to form composites with modified properties and enhanced performances [5, 6].

There is growing interest in developing polymer composites derived from renewable, environmentally friend and sustainable resources to alleviate the commonly cited drawbacks of conductive polymers upon surface deposition. Fibrous materials such asflax, banana, coconut and sisal are rich in hydroxyl groups with excellent mechanical properties, low cost, less dense and biodegradability rendered them good candidates to reinforce conductive polymer-matrices [7–9].

Fiber-reinforced polymer composites can be produced using *in situ* oxidation, electrochemical and dispersion polymerization methods. In situ chemical deposition of polymers on surface substrates has emerged as a promising method to alleviate solubility issues, prevent aggregation and is suited for bulk production. The immersion of a fiber into reaction mixture with monomer and oxidant solution results submicrometer thin coating over the surface of the reinforcement phase [10–12].

However, application of natural fibers as reinforcement for polymer-based composite materials has certain shortcomings: high moisture uptake and water absorption cause swelling so as to reduce mechanical property and aggregate formation while processing restrict polymer-matrix selection as well cause reinforcement degradation, and poor compatibility between plant particles and polymeric phase resulting non-uniform surfaces which weaken further the mechanical strength [13, 14].

Polyaniline has reactive N–H group, the source of polyfunctionality, which made it suitable for adsorption of different pollutants from water [1, 2]. Many research outputs have been published on application of PAni composites for heavy metal ions removal such as PAni/sawdust, PAni/agrowaste, PAni/chitosan and PAni/clay from aqueous system [15–17]. Removal efficiency of PAni composites for Cd^{2+}, Cr^{6+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and fluoride ions from contaminated water

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was appreciable even though they have their own limitations [18, 19].

The present work is primarily aspired to explore sisal fibers as new reinforcement phase in the production of PAni coated sisal fiber with the advantage of being lightweight [20], mechanically fairly good and cheap with surface functionalized and potentially applicable for water pollutant remediation from an aqueous system. Besides, the influence of surface coating of sisal fibers on thermal, mechanical and morphological structure was investigated using modern instruments such as: thermogravimetric analysis, Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy, scanning electron microscopy, X-ray diffraction, electrical conductivity and single fiber tensile testing machine.

EXPERIMENTAL

Materials

Aniline, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), hydrochloric acid (HCl), chloroform ($CHCl_3$) and acetonepurchased from Merck Chemical Co. (Germany) through a local agency. They were all analytical reagent grade and used without further purification.

Sisal (*Agave sisalana*) was obtained from Tigray region, Ethiopia. The fibers were extracted using hand decortication method [21], air dried and washed with distilled water, followed by acetone and dried in air at room temperature [22].

Surface Coating of Sisal Fibers with Polyaniline

In situ polymerization of polyaniline in the presence of sisal fibers was carried out using the following procedure: 5 g of sisal fiber was immersed in 0.1 M HCl on stirring to soak uniformly. 0.5 M aniline solution was added to the flask containing acidified fiber on continuous stirring in order to maintain homogeneity throughout the system. To undergo *in situ* oxidative polymerization, 0.5 M $FeCl_3 \cdot 6H_2O$ oxidant solution was added into the mixture drop wise while stirring and the reaction was allowed to continue for 12 h at room temperature. The polyaniline coated sisal fiber was filtered, washed with dilute HCl solution followed by double distilled water repeatedly until the filtrate becomes colorless to remove monomers and oligomer impurities remaining. It was an oven dried at 50°C [23].

Characterization

Fourier transform infrared spectrometer (Bruker Vector 22) was used to record the spectra of untreated sisal fiber (USF), pure polyaniline (PAni) and polyaniline coated sisal fiber (PAni/USF) samples. KBr disk technique was used in a spectral range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

Thermogravimetric analysis of USF and PAni/USF samples were performed on the simultaneous thermal analyzer (DSC-TGA SDT-Q600). The analyzer settings were: a continuous nitrogen flow (20 mL/min) and a heating rate of 40 grad/min from 25 to 600°C.

X-ray diffraction studies were performed under ambient condition on X-ray diffractometer (XRD-7000, Shimadzu) using CuK_α ($\lambda = 1.5418$ Å) radiation with 40 kV and 30 mA on rotation between 10° to 70° at 2θ scale.

Morphology of free sisal fiber (USF) and polyaniline coated sisal fiber (PAni/USF) were observed using a highly customizable scanning electron microscope (JSM-IT300LV, JEOL, USA) coupled with a port for analytical attachment of energy dispersive X-ray (EDX) spectrometry. The samples were gold coated by sputtering technique to avoid charging and observed under different magnifications.

Electrical conductivity of PAni and PAni modified fibers was measured using portable conductometer device (Hanna Instruments HI 8033) by dissolving in deionized chloroform solution.

Elongation at break and breaking tensile strength of original length of 25 mm fiber samples were performed on single fiber tensile testing machine.

RESULTS AND DISCUSSION

FTIR Spectroscopy

The FTIR spectra of USF and polyaniline coated fibers (PAni/USF) are shown in Fig. 1. Comparing the spectra of USF and PAni/USF, they have several bands in common. The bands at 2913 and 2900 cm^{-1} correspond to the C−H symmetrical stretching vibrations of aliphatic hydrocarbons belonging to the sisal fibers from USF and PAni/USF respectively [24]. The bands at 1732 and 1737 cm^{-1} attributed to the C=O stretching of acetyl groups [25] of hemicellulose and lignin of sisal fibers as mentioned in the above order. One basic difference between the free fibers (USF) and polyaniline coated fibers (PAni/USF) is the presence of a band at 1240 cm^{-1} in USF which disappeared in PAni/USF sample. This strong absorption band represents the C−O stretching vibration of aryl groups from lignin [26].

New bands appear in the FTIR spectrum of pure PAni which is quite different from that of USF. Presence of stronger and broader bands at 1480 and 1600 cm^{-1} signifies the existence of benzoid and quinoid ring, respectively. This is an indication that PAni exists in emeraldine form. The band at 1132 cm^{-1} is characteristic of PAni conductivity, which is a measure of electron delocalization. Deposition of polyaniline through in situ oxidative polymerization onto the surface of USF has shown new characteristic bands. The strong band at 1160 cm^{-1} in PAni/USF is characteris-
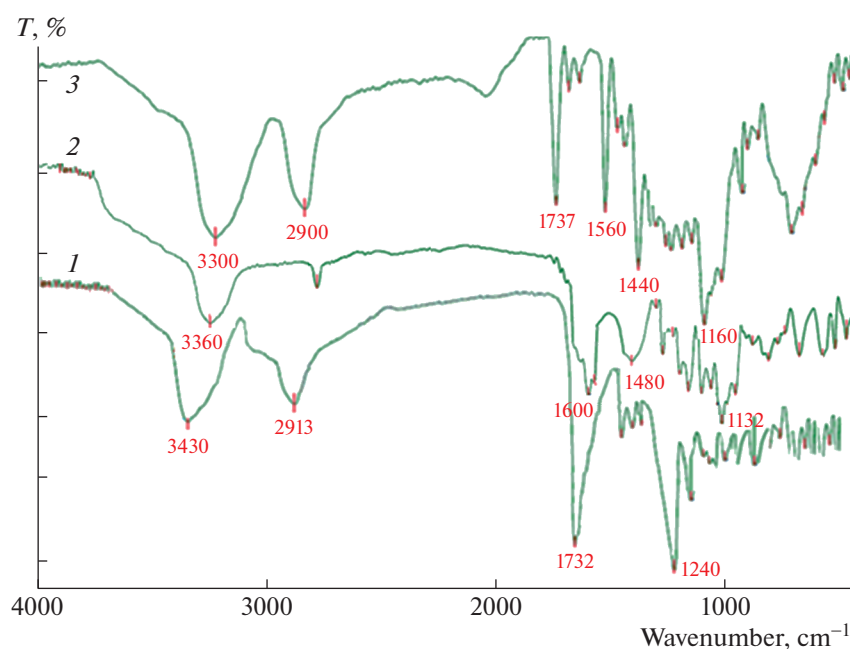
Fig. 1. FTIR spectra of (*1*) USF, (*2*) pure PAni, (*3*) PAni/USF.

tic feature of PAni conductivity, which indicates the degree of electron delocalization [27]. Another important observation from the FTIR spectra of PAni coated sisal fibers was the presence of a benzoid ring (N=B=N) band at 1440 cm^{-1} [28] and a quinoid ring (N=Q=N) vibration at 1560 cm^{-1}, indicating that PAni exists in oxidized form, emeraldine salt [29, 30]. Benzoid and quinoid bands are absent on the free fibers, USF. This further confirmed the surface deposition of polyaniline through *in situ* oxidative polymerization on sisal fibers was successful.

Furthermore, characteristic bands of N−H stretching of amine groups of PAni/USF appears around 3300 cm^{-1}, representing the presence of polyaniline on the surface of the fibers [31]. Comparing the FTIR spectra of free fibers (USF) with polyaniline coated fibers (PAni/USF); there is a visible difference in the higher absorption bands. In the free fibers (Fig. 1, curve *1*), the band at 3430 cm^{-1} belongs to the O−H stretching vibrations of intermolecular and intramolecular H bonds from cellulose [14].

Thermal Analysis

The thermal properties of USF and PAni/USF were analyzed by TGA. The results are shown in Fig. 2, the upper stage of USF thermogram (curve *1*) extends up to 100°C, is due to the removal of moisture present in the fiber. The second step at approximately 350°C is attributed to the decomposition of glycosidic linkages of hemicellulose, cellulose and lignin [25, 32].

In case of PAni/USF (curve *2*), at the first stage removal of moisture, impurities and unreacted mono-

mers may be assigned as in the USF. The second stage around 375°C shows the bond cleavage of C−H, C−C and C−O from hemicellulose, cellulose and lignin. The last stage beyond 450°C is thermally stable compared to the free fiber, which represents the polymer backbone degradation [2, 6, 33]. From the thermograms, it is clearly visualized that weight loss due to moisture USF was significant in USF compared to the PAni/USF. This is clear evidence that most natural fibers possess hydrophilic nature and removes more moisture in comparison with hydrophobic polymers.

X-ray Diffraction Analysis

The diffractograms of USF and PAni/USF trace two distinct reflection peaks, corresponding to 2θ values approximately between 16° and 23°. The peaks for USF (Fig. 3, curve *1*) are exactly located at 2θ = 16° and 22.4°, representing the crystallographic plane reflections of (101) and (002) which are quite similar to the characteristic peaks of cellulosic matter [24, 34]. The difractograms of USF and PAni/USF exhibit considerable overlap of the diffraction peaks. This clearly indicates that there is no significant crystalline transformation of the fiber upon surface deposition of polyaniline. One peculiar difference between the difractograms of USF and PAni/USF is the appearance of new peaks around 26° and 32° on the PAni/USF designating (200) and (212) reflections respectively which signify the deposition of polyaniline on the sisal fiber in emeraldine salt form [6, 35].
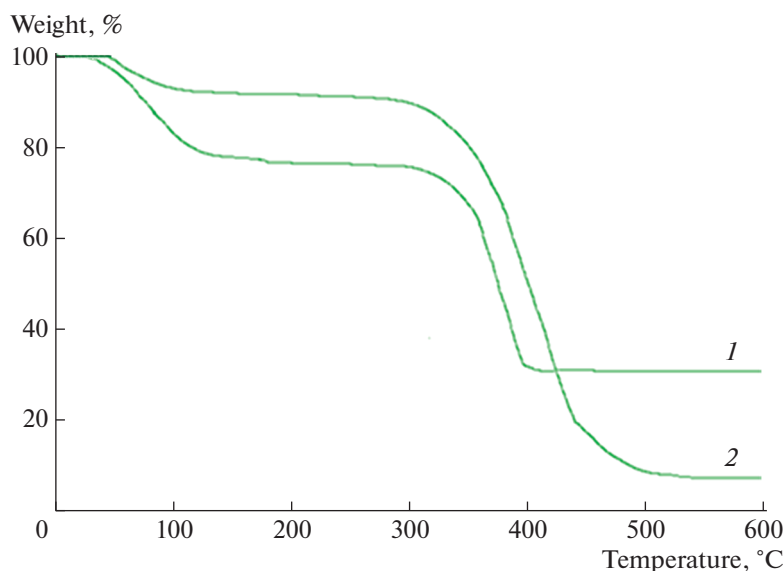
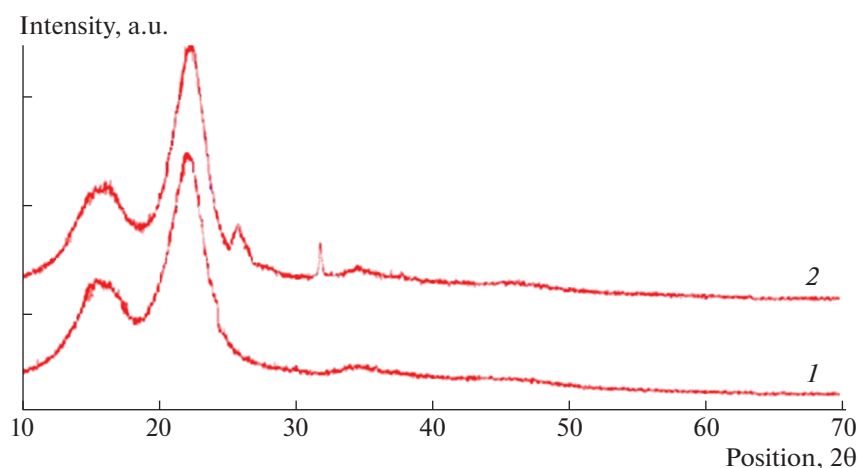**Fig. 2.** TGA curves of (*1*) USF and (*2*) PAni/USF.

Fig. 3. XRD diffractograms of (*1*) USF and (*2*) PAni/USF.

*Scanning Electron Microscopy
and Energy Dispersive X-ray Spectroscopy*

The scanning electron microscopy (SEM) analysis was carried out to study the morphology of the USF and the effect of polyaniline coating upon sisal fiber (PAni/USF). SEM micrograph of USF (Fig. 4a), a major portion of the surface of sisal fiber covered by hemicellulose and lignin was observed. This microstructure revealed the surface is rough with so many cracks. The corresponding EDX spectra (Fig. 4c) further confirmed existence of impurities like aluminum and sulfur incorporated with the fiber. These impurities may be introduced from the reactants, solvents and the fiber itself.

The SEM micrograph of PAni/USF (Fig. 4b) revealed that surface of PAni/USF is smooth com-pared to that of USF. This morphological variation can be the result of surface coating of sisal fiber by polyaniline through in situ oxidative polymerization. The EDX spectrum (Fig. 4d) further confirmed the removal of impurities was successful during the in situ polymerization process. This spectrum in turn confirmed the deposition of PAni on the surface of sisal fiber, which shows detection of intense chlorine and nitrogen from polyaniline backbone [6].

Electrical Conductivity Studies

The electrical conductivity of free sisal fibers is 4.6×10^{-10} S/cm while that of pure PAni and PAni/USF were found 0.91×10^{-4} and 1.37×10^{-4} S/cm, respectively. The conductivity of PAni/USF is in the semi-
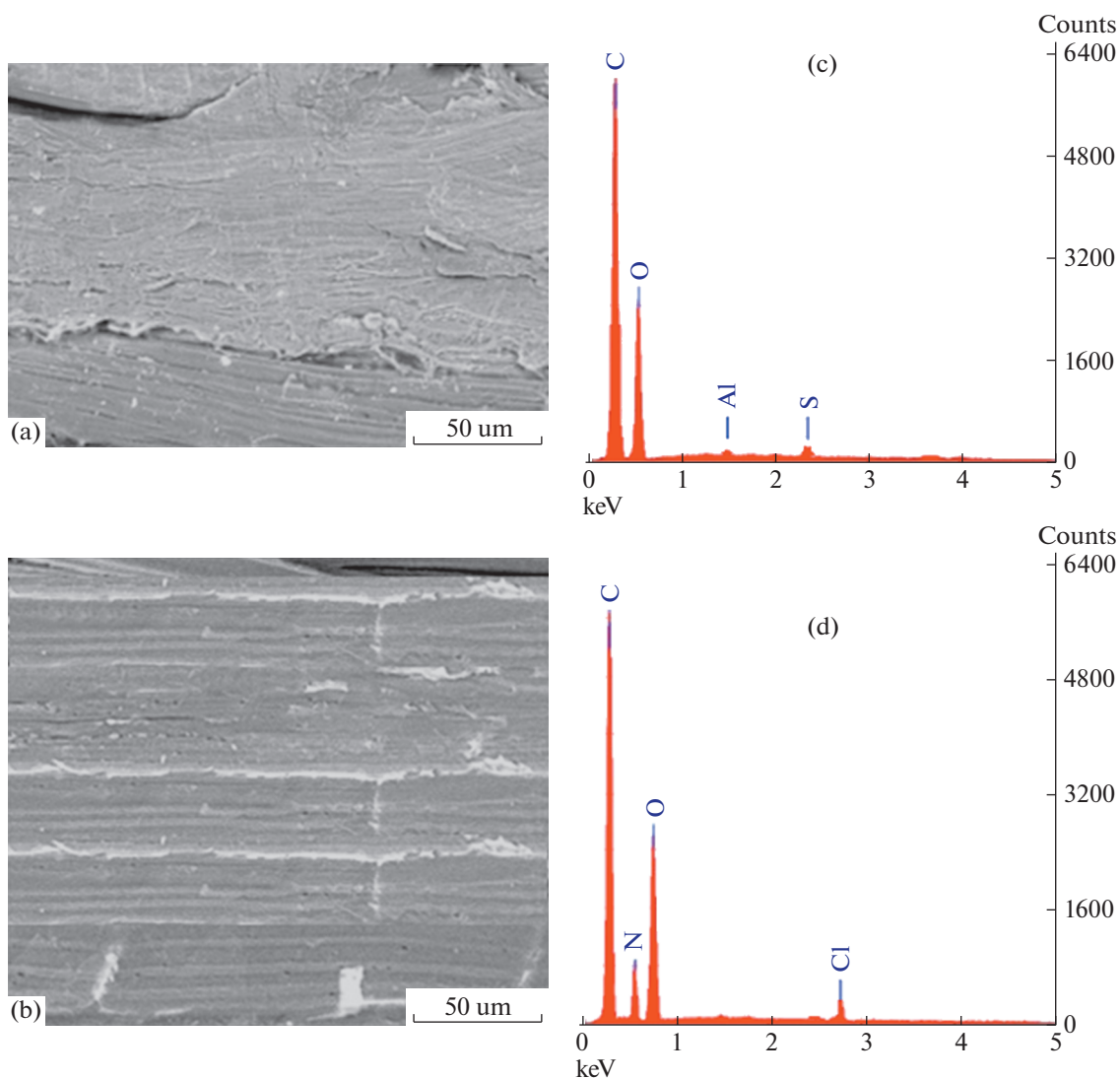
Fig. 4. SEM micrographs of (a) USF, (b) PAni/USF and EDX spectra of (c) USF and (d) PAni/USF.

conducting level which is a clear evidence that PAni is deposited in its oxidized form. PAni coated sisal fiber is rich in hemicellulose, lignin and other waxy substance confirmed from the FTIR and EDX spectra. These impurities including the fiber itself restricted the movement of ions in the solution [6].

Elongation at Break and Tensile Strength

The elongation at break and breaking tensile strength results of USF and PAni coated sisal fibers are summarized in the table 1. Elongation at break is a parameter used to analyze how much the fiber is resistant to an applied load. PAni/USF was found to have 2.8% of elongation from the 25 mm original length. Numerical analysis shows the fiber was elongated about 700 μm until the breaking point against the applied load which is somewhat higher than the value

of USF. The surface coating by PAni on the fiber is responsible for enhanced elongation. It is interesting to note that PAni/USF showed higher tensile strength compared to USF. The slight enhancement in tensile strength could be associated with PAni coating on the surface of the fiber. This result in turn confirmed hemicellulose, lignin and other impurities were partially removed during acidification in the process of polymerization.

CONCLUSIONS

The SEM micrograph confirmed the surface of sisal fiber was rough which becomes uniform upon polyaniline coating. An observation from FTIR stretching vibrations proved the existence of lignin and hemicellulose abundantly on the surface of sisal fibers.

Table 1. Mechanical properties of USF and PAni/USF

Sample	Breaking tensile strength, MPa	Elongation at break, %
USF	264	2.5
PAni/USF	267.5	2.8

Results from EDX spectra shows polyaniline was successfully deposited on the surface of the fiber which was confirmed by the detection of intense chlorine and nitrogen from the polymer backbone. This incidence was supported by the results of FTIR and conductivity that polyaniline was deposited in its conducting form, emeraldine salt, which further enhanced the active surface functionalities of the fiber. Therefore, *in situ* oxidative polymerization is an effective method to deposit polyaniline on the surface of sisal fibers. From thermal, spectroscopic microscopic and conductivity results found so far, sisal fiber was found as a suitable reinforcement substrate for coating of polyaniline.

Experiments are now under way to test the impact of alkali treatments and polyaniline coating onto the mechanical features, water absorption and fiber fineness of the sisal fibers and polyaniline coated sisal fibers.

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SPELL: 1. asflax, 2. acetonepurchased, 3. cellulosic, 4. difractograms