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Preparation of conductive paper composites based on natural cellulosic fibers for packaging applications

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ABSTRACT

Conducting paper based on natural cellulosic fibers and conductive polymers was prepared using unbleached bagasse and/or rice straw fibers (as cellulosic raw materials) and polyaniline (PANi) as conducting polymer. These composites were synthesized by in situ emulsion polymerization using ammonium persulfate (APS) as oxidant in the presence of dodecylbenzene sulfonic acid (DBSA) as emulsifier. The prepared composites were characterized using Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA), differential scanning calorimeter (DSC), and their morphology was investigated using scanning electron microscope (SEM). Electrical conductivity measurements showed that the conductivity of the paper sheets increases by increasing the ratio of PANi in the composite. Mechanical properties of the paper sheets were also investigated, the results revealed that the values of breaking length, burst factor, and tear factor are decreased with increasing ratio of added PANi, and this effect is more pronounced in bagasse-based composites. The new conductive composites can have potential use as anti-static packaging material or anti-bacterial paper for packaging applications.

1. Introduction

Nowadays, coated paper with a conducting polymer has great attention in new functional papers and packaging applications, such as anti-static and electro-magnetic shielding papers, novel wall coverings, electrical resistive heating papers and anti-bacterial papers (Johnston, Moraes, & Bommann, 2005; Johnston, Kelly, Moraes, Bommann, & Flynn, 2006). Among the known conducting polymers used for coating fibers, polypyrrole (PPy) is the preferred polymer because of its low toxicity, chemical stability and commercial availability (Kuhn, Child, & Kimbrell, 1995). Moreover, polyaniline (PANi) as another type of conducting polymer is characterized by its highly p-conjugated polymeric chain, metal-like conductivity, reversible chemical, different morphology (Abdel Rehim, Youssef, Ebtesam, Khatab, & Turky, 2010) and electrochemical properties and physical properties upon a novel doping/de-doping process, in general that leads to promising applications in different fields (Ding, Qian, Shen, & an, 2010 & Wan, 2008). Coating of cellulosic fibers with conductive polymer can be carried out with more than one method; the most popular is the in situ polymerization of monomer in the presence of pulp fibers (Huang, Kang, & Ni, 2006; Kelly, Johhnston, Borrmann, & Richardson, 2007; Wan, 2004; Youssef et al., 2011). Recent studies focused on the effect of structure, morphology and the properties of pulp fiber substrates which are used in PANi- or polypyrrole conductive paper, on the final performance of the composite materials. The effect of fiber morphology on the conductivity of PPy-coated paper was investigated (Kang & Ni, 2006) and the results revealed that above a critical fiber length of about 0.5 mm the conductivity of the coated paper is low. Also, the influence of pulp type, content of acidic groups (sulfonic or carboxylic groups) was studied, Kappa number (residual lignin content) of unbleached Kraft pulp, and beating degree of bleached Kraft pulp on the conductivity of PANi-coated paper (Qian, Shen, Yu, & An, 2010). It was found that the amount of coated PANi increased with increasing content of sulfonic groups or decreasing kappa number of unbleached Kraft pulp. Moreover, the percolation behavior of polyaniline-coated conductive paper was investigated (Li, Qian, Wang, & An, 2010). This parameter is important since it determines the concentration of conductive particles at which the dramatic change in conductivity occurs. It was found that the upper and lower threshold values are around 4% and 30% respectively. XPS confirmed that the bond between PANi and cellulose existed in the form of hydrogen bonding. In principle, one could produce polymers in these cellulosic raw materials so that the polymer is fully encapsulating the fiber of cellulosic raw materials, which provide the possibility to develop new hybrid materials that demonstrate the inherent proprieties of both components. These properties contain the tensile strength, flexibility and comparatively high surface areas that are related to cellulosic materials. In recent work we keen to prepare conducting

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Table 1
Analysis of used raw materials.

Composition, %	Rice straw	Bagasse	Method
Extractives	5.1	2.4	Tappi T204 om-88
Ash content	14.1	2.15	Tappi T211 om-86
Lignin	17.8	15.5	Tappi T222 om-88
Pentosan	12.5	14.4	Tappi T223 om-84
Hollocellulose	71.9	00	Tappi T9 wd-75
α-Cellulose	44	63	Tappi T203 om-88
β & γ-Cellulose	13.4	00	Tappi T204 om-88

paper based on cellulosic raw materials approximating unbleached bagasse and/or rice straw fibers and The resulting hybrid materials can then be included into other consumer type materials such as plastics, packaging materials, surface coatings and new application as anti-static packaging material or anti-bacterial paper.

2. Materials and methods

2.1. Materials

Rice straw (R) raw material is kindly provided by Rakta Company, Alexandria, Egypt, while bagasse (B) raw material and unbleached bagasse pulp are provided by Edfu Company, Egypt. They were analyzed according to the standard methods in the field of cellulose chemistry & technologies are shown in Table 1. Aniline monomer (99% purity), ammonium persulfate (APS) and dodecylbenzene sulfonic acid (DBSA) are products of Tokyo Kasei Kogyo Co. HCl was received from Alfa Aesar. Unless otherwise noted, all other chemicals were reagent grade and used as received.

2.2. Experimental part

2.2.1. Preparation of pulp

Rice straw pulp is prepared by kraft method (Ziaie-Shirkolaee, 2009) while bagasse pulp was prepared by enzyme method.

2.2.2. Preparation of PANi/paper composite via emulsion polymerization

Composites of polyaniline/cellulosic fibers prepared using 3 different ratios of PANi/pulp, these ratios are 2.5, 5 and 10% PANi/pulp amount. The method is as follows: the desired amount of pulp is loaded in 500 mL beaker then a solution of 3 g DBSA (0.09 mol) dissolved in 50 mL de-ionized water was added, the mixture was slowly stirred until a homogeneous solution was formed. Aniline monomer 9 g (0.097 mol) was added and kept stirring to become emulsified then 9 mL of 1 M HCl was mixed with mixture. The mixture became less transparent with the addition of HCl. An ammonium persulfate (APS) aqueous solution prepared in another beaker by dissolving 7.3 g (0.032 mol) APS in 30 mL de-ionized water and kept at low temperature in a freezer several hours before using. The oxidant was poured directly into the reaction mixture followed by a vigorous stirring with a mechanical stirrer using 500 rpm. The polymerization reaction proceeded at room temperature for 6 h and finally the obtained composites are isolated by filtration.

2.2.3. Formation of paper sheets

The paper sheets were prepared according to the S.C.A. standard, using the model S.C.A. sheet former (AB Worentzen and Wettre). In the apparatus a sheet of 165 mm. diameter and 214 cm^2 surface area was formed. The weight of oven dry pulp used for every sheet was about 3.2 g. After sheet formation, the sheet was pressed for 4 min (at 5 kg/cm^2) using a hydraulic press. Drying of the test sheets was made using a rotating cylinder or drum at 60 °C + 5 for 2 h. The sheets were then placed for conditioning at 65% relative humidity and temperature ranging from 18 to 20 °C.

2.2.4. Characterization

The XRD patterns of the composites sheet were carried out in a Bruker D8 Advance X-ray diffractometer with CuK-α radiation (λ = 0.1542 nm, 40 kV, 30 mA). The FTIR measurements, paper and polyaniline – Paper Composite were inserted onto KBr disks. Spectra were carried out in a (Shimadzu 8400S) FTIR spectrophotometer. Also, the electric measurements were carried out using HIOKI Z-HITESTER 3531 LCR Bridge and HIOKI 9261 TEST FIXTURE in frequencies ranging from 100 Hz up to 100 kHz, Corporation-Japan. The powder samples were pressed between two parallel brass plates in a special measuring cell for powders. The thermal stability was studied using a Perkin Elmer thermogravimetric analyzer (TGA), with a heating rate of 10 °C/min in nitrogen atmosphere and differential scanning calorimeter DSC, Perkin Elmer with a heating rate of 10 °C/min was used for the determination of the crystallinity of the prepared sheets. Scanning electron micrographs (SEM) were taken using a JOEL scanning electron microscope. All samples were coated with gold.

3. Results and discussion

In this study, composites based on unbleached bagasse or rice straw fibers (as cellulosic raw material) and polyaniline (PANi) as very simple conducting polymer were synthesized via in situ polymerization. Polyaniline was prepared by emulsion polymerization through oxidation of aniline by APS in the presence of a definite amount of pulp fibers and n-dodecylbenzenesulfonic acid (DBSA) as emulsifier and HCl as the dopant. Generally, aniline polymerization proceeds via cation-radical mechanism (Ding, Padias, & Hall, 1999). It was previously indicated in a study based on model compounds (Chen, 2003) that, phenolic hydroxyl groups could inhibit the polymerization of aniline since they trap aniline cation radicals. Lignin is a polymer having phenolic hydroxyl groups, so it is possible that lignin could inhibit the polymerization of PANi. However, DBSA is used as emulsifier to catalyze the polymerization reaction of aniline in the presence of unbleached pulp fibers and also to increase the electrical conductivity of the formed PANi/pulp fiber composites. Moreover, it was illustrated that any surface is present in contact with aniline during polymerization step will be covered by the formed polymer; this applies also to the cellulosic fibers (Stejskal, Trchova, Fedorova, Sapurina, & Zemek, 2003).

3.1. Scanning electron microscopy (SEM)

The surface morphological properties of the PANi-raw materials were investigated by SEM and demonstrated in (Fig. 1) since the percolation threshold in composites is related to the homogeneousness of the mixing of individual components of the composites. Fig. 1 illustrates the SEM photographs of the composites prepared using different ratios of PANi, which support the homogeneity of the composites and uniformity of sheet surface which produced with high content of polyaniline in the sheet at zero temperature and this homogeneity increased as the concentration of polyaniline increased. A comparison of the original sheet matrix with that of the PANi-cellulosic raw materials composite reveals that although the polymer appear to form largely on the rice straw or bagasse fibers, the open structure of the cellulosic matrix has been retained. This provides a large available surface area of the polymer for chemical and physical interactions and electronic conduction.

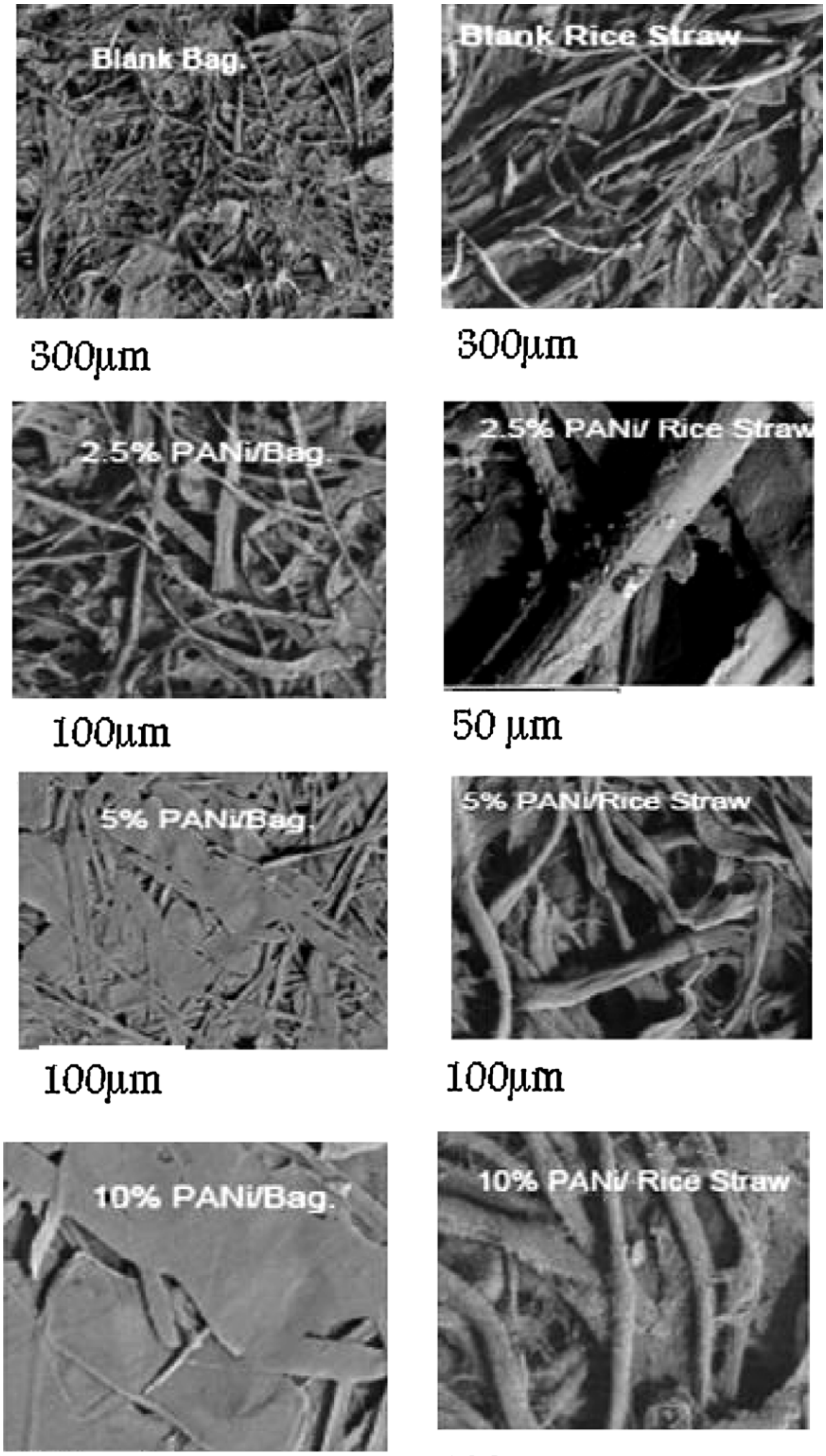

Fig. 1. SEM images of PANi/raw materials composites with different ratios of PANi.

3.2. *FTIR spectra*

To confirm the formation of polyaniline on the cellulosic raw materials (bagasse or rice straw) sheets we recorded the FTIR spectra of the polyaniline incorporated raw materials in the diffuse reflectance mode. FTIR spectroscopic evidence confirmed that PANi synthesized in the cellulosic raw materials had the same characteristic vibrational transitions as those of emeraldine salt in the bulk under identical experimental conditions. In other words, the characteristic broad band for O–H group of cellulosic materials appears around 3500 cm^{-1} and a band around 2950 cm^{-1} because of C–H presented in CH_2OH group, this part of the spectra is not shown. On the other hand, the bands around 1575, 1487, and 795 cm^{-1} correspond to polyaniline in the blend films as shown

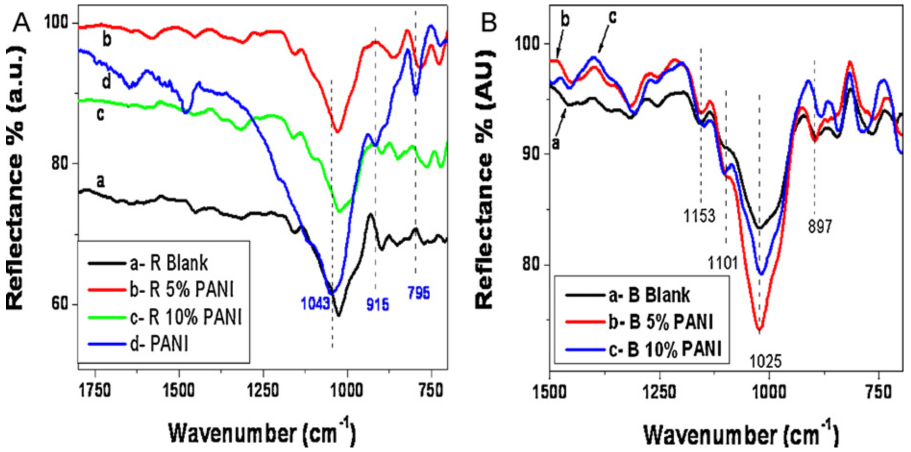

Fig. 2. (A) FTIR spectra for PANi, rice straw fibers and paper sheets based on PANi/rice straw fibers, and (B) FTIR spectra for bagasse blank and composites of PANi/bagasse fibers.

in (Fig. 2), a sift in the bands can be observed due to the interaction of PANi and OH groups in the cellulosic fiber (Fig. 2A and B). The band corresponding to out of plane bending vibration of C—H bond of p-substituted benzene ring appears at 806 cm^{-1}. The bands corresponding to stretching vibrations of N—B—N and N═Q═N structures appear around 1487 and 1575 cm^{-1}, respectively (where —B— and ═Q═ stand for benzenoid and quinoid moieties in the polyaniline backbone). Fig. 2B shows the FTIR spectra of PANi/bagasse composites and reveals that the band characteristic of the conducting protonated form can be observed at 1251 cm^{-1}. The prominent 1153 cm^{-1} band, assigned to a vibration mode of the —NH$^{\bullet+}$ = structure in the spectrum of PANi hydrochloride.

3.3. X-ray diffraction (XRD) pattern study

The XRD diffraction pattern of polyaniline/rice straw composites sheets with different polyaniline concentrations (b and c) during making the sheet as well as rice straw blank (a) which shown in (Fig. 3A). The XRD pattern shows two characteristic peaks at $2\theta = 16°$ and 22.46° which corresponding to 5.6 and 4 Å respectively. These peaks appear in all composites which means that the polyaniline intercalated into the cellulosic matrix. Whereas, the (Fig. 3A, d) shows the rice straw sheet coated by polyaniline prepared by emulsion polymerization new characteristic at two theta = 4°, which corresponding to 21 Å that demonstrated to the order structure of polyaniline (phenazine ring) and the other two peaks for pure rice straw itself.

Fig. 3B shows the XRD pattern of polyaniline/bagasse composites sheets with different PANi concentrations (b and c) during making the sheet as well as bagasse straw blank (a) illustrated the same two characteristic peaks for Rice straw at $2\theta = 16°$ and 22.46° which corresponding to 5.6° and 4 Å respectively. These peaks appear in all composites which means that the PANi intercalated into the cellulosic matrix.

3.4. Thermal analysis

Fig. 4a shows the TGA profiles of PANi/rice straw composites of different concentrations (B 5% and C 10%) as well as rice straw blank (A) without polyaniline, the weight loss between 180 and 230 °C is probably attributed to the increase the amount of polyaniline in the sheet also the amount of emulsifier (DBSA), the weight loss of the samples containing (5 and 10% of polyaniline) appears less thermal stability than the pure Rice straw sheet. Whereas, in case of using bagasse as raw materials the weight loss between 120 and 210 °C is may be related to the nature of the precursor (bagasse) and also the amount of polyaniline present in the sheet. All in all, the sample containing high percent of polyaniline (10%) demonstrated less thermal stability than the sample contains 5% and pristine bagasse sheet as shown in (Fig. 4b).

Supplementary information about crystallinity behavior of the prepared composites from bagasse loaded with 10% of PANi, is represented in (Fig. 5a), where it can fascinatingly be found that the crystallinity of bagasse sheet itself showed two endothermic peaks at 327 and 442 °C while after the addition of the Polyaniline by 10% this peaks became broaden and shifted to low value at 320

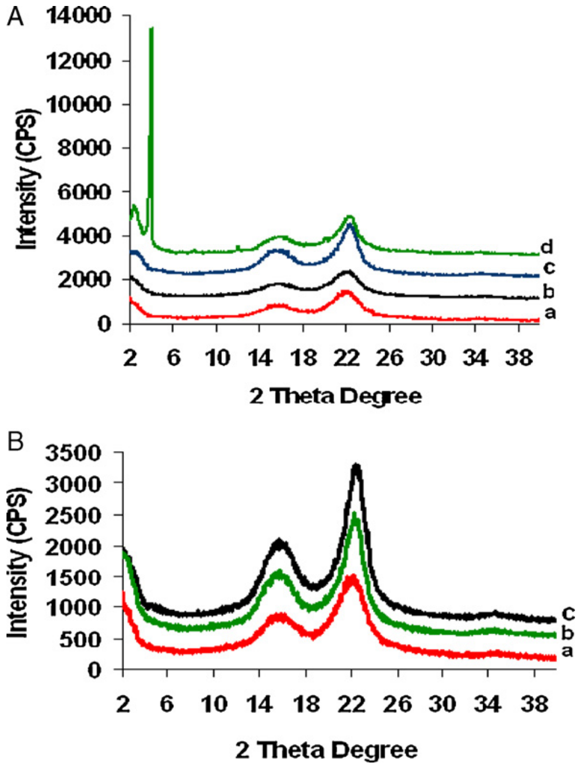

Fig. 3. (A) XRD diffraction pattern of polyaniline/ rice straw composites sheets with different polyaniline concentrations (b 5% and c 10%) during making the sheet as well as rice straw blank (a) and rice straw sheet coated by polyaniline prepared by emulsion polymerization (d), and (B) XRD diffraction pattern of polyaniline/bagasse composites sheets with different polyaniline concentrations (b 5% and c 10%) during making the sheet as well as bagasse straw blank (a).

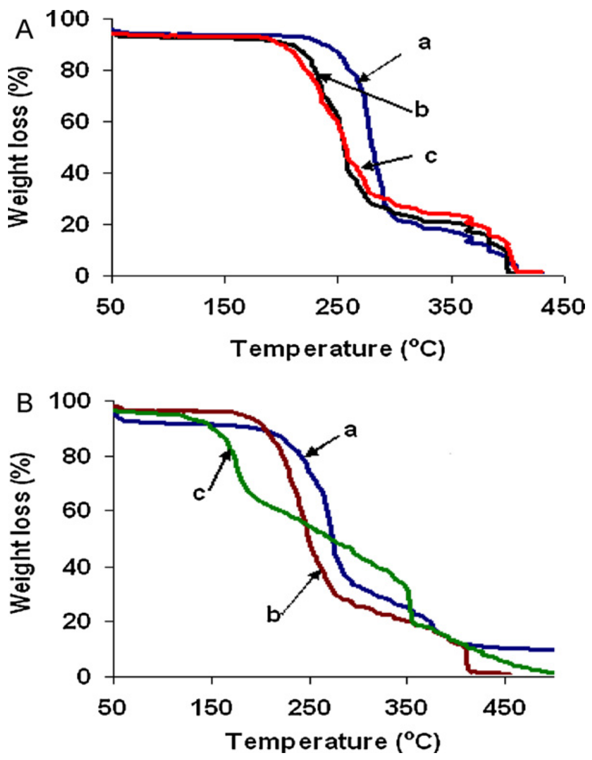

Fig. 4. (a) TGA profile of polyaniline/rice straw composites sheets with different polyaniline concentrations (b 5% and c 10%) during making the sheet as well as rice straw blank (a) without polyaniline, and (B) TGA profile of polyaniline/bagasse composites sheets with different polyaniline concentrations (b 5% and c 10%) during making the sheet as well as bagasse straw blank (a) without polyaniline.

and 437 °C, respectively. Otherwise, in (Fig. 5b) the crystallinity of rice straw/PANi sheet enhanced by the loading polyaniline by 10%, besides, there are two characteristic peaks for rice straw sheet appears at 325 and 422 °C that increase to 450 °C by the totaling polyaniline to the sheet.

3.5. Mechanical properties of PANi/cellulosic raw materials

The mechanical properties of the prepared sheets which fashioned from bagasse as cellulosic raw materials and different concentrations of polyaniline as shown in Table 2, the breaking length, burst factor, and tear factor decrease steadily by increasing the amount of polyaniline in the composites sheet this due to that polyaniline intercalated between the cellulosic fibers also the polyaniline has some drawbacks that polyaniline is inherently brittle and poor in processability due to its insolubility in common organic solvents (Duke, 1987). In addition, Table 2 shows the mechanical properties of PANi/rice straw composites which illustrated that the breaking length and burst factor decreased by the addition of 5% of PANi to the rice straw during making the sheet and we notice higher decrease in all mechanical properties by the rising the amount of polyaniline to 10%, although the tear factor decreasing by increasing the amounts of polyaniline into the matrix when compare with the rice straw itself this is because of the nature of polyaniline mention above.

Table 2
Mechanical Properties of PANi/bagasse composites and PANi/rice straw at different PANi ratios.

Samples	Mechanical properties		
	Breaking length (m)	Burst factor (kg/cm^2)	Tear factor
Blank (bagasse)	4073.28	0.0175	571.02
2.5% PAni/bagasse	1365.69	0.0063	399.72
5% PAni/bagasse	999.29	0.0053	314.06
10% PAni/bagasse	666.19	0.0028	285.51
Blank (rice straw)	701.23	0.0041	480.84
5% PANi/rice straw	691.21	0.0041	480.84
10% PANi/rice straw	601.05	0.0037	420.74

3.6. Electrical conductivity

The electrical conductivity values of the polyaniline/cellulosic raw materials are shown in Table 3, the blank of rice straw has electrical conductivity (8×10^{-13} S cm^{-1}) and by coating the fibers with PANi in different ratios (2.5, 5, and 10%), The electrical conductivity of the composites starts to increase by (1.56×10^{-10}, 4.56×10^{-7} and 2.5×10^{-5} S cm^{-1} respectively). The value of electrical conductivity increases by increasing the amount of polyaniline compared to the original sheet of rice straw. It is worthy to notify that the electric conductivity of pure PANi prepared under the same conditions in the absence of rice straw is 0.37 S cm^{-1}. However, in case of PANi/bagasse composites, the electrical conductivity of the bagasse blank is 4.8×10^{-11} S cm^{-1} and the values of the electrical conductivity of the prepared sheets rising by the addition of polyaniline in different ratios (2.5, 5, and 10%), the electrical conductivity enhanced by (7.6×10^{-10}, 1.8×10^{-7} and 1.3×10^{-5} S cm^{-1} respectively) as shown in Table 3. Therefore, the cellulosic raw materials sheets will be coated with polyaniline after polymerization process, wherein the cellulose fibers on the sheets are encapsulated with polyaniline particles or fused to gather in a sheet as confirmed by SEM image. Hence, the polyaniline is apparently bonded to the surface of cellulose fibers thought hydrogen bonding between the

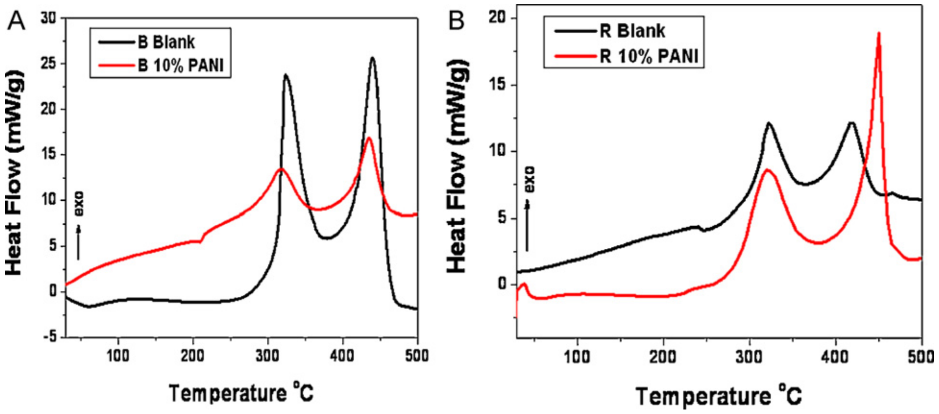

Fig. 5. (A) DSC profiles of blank bagasse and 10% PANi/bagasse coated fibers, and (B) DSC profiles of blank rice straw and 10% PANi/rice straw coated fibers.

Table 3
Electrical conductivity of paper sheets prepared from PANi/cellulosic raw materials composites.

Samples	Blank (Rice straw)	2.5% PANi	5% PANi	10% PANi
Electrical conductivity (S cm^{-1})	8×10^{-13}	1.56×10^{-10}	4.56×10^{-7}	2.5×10^{-5}
Samples	Blank (Bagasse)	2.5% PANi/B	5% PANi/B	10% PANi/B
Electrical conductivity (S cm^{-1})	4.8×10^{-11}	7.6×10^{-10}	1.8×10^{-7}	1.3×10^{-5}

N in the aniline monomer unite of polyaniline and OH groups in cellulose molecules of paper sheet which demonstrated by IR investigations. Moreover, this level of electrical conductivity is more essential and facilities the devolvement of anti-static paper for packaging application and also for electronic paper for new applications.

4. Conclusions

Novel conducting-paper composite materials have been produced through coating unbleached pulp of rice straw and bagasse with PANi using in situ emulsion polymerization. The morphology of the formed paper sheets showed that using high PANi ratio in the coating formulation, affords a large specific area which enhances the physical and chemical properties of the polymer. Electrical conductivity of the paper sheets was increased remarkably with increasing the different amounts of PANi in the prepared composite (from 8×10^{-13} to 2.5×10^{-5} S cm^{-1} in case of rice straw), while it is enhanced (from 4.8×10^{-11} to 1.3×10^{-5} S cm^{-1} in case of bagasse) when added only 10% of PANi. On the other hand, values of breaking length, burst factor, and tear factor are decreased with increasing the ratios of the added PANi, and this effect is more pronounced in bagasse-based composites. The novel conductive paper can find interesting applications.

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