Carbohydrate Polymers 90 (2012) 1003–1007

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Structural and electrical properties of paper–polyaniline composite

A.M. Youssef[a,*], S. Kamel[b], M. El-Sakhawy[b], M.A. El Samahy[a]

[a] Packing & Packaging Materials Department, National Research Center, Dokki, Cairo, Egypt
[b] Cellulose & Paper Department, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article history:
Received 19 May 2012
Received in revised form 10 June 2012
Accepted 12 June 2012
Available online 20 June 2012

Keywords:
Polyaniline
Paper
Composite
SEM
TGA
Conductivity

ABSTRACT

Conducting polymers have generated a great deal of interest because of their physical and chemical properties as well as their potential application in industry particularly in packaging applications. However one of short comings of most conducting polymer is that they are often formed as intractable films that are difficult to process. To overcome this problem we have incorporated conducting polymer, namely polyaniline into sheets of paper in order to create new composite material which combine the universal properties of paper product with the chemical and electrically conducting properties of the conducting polymer. Paper conducting polymer composite have been prepared by polymerizing aniline directly onto the paper sheet using ammonium peroxydisulfate (APS) as an oxidant at different temperatures. The prepared composite was characterized by FT-IR and SEM. The thermo-oxidative degradation was studied by thermo gravimetric analysis (TGA); electrical conductivities measurements of the composites were significantly increased over those of the precursor paper.

1. Introduction

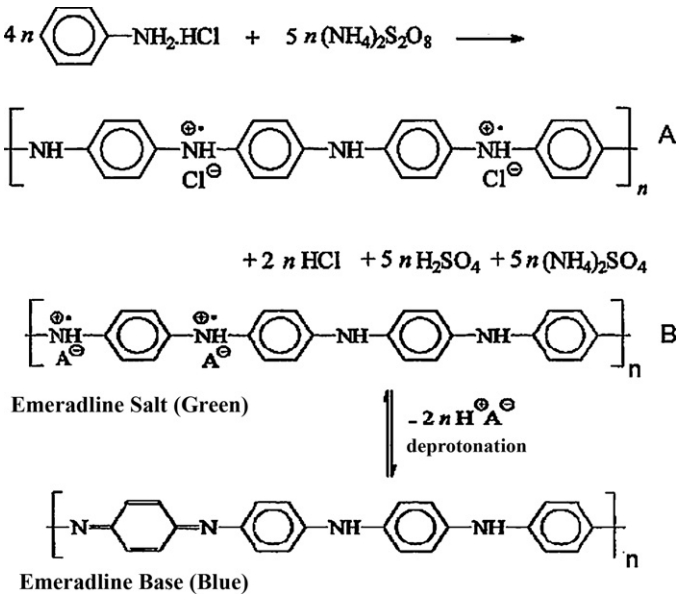
Intrinsically conducting polymers (ICP's), first reported by Chiang et al. (1977) are organic polymers containing repeated units of oxidized or reduced monomers. Extensive international research effort has followed the initial discovery, resulting in detailed studies into the effect of various substituents, oxidants and dopants (Youssef, 2012). In situ polymerization of pyrrole with paper fibers has been undertaken, resulting in spheres of PPY of 5–10 nm it was concluded that the polypyrrole (PPY) was bound via the N at the pyrrole ring to the hydroxyl groups on the surface of the cellulose (Liu, Moon, Maruyama, & Yamamoto, 1993).

Paper is a universal material that is used widely as a communication and packaging medium. It comprises a matrix of cellulose fibers held together in a sheet by hydrogen bonding between hydroxyl groups on adjacent fibers (Johnston, Moraes, & Thomas, 2005). With the advent of newer and newer technologies, the demand for materials possessing a combination of a wide range of desirable properties is increasing day by day for instance in packaging application (Nassar & Youssef, 2012). One of the techniques to develop such materials is the formulation of composites from compatible materials individually possessing the desirable properties. In view of lightweight, low cost, low temperature fabrication as well as good mechanical strength and environmental stability, electrically conducting composites based on an electrically conducting polymer, polyaniline (PANi) with an insulating polymer, paper sheet were selected for this study (Billmeyer, 1994; Gowariker, Viswanathan, & Sreedhar, 1999; Pron, Zagorska, Nicolan, Genond, & Nechtschein, 1997; Sinha, 2002). Polyaniline occupies a high place among intrinsically conducting polymers because of its very simple preparation, good environmental stability and the fact that it can be doped by protonic acids to high electrical conductivities (Al-Ahmed, Mohammad, & Rahman, 2004). Also due to its ease of synthesis, low cost, high yield, and relatively stable electrical conductivity (Tabellout, Fatyeyeva, Baillif, Bardeau, & Pud, 2005). However, the major drawback of these conducting polymers is the unprocessability and intractability which has made their processing into the desired form is rather difficult. The discovery of counter-ion of functionalized doping acid strongly influences the solubility and consequently induced processability of the PANi (Laska, Pron, & Lefrant, 1995). Therefore PANi can be processed without altering its structure by blending it with some other conventional polymers. These blends are designed to combine the desired properties of both components, i.e. good electrical conductivity of PANi with processability and physical properties of the matrix polymer.

In situ polymerization of pyrrole, aniline and their derivatives with cellulosic substrates have been studied and provided composites with potentially useful properties. Conductivity relative to the untreated substrate is increased, and an inverse relationship of conductivity to dielectric, and hence capacitance is observed. A metallic layer such as copper may be deposited electrochemically

* Corresponding author at: Packaging and Packing Materials Department, National Research Center, P.O. Box 12622, Dokki, Cairo, Egypt. Tel.: +20 2 33322418; fax: +20 2 33370931.
E-mail address: amyoussef27@yahoo.com (A.M. Youssef).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.06.034



Scheme 1. (A) The oxidation of aniline hydrochloride with APS yields PANi (emeraldine) and (B) the conducting PANi in the protonated emeraldine salt (green color), as well as the deprotonated in alkalis to the corresponding emeraldine base (blue) and non-conducting.

onto the surface of the composite, and the metal surface may then be oxidized to form either the green carbonate patina commonly seen on bronze statues, or a deep red oxide layer. When the polymer used is polypyrrole, silver may be reduced onto the surface following reduction of the polymer via hydrazine or sodium borohydride (Richardson, Johnston, & Borrmann, 2006). The development of conducting polymer composites with cellulose (wood) and protein fibers (wool) with the polymer fully encapsulating the fiber provide the opportunity to develop new hybrid materials that exhibit the inherent proprieties of both components. These properties include the tensile strength, flexibility and relatively high surface areas that are associated with cellulose (wood) and wool fibers, and the electronic and chemical properties of conducting polymers. The resulting paper-conducting polymer hybrid materials can then be incorporated into other commodity/consumer type materials such as plastics, surface coatings and films to impart new or enhanced properties to them (Johnston, Kelly, Moraes, Borrmann, & Flynn, 2006). In this study we tried to improve the electrical properties of prepared paper composite by combining the PANi as conducting polymer onto and/or into the paper surfaces by different methods.

2. Materials and methods

2.1. Materials

Filter paper, aniline hydrochloride monomer (99% purity) was obtained from Aldrich. Ammonium persulfate (APS), sodium dodecyl sulfate (SDS), and hydrochloric acid (HCl) were used as received from Alfa Aesar. p-Dodecyl benzyl sulfonate (DBS) was obtained from King Industries. Unless otherwise noted, all other chemicals were reagent grade and used as received.

2.2. Experimental part

Filter paper was selected for this study as an open matrix structure on a sub-micron scale (Whatman 40 filter papers), and does not contain filler materials or a surface coating as most printing and writing papers do. The fibers in the filter paper sheet were

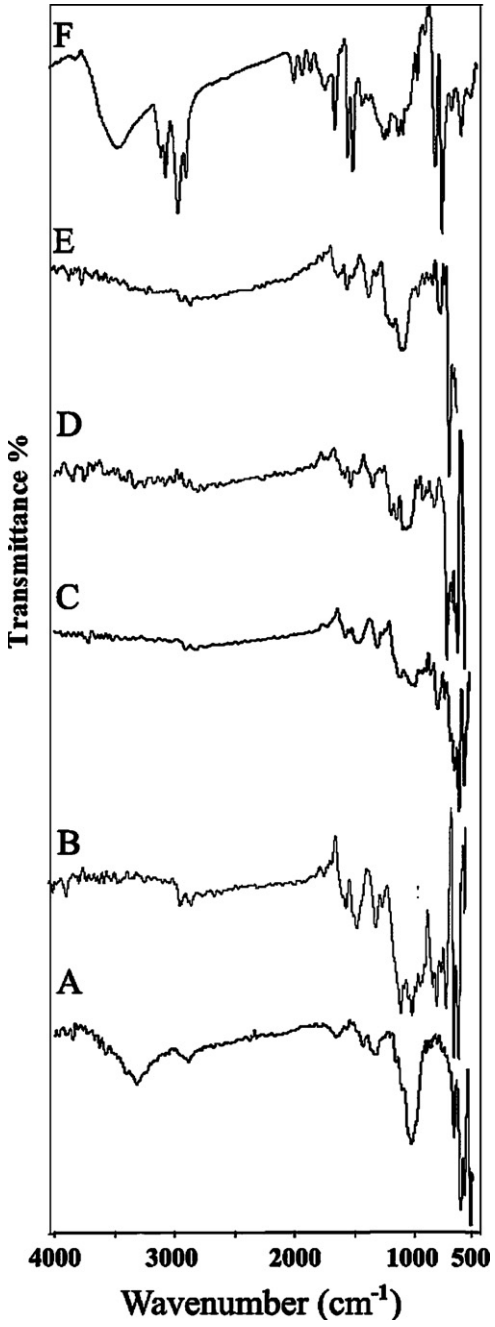


Fig. 1. FT-IR spectra of (A) uncoated filter paper; (B–D) filter paper coated in situ with PANi at different temperature 0, 25, and 50 °C respectively; (E) filter paper coated by dipping in PANi, and (F) pure PANi.

encapsulated with conducting polymers (polyaniline). The aniline hydrochloride (0.2 M) was allowed to dissolve in water and absorb onto the surface of the individual filter paper then p-dodecyl benzyl sulfonate (0.02 M) was dissolve in water (200 ml as a 70:30%, w/w solution in xylene) to form a milky white emulsion. The emulsion was carried out with effective stirring by adding a solution of ammonium peroxydisulfate (APS) (0.074 mol in 40 ml of water) as the oxidant dropwise to the mixture over a period of approximately 1 h. During this period the emulsion changed color from brown/orange to dark green to black over a period of about 5 min. The reaction was allowed to proceed for 24 h, to ensure complete polymerization. Using the same process for synthesizing the

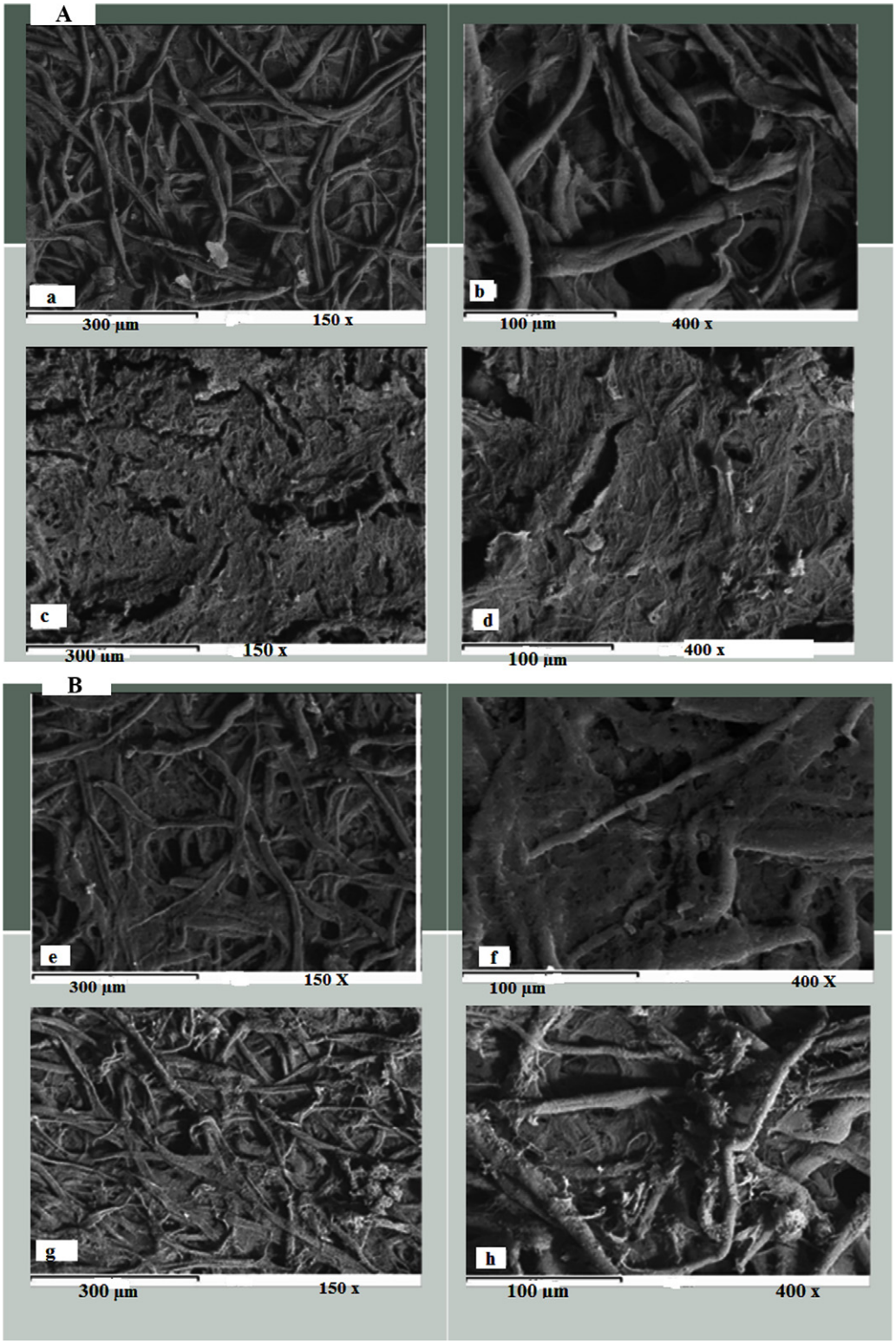


Fig. 2. (A) SEM photographs of uncoated filter paper and filter paper coated with PANi at different temperatures and different magnifications (a and b) uncoated, (c and d) coated at 0 °C. (B) SEM photographs of filter paper coated with PANi at different temperatures and different magnifications (e and f), (g and h) coated at 25°C and 50°C respectively.

polyaniline coated filter paper by dipping process, the emulsion of polyaniline was poured in several drops over the filter paper using a pipette and the filter paper was allowed to remain soaked in the emulsion of polyaniline for 30 min. Then, the resulting polyaniline-coated filter paper was washed thoroughly with distilled water to remove any free polyaniline and unreacted ammonium peroxydisulfate and emulsifier. The coated filter paper were then washed with hydrochloric acid (0.1 M) to effect doping by Cl^- ions, followed by washing with water. After thorough washing of the filter papers with acetone and drying.

2.3. Characterization

For the FT-IR measurements, paper and polyaniline – paper composite were inserted onto KBr disks. Spectra were carried out in a (Shimadzu 8400S) FTIR spectrophotometer. Electrical 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 samples were pressed between two parallel brass plates in a special measuring cell for this sample. Thermo gravimetric analysis (TGA) was performed on some selected composites by using Perkin-Elmer (Pyris Dimond) instrument from 25 to 600 °C at a heating rate of 10 °C min^{-1} with a dry air flow rate of 200 ml min^{-1}. Scanning electron microscopy (SEM) micrographs were taken using a JOEL scanning electron microscope. All samples were coated with gold.

3. Results and discussion

The oxidation of aniline in acidic aqueous media using ammonium peroxydisulfate as oxidant has become the most widely used synthetic route to conducting PANi and is obtained as the protonated emeraldine salt (green color). It is deprotonated in alkalis to the corresponding emeraldine base, which is blue and non-conducting (Scheme 1).

3.1. FT-IR spectra

Fig. 1 represents the FT-IR spectra of (A) uncoated filter paper; (B–D) filter paper coated with polyaniline via in situ emulsion polymerization at different reaction temperature 0, 25, and 50 °C respectively; (E) filter paper coated by dipping in polyaniline solution and (F) pure polyaniline prepared by using the same method. The characteristic broad band for hydroxyl group (O—H) of filter paper appears around 3500 cm^{-1} and a band around 2950 cm^{-1} because of C—H presented in CH_2OH group has been observed in Fig. 1A (Rajini, Venkateswarlu, Rose, & Sastry, 2001; Valentea et al., 2005). On the other hand, the bands around 3235, 1575, 1487, and 806 cm^{-1} correspond to polyaniline in the blend films as shown in Fig. 1B and C. 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 itself (Ebrahim, Kashyout, & Soliman, 2007). The peak detected at 3235 $cm^{-}1$ may be attributed to —NH— group.

3.2. Scanning electron microscopy (SEM)

Composite materials containing cellulose have been of interest due to their environmentally friendly origin and high specific strength. The percolation threshold in composites is related to the homogeneousness of the mixing of individual components of the composites, hence, the surface morphological properties of the PANi–paper were investigated by SEM. The SEM photographs of the composites support the homogeneity of the composites and uniformity of film surface which produced at zero temperature (Fig. 2A(c, d)) compare with the pristine filter paper without any polyaniline (Fig. 2A(a, b)) and this homogeneity decreased as reaction temperature increased as evident from Fig. 2B(e–h).

A comparison of the original paper matrix with that of the PANi–paper composite shows that this polymer appears to form largely on the paper fibers and that the open structure of the paper matrix has been retained. This provides a large available surface area of the polymer for chemical and physical interactions and electronic conduction. It opens up the possibility of developing new grades of paper and new applications in the field of packaging and packing materials.

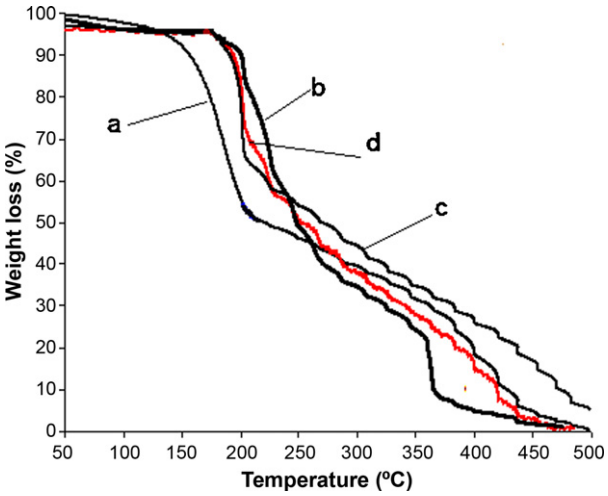


Fig. 3. Thermogravimetric analysis (TGA) of (a) original filter paper, as well as PANi–filter paper composites prepared using emulsion polymerization at different temperature, (b) 0 °C, (c) 25 °C, and (d) 50 °C.

3.3. Thermal analysis of the prepared PANi–paper composite

Fig. 3 illustrated the thermo-gravimetric analysis of original filter paper as well as in the various paper composites containing PANi at different reaction temperature. The original filter paper loss around 6% at 126 °C whiles all the other composites loss 8% at 182 °C at the first weight loss step. Also in the results of the thermo-gravimetric analysis enhanced reduction of the composite mass below 400 °C, compared with the original filter paper, may be because of the deprotonation of protonated PANi to PANi base (Stejskal & Gilbert, 2002) which is related to the loss of acid. Conversely, thermal stability of the prepared filter paper–PANI composites is greater than that of filter paper itself, especially at 5 °C which showed higher thermal stability than the other composites at different reaction temperatures.

3.4. Electrical conductivity

The electrical conductivity of the filter paper without polyaniline it was (2×10^{-11} S cm^{-1}) and by carrying out the emulsion polymerization of (aniline hydrochloride/APS) in presence of sodium dodecyl benzyl sulfonate (DBS) as emulsifier at different reaction temperature (0, 25, and 50 °C). The low electrical conductivity of the filter paper starts to upsurge compare to the original filter paper (5.8×10^{-5}, 3.6×10^{-5} and 1.274×10^{-8}, respectively). Furthermore, the conductivity of PANi prepared under the same conditions in the absence of filter paper was 0.37 S cm^{-1} (see Table 1). Consequently, the filter paper will be coated with polyaniline after polymerization process, wherein the cellulose fibers on the filter paper are encapsulated with polyaniline particles or fused

Table 1
Conductivity of PANi prepared by emulsion polymerization and filter paper as well as, PANi–filter paper composites prepared at different reaction temperatures.

Samples	Conductivity (S cm^{-1})
Filter paper	7×10^{-11}
Pure polyaniline	37×10^{-2}
PANi–filter paper composites prepared at 0 °C	3.6×10^{-5}
Filter paper/PANi composites prepared at 25 °C	5.7×10^{-5}
Filter paper/PANi composites prepared at 50 °C	1.28×10^{-8}
Filter paper/PANi composites prepared by dipping	1.9×10^{-5}

to gather in a sheet as proven by SEM image (Fig. 2). Hence, the polyaniline is apparently bonded to the surface of cellulose fibers thought hydrogen bonding between the N in the aniline monomer unite of polyaniline and OH groups in cellulose molecules of filter paper 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 as electronic paper for new applications.

4. Conclusion

Paper–PANi composites have been successfully prepared by polymerizing aniline monomer directly onto the filter paper sheet using ammonium peroxydisulfate (APS) at different reaction temperatures. The thermal properties were enhanced by the addition of polyaniline to filter paper sheet. In addition, the morphology of the prepared composites were characterized using scanning electron microscopy and the SEM photographs of the prepared composites maintain the homogeneity of the composites and uniformity of film surface which produced at zero temperature in addition to this homogeneity decreased as reaction temperature increased. Also, the electrical conductivities of the prepared composites were considerably increased compared with the precursor filter paper (7×10^{-11}) and the low temperature (5.8×10^{-5}) is more appropriate than high temperature (1.274×10^{-8}).

References

Al-Ahmed, A., Mohammad, F., & Rahman, M. Z. A. (2004). Composites of polyaniline and cellulose acetate: preparation, characterization, thermo-oxidative degradation and stability in terms of DC electrical conductivity retention. *Synthetic Metals*, *144*, 29–49.

Billmeyer, F. W., Jr. (1994). *Text book of polymer science*. New York: Wiley.

Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., et al. (1977). Electrical conductivity in doped polyacetylene. *Physical Review Letter*, *39*, 1098–1101.

Ebrahim, S. M., Kashyout, A. B., & Soliman, M. M. (2007). Electrical and structural properties of polyaniline/cellulose triacetate blend films. *Journal of Polymer Research*, *14*, 423–429.

Gowariker, V. R., Viswanathan, N. V., & Sreedhar, J. (1999). *Polymer science*. New Delhi, India: New Age Int. P. Ltd. Publishers.

Johnston, J. H., Kelly, M. F., Moraes, J., Borrmann, T., & Flynn, D. (2006). Conducting polymer composites with cellulose and protein fibers. *Current Applied Physics*, *6*, 587–590.

Johnston, J. H., Moraes, J., & Thomas. (2005). Conducting polymers on paper fibres. *Synthetic Metals*, *153*, 65–68.

Laska, J., Pron, A., & Lefrant, S. (1995). Phosphoric acid diesters protonated polyaniline: Preparation, spectroscopic properties, and processability. *Journal of Polymer Science A: Polymer Chemistry*, *33*, 1437–1445.

Liu, C. F., Moon, T. D. K., Maruyama, T., & Yamamoto, T. (1993). Preparation of polymer blend colloids containing polyaniline or polypyrrole by Fe(II)-, Fe(III)-, and Cu(II)-H_2O_2 catalyst system. *Polymer*, *25*, 775–779.

Nassar, M., & Youssef, A. M. (2012). Mechanical and antibacterial properties of recycled carton paper coated by PS/Ag nanocomposites for packaging. *Carbohydrate Polymers*, *89*, 269–274.

Pron, A., Zagorska, M., Nicolan, Y., Genond, F., & Nechtschein, M. (1997). Highly conductive composites of polyaniline with plasticized cellulose acetate. *Synthetic Metals*, *84*, 89–90.

Rajini, R., Venkateswarlu, U., Rose, C., & Sastry, T. (2001). Studies on the composites of cellulose triacetate (prepared from sugar cane pulp) and gelatin. *Journal of Applied Polymer Science*, *82*, 847–852.

Richardson, M. J., Johnston, J. H., & Borrmann, T. (2006). Electronic properties of intrinsically conducting polymer-cellulose based composites. *Current Applied Physics*, *6*, 462–465.

Sinha, R. (2002). *Outlines of polymer technology*. India: Prentice-Hall.

Stejskal, J., & Gilbert, R. G. (2002). Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report). *Pure and Applied Chemistry*, *74*, 857–867.

Tabellout, T., Fatyeyeva, K., Baillif, P., Bardeau, J., & Pud, A. (2005). The influence of the polymer matrix on the dielectric and electrical properties of conductive polymer composites based on polyaniline. *Journal of Non-Crystalline Solids*, *351*, 2835–2841.

Valentea, A., Burrowsa, H., Polishchukb, A., Dominguesa, C., Borgesc, O., Euse'bioa, M., et al. (2005). Permeation of sodium dodecyl sulfate through polyaniline-modified cellulose acetate membranes. *Polymer*, *46*, 5918–5928.

Youssef, A. M. (2012). Morphological study of novel architecture titanium dioxide nanowires decorated polyaniline nanocomposites and its electrical properties. *Nanoscience and Nanotechanology: An Indian Journal*, *7*, 34-32.