SYNTHESIS AND CHARACTERIZATION OF MODIFIED CELLULOSE AND DOPED-POLYPYRROLE COMPOSITE AS THERMALLY CONDUCTIVE ADHESIVE

S. F. S. Draman[1*], R. Daik[2], F. A. Latif[3], S. M. El-Sheikh[4]

[1]*Faculty of Applied Sciences, Universiti Teknologi MARA (Terengganu),23000 Dungun ,Terengganu, Malaysia*
[2]*School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia,43600 Bangi, Selangor, Malaysia*
[3]*Faculty of Applied Sciences, Universiti Teknologi MARA (Malaysia),40450 Shah Alam, Selangor, Malaysia*
[4]*Nanostructured Materials and Nanotechnology Division, Central Metallurgical Research and Development Institute, 11421 Cairo, Egypt*
**sfauziah@tganu.uitm.edu.my*

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Abstract

In this study, toluene sulfonic acid (TSA) which was used as surfactant and dopant, has been incorporated to polypyrrole backbone via chemical oxidation reaction. Cellulose-based adhesive has been prepared through chemical modification. The obtained cellulose-based adhesive and TSA-doped polypyrrole (PPy) were characterized by using field emission scanning electron microscope (FESEM), Fourier transform infrared (FTIR), elemental analysis CHNS and thermogravimetric analysis (TGA). Then, cellulose-based adhesive and TSA-doped PPy nanocomposite has been prepared via colloidal dispersion method. Fourier transform infrared spectroscopy (FTIR), thermogravimetry analysis (TGA) and high frequency impedence complex spectroscopy were carried out to characterize the nanocomposite. Results from thermal conductivity testing showed that this synthesized material is potentially useful as coating material in small electronic devices.

1 Introduction

Nowadays, there is impressive growth in manufacturing small electronic devices with many functionalities which increase heat dissipation problems. Therefore, heat management become a central task for device design and application. Many researches have been done to develop excellent cooling system including metal heat sink, heat piece liquid-cooler, heat pipe, micro heat sink [1, 2] and thermoelectric water cooling [3]. However, heat dissipation via air cooling like heat sink and fan, also liquid cooling are not suitable for small and light electronic devices. Therefore, there is a critical need to develop a new material to dissipate heat efficiently.

Conjugated polymers have attracted much attention for the past few decades as advanced materials with metal-like electrical conductivity. Among the conjugated polymers, ones based upon polypyrrole has been studied intensively because of its good environmentally stability, facile synthesis and higher electrical conductivity compared with other conjugated polymers

[4]. However, thermal conductivity of PPy and doped-polypyrrole which related to heat dissipation is still not widely explored and thus has been focused in this study. Event though the polypyrrole has many advantages, poor mechanical properties, brittle and few others disadvantages limit its applications [5]. Therefore, the polymer should be combined with other materials to produce a composite enhanced properties.

In this study, cellulose has been selected as matrix for the prepared nanocomposite because it is abundantly available, easy processing, biodegradable and biocompatible [6]. In order to have good adhesion property for applications such as coating material, epoxide group can be incorporated into the cellulose through chemical modification. Toluene sulfonic acid which was used in this study as surfactant and dopant, has been incorporated into polypyrrole backbone via chemical oxidation reaction. Besides to improve the solubility, toulene sulfonic acid also possesses electron mobility which is crucial for high thermal conductvity.

Colloidal dispersion method was used to prepare cellulose-based adhesive and TSA-doped PPy nanocomposite in this study. Colloid system contains two different phases which are dispersed phase and continous phase [7]. Conventional methods, such as powder mixing, solution mixing, or melt mixing are not suitable for mixing of doped-polypyrrole and modified-cellulose due to low solubility and non-melting of doped-polypyrrole.

2 Materials and characterization methods

2.1 Materials

Cellulose and pyrrole (99 % purity) were purchased from Acros Organic, meanwhile ammonium persulfate, APS ($(NH_4)_2S_2O_8$) was acquired from Friendamann Schmidt Chemicals. Dimethyl sufloxide (DMSO) was obtained from R & M Chemicals. Dimethylformamide (DMF) was bought from Fisher Chemicals. Other chemicals were purchased from Sigma-Aldrich. Pyrrole was purified by passing through a column packed with alumina and stored at 4 ^oC before use. Other chemicals were used as received. Deionized water was used in all experiments.

2.2 Methods

2.2.1 Chemical modification of cellulose

Dried cellulose (3.0 g) was immersed in DMSO (90.0 mL) at 60 ^oC and stir for 2 h. Sodium methylate (90.0 mL) was added to the mixture and then stirred for another hour under nitrogen atmosphere at room temperature. The product has been filtered and washed with DMSO. The produced material (2.0 g) was immersed again in DMSO containing 160.0 mL of epichlorohydrin as reagent and stirred for 2 h at 50 ^oC. The obtained product was separated and washed with distilled water and ethanol. Then, the final product (epoxypropyl cellulose) was dried in a vacuum oven for 24 h at 60 ^oC.

2.2.2 *Synthesis of TSA-doped PPy*

Toulene sulfonic acid (0.07 mol) was dissolved in deionized water (100 mL), placed into reaction vessel and stirred vigorously at 0^oC for 15 min. Purified pyrrole monomer (0.07 mol) was added dropwise to the reaction vessel. The mixture was stirred for 20 min. 100 mL of ammonium persulfate (0.52 M) as an oxidant, then was added dropwise to the above solution with vigorously stirring at 0°C. The mixture was stirred for another 7 h. The reaction mixture was poured into a large excess of deionized water and then filtered. The doped PPy was washed with deionized water and methanol several times, and dried in vacuum at 60°C for 2 days. The same procedure was followed to prepare TSA-doped PPy at room temperature (RT).

2.2.3 Preparation of nanocomposite

Colloid A consisted of TSA-doped PPy (5.0 g), DMF (100.0 mL), Sodium Dodecyl Sulphate (SDS) (2.5 g) and deionized water (25.0 mL). Meanwhile, colloid B consisted of epoxypropyl cellulose (3.0 g), DMF (90.0 mL), SDS (1.5 g) and deionized water (15.0 mL).

Firstly, TSA-doped PPy was dispersed in DMF and stirred with magnetic stirrer at 400 rpm until homogeneous dispersion obtained. After that, SDS solution was added slowly into the mixture and stirred to form colloid A. Then, the process was repeated to produce colloid B. Both colloids were mixed together and stirred for 3 hrs to produce a uniform and homogenous colloid. The mixture was poured into methanol and stirred with magnetic stirrer at 400 rpm for 30 min. The obtained product was filtered and dried in fume hood for 24 h. The product was further dried in vacuum oven.

2.3 Characterization

Infrared spectra of samples were analyzed using Bruker, Fourier Transform Infrared system (FTIR) model Tensor 27 with OPUS 6.0 software. Samples in powder form were tested using Attenuated Total Reflectance (ATR). The scans were carried out from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) of all the samples was carried out using a Mettler Toledo model TGA/SDTA 851^e. Samples of 5-6 mg were placed in alumina pans and heated from 30 to 600°C at 10 $^oCmin^{-1}$, under a dynamic flow of nitrogen (50 $mLmin^{-1}$).

Morphology of the samples was analyzed by using a Zeiss, field emission scanning electron microscope (FESEM), model Supra 46VP. SEM images were examined using accelerating voltage at 5 kV. The doping level of TSA-doped PPy was determined via elemental analysis using a CHNS/Thermo Finnigan/Eager 300 for EA 1112 elemental analyzer.

Samples in pellet form were analyzed using frequency response analyzer (HIOKI 3532-50 LCR HiTester) over a frequency range of 10^2 Hz-10^6 Hz at room temperature to measure electrical conductivity. Samples obtained Meanwhile, thermal conductivity was measured by using C-Therm Tci thermal analyzer.

3 Results and discussion

3.1 FTIR spectroscopy

Figure 1 shows FTIR spectra of cellulose, modified cellulose, PPy and TSA doped-PPy. FTIR spectra for cellulose and modified counterpart are similar to each other. The peak observed at 898 cm^{-1} is attributed to glucose ring stretching in cellulose [8, 9]. Other observed peaks that attributed to cellulose are 2890 cm^{-1} (C-H stretching), 1373 cm^{-1} (O-H in plane deformation), 1053 cm^{-1} (C-O stretching). However, there are additional three peaks observed for modified cellulose. The bands at 1588 cm^{-1} (C-O stretching), 952 cm^{-1} (C-H bending) and 1263 cm^{-1} due to epoxide groups [10]. This indicated that epoxy group has been incorporated successfully onto cellulosic chain.

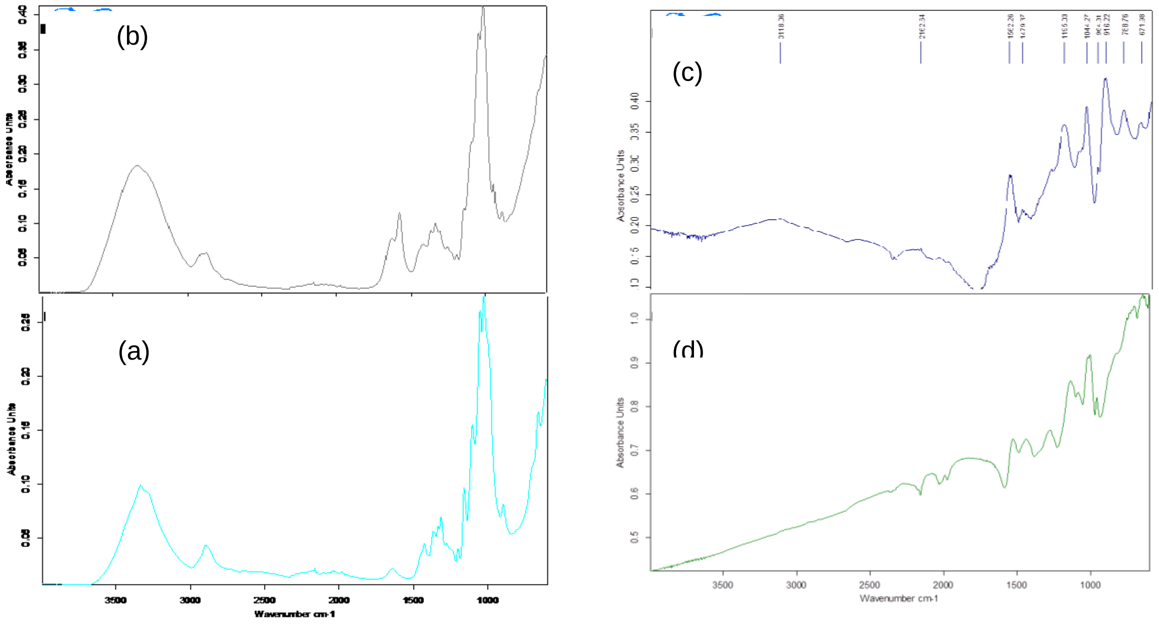

Figure 1. FTIR spectra for pure cellulose (a), modified cellulose (b), PPy (c) and TSA doped- PPy (d).

FTIR spectra for PPy and TSA doped-PPy are also similar to each other, indicating the main polymer chains are alike. The bands at 1562 cm^{-1} (C=C stretching), 1479 cm^{-1} (C-N stretching), 1195 cm^{-1} (C-H in plane bending), 1044 cm^{-1} (C-H in plane deformation vibration) are the characteristics for PPy. All the observed peaks are in accordance to that reported previously [11, 12]. The broad absorption band above 2000 cm^{-1} is more obvious in the spectrum for TSA-doped PPy. The peak at 1004 cm^{-1} of TSA-doped PPy FTIR spectra is attributed to the mode of in-plane deformation vibration of N^+H_2 on protonated nitrogen which is an important characteristic for doped polypyrrole [13].

3.2 Elemental analysis

Charge carriers for doped PPy are usually thought to be responsible for electronic motion along polymeric chain [14]. It means that the doping level will affect some properties of produced nanocomppsite including electrical and thermal conductivity and will be discussed in section 3.5.

$$\text{Doping level}(\%) = \left(\frac{(\frac{S}{N})}{2.3}\right) x\ 100 \tag{1}$$

where S and N are the sulphur and nitrogen content calculated from elemental analysis, respectively. Results of elemental analysis, percentage of yield and doping levels are shown in Table 1.

Samples	N (%)	C (%)	S (%)	H (%)	Yield (%)	Doping level (%)
TSA-doped PPy, RT	13.98	54.35	7.77	4.21	61.55	24.16
TSA-doped PPy, 0°C	13.72	55.50	8.84	5.06	67.19	26.87

Table 1. Doping level of doped PPy as calculated from the elemental analysis

TSA-doped PPy synthesized at 0 °C has higher doping level compare to the one that synthesized at room temperature. This is because the free radical at the growing site of PPy is stabilized at low temperatue. Furthermore, polymerization at low temperature can avoid cross linking reaction [15].

3.3 The Morphology

The physical appearance of cellulose-based adhesive and TSA-doped PPy and its nanocomposite is shown in Figure 2. The colour of modified cellulose is white, while TSA-doped PPy is black. The final product is black greyish in colour.

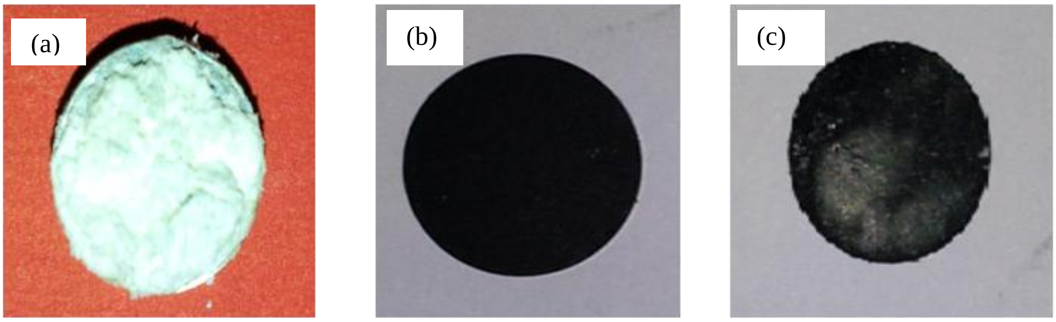

Figure 2. Photographs of modified cellulose (a), TSA doped-PPy (b) and their nanocomposite (c)

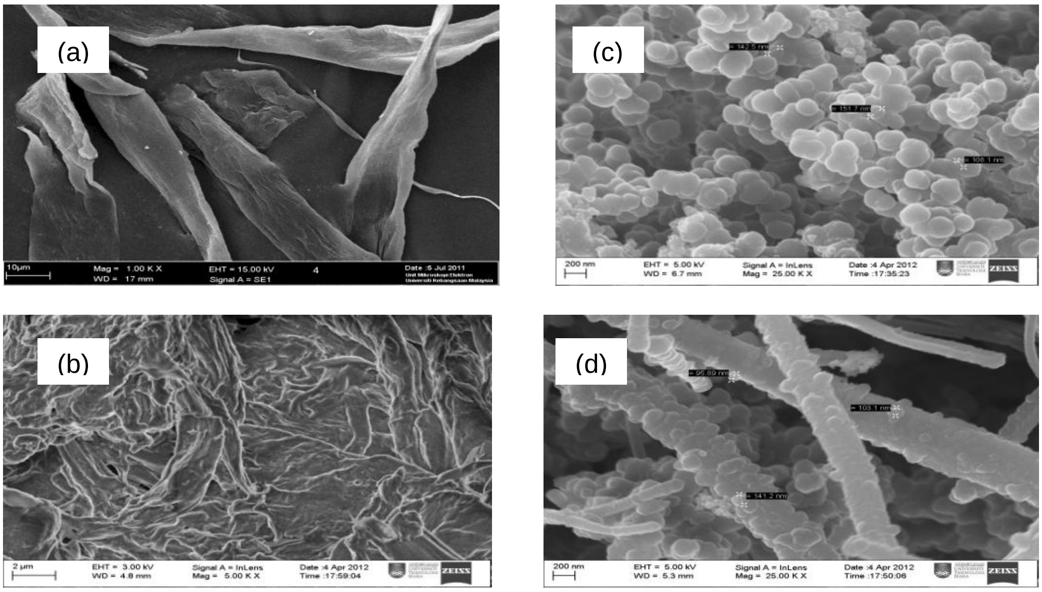

Figure 3. Scanning electron micrograph for cellulose (a), epoxypropyl cellulose (b), PPy (c) and TSA doped-PPy (d)

Scanning electron micrographs (SEM) for cellulose, modified cellulose (epoxypropyl cellulose), PPy and TSA-doped PPy are shown in Figure 3. It is clearly observed, chemical modification changes the morpohology of cellulose. According to Johar et al. [16] who studied about cellulose from risk husk, mentioned that chemical treatment reduced the size of cellulose fiber which can provide higher reinforcing capability for composite application. Morphology for PPy (Figure 3 (c)) changes from spherical shape to rod-like shape for TSA-doped PPy (Figure 3 (d)) with the size of 95-140 nm. The rod-like shape nanoparticle of TSA-doped PPy are closely packed and thus may lead to the interparticle electron hopping and thus high electrical conductivities relatively [11, 17].

3.4 Thermal stability study

Based on Figure 4 (a), it can be seen that cellulose exhibited two stages of mass loss. The initial mass loss which is below 100 ^{o}C is attributed to the release of absorbed moisture. The second mass loss is thermal decomposition of cellulose starting around 300 ^{o}C**.** In general, the thermolysis reaction of cellulose occurs by the cleavage of glycoside bonds, C-H, C-O and C-C bonds. Dehydration, decarboxylation and decarbonylation are also involved in the process[18]. For the modified cellulose, there are three step of weight loss. The first mass loss due to evaporation of water. The second step indicated the decomposition of epoxy group that has been incorporated in the cellulose backbone. Meanwhile, the third mass loss is attributed to cellulose decomposition.

The first significant mass loss for PPy and TSA-doped PPy was at temperature below 100 ^{O}C are due to the evaporation of water molecules. The second mass loss corresponds to decomposition of PPy and TSA-doped PPy, starting around 230 ^{O}C. Based on the TGA results, it is found that thermal stability of TSA-doped PPy is higher than PPy. This is due to the presence of aromatic group in doped PPy causes difficulties for degradation of PPy chains. Therefore, it can be pointed out that PPy is quite thermally stable as also reported by other researchers [11].

In the case of modified cellulose-based adhesive and TSA-doped PPy composite, the first step mass loss which is below 100 ^{o}C due to the release of adsorbed moisture in the composite. The second mass loss, ranging from 130-230 ^{o}C, can be attributed to the epoxy group that have been incorporated in cellulose chains. The third mass loss starting around 230 ^{o}C corresponds to TSA-doped PPy. Lastly, the four step starting around 300 ^{o}C is attributed to the decomposition of cellulose.

3.5 Electrical and thermal conducticity

Based on results shown in Table 2, PPy and doped PPy gave the reading of electrical conductivity in semi conductive range. The delocalization of π electrons over the polymeric backbone, co-existing with unusual low ionization potentials and high electron affinities make possible unique electrical properties of conjugated polymer including PPy and doped PPy [19]. The higher doping level of TSA-doped PPy (0^{o}C) (27 %) compared to TSA-doped PPy (RT) (24 %) resulting higher electrical and thermal conductvity. This is because the charges and electron mobility are increased [20]. However, as expected the nanocomposite showed a decrease in electrical conductivity since cellulose-based adhesive is an insulator [21]. The results obtained in Table 2 showed that semi conductor materials in electrical conductivity analysis gave good value in thermal conductivity and in the range of conventional polymer [22].

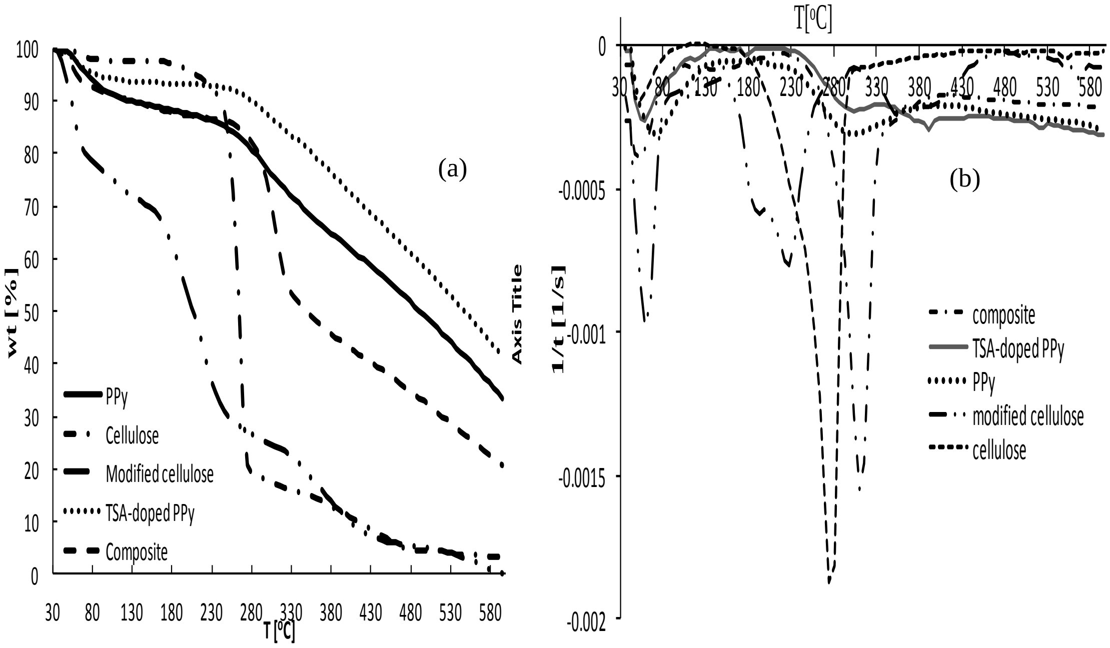

Figure 4. TG (a) and DTG (b) thermograms for pure cellulose, modified cellulose, PPy, TSA-doped PPy and modified celluloae : TSA-doped PPy nanocomposite

Samples	Electrical conductivity ($S\ cm^{-1}$)	Thermal conductivity K (W/Mk)
PPy	5.42×10^{-6}	0.343
TSA-doped PPy, RT	9.95×10^{-4}	0.406
TSA-doped PPy, 0°C	8.42×10^{-3}	0.431
Nanocomposite	2.68×10^{-3}	0.422

Table 2. Thermal conductivity and electrical conductivity results

4 Conclusion

Cellulose-based adhesive has been succesfully prepared via chemical modification. The incorporation of epoxy group onto celluloisic chains was confirmed by FTIR spectroscopy and TGA analysis. The prepared nanocomposite was relatively stable at high temperature and its electrical conductivity (2.68×10^{-3} S cm^{-1}**)** is in the range of semi conductive materials. Results from thermal conductivity testing showed that this prepared material is potentially useful as coating material in small electronic devices.

References

[1] Dobre T., Pârvulescu O. C., Stoica A.,Iavorschi G. Characterization of cooling systems based on heat pipe principle to control operation temperature of high-tech electronic components. *Applied Thermal Engineering* **Vol. 30**, pp. 2435-2441 (2010).

[2] Zhang H.,Zhuang J. Research, development and industrial application of heat pipe technology in China. *Applied Thermal Engineering* **Vol. 23**, pp. 1067-1083 (2003).

[3] Huang H. S., Weng Y. C., Chang Y. W., Chen S. L.,Ke M. T. Thermoelectric water-cooling device applied to electronic equipment. *International Communications in Heat and Mass Transfer* **Vol. 37**, pp. 140-146 (2010).

[4] Ansari R. Polypyrrole conducting electroactive polymers: Synthesis and stability study. *E- Journal of Chemistry* **Vol. 3**, pp. 186-201 (2006).

[5] Blinova N. V., Stejskal J., Trchová M., Prokes J.,Omastová M. Polyaniline and polypyrrole: A comparative study of the preparation. *European Polymer Journal* **Vol. 46**, pp. 871-876 (2007).

[6] Bindu S. P., Ray D., Sengupta S., Kar T., Mohanty A.,Manju M. Isolation of Cellulose Nanoparticles from Sesame Husk. *Industry Engineering Chemical Research,* **Vol. 50**, pp. 871-876 (2012).

[7] Levine I. N. *Physical Chemistry (5th ed.).* McGraw-Hill, Boston (2001).

[8] Bono A., Ying P. H., Yan F. Y., Muei C. L., Srabatly R.,Krishniah D. Synthesis and characterization of carboxymethyl cellulose from palm kernel cake. *Advances in Natural an Applied Sciences,* **Vol. 3**, pp. 5-11 (2009).

[9] Sun J. X., Sun X. F., Zhao H.,Sun R. C. Isolation and characterization of cellulose from sugarcane baggase. *Polymer Degradation and Stability,* **Vol. 84**, pp. 331-339 (2004).

[10] Pedroso L. M., Margarida M., Castro C. A., Simoes P.,Portugal A. Melamine/epichlorohydrin prepolymers : synthesis and charaxterization. *Polymer* **Vol. 46**, pp. 1766-1774 (2005).

[11] Ghalib H., Abdullah I.,Daik R. Synthesis of polypyrrole nanoparticles in natural rubber-polystyrene blend via emulsion polymeriation. *Journal of Applied Polymer Science,* **Vol. 123**, (2012).

[12] Li X., Wan M., Wei Y., Shen J.,Chen Z. Electromagnetic funtionalized and core-shell micro/nanostructure polypyrrole composites. *Journal of Physical Chemistry B,* **Vol. 110**, (2006).

[13] Omastova M., Trchova M., Kova´rˇova J.,Stejskal J. Synthesis and structural study of polypyrroles prepared in the presence of surfactants. *Synthetic Metals,* **Vol. 138**, pp. 447-455 (2003).

[14] Wan M. X. *Conducting polymers with micro or nanometer structure*. Springer-Verlag, Heidelberg (2008).

[15] Jang J. Conducting polymers nanonaterials and their application *Emmisive Materials Nanomaterials,* **Vol. 199**, pp. 189-260 (2006).

[16] Johar N., Ahmad I.,Dufresne A. Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk. *Industrial Crops and Products,* **Vol. 37**, pp. 93-99 (2012).

[17] Yang Y., Liu J.,Wan M. Self-assembled conducting polypyrrole micro/nanotubes. *Nanotechnology,* **Vol. 13**, pp. 771-773 (2002).

[18] Trindade W. G., Hoareau W., Megiatto J. D., Razera A. T., Castellan A.,Frollini E. Thermoset Phenolic Matrices Reinforced with Unmodified and Surface-Grafted Furfuryl Alcohol Sugar Cane Bagasse and Curaua Fibers: Properties of Fibers and Composites. *Biomacromolecules,* **Vol. 6**, pp. 2485-2496 (2005).

[19] Stenger-Smith J. D. Intrinsically electrically conducting polymers. Synthesis, characterization, and their applications. *Progress in Polymer Science,* **Vol. 23**, pp. 57-79 (1998).

[20] Callister W. D. *Material Science and Engineering : An Introduction*. John Wiley & Sons Ltd., New York. (2007).

[21] Serth R. W. *Process heat transfer : principles and applications*. Academic Press, USA (2007).

[22] Bahadur R.,Bar-Cohen A. Orthotropic Thermal Conductivity Effect on Cylindrical Pin Fin Heat Transfer. *International Journal of Heat and Mass Transfer* **Vol. 50**, pp. 1155-1162 (2007).