

Preparation and Characterization of Polypyrrole Nanocomposites using Various Surfactants in Aqueous and Aqueous/Non-Aqueous Media

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Abstract: Polypyrrole nanocomposites were prepared to study some characteristics such as morphology and chemical structure. Polypyrrole nanocomposites have been prepared to in aqueous and aqueous/nonaqueous media by chemical oxidative polymerization using ferric chloride as an oxidant and in the presence of various surfactants such as sodium dodecylbenzenesulfonate, poly (vinyl alcohol) and hydroxypropylcellulose. The nanocomposites were characterized in terms of morphology, particle size, chemical structure and glass transition temperature. The morphology of products was characterized by using Scanning Electron Microscope (SEM). The results indicate that the surface morphology and particle size are dependent on the type of surfactant. Also the chemical structure and glass transition temperature of product were determined by fourier-transform infrared spectroscopy and differential scanning calorimetry respectively.

Key words: Glass transition temperature, morphology, nanocomposite, polypyrrole, surfactant

INTRODUCTION

Conducting polymers have become a popular basic material for advanced applications such as static electricity dissipation (Skotheim *et al.*, 1998), metal anti-corrosion and marine fouling prevention (Nalwa, 1997; Wang *et al.*, 1999), rechargeable batteries (Scrosati, 1998), conductive paints (Eisazadeh *et al.*, 1993), heavy-metals separation (Eisazadeh, 2007a, 2007b), optical devices (Falcao and De Azevedo, 2002), membranes (Misoska *et al.*, 2001), sensors and biosensors (Guernion *et al.*, 2002; Yamato *et al.*, 1997), electromagnetic interference (EMI) shielding (Dhawan *et al.*, 2002), antistatic coatings (Ohtani *et al.*, 1993), biomedical applications (Benabderrahmane *et al.*, 2005), etc.

Conjugated polymers are easily synthesized through chemical or electrochemical processes and their conductivities can be controlled through doping or dedoping procedures (Cho *et al.*, 2007). Conducting polymer presents advantages such as low specific mass and versatility of the synthesis. However, its technological application still introduces some limitations, such as low environmental stability, poor mechanical properties (Zoppi *et al.*, 1994), and low processability due to the insolubility and infusibility of most of these polymers.

Research interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene, etc. has increased tremendously because of the versatility of their applications (Mahmud *et al.*,

2005). Among conducting polymers, PPy has been extensively studied, motivated by its high conductivity, environmental stability and high yield in redox processes (Planche *et al.*, 1994). This polymer is one of the best-known conducting polymers and has been intensively studied as an electroactive material for several years (MacDiarmid, 2001; MacDiarmid, 1997; Skotheim, 1986). PPy can be prepared by plasma and vapor phase polymerization techniques. Due to its ability to provide high conductivity by creating suitable thickness and uniform film, in situ chemical polymerization is the best process coating dielectric materials (Ferenets and Harlin, 2007). In this study PPy prepared chemically by using various surfactants in aqueous and aqueous/non aqueous media.

EXPERIMENTAL

Instrumentation: Magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope model LSM50A, differential scanning calorimeter model PL-DSC and fourier transform infrared spectrometer model shimadzu 4100 were employed.

All of the experiments were performed in Polymer Laboratory of Babol University of Technology on February 2011.

Reagents and standard solutions: Materials used in this study were pyrrole ($d = 0.97 \text{ g/mL}$), hydroxypropylcellulose (HPC, $M_w = 10^6$), poly(vinyl alcohol) (PVA,

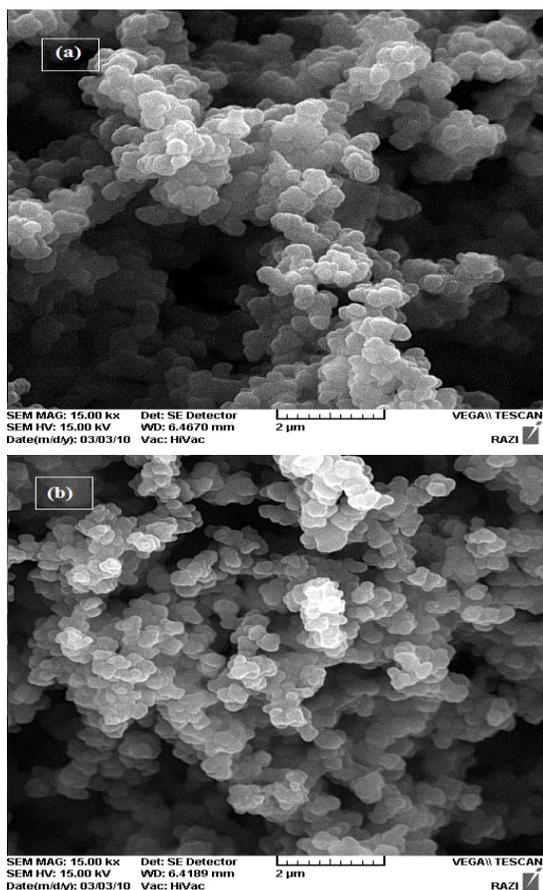


Fig. 1: Scanning electron micrograph of polypyrrole nanocomposite generated in aqueous media, (a) without surfactant and (b) DBSNa (2 g/L) used as surfactant. Reaction conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, pyrrole monomer = $14.45 \times 10^{-2} \text{ mol/L}$, volume of solution = 100 mL, reaction time 5 h at room temperature

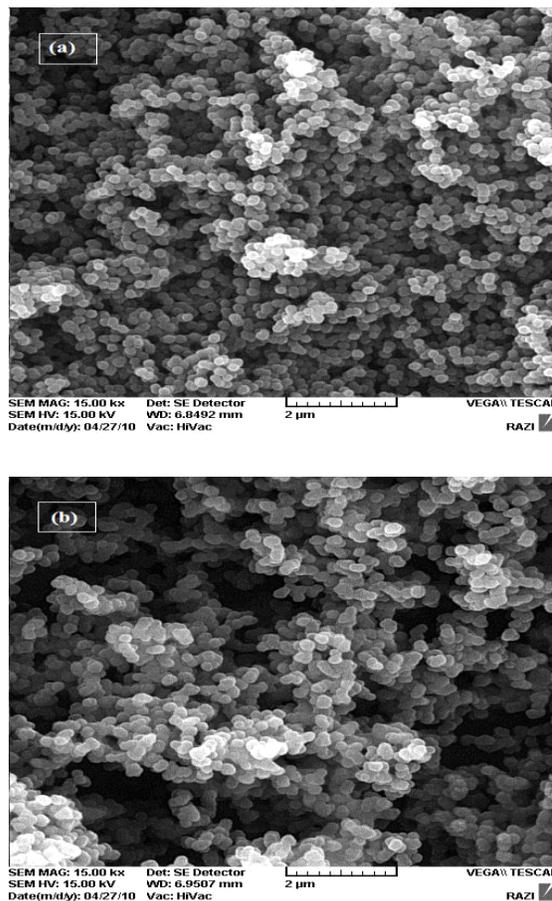


Fig. 2: Scanning electron micrograph of polypyrrole nanocomposite generated in aqueous media, (a) HPC (2 g/L) and (b) PVA (2 g/L) used as surfactants. Reaction conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, pyrrole monomer = $14.45 \times 10^{-2} \text{ mol/L}$, volume of solution = 100 mL, reaction time 5 h at room temperature

Table 1: Preparation conditions and impact of the type of surfactant on the yield and particle size

Type of solution	Type of surfactant	Concentration of surfactant (g/L)	Particle size (nm)	yield of monomer to polymer (% w/w)
Water			215	85
Water	DBSNa	1	198	75
Water	DBSNa	2	167	70
Water	HPC	1	152	65
Water	HPC	2	95	60
Water	PVA	1	103	60
Water	PVA	2	90	55
Water + ethyl acetate-			160	80
Water + ethyl acetate	DBSNa	1	99	65
Water + ethyl acetate	HPC	1	161	60
Water + ethyl acetate	PVA	1	153	55

$M_w = 72000$), sodium dodecylbenzene-sulfonate (DBSNa), ethyl acetate and ferric chloride, from

Merck and Aldrich. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this study. Pyrrole monomer was purified by simple distillation.

Nanocomposite preparation: The reaction was carried out in an aqueous and aqueous/non-aqueous media at room temperature for 5 h. In a typical experiment 1 mL pyrrole monomer was added to a stirred aqueous solution (100 mL) containing 5.4 g FeCl_3 and 0.1 - 0.2 g of one of the surfactants. After 5 h, the polymer was collected by filtration, and in order to separate the oligomers and impurities, the product was washed several times in succession with deionized water. It was then dried in a vacuum oven at 40°C for 12 h.

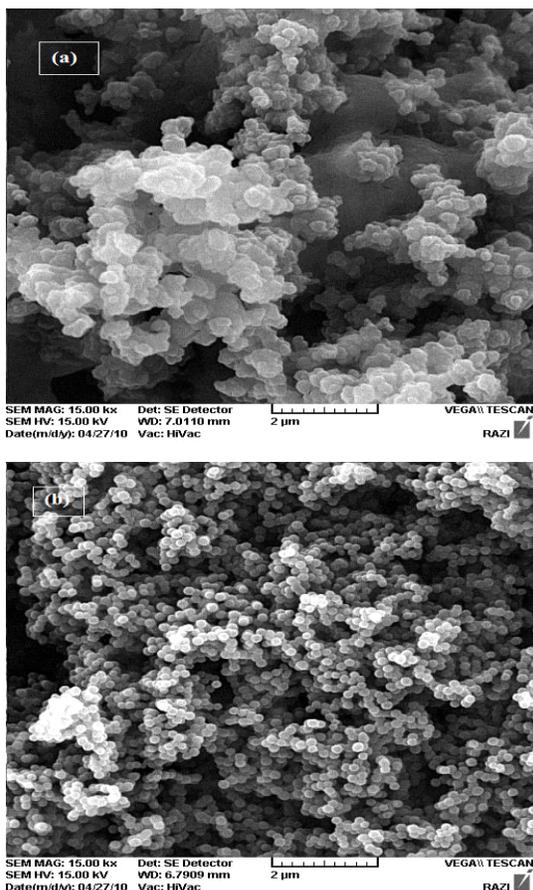


Fig. 3: Scanning electron micrograph of polypyrrole nanocomposite generated in aqueous/non aqueous (water/ethylacetate) media, (a) without surfactant and (b) DBSNa (2 g/L) used as surfactant. Reaction conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, pyrrole monomer = $14.45 \times 10^{-2} \text{ mol/L}$, volume of solution = 100 mL, reaction time 5 h at room temperature

RESULTS AND DISCUSSION

Scanning electron microscope analysis: The yield of monomer to polymer, particle size and surface morphology are dependent on the type and concentration of surfactant, because the surfactant was adsorbed physically to the growing polymer (Aldissi and Armes, 1991). As can be seen in Table I, the type and concentration of surfactant influence the size of particles. Particle size decreases by increasing concentration of surfactant, because surfactant prevented from gross aggregation of particles. Also the type of solution affect the size, homogeneity and yield of monomer to polymer due to, the type of solution influence the rate of polymerization.

The surface morphology of product was characterized by Scanning Electron Microscope (SEM). As shown in

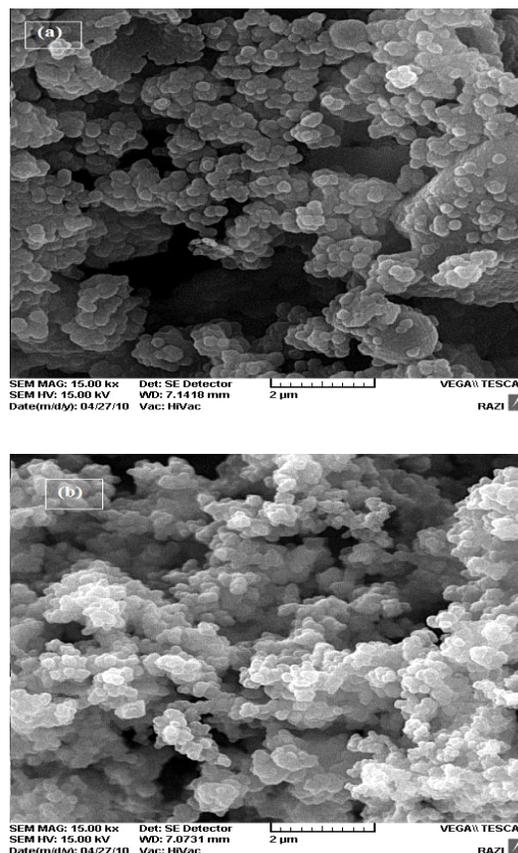


Fig. 4: Scanning electron micrograph of polypyrrole nanocomposite generated in aqueous/non aqueous (water/ethylacetate) media, (a) HPC (2 g/L) and (b) PVA (2 g/L) used as surfactants. Reaction conditions: $\text{FeCl}_3 = 54 \text{ g/L}$, pyrrole monomer = $14.45 \times 10^{-2} \text{ mol/L}$, volume of solution = 100 mL, reaction time 5 h at room temperature

Fig. 1 to 4, the size and homogeneity of the particles are dependent on the type of surfactant and solution. By comparison between Fig. 1 and 2, and also between Fig. 3 and 4, particle size and homogeneity of particles related the type of surfactant and solution, because in the polymerization of pyrrole surfactant adsorbed physically to polymer and influence the physical and chemical properties of solution and rate of polymerization.

As can be seen in aqueous solution (Fig. 2) small monodisperse spherical particles were obtained by using HPC and PVA. But, in aqueous/nonaqueous solution homogeneity increases and particle size decreases by using DBSNa.

Fourier-transform infrared spectroscopy analysis: The molecular structures of the obtained products were determined by FTIR spectroscopy, which provided valuable information regarding the formation of

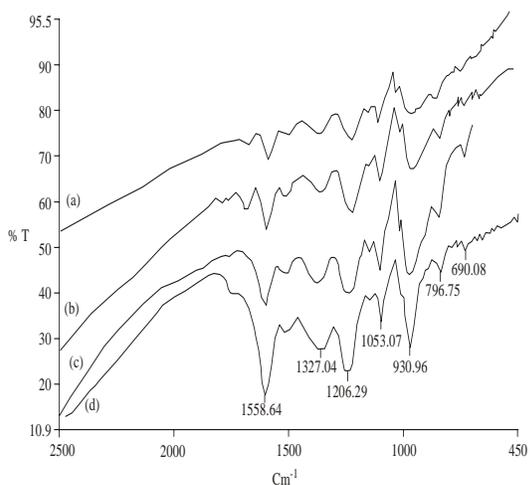


Fig. 5: FTIR spectra of (a) polypyrrole nanocomposite without surfactant, (b) DBSNa, (c) HPC, and (d) PVA used as surfactants. FeCl₃ used as oxidant in queous solution

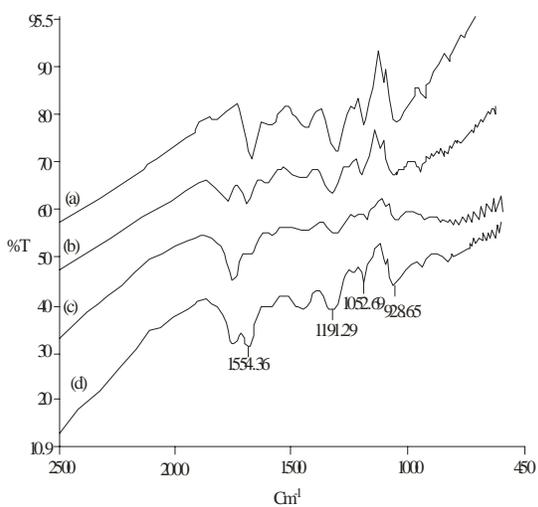


Fig. 6: FTIR spectra of (a) polypyrrole nanocomposite without surfactant, (b) DBSNa, (c) HPC, and (d) PVA used as surfactants. FeCl₃ used as oxidant in solution of (water/ethyl acetate)

polypyrrole nanocomposites. The FTIR spectra analysis was done to identify the characteristic peaks of the products. The FTIR spectra in the 2500-450 cm⁻¹ region for various polymers are shown in Fig. 5 and 6. As can be seen, the FTIR spectrum changed when the nanocomposite was obtained by using various surfactants and solutions. As can be seen in Fig. (5d) the peak related to pyrrole unit at 1558 cm⁻¹. The peaks are at 1327 cm⁻¹ (C-N stretching vibration), 1206 cm⁻¹ (C-H in-plane deformation), 1053 cm⁻¹ (N-H in-plane deformation), 930 cm⁻¹ (C-H out-of-plane deformation) and 796 cm⁻¹ (C-H out-of-plane ring deformation).

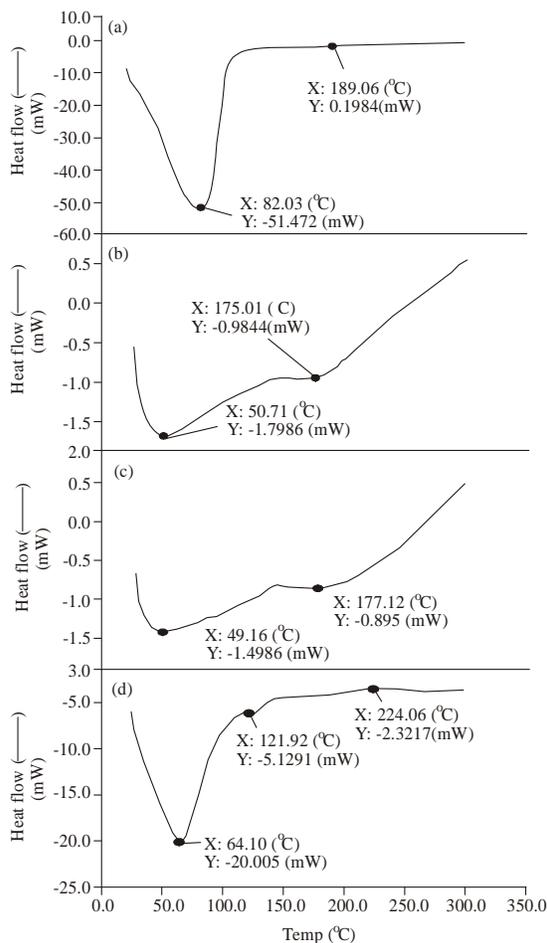


Fig. 7: DSC thermograms of polypyrrole nanocomposite (a) without surfactant, (b) PVA, (c) HPC and (d) DBSNa used as surfactants in aqueous media.

Differential scanning calorimeter analysis: Thermal properties of polypyrrole have been studied using Differential Scanning Calorimeter (DSC). The DSC thermograms of the polypyrrole nanocomposites are shown in Fig. 7.

Generally, a glass transition appears as a sudden change in slope in the DSC curve but sometimes it appears as an endothermic peak. The endotherms observed in thermogram (Fig. 7) are attributed to the glass transition of the polypyrrole (189, 175, 177.1 and 121.9°C), respectively. According to thermograms, surfactants can shift the glass transition to lower temperatures in the PPy nanocomposite.

CONCLUSION

In this study the characteristics of PPy nanocomposites, such as morphology, glass transition temperature and molecular structure, were investigated in

aqueous and aqueous/non-aqueous media by using various surfactants. It was found that the type of surfactant has a considerable effect on the particle size and morphology of the resulting product which is probably due to the adsorption of the surfactant to polymer physically, and also the influence of the surfactant on the chemical and physical properties of the solution. The SEM micrographs show that the type of surface active agent plays a major role on the size and monodispersity of particles. The molecular structures of the products were determined by FTIR spectroscopy. The results indicate that the intensity of the peaks is dependent on the type of surfactant, presumably due to the interaction of surfactant and polypyrrole. The DSC thermograms clearly demonstrate the relationship between type of surfactant and Tg for the PPy nanocomposite. As shown in the thermograms, the presence of surfactant can decrease the glass transition temperature of polypyrrole.

REFERENCES

- Aldissi, M. and S.P. Armes, 1991. Colloidal dispersion of conducting polymers. *Prog. Org. Coat.*, 19(11): 21-58.
- Benabderrahmane, S., S. Bousalem, C. Mangeney, A. Azioune, M.J. Vaulay and M.M. Chehimi, 2005. Interfacial Physicochemical Properties of Functionalized Conducting Polypyrrole Particles. *Polymer.*, 46(1): 1339-1346.
- Cho, S.H., K.T. Song and J.Y. Lee, 2007. *Handbook of Conducting Polymers*. 3rd Edn., CRC Press, New York.
- Dhawan, S.K., N. Singh and S.Venkatachalam, 2002. Shielding behaviour of conducting polymer-coated fabrics in X-Band, W-Band and radio frequency range. *Synth. Met.*, 129(2): 261-267.
- Eisazadeh, H., G. Spinks and G.G. Wallace, 1993. Electro-chemical properties of conductive electroactive polymeric colloids. *Mater. Forum.*, 17(3): 341-344.
- Eisazadeh, H., 2007a. Removal of Chromium from Waste Water Using Polyaniline. *J. Appl. Polym. Sci.*, 104(3): 1964-1967.
- Eisazadeh, H., 2007b. Removal of mercury from water using polypyrrole and its composites. *Chin. J. Polym. Sci.*, 25(2): 393-397.
- Falcao, E.H.L. and W.M. De Azevedo, 2002. Polyaniline-polyvinyl alcohol composite as an optical recording material. *Synth. Met.*, 128(2): 149-154
- Ferenets, M. and A. Harlin, 2007. Chemical in Situ Polymerization of Polypyrrole on Poly(methyl methacrylate) Substrate. *Thin Solid Films*, 515(13): 5324-5328.
- Guernion, N., R.J. Ewen, K. Pihlainen, N.M. Ratcliffe and G.C. Teare, 2002. The fabrication and characterisation of a highly sensitive polypyrrole sensor and its electrical responses to amines of differing basicity at high humidities. *Synth. Met.*, 126(2-3): 301-310.
- MacDiarmid, A.G., 2001. *Synth. met: A novel role for organic polymers (Nobel Lecture)*. *Angew. Chem. Int. Ed.*, 40(1): 2581-2590.
- MacDiarmid, A.G., 1997. Polyaniline and polypyrrole: Where are we headed? *Synth. Met.*, 84(1-3): 27-34.
- Mahmud, H.N.M.E., A. Kassim, Z. Zainal and W.M.M. Yunus, 2005. Electronic Conducting Polymer Composite Films with Enhanced Mechanical Properties. *J. Appl. Polym. Sci.*, 100(3): 4107-4112.
- Misoska, V., J. Ding, J.M. Davey, W.E. Price, S.F. Ralph and G.G. Wallace, 2001. Polypyrrole membranes containing chelating ligands: Synthesis, characterisation and transport studies. *Polymer.*, 42(21): 8571-8579.
- Nalwa, H.S., 1997. *Handbook of Organic Conductive Molecules and Polymers*. Wiley, Chichester.
- Ohtani, A., M. Abe, M. Ezoe, T. Doi, T. Miyata and A. Miyake, 1993. Synthesis and properties of high-molecular-weight soluble polyaniline and its application to the 4mb-capacity barium ferrite floppy disk's antistatic coating. *Synth. Met.*, 57(1): 3696-3701.
- Planche, M.F., J.C. Thibblemont, M. Mazars and G. Bidan, 1994. Kinetic study of pyrrole polymerization with iron (iii) chloride in water. *J. Appl. Polym. Sci.*, 52(13): 1867-1877.
- Scrosati, B., 1998. Conducting polymers: Advanced materials for new design rechargeable lithium batteries. *Polym. Int.*, 47(2): 50-55.
- Skotheim, T.A., R.L. Elsenbaumer and J.F. Reynolds, 1998. *Handbook of Conducting Polymers*. 2nd Edn., Marcel Dekker, New York.
- Skotheim, T.A., 1986. *Handbook of Conducting Polymers*. Marcel Dekker, New York.
- Wang, X.H., J. Li, J.Y. Zhang, Z.C. Sun, L. Yu, X.B. Jing, F.S. Wang, Z.X. Sun and Z.J. Ye, 1999. Polyaniline as marine antifouling and corrosion-prevention agent. *Synth. Met.* 102(1-3): 1377-1380.
- Yamato, H., T. Koshiba, M. Ohwa, W. Wernet and M. Matsumura, 1997. A new method for dispersing palladium microparticles in conducting polymer films and its application to biosensors. *Synth. Met.*, 87(3): 231-236.
- Zoppi, R.A., M.I. Felisberti and M.A. De Paoli, 1994. Chemical preparation of conductive elastomeric blends: Polypyrrole/EPDM. I. oxidant particle-size effect. *J. Polym. Sci.*, 32(6): 1001-1008.