



PREPARATION AND CHARACTERIZATION OF FIBROUS CELLULOSE/POLYPYRROLE NANOCOMPOSITES

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Introduction

Polypyrrole has been one of the most widely studied polymers in the area of conductive polymers because of its environmental stability, physical and electrical properties [1]. The properties of conducting polymers such as redox activity, ion exchange, ion discrimination capacities and corrosion protection are highly dependent on the synthesis procedure as well as on the nature of dopant, monomer and solvent [2]. Polypyrrole is one of the conductive polymers readily synthesized from a range of aqueous and non-aqueous solvents and have many potential advantages such as low cost and low potential oxidation. All these properties made polypyrrole as a good candidate in many potential applications such as electronic and electrochromic devices, light-weight batteries, membrane separation, sensors, drug delivery, rechargeable batteries, and chromatographic stationary phases [3,4]. However, it is an infusible, improcessable polymer which has relatively poor mechanical, and processability properties. Because of that, the study on the new approaches, to synthesize conductive polymers composite with enhanced mechanical and electrical properties is still continuing. In recent years, composite materials of cellulose and conductive polymers have received significant attention. It has been shown that polypyrrole (PPy) can be uniformly coated on cellulose fibers from commercial filter paper by a chemical polymerization-induced adsorption process [5]. More recently, it was demonstrated that pyrrole was *in situ* polymerized on the individual cellulose fibers extracted from the *Cladophora* green [6]. Microfibrillated cellulose (MFC), was first developed in the early 1980s, by high-shear mechanical homogenization in water. The word "fibril" has been used by various researchers to describe relatively long and very thin pieces of cellulosic material [7]. Due to the mild character of the enzymatic hydrolysis, the cellulose fibers in MFC are substantially longer than Cellulose nanocrystal (CNC) which produced by acid hydrolysis. In this research, composite of

Polypyrrole-Microfibrillated Cellulose (PPy-MFC) was prepared in the presence of different surfactant. Microfibrillated celluloses (MFC) are generally considered to be fibrils with diameters in the range of 10-100 nm liberated from larger plant based cellulose fibers. Conducting Polypyrrole (PPy) composites were synthesized via chemical polymerization method using different concentration of Pyrrole, MFC, and Ammonium persulfate (NH₄)₂S₂O₈ as oxidant.

Results and Discussion

2.1. Field Emission Scanning Electron Microscopy (FE-SEM)

The morphologies of resulting composites were greatly depend on the monomer concentration and surfactant chain length. The FE-SEM micrographs of polypyrrole exhibited the presence of globular, micrometer-sized particles with a bulky and non-porous structure. However, the composite of PPy-MFC showed an open porous structure of fiber with average size of nanometer (Fig 1).

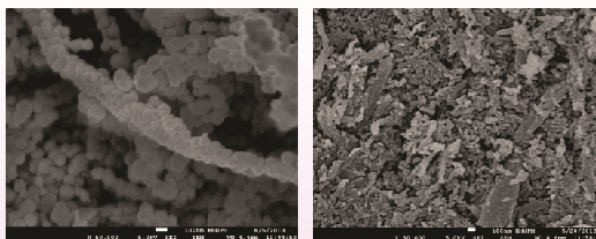


Figure 1: FESEM micrographs of PPy-MFC, AND PPy-MFC-CTAB at 50,000 x magnification

Ribbon-like polypyrrole nanostructures were prepared by chemical polymerization of pyrrole in the presence of long-chain cationic surfactant, Cetyltrimethylammonium bromide (CTAB), whereas no polypyrrole nanostructure was obtained in the presence of anionic surfactant of Sodium dodecylbenzenesulfonate (SDBS). The composite of PPy-MFC prepared in the presence of CTAB, nanofibers presented the mean diameter of 71.27 nm that showed a value between the size of PPy-MFC and PPy-CTAB.

2.2. Transmission Electron Microscopy

The size of nanostructure, and fiber size distribution was studied by Transmission electron microscopy (TEM). Figure 2 shows the TEM images of PPy-MFC prepared from solution containing 0.03M pyrrole and 0.025M MFC

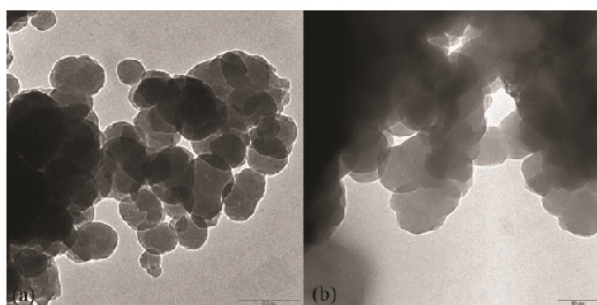


Figure 2: TEM images of PPy-MFC at magnifications of (a) 16,000 and (b) 20,000

The composite of PPy-MFC prepared in the presence of CTAB as shown in Figure 3, nanofibers presented the mean diameter of 71.27 nm that showed a value between the size of PPy-MFC and PPy-CTAB.

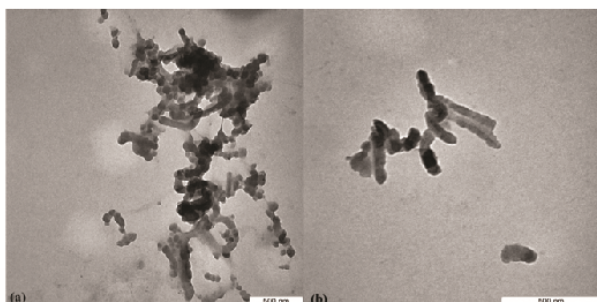


Figure 3: TEM image of PPy-MFC-CTAB at magnifications of (a) 40,000 and (b) 80,000

Reaction between cationic surfactant of CTAB with anion of oxidizing agent which is persulphate ion acted as templates for the formation of ribbon-like polypyrrole nanostructures. However, anionic surfactant of SDBS cannot serve as a template for the polymerization of pyrrole probably because of its role as counterions in the polymer chains.

2.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR spectra showed that pyrrole was polymerized successfully on the MFC fibers and when an anionic surfactant was used to prepare the composites; it served as counter ion for the PPy chains. The infrared absorption spectra of PPy, MFC, CTAB and a composite prepared from solution containing 0.06M PPy, 0.1% MFC and 12cmc of CTAB are shown in Figure 12. The characteristic peaks of polypyrrole at 1022.74 cm^{-1} (C-H in-plane), 1138.29 cm^{-1} (C-N stretching), and 1525.41 cm^{-1} (ring vibration), confirmed the formation of

polypyrrole doped by oxidizing agent which was Ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The peak at 3327.46 cm^{-1} and 2913.16 cm^{-1} which are due to O-H and C-H stretching in MFC indicating the polymerization of Pyrrole on the surface of MFC. The peak at 1307.09 cm^{-1} which is related to C-O and C-H bending in MFC, is another evidence of presence of MFC in the structure of PPy-MFC-CTAB composite. The absorption at 1698.66 cm^{-1} was assigned to the C=C ring stretching of pyrrole in benzoic form. A sharp peak at 909.26 cm^{-1} is characteristic peak of CTAB inside structure of composite.

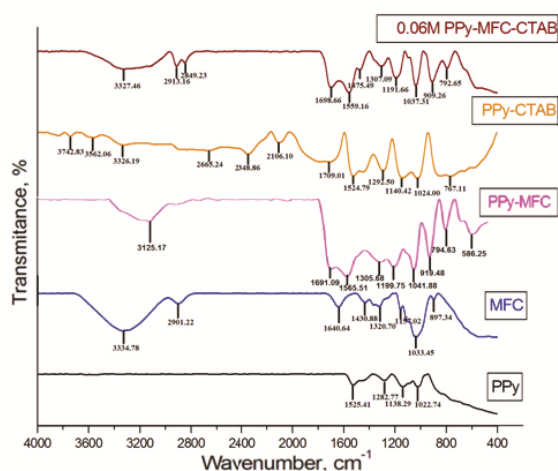


Figure 4: The FT-IR spectrum of PPy, MFC, PPy-MFC, PPy-CTAB, and composite prepared from solution containing 0.06M Pyrrole, 0.1% MFC and 12cmc of CTAB.

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