In-situ Polymerization of Polyaniline/Polypyrrole Copolymer using Different Techniques

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Abstract. The morphology and surface area of the poly(aniline-co-pyrrole) copolymer (PANPY) are important properties which improve the efficiency of the copolymer in various applications. In this investigation, different techniques were employed to produce PANPY in different morphologies. Aniline and pyrrole were used as monomers, and ammonium peroxysulfate (APS) was used as an oxidizer with uniform molar ratio. Rapid mixing, drop-wise mixing, and supercritical carbon dioxide (ScCO2) polymerization techniques were appointed. The chemical structure, crystallinity, porosity, and morphology of the composite were distinguished by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) analysis, and transmission electron microscopy (TEM) respectively. The characterization tests indicated that the polyaniline/polypyrrole copolymer was successfully prepared with different morphologies. Based on the obtained TEM, hollow nanospheres were formed using rapid mixing technique with acetic acid that have a diameter of 75 nm and thickness 26 nm approximately. Also, according to the XRD, the produced structures have a semi-crystalline structure. The synthesized copolymer with ScCO2-assisted polymerization technique showed improved surface area (38.1 m²/g) with HCl as dopant.

1. Introduction

Polyaniline (PANI) and polypyrrole (PPy) are extensively studied conductive polymers. Both have unique characteristics such as a high conductivity and environmental stability. In the past, there was a difficulty to make a copolymer of aniline and pyrrole because of synthesis method for each of them [1]-[2]. Now, there are two main ways to synthesize a copolymer of aniline and pyrrole by chemical [3]-[7] or electrochemical [8]-[10] methods. Chemical oxidation process has been checked in previous studies where ammonium peroxysulfate solution (APS) is used as oxidant [3]-[7]. Modifications to the chemical oxidation method have been conducted to improve the conductivity such as surfactant-assisted chemical oxidative polymerization [11], inverted emulsion [12], pre-polymerization [13] and...
template synthesis method [14]. Recently, extensive studies were conducted to investigate the idea of using supercritical CO2 (ScCO2) as an alternative aid in polymer synthesis. Supercritical CO2 (ScCO2) have some interesting properties due to the intermediate phase between liquid and gas phase such as density like liquids, viscosity and diffusivity like a gas. It is clean, non-toxic, non-flammable, chemically inert, inexpensive and considerable in the atmosphere. By small changes in temperature and pressure, a supercritical CO2 can be tuned and controlled. It is easy to remove after the polymerization process by reverting to ambient conditions. Moreover, it was stated that the employment of compressed CO2-assisted polymerization process has a significant effect on the produced morphology of the produced polymer [15],[16].

This investigation deals with the first chemical copolymerization of polyaniline/polypyrrole using three distinct preparation chemical polymerization methods to prepare various copolymers with different morphologies and properties. Conventional chemical oxidation, rapid mixing, supercritical carbon dioxide ScCO2-assisted polymerization techniques were utilized with the same molar ratios of the reactants. The copolymer was characterized by TEM, XRD, FT-IR, and BET surface area analysis for different physical and chemical examinations.

2. Experimental

2.1. Materials

Aniline, Pyrrole, Ammonium peroxydisulfate solution (APS), Acetic acid, Hydrochloric acid, Ethanol, and Methanol were purchased from Sigma-Aldrich. All chemicals were used without further refining. Freshly distilled water was used for the preparation of all aqueous solutions and the washing process.

2.2. Synthesis of copolymer by conventional chemical oxidation

In conventional chemical oxidation process, 25 mL of aniline/pyrrole mixture was prepared by dissolving aniline and pyrrole in aqueous dopant solution (0.2 M acetic acid or 0.2 M HCl) with molar ratio 1:1. At the same time, 25 mL ammonium persulfate solution (APS) was added drop-wise in a flask with stirring. The resultant mixture was left for 24 h seeking the full polymerization. The precipitates were collected and washed with diluted HCl, ethanol, methanol, and finally distilled water. Then, it was centrifuged for 10 min at 6000 rpm. Finally, the copolymer was dried for 24 h at 80 °C.

2.3. Synthesis of PANPY by rapid mixing

Rapid mixing was used to produce the aniline/pyrrole copolymer. The same molar ratio of oxidant: monomer with the same solutions were prepared at the same conditions of previous technique. The oxidizer solution was added at once to the monomers solution followed by continuous stirring at 1000 rpm for 2 h. The produced solution was kept at room temperature for 24 h. The same steps of collecting, filtering, washing, and drying was conducted.

2.4. Synthesis of PANPY by CO2-assisted method

CO2-assisted polymerization method in which supercritical CO2 is used to improve the morphology of the polymers. The same amount of aniline, pyrrole, acid and APS solutions were used. The mixture of aniline and pyrrole were placed in the autoclave which is connected to the CO2 pump and placed in an oven. The temperature was increased to 40 °C before the injection of CO2 inside the autoclave until the pressure reaches 9 MPa. Then, APS solution was fed by another high-pressure pump at a uniform flow rate of 0.5 mL/min. Then, the mixture was left to polymerize for 3 h. After polymerization, a valve was opened to release the CO2 from the vessel in 3 min completely. The prepared polymer was collected, filtered, washed, and dried at 80 °C for 24 h.

2.5. Characterization
The copolymer samples were characterized using TEM, FT-IR, XRD, and BET respectively. The morphology of the samples was investigated by using Transmission electron microscopy (TEM, JEOL Ltd., JEM-1010). Infrared spectra were recorded using a Fourier transform infrared (FT-IR) spectrometer (Vertex 70, Bruker scientific instruments, Germany) to identify the chemical structure of the samples. To measure crystallinity, X-ray diffraction was used (LabX XRD-6100 Shimadzu, Japan). N2 adsorption/desorption isotherms at 77 K and the Brunauer-Emmett Teller (BET) surface area analysis were conducted using (BelsorbminiII, BEI Japan Inc., Japan). All the samples were degassed under vacuum at 150 °C for 2 h.

3. Results and Discussion

3.1. PANPY morphology

![TEM images of PANPY copolymer samples](image)

**Figure 1.** TEM for the produced PANPY copolymer (a) CH₃COOH dropwise polymerization, (b) CH₃COOH rapid mixing polymerization, (c) CH₃COOH CO₂-assisted polymerization (d) HCl dropwise polymerization, (e) HCl rapid mixing polymerization, and (f) HCl CO₂-assisted polymerization.
TEM images of the manufactured PANPY copolymers using the two different dopant acids with the employment of the three different polymerization techniques are shown in Figure 1. The results indicate that samples prepared using acetic acid as a dopant acid produced different shapes. When the conventional polymerization process (Oxidizer dropwise adding) were used, a core and shell shape was produced. The shell which may return to PANI had a 25 nm thickness which may be due to the pre-polymerization of the two polymers separately. Also, Figure 1(b) reveals that nanospheres with hollow interiors at the centers was produced when rapid mixing technique was taken into consideration. The interior part has a diameter of 75 nm and thickness 26 nm approximately. Furthermore, the copolymer produced using the ScCO₂-assisted polymerization method was more homogeneous and had a one-phase net structure. Therefore, the ScCO₂-assisted polymerization process may have a unique mixture which helps to produce the copolymer without separation between PANI and PPY. Using HCl acid (Error! Reference source not found.1) produced nanoparticles morphology with an average diameter of 53 nm when dropwise adding polymerization was utilized. Fibrous structure with an average diameter of 80 nm was prepared when rapid mixing polymerization process was used. Finally, using ScCO₂-assisted polymerization method produce an aggregated structure copolymer.

### 3.2. PANPY chemical structure

FT-IR images of PANPY copolymers prepared by different methods are shown in Figure 2. The spectrum of the copolymer prepared by HCl and acetic acid by the three different methods showed characteristic band at 1113 cm⁻¹ and 1194 cm⁻¹ which are assigned to C=C stretch, C-C in ring stretch, and C-N stretch of polypyrrole and polyaniline [14]. This peak disappeared in the samples prepared using acetic acid as a dopant acid by CO₂ assisted polymerization. Another feature in the spectra is

![Figure 2. FT-IR curve for PANPY samples](image)

Figure 2. FT-IR curve for PANPY samples (a) CH₃COOH CO₂-assisted polymerization (b) CH₃COOH dropwise (c) CH₃COOH rapid mixing (d) HCl dropwise polymerization (e) HCl CO₂-assisted polymerization (f) HCl rapid mixing polymerization
the band at 3438 cm\(^{-1}\), which corresponds to the N-H stretch of both polyaniline and polypyrrole [5]. The prepared copolymers with acetic acid showed a peak at 1492 cm\(^{-1}\) which are assigned to the C=C, N-N, and C-N stretch mode of pyrrole [14]. The semiquinonoid ring (-N-ring) of PANI (1378 cm\(^{-1}\)) was shifted to around 1396 cm\(^{-1}\) which appeared in the samples synthesized with HCl. A sharp peak at 1565 cm\(^{-1}\) which corresponds to C=C stretch showed in the HCl samples, was shifted to around 1626 cm\(^{-1}\) in acetic acid samples. This result confirms the successful preparation of the copolymer that includes both polymers.

3.3. PANPY crystallinity
XRD patterns of the six PANPY samples are shown in Figure 3 to investigate its crystallinity. It indicates that the main diffraction peaks centred between 2\(\theta\) = 20 and 24° which can be attributed to the characteristics peaks of PANI (2\(\theta\) = 19.5 and 25.2°) [16] and PPy (2\(\theta\) = 24°) showing that the two polymers are present in the copolymer and all prepared copolymers have semi-crystalline structures.

3.4. PANPY surface area and pore size
Table 1 shows the BET surface area, total pore volume, and average pore diameter of the produced copolymer using the different preparation conditions. For acetic acid, rapid mixing technique gives the best values of surface area (30.73 m\(^2\)/g) compared with other preparation techniques which indicate that the ScCO\(_2\)-assisted polymerization technique has a noticeable effect on the surface area of the prepared copolymer. Also, the hollow structure characteristics produced using the rapid mixing
technique (as shown in Figure 1(b)) play a significant role in the material surface area. The dropwise adding technique shows the worst surface area compared with other preparation techniques. On the other hand, the effect of using HCl as a dopant for the preparation of PANPY by the mentioned polymerization processes on the surface area has a different ranking. The surface area produced by CO₂ assisted polymerization is better than the dropwise technique.

The N₂ adsorption/desorption curve and pore size distribution of the produced PANPY structures are shown in Figure 4 and Figure 5. Based on the data obtained, the prepared PANPY structures showed a hysteresis loop of H3 type according to the classification [17]. H3 means that the pores are slit-shaped. Additionally, the prepared PANPY structures have a wide pore size distribution, and it is considered as a macroporous structure according to the IUPAC pore classification.

**Table 1.** Surface area, total pore volume, and average pore diameter of different PANPY samples.

| Parameters                        | HCl rapid mixing | HCl dropwise | HCl CO₂-assisted | CH₃COOH rapid mixing | CH₃COOH dropwise | CH₃COOH CO₂-assisted |
|----------------------------------|-----------------|--------------|------------------|----------------------|------------------|----------------------|
| Surface Area (BET) (m²/g)        | 10.34           | 23.33        | 38.1             | 30.73                | 12.02            | 27.8                 |
| Total Pore Volume (BJH) (cm³/g)  | 0.050           | 0.028        | 0.157            | 0.182                | 0.070            | 0.145                |
| Average Pore Size (BJH) (nm)     | 2.50            | 1.96         | 2.26             | 2.21                 | 2.21             | 2.1                  |

**Figure 4.** Pore size distribution curve for prepared PANPY samples
Figure 5. N₂ adsorption/desorption isotherm for (a) HCl rapid mixing polymerization (b) CH₃COOH rapid mixing (c) HCl dropwise polymerization (d) CH₃COOH dropwise polymerization (e) HCl CO₂-assisted polymerization (f) CH₃COOH CO₂-assisted polymerization
4. Conclusion
In this paper, three different polymerization methods were implemented to synthesize PANPY copolymer. The copolymers were successfully prepared and have a semi-crystalline structure with six different morphologies. In case of acetic acid medium with; adding APS dropwise to the aniline/pyrrole solution produced PANPY with core & shell structure with 25 nm as shell thickness. While adding APS at once with rapid stirring produced PANPY with hollow nanospheres structure with an average diameter of 75 nm and thickness of 26 nm. The ScCO$_2$-assisted polymerization was conducted at 80 °C, CO$_2$ at 9 MPa was pumped into the aniline/pyrrole solution, resulting in homogenous copolymer structure. In case of HCl acid medium; PANPY nanoparticles with an average diameter of 53 nm were produced by adding APS dropwise to the aniline/pyrrole solution. Fibrous structure with an average diameter of 80 nm. Finally, the ScCO$_2$-assisted polymerization was conducted at the same conditions as in acetic acid medium produced aggregated structure copolymer. The specific surface area of the different morphologies showed that CO$_2$-assisted PANPY polymerization with HCl showed improved surface area. Also, macroporous structures were attained from all the studied polymerization methods.

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