Chemical, Electrochemical and Plasma Polymerization of Pyrrole-Aniline Copolymers and Their Characterization

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ABSTRACT

Pyrrole-aniline copolymers were synthesized using both three chemical, electrochemical and plasma polymerization methods. Comparison of the copolymers synthesized with three methods was investigated. Fourier transform infrared spectroscopy (FT-IR), thermogravymetric analysis (TG-DTA), scanning electron microscopy (SEM) and conductivity results confirmed that the poly(Py-co-Ani) copolymers were successfully obtained in all cases with some differences according to synthesis methods. It was found that plasma method enhanced the thermal stability of the pyrrole-aniline copolymer. The first thermal decomposition temperatures of chemically, electrochemically and plasma polymerized copolymers are 210, 190 and 250 °C, respectively. However, the conductivity value of plasma polymerized copolymer (1,97x10^{-4} S.cm^{-1}) is lower than that of chemical (4,40x10^{-4} S.cm^{-1}) and electrochemical (3,14x10^{-4} S.cm^{-1}) synthesized copolymers. According to findings chemical and electrochemical polymerization methods provides nearly the same properties to the copolymers. Plasma polymerization method provides better thermal properties to copolymer. The both three methods can be used for preparing the pyrrole and aniline copolymers. .

Keywords: Pyrrole, aniline, chemical polymerization, electrochemical polymerization, plasma polymerization and copolymer.

1. INTRODUCTION

Conducting polymers (CPs) have been widely studied due to their unique properties and wide application areas. Among these CPs, polypyrrole (Ppy) [1] and polyaniline (Pani) [2] has received significant attention because of their good environmental stability, easy synthesis, low fabrication cost, and high electrical conductivity and favorable physicochemical properties.

Both Ppy and Pani are usually synthesized through chemical or electrochemical methods. Chemical method is generally used when large quantities of polymer are required and this method include an oxidant such as $FeCl_3$, ammonium persulfate $[(NH_4)_2S_2O_8]$. On the other hand, electrochemical method can be used for preparation of polymer films and can provide better film thickness control and morphology. Moreover, the materials can be directly deposited on the conductive substrates. Compared with chemical and electrochemical methods, plasma polymerization is expected to be suitable to obtain polymers for different applications, without using solvents, oxidants and any additives. These specifications make plasma treatment to be environmentally friendly method [3, 4].Several approaches include derivation of monomers, blending, composite synthesis and copolymerization have been taken to obtain polymers with better properties. Among these methods, copolymerization could be the attractive way for preparing new materials. Combination of the unique properties of Ppy and Pani described above can give materials with significant properties. Copolymers of pyrrole and aniline have been obtained by different techniques and studied by means of their morphology, thermal, electrical and electrochemical properties [5, 6].

In the present study, copolymerization of pyrrole and aniline was carried out by using three different methods include chemical, electrochemical, and plasma polymerization. The copolymers obtained via different methods were characterized and compared by means of structure, morphology, thermal behaviors and conductivity. To the best of our knowledge, there is no report on the properties of pyrrole-aniline copolymers synthesized by three different methods. Comparison of the properties of these copolymers were investigated for the first time in this study.

2. MATERIAL AND METHODS

1.1. Materials

Pyrrole (Sigma Aldrich), aniline (Sigma Aldrich) $(NH_4)_2S_2O_8$ (Sigma Aldrich) and Hydrochloric acid fuming 37% (Merck, Millipore) were used without further purification.

1.2. Synthesis

1.2.1.Chemical polymerization

In chemical polymerization, different molar ratios of pyrrole and aniline were used to determine the optimal molar condition. The molar contents of Py to Ani are determined as 40% and 60%, respectively. The synthesis of copolymers were carried out in aqueous solution containing ammonium persulphate $[(NH_4)_2S_2O_8]$ as an oxidant. The molar ratio of oxidant to total monomer was selected as 2.5. The oxidant of $(NH_4)_2S_2O_8$ was added dropwise to the monomer dispersed aqueous solution under constant stirring at room temperature. After addition of the oxidant, the reaction mixture was stirred at room temperature for 16 hours. Then, the reaction mixture was filtered and washed with plenty of water. The obtained solid was dried under vacuum at 50 °C for 24 h.

1.2.2.Electrochemical polymerization

The experiments were carried out in a typical three electrode cell in which a glass sheet with deposited indium-tin-oxide (ITO) was used as the working electrode (WE), a platinum wire was used as the counter electrode (CE), and an Ag/AgCl electrode was used as the reference electrode (RE). 0.1 M HCl solution containing 40% pyrrole and 60% aniline was prepared for polymerization. Potential of 0.8 V was applied to the working electrode for 15 min. Then the ITO electrode was removed from the solution, rinsed thoroughly with the xxx to remove the soluble monomer and oligomers on the film and finally dried in the air to obtain poly(Py-co-Ani).

1.2.3. Plasma polymerization

Poly(Py-co-Ani) was synthesized using plasma treatment. The plasma produced at low pressure (80 mTorr) with 13.56 MHz frequency at a power of 150 W for 30 min.

1.3. Characterization

Fourier transform infrared (FTIR) spectra of the polymers were measured between 400 and 4000 cm-1 from potassium bromide (KBr) pellets on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, HP91QA, England). Thermogravimetric analysis (TGA) was performed on a Perkin Elmer (USA) thermogravimetric analyzer in the presence of N_2 atmosphere from 30 to 900°C with the heating rate of 10°C/min. The morphology of the films was characterized using scanning electron microscopy (SEM) (Philips XL-30S FEG) (Holland). The conductivity was measured using the four probe technique with a PCIDAS6014 current source, a voltmeter and a temperature controller. Dry powders were pressed into pellets using a steel die having a diameter of 13 mm in a hydraulic press at 700 MPa.

3. RESULTS AND DISCUSSION

3.1. FT-IR results

Figure 1 shows the FTIR spectrum of PPy and poly(py-co-ani) synthesized with three different methods. The bands at around 793 and 1042cm^{-1} correspond to C-H out of plane and C-H in plane deformation vibrations respectively for polypyrrole. The strong C-N stretching vibrations of the Ppy ring can be seen at 1295 cm^{-1} for both Ppy and chemicaly synthesized poly(py-co-ani). That band is not as strong as electrochemically and plasma synthesized copolymer. Nevertheless, the strongbands in the region 900-1800 cm^{-1} for all polymers indicates that the conductive form of PPy is formed [7].In spectrum of copolymers the peaks at around 1571cm-1 and 1467cm^{-1} with some shifts are characteristic bands which are belongs to quinoid and benzenoid ring stretching vibrations respectively for polyaniline [8, 9]. These bands were seen prominently in the spectrum of all three copolymers. The band at 1146cm^{-1} is due to conducting form of polyaniline, the emeraldine salt [7]. Furthermore, the bands at around 2300 and 2320 cm^{-1} attributed to aliphatic amines. A lot of common bands were seen in the spectrum. It is observed that the bands shifted to a lower wavenumber for copolymers indicate the presence of neighboring aniline and pyrrole constitutional units.The bands at 607cm-1, 762cm^{-1}, 1042cm^{-1}, 1178cm^{-1}, 1302cm^{-1}, 1571cm^{-1} and 1467cm^{-1} indicates the formation of poly(aniline-co-pyrrole) both three synthesis methods [10]

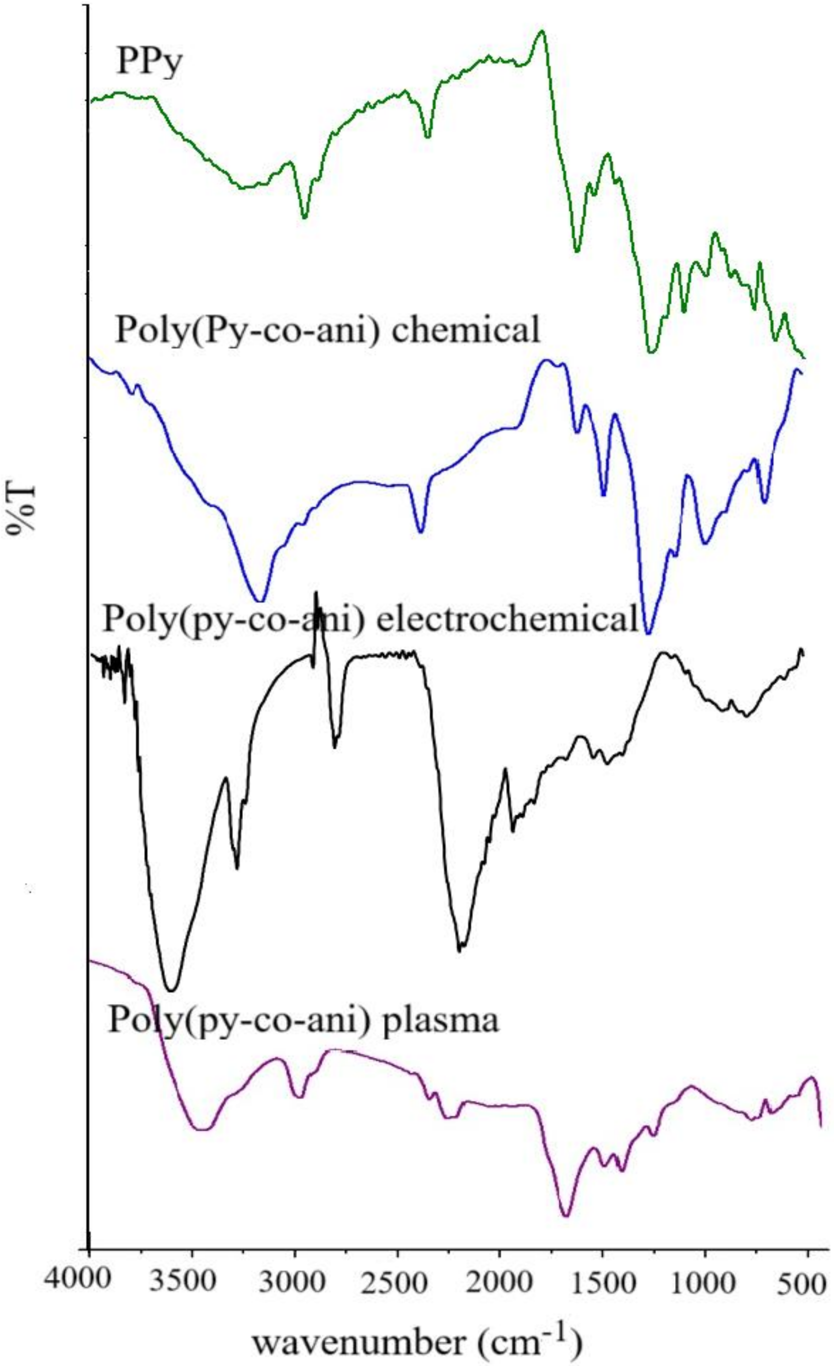

Figure 1. FTIR spectrum of Ppy and copolymers

3.2. SEM Results

The influences of the polymerization methods on the morphology of copolymer have been investigated by SEM. Figure 2a-c depicts the morphologies of copolymers synthesized with three methods. Generally, Pani has fibrillar and granular structure and Ppy has cauliflower like structure as known according to literature [11, 12]. The chemically synthesized copolymer shows the most similar morphology with the literature. All the morphologies have a tendency to agglomerate into irregular morphologies as p* interaction between the pyrrole chains [13]. These assemblies have a spherical shape, which is more energetically favorable. The fibril structure belonging to the PAni was more dominant in the copolymer obtained by electrochemical synthesis, which provides more controlled polymerization. The particle sizes of copolymers synthesized by electrochemical and plasma methods were smaller than that of copolymer synthesized by chemical method. Althought the particle sizes different from each other, the morphology of the copolymers was similar in all cases. The morphology of the copolymers combines both the fibrillar and granular structure of Pani and the cauliflower structure of Ppy, which confirm the formation of copolymers by the three different methods.

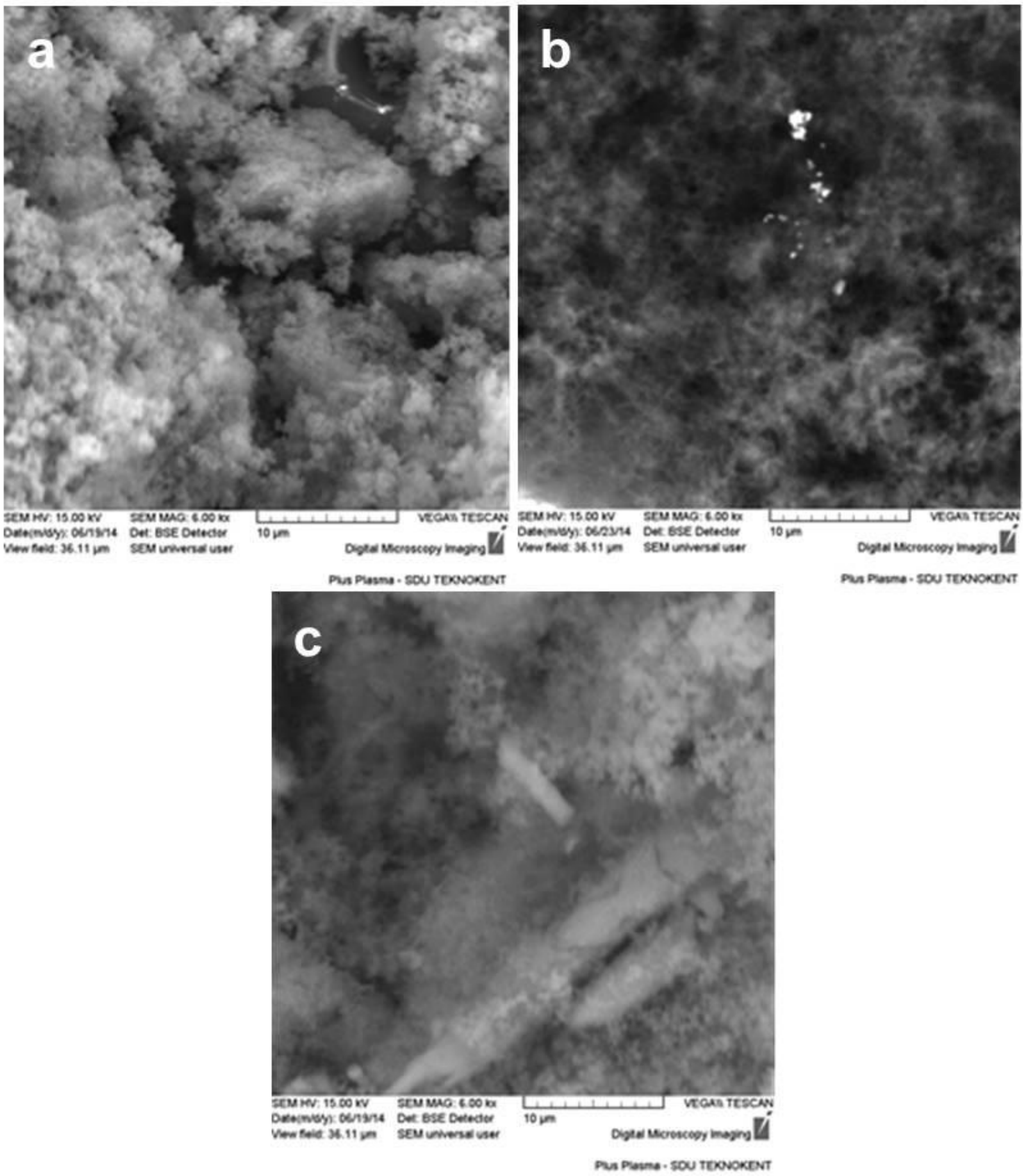

Figure 2. SEM images of copolymers synthesized by chemical polymerization (a), electrochemical polymerization (b), and plasma polymerization (c).

3.3. TGA Results

Thermal degradation behaviors of copolymers were investigated by thermal gravimetric analysis (TGA). Figure 3a-c shows the weight loss of copolymers upon heating in a nitrogen atmosphere at a rate of 10 °C/min.

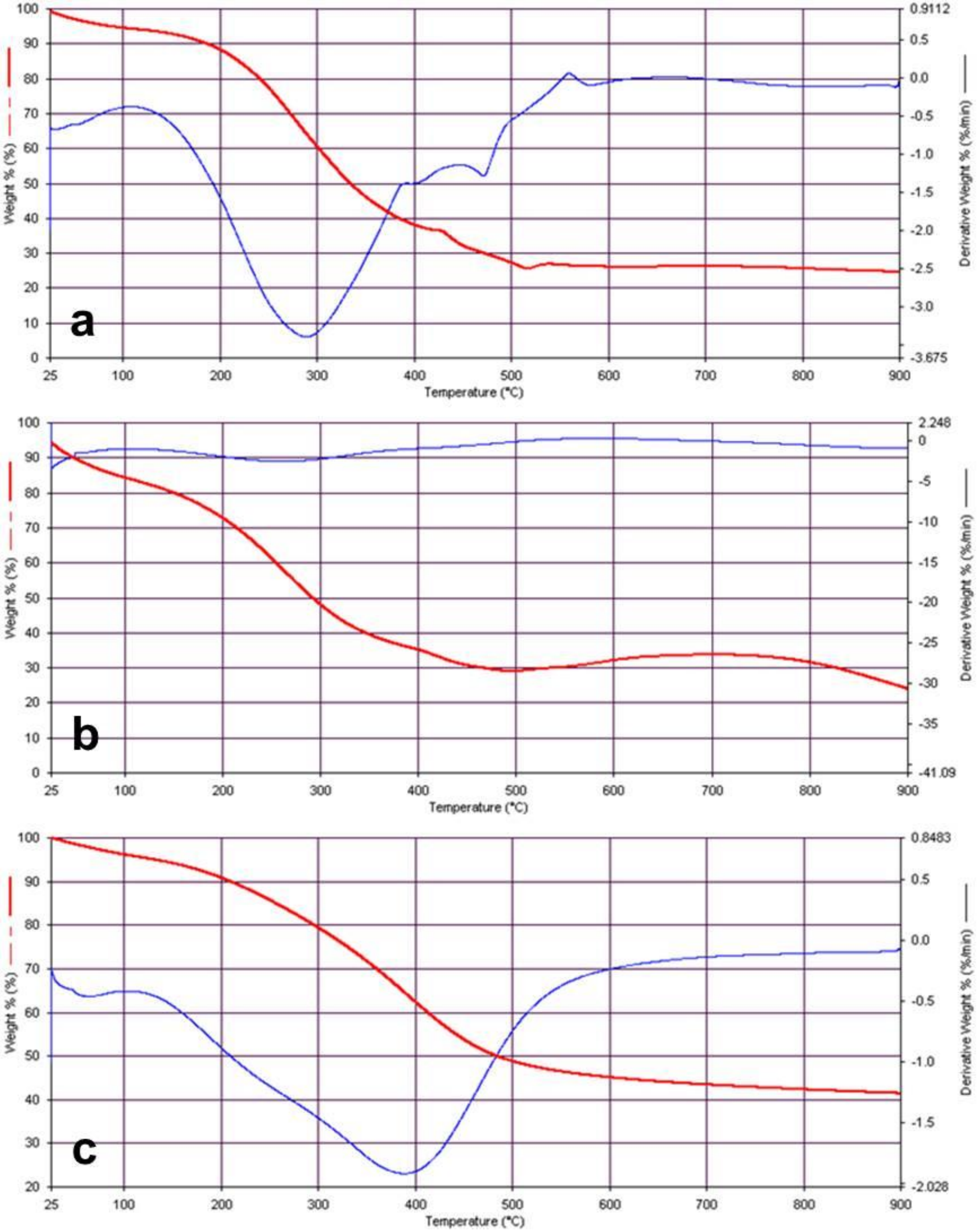

Figure 3. TGA results of copolymers synthesized using chemical polymerization (a), electrochemical polymerization (b), and plasma polymerization (c).

The low weight loss (8-15%) observed in the range of 70-100°C is due to moisture being removed from copolymer structure for all copolymers [14]. Thermal degradation temperatures and residues% at 900°C shown in Table 1, which are determined from thermograms. The chemically synthesized copolymer shows two step weight loss while the electrochemically and plasma synthesized copolymers show one step weight loss except for the low mass due to moisture. The first weight loss (210-370 °C) indicates removing dopant anions from polymer structure while the second weight loss (430-510°C) is related to the thermal decomposition of the polymer chains for chemically synthesized copolymer. A sharp weight loss appears in the temperature range of for 190-340°C for electrochemically synthesized copolymer and 290-490°C for plasma synthesized copolymer, which is related to removel of dopant anion and thermal decomposition of the polymer chains simultaneously [15].

When the thermal stability of the copolymers were compared with each other, the most stable copolymer was plasma polymerized according to the initial decomposition temperature of copolymers. Besides, the residues of the copolymers at 900°C show that plasma polymerization increases the thermal stability of copolymer, while the copolymers obtained from chemical and electrochemical polymerization exhibits similar result with each other.

Table 1. Thermal degradation temperatures of copolymers. (Ti, Initial decomposition temperature; Tm, Maximum decomposition temperature; Tf, Final decomposition temperature)

Copolymer	Ti	Tm	Tf	% residue at 900 °C
Chemical polymerization	210	290	370	25
	430	470	510	
Electrochemical polymerization	190	265	340	25
Plasma Polymerization	250	370	490	42

3.4. Conductivity Results

The conductivity values of all samples are given in Table 2. It was seen that the synthesis method effects conductivity value of copolymer. Althought the conductivity value of copolymer is effected by the synthesis method, the conductivity values are in the similiar range. The conductivity values of chemically and electrochemically synthesized poly(Py-co-ani) almost closed to each other. The plasma polymerized copolymer showed relatively lower conductivity value than that of the other copolymers. Since the plasma polymerization method offers a faster and uncontrolled synthesis environment compared to other methods, the conjugation may not be smooth enough. This may have caused the conductivity of the copolymer to be lower than those synthesized by other methods. Nevertheless the conductivity values of copolymers are compatible with the literature [16, 5]

Table 2.The conductivity of poly(Py-co-Ani) synthesized by three different method.

Method	**Conductivity** **($S.cm^{-1}$ at 25 ˚C)**
Chemical	$4{,}40x10^{-4}$
Electrochemical	$3{,}14x10^{-4}$
Plasma	$1{,}97x10^{-4}$

4. CONCLUSION

Poly (Py-co-ani) copolymers were synthesized with three different synthesis methods. These synthesis methods were selected for this study showed acceptable characteristic properties. All of the coplymers were successfully characterized with FTIR,TGA,SEM and conductivity measurements. FTIR and SEM studies indicated that thecopolymers were formed by all three polymerization method. The thermal and conductivity properties of the preparedcopolymers were affected by the synthesis methods. The copolymer synthesized with plasma polymerization have higher thermal stabilities than thatof copolymers synthesized by chemical and electrochemical methods. However, the conductivity value of the plasma polymerized copolymer is lower than that of other copolymers.

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