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

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 an attention from the research community and have been widely studied widely due to the extraordinary properties such as tunable electrical conductivity, easy preparation, lightness and processability. Various conducting polymers such as polyaniline (Pani), polyacetylene (PA), polypyrrole (PPy) and polythiophene (PTh) have been investigated by researchers due to their application in different fields [1]. Among these CPs, Ppy [2] and Pani [3] has received significant attention because of their good environmental stability, easy synthesis, low fabrication cost, and high electrical conductivity and favorable physicochemical properties. Pani and Ppy exhibits potential for application in the adsorption [4], fuel cell [5], actuators [6], sensors [7] and electronic devices and supercapacitors [8].

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. Especially, lots of researchers have been mainly studied on the synthesis of conducting polymers using conventional chemical or electrochemical method in order to develop the electrical conductivity, thermal stability, and mechanical properties [9]. However, these conventional methods have some limitations and disadvantages such as toxicity, complex process, to be expensive, thermal heating or cooling process, and environmental problems. In order to overcome these disadvantages, plasma polymerization method is a promising alternative for synthesizing the conducting polymers. 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. Also it has various benefits such as a simple of equipment, ease of synthesis, economic, and thermal heating or cooling free process [10]. These specifications make plasma treatment to be environmentally friendly method [11, 12]. 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 [13, 14].

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. Changes in the use of energy resources require less dependence on fossil fuels. Future demands for greener processes will support the reduction or elimination of chemical processes that use high amounts of solvents. At this point, plasma polymerization, which allows thinner production of polymeric films, can increase competitiveness. Because plasma polymerization can be used to deposit thin polymeric films on various substrates. Coating a substrate with thin polymeric films can be used to alter its surface physicochemical properties. These properties provide the opportunity to design materials for different applications by improving barrier properties, changing surface wettability, and changing surface functional groups [15], The fact that it is difficult to provide these advantages of polymers synthesized by chemical and electrochemical methods motivated us to compare the properties of materials obtained using plasma polymerization 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 0.1 M HCl and distilled water, respectively 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

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 strong bands in the region 900-1800 cm^{-1} for all polymers indicates that the conductive form of PPy is formed [16]. 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 [17, 18]. 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 [16]. 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 [9]. Also there are some shifts in the spectrum of copolymers according to PPy (Fig 1). These shifts are trough to smaller wavenumbers for copolymers. It can be seen that these shifts are bigger in plasma polymerized copolymer than that of chemically and electrochemically polymerized copolymers. In this situation, we can interpret that the plasma polymerized copolymer is more stable than the other copolymers.

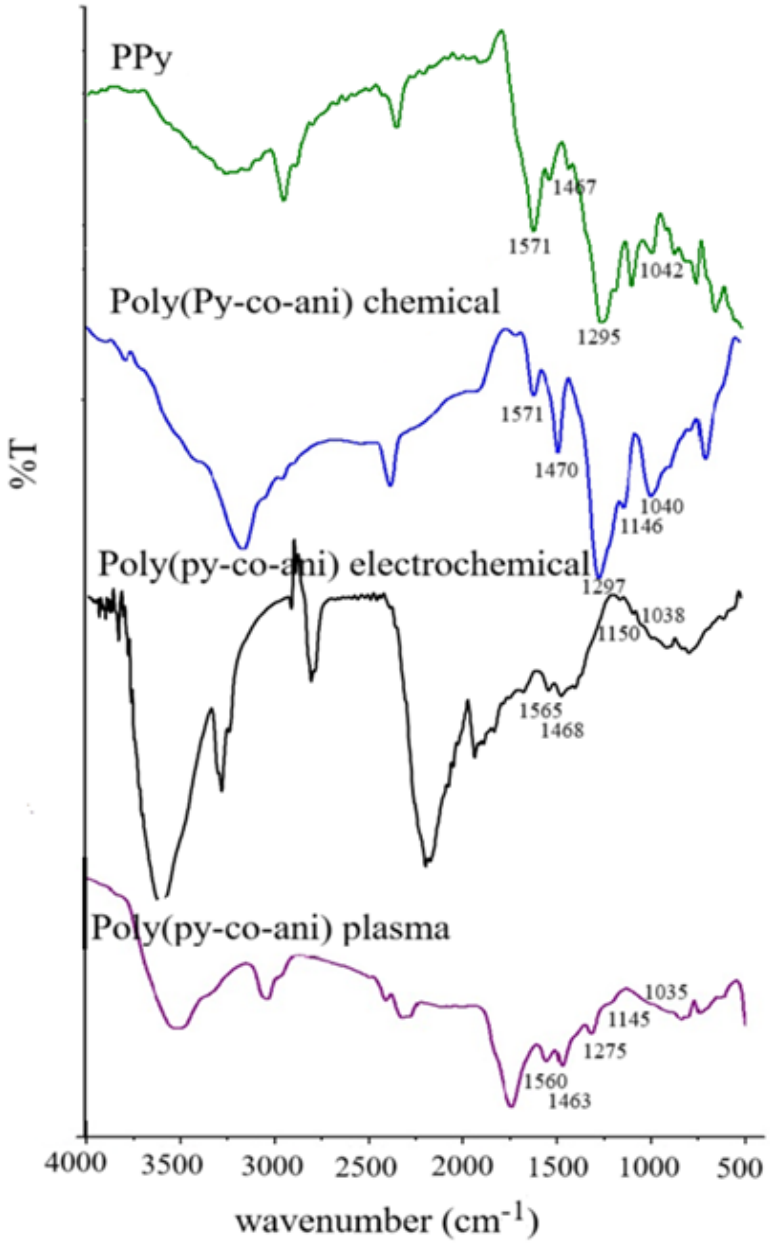

Figure 1. FTIR spectrum of Ppy and copolymers

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 [19, 20]. The chemically synthesized copolymer shows the most similar morphology with the literature (Fig 2a). All the morphologies have a tendency to agglomerate into irregular morphologies as p* interaction

between the pyrrole chains [21]. 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 (Fig 2b). The particle sizes of copolymers synthesized by electrochemical and plasma methods (Fig 2c) were smaller than that of copolymer synthesized by chemical method. Althought the particle sizes different from each other (between 200 and 800 nm), 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.

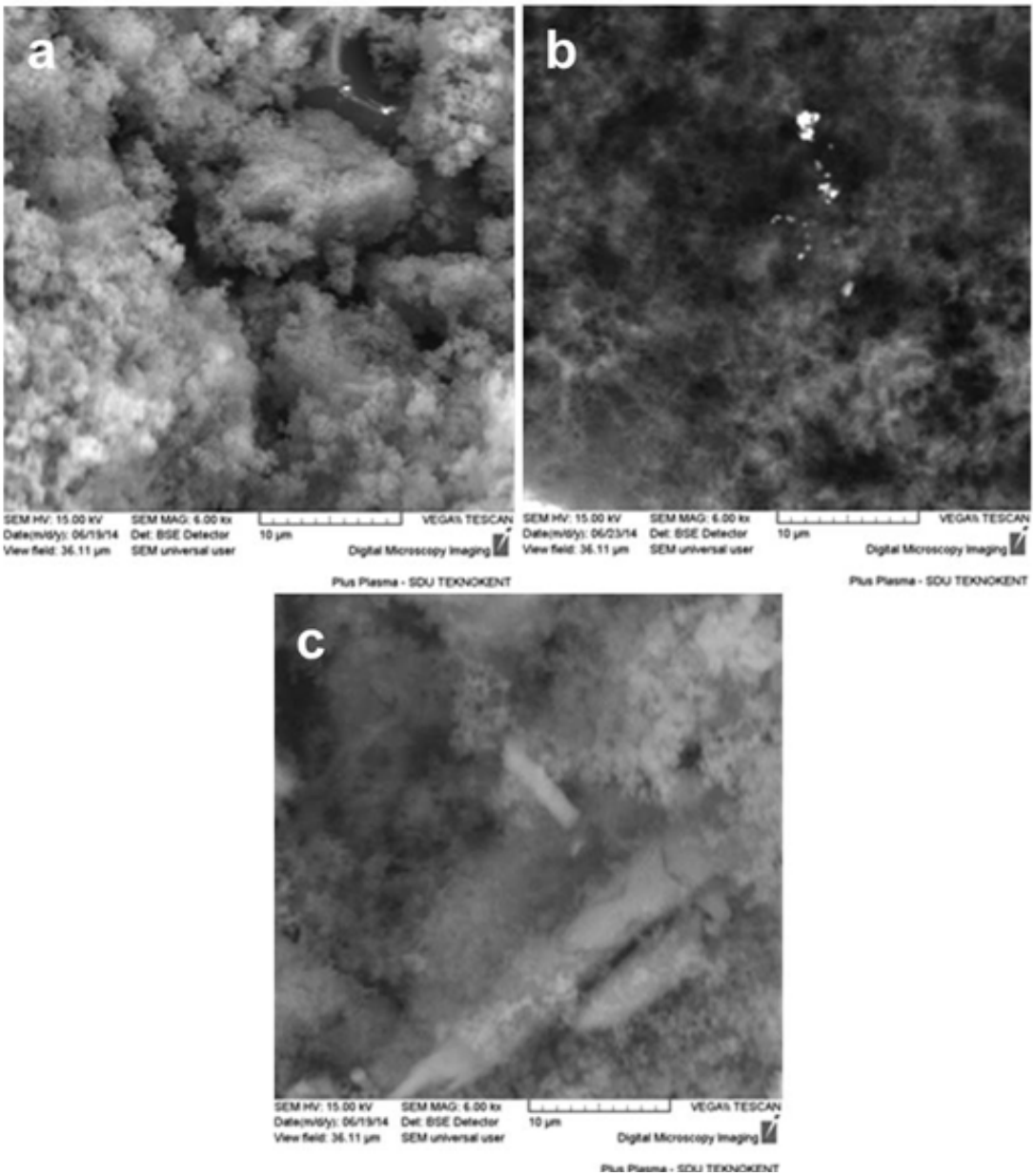

Figure 2. SEM images of copolymers synthesized by chemical polymerization (a), electrochemical polymerization (b), and plasma polymerization (c).

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.

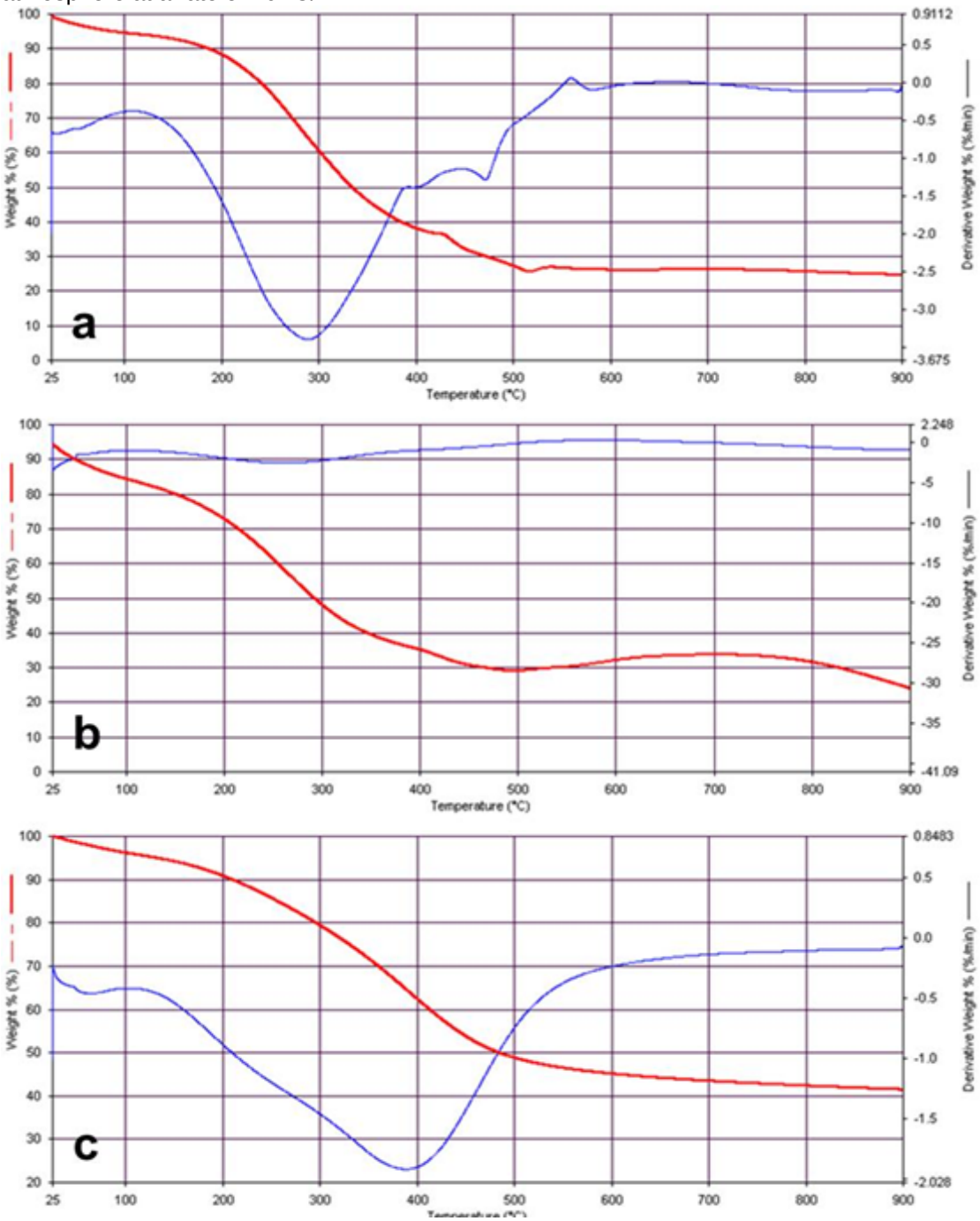

Figure 3. TGA results of copolymers synthesized using chemical polymerization (a), electrochemical polymerization (b), and plasma polymerization (c).

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 [22]. 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 [23].

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 [24].

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 supported the characteristic properties of copolymer. All of the copolymers were successfully characterized with FTIR, TGA, SEM and conductivity measurements. FTIR and SEM studies indicated that the copolymers were formed by all three polymerization method. The thermal and conductivity properties of the prepared copolymers were affected by the synthesis methods. FTIR results showed that the copolymer synthesized by plasma polymerization has more stable structure than the others. Besides, the copolymer synthesized by plasma polymerization have higher thermal stabilities than that of copolymers synthesized by chemical and electrochemical methods. Althought, the conductivity value of the plasma polymerized copolymer is lower than that of other copolymers, its conductivity value is not too low for various application areas. However, plasma polymerization allows ultra-thin film formation, good interaction with the substrate material and applicable onto each type of substrate. As a result of this study, plasma polymerization is a recommended technique for Poly (Py-co-ani) synthesis.

REFERENCES

[1] Sharma AK, Sharma YJ. p-toluene sulfonic acid doped polyaniline carbon nanotube composites: synthesis via different routes and modified properties. Electrochem. Sci. Eng. 2013; 3(2): 47-56.
[2] Jyothibasu JP and Lee RH Jyothibasu JP and Lee R. Green synthesis of polypyrrole tubes using curcumin template for excellent electrochemical performance in supercapacitors, J. Mater. Chem. A, 2020.
[3] Khaw LF, Koh WS, Yeap SP, Lim JK, Ahmad AL, Toh PY, Khosravi V. Shape-controlled synthesis of polyaniline and its synergisticeffect with reduced graphene oxide for the fabrication offlexible electrode. Polym Eng Sci. 2023; 63: 2295-08.
[4] Javadian H. Application of kinetic, isotherm and thermodynamic models for the adsorption of Co(II) ions on polyaniline/polypyrrole copolymer nanofibers from aqueous solution. Journal of Industrial and Engineering Chemistry. 2014; 20(6): 4233-41.
[5] Jia Y, Ma D, Wang X. Electrochemical preparation and application of PANI/MWNT and PPy/MWNT composite anodes for anaerobic fluidized bed microbial fuel cell. Biotech. 2020; 10: 3-12.

[6] J Li, J Markmann, N Mameka. Enhanced electrochemical actuation of nanoporous gold-polypyrrole hybrid under load. Appl. Phys. Lett. 2022; 121: 021901.
[7] Zea M, Texidó R, Villa R, Borrós S and Gabriel G. Specially Designed Polyaniline/Polypyrrole Ink for a Fully Printed Highly Sensitive pH Microsensor. ACS Appl. Mater. Interfaces. 2021; 13(28): 33524-35.
[8] Zhao Z , Wang H, Huang H, Li L, Yu X, Graphene oxide/polypyrrole/polyaniline composite hydrogel synthesized by vapor-liquid interfacial method for supercapacitors, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2021; 626: 127125-33
[9] Sharma AK, Bhardwaj P, Dhawan SK, Sharma Y. Oxidative Synthesis And Electrochemical Studies Of Poly(aniline-co-pyrrole)-hybrid Carbon Nanostructured Composite Electrode Materials For Supercapacitor. Adv. Mater. Lett. 2015; 6(5): 414-20.
[10] Park CS, Kim DH, Shin BJ, Tae HS.Synthesis and Characterization of Nanofibrous Polyaniline Thin Film Prepared by Novel Atmospheric Pressure Plasma Polymerization Technique. Materials. 2016; 9 (39): 1-12.
[11] Kim JY, Iqbal S, Jang, HJ, Jung EY, Bae GT, Park CS, Shin BJ, Tae HS. Transparent Polyaniline Thin Film Synthesized Using a Low-Voltage-Driven Atmospheric Pressure Plasma Reactor. Materials. 2021; 14: 1278-89.
[12] Tanasă F, Zănoagă M, Teacă CA, Nechifor M, Shahzad A. Modified hemp fibers intended for fiber-reinforced polymer composites used in structural applications-A review. I. Methods of modification. Polymer Composites. 2020; 41: 5-31.
[13] Lü QF, He ZW, Zhang JY, Lin Q. Fabrication of nitrogen-containing hollow carbon nanospheres by pyrolysis of self-assembled poly(aniline-co-pyrrole). Journal of Analytical and Applied Pyrolysis. 2012; 93: 147-52.
[14] Oua X and Xu X. A simple method to fabricate poly(aniline-*co*-pyrrole) with highly improved electrical conductivity *via* pre-polymerization. RSC Adv. 2016; 6: 13780-85
[15] Hossain M, Trinh QH, Nguyen DB, Sudhakaran MSP, Mok YS. Formation of plasma-polymerized superhydrophobic coating using an atmospheric-pressure plasma jet. Thin Solid Films. 2019; 675: 34-42.
[16] Mavundla SE, Malgas GF, Motaung DE, Iwuoha EI. Physicochemical and morphological properties of poly(aniline-co-pyrrole). J Mater Sci. 2010; 45: 3325-30, DOI: 10.1007/s10853-010-4351-5
[17] Sharma, AK, Sharma Y, Malhotra R, Sharma J. Solvent Tuned PANI-CNT Composites As advanced Electrode Materials For Supercapacitor application. Adv. Mat. Lett. 2012; 3(2): 82-86. DOI: 10.5185/amlett.2012.1315
[18] Sharma Y, Tiwari A, Hattori S, Terada D, Sharma AK, Ramalingam M, Kobayashi H. Fabrication of conducting electrospun nanofibers scaffold for three-dimensional cells culture. Int. J. Biol. Macromol. 2012; 51: 627-31. DOI: 10.1016/j.ijbiomac.2012.06.014
[19] Bibi A and Shakoor A. Charge transport mechanism in dodecylbenzenesulfonic acid doped polyaniline/carbon black composites Polymers and Polymer Composites. 2021; 29(9S): 1044-51, DOI: 10.1177/09673911211040376
[20] Trung VQ, Hanh TH, Quang TH, Hung HM, Linh DK, TuyetLan HT and Duc LM. Corrosion protection of molybdate doped polypyrrole film prepared in succinic acid solution. Corrosion Engineering, Science and Technology. 2018; 53(S1): 59-66 https://doi.org/10.1080/1478422X.2017.1389370
[21] Yang C, Liu P, Zhao Y. Preparation and characterization of coaxial halloysite/polypyrrole tubular nanocomposites for electrochemical energy storage. Electrochim. Acta. 2010; 55: 6857-64.
[22]. Sen Gursoy S, Cogal S, Uygun Oksuz A. Influence of surfactants on properties of electrochemically synthesized pyrrole/1-dimethylaminopyrrole copolymer. Iran Polym J. 2014; 23:783-792.
[23] Cakmak G, Küçükyavuz Z. and Küçükyavuz S. Conductive copolymers of polyaniline, polypyrrole and poly(dimethylsiloxane). Synthetic Metals. 2005; 151: 10-18.

[24] Sankar S, Ramesan MT. Synthesis, characterization, conductivity, and gas-sensing performance of copolymer nanocomposites based on copper alumina and poly(aniline-co-pyrrole). Polym Eng Sci. 2022; 62:2402-10.