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Effect of the Sizing Compound on the Electropolymerization of Pyrrole and the Impedance of Carbon Fiber Coated with Polypyrrole

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Abstract: Carbon Fiber (CF) is used as a strengthening material in resin composites having high performance in most industrial areas due to the fact that it has mechanical properties such as low weight, high durability, and toughness. The mechanical performances of composite materials depend on the features of fiber and matrix which composed them. The one of methods which improves the features of fiber surface is the coating on fiber surface with thin film. When the fiber was coated with electropolymer, the mechanical durability of the composite was increased. In this study, carbon fibers were electrochemically coated with polypyrrole (PPy) in the presence of sizing compound (SC) based on epoxy. During the process, it was investigated that how current, obtained coating weights and impedance data, especially capacitance, changed by the amount of SC. For this reason, different amounts of SC (%0; % 0.18; %1.8 v/v) was added into the electrolyte solution (0.1 M $NaClO_4$-ACN) including 0.1 M Pyrrole (Py). Coating process was carried out by using Constant Potential or Cyclic Voltammetry Techniques. Other techniques for investigations were gravimetrical analysis, electrochemical impedance spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR) and Light Microscopy. At the end of the coating, the weight of coating and specific capacitance (Csp) values were 0.8 mg/g and 114 µF for % 0 of SC 10 mg/g and 57 µF for %0.18 of SC and 1.73 mg/g and 166 µF for %1.8 of SC, respectively. As a result, the coating weight and capacitance data (especially, Csp,) of carbon fiber coated with PPy were inversely changed with the amount of SC added into electrolyte.

Keywords: Electropolymerization, Sizing, Impedance and Capacitance.
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INTRODUCTION

Carbon Fiber (CF) is used as a strengthening material in resin composites having high performance which is mostly used in the fields of industry, space, and textile due to having mechanical properties such as low weight, high durability, and strength [1-4]. The mechanical properties of composite materials are based on the properties of fiber and matrix which constitute it. Developing these properties is possible the control of intermediate surface formed between fiber and matrix. Intermediate surface plays an important role for controlling the mechanical properties such as the shearing inter layers and impact resistance of composite. A strong and durable intermediate surface can effectively transfer the load from matrix to fiber. Fiber/matrix interaction depends on chemical bonds formed from interaction between active groups existing in matrix resin and polar group such as hydroxyl and carboxyl on the surface of fiber [5-7]. Various methods were developed for raising the wettability of and functional group number on fiber surface [8-11]. Methods such as the electrochemical oxidizing [12-14], the oxidizing in acidic medium using nitric or phosphoric acid [15-19], plasma [20-22], and radiation [23, 24] were used for developing the performance of intermediate surface between fiber and matrix. Another method is coating with thin polymer film [25-27]. The film thickness and functionality of the formed coating can control with electrochemical coating method using method parameters (current density, potential, monomer concentration, and temperature, *etc*.) [28-33]. It is well known that while CF is obtained, it is sized with various adding (sizing) compounds. Also, the effect of sizing compound (SC) on the surface roughness, surface reactive group number, and wettability of the fiber were investigated [34]. When CFs based on polyacrylonitrile (Poly(AN), PAN) was treated with J4 and A436 emulsion type sizing compound, it was observed the decreasing on the average surface roughness (Ra) [35]. Acidic filling materials demonstrate more interaction durability with epoxy matrix [36]. It is considered that Ra decreased because of the filling of hollow between strains on surface of the fiber [37]. As CF was sized by electropolymerization, the mechanical strength of composite was increased. The impact, bend and shear strength of phenolic resin-based composite respectively were 44%, 68% and 87% when CF was reinforced with m-phenylenediamine. During mechanical test, composite including unsized CF possessed holes due to getting out the CF [38]. This behavior is caused that unsized CF surface does not carry convenient groups to hold on to matrix. This problem could be decreased when CFs are sized by electropolymerization. As a result, electropolymerization is a convenient method for CF sizing process [38].CF were electropolymerized with monomers including groups such as –OH, $–NH_2$ or –COOH by using Cyclic Voltammetry (CV) or Chronoamperometry to develop surface features. At the end of this process, CFs were sized [38].CF was electrochemically coated with polyethylendioxythiophene (PolyEDOT) [39], PolyAN [40, 41], Polypyrrole (PolyPy) [42],

and their derivatives (43, 44). The capacitivity and roughness of CF were increased by using this method [45]. Also it was reported that Poly(Py) contribute to the strength of composite [42]. Electrochemical Impedance Spectroscopy (EIS) was used as a spectroscopic technique to analyze electrochemical process occurring at the electrolyte/electrode interface and to investigate the charge transfer, ion diffusion and capacitor behavior of conducting polymer modified electrodes [46-48]. In the literature, the capacitive features of carbon fiber (CF) electrodes modified by conducting polymer such as poly(N-methyl pyrrole) [45], polythiophene and poly(N-methylpyrrole) [49], N-pyrrole, N-phenylpyrrole, and 1[4-methoxyphenyl]-1H-pyrrole homopolymers [50], poly(3-dodecylthiophene) [48], poly(3-methylthiophene) [51], poly(thiophene-imidazole) [52], were characterized by EIS. It was signed that the value of impedance for the electrode coated poly(3-methylthiophene) was affected with the morphology of coating and also the morphology was affected with the present electrolyte [51]. In this study, we aimed to investigate how SC affects on and the electropolymerization of Py and the impedance data of PolyPy coated CF. For this reason, CFs was electrocoated with polypyrrole (PolyPy) conducting polymer by using constant or cyclic potential in the presence of epoxy based sizing compound (SC) in electrolyte solution. The coating thickness (as weight) and capacitive features of obtained coated CF and the current flown through system were investigated.

EXPERIMENTAL

In this study, we used CFs that were coated electrochemically with Py monomer (0.1 M) by using Constant Potential (1.5 V) in three electrode system, Ag wire (calibrated with 0.1 M ferrocene) as reference electrode, Pt wire as counter electrode and CF (0.003 ± 0.0005 g and 6 cm) as the working electrode. Electrolyte solution contained different amounts (0%; 0.18% and 1.8%) of epoxy based SC (Chemetylen AK-2 (SANYO Chemical Industries, Ltd.) in 0.1 M sodium perchlorate (0.1 M $NaClO_4$)-acetonitrile (ACN) [48-50].

The Constant Potential Electropolymerization (CPE) of Fibers

The aim of this part was to investigate the effect of SC on current which is flown in the circuit, so to follow the change of weight of coating with amount of SC in the electrolyte solution. During 60 min, the current flown through the system was recorded in CPE. Obtained data vs. time were given in Table 1.

Table 1: Obtained from CPE the current-time data. ($NaClO_4$/ACN; 0.003 g CF; 1.5 V)

Current/μA	18	17.94	17.65	17.65	17.21	17.14	17.21	17	17	16.6
Time/min.	0.1	3.52	9.86	16.1	28	33	41	47	58	60

In the first experiment, SC was not added into the electrolyte to see the difference of SC. Other experiments were carried out by adding 0.18% (w/v) and 1.8% (w/v) of SC to compare and find the convenient amount of SC. Obtained data were given Table 2 and Table 3.

Table 2: Obtained from CPE the current-time data. (SC: 0.18%; $NaClO_4$/ACN; 0.003 g CF; 1.5 V)

Current/μA	10.9	11.28	12	13.09	13.59	13.52	13.45	13.67	13.74	13.59	13.59
Time/min.	1.71	5.88	9.86	17	27	32	40	46	50	54	60

When the amount of SC was 0%, current changing was not observed during process, at 60 min and its value was about 17 μA. This current value was recorded as 13 μA for 0.18% of SC. This result pointed to the finding that the SC decreased current value. However, the current increased during the process and the weight of coating reached 10 mg/g for 0.18% SC. It was, however, 0.8 mg/g for 0% SC.

Table 3: Obtained from CPE the current-time data. (SC: 1.8%; $NaClO_4$/ACN; 0.003 g CF; 1.5 V)

Current/μA	10.7	0.6	0.4	0.42	0.49	0.49	0.42	0.63	0.7	0.63	0.63
Time/min.	0.1	4.07	9.6	14	19	28	36	45	53	57	60

According to Table 3, in these conditions the current passed from circuit was 10.7 μA within the first minute. Then the value decreased to 0.4 μA. The weighed amount of coating was 1.73 mg/g. As a result, the coating came true in the first minute. The amount of SC promoted the coating. It was however seen that the excess amount of SC was inhibited the current passing. When coating weight was 0.8 mg/g for 0% SC, it was 10 mg/g for 0.18% SC. Surprisingly, while the weight was decreased to 1.73 mg/g, the current was decreased 0.63 μA for 1.8% SC. When compared with 0.18% SC, the reason of this decrease was thought that the current passing and coating were blocked by the excessive amount of SC.

Gravimetric Analysis

To see how the adding of various amount of SC in electrolyte solution affected on the amount of coating, after CPE, CFs coated with PolyPy were weighted by using a five-digit analytical balance. The obtained data were given in Table 4.

Table 4: The amount of coating as compared the different amount of SC. (0.003 gr CF; 1.5 V)

SC (%)	0	0.18	1.8
Weight (mg/g)	0.8	10	1.73

According to obtained data, as SC was added in electrolyte solution during electrocoating, a decrease in the coating amount was observed. When SC amount was 0.18%, coating amount was 10 mg/g. This increasing was attributed to including into the structure of coating. But it was determined that the increasing in the amount was inhibited, while the amount of SC added in electrolyte solution was more than 0.18%, the increasing of coating amount was inhibited. Also, this increase was supported with the current rise (Table 2 and 3). Depended on these results, it is concluded that the current and SC amount were important parameters on the controlling of the thickness or amount of coating.

Structural Analysis (FTIR-ATR)

In the data, FT-IR peaks were investigated to understand whether if SC was included into the structure of the coating. The FT-IR spectra of CF coated with PPy in the presence of the various ratios of SC were compared in Figure 1. When we look at the figure, it was considered that the characteristic peaks of CF were covered with coating (PolyPy) and the characteristic peaks of coating were seen in the spectrum. The peak of PPy was seen in 3800-3600 cm^{-1}, and the ones of SC in 2900-2800cm^{-1}. The related peak assignments were given in Table 5.

Table 5. The FTIR-ATR peak assignments.

Peak (cm^{-1})	**Peak Type**
3748	N-H stretching[53]
2872, 1682, 1711	SC
1537, 1452,	PolyPy ring vib.[53]
1312, 1089, 1072, 1040 and 889	=CH band vib. of PPy[53]

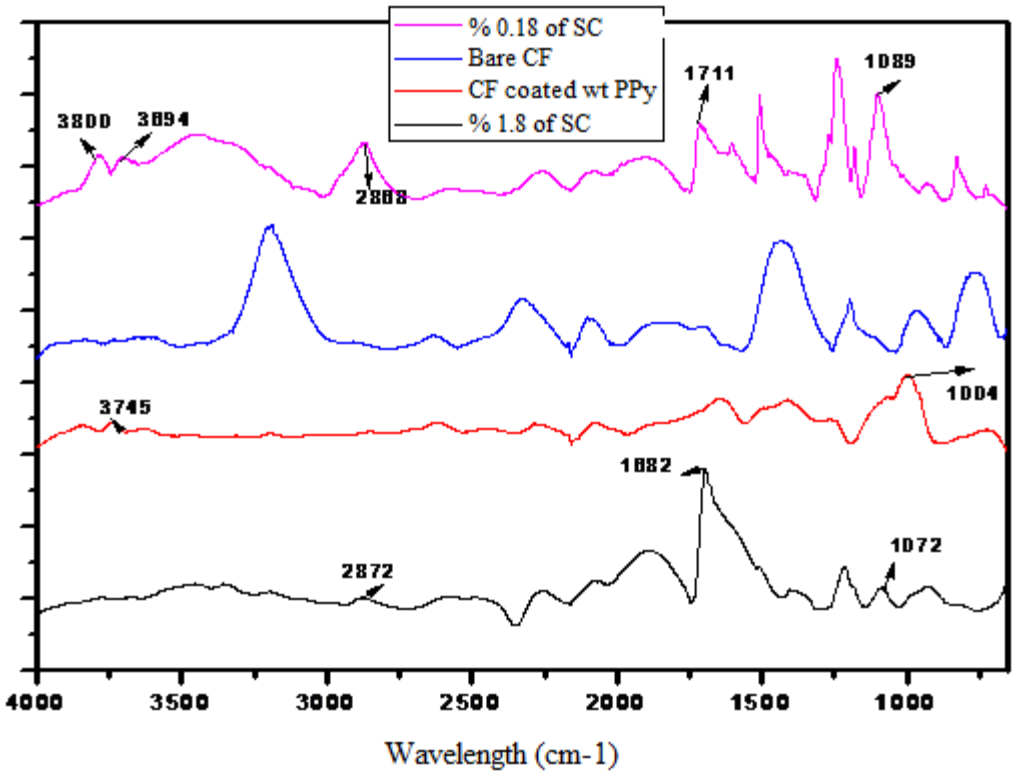
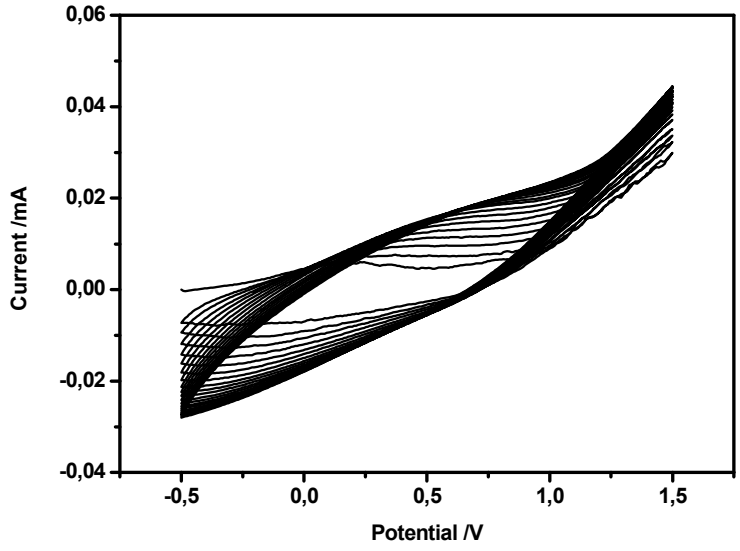
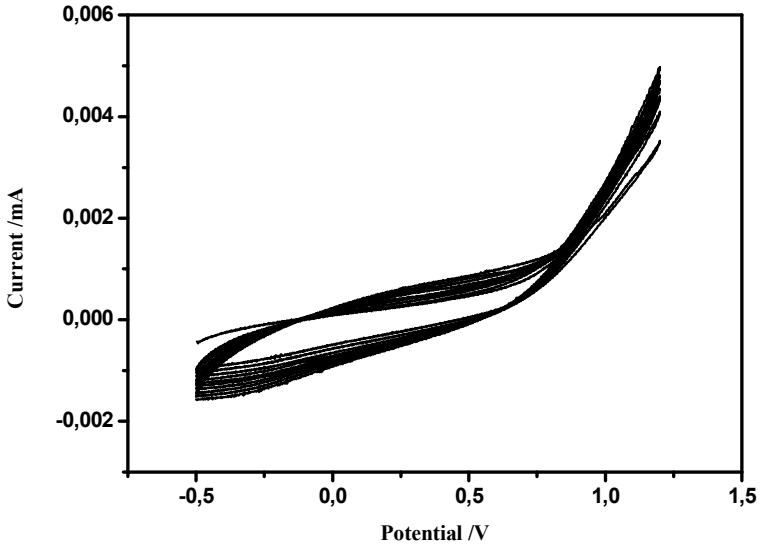


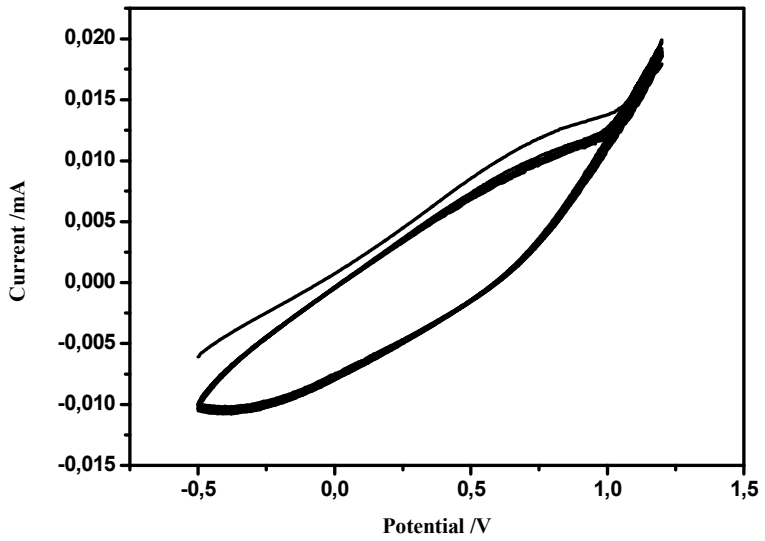
Figure 1. The FTIR-ATR spectra of CF coated with PolyPy in presence of SC (0.18%; 1.8%).

Peaks at 1452 and 1537cm^{-1} were assigned to Py ring vibration. The ones at 1312 and 1040 cm^{-1} were presented as the =C-H band vibrations. The N-H stretching vibration was observed at 3745 cm^{-1}. The peaks at 1178, 1089, 1072 and 889 cm^{-1} were characteristic peaks of =C-H out of plane vibration, demonstrating the polymerization of Py [53]. It was considered that the peaks at 2872, 1682 and 1711 cm^{-1} belonged to SC.

The Cyclic Voltammetry-Induced Electropolymerization of Fibers:

To investigate the effect of SC on the impedance values (or capacitance values), it was required to prepare CFs thin layer coated with PolyPy. For this reason, cyclic voltammetry technique was used. A three-electrode system consisted of Ag wire as a reference electrode, Pt wire as a counter electrode, and single CF as a working electrode like CPE. SC was added in 0.1 M Py including electrolyte solution ($NaClO_4$-ACN) in various ratios, which were 0%; 0.18% and 1.8%. So, obtained CV graphs were given in Figure 2.

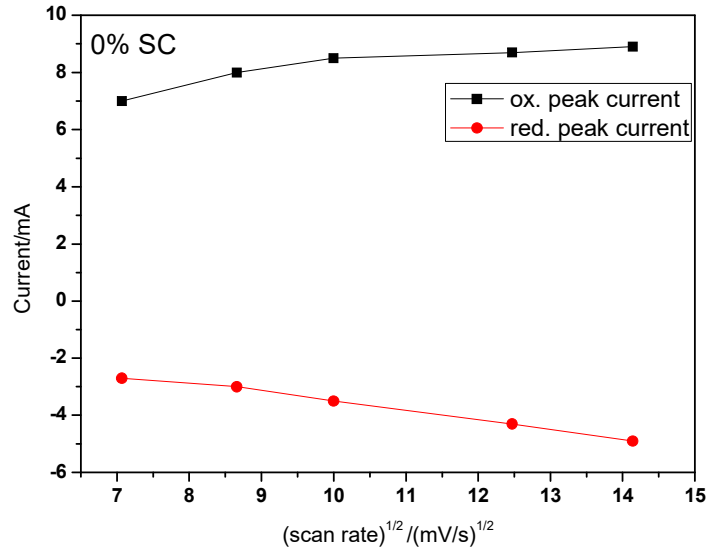
	**a.** $NaClO_4$/ACN 0% SC
	**b.** $NaClO_4$/ACN 0.18% SC



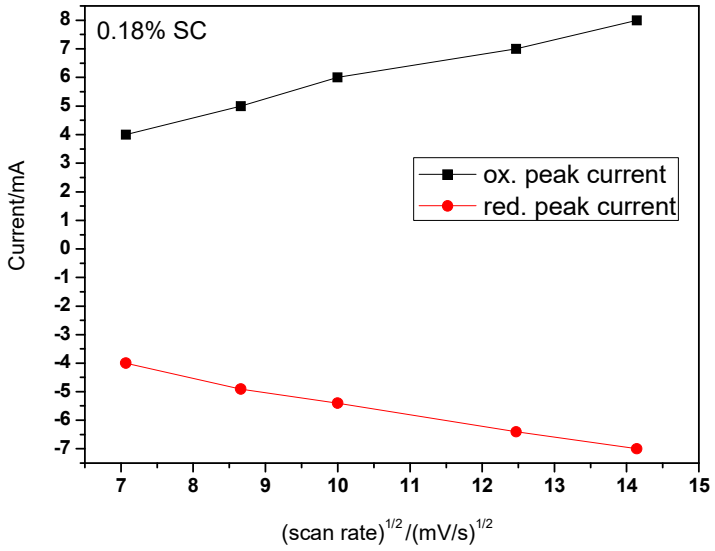
c. $NaClO_4$/ACN
1.8% SC

Figure 2. The CVs showing the effect of SC on polymerization of Py in $NaClO_4$-ACN including various ratios of SC.

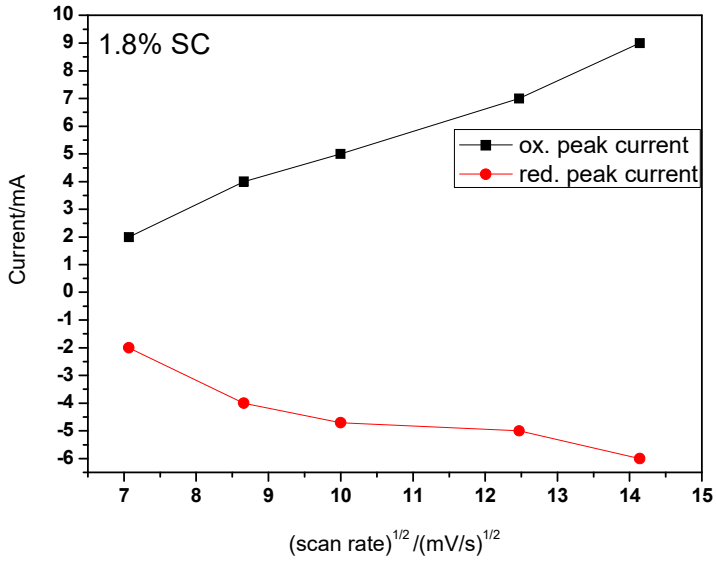
It was seen clearly that adding SC affected the shape of CV. Py was oxidized at 0.9 V and current value was 0.04 mA (Figure 2a). As SC was added in electropolymerization medium, the value was decreased at 0.005 mA for %0.18 SC and 0.02 mA for 1.8% SC. It was thought that the cause of raising value at 1.8% SC might be due to the increasing amount of SC. To determine the electrical properties and if the mechanism of polymerization reaction is controlled by diffusion or not, it is required that CFs coated with PolyPy are investigated under CV conditions. Used electrolyte solution cannot include the monomer (here Py). For this reason, various scan rates were applied to CF coated with PPy and obtained CV graph, which were monomer-free graphs. The current responses to the scan rate from the polymer, oxidation (ox.) and reduction (red.) of the polymer peak current potentials and oxidation and reduction of the polymer peak current values were obtained from the graphs. Figure 3 illustrated scan rate vs. oxidation-reduction peak current values.



a. $NaClO_4$/ACN
0% SC



b. $NaClO_4$/ACN
0.18% SC



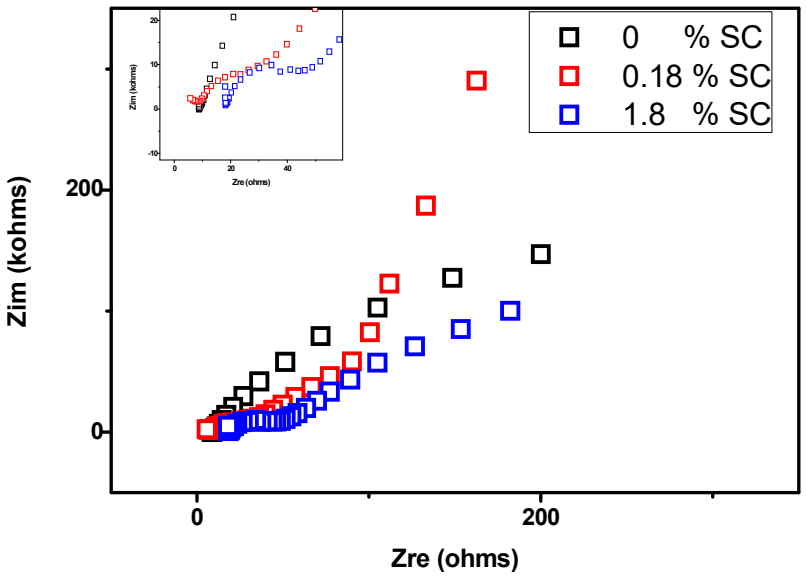
c. $NaClO_4$/ACN
1.8% SC

Figure 3. The monomer-free graphs of CFs coated with PPy in different conditions.

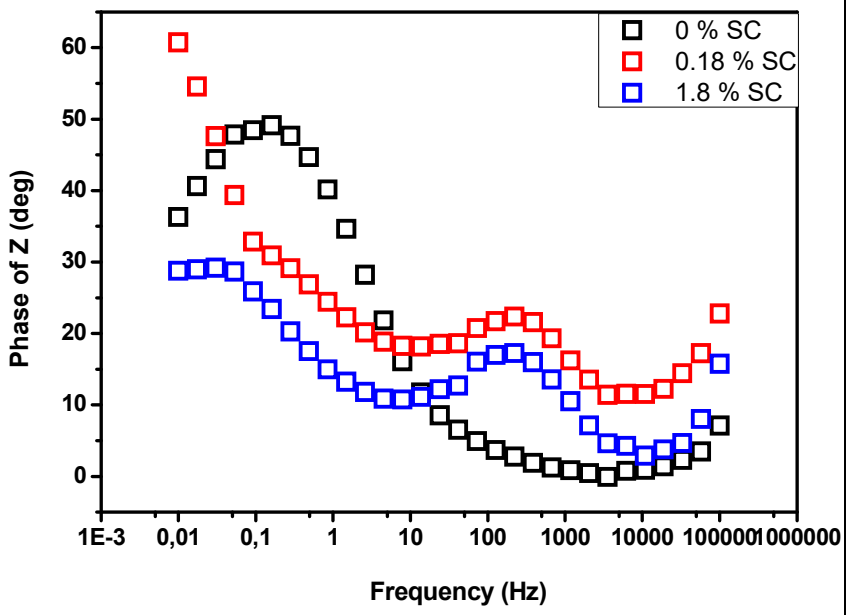
As the curve obtained from this data is approximated to a linear form, it could be concluded that the mechanism of polymerization reaction was controlled by diffusion. It can however be seen clearly that this control was destroyed by using of 1.8% SC in electrolyte medium.

The Electrochemical Impedance Analysis of Coated Fibers

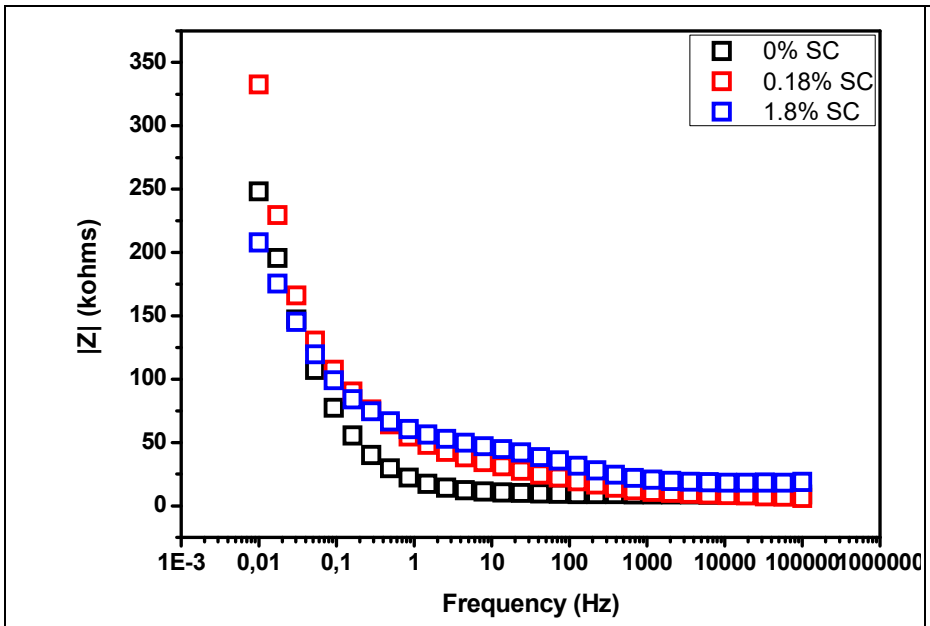
To show and compare the effect of SC on electrochemical impedance, namely capacitance, the CFs obtained from related experiments were used. The measurements were taken in $NaClO_4$-ACN solution by using Electrochemical Impedance Spectroscopy (EIS). Figure 4 illustrated EIS graphs (Nyquist, Bode-Phase, Bode-Magnitude, and admittance).



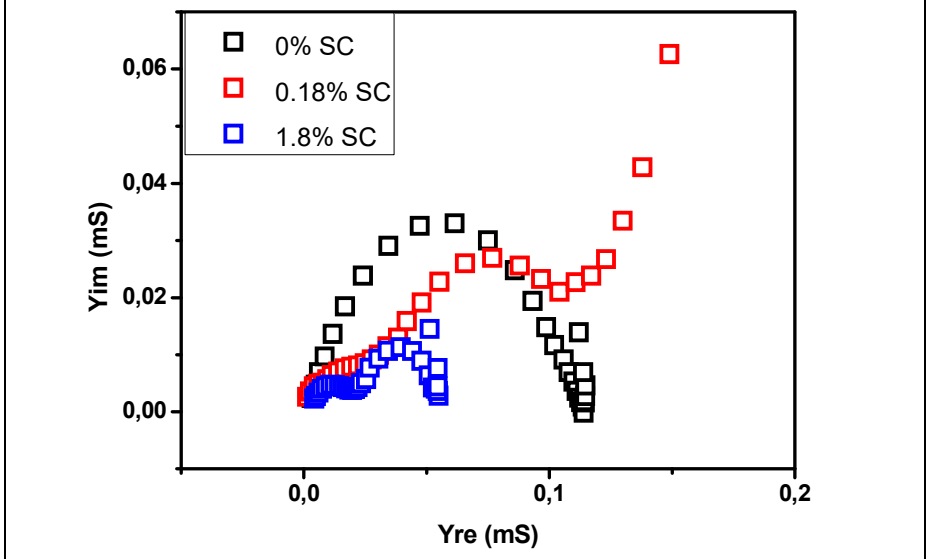
a. Nyquist graph



b. Bode-Phase graph



c. Bode-Magnitude graph



d. Admittance graph

Figure 4. The EIS graphs of CFs coated with PPy in different conditions.

Different Capacitance values were obtained from these impedance graphs [54]. One of them was specific capacitance (C_{sp}) calculated from Nyquist graph by using Z_{im} at lowest frequency. The other was Double Layer Capacitance (C_{dl}) calculated from Bode-Magnitude graph by using IZI at 1 Hz. Calculated C_{sp} and C_{dl} values were 114 µF and 45 µF ; 57 µF and 19 µF; 166 µF and 17 µF for 0%; 0.18%; 1.8% of SC, respectively. Phase angle and admittance values were changed as 36° and 32 µS; 61° and 26 µS; 29° and 11 µS for 0%; 0.18%; 1.8% of SC, respectively.

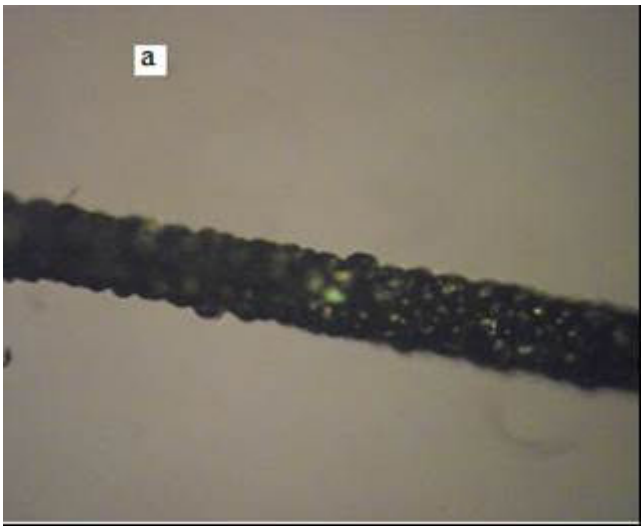
In the light of this information, values obtained from these impedance graphs were given in Table 5. According to the values C_{sp} value was changed by adding SC in electrolyte solution. This change was shaped bell curve reversely, but the changing of the coating weight was shaped bell curve.

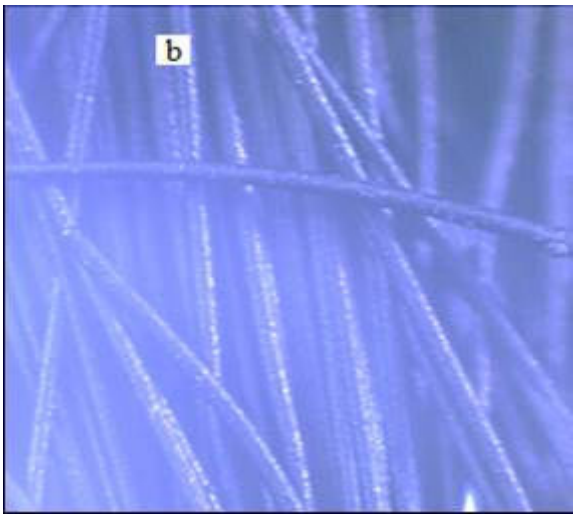
Table 5. The changing of Csp and coating weight vs. the ratio of SC.

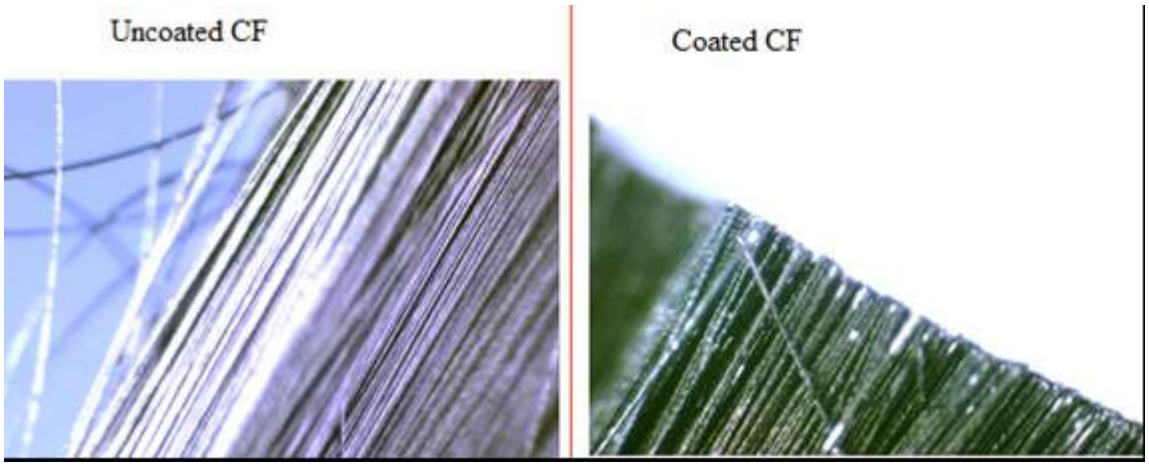
SC (%)	0	0.18	1.8
Csp (μF)	114	57	166
Weight (mg/g)	0.8	10	1.73

Light Microscopic Images

CF was coated with PolyPy in the presence of various ratios (0%, 0.18%, and 1.8%) of SC in the electrolyte. CF was used as brush (in CPE technique) or single (in CV technique) form. The images captured from light microscopy of CFs coated with PolyPy were shown in Figure 5. Single CF was illustrated in Fig.5a, brush CF in Fig.5b and the comparison of coated and uncoated of CFs in Fig5c. As seen in the figure, the coatings were homogenous.







c)

Figure 5. The images of light microscopy of Single CF (a), brush CF (b) and the comparison of uncoated and coated CFs (c).

DISCUSSIONS

In this study, it was proved that SC presented in electrolyte affected to the electropolymerization of Py, the weight of coating, the electrical, impedance, and capacitance properties of CF coated with PPy by using convenient techniques (CPE, Analytical Balance, CV, EIS and Light Microscopy). As a result, the weights and the capacitance values of CFs coated with PolyPy in conditions such as 0.1 M $NaClO_4$-ACN electrolyte solution including 0.1M Py and various ratios of epoxy based SC (0%; 0.18% and 1.8%) was changed with the SC ratios.

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Türkçe Öz ve Anahtar Kelimeler

Pirolün Elektropolimerleşmesi Üzerine Boyutlandırıcı Bileşiğin Etkisi ve Polipirol ile Kaplanmış Karbon Lifinin İmpedansı

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Öz: Karbon Lifi (CF), düşük ağırlık, yüksek dayanırlık ve sertlik gibi mekanik özelliklerinden ötürü pek çok endüstri alanında yüksek performansa sahip reçine kompozitlerinde kuvvetlendirici malzeme olarak kullanılmaktadır. Kompozit malzemelerin mekanik performansları, onu oluşturan lif ve matrisin özelliklerine dayanır. Lif yüzeyinin özelliklerine etkide bulunan yöntemlerden biri, lif yüzeyinin ince filmle kaplanmasıdır. Lif elektropolimer ile kaplandığı zaman, kompozitin mekanik dayanıklılığı artmıştır. Bu çalışmada, karbon lifleri polipirol (PPy) ile elektrokimyasal olarak kaplanmış olup ortamda epoksi esaslı boyutlandırıcı bileşik (SC) vardır. Süreç boyunca SC'nin miktarı ile akımın, elde edilen kaplama ağırlıklarının ve impedans verisinin, özellikle kapasitansın, nasıl değiştiği incelenmiştir. Bu sebeple, farklı miktarda SC (%0, %0,18, %1,8 v/v) elektrolit çözeltisi olan ve 0,1 M pirol (Py) içeren 0,1 M $NaClO_4$-ACN'ye ilave edilmiştir. Kaplama işlemi Sabit Potansiyel veya Döngülü Voltammetri teknikleri ile yürütülmüştür. Diğer inceleme teknikleri gravimetrik analiz, elektrokimyasal impedans spektroskopisi, Fourier Transform İnfrared Spektroskopisi (FT-IR) ve Işık Mikroskopisidir. Kaplamanın sonunda, kaplamanın ağırlığı ve özgül kapasitansı (Csp), %0 SC için 0,8 mg/g ve 114 μF, %0,18 SC için 10 mg/g ve 57 μF ve %1,8 SC için 1,73 mg/g ve 166 μF olarak bulunmuştur. Sonuç olarak, PPy ile kaplanmış karbon lifinin kaplanma ağırlığı ve kapasitans verisi (özellikle Csp), elektrolite ilave edilmiş SC'nin miktarı ile ters orantılı olarak değişmiştir.

Anahtar kelimeler: Elektropolimerleşme, Boyutlandırma, İmpedans ve Kapasitans.

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