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A Systematic Study on Morphological, Electrical and Electromagnetic Shielding Performance of Polypyrrole Coated Polyester Fabrics

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ABSTRACT

Functional conducting polymeric composites with micro and nano structures have received great attention due to technological applications in electrical, optical, and magnetic materials and devices. Electrically conductive polymeric textile surfaces are used for smart/functional textile applications such as electromagnetic shielding, anti static coatings, wearable electronic sensors, heat generating textiles etc. In this study, micro/nano scale conductive polymer coatings were obtained on polyester fabrics by in-situ chemical polymerization of pyrrole. Electromagnetic shielding performance of polyester-polyprrole (PES-PPy) conductive composite fabrics were investigated by coaxial holding method of ASTM D 4935. Spectroscopic (FTIR-ATR, XPS), morphologic (SEM), thermal (TGA) and electrical (Four Point Probe) characterizations were performed. Direct Current (DC) electrical conductivity of PES-PPy composite fabrics increased linearly with the fabric coating thickness. The electromagnetic shielding effectiveness of PES-PPy composite fabrics were enhanced by coating them in the presence of different PPy contents and $FeCl_3$+*p*-TSA initiator-dopant system.

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Conductive textiles, Conductive polymers, Polypyrrole, Electromagnetic shielding

1. INTRODUCTION

Development of electrically conductive textiles has gained great attention in recent years especially in protective technical textile applications for the purpose of controlling electromagnetic shielding. Conductive textiles are structures that have the ability to transfer electrical charges like metals. Conductive textile applications are carried out by integrating conductive metal wires or yarns into the fabric structure in the weaving and knitted fabric production process or by surface coating with conductive polymers or particles. The development of smart technical textiles requires fabrics that conduct electricity. One of the practical techniques to make textile materials electrically conductive is to apply a coating layer of conjugated polymers onto fiber or fabric surface [1-3].

Conjugated polymers have been commonly preferred due to their excellent electrical properties. The most widely used polymers among the conductive polymers known as synthetic metals are polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) [4]. Polypyrrole is the most widely used conjugated polymer which is due to its ease of synthesis, good redox properties, stability in the oxidized form, high electrical conductivity and water solubility [5]. The most important difference of these polymers from insulating polymers is the conjugation of π-electrons formed by the overlapping of the carbon p-orbital along the backbone and doping with a suitable dopant to reach metallic conductivity levels.

Conductive polymeric textiles are a part of composite materials and have gained much interest in many fields such as defence, medical, electrical, and electronics

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applications. These composite fabrics could be used in protective clothing, solar cells, electrochromic devices, flexible sensors, as well as home and business applications including electromagnetic interference shielding, electrostatic charge dissipation and dust free clothes. These conductive composite fabrics are used in military applications for radar protective composite fabrics due to desirable microwave absorption characteristics. Furthermore conductive woven or knitted fabrics structural order and flexibility offer an opportunity for desirable electromagnetic shielding properties [6-8].

Electromagnetic shielding effectiveness (EMSE) is a process of restricting the electromagnetic wave penetration by blocking them by a barrier made of conductive material in rapidly growing field of electronics. The metal composite materials which have low elasticity, easy to corrosion, high weight and poor regeneration capacity are used due to their good shielding performance properties in the former electromagnetic shielding studies. However nowadays the potential of conductive polymer coated composites in the field of electromagnetic shielding wave applications have gained great attention because of their superior electrical properties, versatility, light weight, high flexibility and mechanical properties [7-10]. There are many methods to produce electrically conductive fabric composites to obtain electromagnetic shielding textiles. The fabrics can be easily coated with intrinsically conductive polymers (ICPs) to form a very thin layer on fabric surfaces by in situ chemical polymerization, drop casting-drying and vapour phase polimerization [8,9]. The direct coating methods via in-situ chemical polymerization is reported that provide good electrostatic charge dissipation (ESD) characteristic as well electromagnetic radiation energy blocking response. Also $FeCl_3$ based oxidative agents are used to initiate the pyrrole during the in-situ coating process since it has both conducting and magnetic properties [13].

Hakansson et al. studied the electromagnetic shielding effectiveness of polypyrrole/polyester composites over the 1 - 18 GHz and they measured the maximum EMSE as 8.68 dB [14]. Kaur et al. synthesized polypyrrole nanoparticles (PPy NPs) by chemical oxidation method under surfactant directed process and determined the PPy nanoparticle size decreases while the DC conductivity and EMSE values increase with surfactant concentration. They found the highest EMSE value of 49 dB [15]. Rubeziene et al. prepared poly (3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS) coated polyester/cotton plain weave woven fabrics to investigate the electromagnetic shielding properties. They determined certain advantages of conductive coated fabrics in comparison with metallized fabrics within the range of 2 GHz - 20 GHz [16]. Saini et al. studied the electromagnetic shielding behavior of conductive polyaniline (PANI) –multi-walled carbon nanotube (MWCNT) nanocomposites produced by in situ polymerization. The higher electrical conductivity values due to the synergistic effect of two seperate phases (i.e. PANI and MWCNT) were determined in the case of PANI–MWCNT composite (19.7 S cm^{-1}) in comparison with MWCNT (19.1 S/cm^1). The absorption dominated EMSE values of 27.5−39.2 dB was measured which indicates a candidate material for microwave shielding in the 12.4–18.0 GHz frequency range [17].

In this study, electrically conductive polypyrrole coated polyester composite fabrics were produced by in-situ chemical polimerization and a systematic study was performed on the morphological, spectroscopic, electrical, thermal and electromagnetic shielding performance of PPy coated polyester fabrics. The effect of PPy content and initiator-dopant system on the electrical conductivity, coating thickness, surface morphology, electromagnetic shielding performance and weight loss (%) of PES-PPy composite fabrics was investigated. It is emphasized that the 0.4% (v/v) PPy content in the presence of p-TSA dopant has been determined as a main threshold for higher electrical conductivity and electromagnetic shielding effectiveness unlike the literature. In addition, it was determined that higher EMSE performance was obtained by increasing the coating thickness and the total thickness of the layered shield fabric in the presence of p-TSA.

2. MATERIAL AND METHOD

2.1 Material

Pyrrole (98%) was used as a conductive monomer to coat polyester fabrics by in-situ chemical polymerization. Iron(III) chloride ($FeCl_3$) and *p*-toluenesulfonic acid monohydrate (*p*-TSA) were selected as an initiator and dopant, respectively. Ethanol, methanol, acetone and distilled water were used for further washing and removing impurities. All chemicals were Sigma-Aldrich products and were used as received without any purification. An undyed and ready to dye 100% polyester woven fabric was supplied by Kipas-Turkey (Table 1).

2.2 Method

2.2.1 Preparation of Polypyrrole Coated Polyester Fabrics

Polypyrrole coated polyester fabrics (PES-PPy) were produced by in situ chemical polymerization method. A polyester fabric with an area of 36 cm^2 was washed with acetone and was dried in an oven to remove impurities. Before the coating, $FeCl_3$ and *p*-TSA were mixtured with a magnetic stirrer for 1h to obtain a 50 mL aqueous solution. Then polyester fabric was immersed into $FeCl_3$+*p*-TSA aqueous solution to acquire a homogeneously wetted fabric. Pyrrole was added drop by drop to the $FeCl_3$ + *p*-TSA aqueous solution including polyester fabric and polymerization was continued for 3 hours at 25^oC. At the end of polymerization, the PPy coated polyester fabric was washed with methanol, ethanol, distilled water and dried in laboratory conditions for 24 hours. The polymerization process is given in Figure 1.

Table 1. Polyester fabric constructional properties

Fabric Weight (g/m^2)	Weft Density (picks/cm)	Warp Density (ends/cm)	Weave pattern
256	24	36	2/1 S Twill

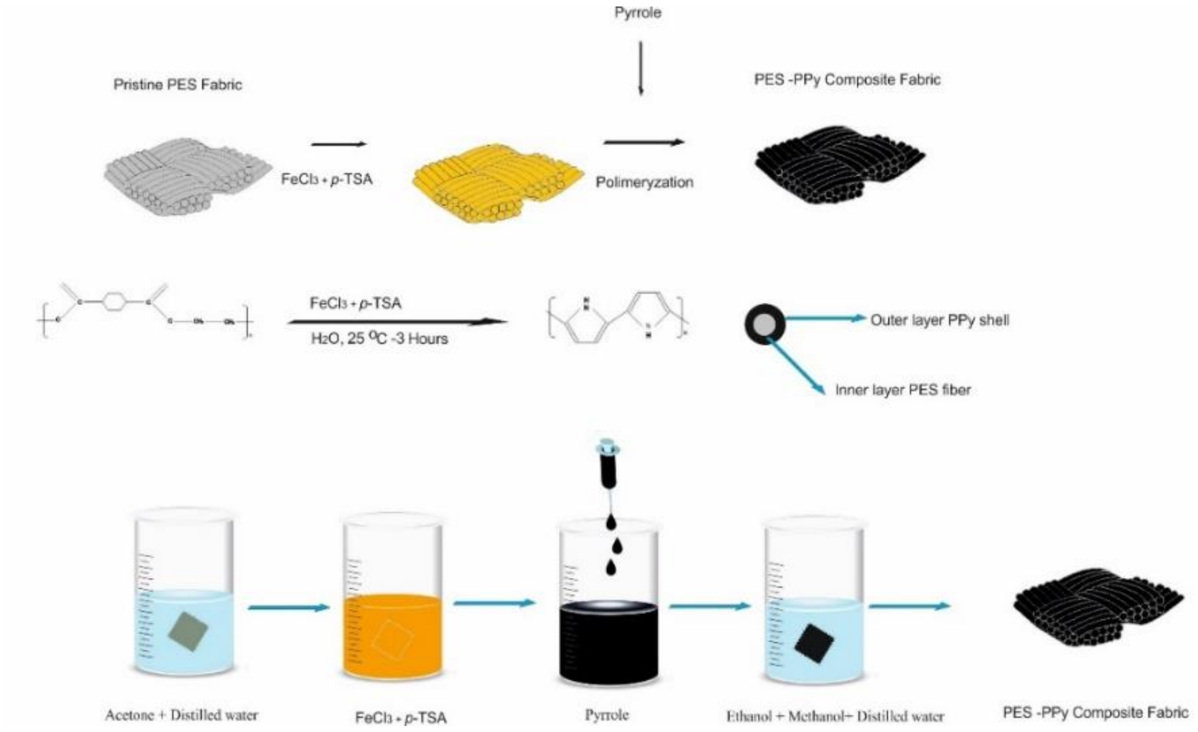

Figure 1. Preparation of PPy coated polyester fabric (Molar Ratio: [FeCl$_3$]/[Py]=2.2, [*p*-TSA]/[Py]=0.2)

2.2.2 Characterization

Fourier Transform-Infrared (FTIR) analysis of PPy coated polyester fabrics was performed by a Perkin Elmer Spectrum 400. X-Ray Photoelectron Spectroscopy (XPS) Analysis was carried out by PHI 5000 *Versa Probe.* Surface morphology was determined a scanning electron microscope (SEM) by a Quanta 400F. Thermal gravimetric characteristics (TGA) were investigated by Exstar TG/DTA 6300 thermo gravimetric calorimeter under N$_2$ atmosphere from 25 to 550°C at a heating rate of 20°C/min. Four point probe DC conductivity measurements were performed on Entek Elektronics FFP 510 Four Point Probe Measuring System. Electromagnetic interference shielding effectiveness measurements were carried out based on ASTM D4935 standard for planar materials using a network analyser by holding the specimen between a test fixture (EM-2107A) according to the coaxial transmittance line method [17-20].

3. RESULTS AND DISCUSSION

3.1 FTIR Spectrocopy

Figure 2 shows the FTIR spectra of PPy coated polyester fabrics.

In pristine polyester fabric; a strong absorption band was observed at 1712 cm^{-1} which was attributed to C=O stretching vibration (Figure 2). Other absorption peaks of polyester fabric are aromatic ring stretching (1408 cm^{-1}), carboxylic ester or anhydride (1338 cm^{-1}), O=C–O–C or secondary alcohol (1090 and 1015 cm^{-1}), C=C stretching (969 cm^{-1}), five substituted H in benzene (871 cm^{-1}), two neighboring H in benzene (847 cm^{-1}) and heterocyclic aromatic ring stretching (722 cm^{-1}) vibrations [21]. After the PPy coating process, a new absorption peak (C=C ring vibration) was observed at 1558 cm^{-1} and shifted to 1531 cm^{-1} by the increasing of PPy content that indicates the PPy was included to the polyester composite fabric. PPy ring bending peak observed at 1168 cm^{-1} is shifted to 1149 cm^{-1} by the incorporation of PPy in the composite structure. The absorption peaks between 1040 and 1080 cm^{-1} were attributed to the in-plane vibration of NH$^+$ groups of PPy chains by protonation [22,23].

3.2 X-Ray Photoelectron Spectroscopy

XPS analysis was performed to identify the PPy formation on the polyester fabric surface. Figure 3 ve Figure 4 present the wide scan (0-1200 eV) spectra of uncoated and PPy coated polyester fabrics, respectively.

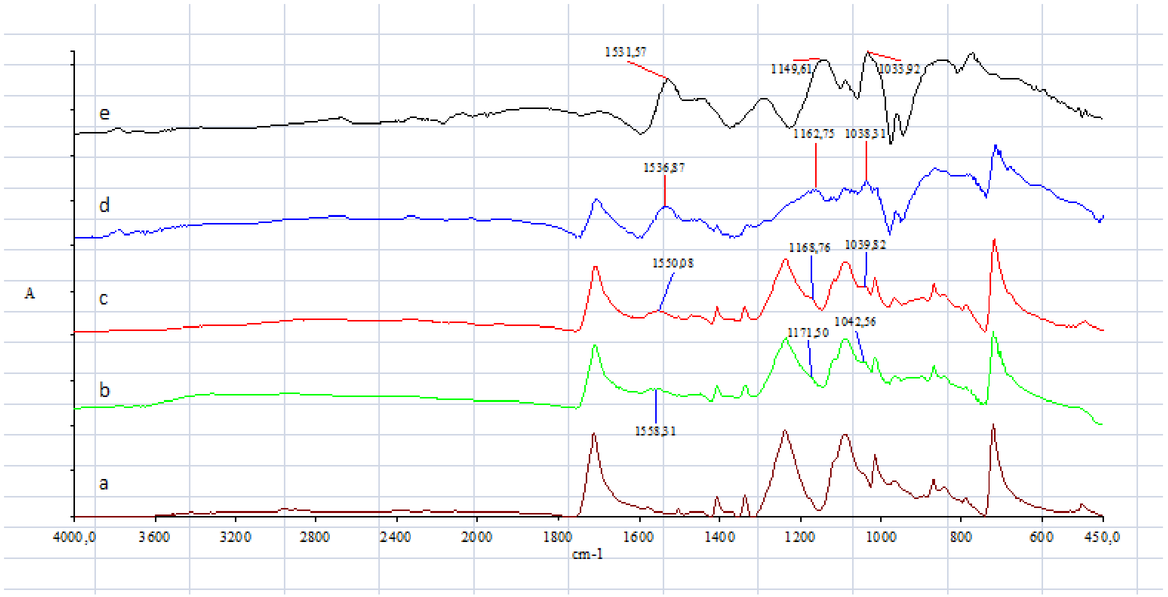

Figure 2. FTIR spectra of PPy coated PES fabrics (a. uncoated fabric, b. %0.1 (v/v) PPy, c. %0.2 (v/v) PPy, d. %0.3 (v/v) PPy, e. %0.4 (v/v) PPy)

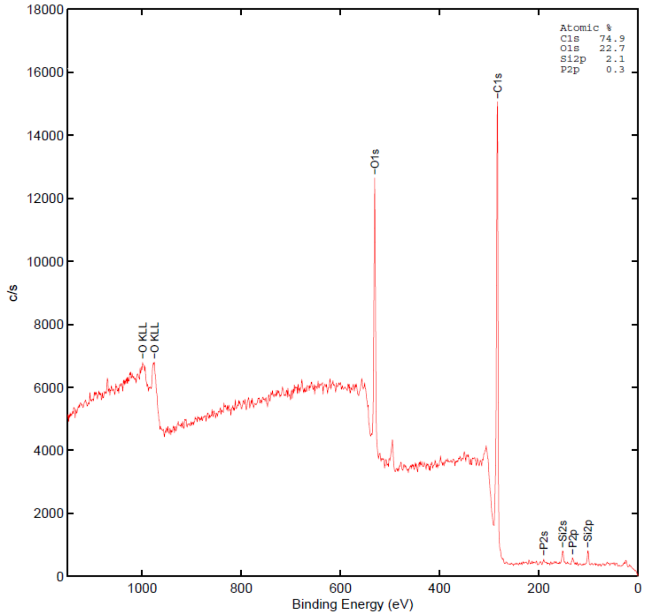

Figure 3. XPS spectra of uncoated polyester fabric

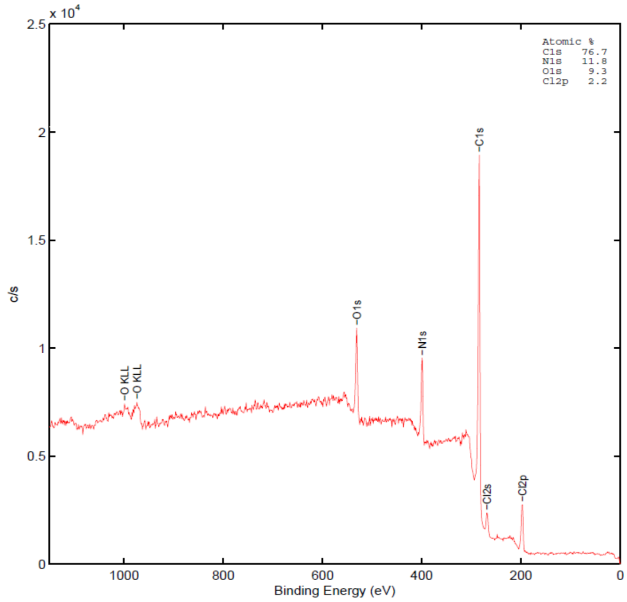

Figure 4. XPS spectra of 0.4% (v/v) PPy coated polyester fabric

The percentage of atoms for uncoated polyester fabric and PES-PPy coated fabric with 0.4% (v/v) PPy were given in Table 2.

Table 2. Atoms ratio of uncoated and %0.4 (v/v) PPy coated PES composite fabrics

Fabric	C (%)	O (%)	N (%)	Cl (%)
PES	74.9	22.7	-	-
PES-PPy	76.7	9.3	11.8	2.2

Carbon and oxygen atoms were detected for PES and PES-PPy coated fabrics whereas nitrogen and chloride atoms were detected only for the PPy coated polyester fabric. Compared with the uncoated fabric, the P2s, P2p, Si2p and Si2s peaks were disappeared in the PES-PPy composite fabric due to in situ chemical polymerization of pyrrole. The N1s, Cl2p and Cl2s peaks were observed only for the spectra of PPy coated polyester composite fabric. In PES-PPy composite fabric, a new peak appeared at 400 eV depicted that NH^+ groups were introduced to polyester macromolecule chains by in-situ polymerization process with $FeCl_3$ indicating the incorporation of PPy particles (Figure 3, Figure 4, Table 2).

3.3 Surface Morphology

The SEM images of %0.4 (v/v) PPy coated polyester fabrics in the presence of $FeCl_3$ and $FeCl_3$+*p*-TSA initiator-dopant system were presented in Figure 5.

Compared to the smooth surface of polyester fabric (Figure 5 (a-c)), a significant change on the surface of polyester fabrics was occured after *in-situ* chemical polymerization of pyrrole. The homogeneously distributed PPy nanoparticle coatings were observed on the fabric surfaces for both $FeCl_3$ and $FeCl_3$ + *p*-TSA polymerization system (Figure 5(d-i)). While a homogeneously coated PPy layers were observed on the yarns in the presence of $FeCl_3$; an extremely dense PPy nanoparticle layer were observed on the fabric surface which is coated with PPy in the presence of $FeCl_3$ + *p*-TSA initiator-dopant system. Unlike the $FeCl_3$, PPy coated regions having denser and smaller globular nanoparticles were observed in the $FeCl_3$ + *p*-TSA initiator-dopant coating system which shows some small particles of PPy deposited on the surface that increase the overall roughness of the fibers. The presence of p-TSA dopant may increase the solubility of the pyrrole during polymerization, causing the surface morphology to change. In the composite fabrics coated with PPy in the presence of p-TSA dopant, the droplets could reduced in size and could were well dispersed due to the improved dispersion efficiency. The cauliflower and dentritic morphology of PPy were observed in agreement with literature [23,24].

In the coating process, the p-TSA sulfonic acid group makes hydrogen bonding with the nitrogen atoms in the pyrrole ring. Therefore, hydrogen bonding continues along the polyester macromolecule chains, and as a result of the coating process, the pyrrole polymerization takes place on the polyester fabric surface. The resulting polypyrrole and polyester macromolecules interact by hydrogen bonds. The polyester-polypyrrole interaction is given in Figure 6.

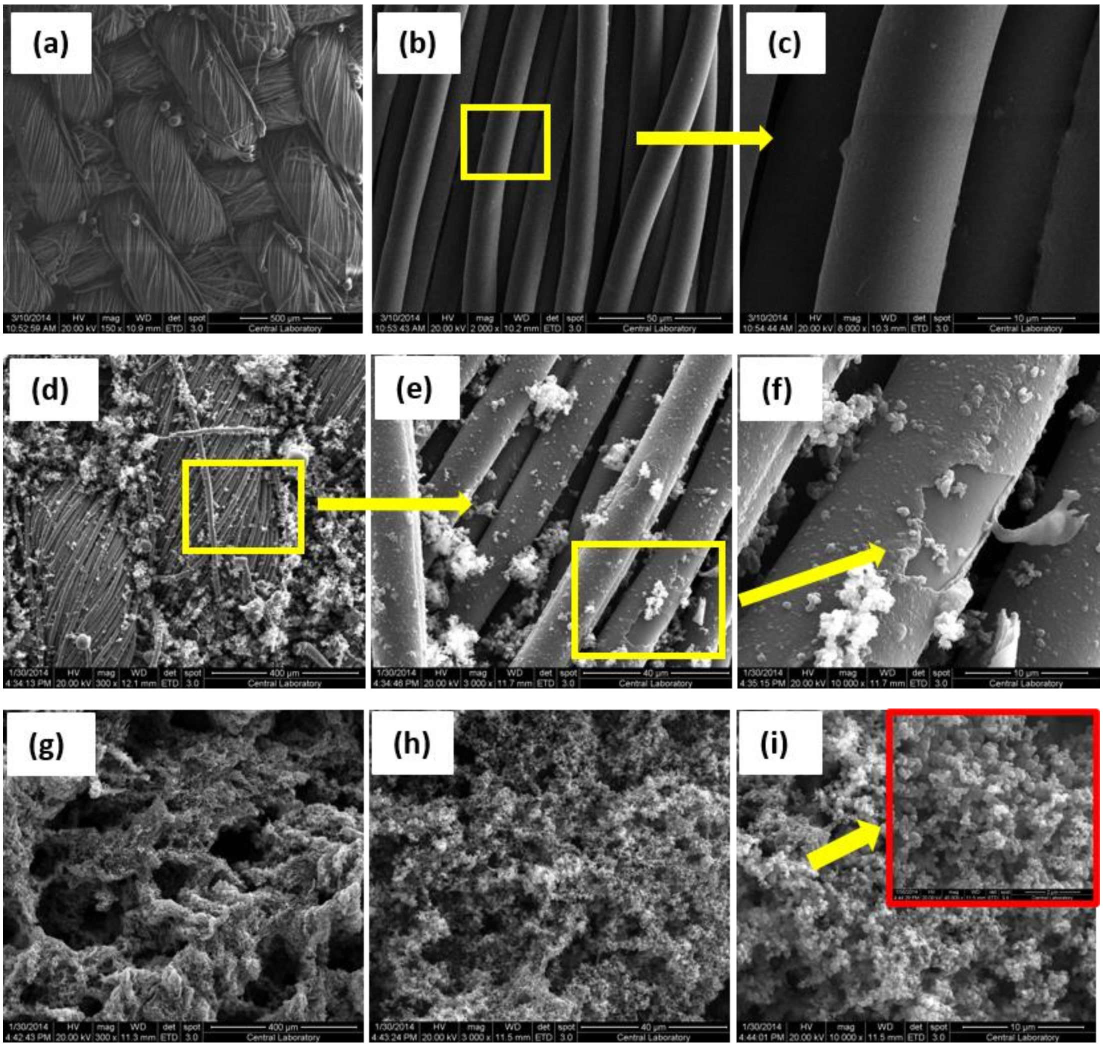

Figure 5. SEM images of uncoated polyester fabric (a-b-c), PES-PPy fabrics doped with $FeCl_3$ (d-e-f) and PES-PPy fabrics doped with $FeCl_3$ + *p*-TSA initiator-dopant system (g-h-i)

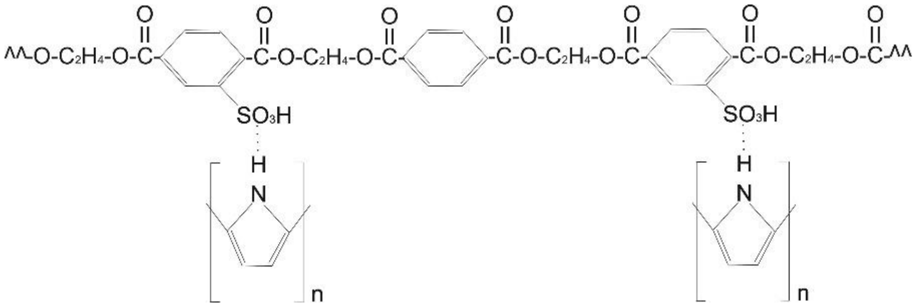

Figure 6. Polyester-polypyrrole interaction

3.4 Electrical Characteristics

The DC conductivity comparison of %0.4 (v/v) PPy coated PES-PPy composite fabrics in the presence of $FeCl_3$ and $FeCl_3$+*p*-TSA initiator-dopant system was given in Table 3.

Table 3. DC conductivity comparison of %0.4 (v/v) PPy coated PES-PPy composite fabrics

Fabric Sample	DC Conductivity (S/cm)	Thickness (µm)	Coating (%)
PES	1×10^{-12}	357	-
$FeCl_3$	1×10^{-2}	401	12.3
$FeCl_3$+*p*-TSA	5.8×10^{1}	436	22.1

Doping process has a significant role in the conductive polymer composites. The neutral polymer backbone is converted to a charged π-conjugated system which allows electrons to flow through π-conjugated system due to the formation of conduction bands of conductive polymers [25]. The higher conductivity values have been determined in the presence of *p*-TSA dopant in polymerization medium. The DC conductivity of $FeCl_3$+*p*-TSA doped PES-PPy composite fabric is 5800 times higher than $FeCl_3$ doped PES-PPy composite fabric which could be due to the homogeneously distribution of PPy nanoparticles in the presence of *p*-TSA dopant. The $FeCl_3$+*p*-TSA initiator-dopant system can show enhanced electron mobility and higher polymerization degree of pyrrole than $FeCl_3$ for the %0.4 (v/v) PPy coated PES-PPy composite fabrics [26]. According to the morphological analysis, an extremely dense PPy nanoparticle layers were observed on the fabric surface which was coated with PPy in the presence of $FeCl_3$+*p*-TSA initiator-dopant system (Figure 4). The interconnected PPy network structure having denser and smaller globular nanoparticles of PES-PPy conductive composite fabrics in the presence of $FeCl_3$+*p*-TSA initiator-dopant system improves the electronic pathways resulting in the higher electrical conductivity.

The effect of PPy content on the DC conductivity and fabric thickness of PES-PPy composite fabrics coated with $FeCl_3$+*p*-TSA initiator-dopant system is presented in Table 4 and Figure 7.

Table 4. Effect of PPy content on the DC conductivity and thickness of PES-PPy composite fabrics coated with $FeCl_3$+*p*-TSA initiator-dopant system

Fabric Sample	DC Conductivity (S/cm)	Thickness (µm)	Coating (%)
PES	1×10^{-12}	357	-
0.1% (v/v) PPy	3.6×10^{-3}	377	5.6
0.2% (v/v) PPy	1.5×10^{-2}	392	9.8
0.3% (v/v) PPy	2.1×10^{-1}	408	14.2
0.4% (v/v) PPy	5.8×10^{1}	436	22.1

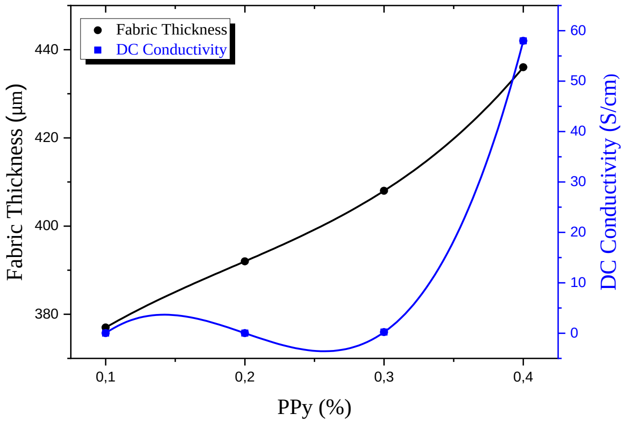

Figure 7. The effect of PPy content on the DC conductivity and fabric thickness of PES-PPy composite fabrics

Table 4 and Figure 7 show the relationship between the DC electrical conductivity and coating thickness values of PES-PPy conductive composite fabrics coated with $FeCl_3$+*p*-TSA initiator-dopant system. According to the measurements, the DC conductivity of PES-PPy composite fabrics increased with the fabric coating thickness. When the uncoated PES fabric was an insulator, PES-PPy fabrics became conductive at certain rates with the addition of PPy to the fabric structure. While the DC conductivity values were realized as a semiconductor level for the PES-PPy composite fabrics in the presence of 0.1% (v/v) PPy and 0.2% (v/v) PPy; the conductive level was realized for the contents of 0.3% (v/v) PPy and 0.4% (v/v) PPy. In particular, the conductivity of PES-PPy conductive composite fabric including 0.4% (v/v) PPy increased 275 times to 5.8×10^{1} S/cm compared to the composite fabric including 0.3% (v/v) PPy. Therefore, 0.4% (v/v) PPy content has been determined as a main threshold for higher DC electrical conductivity. In the literature, conductivity levels varying between semiconductor and metallic levels have been reported in studies performed with different initiators and dopants **[27-29].** Wang et al. (2001) determined the conductivity of polypyrroles synthesized in-situ in the presence of different sulfonic acid dopants and surfactants in the range of 0.57-40.7 S/cm [27]. Kaynak et al (2003) studied the effects of reactant concentration and synthesis parameters on the electrical properties of conductive PPy coated poly(ethylene terephthalate) (PET) fabrics. They reported higher conductivity and/or resistance results between the 10 ohm and 60 ohm depend on synthesis parameters [28]. Oh et al. (2001) reported higher conductivity results of PPy films doped with various dopants and dopant mixtures such as 1 S/cm or 43.3 S/cm [29]. The conductivity increase with coating thickness in the PES-PPy composite fabric structure suggests that PPy is homogeneously coated on PES fabric surface in agreement with the SEM images (Figure 4). Furthermore, it has been found that the $FeCl_3$+*p*-TSA initiator-dopant system used in the coating process improved considerably the DC conductivity. If the coating thickness increases, conductive channels can rise in the composite structure. Thicker coatings lead to pathways that are more conductive, higher conductivity and lower surface resistance [30]. The *p*-TSA used in addition to the $FeCl_3$ initiator in the coating process of PES-PPy fabric markedly reduced the resistance values. Therefore, the electronic properties of conducting polymeric composites in the presence of doping materials improves due to the presence and density of the bipolarons [31-33].

3.5 Electromagnetic Shielding Effectiveness

The coaxial transmission line method determines the electromagnetic shielding ability in frequency range of 30 MHz to 1.5 GHz. The measurement set-up consists of a sample holder with its input and output connected to the network analyzer. The network analyzer is used to generate and receive the electromagnetic signals. The coaxial test fixture is shown in Figure 8.

Electromagnetic shielding is defined as the mitigation of propagating electromagnetic waves incurred by the shielding materials. When an electromagnetic wave come across a fabric surface it can be absorbed, reflected or transmitted and electromagnetic shielding through fabrics can be carried out by absorption or reflection of an electromagnetic signal. The efficacy of the electromagnetic shielding is often characterized as shielding effectiveness measured in decibels (dB) [34,35].

For a single layer of material the SE_T is a sum of three different shielding mechanisms:

$$SE_T(dB) = SE_A + SE_R + SE_{MR} \qquad (1)$$

where SE_A represents the absorption loss of the wave through attenuation in the medium, SE_R represents the shielding by reflection in the medium, and SE_{MR} represents the additional effects due to multiple reflections and absorption in the medium. The effect of multiple reflections between two interfaces of material is neglected if $SE_A \geq 10$ dB.

Metal-coated electromagnetic shield materials reflects electromagnetic waves due to having higher conductivity. Intrinsically conducting polymer coated materials such as conductive fabrics are able to absorb electromagnetic waves and can provide effective protection against electromagnetic radiations. Hence, the EMSE of such conductive polymer coated fabrics is basically a function of surface resistivity or electrical conductivity [16].

The total electromagnetic shielding effectiveness SE_{total} that includes contributions due to reflection and absorption can be expressed as follows: [36,37].

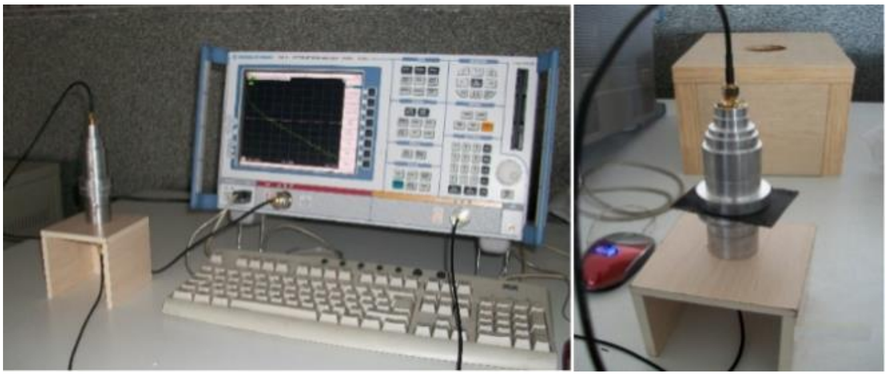

Figure 8. Coaxial transmission line test fixture

$$SE_{Total}\ (dB) = 20\ log\left({}^{E_1}/_{E_2}\right) = 10\ log\left({}^{P_1}/_{P_2}\right) = 20\ log\left({}^{H_1}/_{H_2}\right) \qquad (2)$$

where P_1 (E_1 or H_1) is received power (electric field or magnetic field strength) with the PES-PPy conductive fabric present and P_2 (E_2 or H_2) is received power (electric field or magnetic field strength) without the PES-PPy conductive fabric.

The frequency-dependent EMSE of PPy coated PES fabrics is presented in Figure 9.

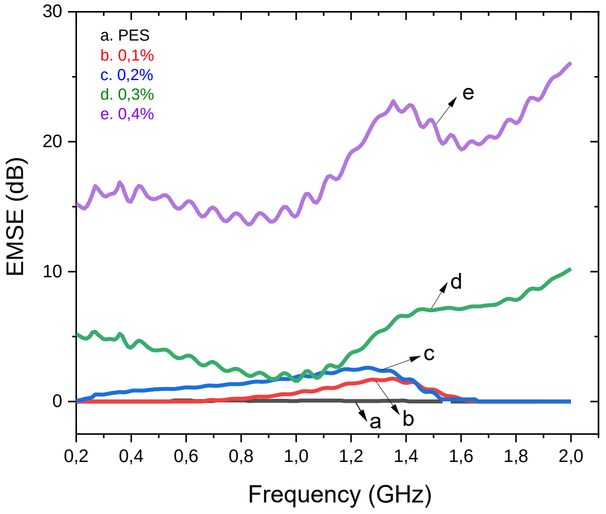

Figure 9. Electromagnetic shielding effectiveness of PES-PPy composite fabrics in the presence of different PPy contents [a. uncoated PES fabric, b. 0.1%, c. 0.2%, d.0.3%, e.0.4%]

The EMSE values of PES-PPy composite fabrics increased with an increasing PPy content. This increase became obvious especially in coated fabrics for 0.4% (v/v) PPy which exhibited higher EMSE comparing with other tested PPy contents in the frequency range between 0.2 and 2 GHz. PES-PPy composite fabrics with coated lower than 0.4% (v/v) PPy exposed the significantly worse electromagnetic shielding effectiveness comparing with the composite fabric coated with 0.4% PPy. This could be expressed by the fact (see Table 4) that PES-PPy composite fabrics with lower dc electrical conductivity and EMSE have similar electromagnetic radiation protection and concluded that the control of EMSE depends on conductivity level of conductive composite fabrics [16,38].

Figure 10 shows the relationship between the DC Conductivity and PPy content of PES-PPy composite fabrics with the shielding efficiency at a frequency of 1.4 GHz.

The in situ chemical coated composite fabrics by conducting polymers ensure better electrostatic discharge (ESD) and electromagnetic shielding effectiveness. The higher electrostatic response of conductive polymer coated woven fabrics arises due to coated fiber that forms conducting domains having high aspect ratio. The woven fabric structure with micropores enhances the charge transport due to formation of continuous network of interconnected conductive regions on the fabric surface and eases the mobility of charge carriers. Since both electrical conductivity as well as magnetic properties are important; the $FeCl_3$+*p*-TSA doped PPy with inherent ferromagnetic behavior was selected. The conductive polymer coated fabrics recommend the electrical conductivity between the 10^{-3} S/cm and 10^{1} S/cm for good shielding efficiency [39,40].

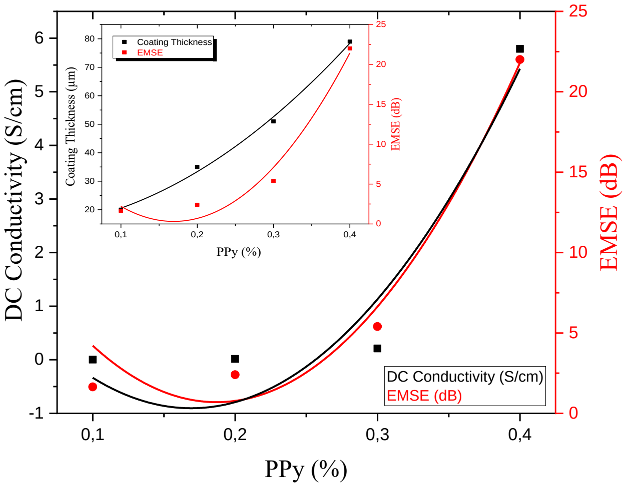

Figure 10. The correlation between the DC Conductivity and PPy content of PES-PPy composite fabrics with the shielding efficiency at a frequency of 1.4 GHz (Inset Figure: The relation between the coating thickness and EMSE of PES-PPy composite fabrics depending on PPy content)

While the PES-PPy composite fabric coated with 0.4% (v/v) PPy shows the highest coating thickness and dc conductivity offers EMSE of 23 dB at 1.4 GHz and 28 dB at 2 GHz; however the EMSE values were measured approximately 5 dB for composite fabrics coated with lower than 0.4% (v/v). The electromagnetic shielding effectiveness of PES-PPy composite fabrics can be enhanced by coating them in the presence of different PPy contents and $FeCl_3$+*p*-TSA initiator-dopant system. The reason for better EMSE of PES-PPy composite fabric can be attributed to the homogeneously coated denser and smaller fibrilar structure as can be seen in Figure 4. As a result, the $FeCl_3$+*p*-TSA initiator-dopant system increased the coating thickness, DC conductivity and electromagnetic shielding behavior of PES-PPy composite fabrics (Figure 10). The effect of composite fabric layer on electromagnetic shielding performance of PES-PPy composite fabrics was presented in Figure 11.

While PES-PPy composite fabric has a certain EMSE value in a single layer for 0,2% (v/v) PPy and 0,3% (v/v) PPy; shielding performance significantly improved when the layered fabric structure was introduced (Figure 11).

The correlation between shielding effectiveness and thickness of a single-layer composite structure has been expressed as follows [41]:

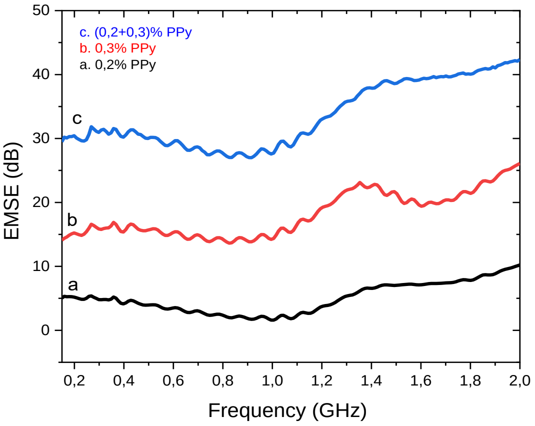

Figure 11. Effect of fabric layer on electromagnetic shielding performance of PES-PPy composite fabrics [a. 0.2% PPy, b. 0,3% PPy, c.(0,2+0,3)%PPy]

$$EMSE\ (dB) = 20\ log\left(1 + \frac{1}{2}\sigma\ dZ_0\right) \qquad (3)$$

σ = DC Conductivity

d = Thickness

Z_0 = Wave impedance in the free space (377Ω)

The Equation (3) deals with EMSE formulation of single layered composite structure which is directly proportional to the DC conductivity and thickness. PES-PPy composite fabrics doped with 0.2% (v/v) PPy and 0.3% (v/v) PPy offer total shielding effectiveness for seperate single layers (layer 1 and layer 2) of PES-PPy composite fabrics was around 10 dB and 26 dB, respectively at a frequency of 2 GHz. However, on increasing the coating thickness by locating successive layers of PES-PPy composite fabrics, the value of total shielding effectiveness reached up to 42.3 dB, for a composite shield fabric containing two layers. Thus, with an increase of ~100% in the thickness of PES-PPy composite fabric structure, its EMSE has been expanded by ~130% (Figure 11).

3.6 Thermal Characteristics

The TGA comparison of uncoated PES fabric and %0.4 (v/v) PPy coated PES composite fabrics in the presence of $FeCl_3$ and $FeCl_3$+*p*-TSA initiator-dopant system were presented in Figure 12.

When the temperature at which polyester fabric begins to degrade is 400 °C; the thermal decomposition start temperatures of PET-PPy fabrics which are coated with 0,4% (v/v) PPy in the presence of $FeCl_3$ and $FeCl_3$+*p*-TSA initiator-dopant system were measured as 395 °C and 390 °C, respectively. Thermal decomposition temperature of polyester fabric has been reported as 350-470 °C in the literature [42]. It has been determined that uncoated PES fabric and PPy coated PES conductive composite fabrics retain their weights up to the temperature when they begin to thermally degrade. While uncoated PES fabric and PPy coated PES composite fabric in the presence of $FeCl_3$ initiator have lost 85% of their weights up to 600 °C; the PPy coated PES fabric in the presence of $FeCl_3$+*p*-TSA initiator-dopant system has kept 25% of its weight (Figure 12). According to TGA results, it can be stated that PES-PPy composite fabrics coated with $FeCl_3$ + *p*-TSA initiator-dopant system have more desirable results in terms of weight loss, especially in high temperature applications.

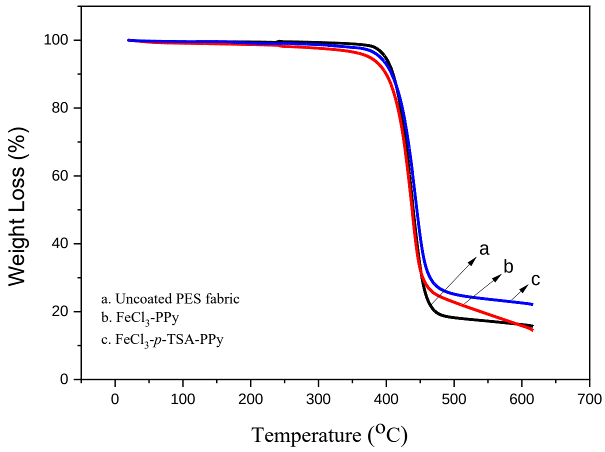

Figure 12. TGA thermograms of uncoated PES fabric and %0.4 (v/v) PPy coated PES composite fabrics in the presence of $FeCl_3$ and $FeCl_3$ +*p*-TSA initiator-dopant system

4. CONCLUSION

In this study, electrically conductive PES-PPy composite fabrics were produced by in-situ chemical polimerization. The effect of PPy content and initiator-dopant system on the electrical conductivity, coating thickness, surface morphology, electromagnetic shielding performance and thermal weight loss was investigated. However the effect of fabric layer was examined in terms of shielding effectiveness.

In PES-PPy composite fabric, a new absorption peak (C=C ring vibration) was observed at 1558 cm^{-1} and shifted to 1531 cm^{-1} by the increasing of PPy content that indicates the PPy was included to the polyester composite fabric. A new peak appeared at 400 eV depicted that NH^+ groups were introduced to polyester macromolecule chains indicating the incorporation of PPy particles. While a homogeneously coated PPy layers were observed in the presence of $FeCl_3$; an extremely dense PPy nanoparticle layer were observed on the fabric surface in the presence of $FeCl_3$ + *p*-TSA initiator-dopant system. Unlike the $FeCl_3$, PPy coated regions having denser and smaller globular nanoparticles were observed in the $FeCl_3$ + *p*-TSA initiator-dopant coating system. The DC conductivity of $FeCl_3$+*p*-TSA doped PES-PPy composite fabric is 5800 times higher than $FeCl_3$ doped PES-PPy composite fabric which could be due to the homogeneously distribution of PPy nanoparticles in the presence of *p*-TSA dopant. DC conductivity of PES-PPy composite fabrics increased linearly with the fabric coating thickness. 0.4% (v/v) PPy content has been determined as a main threshold for higher

DC electrical conductivity. The EMSE values of PES-PPy composite fabrics increased with an increasing PPy content. This increase became obvious especially in coated fabrics for 0.4% (v/v) PPy which exhibited higher EMSE comparing with other tested PPy contents in the frequency range between 0.2 and 2 GHz. The electromagnetic shielding effectiveness of PES-PPy composite fabrics was enhanced by coating them in the presence of different PPy contents and $FeCl_3$+*p*-TSA initiator-dopant system. A correlation was found between shielding effectiveness and thickness of a single-layer composite structure. Increase in the coating thickness by locating successive layers of PES-PPy composite fabrics, the value of total shielding effectiveness reached up to 42.3 dB for a composite shield fabric containing two layers. According to TGA results, it can be stated that PES-PPy composite fabrics coated with $FeCl_3$ + *p*-TSA initiator-dopant system have more desirable results in terms of weight loss, especially in high temperature applications. PES-PPy composite fabric doped by 0.4% (v/v) PPy supports the its conformity as a promising shield material.

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