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Research paper

Electrically Conductive Polyester Fabrics Embedded Polyaniline

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Abstract

Recently, conductive fabric has attracted massive attention among researchers due to their unique conductive properties with a wide range of possible applications. This study explores the fabrication of poly aniline (PANI) conductive fabric through an immersion technique of polyester fabric in PANI solution. Two types of acids (sulphuric acid (H_2SO_4) and *p*-toulene sulfonic acid (*p*TSA) have been employed as the doping agent to induce the conductivity in various weight percentages (0.3, 0.6 and 0.9 wt%) with immersion time of 5, 10 and 15 minutes. The fabricated conducting fabrics were then characterized by Fourier Transform Infrared Spectroscopy with attenuated total reflection (FTIR-ATR) and X-ray Diffraction (XRD) for analyses of chemical structure and phase identification respectively. Their morphologies were observed by Scanning Electron Microscope (SEM) which revealed the various fibrous structure. The finding is in line with the electrical conductivity properties of the fabrics observed using Four-point probe technique. Optimum conductivity of the conductive fabrics were found to be at 0.6 wt. % for both types of acid which are 1.30 x 10^{-2} S/cm (H_2SO_4) and 1.39 x10^{-3} S/cm (*p*TSA). Meanwhile, the varied immersion time showed no significant changes on this property, due to the short time laps. For FTIR results, the peaks confirmed the presence of PANI-EB together with the introduced acid within the PANI backbone. Collectively, H_2SO_4 is found to be a good candidate as doping agent, deduced from obtained conductivity values and structural properties.

Keywords: *Polyaniline; Conductive fabric; Polyester; HCl; pTSA.*

1. Introduction

In the past 20 years, various types of different conducting polymer have been developed. This leads to a Nobel Prize award in the year 2000 for Alan J. Heeger, Hideki Shirakawa and Alan G. MacDiarmid (1977), for their development and discovery of electrically conducting polymer. According to G. Kaur *et al*.[4], conducting polymer otherwise known as intrinsically conductive polymer (ICP) is created from engineered polymer found in the last decade for instance, Polyaniline (PANI), Polypyrole (PPy) and Polythiophene (PT). The ability of these polymers to conduct electricity have attracted scientists all over the world from many fields such as polymer science, electrical engineering, electronics, synthetic chemistry, and electrochemistry. With the growth of Research and Development (R&D) community nowadays, further stability of the materials and enhancing the properties of these polymers are currently being studied and explored.

Among numerous of CPs, PANI is a standout conducting polymer with numerous advantages. It receives numerous surveillance because it is environmentally stable, able to mix with thermoplastics, has high conductivity, minimal cost, simplicity of synthesis, has special redox behaviour and able to electrically switch between its conductive and insulator states by doping or dedoping process [11]. The reasons on the interest in many areas of fields are due to the fact that it can easily be synthesized and processed. PANI exists at various oxidation states which can be doped by using different types of dopant in order to induce the conductivity property [6]. The capacity of PANI to be used in bioelectronics gadget has roused numerous investigations to be directed to release its capability to fit in different controls [3]. As a standout amongst conducting polymers, PANI has major limitation in rendering the electrical properties. This is expected to be due to the crucial dopant selection process [5]. Distinctive sort of dopants may indicate diverse conductivity in PANI system [7].

Recently, the development of fabrics with new properties and applications has received great attention and one of these properties is the electrical conductivity [14]. General approaches to improve the properties of textile fabrics include the embedment of relevant non-textile particles within the structure or covering the surface with those particles via various techniques. A conductive fabric is a fabric or textile that can lead and conduct electricity which is an incredible consideration and offers numerous development for applications. The use of PANI embedded fabric as an ammonia sensor, electromagnetic protection, static charge dissemination, electrochemical gadgets or valuable metals recuperation has been accounted recently [14]. The embedment of polyaniline in fabric will hold the adaptability of the fabric and electrical conductivity of conducting polymer [2]. The fabric itself has an electrical resistance which is supported by the properties of the con-

ductive fibers, their interconnection inside the fabric and the geometry of the fabrics [11]. In this study, polyester fabric will be used as a substrate due to its ability to retain its original shape from stretching, shrinking or wrinkling and is stable in acid media [15].

The conductivity of PANI embedded on polyester fabric will be upgraded by doping with acid, which in this situation are *p*-touloune sulfonic acid (*p*TSA) and sulfuric acid as the doping agents. The doped polyaniline will influence the electrical conductivity property of PANI. As the acid has the ability in making conductive fabric, this fabric will have great properties and give a strong platform for incorporating process ability and show a variety of functionalities for the polymer in conductive fabrics.

2. Experimental

2.1. Materials

Polyaniline emeraldine base (PANI-EB, 50 kDa), p-toluene sulfonic acid (*p*TSA) and sulphuric acid were purchased from Sigma Aldrich. N, N-Dimethylformamide (DMF) which acts as a solvent was taken from the laboratory. While the polyester fabric that is used in this study was purchased from Jakel (M) Trading.

2.2. Sample preparation

Doped polyaniline was prepared by dissolving 0.3 wt. % of PANI-EB (0.18 g) into DMF solution (60 ml). 0.3 wt. % of pTSA acid or sulphuric acid (0.18 g) were prepared. For doped solution, pTSA acid or sulphuric acid were added into the solution. The solution turned from blue to green indicating that the solution is in conductive state (emeraldine salt). This step was repeated for another weight percent of dopant (0.6 wt. % and 0.9 wt. %). A solution of dissolved (0.3 wt. %) PANI-EB without addition of acid acted as a control (blue colour) which is non-conductive (undoped PANI). This step was followed by a centrifuged process for 1 hour at 4000 rpm to separate the solutions from the precipitate. Then, the precipitate was filtered from the solutions to obtain pTSA or sulphuric acid-doped PANI solutions free from any undissolved particles. Polyester fabric was prepared and cut into 3 cm x 3 cm dimension. Then the fabrics were immersed into the doped and undoped PANI solutions for 15 minutes. Next, the samples were dried at room temperature and kept in the dark until used. This was followed by characterisation using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Four Probe point for analyses of their chemical structure, phase identification, morphology and conductivity respectively.

2.3. Material Characterization

All fabrics were analysed using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Four Point Probe to investigate any changes in the functional group, phase identification, morphology and optical conductivity respectively.

2.3.1. FTIR spectroscopy

Fourier Transform Infrared spectroscopy was conducted on Perkin-Elmer spectrometer (model spectrum RX-1) in the range of 400-4000 cm^{-1} and with a resolution of 2 cm^{-1}.

2.3.2. XRD

X-ray Diffraction (XRD) instrumentation is used to confirm the presence of PANI's phase in the sample. X-ray diffraction patterns were taken using a diffractometer fitted with CuKα radiation (λ= 1.5404 nm) at 40 kV and 40 mA in the 4-60°2 region.

2.3.3. SEM

A Jeol JSM-6300 Scanning Electron Microscope (SEM) was used to examine the morphology of doped and undoped PANI. The undoped and doped fabric samples were sputter coated with a thin layer of Au. SEM analyses were performed using an acceleration voltage of 20 kV

2.3.4. Four-point probe

The conductivity of the sample was measured using model 2450 Source Meter four-point probe. Four-point probe is a simple testing of resistance of a sample by passing through two probes for measuring voltage and another two probes to measure the current flow. The conductivity of the sample was obtained by plotting voltage and current.

3. Results and discussion

3.1. Visual assessment

Fig.1: Visual assessment of the immersed fabric into the undoped (blue color) and doped PANI (green color).

Figure 1 shows the polyester fabric undergoing colour transition from white to blue and finally became green colour. The bare fabric is in its normal colour which is white due to no immersion solution of PANI and acid dopant. The bare fabric then changed its colour to blue after immersion into undoped PANI solution which is no addition of dopant in the solution. This shows that PANI-EB is in emeraldine base state (undoped). Meanwhile, the green colour polyester fabric shows that PANI is in emeraldine salt (doped) state after immersion in doped PANI solution where a dopant agent (sulphuric acid or *p*TSA) was added into PANI solution to induce its conductivity properties. This proves that doping has successfully taken place where the acid dopant works to protonate the PANI, resulting in changing colour from blue to green [9].

3.2. FTIR analysis

Functional groups present in PANI fabric were identified by using Fourier Transform Infrared Spectroscopy (FTIR). Figure 2 shows the spectra of FTIR of polyaniline fabric undoped and doped with *p*TSA and sulphuric acid. All spectra show similar bands and peaks. There are no significant differences and changes in the FTIR analysis of all undoped and doped PANI fabrics [7]. The only obvious difference in peak occurs at 1021 cm^{-1} for PANI-EB with sulphuric acid and 1023 cm^{-1} for PANI-EB with *p*TSA, which are attributed to the presence of S=O and SO_3 respectively. For PANI-EB doped with sulphuric acid, the presence of S=O peak at 1021 cm^{-1} indicates that PANI-EB was successfully doped with sulphuric acid. While for the PANI-EB doped with *p*TSA, the peak at 1023 cm^{-1} for SO_3 indicates the presence of dopant. There is C=C bond stretching of vibration for benzene unit of

PANI-EB doped with sulphuric acid at 1501 cm^{-1} and 1509 cm^{-1} for PANI-EB doped with *p*TSA [11]. The bands at 1417 cm^{-1} are attributed to C-C aromatic ring for benzoid unit for undoped PANI-EB and PANI-EB doped with *p*TSA while for PANI-EB doped with sulphuric acid, the peak for C-C was located at 1410 cm^{-1}. The main feature of PANI could be observed at C-N stretching mode of benzenoid units and C-N secondary aromatic amine (-N-benzenoid-N-). For C-N stretching mode of benzenoid unit of undoped PANI-EB, the band is located at 1350 cm^{-1}. This peak is also identical and present in PANI-EB doped with sulphuric acid. While for PANI-EB doped with *p*TSA the peak is at 1339 cm^{-1}. For C-N secondary aromatic amine, the band is at 1242 cm^{-1} and this applies for all samples. This result is consistent with those observed by Molina, Esteves, Fernández, Bonastre, & Cases [7]. Table 1 lists the FTIR peaks for undoped PANI-EB, PANI-EB doped with *p*TSA and PANI-EB doped with sulphuric acid.

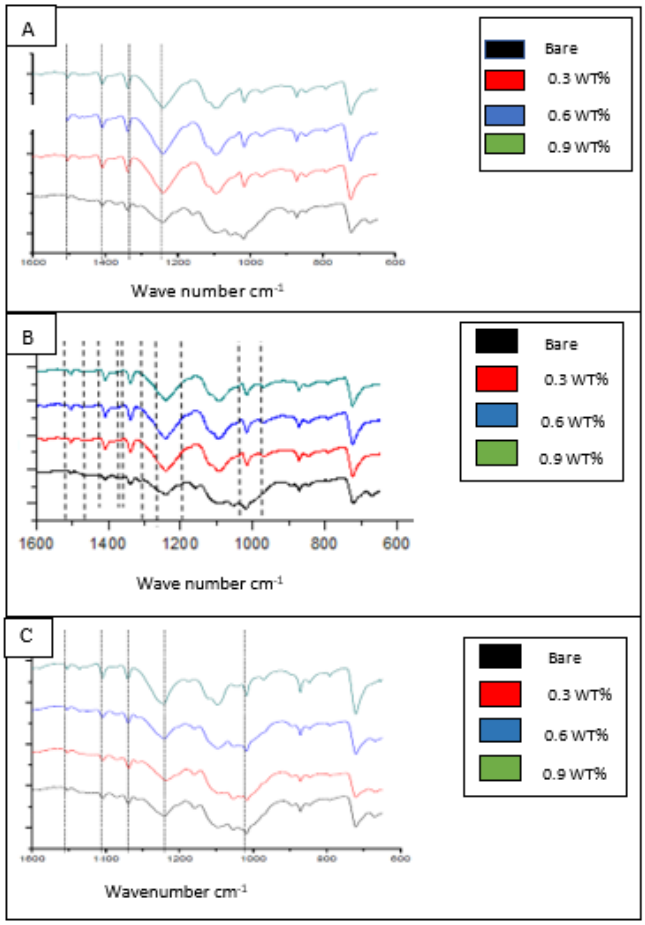

Fig. 2: FTIR spectra of A) undoped PANI-EB, B) PANI-EB doped with *p*TSA C) PANI-EB doped with sulphuric acid

Table 1: FTIR peaks for PANI-EB, PANI-EB doped with *p*TSA and PANI-EB doped with sulphuric acid

Functional Group	PANI-EB	PANI-EB + *p*TSA (cm^{-1})	PANI EB + sulphuric acid (cm^{-1})
S=O	-	-	1021
C=C bond stretching	1501	1509	1501
C-C aromatic	1417	1417	1410
C-N stretching mode of benzenoid unit	1350	1339	1350
C-N secondary aromatic	1242	1242	1242
SO_3	-	1023	-

3.3. XRD

XRD was used to determine the phase and crystallographic information of undoped and doped PANI fabrics. X-ray diffraction pattern of Figure 3 indicates a broad angle asymmetric scattering peak from 10^o to 30^o.

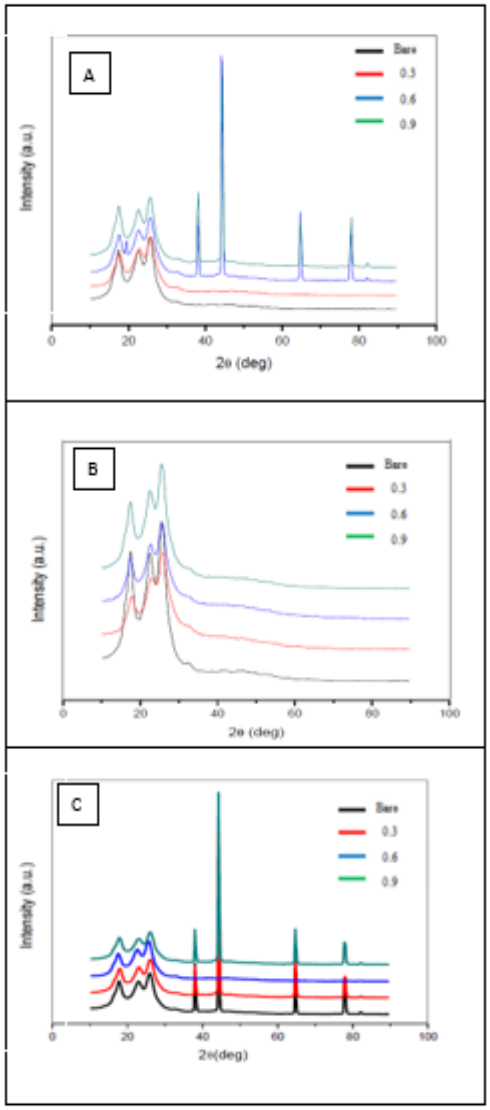

Fig. 3: X-Ray diffractogram of A) undoped PANI-EB B) doped PANI with sulphuric acid C) doped PANI with *p*TSA

The diffractogram of undoped PANI EB embedded in polyester fabric shows high relative intensity at 2□ = 25.67°. For doped PANI-EB with sulfuric acid, the high relative intensity was found to be located at 2□=25.67°, while for doped PANI-EB with *p*TSA this was found at 2□ = 25.70° ~ 26.05°. These results are similar to those reported by by Sakthivel & Boopathi [14] where the maxima peak of PANI coated on polyester fabric was found to be at 2□= 21.17° and 26.49°. The other peaks in the diffractograms correspond to impurities present in the fabric. The intensity values of doped PANI with acid is higher than undoped PANI-EB.

3.4. SEM

The surface morphology of the PANI fabrics were determined using Secondary Electron Microscope (SEM) at two different magnification images (180x and 500x). SEM images shown in Figure 4 for the PANI embedded fabrics were found to be quite irregular and scattered.

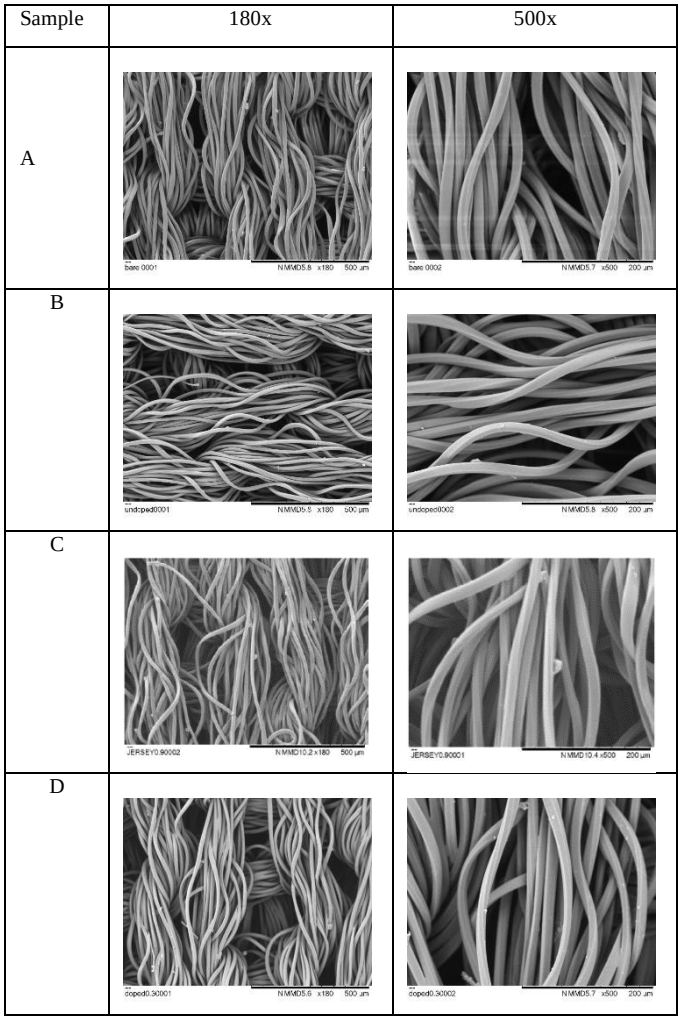

Fig. 4: SEM images of A) bare fabric B) undoped PANI-EB fabric C) doped PANI-EB with sulphuric acid fabric D) doped PANI-EB with *p*TSA fabric with 180x and 500x magnification

As can be seen in the SEM micrographs of Figure 4 the morphology surface of all the samples showed no significant changes. The surfaces' fibres of the fabric are smooth [13]. Although the samples have different compositions, the bare fabric, undoped and doped fabric showed no difference in surface structure which is fibrous [1]. Thus it can be assumed that relatively small amount of PANI has dissolved into the fabric, hence no distinctive differences could be seen from the images. For future study, Energy Dispersive X-ray analyser (EDX) needs to be done to examine the elemental composition of the sample. This is important to be performed to differentiate and determine any changes of the element present on the sample.

3.5. Electrical conductivity

The electrical conductivity of the dried fabric was determined at ambient room temperature using four-point probe. As we can see in Table 2 bare polyester fabric and undoped PANI-EB fabric resulted in negative conductivity which means that the electrical conductivity cannot be detected. The instrument was unable to produce the data due to the relatively low conductivity of the samples. The samples have shown no signal; thus negative values were recorded. This is due to the absence of acid within the PANI that acts as a dopant to render the conductivity.

Table 2: Electrical conductivity for doped PANI with sulphuric acid and doped PANI with *p*TSA.

Acid	Weight percent (wt. %)	Conductivity (S/m)
Doped PANI with sulphuric acid	0.3	6.50×10^{-3}
	0.6	1.30×10^{-2}
	0.9	2.50×10^{-3}
Doped PANI with *p*TSA	0.3	1.47×10^{-3}
	0.6	1.39×10^{-3}
	0.9	6.48×10^{-4}

PANI-EB doped with sulphuric acid have conductivity of 6.5×10^{-3} S/cm, 1.3×10^{-2} S/cm and 2.5×10^{-3} S/cm for 0.3, 0.6 and 0.9 wt. % respectively while PANI-EB doped with *p*TSA, have conductivity of 1.47×10^{-3} S/cm, 1.39×10^{-3} S/cm, 6.48×10^{-4} S/cm for 0.3, 0.6 and 0.9 wt. % respectively. This result is acceptable and proved that acid dopant had induced the conductivity properties into PANI-EB. This claim can also be supported by Mostafaei & Zolriasatein [8] which stated that common acceptable range for conductivity of PANI is in the range of 10^{-3} to 10^{3} S/cm.

From these results, it is shown that the highest conductivity for all samples were obtained at 0.6 wt. %. This work proved that the optimum composition of PANI EB with acid dopant is 0.6 wt. %. This study can also conclude that sulphuric acid works best as a dopant agent since it gave higher conductivity when compared with *p*TSA which are 1.30×10^{-2} S/cm and 1.39×10^{-3} S/cm respectively. The conductivity of the PANI fabric increased due to the increase in presence of polaron at the backbone of PANI. This is obtained from the available protons from the acid dopant [10].

4. Conclusion

The fabrication of polyaniline conductive fabric using sulphuric acid or *p*TSA as a dopant were successfully prepared by immersion technique. The structural properties of the fabrics have been determined by FTIR that confirmed PANI fabric with different acid dopant were successfully doped. The morphology of these fabrics showed no significant difference but it gives good respond on electrical conductivity. This proves that the conductivity property of PANI is not affected by the structure of the fabric. XRD was performed in this study and can conclude that PANI was present on the surface of the fabric. The optimum conductivity was found to be at 0.6 wt. % and sulphuric acid works as the best dopant agent which gave higher conductivity than *p*TSA.

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References

[1] Bajgar, V., Penhaker, M., Martinková, L., Pavlovič, A., Bober, P., Trchová, M., & Stejskal, J. (2016). Cotton fabric coated with conducting polymers and its application in monitoring of carnivorous plant response sensors; 16(4): 498.

[2] Geetha, S., Satheesh, K.K., Trivedi, D.C. (2005). Polyaniline reinforced conducting E-Glass fabric using 4-chloro-3-methyl phenol as secondary dopant for the control of electromagnetic radiations. Composites Science and Technology; 65: 973-980.

[3] Huanhuan, W., Jianyi, L., & Ze, X.S. (2016). Polyaniline (PANI) based electrode materials for energy storage and conversion, Journal of Science: Advanced Materials and Devices; 72: 225-255.

[4] Kaur, G., Adhikari, R., Cass, P., Bown, M., & Gunatillake, P. (2015). Electrically conductive polymers and composites for biomedical applications. Retrieved from https://pubs.rsc.org/en/content/articlelanding/2015

[5] Li, Y. (2015). Organic Optoelectronic Materials, 91. Retrieved from https://doi.org/10.1007/978-3-319-16862-3

[6] Mahat, M. M., Mawad, D., Nelson, G. W., Fearn, S., Palgrave, R. G., Payne, D. J., & Stevens, M. M. (2015). Elucidating the deprotonation of polyaniline films by X-ray photoelectron spectroscopy. J. Mater. Chem. C; 3(27): 7180–7186.

[7] Molina, J., Esteves, M. F., Fernández, J., Bonastre, J., & Cases, F. (2015). Polyaniline coated conducting fabrics chemical and electrochemical characterization. European Polymer Journal; 47(10): 2003–2015.
[8] Mostafaei, A., & Zolriasatein, A. (2012). Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods. Progress in Natural Science: Materials International; 22(4): 273–280.
[9] Nicolas-Debarnot, D., & Poncin-Epaillard, F. (2003). Polyaniline as a new sensitive layer for gas sensors. Analytica Chimica Acta; 475(1–2): 1–15.
[10] Nurzatul, S., O, I., Zainal, Z., & Adawiyah, R. (2017). A conductive fabric with anti-infection properties. ScienceDirect; 00: 1–9.
[11] Parel, M. M. P., Gillado, A. V., & Herrera, M. U. (2018). Morphology and electrical conductivity of polyaniline coating on acetate film. surfaces and interfaces, (2017); 74–77.
[12] Petersen P. H. R., Pate M, & Eichhoff, J. (2011) Electronic textile resistor design and fabric resistivity characterization.. Text Res J8:1395-1404.
[13] Rehnby, W., Gustafsson, M., & Skrifvars, M. (2008). Coating of textile fabrics with conductive polymers for smart textile applications. Welcome to Ambience'08; 100–103.
[14] Sakthivel, S., & Boopathi, A. (2015). Study of polyaniline coated conducting polyester fabric structural characterizations; 123–129.
[15] Zhao, Z., Zhou, J., Fan, T., Li, L., Liu, Z., Liu, Y., & Lu, M. (2018). An effective surface modification of polyester fabrics for improving the interfacial deposition of polypyrrole layer. Materials Chemistry and Physics; 203: 89–96.