Effect of Polymerization Variables on the Electrical Conductivity of Polyaniline Functionalized Cotton Textiles

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ABSTRACT
Polyaniline functionalized cotton textiles were synthesized via in situ oxidative polymerization of aniline using hydrated ferric chloride solution in acidic media. Variation in conductivity was examined against polymerization variables such as amount of aniline, oxidant, reaction media, and time. Effects of polyaniline functionalization on the structural features of cotton textiles at optimum polymerization conditions were screened by FT-IR, TGA, and SEM instruments. FT-IR profiles at 1440 cm\(^{-1}\) and 1560 cm\(^{-1}\) proved the existence of benzoid and quinoid rings within the cotton structure, which confirmed the introduction of polyaniline in its conductive form, emeraldine salt. Thermal studies revealed the existence of polyaniline, which further enhanced the thermal stability of cotton textiles. SEM microstructure also proved the formation of nonuniform surfaces with a considerable amount of debris, buds, and channels due to the inclusion of polyaniline. Polyaniline functionalization has shown substantial enhancement of electrical conductivity by changing insulating cotton to semiconductor. At optimum polymerization variables ([aniline] = 1 M, [oxidant] = 1 M, [acid] = 0.5 M, and time = 24 hrs), maximum conductivity was registered at 7.63 \(\times\) \(10^{-3}\) S/cm, which is equivalent to the conductivity of semiconductor materials.

Keywords: Conductivity, Cotton fibers, Functionalization, Oxidation, Polyaniline.

1. INTRODUCTION
Organic polymers such as polyaniline, polypyrrole, and polythiophene are commonly known as conducting polymers, which mimic metallic conduction (Guarino et al., 2016). As a result, they have attracted considerable attention from scientists and industrialists for their wonderful electrical conductivity, optical properties, and ion exchange characteristics. Polyaniline (PAni) is one of the most applicable conductive polymers using the cheapest monomer with the advantage of facile polymerization (Teklu et al., 2017). Addition of oxidizing or reducing agents and variation of reaction media can alter the electronic structure of polyaniline by varying the ratio of oxidation-reduction states of amino functionalities from fully oxidized pernigraniline to completely reduced luecoemeraldine base (Fig 1) (Jamadade et al., 2010).

Polyaniline backbone is saturated with reactive amino-functionalities comprising of benzoids and quinoids which are accountable for the fascinating surface phenomenon. Sole
polyaniline commonly exists in the form of aggregated powder which possesses limited surface area, poor mechanical strength, and difficult to process in aqueous media (Kanwal et al., 2013; Teklu et al., 2020). These limitations hamper the scope, versatility and multidisciplinary applications of polyaniline. Consequently, polyaniline can be blended with other polymers (Bhadra et al., 2017) or coated on flexible supporting substrates such as textiles and fibers (Zareh et al., 2011) to maximize surface area, improve mechanical strength, and alleviate the processability issues (Onar et al., 2009) associated with bulk polyaniline to display enhanced properties and better performance.

Figure 1. Electronic structure of different forms of polyaniline, where $\text{A}^-$ denotes arbitrary anion (Ray et al., 1989).

The demand to develop textiles or fabrics with enhanced functionalities is growing rapidly (Kim et al., 2006; Gicevicius et al., 2020). Polyaniline salt has played a key role as a conductive filler to synthesize electrically conductive textiles (Hoghoghifard et al., 2015). Different scholars have reported that polyaniline modified textiles are used as smart textiles, sensors, EMI shielding, and medical clothes (Dhawan et al., 1998; Bhat et al., 2006). Cotton (*Gossypium hirsutum*), which grows comfortably in Tigray, northern Ethiopia, is one of the most important natural fibers used in the textile industry (Teklu et al., 2020). It is commonly used as a
supporting substrate (Bajgar et al., 2016) to carry conducting species because it is abundant, light weight, and low cost (Mondal et al., 2018).

Polymerization of aniline and functionalization of textiles can be done at the same time using in situ chemical polymerization (Jiang et al., 2008) which is known as a nondestructive technique. Moreover, in situ oxidative polymerization is a proven method to avoid aggregate formation and maximize surface area, which is known to be a suitable technique for mass production at a reasonable cost (Lekpittaya et al., 2004). However, the application of cotton fibers as a substrate phase has certain shortcomings such as high moisture regain when exposed to water resulting in swelling (Cruz et al., 2017). Consequently, in situ oxidative polymerization and subsequent functionalization play synergistic effect by enhancing conductivity and hydrophobic nature, thereby reducing water absorption feature of cotton textiles (Nouri et al., 2000).

Research findings also suggested the electrical conductivity of electroactive polymers depends on polymerization variables such as type of monomer, oxidant and dopant, concentrations, solution media, and other reaction conditions (Qiu et al., 2020). An investigation on polyaniline coated cellulose composites proved that changing dopant concentration greatly affects the electrical conductivity. However, severe acidity causes degradation of polymer chains resulting in a decline in the electrical conductivity of the system (Yuningsih et al., 2017). There are also opposite reports about the effects of the monomer-oxidant ratio on the electrical conductivity of polyaniline and polyaniline functionalized fabrics (Patil and Deogaonkar, 2012). Hence, the investigation of polymerization variables that are expected to influence the electrical conductivity of polyaniline functionalized textiles has become mandatory.

Therefore, the purpose of this research is to study the effect of polymerization variables such as amount of aniline, oxidant, reaction media, and time on the structure and electrical conductivity of polyaniline functionalized cotton textiles.

2. MATERIALS AND METHODS
2.1. Chemicals and Materials
The following reagents were of analytical grade and used without further purification: aniline, ferric chloride hexahydrate, hydrochloric acid, chloroform, acetone and ethanol purchased from Merck Chemical Co. (Germany) through a local agency. Cotton (Gossypium hirsutum) textiles
were obtained from the local market in Humera, Tigray, Northern Ethiopia. It was washed with double distilled water, followed by acetone and ethanol, and finally dried in the air at room temperature.

2.2. In situ Polymerization of Aniline on Cotton Textiles

The effects of polymerization variables were studied by varying the amount of aniline, oxidant, solution media and reaction time at room temperature. In situ chemical polymerization of aniline on cotton textiles were carried out using the following procedure: 10 g of cotton textile was soaked in 150 mL of hydrochloric acid concentrations (0.1, 0.3, 0.5, 0.7, 1, 1.5, and 2 M) with stirring. 150 mL of aniline concentrations (0.1, 0.5, 1, 1.5, and 2 M) were added to the flask containing acidified textile with subsequent stirring. Equal volumes of hydrated ferric chloride solution at different concentrations (0.1, 0.5, 1, 1.5, and 2 M) were added drop wise while stirring (Razak et al., 2012; Engin and Usta, 2014), and the polymerization process was allowed for (1, 6, 12, 24, and 48 hrs) at room temperature.

Upon addition of the hydrated ferric chloride solution, the mixture changed first to blue, then to green, and then to dark green in a few minutes. Polyaniline functionalized cotton textiles were filtered and washed with a 0.3 M HCl solution followed by double distilled water until the filtrate became colorless. It was oven dried at 50 °C. After determination of optimum values, corresponding structural experiments were adjusted at a concentration of 1.0 M aniline, 1.0 M oxidant [FeCl₃.6H₂O], 0.5 M HCl, and 24 hrs of polymerization time.

2.3. Characterization of Polyaniline Functionalized Cotton Textiles

Sole polyaniline and polyaniline functionalized cotton textiles were characterized using a Fourier transform infrared (FT-IR) spectrometer (Bruker Vector). They were subjected to thermal analysis on a simultaneous thermal analyzer (DSC-TGA SDT-Q600) from 25 °C to 600 °C to monitor the weight loss as a function of temperature. Surface microstructures were examined by a scanning electron microscope (SEM) (JSM-IT300LV, JEOL, USA) at a magnification of 300X.

2.4. Electrical Conductivity

Polyaniline functionalized cotton textiles were immersed in chloroform and subjected to Mesdan Autowash at a speed of 40 rpm at 60 °C for 90 minutes. The electrical conductivity of the liquid extract was measured using a portable conductometer device (Hanna Instruments HI 8033) (Teklu et al., 2020).
3. RESULTS AND DISCUSSION

3.1. Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectra of sole cotton textile and polyaniline functionalized cotton textile are shown in figure 2. The band at 3400 cm$^{-1}$ (Fig 2B) represents N-H stretching vibration of amino functionalities in conjunction with H-bonding, while the peak at 3300 cm$^{-1}$ (Fig 2A) corresponds to O-H stretching vibration of hydroxyl groups in cellulose (Xu et al., 2016) of cotton textile. There is a noticeable shift towards higher wavenumber on polyaniline functionalization of cotton textiles as compared to the control sample, bare cotton textiles. A very weak signal at 2900 cm$^{-1}$ belongs to C-H stretching vibration of aliphatic hydrocarbons from the cellulose of cotton textiles. The band at 1730 cm$^{-1}$ corresponds to the presence of C=O stretching vibrations of carbonyl groups introduced from cotton textiles (Sakthivel and Boopathi, 2015). However, the peak intensity was noticeably lessened by the functionalization of polyaniline.

New bands were observed at 1440 cm$^{-1}$ and 1560 cm$^{-1}$, which could be distinguished as C-N stretching vibration of benzoid (N-B-N) and C=N stretching modes of quinoid (N=Q=N) ring structures of polyaniline, respectively (Hoghoghifard et al., 2015). Another confirmatory peak at 1160 cm$^{-1}$ is peculiar to the presence of delocalized electrons in the system, which is derived from polyaniline (Onar et al., 2009). The peak at 1030 cm$^{-1}$ and 1070 cm$^{-1}$ represents to C-O β-glycosidic linkage of glucose in cellulose (Zhang et al., 2014).

![Figure 2. FT-IR spectra of (A) cotton textile and (B) polyaniline functionalized cotton textiles.](image-url)
3.2. Thermogravimetric Analysis (TGA)

Thermal stability of cotton textiles (used as a control) and polyaniline functionalized cotton textiles were examined gravimetrically, and the results are presented in figure 3. The first degradation peak, which extends up to 105 °C, shows mass loss due to evaporation of moisture and water (Razaq et al., 2015). However, the mass loss is less for polyaniline functionalized cotton textiles (Fig 3B). This result further supported the hypothesis that the introduction of polyaniline can suppress the hygroscopic nature of cotton textiles by empowering hydrophobicity. A very sharp degradation peak at 290 °C represents the decomposition of organic matter from cotton textiles. The last stage beyond 400 °C (Fig 3B) represents the degradation of the polyaniline backbone, which is absent in the control sample, cotton textiles (Fig 3A). The introduction of polyaniline further enhanced the thermal stability of cotton textiles (Muthukumar and Thilagavathi, 2012).

Figure 3. TGA thermogram of (A) cotton textile, (B) polyaniline functionalized cotton textiles.

3.3. Surface Morphology (SEM)

SEM micrographs of cotton textiles and polyaniline functionalized cotton textiles are presented in figure 4. It is clearly visible that cotton textile naturally possesses smooth surfaces. SEM microstructure of polyaniline functionalized cotton textile revealed the formation of nonuniform
surfaces and a considerable amount of debris (Nouri et al., 2000), buds, and channels compared to the uniform surface of cotton textiles.

![SEM microstructures of (A) cotton textiles, (B) polyaniline functionalized cotton textiles.](image)

Figure 4. SEM microstructures of (A) cotton textiles, (B) polyaniline functionalized cotton textiles.

### 3.4. Optimizing Effect of Polymerization Variables on Electrical Conductivity

#### 3.4.1. Effect of Monomer Concentration on Electrical Conductivity

The monomer (aniline) concentration used for this study was 0.1, 0.5, 1, 1.5, and 2 M at constant [FeCl₃·6H₂O] oxidant and [HCl] acid concentration (both 0.5 M) for 12 hrs of polymerization time at room temperature.

Subsequent results of electrical conductivities of sole polyaniline and polyaniline functionalized cotton textiles are presented in figure 5A. The maximum electrical conductivity achieved for sole polyaniline is 0.76 S/cm, which lies in the metallic conduction, while that of polyaniline functionalized cotton textiles is equivalent to semiconductors (10⁻⁶ S/cm to 10⁻⁴ S/cm) for the ranges of aniline concentrations. This result confirmed polyaniline is introduced to the system in the partially oxidized form called emeraldine salt (Teklu et al., 2017; Razaq et al., 2015). Electrical conductivity was linearly increased with an increase in concentration of aniline up to some level. Boosting electrical conductivity with an increased amount of aniline is evidence for enhanced level of doping by adding mobile charges along with polyaniline backbone.

On the contrary, the electrical conductivity was decreased to some extent with further increase of aniline beyond 1 M, which might be partially attributed to the existence of unreacted leftovers as the oxidant exists in limited amount in the polymerization process. Furthermore, larger polymer chains and oligomers might exist in dynamic equilibrium causing partial
dedoping. For this reason, the electrical conductivity is significantly decreased from $10^{-3}$ S/cm to $10^{-4}$ S/cm (Bhadra et al., 2017; He et al., 2016). Although the method of preparation is different, the findings of the present study are equivalent with the existing literature values, which ranges from $1.07 \times 10^{-4}$ S/cm to $2.06 \times 10^{-4}$ S/cm (Teli et al., 2014). However, the electrical conductivity of the current study is significantly smaller than that of polyaniline functionalized cellulose sheet ($9 \times 10^{-2}$ S/cm) (Razaq et al., 2015).

Figure 5. Effect of (A) aniline concentration [oxidant = 0.1 M & HCl = 0.1 M] for 12 h and (B) polymerization time [aniline = 1.0 M, oxidant = 1.0 M, & HCl = 0.5 M] [(A) sole polyaniline and (B, C, D, E, and F) represent polyaniline functionalized cotton textiles at room temperature.

3.4.2. **Effect of Oxidant Concentration on Electrical Conductivity**

The effect of [FeCl$_3$·6H$_2$O] oxidant was carried out at 5 different concentrations (0.1, 0.5, 1, 1.5, and 2 M) at constant monomer (1 M), and HCl acid (0.1 M) concentrations for 12 hrs of polymerization time at room temperature.

The corresponding results of the effect of oxidant concentration on the electrical conductivity of polyaniline functionalized cotton textiles are summarized in figure 6A. These results depicted an enhancement of electrical conductivities along with an increase in oxidant concentration (Deng et al., 2014). The electrical conductivity of polyaniline functionalized cotton textiles at low oxidant [FeCl$_3$·6H$_2$O = 0.1 M] is $10^{-6}$ S/cm. This result proved that polyaniline is converted to a partially oxidized form to some extent even at very low oxidant concentrations. Maximum conductivity was achieved at an equimolar oxidant - monomer ratio 1.0:1.0, which shows completion of polymerization of aniline and saturation of polyaniline through dopants.
However, the electrical conductivity remained almost constant with further increase in the oxidant concentration (beyond 1 M), which confirmed the completion of aniline (Oh et al., 1999) acting as a limiting factor.

![Figure 6](image)

Figure 6. Effect of (A) oxidant concentration [aniline = 1.0 M & HCl = 0.1 M] and (B) acid concentration [aniline = 1.0 M & oxidant = 1.0 M] on electrical conductivity of polyaniline functionalized cotton textiles for 12 hrs at room temperature.

### 3.4.3. **Effect of Acid Concentration on Electrical Conductivity**

Results of oxidative polymerization of aniline due to variations in acid concentration are displayed in figure 6B. The reaction can be explained as vigorous and fast exothermic with an increase in hydrochloric acid concentration from 0.3 M to 2 M. The pH of the polymerization process of aniline at [HCl = 0.3 M] was measured every two hrs and characterized by a subsequent reduction in acidity (Navarchian et al., 2013) when the elapsed time increased. The initial pH of the solution at [HCl] = 0.3 M was 2 while pH of the polymerization reaction reached 4.7 due to its completion.

A noticeable enhancement of electrical conductivity was observed with an increase in acid concentration (HCl). This trend might be justified by the availability of electron delocalization and accessible protons, which are responsible for an increased degree of doping. This can be considered confirmation of the successful attachment of protons to the backbone of polyaniline. However, the increase in electrical conductivity remained steady up on further increase in the acid concentration (beyond 1 M). This phenomenon can be explained by the degradation of polymer chains into small, conjugated molecules and oligomers due to hydrolysis.
Besides, increasing acid concentration after 0.5 M weakens the strength of cotton textiles, leading to the disintegration of component fibers (Yuningsih et al., 2017).

3.4.4 Effect of Polymerization Time on Electrical Conductivity

The polymerization process was carried out at 5-time intervals (1, 6, 12, 24, and 48 hrs) at constant concentration of monomer, and oxidant (both 1 M), and acid (0.5 M) concentrations at room temperature. Electrical conductivities of polyaniline functionalized cotton textiles achieved with respect to variation in polymerization time are presented in figure 5B. It is clearly observed that a longer polymerization time enhances the electrical conductivity of polyaniline. This can be justified by the logic; increasing reaction time increases the probability of dispersing aniline on the surface and interface of cotton textiles, which in turn allows growth of linear polymer chains at a slower polymerization rate. Maximum conductivity was registered 7.63 X 10^{-3} S/cm at 24 hrs of reaction time which is taken as an optimum time. However, electrical conductivity starts to drop to some extent after the optimum time. This could be associated with the completion of polymerization of aniline and saturation of the surface of cotton textiles with polyaniline. There is also a possibility of chain fragmentation into oligomers and smaller molecules after completion of the polymerization reaction caused by the hydrolysis process (Hoghoghifard et al., 2015).

4. CONCLUSION

This study attempted to investigate the relationship between polymerization variables and electrical conductivity of polyaniline functionalized cotton textiles. Accordingly, the main findings are summarized in the following manner.

The FT-IR band at 1160 cm^{-1} confirmed inclusion of polyaniline in the system in its conductive form, emeraldine salt. Thermal analysis proved that thermal degradation proceeds in two main stages: evaporation of moisture and a sharp degradation peak that represents the decomposition of organic matter. SEM microstructures also confirmed the formation of debris, buds, and channels on the functionalization of cotton textiles using polyaniline compared to the uniform surface of cotton textiles used as control sample. Finally, electrical conductivity of polyaniline functionalized cotton textiles increased with an increase in the amount of aniline, oxidant, acidity and polymerization time up to the optimum values ([aniline] = 1 M, [oxidant] = 1 M, [acid] = 0.5 M, and time = 24 hrs).
Hence, conductive cotton textiles were successfully produced using polyaniline synthesized via an in situ oxidative polymerization route.

5. ACKNOWLEDGMENTS
The author gratefully acknowledges the financial support from Mekelle University {Scheme number: MU/CNCS/ 001/2011}. The author also wants to acknowledge Ethiopian Leather Development Institute for allowing the laboratory to analyze the sample using FT-IR, TGA, and SEM instruments.

6. CONFLICT OF INTEREST
The author wants to declare that there is no conflict of interest.

7. REFERENCE


