Preparation of Conducting Polyester Textile by *in situ* Polymerization of Pyrrole

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A method to produce conducting polypyrrole/polyester composite textile has been optimized using *in situ* chemical polymerization. The properties of the composite textiles were characterized by conductivity measurement (Four-point Probe Technique) and Scanning Electron Microscopy (SEM). Investigation of the preparation conditions was carried out by varying the dopant/oxidant concentration (0.2-2 M FeCl₃), diffusion time (1-8 h), polymerization time (2-24 h) and polymerization temperature (5-60° C). The best result with respect to conductivity and coating uniformity was obtained when pyrrole was allowed to diffuse in the polyester textile for 2 h and polymerized for 6 h using 1.0 M FeCl₃ at low temperature. The conductivity improved from 10⁻¹⁰ to 10⁻¹ Scm⁻¹ (RSD=0.35%, n=5). The prepared composite textile can find possible application in electromagnetic interference shielding, microwave attenuation, static electric charge dissipation and electrotherapy.

Key Words: composite textile, conducting polymer, polypyrrole, polyester

INTRODUCTION

The science of textile materials is continuously progressing. Nowadays, textile fibers broaden their field of use beyond traditional application. They are now being explored in different applications like heat generation (Varesano et al. 2009), electromagnetic interference shielding (Chen et al. 2007), electrotheraphy (Oh et al. 2004), electrostatic discharge protection (Dhawan et al. 2002) and sensor (Kincal et al. 1998). These applications are dependent on electrical conductivity; hence, these materials are called conducting textiles. These are commonly produced by insertion of metallic wires inside the yarns, which incorporate conductive fillers or coating with carbon/metal powders (Dall’Acqua et al. 2004). However, they have the disadvantages of limited mechanical flexibility, heavy weight and corrosion. In order to overcome these weaknesses, another technology was explored – coating with conducting polymer (Gregory et al. 1989).

Among the conducting polymers, polypyrrole (PPy) has attracted much attention because of its high electrical conductivity, low toxicity and high stability in air relative to other conducting polyheterocycles (Chandrasekhar 1999). However, like many other conducting polymers, the electrons of the polypyrrole are delocalized in the conjugated structure. This leads to insolubility in ordinary solvent and infusibility since it decomposes before melting (Yin et al. 1997). This is why their industrialization is considerably hampered despite their potential applications. In order to maximize their use, researchers focused on producing composite materials by incorporating the conducting polymer in insulating bases. Textiles are substrate candidates for composite materials because of their flexibility and resiliency.

Conductive polymer composites can be produced by *in situ* chemical polymerization through bulk, diffusive or
vapor-phase polymerization. Researchers that reported the impregnation of polypyrrole with substrates like cellulose, nylon, polyester and wool using bulk polymerization obtained a conductivity of around 0.1 S/cm (Varesamo et al. 2005; Dall’Acqua et al. 2004; Gregory et al. 1989). The disadvantage of this technique is that chemical polymerization occurs in the bulk of the solution and the resulting polymers precipitate as insoluble solids, although a part of the polymer formed can deposit spontaneously on the surface of the substrates (Malinauskos 2001).

Other researchers who used vapor-phase polymerization carried out the method by passing the fiber substrates through the vapors of the monomer, followed by the exposure to an oxidizing agent (Kaynak et al. 2008; Najar et al. 2007; Dhawan et al. 2002; Tan and Ge 1996). This method produces a more uniform coating than the bulk polymerization but requires additional set-up. The level of conductivity obtained using the two methods is the same.

Conducting textile can also be achieved via diffusive polymerization. Studies focused on this route reported a conductivity of $10^{-1} - 10^{-4}$ S/cm (Kassim et al. 2002; Malinauskos 2001; Meador et al. 1997; Li and Song 1991). In this method, polymerization occurs almost exclusively at the fibers whereas no bulk polymerization in the solution takes place; which leads to cheaper production cost. Thus, this route was chosen in this study. The conductivity of polypyrrole is combined with the flexibility of one of the most durable man-made fibers, polyester (PET).

Gregory and co-workers (1989) found out that the physical and chemical properties of the composite can be varied by the choice of dopant and reaction conditions. These processing parameters could significantly affect the resulting conductivity. In this study, these variables were investigated in terms of conductivity, absorbed pyrrole and morphology. The research sought to identify the best condition to produce a conducting polyester textile.

MATERIALS AND METHOD

Chemical Diffusive Polymerization
The surface of the PET textile was first enriched with the monomer using 50% aqueous pyrrole solution. After specific diffusion time, it was removed from the diffusion bath and air dried for 5 min before being soaked in the polymerization bath consisting of aqueous FeCl$_3$ at a specific polymerization temperature. After the polymerization, the polypyrrole/polyester (PPy/PET) composite textile was washed with water and air-dried for 24 h before characterization. The experimental design is presented in Figure 1.

Characterization
The conductivity ($\sigma$) was measured using Four-point Probe Technique. Four hair-thin nichrome wires (diameter=0.05 cm, length=2 cm) were attached in equally spaced points in the textile using minute amount of silver paste (Electrolube). A constant voltage source from a power supply (Lodestar) was used to apply a steady potential through the two innermost probes and the current across the outer two was measured using a DMM2400 bench top digital multimeter. The conductivity was computed according to equation 1.

$$\sigma = \frac{I}{TWV}$$

where $I = \text{current reading (A)}$.

Figure 1. Schematic Diagram of the Experimental Design.
*condition that yields the highest conductivity

CONSTANT CONDITIONS
8 hours diffusion time, 1.0 M FeCl$_3$
25° C polymerization temperature
*best polymerization time, 1.0 M FeCl$_3$
25° C polymerization temperature
*best polymerization time, *best diffusion time 25° C polymerization temperature
*best polymerization time,*best diffusion time
*best oxidant/dopant concentration 25° C polymerization temperature
RESULTS AND DISCUSSION

Polymerization Time

Synthesis time can significantly affect the conductivity of the composite textile. Table 1 shows the results of the conductivity measurement using different conditions. The best polymerization time is 6 h since the difference for the higher time is small.

Polymerization time has a considerable effect on the surface morphology on the textile composite as shown in Fig. 2. The uncoated PET fibers (Fig. 2A) are cylindrical and have a featureless surface morphology. More of the polypyrrole particles are produced when polymerization is carried out at increasing time. Comparative with Figure 2C, the Figure 2D reveals dendritic deposits of polypyrrole in the surface and crossovers in the weaves of the textile but looking at the Table 1, there is no significant conductivity increase between samples prepared at the polymerization time of 6 and 12 h. When polymerization is carried out at 4 h (Fig. 2B), lesser globular spots on the interstices of the fibers reveal that polymerization is not yet complete. Some of the polypyrrole have not yet form adherent coating in the surface and can be taken off when the samples are washed with water.

Since the polyester becomes saturated with pyrrole due to the long soaking time (8 h), some of the bulk polypyrrole may also precipitate on the surface of the substrate, which can also be easily washed off with water. Some of it may be deposited at the crossovers in the weaves as shown in Figures 2C and 2B. This impregnation can be difficult to remove by rinsing. As it is known from literature the dendritic deposits are not desirable since they do not contribute to increase the conductivity (Hakansson et al. 2004). This is confirmed in the present study wherein an increase in the amount of polypyrrole particles in the surface (Figure 2 C in comparison with Figure 2 D) does

Table 1. Conductivity measurements of PPy/PET composite textile at different experimental conditions.

<table>
<thead>
<tr>
<th>Constant Conditions</th>
<th>Experimental condition</th>
<th>Conductivity (Scm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average (n=5)</td>
</tr>
<tr>
<td>Untreated*</td>
<td></td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>Polymerization time (h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 h diffusion time</td>
<td>2</td>
<td>2.45 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.55 x 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.57 x 10⁻³</td>
</tr>
<tr>
<td>1 M FeCl₃</td>
<td>12</td>
<td>1.54 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>1.79 x 10⁻³</td>
</tr>
<tr>
<td>25°C polymerization temperature</td>
<td>12</td>
<td>5.09 x 10⁻⁵</td>
</tr>
<tr>
<td>6 h polymerization time</td>
<td>2</td>
<td>7.52 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.80 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>8.13 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>8.43 x 10⁻³</td>
</tr>
<tr>
<td>Diffusion time (h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 h polymerization time</td>
<td>1</td>
<td>5.09 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.52 x 10⁻³</td>
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<td></td>
<td>4</td>
<td>7.80 x 10⁻³</td>
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<td></td>
<td>6</td>
<td>8.13 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>8.43 x 10⁻³</td>
</tr>
<tr>
<td>FeCl₃ concentration (M)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
<td>4.74 x 10⁻⁵</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>6.69 x 10⁻⁵</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>6.90 x 10⁻⁵</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5</td>
<td>6.55 x 10⁻⁵</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>6.44 x 10⁻⁵</td>
</tr>
<tr>
<td>Polymerization temp (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 h diffusion time</td>
<td>5</td>
<td>6.69 x 10⁻²</td>
</tr>
<tr>
<td>6 h polymerization time</td>
<td>25</td>
<td>3.55 x 10⁻²</td>
</tr>
<tr>
<td>1 M FeCl₃</td>
<td>60</td>
<td>2.56 x 10⁻⁵</td>
</tr>
</tbody>
</table>

*pristine polyester textile
not affect the conductivity (Table 1). It therefore shows that conductivity depends not only on the conducting polypyrrole deposited on the surface of the base polyester textile but also with the penetration of polypyrrole within the fibers of the polyester. This property covers the bulk conductivity and not just the surface conductivity. This may be due to the continuity and connectivity of the conducting particles inside and outside the fibers which could enhance the conductivity of the composite textile.

**Diffusion Time**

It is important that the pyrrole monomer is allowed to diffuse well in the polyester textile. The amount of absorbed pyrrole will depend on how long the textile is exposed with the monomer in the diffusion bath. Figure 3 shows the changes of absorbed pyrrole as a function of the diffusion time. Polypyrrole content kept on increasing as the diffusion time increases. However, an increase in the amount of absorbed pyrrole did not significantly increase
the conductivity as shown by the plateau of conductivity after 2 h diffusion time (Table 1). Polypyrrole coated on the fabric during the later stages of the diffusion process cannot contribute to increase the conductivity of the composite. This is possibly because a conduction path of the composite was already saturated by polypyrrole coated during the early stages (Bhat et al. 2004). The diffusion time of 2 h which yields an absorbed pyrrole of 6.02 % (n=5, 0.92% relative standard deviation- RSD) is enough to produce a good conductivity.

Figure 4 shows the surface morphologies using different diffusion time. For the composite textiles subjected to lower diffusion time (Fig. 4A), small amount of polypyrrole particles is observed. The low conductivity of these composite textiles (see Table 1) suggested that 1 h diffusion time is not enough to allow the deposition of polypyrrole within the fibers, hence a minute amount of particles is formed in the surface of the textile. At increasing diffusion time, more of the polymerized products are also visible (Fig. 4C). However, the conductivity increases very minimally. The saturation of the conductivity is already been reached at 2 h diffusion time.

**Oxidant/Dopant Concentration**

Another important parameter to consider in the polymerization process is the choice of dopant/oxidant. Ferric chloride hexahydrate was used in this study. It is cheaper than most of the dopant used in pyrrole polymerization like anthraquinone-2,6-disulfonic acid disodium salt, 2,6- naphthalene disulfonic acid disodium salt and 1-naphthalene sulfonic acid. It does not only serve as an oxidant but as a dopant as well (Wallace et al. 2003). This study produced a level of conductivity which is comparable to those reported in literature.

Table 1 shows significant conductivity increase at 1.0 M FeCl₃. At the further growing of the concentration, minimal increase can be noted. This concentration is taken as the best ferric chloride concentration.

Theoretically, for one electron oxidant such as ferric chloride, an oxidant/dopant molar ratio of 2.3 is consumed. Two electrons are required for the oxidation of each pyrrole unit with the remaining 0.3 electrons being used for the 30% oxidative doping of the neutral polypyrrole product into its conducting form which carries a positive charge on about every third pyrrole unit (Wallace et al. 2003). This is precisely applied for the process of bulk polymerization. For the present study where diffusive polymerization is employed, it is difficult to ascertain the exact molar ratio of ferric chloride with pyrrole. Nevertheless, a high ratio of 4 is computed for this study since not all the pyrrole can be consumed -- some remain in the diffusion bath, giving way for redistillation and reuse.

![Figure 4](image-url)  
**Figure 4.** SEM Micrographs at 500x magnification prepared at diffusion time of (A) 1 h (B) 2 h and (C) 4 h using 6 h polymerization time, 1.0 M FeCl₃, and 25°C polymerization temperature.
Solvent effects have also been reported for the polymerization of pyrrole in ferric chloride as oxidant. The conductivity of the polypyrrole product prepared in water and alcohol is considerably higher than that of the polymers prepared under the same conditions in organic solvents such as chloroform and benzene (Wallace et al. 2003). Hence, water is chosen in this work to aid in the polymerization. It is non-toxic and at the same time, the cheapest solvent.

**Polymerization Temperature**

Another factor that is considered in this study is the polymerization temperature. In earlier studies on the chemical polymerization of pyrrole, the temperature of synthesis is already identified as the key factor affecting the conductivity of the resulting polymer. Kassim et al. (2002) reported an optimal reaction temperature between 0-10°C which is coherent with the result of the present study. This trend of higher conductivities at lower temperature is generally attributed to an increase in the number of defects of the polymer structure when it is obtained at higher temperature. These defects break the delocalization through the π system. The low temperature seems to promote an orderly growth of chains with a greater conjugation and smaller amount of defects. (Torres & Gomez 1998)

Figure 5 displays morphologies of samples at different polymerization temperatures. The composite textile prepared at 60°C contains particles with myriad globules, whereas the composite textiles polymerized at 5°C shows tiny uniform coating in the fibers. For the sample prepared at ambient temperature, lesser nodules are spotted with small islands of polypyrrole moieties. These globular polypyrrole moieties are similar to that obtained by Torres and Gomez (1998) who synthesized polypyrrole in the form of dense precipitates at low temperature while spongy precipitates are seen at higher temperature.

The sample prepared at 60°C has a conductivity which is three orders of magnitude lower than that polymerized at 5°C. Polymerization naturally starts at the first layer of contact with the monomer on the surface of the fibers. The high temperature caused rapid polymerization on the surface, thereby hindering the penetration of the oxidant (Kim et al. 2002). This is also confirmed by the observation of rapid decoloration (from white to black) of the composite textile when polymerized at high temperature.

At low temperature, polymerization proceeds very slowly (Kassim et al. 2002). The slow process allows the polymerization products to penetrate inside the fibers and the polypyrrole to be deposited evenly (Kim et al. 2003). It was also thought that the polymerization time of 6 h was not enough for the slow process to be completed, so a test was run using a longer polymerization time of 24 h. However, there was no significant effect on the conductivity.

The rapid polymerization may have also caused some of the FeCl₃ oxidant/dopant molecules to be trapped within the fibers of the textile (Bhat et al. 2004). This was confirmed in the present study using semi-quantitative analysis by EDX. Numerical conversion of the peaks in the EDX spectra is presented in Table 2. The high
Table 2. Composition of Ppy/PET composite textiles at different polymerization temperatures using SEM-EDX.

<table>
<thead>
<tr>
<th>Polymerization temperature</th>
<th>Percentage Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>5° C</td>
<td>30.44</td>
</tr>
<tr>
<td>25° C</td>
<td>30.45</td>
</tr>
<tr>
<td>60° C</td>
<td>30.26</td>
</tr>
</tbody>
</table>

% nitrogen at 5°C indicates greater polypyrrole with the greatest % Cl dopant formed. At this temperature, negligible amount of iron was also obtained. On the other hand, iron was detected in the samples polymerized at high temperature, suggesting that the oxidant FeCl₃ was incorporated inside the fibers. This contributes to higher defects which degrades the conductivity.

The level of conductivity ($10^{-1}$ Scm⁻¹) obtained using the optimized condition (2 h diffusion time using 1.0 M FeCl₃ at 6 h polymerization time and low temperature 5° C) is suitable for myriad application (Chandrasekhar 1999). Thus, the prepared conducting PPy/PET composite textile can be explored in electromagnetic interference shielding and static electric charge dissipation.

CONCLUSION
This study describes the preparation of a conducting polyester textile by in situ polymerization of pyrrole. The highest conductivity is obtained when the polyester textiles are soaked in 50% aqueous pyrrole solution for 2 h; air dried for 30 min and soaked in the polymerization bath containing 1.0 M FeCl₃ for 6 h at 5° C. It yields a conductivity of $0.0689 \pm 0.0239$ Scm⁻¹. This is a significant improvement in the conductivity levels compared to the pristine polyester textile whose conductivity is about $10^{-10}$ Scm⁻¹. The composite textile undergoes weight uptake of 6%, revealing that the diffusion of the monomer pyrrole has taken place. SEM confirms the incorporation of pyrrole in the polyester textile which proves that the good conductivity of the composite textile is due to the presence of even polypyrrole coating as well as the penetration of the polypyrrole inside each fiber.

REFERENCES


