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Methods of Coating Textiles with Soluble Conducting Polymers

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ABSTRACT

Soluble conducting alkyl polypyrrole polymers have been applied by either chemical polymerization of the 3-alkyl monomers or direct application of polymer emulsion to the surface. Solution, vapor and spray polymerization methods of coating poly(3-alkylpyrroles) to the surface of woven wool fabrics are explored. Conductive textile samples have also been prepared by applying emulsions of soluble prepolymerized 3-alkylpyrrole to the fabric surface. Direct applications of a conductive paint to the textile surface eliminate the exposure of the substrate to damaging oxidizing agents which allow the coating of more sensitive and delicate substrates. All textiles produced are tested for abrasion resistance and conductivity. For alkyl polypyrrole coated fabrics, the optimum carbon chain lengths are between \(n=10\) and \(n=14\), which result in optimum values of conductivity and solubility. The darkness of the tone is inversely related to the surface resistivity of the resulting conductive fabric. Therefore, deep black coatings have low resistivity whereas light gray coatings on a white fabric surface have higher surface resistivity. Longer alkyl chains result in higher surface resistivity in fabrics. The conductive coating of poly(3-decanylpyrrole) on the textile surface has a better abrasion resistance compared to that of an unsubstituted polypyrrole coating.

Keywords: Wool, Surface treatment, Experimental, Delamination

1. Introduction

Conductive polymers have hundreds of applications which range from thermal clothing to circuit boards to microwave absorbers (Hakansson et al., 2004; Kanatzidis et al., 1990; Hakansson et al., 2007; De Paoli et al., 1999).

However, the textile industry has been reluctant to manufacture these fabrics due to the hazardous conditions in which they are produced. Therefore, we have made soluble conducting polymers in the form of a non-damaging conductive paint which is applied to fabrics by various techniques (Foitzik et al., 2005).

In a previous article, we presented the synthesis of a range of soluble alkyl polypyrroles and characterized the resulting polymers with respect to solubility and conductivity. We observed that the solubility increases with the length of the alkyl chain attached to the pyrrole ring without significantly affecting the conductivity of the resulting polymer in the form of powder or free standing film. In this work, all the polymerization and characterization techniques are performed on coated fabrics. The main advantage of soluble conducting polymers is that they can be directly applied to any substrate, which avoids exposure of the surfaces to damaging oxidizing agents and fulfil the requirements for controlled laboratory conditions. In addition to solution and vapour polymerization, soluble conducting poly-3-alkylpyrroles can be pre-packaged in aerosol cans or as commercially available paints, and applied directly to any surface in any desired pattern for intelligent textile applications. In this paper, we present methods of application of these soluble conducting polymers onto the surface of fabrics by solution and vapor polymerization, spraying and brushing the polymers onto the fabrics and characterizing the products with respect to resistance, binding strength, handle and surface morphology.
2. Experimental

Two-point probe methods are generally used for the electrical characterization of conductive textiles (Lin, 2005). Two electrodes (20.0 × 30.0 mm), which were separated a distance of 20.0 mm on a block that weighed 1.008 g (10 N), were placed onto a fabric surface and the resistance was measured. This allows the results to be reported in surface resistivity, \( R_s \), in ohms per square (\( \Omega/\square \)), given by Equation 1, where \( R \) is the resistance, \( l \) is the distance between the electrodes and \( w \) is the width of the electrode.

\[
R_s = R \left( \frac{w}{l} \right)
\]  

(1)

Another accepted method is for the two-probe measurement to be directly taken on the textile surface and the resistance reported in ohms (\( \Omega \)). This is reported as surface resistance as opposed to surface resistivity, which is in ohms per square (\( \Omega/\square \)). All methods of testing were repeated several times and the average was taken. Although these polymers can be applied to any surface, in this investigation, wool fabrics are chosen as the substrate material.

The binding strength of conducting polymers on fabrics was tested by using a Martindale abrasion tester. A textile sample was mounted on the abrasion tester. The abrasion test was carried out by a random rubbing action against a standard woven material for a fixed number of cycles with a standard weight applied. A wide range of conductive coatings were tested for fastness.

The details of a chemical synthesis and characterization of alkyl pyrrole monomers were given in the first part of this work. We will now focus on coating techniques on fabric surfaces using polymers generated from these alkyl pyrrole monomers. Although the coatings can be applied to any surface, wool fabrics are used as the substrate material for this research.

3. Coating Techniques, Results and Discussion

3.1 Solution Polymerization of 3-alkylpyrroles onto Textiles

Solution polymerization of 3-alkylpyrrole with an oxidant, ferric chloride (FeCl\(_3\)), in the presence of wool fabric, produces polymer coated textiles. The fabric was stirred with 9.60 mmol of alkyl pyrrole and 2 mL of Albegal FFA for 10 minutes. Then, 10 mmol of the oxidant, FeCl\(_3\), was added to the solution and the solution was stirred for 3 hours at room temperature. The textile sample was washed and dried before surface resistivity measurements. The original white fabric turned gray and finally black as the polymerization proceeded. The darkness of the tone is directly related to the thickness of the coating and inversely related to the surface resistivity of the resulting conductive fabric. Therefore, deep black coatings are highly conductive and medium gray or light gray coatings on a white fabric surface results in higher resistance readings. A visual assessment of an originally white wool fabric coated with solution polymerized 3-alkylpolypyrroles showed that the tone of the coating is lighter for longer alkyl chains. As mentioned before, the alkyl chains were attached to the pyrrole ring to render the polymer soluble. This is due to the increase of lipophilicity of the polymers by the addition of alkyl groups covalently bound to the polypyrrole. Amongst the alkyl polypyrroles coated on fabrics by solution polymerization, poly(3-decanylpyrrole) resulted in the darkest and thickest coating, whereas poly(3-behenylpyrrole) resulted in the lightest coating, i.e. highest surface resistance. For conductive textiles, when both the solubility and conductivity of the polymer films were taken into consideration, the optimum carbon chain lengths are between n=10 and n=14, which result in optimum values of conductivity and solubility.

Figure 1 is an electron microscope image of chemically polymerized 3-decanylpyrrole on the surface of wool fabric at a magnification of 1000X. As the soluble conductive polymer dried, it forms a more cohesive solid layer that bonds the fibers together. The formation of this morphology is attributed to the slow evaporation of the solvents as the polymer dried. The loosely bound bulk polymerized particles of conventional solution polymerization were not observed in soluble conducting polymer coated fabrics. On the other hand, the surface resistance was higher than textiles coated by the conventional chemical polymerization of pyrrole.
Fig. 1. Electron micrograph of a chemically polymerized 3-decanylpyrrole on wool. Magnification 1000×. 3-decanylpyrrole, AQSA, FeCl₃ (2:1:4). Polymerized for 4 hours at 25°C

When polymerization of 3-decanylpyrrole was conducted in an aqueous medium, the thickness of the polymer coating is much greater than that obtained by polymerization in chloroform. This is due to the bulk polymer dissolving in excess chloroform, whereas in water, the bulk polymer settles onto the textile surface. Figure 2 shows an electron micrograph of aqueous solution polymerized 3-decanylpyrrole on wool, which smoothly and evenly coats the fabric compared to the uneven surface shown in Figure 1.

Fig. 2. Electron micrograph of aqueous solution polymerized 3-decanylpyrrole on wool. Magnification 100×. 3-decanylpyrrole, FeCl₃ (1:2). Polymerized for 4 hours at 25°C

3.2 Vapor Polymerization onto Textiles

In our previous work, we showed that vapor polymerization of pyrrole on textiles results in a thinner and more homogeneous coating compared to solution polymerization (Najar et al., 2007; Kaynak et al., 2008).

Solution polymerization was carried out for periods ranging from 60 minutes to 180 minutes by exposure of the fabric to a solution of monomer and oxidant with regular agitation. As discussed in an earlier publication (Kaynak et al., 2003), long solution polymerization times result in thicker, highly conductive coatings with substantial bulk polymer deposits on the fabric, whereas vapor polymerization of pyrrole on textiles has been shown to produce a more homogenous thin coating (Lin et al., 2005).

When the vapor is applied using a carrier gas, a thin coat of polypyrrole is produced with no bulk polymer particles on the surface. The polymerization in vapor coating is accomplished within minutes, in a much shorter time than solution polymerization. An example of vapor polymerization of pyrrole can be seen in Figure 3, where a smoother surface morphology is evident.

Fig. 3. Polypyrrole applied to a wool substrate by the vapor polymerization method. Magnification 6590×

The application of a polymer coating to a textile surface by vapor polymerization involves a pre-treatment of the textile with a strong oxidizing agent, such as FeCl₃. The textile was dried in order to remove all traces of solvent, otherwise the morphology of the coating would appear to be similar to that of solution polymerization. When the oxidized and dried sample was exposed to the monomer vapour by using an inert carrier gas, a very thin coating formed on the sample very rapidly. The coating procedure was repeated to build up the polymer layer and enhance the
conductive. Polypyrrole was readily produced by vapor polymerization. However, in the case of 3-alkylpyrrole monomers, vapor polymerization took an extremely long time, exceeding 8 hours. Therefore, vapor phase polymerization is not suitable for the polymerization of alkyl pyrrole monomers.

### 3.3 Spray Polymerization onto Textiles

Alkyl pyrrole monomer was sprayed onto a pre-oxidized surface where the polymerization took place. The oxidation was accomplished by spraying the fabric surface with a fine mist from a solution of FeCl$_3$ in ethanol (50 g/L). Then, the fabric was dried with a heat gun to yield an oxidized sample, which was sprayed with the 3-iso-alkylpyrrole in ethanol (1:2 wt/wt). The textile gradually turned black as the polymerization took place on the surface. The entire process was repeated 4 to 5 times to achieve a thicker coating, which was deep black in color. Finally, the samples were washed and dried. The surface morphology of the resultant poly(3-decanylpyrrole) (Figure 4) is significantly different from that of the solution or vapor polymerized pyrrole. It appears that there is some bonding between the fibers as the coating seems to penetrate into the inter-fiber structure and bond the fibers together.

![Fig. 4. Spray polymerized 3-decanylpyrrole onto a wool substrate. Magnification 1000×](image)

Although the fabric was not soaked in the solution for prolonged coating times, the spray polymerization produced coatings with greater abrasion resistance than both the conventional vapor and solution polymerization methods. Spray polymerization gives the best results with a single application of the spray. Repeated coatings give rise to poor surface morphology and some loss of drape of the fabric.

### 3.4 Applying solutions of poly(3-alkylpyrroles) onto textiles

One of the main advantages of soluble conducting polymers is the ability for direct application to any desired surface without exposure to corrosive oxidizing agents. Soluble polymers can be pre-packaged as paint and applied by spray painting or hand brushing. The polymer solution can be sprayed to coat the surface with a conductive film. The morphology and resulting surface properties are dependent on the nature of the spray and the number and dynamics of the applications. Nevertheless, a coating was produced by spraying poly(3-decanylpyrrole) 5 times, and the fabric was allowed to dry between coatings. The resulting surface morphology of the film is smooth and thicker than vapor phase coated fabrics (Fig.5).

![Fig. 5. Electron micrograph of poly(3-decanylpyrrole) applied by spray painting, magnification 2000×](image)

The polymers were also applied by using brush strokes and dipping the fabric into the polymer solution. In these cases, the polymer uniformly covered the surface. A visual inspection of these coatings indicated a uniform coating. However, when examined under a microscope, these coatings had surfaces with much higher surface roughness.

### 3.5 Conductivity of Poly (3-alkylpyrroles) Coated Textiles

The conductivity of coated fabrics is generally lower than their free standing forms. The
difference may be attributed to the thickness of the coating, structure of the textile, fineness of the fibers and yarns in the fabric, and the chemical and physical nature of the substrate surface. For example, in one of our earlier studies, we showed that surface treatment by plasma gas has a significant effect on the binding strength of the coating and conductivity of the textile (Garg et al., 2007).

A single exposure vapor phase coating produces very thin and smooth coatings, but the surface resistivity of the fabric is significantly lower than that of free standing films and also fabrics coated by solution polymerization. The fibrous nature of the textiles also play a significant part in the difference in conductivity between coated fibrous assemblies and free standing conducting films. In a fibrous network, the electrical path would have local discontinuities, and electrical contact between fibers is influenced by the state of stress to which the fabric is subjected. Therefore, surface resistance measurements are taken when the fabrics are relaxed. When the fabrics are stretched, the resistivity decreases two orders of magnitude. The piezoresistive-like behaviour is due to lateral compressive forces generated by axial tension, which causes improved contact between fibres, and hence enhances the electrical properties. A cyclic stretch and release of the fabric result in large amplitudes of cyclic variation in resistivity.

As mentioned in the previous publication, alkyl chain length has an influence on the conductivity of polymer. This influence is minor in the case of free standing films or conducting polymer pellets. However, when coated on textiles, the surface resistance increases rapidly beyond a carbon chain length of $n=14$. For the purpose of conductive textiles, the optimum value for $n$ is around $n=10$, which considers both conductivity and solubility as these two parameters are inversely proportional to each other.

The conductivity of the final coated textile greatly depended on the thickness of the coating and the chemical and physical nature of the substrate surface. Thinner coatings generally revealed the colour of the fabric substrate, which resulted in a higher surface resistance of the coated fabric, and did not have any significant effect on the flexibility, handle and drape properties of the fabric. Thinner coatings are therefore suitable for applications for which appearance and handle are more important than low surface resistivity. In contrast, a thicker coating results in a darker and more conductive fabric.

![Surface resistance vs. alkyl chain length of poly(3-alkylpyrroles) on wool. Probe separation = 10 mm](image)

3.6 Abrasion of Poly (3-alkylpyrroles) Coated Textiles

A conductive coating of poly(3-decanylpyrrole) on the textile surface has a greater fastness with a more even dispersion compared to that of an unsubstituted polypyrrole coating. If the amount of vapor exposed to the wool substrate was increased, the poly-3-decanylpyrrole coating remains homogeneous compared to that of polypyrrole.

A visual assessment based on the results of the Martindale abrasion testing showed that textiles coated by the solution polymerization have better abrasion resistance than those coated by the vapor polymerization method. The spray-painted polymer shows an increased fastness with increasing coating thickness. The brushed coating has approximately the same color fastness as solution polymerization. The addition of polymer as a vapor has been shown to have a poor color fastness, which is due to the vapor settling only on the surface of the textile. Conversely, solution polymerization allows better penetration of the monomer into the textile matrix and polymerization takes place deep into the interstices of the textile structure.

Polymerization on the surface of textiles produced resulted in lower surface resistivity compared to coatings produced by the application of polymer emulsions to textiles. Figure 7 shows the surface...
resistance of the coated textiles by each method before and after abrasion testing. Although each sample has a large conductivity loss due to abrasion testing, the loss is greater for poly(3-decanylpyrrole) samples coated by the vapor polymerization technique. This result is in agreement with the results found with colour fastness testing. Although the solution polymerization method produced coated textiles with a lower conductivity, the coating has better durability.

![Comparison of application of poly(3-decanylpyrrole) and the surface resistance before and after abrasion testing](image)

Fig. 7. Comparisons of application of poly(3-decanylpyrrole) and the surface resistance before and after abrasion testing

When the results for poly(3-decanylpyrrole) were compared to polypyrrole, they showed the same trend, whereas the increase in resistance due to abrasion is much more notable in the case of the vapor polymerized samples.

The solution polymerization method always gave a product with a better coating fastness than the vapor and spray polymerization method. This is attributed to the extended time that is required for the solution polymerization process. As the textile sample was left in water for 3-4 hours, the oxidant had sufficient time to fully penetrate into the wool strands, whereas vapor polymerization occurred much more rapidly and only thin coatings were applied in one step.

3. Conclusion

A range of 3-alkylpyrrole monomers have been synthesized and then polymerized to form soluble conducting polymers, which are applied onto fabrics by polymerization of the monomer on the fabric or directly applied to the surface as soluble polymers. The conductivity of alkyl polypyrrole coated fabrics is observed to sharply decrease beyond a carbon chain length of n=14. The conductivity of free standing soluble conducting films or soluble conducting polymer pellets is much less affected by the alkyl chain length compared to that of fabrics coated by soluble poly(3-alkylpyrroles). This difference in behaviour is attributed to the fibrous nature of the fabrics which gives rise to discontinuities in the electrical path and thinness of the coatings on the fabrics compared to that of free standing polymer films and pellets. Single exposure vapor phase coatings result in very thin and smooth coatings with lower conductivity and abrasion resistance.

A series of conductive textiles are produced by chemical polymerization of a range of 3-n-alkylpyrrole monomers by using both solution and vapor and spray polymerization methods. Fabrics coated with polymers formed from 3-n-alkylpyrrole by using the solution polymerization method have lower surface resistance than those formed by using the vapor or mist polymerization method. The vapor polymerization method of pyrrole yields a quick coating with smooth surface morphology and good resistivity values. Since the exposure to the monomer vapor is for a short duration of time, the resulting coating is much thinner than solution polymerization of pyrrole and hence, has a comparatively higher surface resistivity. On the other hand, vapor coating of 3-alkyl pyrroles takes a long time, exceeding 8 hours. Therefore, the vapor phase polymerization is not suitable for the polymerization of alkyl pyrrole monomers.

Polymerization onto the surface of textile by using solution, vapor or spray polymerization, produces more highly conductive textiles than those obtained by direct application of poly(3-alkylpyrrole) solutions. However, a direct application has the advantage of avoiding the use of corrosive oxidizing agents at the time of coating. Although the fabric is not soaked into the solution for prolonged coating times, the spray polymerization produces coatings with greater abrasion resistance than both the conventional vapor and solution polymerization methods we used for 3-alkyl pyrroles.
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