**Olney Medal Address**

# Adsorption at the Liquid/Solid Interface: Conductive Textiles Based on Polypyrrole

By ***Hans H. Kuhn***, Milliken Research Corp., Spartanburg, SC

**ABSTRACT**

**Adsorption at the liquid-solid interface is widely used by the textile industry in processes such as dyeing, finishing, wastewater treatment, and many others. Precipitates of nano dimensions formed *in situ* have been used to form coherent, usually amorphous, films of metal oxides, sulfides, etc. on solid surfaces including textiles.**

**This phenomena has been successfully used to polymerize pyrrole on the surface of textile fibers, fabrics, or yarns. While pyrrole is particularly suitable for this process, other monomers such as aniline or thiophene may be used. Polypyrrole is one of the more environmentally stable conductive materials and the above process has been successfully used in industrial production. The electrical properties and the environmental stability of the product depend on a number of variables such as concentration of the chemicals and particularly the dopants used. Furthermore, the environmental stability of the conductive textiles can be significantly improved by the use of certain additives in the polymerization.**

**Numerous applications have been found for conductive textiles, especially in the field where their microwave adsorption characteristics are highly desirable. This is the case in military applications like camouflage and stealth technology.**

**KEY TERMS**

**Adsorption**
**Conductive Textiles**
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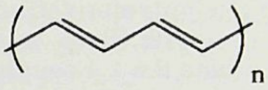
Adsorption at the liquid/solid interface is not only of great importance in many fields of natural sciences such as biology and geology, but plays a significant role in the field of textile finishing. In most cases of textile finishing, the interface is between the fabric (solid) and water. Processes such as scouring, dyeing, and application of soil release finishes all depend on the adsorption at the liquid/solid interface. While many of these interactions occur at the molecular level, similar reactions can be conducted with colloidal particles of nanometer size or even with dispersions of particles in aqueous solutions.[1-3] These reactions may be driven by chemisorption, physisorption, or possibly only by hydrophobic bonding. This paper discusses one of these reactions which leads to an entirely new and exciting product.

Conducting polymers have been known for more than two decades. They consist of conjugated unsaturated polymers of which polyacetylene is the basic structure:



The oxidized polymer contains cationic moieties that are neutralized or doped with a counter-ion. These charge-defects, called bipolarons, are electron holes that serve as the charge carriers and allow the flow of electrons along the polymer chain, similar to a molecular wire.[4] Weight-based conductivities approaching that of copper have been reported for doped polyacetylene. Unfortunately, polyacetylene is highly unstable and loses its properties if not held under anhydrous and oxygen free environment. There are, however, a number of polymers that are much more stable under ambient conditions such as polypyrrole, polythiophene, and polyaniline. These polymers can be prepared by the oxidative polymerization of their respective monomers which may be conducted either chemically or electrochemically.[5-7] Usually these polymerizations are conducted in dilute solutions. If the monomers are water soluble, which is the case, for instance, for aniline and pyrrole, the polymerization can be conducted in aqueous solutions. The conductivity of these polymers are not quite as high as in polyacetylene and lay in between the conductivity of metals and semiconductors.

### Polymerization of Pyrrole

The oxidative polymerization of pyrrole has been examined by a large number of investigators and is believed to follow the mechanism shown in Fig. 1.[8]

Some of the lower molecular weight oligomers have actually been isolated during the polymerization.[9] Pyrrole is soluble in water to about 6%. This solubility drastically decreases for the dimer and oligomers which causes precipitation of the polymerizing species. If the polymerization is conducted in the presence of a high surface area structure such as a textile fabric, the entire polymerization occurs on the surface provided without any visible precipitate in the aqueous phase. For the chemical polymerization of pyrrole, iron (III) salts have been found to yield superior products over other oxidizing agents such as hydrogen peroxide or alkali persulfates. It is suspected that complex formation between the

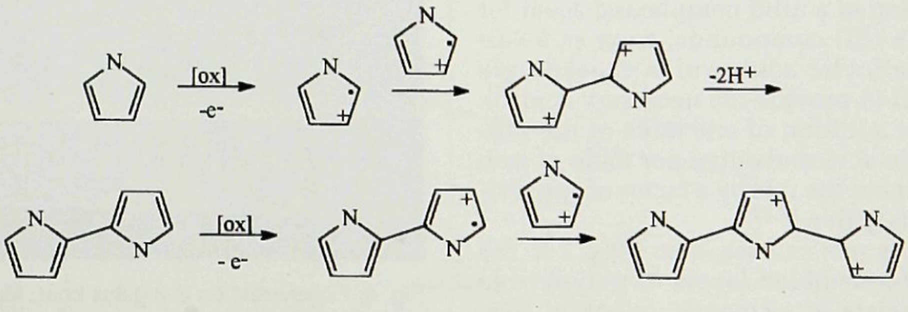


Fig. 1. Polymerization mechanism for pyrrole.

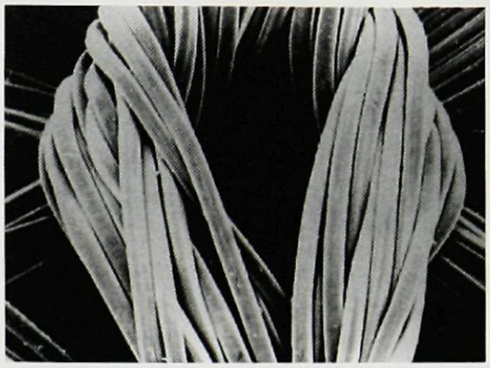


Fig. 2. Polypyrrole on knitted nylon fabric. Magnification 200X.

tri-valent iron and pyrrole and the relatively low oxidation potential of this oxidant may be responsible for these findings.[10]

To directly obtain the oxidized and doped form of the polypyrrole, at least 2.33 moles of iron (III) salt are necessary. Iron perchlorate has been shown to yield the best products, but for safety and economic reasons, iron chloride is preferred and yields products of similar properties. If no other dopants are added to the reaction mixture, the polypyrrole obtained is doped with chloride ions. However, it is possible to add other anions, particularly arylsulfonic acids, which compete with the chloride ion for the doping of the polymer. If the organic sulfonic acid is barely soluble in water, chloride doping can be suppressed so that eventually less than 10% of the dopant is provided by chloride ions.[11]

It was found that the polymerization is typical of a second order autocatalytic reaction with a rate constant of $1.3 \times 10^{-1}$ $M^{-1}sec^{-1}$ at 25C in the presence of textile fibers. The rate is considerably slower if no fibers are present resulting in a rate constant of $3.2 \times 10^{-2}$ $M^{-1}sec^{-1}$.[10]

These reactions work very well if conducted at relatively low concentrations, preferably 0.01 to 0.02 moles/liter of the monomer. To obtain thicker coatings, resulting in higher conductivities, it is often desirable to use higher concentrations of pyrrole. Under these conditions, polymerization may occur in the liquid phase resulting in the deposition of particulate material on the fabric surface. To slow the reaction, it has been found that the addition of a mild complexing agent for iron (III) compounds, such as 5-sulfosalicylic acid, works exceedingly well to provide the necessary control. The addition of one mole of the salicylic acid derivative per mole of iron reduces the rate by a factor of approximately five.[12,13]

As one can see from Figs. 2-5, the self-assembled layers of polypyrrole consists of a smooth, coherent film composed of nanometer size nuclei which have grown into each other during the polymerization. It is known that self-assembled thin layers of polymers deposited on substrates often result in a higher order than polymers obtained by precipitation from solution. We have indeed been able to show a similar effect in our process. X-ray photoelectron spectroscopy analysis indicates that polypyrrole powders produced by the chemical oxidation of pyrrole in water consists of about 45% of the desirable 1,4-coupling, with the remainder consisting of a mixture of non-conjugated polymers resulting from substitution in the 2 and 3 positions and other oxidized species. Conducting the polymerization on the surface of quartz fibers results in a product where the 1,4 coupling is increased to almost 70%, showing a significantly higher degree of order in the self-assembled thin film. These findings are further supported by the increased volume conductivity found in the adsorbed polypyrrole on textile fabrics.[13]

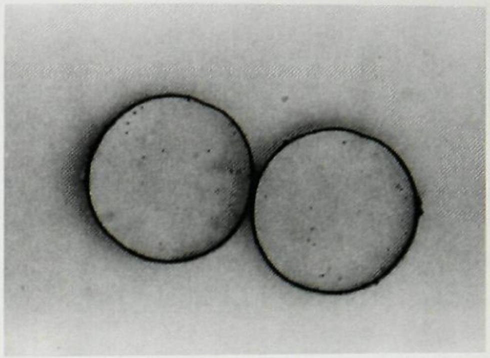


Fig. 3. Cross section of nylon 6 fiber treated with polypyrrole. The dark area shows the polypyrrole coating. Magnification 960X.

At this point it may be appropriate to discuss some of the units used in the following discussions. The volume conductivity, also called specific conductivity, is expressed in Siemens/cm. It is the reciprocal of the specific resistance, which is defined as the resistance measured in ohms along 1 cm of material with a cross-sectional area of 1 cm$^2$. For thin films such as textiles, however, the term of surface or sheet resistance is used, measured according to AATCC Test Method 76-1987. The resistance is measured with the separation of the resistance probes equal to their length and is reported in ohms/square. The resistance is the same for 1 cm$^2$, 1 in.$^2$, etc. The stability of conductive fabrics is expressed as $R_o/R_x$ where $R_o$ represents the original surface resistance and $R_x$ is the surface resistance at time $t$.

Figs. 2 and 4 show that there is no fiber-to-fiber bonding in the final product. As a result, the textile properties such as breaking strength, elongation at break, etc. are largely unaffected.[14] Drape and formability of the textile are preserved as is the capability of being saturated by resins for composite structures. Depending on the amounts of monomer used and the weight and construction of the fabric, surface resistances of 10-10,000 ohms/sq can be produced. Surprisingly, no significant differences could be found by the use of different fibers. Polyester, nylon, rayon, acrylics, Kevlar, Nomex, wool, and cotton all seem to perform very similarly. Glass fibers, however, are too hydrophilic and must be treated with aminosilane to respond properly to the treatment with polypyrrole.

As stated previously, different counterions or doping agents can be used in the polymerization of pyrrole. It is one of the most important variables in this process, affecting not only the degree of conductance, but surprisingly also the degree of stability. A wide range of properties can be obtained by simply adding various organic sulfonic acids to the polymerization mixture (Table I). The performance, in terms of conductance and stability, improves with the concentration of sulfonic acid used. The performance is further improved if sparingly soluble aromatic sulfonic acids, such as naphthalene-2-sulfonic acid and particularly anthraquinone-2-sulfonic

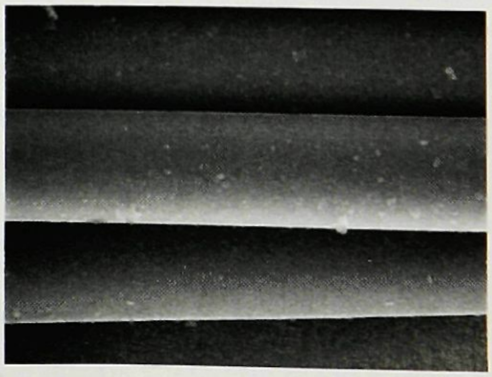


Fig. 4. Polypyrrole on S-2 glass fiber. Magnification 1000X.

Fig. 5. Polypyrrole on glass fiber. Magnification 100,000X.

Table I. Polypyrrole on 100% Textured Woven Polyester Fabric[a]

| Dopant | Amount (%owf) | Resistance (Ohms/sq) | Stability (*Ro/Rx*)[b] |
|---|---|---|---|
| Hydrochloric acid[c] | - | 1250 | .08 |
| Sulfuric acid[d] | - | 8300 | .08 |
| Methanesulfonic acid | 10 | 1100 | .05 |
| Trifluoromethanesulfonic acid | 10 | 500 | .05 |
| Benzenesulfonic acid | 10 | 522 | .16 |
| Benzenesulfonic acid | 100 | 176 | .25 |
| *p*-Toluenesulfonic acid | 10 | 240 | .24 |
| *p*-Toulenesulfonic acid | 100 | 78 | .45 |
| *p*-Ethylbenzenesulfonic acid | 10 | 145 | .36 |
| *p*-Ethylbenzenesulfonic acid | 100 | 60 | .65 |
| 1,3-Benzenedisulfonic acid | 10 | 276 | .35 |
| 2-Naphthalenesulfonic acid | 10 | 68 | .70 |
| 1,5-Naphthalenedisulfonic acid[e] | 10 | 89 | .39 |
| 1,5-Naphthalenedisulfonic acid[e] | 100 | 74 | .38 |
| 2-Anthraquinonesulfonic acid[f] | 2 | 50 | .63 |
| 2-Anthraquinonesulfonic acid[f] | 4 | 46 | .65 |
| 2-Anthraquinonesulfonic acid[f] | 5 | 41 | .65 |

[a]Polymerized at room temperature using 1.33 g/L pyrrole, 2.4 moles of ferric chloride in a 1:30 fabric to liquor ratio for 4 hours. [b]30 hrs, 100C. [c]Polymerized with ferric chloride only. [d]Polymerized with ferric sulfate only. [e]Disodium salt. [f]Sodium salt.

Table II. Elemental Analysis of Polypyrrole Powders[a]

| Dopant | Concentration (in g/L) | Atomic Ratio | | | |
|---|---|---|---|---|---|
| | | Cl/N | S/N | (Cl+S)/N | O/N[b] |
| Ferric chloride | | .22 | | .22 | .83 |
| *p*-Toluenesulfonic acid | 3.3 | .15 | .12 | .27 | .83 |
| *p*-Toluenesulfonic acid | 10.0 | .11 | .18 | .29 | .57 |
| 2-Anthraquinonesulfonic acid | 3.3 | .07 | .27 | .34 | .36 |

[a]Polymerized in water at room temperature using 0.2 mol/L of pyrrole and a ferric chloride/pyrrole ratio of 2.4 in the absence of textiles. [b]In excess of oxygen in sulfate ions.

acid are used.[15] Analytical investigations reveal that the less water soluble acids suppress the doping with chloride ions resulting in doping predominantly with the aryl sulfonates. It is further suspected that the relatively planar structure of naphthalene- or anthraquinone-2-sulfonic acid allows stacking of these molecules between the layers of the conjugated polymer. This facilitates hopping of electrons from chain to chain where defects in the chain occur, a process necessary to achieve reasonable conductance values.

If pyrrole is oxidized electrochemically, appropriate doping can be obtained by the selection of the electrolyte used. If, however, ferric chloride is used for the chemical oxidation of pyrrole, doping with chloride ions, which are present in a relatively high concentration, is always possible. It has been suggested that the use of iron (III) salts, derived from the desired organic sulfonic acid, when used as a doping agent would eliminate this problem. This is indeed possible, for instance, with the commercially available ferric tosylate.[16] The 3.5 times higher molecular weight together with a many fold higher price makes this approach economically unattractive.

Only very few publications discuss the elemental analysis of conducting polymers. This may originate from the fact that the results always indicate the presence of excess oxygen, which is often explained by the adsorption of oxygen and carbon dioxide on the surface of the polymer. Recently, Martin and Lei have shown that polypyrrole synthesized in the presence of a small amount of water is most likely a copolymer of pyrrole and 3-hydroxypyrrole.[17] While this substitution in position three does not reduce the length of the conjugated chain, and with it the volume conductivity, it certainly makes it more sensitive to oxidation and the formation of defects in the chain. Table II shows the amount of excess oxygen, determined by direct oxygen analysis, for polypyrrole synthesized with various doping agents. When the polymer is doped with chloride only, enough excess oxygen is found for 80% of the pyrrole moieties to be hydroxy functionalized. Whereas in the presence of anthraquinone-2-sulfonic acid, this substitution is reduced to about 30% of the pyrrole molecules. This may present an additional reason for the observed improvement in stability.

There have been reports that the addition of certain chemicals can improve the properties of the polypyrrole obtained. Such improvements have, for instance, been reported for the addition of *p*-nitrophenol.[18] It was found in this study that the addition of the sparingly water-soluble 2,4-dihydroxybenzophenone (DHBP) leads to an interesting improvement in the stability of the polypyrrole deposited onto the surface of textiles. DHBP is, for all practical purposes, insoluble in water. It can, however, be dissolved in methanol. If such a solution is added to an aqueous solution of ferric chloride, the complex formed between the iron and the DHBP shows a limited water solubility. Fig. 6 shows the normalized stability of a polypyrrole-coated fabric polymerized in the presence of DHBP at elevated temperature as a function of time.

The initial increase in conductance is dependent upon the DHBP/pyrrole ratio and is more pronounced for higher values. The initial increase in conductivity is most likely due to morphological changes in the deposited polymer.[19] The mechanism for this improvement has not been established. There are reasons to believe that the compound is not incorporated into the

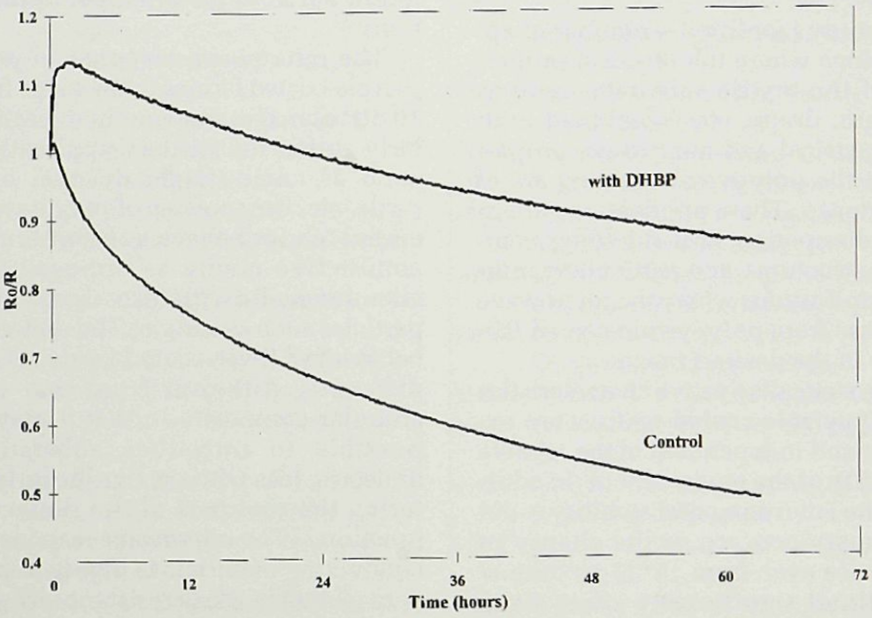


Fig. 6. Degradation of polypyrrole-coated polyester fabric at 100C with and without DHBP.

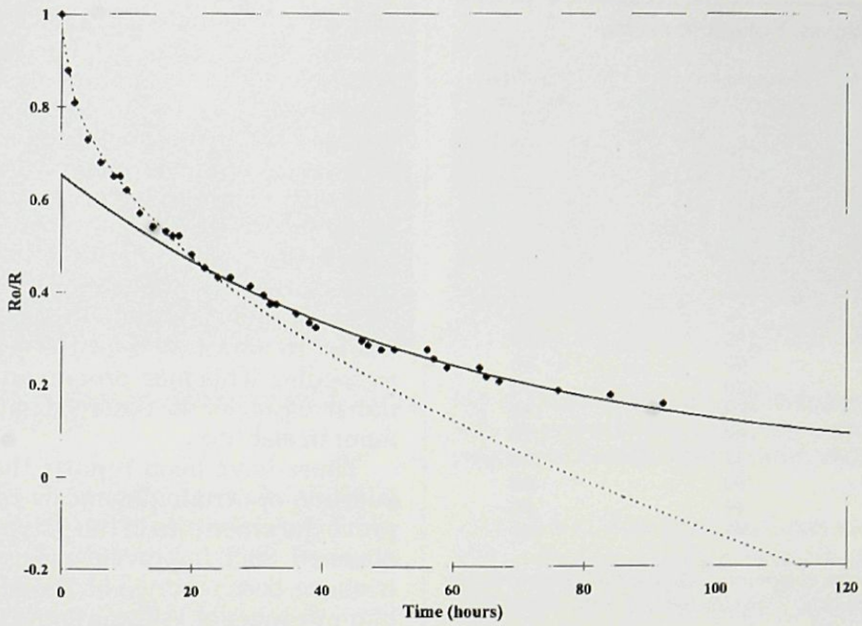


Fig. 7. Conductivity decay of polypyrrole-coated PET Fabric at 100C (◆). Best fit diffusion controlled curve (- - -). Best fit first-order decay curve (——).

polymer. It is suspected that the dihydroxybenzophenone may further reduce the doping with chlorine ions, but this has not yet been determined.

Numerous papers discuss the degradation of polypyrrole and find either a diffusion-controlled or first-order decay reaction. Although the exact mechanism for degradation has not been established, oxidation of the polymer backbone leading to non-conjugated defects is generally thought to be responsible for the loss of conductivity with time. Samples aged at the elevated temperature under argon and doped only with toluenesulfonic acid show no degradation over time. The decay resembles diffusion-controlled kinetics at the initial stages of degradation and first order kinetics during the later stages (Fig. 7).

## Applications

This study identified a number of applications where the physical properties of the textile substrate, such as strength, drape, etc., combined with the electrical and microwave properties of the polypyrrole coating are of importance. These applications are in static dissipation, EMI-shielding, composite structures, and particularly military applications where the microwave response from polypyrrole-coated fabrics is in the desired range.

The static dissipative characteristics of polypyrrole-coated textiles are excellent and independent of the relative humidity of the environment. In addition, the environmental stability is not of primary concern as the change in resistance even from $10^4$ to $10^6$ ohms/sq will not significantly affect static dissipation. Applications such as in sanding belts, transport belts, filtration, and others are promising.

Applications for electromagnetic shielding have been found in a number of areas where the elimination of electromagnetic interference is of importance, such as in electronic packaging, electronic instruments, power generation equipment, and many others.[20,21]

Textile fabrics have wide applications in the field of reinforced composite structures. It is essential that good adhesion to the fiber substrate is obtained. Polypyrrole-coated quartz fabrics used in composite structures with epoxy resins for aircraft wings have shown strength properties comparable to the uncoated control. One of the benefits from encapsulating the conductive fabrics into a polymer matrix is the increase in environmental stability obtained. Such combinations have been found suitable for practical applications.[22]

The microwave response of polypyrrole-coated fabrics in the range from $10$-$10^3$ ohms/sq renders them particularly suited for military applications such as camouflage, decoys, edge cards, etc. Composites of polypyrrole-coated fabrics behave as a continuous conductive media as opposed to a granular media with disperse polymer particles such as carbon. The dielectric behavior of these coated fabrics is significantly different from that of a granular composite in that it may be possible to introduce substantial dielectric loss without significantly altering the real part of the dielectric function.[23] The microwave response to conducting materials is highly dependent on their surface resistance. Highly conducting materials, such as metals, are highly reflective and insulating materials transmit GHz radiation. The ability to tailor the sheet resistance in polypyrrole-coated fabrics enables the production of materials with tunable reflection, transmission, and absorption properties. Multispectral fabrics combining the radar properties of polypyrrole-coated fabrics with visible, near infrared, and thermal camouflage properties are used to produce camouflage nets for military applications.

A number of military applications use polypyrrole coated fabrics to alter their radar signature. Materials with conductivity gradients, such as edge cards, and layered structures, such as Jaumann absorbers and Salisbury screens, represent some of the military applications of these fabrics.[24,25]

## Conclusions

Using the interaction at the liquid/solid interface, we have been able to self-assemble a layer of the conductive polymer polypyrrole at the surface of textiles such as fabrics, yarns, or loose fibers. The electrical properties and environmental stability of these products depend upon the processing conditions and particularly on the counterions used. Applications of these commercially available products (sold under the trademark Contex) in static dissipation, EMI shielding, composite structures, and military applications have been discussed.

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## Author's Address

Hans H. Kuhn, Milliken Research Corp., M-405, P.O. Box 1927, Spartanburg, SC 29304; telephone 864-503-2320; fax 864-503-2417.

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