

Pyrrole Chemical Polymerization on Textiles: Kinetics and Operating Conditions

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ABSTRACT: The chemical polymerization of pyrrole was studied with the aim of defining the best operating conditions for obtaining conductive fabrics of synthetic fibers. Ammonium persulfate was chosen as the oxidant, and various dopants were tested. Among these, naphthalene-2,6-disulfonic acid disodium salt enabled the lowest surface resistivity to be reached. Hence, several kinetic runs were performed to explain the influence of some operating conditions as oxidant concentration and temperature. A pseudo-first-order kinetic equation was derived, and the reaction rates were found to

be practically unaffected by the presence of the textile substrate. Pyrrole polymerization was faster than adsorption of the monomer, suggesting the hypothesis of fast polymerization outside the fibers followed by adsorption onto the fiber surface. The surface coating of polypyrrole was evidenced by microscopic observation of the fiber cross sections. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4121–4126, 2006

Key words: polypyrroles; fibers; conducting polymers; kinetics (polym.); coatings

INTRODUCTION

Electrically conducting textiles prepared by the deposition of thin layers of conductive polymers on the fiber surface of fabrics and yarns recently have been proposed for antistatic, heating, or EMI shielding applications.^{1,2} Among the conjugated polymer group, including PEDOT, polyaniline, and polythiophene, polypyrrole (PPy) is one of the most promising candidates for this kind of applications because of its physical and electrical properties.^{3–18} Intrinsic conductive textiles with good electrical and thermal properties were prepared by our group by *in situ* polymerization of pyrrole on the surface of wool fibers and inside the fiber bulk of cellulose fibers, without noticeably changing the flexibility and tensile properties of the original material.^{19–21} The synthesis of PPy on textile substrates was generally carried out by using ferric chloride or ammonium persulfate (APS) as the oxidizing agent in the presence of an organic dopant such as anthraquinone-2-sulfonic acid (AQSA), *p*-toluene sulfonic acid (PTSA), dodecylbenzene sulfonic acid (DBSA), or naphthalene disulfonic acid (NDSA). Most treatments were performed by wet impregnation of fabric in aqueous pyrrole solution containing the oxidant and the dopant. The best conductivity performances were obtained at

room or lower temperature with a molar ratio oxidant/pyrrole up to 2.5 and were strongly affected by the nature and concentration of the dopant.^{1,22–24} Very little data about the polymerization rate of pyrrole onto textile substrates have been reported in the literature. Gregory et al.⁶ followed the monomer depletion versus time by gas chromatography, but other literature references about the kinetics of this reaction are poor, and the influence of the operating conditions is not yet completely understood.

In this work, we prepared PPy-coated conductive polyester, polyamide, polypropylene, and acrylic fabrics, using APS as the oxidant and different organic dopants. The influence of oxidant concentration and temperature were investigated monitoring the concentration of the monomer versus time by high-performance liquid chromatography (HPLC), and a kinetic equation was derived. Moreover, microscopic observation was performed to find evidence the PPy coating.

EXPERIMENTAL

Materials

The following textiles were used:

- two PET fabrics—light (LPET), 64 g/m², and heavy (HPET), 130 g/m²;
- polyamide 6 (PA6), 132 g/m²;
- polypropylene (PP), non-woven, 34 g/m²;
- acrylic (PAC), for outdoor use, 335 g/m².

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LPET is a polyester fabric for transfer printing kindly supplied by TPB Barzaghi (Giussano, Italy). HPET and PA6 were purchased from EMPA Testmaterialen (St. Gall, Switzerland). The nonwoven PP was supplied by Albis (Roasio, Italy) and the PAC fabric by Montefibre (Porto Marghera, Italy).

Because the fabrics had different surface densities, the specific surface area of the fibers was calculated from their size and density, and these values are reported in Table I. Before treatment, the fabrics were washed and dried at 100°C for 12 h.

All the reagents were from Aldrich. Pyrrole was freshly distilled. The oxidant used was ammonium persulfate (APS) in the presence of the following dopants: antraquinone-2-sulfonic acid sodium salt (NaAQS), sodium dodecylbenzene sulfonate (NaDBS), naphthalene-2,6-disulfonic acid disodium salt (Na₂NDS), or *p*-toluene sulfonic acid (PTSA).

Polymerization runs

Fabric strips of about 0.8 g were introduced into test tubes and treated with 15 cm³ of the dopant solution. The proper amount of pyrrole was added with a microsyringe, and the tubes were sealed and stirred in a thermostatic bath for 15 min. Then polymerization was started by adding 10 cm³ of APS solution. After the required time, the fabrics were repeatedly washed with nonionic surfactant solution and water. The products were finally dried at 75°C for 12 h and immediately subjected to surface resistivity measurement.

In the kinetic runs, the same operating conditions were adopted, but the solution volume was increased to 50 cm³, and the fabric was cut into small pieces to achieve fast homogeneity of the solution. Samples of 1 cm³ of the reaction mixture were taken with a syringe every 10 min and introduced into 4 cm³ of 0.004M sodium thiosulfate solution to stop the polymerization. The samples were then diluted with 5 cm³ of distilled water, filtered, and subjected to HPLC analysis.

HPLC analysis

In the kinetic runs Na₂NDS was introduced as the dopant; therefore, the HPLC analysis was performed to separate and evaluate the residual pyrrole and dopant. The apparatus used was a Varian 5000 equipped with a binary gradient pump and a variable wavelength UV-vis detector. The selected wavelength was 210 nm, corresponding to the absorption peak of both substances without interference of persulfate. A TSK MCH10 column, 15 cm long, was used with a mobile phase water/methanol 40 : 60 at a 0.7 cm³/min flow rate. For quantitative analysis, the internal standard method was adopted, and pure caprolactam was chosen as the internal standard. Caprolactam did not interfere in chromatograms and was found to be unaffected by the reagents; hence, it was introduced into the polymerization solution at the beginning.

TABLE I
Influence of Various Dopants on Weight Increase and Surface Resistivity of Synthetic Fabrics Coated with PPy

Fabric type	Specific surface area of fibers (m ² /g)	Dopant type	Dopant concentration (M)	Weight increase (%)	Surface resistivity (kΩ/square)
HPET	0.186	NaAQS	0.0045	2.9	75.4
			0.009	3.4	102
			0.018	2.0	489
		Na ₂ NDS	0.0045	3.9	14.9
			0.009	4.4	1.3
			0.018	3.7	4.2
			0.0075	2.9	242
		PTSA	0.015	3.0	33.3
			0.030	2.1	157
			0.009	0	>2000
LPET	0.237	NaAQS	0.009	2.6	20.5
		Na ₂ NDS	0.009	3.2	4.3
		PTSA	0.015	1.2	65.2
PA6	0.187	NaAQS	0.009	3.6	14.4
		Na ₂ NDS	0.009	2.9	0.5
		PTSA	0.015	2.9	4.2
PP	0.241	NaAQS	0.009	3.8	93.5
		Na ₂ NDS	0.009	3.5	30.9
		PTSA	0.015	3.9	47.6
PAC	0.252	NaAQS	0.009	1.3	504
		Na ₂ NDS	0.009	2.3	3.6
		PTSA	0.015	1.4	83.7

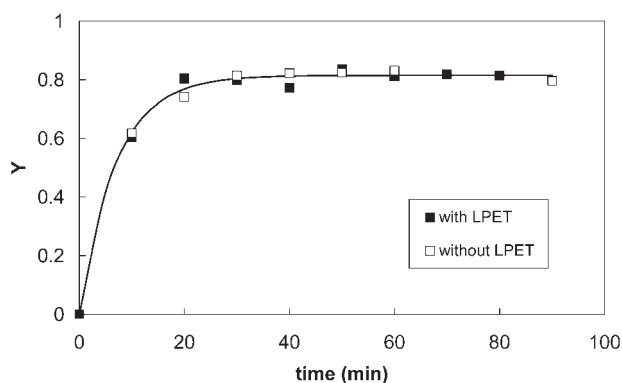


Figure 1 Pyrrole polymerization yield versus time at 25°C (pyrrole 0.020M, APS 0.021M, Na₂NDS 0.009M).

Surface resistivity measurements

The surface resistivity of the fabrics was determined, from the measured resistance value and probe dimensions, according to the following formula:

$$R = R_S \left(\frac{l}{w} \right) \quad (1)$$

where R is the resistance in ohms, R_S is the surface resistivity in ohms/square, l is the distance between electrodes, w is the width of each electrode, and (l/w) is the number of squares of side w that can be fitted between the electrodes without overlapping.¹⁷

Two rectangular gold electrodes measuring 10 × 30 mm and separated by a distance of 10 mm were placed on the sample and pressed onto the fabric by a load of 4N. With this device, the resistance, recorded by a digital multimeter, yielded the surface resistivity directly. The resistance was measured 10 times on each side of the sample and averaged.

RESULTS AND DISCUSSION

Influence of dopants

Initially, the influence of various dopants on weight increase and surface resistivity of PPy-coated synthetic fabrics was investigated. HPET samples of 0.8 g were treated at 25°C for 3 h with 25 cm³ of solution containing equimolar concentrations of pyrrole and APS (0.02M) and various amounts of dopant. The results are reported in Table I and show that NaDBS was practically ineffective; hence it was not considered further. With each of the other dopants, the highest weight increases were found at a 0.009M concentration of NaAQS or Na₂NDS and a 0.015M concentration of PTSA, but Na₂NDS was the most efficient, also yielding the lowest values of surface resistivity.

Therefore, the other fabrics were treated as above, and the results are compared in Table I. It was confirmed that for all the fabrics Na₂NDS had the highest

efficiency in lowering surface resistivity. Moreover, the lowest values with all the dopants were shown by PA6, whereas the highest with Na₂NDS was shown by PP. However, although the surface resistivity mostly showed a minimum corresponding to the maximum weight increase, a clear correlation between these data was not found, nor was such a correlation found at the same specific surface area of the fibers.

Polymerization kinetics

Kinetic runs were performed using Na₂NDS, which was recognized as the most efficient dopant in the previous experiments. The polymerization yields of pyrrole were calculated on the basis of the residual monomer determined by HPLC. Two data series at 25°C are compared in Figure 1: one was obtained in the presence of LPET, the other without textiles. The results practically coincide, and the best-fitting curves (square correlation coefficients higher than 0.99) were achieved using the SigmaPlot program (SPSS Inc.). The following kinetic equation was used for the data processing:

$$Y = Y_{\infty}(1 - e^{-kt}) \quad (2)$$

where Y is the polymerization yield, Y_{∞} is the final value, and k is a pseudo-first-order kinetic constant. Evidently, the reaction involving the monomer was already complete after 60 min. Nevertheless, it is possible that the reaction between oligomers and/or the polymer deposition continued. In fact, according to literature, the resistivity of coated fabrics decreases for a reaction time of up to about 4 h, using FeCl₃ as the oxidant.¹⁶

It was reported by Gregory et al.⁶ that in pyrrole polymerization induced by ferric chloride, monomer depletion follows a pseudo-first-order reaction in the presence of a textile surface, but in its absence, the

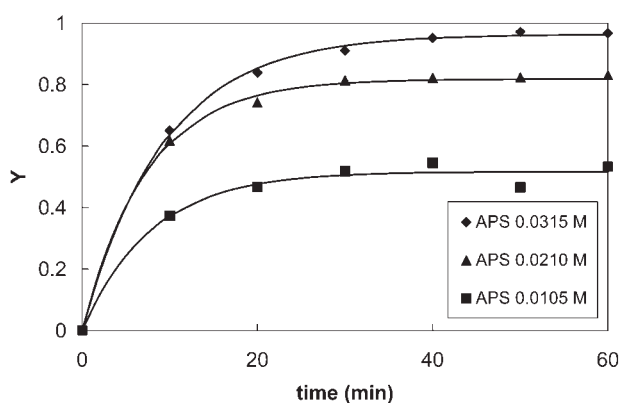


Figure 2 Pyrrole polymerization yield versus time at 25°C with various APS concentrations without textiles (pyrrole 0.020M, Na₂NDS 0.009M).

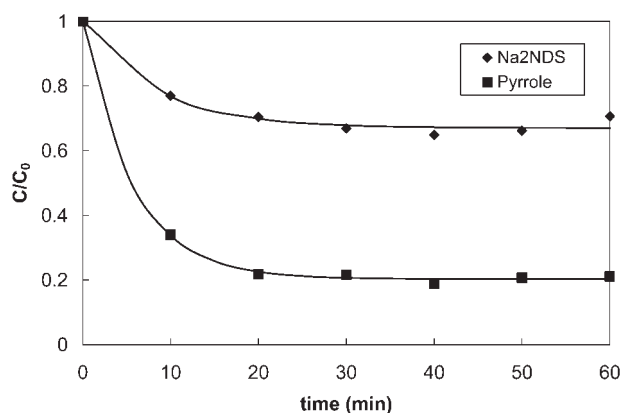


Figure 3 Kinetic curves of dopant and pyrrole depletion at 25°C without textiles (pyrrole 0.020M, APS 0.021M, Na₂NDS 0.0045M).

reaction is significantly slowed, showing a second-order behavior. In our case, the independence of the polymerization kinetics in the presence of a textile substrate could be justified by the use of a different oxidant affecting the polymerization mechanism.

Moreover, oxidant concentration influences both the kinetics and final yield, as shown in Figure 2, where different kinetic curves were obtained in the absence of textiles varying the APS concentration. In these conditions, an APS/pyrrole molar ratio of about 1.5 enabled a polymerization yield very close to 1 to be reached. The dopant depletion followed a kinetic behavior very similar to that of pyrrole, with a residual concentration about 75% of the initial one, as shown in Figure 3, even in the presence of textiles.

However, kinetic runs carried out at different temperatures, in the range of 0°C–50°C, showed that this parameter had a slight effect on the kinetic constants, leaving unchanged the final yields, as can be seen in Table II, which summarizes the parameters of the kinetic curves. In any case, the highest reaction rates were observed at room temperature.

Pyrrole and dopant adsorption by fabrics

Some testing of the pyrrole and dopant distributions in equilibrium conditions between the aqueous solu-

TABLE II
Parameters of Regression Curves of Kinetic Data of Pyrrole Polymerization

Temperature (°C)	APS concentration (M)	Textile	Y_{∞}	k (s ⁻¹)	R^2
0	0.0210	LPET	0.83	6.60	0.999
25	0.0210	LPET	0.82	8.58	0.997
25	0.0210	none	0.82	8.16	0.999
25	0.0105	none	0.52	7.62	0.991
50	0.0105	none	0.53	5.34	0.997

TABLE III
Adsorption by Fabrics at 25°C (Pyrrole 0.020M, Na₂NDS 0.009M, Contact Time 48 h)

Fabric type	Pyrrole adsorbed		Na ₂ NDS adsorbed	
	(mmol/g)	(mmol/m ²)	(mmol/g)	(mmol/m ²)
LPET	0.093	0.393	0.022	0.132
HPET	0.110	0.590	0.014	0.098
PA6	0.134	0.717	0.013	0.081
PP	0.104	0.432	0.003	0.014
PAC	0.155	0.616	0.009	0.043

tion and fabrics was performed to ascertain the affinity between these components and the fibers. The adsorption values, determined by HPLC analysis of the aqueous solutions after a contact time of 48 h, are reported in Table III. The results, expressed as millimoles adsorbed by the weight of the fabric, are compared with those calculated for square meters of fiber surface area.

In any case, the affinity was much higher for pyrrole than for the dopant, but the adsorbed amount of pyrrole was much lower than the observed weight increase after polymerization, without correlation between these values. For example, PAC showed the highest amount of adsorbed pyrrole, but the weight increase (2.3%) was lower than that of LPET (3.2%). This can be understood considering that during oxidative polymerization, the positively charged PPy incorporated more dopant as counterions than the fiber alone and that the fibers were able to adsorb PPy oligomers. However, the highest adsorbed pyrrole by fiber surface area was shown by PA6, which was the fiber with the lowest surface resistivity. Moreover, in the case of PP, the weak affinity for the dopant could justify the low surface conductivity.

On the other hand, in the comparison of the kinetic curve of pyrrole adsorption on LPET with the polymerization yield, shown in Figure 4, the values of the

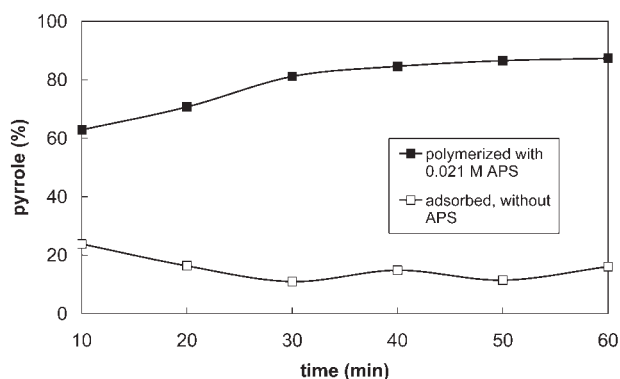


Figure 4 Comparison between the kinetic curves of pyrrole polymerization and adsorption on LPET fabrics at 25°C (pyrrole 0.020M, Na₂NDS 0.009M).

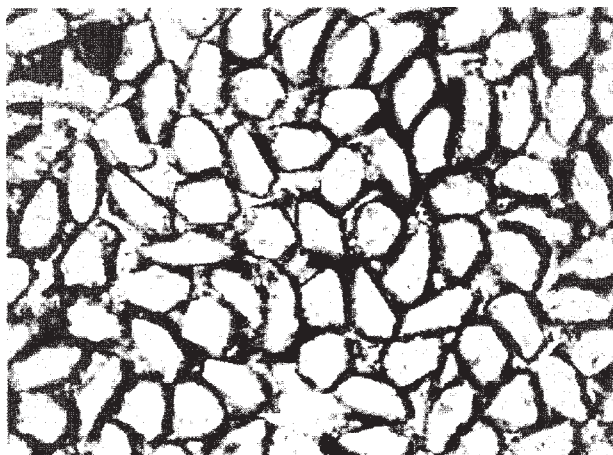


Figure 5 Microscopic image of cross sections of LPET fibers coated with PPy.

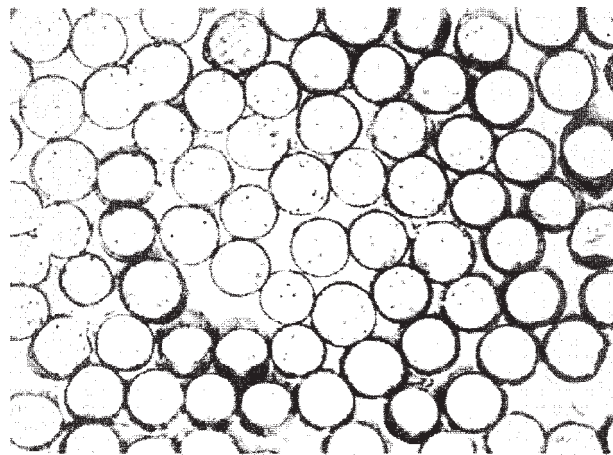


Figure 7 Microscopic image of cross sections of PA6 fibers coated with PPy.

latter are 3–6 times higher than those of the former, indicating a higher reaction rate in any case. Hence, this comparison and the independence of the polymerization kinetics in the presence of a textile substrate suggest the hypothesis of fast polymerization outside the fibers followed by adsorption of PPy onto the fabric surface. In fact, the fiber cross sections observed by transmitted light microscopy, whose images are shown in Figures 5–8, show a surface coating of PPy, which appears as a black layer surrounding the fibers. These results confirmed our hypothesis and agreed with those of several studies of the synthesis of PPy on wool and synthetic fibers.^{2,17,20}

CONCLUSIONS

The results of this study have proven that pyrrole chemical polymerization induced by APS in the

presence of synthetic fabrics enables conductive textiles to be obtained by PPy coating. The nature and concentration of the dopant affected the weight increase and surface resistivity; the best results were obtained with Na₂NDS.

The kinetic data showed that the polymerization yields can be fitted by a first-order equation and that the reaction was complete after 60 min. The kinetic curves were unaffected by the presence of textiles. APS concentration increased the final yield, whereas temperature had a poor influence. Therefore, the best operating conditions were defined.

Synthetic fabrics are able to adsorb pyrrole and dopant, but the polymerization rate is higher, suggesting a fast pyrrole polymerization and successive adsorption of PPy onto the fiber surface. The microscopic observation of fiber cross sections is evidence of a surface coating of PPy.

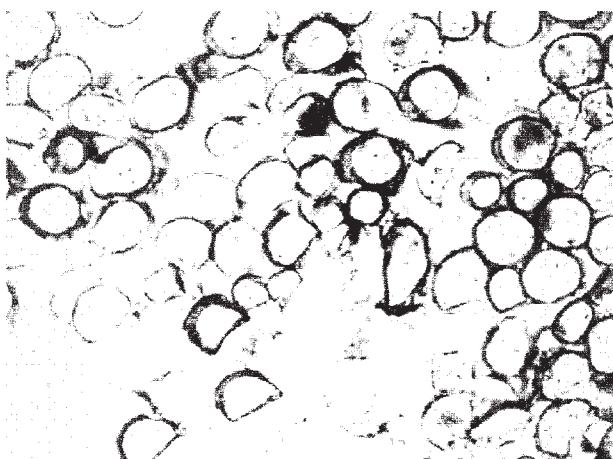


Figure 6 Microscopic image of cross sections of HPET fibers coated with PPy.

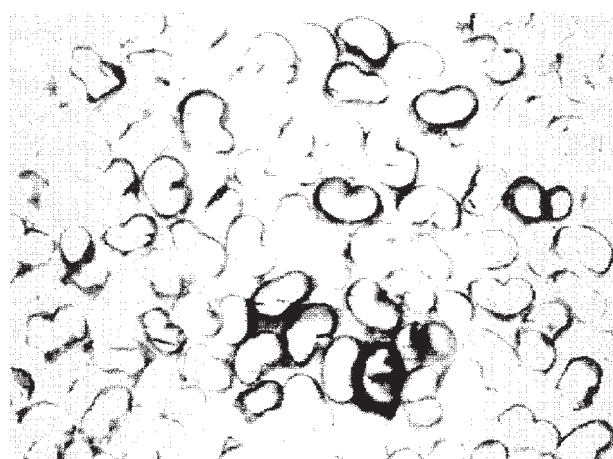


Figure 8 Microscopic image of cross sections of PAC fibers coated with PPy.

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