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Characterization of conducting polymer coated fabrics at microwave frequencies

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Abstract

Purpose – The purpose of this paper is to investigate microwave reflection, transmission, and complex permittivity of p-toluene-2-sulfonic acid doped conducting polypyrrole coated nylon-lycra textiles in the 1-18 GHz frequency with a view to potential applications in the interaction of electromagnetic radiation with such coated fabrics.

Design/methodology/approach – The chemical polymerization of pyrrole is achieved by an oxidant, ferric chloride and doped with p-toluene sulfonic acid (pTSA) to enhance the conductivity and improve stability. Permittivity of the conducting textile substrates is performed using a free space transmission method accompanied by a mathematical diffraction reduction method.

Findings – The real part of permittivity increases with polymerization time and dopant concentration, reaching a plateau at certain dopant concentration and polymerization time. The imaginary part of permittivity shows a frequency dependent change throughout the test range. All the samples have higher values of absorption than reflection. The total electromagnetic shielding effectiveness exceeds 80 percent for the highly pTSA doped samples coated for 3 h.

Originality/value – A non-contact, non-destructive free space method thin flexible specimens to be tested with high accuracy across large frequency range. The non-destructive nature of the experiments enables investigation of the stability of the microwave transmission, reflection, absorption and complex permittivity values. Moreover, mathematical removal of the diffraction enables higher accuracy.

Introduction

Conducting polymers may be used as alternatives to some commonly used metallic shielding materials. In contrast to metallic shielding materials, conducting polymers not only reflect but also absorb electromagnetic radiation in the microwave frequency range of 30 MHz-30 GHz (Kaynak *et al.*, 1993; Kaynak, 1996). Conducting polymer coated textiles may

have potential applications in the minimization of EMI interference by fabricating frequency selective fabric absorbers. A non-contact non-destructive free space method has been refined and used for investigations on thin and flexible specimens of sample sizes greater than 150 × 150 mm across broad microwave bandwidths (Amiet, 2003). Investigation of a range of materials with the free-space transmission method has yielded satisfactory results (Amiet and Jewsbury, 2000; Truong *et al.*, 1998) while an extensive investigation of conducting textiles using this method was lacking. In this paper, the reflection, transmission, and complex permittivity of p-toluene-2-sulfonic acid doped conducting polypyrrole (PPy/pTSA) coated nylon-lycra textiles in the 1-18 GHz frequency were investigated using the free space transmission methods.

Experimental

Synthesis of polypyrrole on textile substrates

A 0.53 mm thick double-sided basket-weave Nylon-Lycra® with an average lycra content of 20 percent was used as substrate textile. After drying fabric samples in a Binder FED 115 Lab oven at 105°C and cooling to room temperature, the samples were introduced into an aqueous solution containing pyrrole monomer (98 percent, Aldrich, Milwaukee, WI, USA), the dopant p-toluene sulfonic acid (pTSA) (98 percent, Sigma-Aldrich), and the wetting agent Albegal FFA (Ciba, Australia) at a concentration of 0.01 percent (w/w). Pyrrole was distilled under vacuum and used at a fixed concentration of 0.045 mol/l in all experiments. The oxidant ferric chloride hexahydrate (minimum 98 percent, Fluka) was added to the solution and a film of conducting polypyrrole (PPy) was formed directly on the textile substrate through oxidative polymerization (Malinauskas, 2001). The optimized ratio of the oxidant ferric chloride hexahydrate ($FeCl_3$, Aldrich) to monomer of 1:2.23 was used (Kaynak and Beltran, 2003), resulting in a fixed concentration of 0.1 mol/l $FeCl_3$, while pTSA was used in concentrations up to 0.036 mol/l. The synthesis was performed at room temperature with a varying polymerization times from 60 to 240 min. After PPy coating and drying, the samples were cut to size (305 × 305 mm or 500 × 500 mm) and stored at 20°C at 65 percent RH.

Characterization

A LEO 1530 FEG-SEM (scanning electron microscopy, SEM) was used to perform a surface morphology study of the conducting textiles. Due to the sufficient conductivity of the PPy coatings, no further conductive coating prior to imaging was necessary.

Fabric thickness measurements were made on preconditioned textile samples in a standard atmosphere using a textile thickness tester (DGTW01B, Mitutoyo, Japan) in accordance with ISO 9073-2 standard (0.5 kPa). The average thickness value from 20 measurements on each sample was used to obtain good accuracy. The original thickness of the uncoated substrate material was 0.53 mm.

After *in situ* polymerization, an approximate thickness of 0.53~0.55 mm was obtained. Fiber diameter measurements of the uncoated and coated fibers were carried out using an optical fiber diameter measurement analysis (OFDA) using an OFDA 2000, which uses optical image analysis to measure the fiber diameters of 2 mm snippets of fibers between two 70 mm

square glass slides. A minimum of 35,000 fibers from each sample were measured and averaged. Optical transmission microscopy analysis was performed on 8 μm microtome transverse sections of PPy coated fabric set in Technovit 7100 resin using an Olympus BX51 equipped with a DP12 camera (3.34 Mpixel).

The surface resistivity of the conducting fabrics was measured according to AATCC test method 76-1995 (American Association of Textile Chemists and Colorists, 1996) using a 34401A multimeter (Agilent Technologies) after conditioning in a standard atmosphere (20°C, 65 percent RH). In the case of coated fabrics, rather than resistivity in Ω/m, surface resistivity R_s in Ω/sq is used to express the electrical property.

Dielectric measurements

Permittivity of the conducting textile substrates was performed using a free space transmission method in conjunction with a mathematical diffraction reduction method as described by Amiet and Jewsbury (2000). The conducting textile sample was placed horizontally flat between two broadband DRG118-A horns operating in the 1-18 GHz frequency range. A radiation output system consisting of an 8510C vector network analyzer (Agilent Technologies) and an 8517A S-parameter test set (Agilent Technologies) with an 83651B synthesized frequency source (Agilent Technologies) generated a swept signal across the pre-set frequency range and collected the data from the measurement. The system covers the frequency range of 45 MHz-50 GHz, where the vector network analyzer has a dynamic range of greater than 100 dB with resolutions of 0.01 dB in magnitude and 0.01° in phase. Software written by Amiet controls the system and to improve accuracy of the permittivity measurements, the diffraction signal was removed using a mathematical method involving two fast Fourier transforms (FFT) and one inverse FFT (Amiet, 2003). A time-gate of 1.0 ns, using a Kaiser-Bessel window, was applied to the frequency domain measurement data, which was converted to time domain to include only signals that reached the output port within the predetermined amount of time. The system was calibrated at least every 5 min during the transmission measurements in order to adjust for changes in the ambient temperature and humidity with time.

The interaction of a material with electromagnetic fields can be characterized by complex permittivity ε^* (related to the electrical component of field), complex permeability μ^* (related to the magnetic component of field), and total (ac + dc) conductivity σ_{tot}. The relative complex permittivity ($\varepsilon^* = \varepsilon_0 \varepsilon_r$ where $\varepsilon_0 = 8.854 \times 10\text{-}12$ F/m) of a material consists of a real part (ε'), mainly associated with amount of polarization occurring in the material, and an imaginary part (ε''), related to dissipation of energy in the material as per: Equation 1 The shielding effectiveness (SE) in [dB] can be calculated as per Balanis (1989): Equation 2 A material is considered a good conductor if $\sigma_{tot} \gg -\omega \varepsilon_0 \varepsilon_r$ and a good dielectric if $\sigma_{tot} \ll -\omega \varepsilon_0 \varepsilon_r$ ($\sigma_{tot} > 0$). This inequality determines how to approximate the skin depth as shown.

For good conductors: Equation 3 For good dielectrics: Equation 4 In the case of the conducting polymers investigated $\sigma_{tot} \approx -\omega \varepsilon_0 \varepsilon_r$.

The materials tested in this work are thin conductive films deposited on non-conductive fabrics, where the skin depth almost exclusively is larger than the total thickness of the

material. The free space method used here produces information about the magnitude and percentages of all amounts of radiation being reflected, absorbed and transmitted through the fabric.

Results and discussion

The morphology of the nylon-lycra filaments coated with PPy-pTSA was smooth and free from cracks (Figure 1). As the polymerization time was increased, the amount of nodular particles on the surface increased. These nodular particles are not strongly adherent to the coating surface, and they can be minimized via control of the process parameters.

A thin layer of conducting PPy on the filament is shown in Figure 2. When the elastomeric lycra fibers are cut off for imaging, they contract slightly, thus causing wrinkling of the coating in the vicinity of the cut ends. The wrinkling, instead of cracking or delaminating of the conducting layer, indicates good adherence and elasticity of the applied coating.

Upon coating by PPy doped with pTSA a color change occurs in the nylon textile as can be seen in Figure 3. As the coating progressed the fabric colour changed from light grey (uncoated), to yellowish towards and finally towards brown. The handle and flexibility of the fabric after coating were very close to that of the untreated fabrics. The PPy coatings had little influence on the mechanical properties of the substrate on which it was formed.

The color change of the fabric was accompanied by an increase in the fiber diameter as the polymerization time was increased. The fiber diameter analysis showed that the mean diameter of the pristine nylon-lycra fibers was 23.84 ± 0.1 µm. During polymerization, the mean fiber diameter increased with time as the polymer deposited on the fabric. The rate of mean fiber diameter increase was higher in the initial stages of polymerization and slower at longer polymerization times due to the higher polymer formation rate in the early stages of coating. The variation of coating thickness with polymerization time was approximated by $d=(1/20)\sqrt{t}$ where, d is the coating thickness in µm and t is the time in minutes. Optical transmission microscopy analysis showed that the coating of PPy surrounded each fiber (Figure 4). The coating was adherent to the fiber even after setting in resin, microtome sectioning and application onto glass slides. The thickness of the coating layer increased as the polymerization time increased and the appearance of bulk polymer (nodular) particles became more pronounced. At long polymerization times of 180 min or more, the coating started to crack due to its larger thickness and incipient brittleness, as indicated by arrow in Figure 4(b).

The surface resistivity as a function of concentration of pTSA at a set polymerization time showed that the surface resistivity dropped quickly as even small amounts of pTSA was added (Figure 5). The initial decrease in surface resistivity for $FeCl_3$ when compared with $FeCl_3+$ 0.004 mol/l pTSA was 65 percent (from 1,010 to 350 Ω/sq). The surface resistivity continued to drop with an increase in dopant concentration, however at a much lower rate than at the initial drop.

Microwave frequency dielectric results

Permittivity of conducting textiles

The imaginary part of permittivity was almost 200 percent larger for the long polymerization time than that of the short time (Figure 6). The difference in surface resistivity between the two samples was approximately one order of magnitude. The real part of permittivity was between 60 percent (0.027 mol/l) and 80 percent (0.015 mol/l) higher for a long polymerization time than the short time. The increase in the real part of permittivity upon addition of larger amounts of dopant may be indicative of the added dopant actively taking part in the charge storage in the material. The same situation was present at the longer polymerization time, however the differences in magnitude between the different dopant concentrations were less pronounced. The smaller effects of higher dopant concentrations on the real part of permittivity at long polymerization times indicates that the increase in energy storage capacity may be possible only up to a certain level of added dopant. Above this concentration, the addition of further dopant ions does not contribute to any further capacitive behaviour of the material.

Reflection, transmission, and absorption of conducting textiles

The results of reflection and absorption of PPy coated nylon is in accordance with those of Kim *et al.* up to 1.5 GHz. PPy-coated plain-weave PET fabrics had a reported contribution to shielding from absorption of up to 7 percent at frequencies up to 1.5 GHz. The absorption contributions to shielding obtained for PPy coated fabrics investigated here were up to six times higher. Another study of similar materials showed a maximum absorption of 33 percent at a resistivity of 2.85 S/cm at 1.5 GHz (Kim *et al.*, 2002; Lee *et al.*, 2002). A common feature of the results is that the longer the polymerization time and the higher the dopant concentration, the lower the transmission and the higher the reflection in the conducting textile samples. The reflection values increase with an increase in frequency. This is expected because the higher frequency will have a smaller penetration depth of radiation and hence less interaction with the polymer. Results indicated that the combination of high values of both real and imaginary parts of permittivity were responsible for the resulting total shielding of radiation.

When pTSA was excluded, significantly lower value of reflection, and almost half the level of absorption was obtained. This is indicative of the dopant ions in the material actively contributing to the conductivity, which has been confirmed by published data (Rodriguez *et al.*, 1997; Nalwa, 1997). The absorption increases by over 40 percent (average value over whole frequency range) with the addition of only small amounts of dopant ions. This is an effective way of improving the microwave absorption in PPy-coated fabrics. The absorption level for a sample doped with 0.018 mol/l pTSA was twice that of a sample with no additional dopant. The amount of reflection steadily increased with the increase in concentration of the dopant in the polymerization bath, reaching maximum levels of 31.36 percent, whereas the sample without dopant displayed an average reflection value of less than 5 percent. The transmission decreased with the increase in the dopant concentration and frequency. Conversely, the reflection levels increased with frequency. Figure 7 shows the average values of reflection, transmission and absorption for samples with different dopant concentrations, but a constant polymerization time of 180 min.

As discussed above, the conductivity increased with an increase in the dopant concentration and/or polymerization time. There sas an upper limit for the conductivity of PPy-coated textiles and some samples with long polymerization times would have approached their threshold conductivity. This is why the total transmission loss reached a plateau at polymerization times above 180 min and dopant concentrations beyond 0.027 mol/l.

The variations in total transmission loss with frequency decreased with an increase in dopant concentration, especially at long polymerization times. This is in accordance with previous reported results for PPy-loaded paper in the 2-18 GHz range. The transmission loss for the samples with a 60 min polymerization time was the lowest, and an increase in total transmission loss was obtained when the polymerization time was extended. However, the increase in the total transmission loss at a very long polymerization time of 240 or 300 min was only a few percent higher compared to that obtained at 180 min.

Conclusion

The permittivity of PPy-coated textiles was measured using a free space transmission measurement technique over the frequency range 1-18 GHz. The measurements are relatively free from diffraction aberration, which indicates that the free space transmission measurement method is suitable for use with the flexible and thin conducting textiles. The real part of complex relative permittivity increased with polymerization time but stabilized after 120 min. The change in the real part of permittivity was not significant beyond 12 GHz irrespective of polymerization time. The imaginary part of permittivity changed with an extension of the polymerization time and varied throughout the frequency range. The influence of an increase in dopant concentration on the permittivity response was also confirmed. Both the real and imaginary parts of permittivity remained stable above dopant concentrations of 0.018 mol/l pTSA.

The polymerization time, dopant concentration and choice of dopant influenced the permittivity and hence reflection, transmission, absorption as well as total SE of the conducting textiles. However, it was difficult to distinguish either of these two factors as being exclusively deterministic of shielding behaviour. All conducting nylon-lycra textiles had higher values of absorption than reflection. The highest absorption levels of around 48.27 to 48.78 percent are obtained for samples with a polymerization times of 120 or 180 min in combination with a dopant concentration of 0.018 or 0.027 mol/l pTSA. The shielding analysis showed that chemical structure influences the SE. The absorption dominated, considerably high shielding proves that conducting polymer coated textiles are good light-weight candidates as shielding materials.

$$\varepsilon_r = \varepsilon_r' + i\varepsilon_r'' \qquad\qquad (1)$$
Equation 1

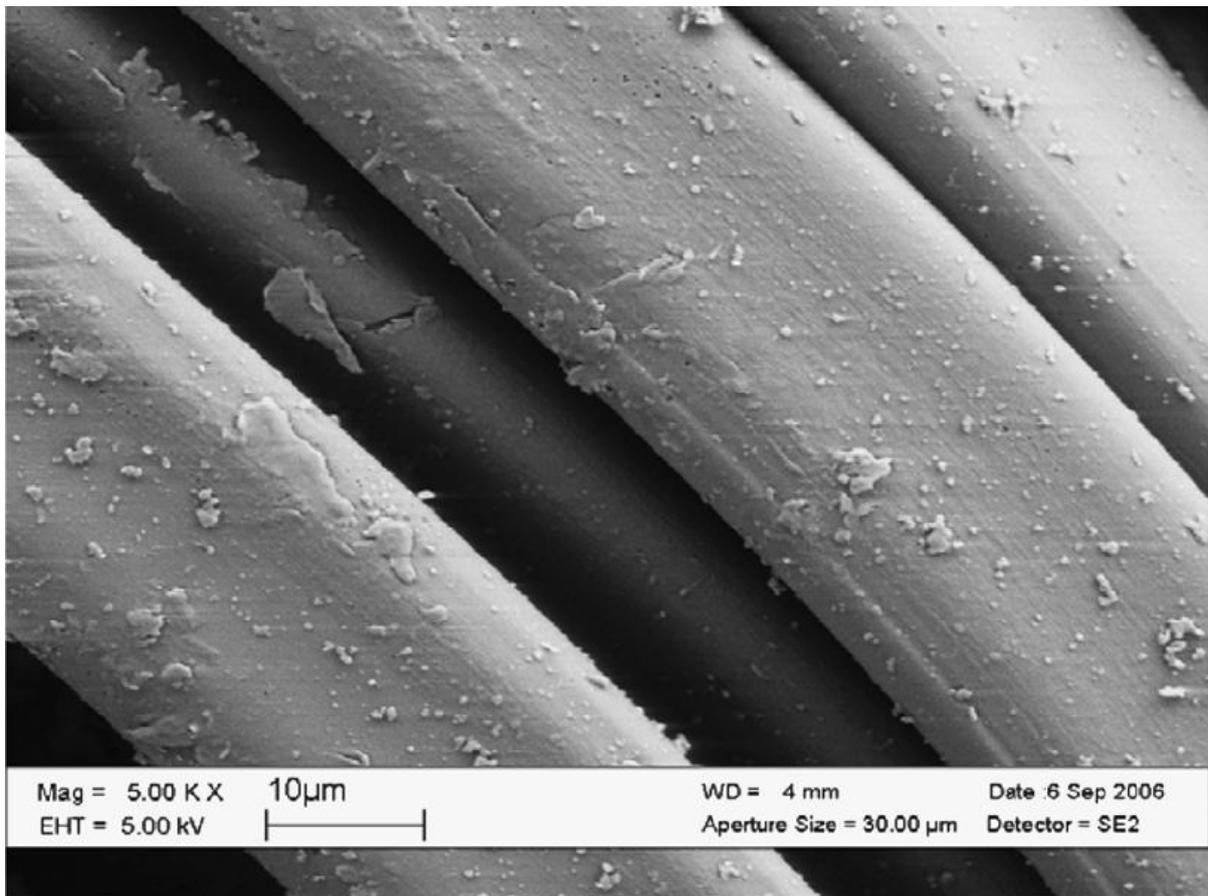$$\mathrm{SE} = 10 \cdot \log_{10}(T[\,\mathrm{percent}]/100) \qquad\qquad (2)$$
Equation 2

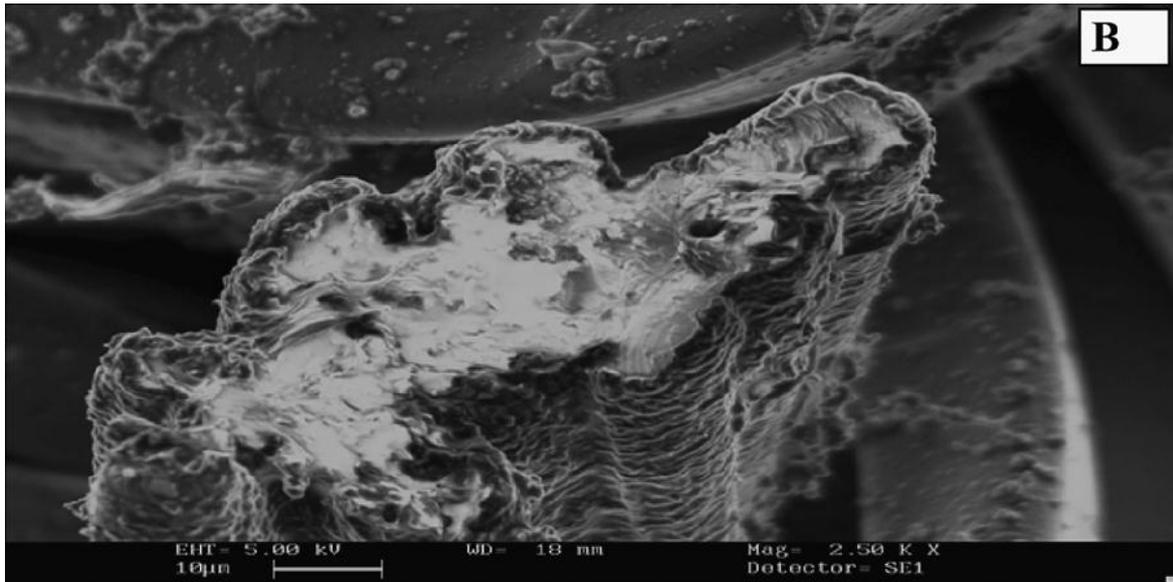$$\delta \cong \sqrt{\frac{2}{\omega\mu_0\sigma_{tot}}}[\text{m}] \qquad\qquad (3)$$

Equation 3

$$\delta \cong \frac{2}{\sigma_{tot}}\sqrt{\frac{\varepsilon'\varepsilon_0}{\mu_0}}[\text{m}] \qquad\qquad (4)$$

Equation 4

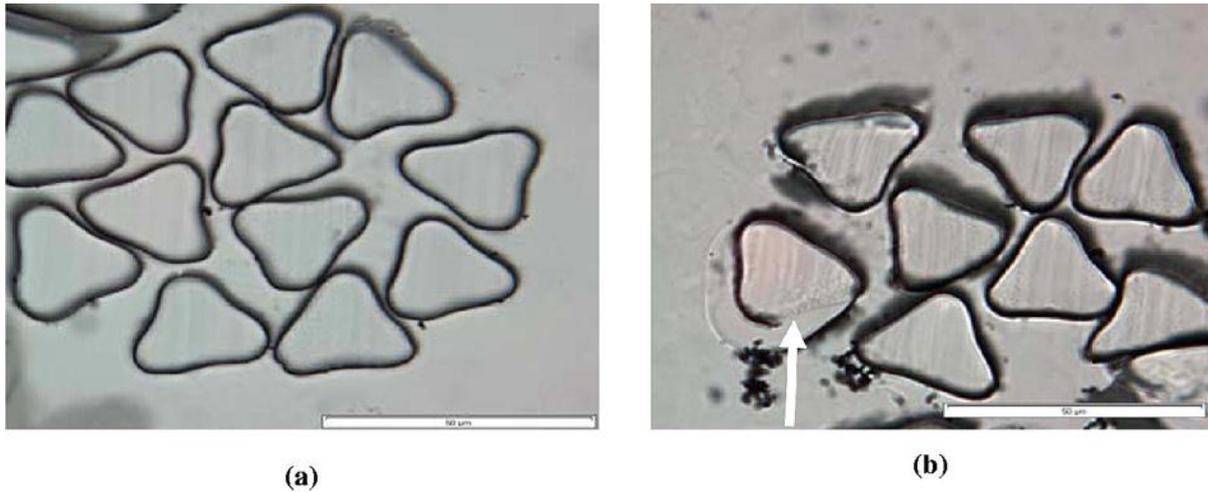**Note:** Polymerization time = 180 min
Figure 1SEM images of PPy-pTSA (0.027 mol/l) coated nylon-lycra

Note: Polymerization time 180min, concentration 0.018 mol/1 pTSA; magnification 2500 × ; scale bar = 10μm
*Figure 2*Micrograph of coated Lycra® fiber (B) ends

Note: From left to right uncoated, 5, 15, 30, 60, 120, 300 min
*Figure 3*Color change in the PPy-pTSA coated nylon-lycra at different polymerization times

Note: (a) 60 min; (b)180 min; scale bar = 50 μm

Figure 4 Optical transmission microscope images of transverse sectioned Ppy-pTSA coated nylon-lycra with different polymerization times
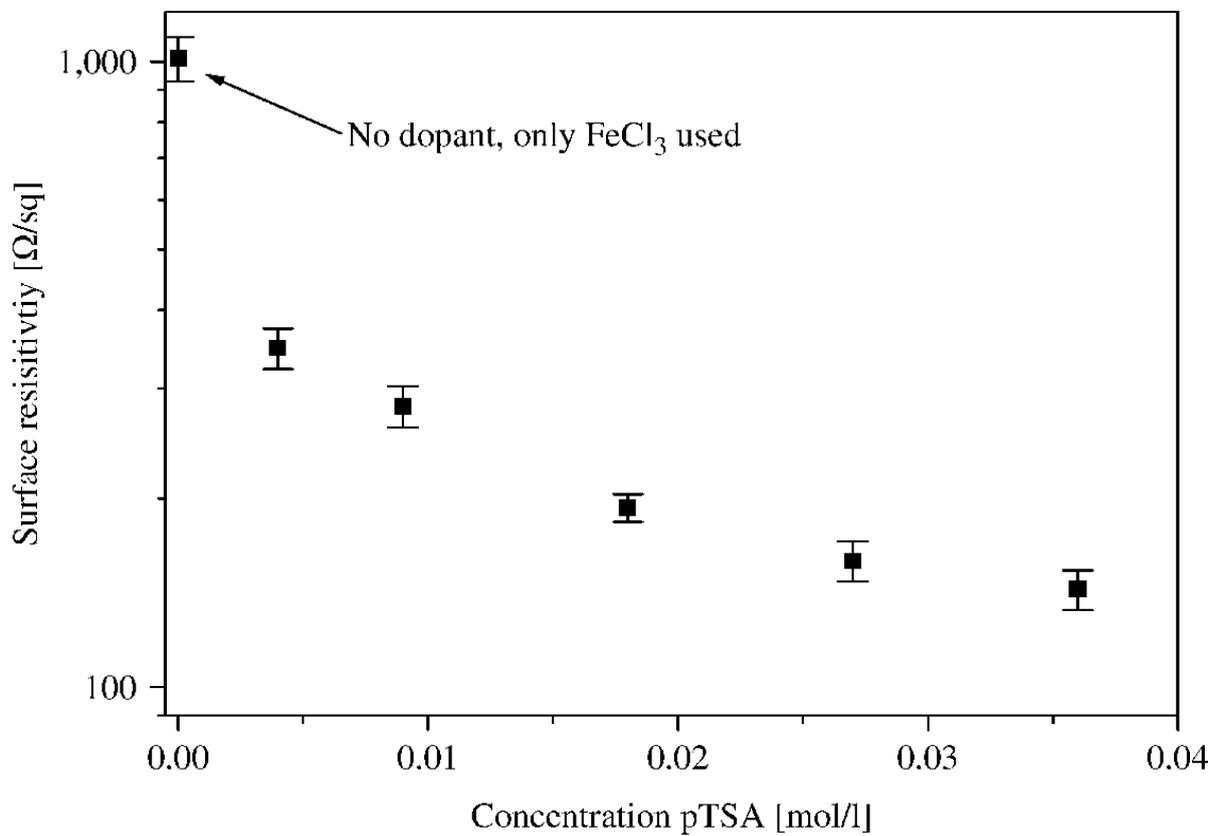
Note: Polymerization time 180 min

Figure 5 Surface resistivity versus dopant concentration for PPy-pTSA coated nylon-lycra
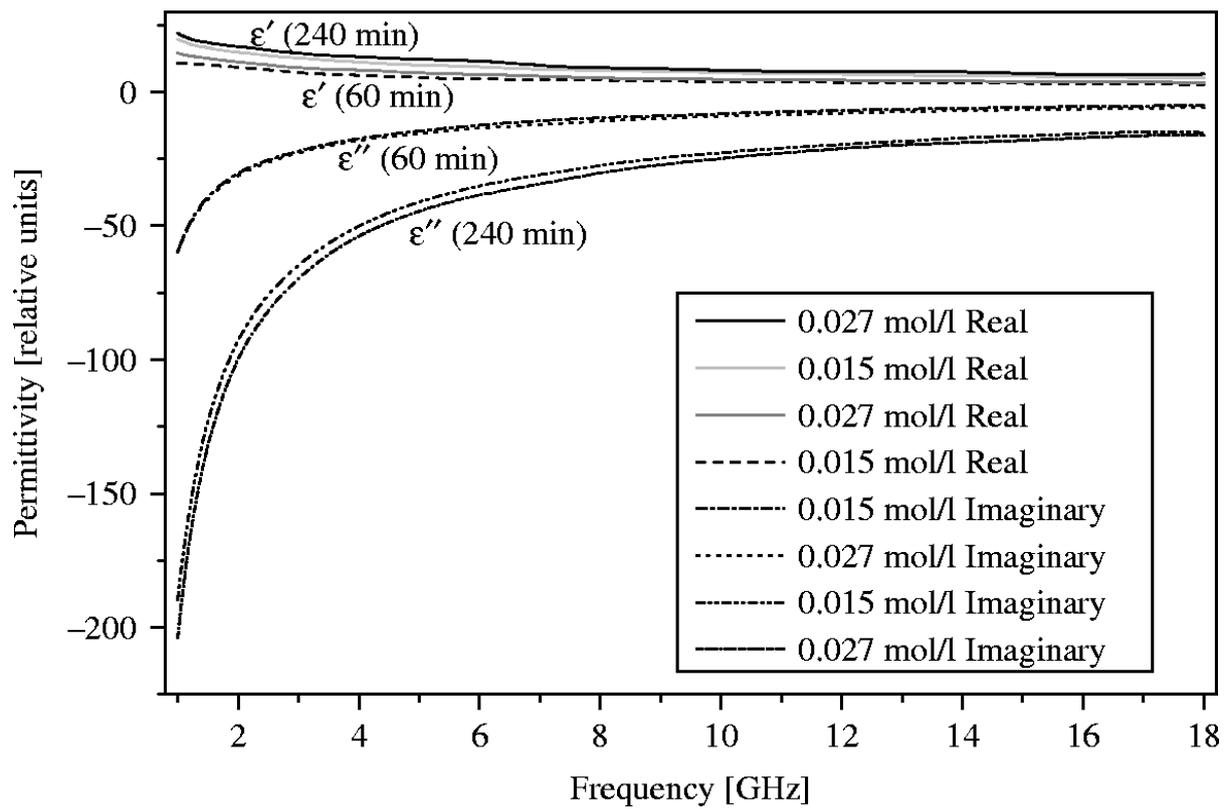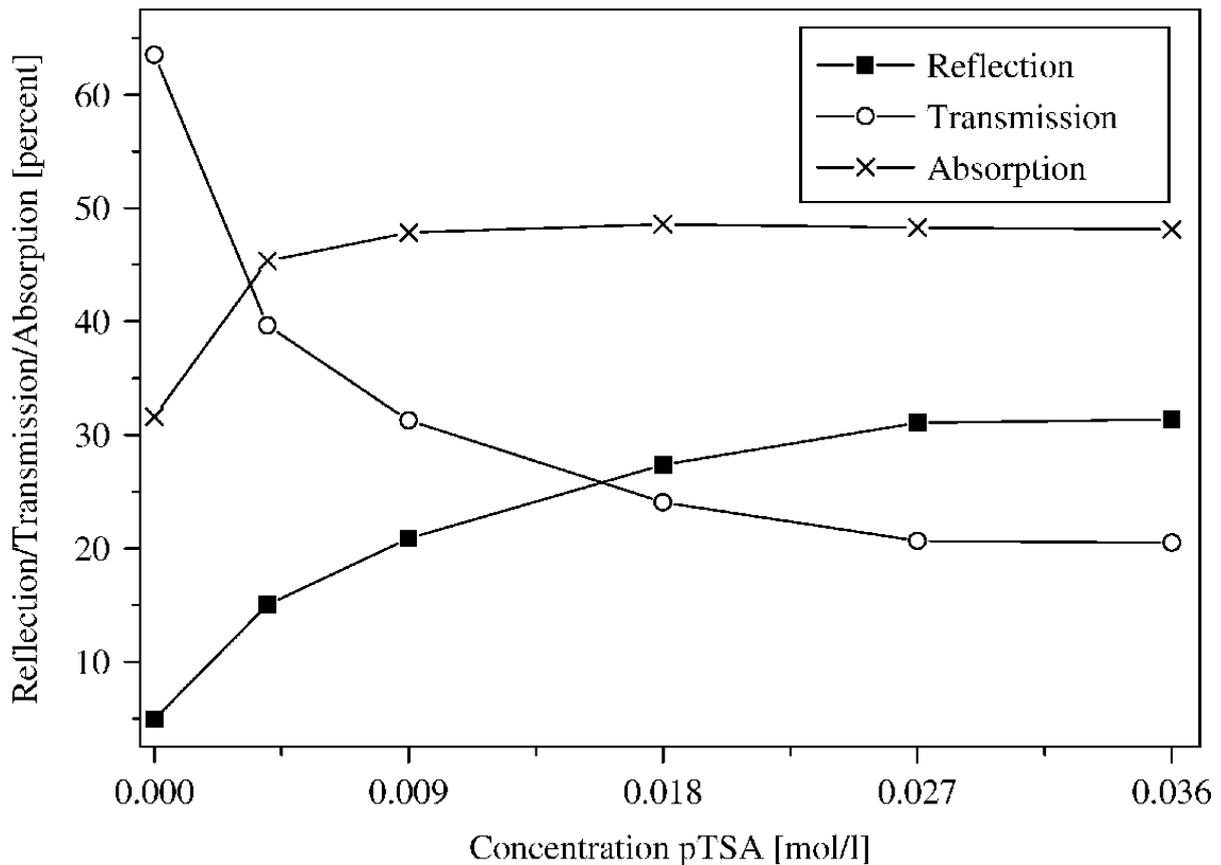
*Figure 6*Permittivity response for PPy-pTSA coated nylon-lycra with 0.015 mol/l or 0.027 mol/l pTSA and 60 or 240 min polymerization time

Note: Polmerization time 180 min

*Figure 7*Reflection, transmission, and absorption values for PPy-pTSA coated nylon-lycra in 1-18 GHz frequency range for different dopant concentrations

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Further Reading

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