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Investigation into the Dielectric Properties of Polypyrrole Coated Fabrics Composites

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Abstract

Flexible polypyrrole coated fabric composites with good dielectric properties were produced using pyrrole as a monomer by in-situ polymerisation on polyester fabric. Initially, the influence of the pyrrole concentration, temperature and time on the dielectric constant of the real and imaginary parts, the loss tangent, and the surface resistance of the composites were investigated. Subsequently, exterior morphologies were analysed. The results show that the pyrrole concentration, the reaction temperature and time had a significant influence on the real and imaginary parts of the dielectric constant, the loss tangent, and the surface resistance of the composites. The polypyrrole composites produced show good performance in terms of dielectric properties and electrical conductivity. In the 0-10⁶ Hz frequency range, the values of the real and imaginary parts of the dielectric constant of the 0.8 mol/l group are both at their largest. Moreover, the value of the surface resistance of the 0.8 mol/l group is at its smallest, and the value of the surface resistance of the 0.2 mol/l group is at its largest, which is 12 times the value given by the 0.8 mol/l group. Values of the real and imaginary parts of the dielectric constant, and the loss tangent for the experimental group produced by polymerisation at ambient temperature are at their largest, which is superior to the other groups. The value of the surface resistance for the experimental group produced at ambient temperature is at its smallest and the electrical conductivity is at its strongest; the higher the reaction temperature, the larger the value of the resistance. The various dielectric properties of the 150 min group are better than for the other groups.

Key words: pyrrole, polypyrrole, dielectric properties, surface resistance, composites.

Introduction

The emission or leakage phenomenon of electromagnetic waves into the air is referred to as electromagnetic radiation, excessive quantities of which may cause electromagnetic pollution. The harm due to electromagnetic waves is mainly divided into two types, one being its effect on human health. Electromagnetic radiation with high intensity acts on the human body in two ways: the thermal effect and non-thermal effect, which can lead to the dysfunction of organisms and public health effects. The oxidation potential of typical aromatic compounds benzene, toluene, thiophene, and pyrrole are + 2.08 V, + 1.98, + 1.60 V, and +0.76 V, respectively (relative to the Ag/Ag⁺ electrode), and pyrrole is one of the monomers which is most easily oxidised due to its relatively low oxidation potential [1-4]. Polyester fibres are generated by a polycondensation reaction of a dibasic organic acid with a glycol. These fibres have excellent wrinkle resistance, elasticity, dimensional stability, and electrical insulating properties. They are also resistant to sunlight, friction, and chemical reagents, and are not susceptible to decay due to mildew, for example [5-7]. Pyrrole polymerises on the polyester fabric surface following interface adsorption at the liquid/solid surface. Initially, under the effect of an oxidant, the neutral pyrrole monomer molecule is oxidised to a cation radical as it loses

an electron. Subsequently, the cation radicals generate di-cations, and then the di-cation generates an electrically neutral pyrrole dimer by disproportionation. Then, the dimer is oxidised again, and combines with cation radicals, thus generating a trimer by disproportionation; and the process ends as catenulated polypyrrole molecules are generated with a degree of polymerisation [8-10]. In the reaction, cation free radicals and their intermediates are readily adsorbed on the solid surface, forming a nucleation center; and then growth leads to the formation of a smooth and agglutinated thin film. Polypyrrole is a polymer containing a conjugated system of π electrons, the electrical conductivity of which changes as a result of a doping reaction. It shows good absorbing properties for electromagnetic waves when the electrical conductivity is such that it is in a semiconductor state [11-15]. An oxidation or reduction reaction of the conductive polymers can lead to electron transfer, and a change in electron distribution alters the energy band, which leads either to the conductive polymer having a semiconductor or conducting state from an insulating state. Oxidation or reduction reactions are involved in the process referred to as doping [16-20]. In this paper, research was conducted to produce flexible polypyrrole coated fabric composites with good dielectric properties using pyrrole as a monomer, iron (III) chloride

as an oxidant, and hydrochloric acid as a doping agent by in-situ polymerisation on polyester fibres. The influence of the pyrrole concentration, reaction temperature and time on the real and imaginary parts of the dielectric constant, the loss tangent, and surface resistance of the composites were investigated. Subsequently, exterior morphologies and the tensile strength were analysed.

Experimental

Materials and reagents

The texture of polyester fabric is plain, warp density – 140/10 cm, weft density – 140/10 cm, and yarn fineness – 18 s. were provided by Hangzhou Rongsheng Chemical Fibres Co., Ltd of Zhejiang Province. Iron (III) chloride, hydrochloric acid, anhydrous ethanol and so on were all analytically pure reagents, provided by Tianjin Guangfu Chemical Technology Co., Ltd.

The preparation process

- Adsorption phase: Plain cloth constructed from polyester fibres was placed into a solution of pyrrole monomers for 40 min to ensure that the pyrrole monomer was sufficiently adsorbed on the cloth of polyester fibres.
- Reaction phase: Iron (III) chloride as an oxidant and hydrochloric acid as a doping agent were added slowly into the liquid at a stable rate of

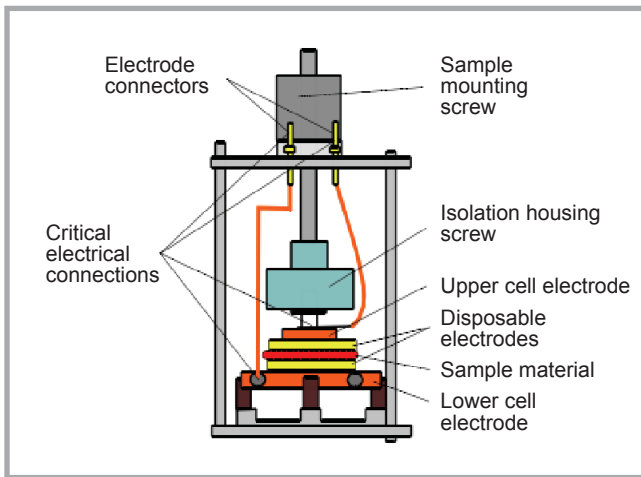


Figure 1. Test cells of dielectric spectrometer.

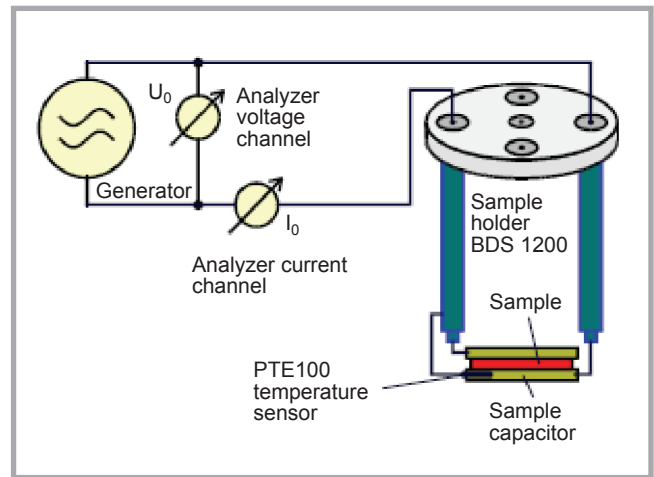


Figure 2. Measuring principle of dielectric spectrometer.

40 drops/min. At a certain temperature, the pyrrole was converted into polypyrrole by in-situ polymerisation.

Test index and method

Tests of dielectric constant and loss tangent

Dielectric constant and loss tangent tests of the polypyrrole coated fabric composites were carried out using a BDS50 die-

lectric spectrometer (German Novocontrol GmbH Company), taking an average after 20 tests. The test temperature was 20 °C, and the humidity – 65%. The test cells were as shown in *Figure 1* [21-22] and test principle as in *Figure 2*.

Surface resistance test

Polypyrrole coated fabrics were put on a clean and insulated laboratory bench,

and then the resistance was determined using a 34410 type agilent bench-type digital multimeter (America FLUKE Corporation). The needle of the multimeter's pen was used to measure a distance of 1 cm on the polypyrrole coated fabric, and the surface resistance between the two points was measured. The test temperature was 20 °C and the humidity – 65%. In this way, 20 groups with different locations of the two points were formed to measure the resistance value, and the average value was calculated.

Table 1. Technological parameters. Note: No. 0 is untreated fabric. Reaction time is 90 min. Ambient temperature is 10 °C.

No.	Dosage of dopant (Hydrochloric acid), mol/L	Mole ratio of oxidant (Iron (III) chloride) to pyrrole	Pyrrole concentration, mol/L	Reaction temperature, °C
1	0.6	1:2	0.2	Ambient temperature
2	0.6	1:2	0.4	Ambient temperature
3	0.6	1:2	0.6	Ambient temperature
4	0.6	1:2	0.8	Ambient temperature
5	0.6	1:2	1.0	Ambient temperature

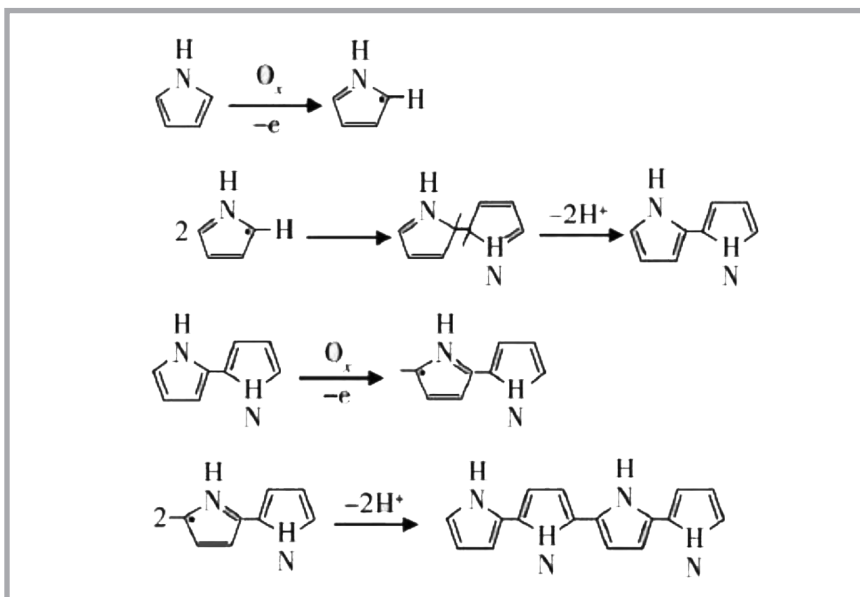


Figure 3. Polymeric reaction process leading to polypyrrole.

Microstructure test

The surface morphology of polypyrrole/polyester fibre composites was observed using a Quanta 200 environmental scanning electron microscope.

Results and discussion

Influence of pyrrole concentration on the dielectric properties and resistance of polypyrrole/polyester fibre composites

To explore the influence of pyrrole concentration on the dielectric properties of the polypyrrole/polyester fibre composites, the pyrrole concentration was varied according to the technological prescriptions given in *Table 1*, to produce five groups of samples.

Pyrrole was generated on the polyester fabric surface following interface adsorption at the liquid/solid surface by a polymerisation reaction according to the oxidative coupling mechanism [23-26]. The process was as follows (see *Figure 3*): Initially, under the effect of iron (III) chloride as an oxidant, the neutral pyrrole monomer molecule

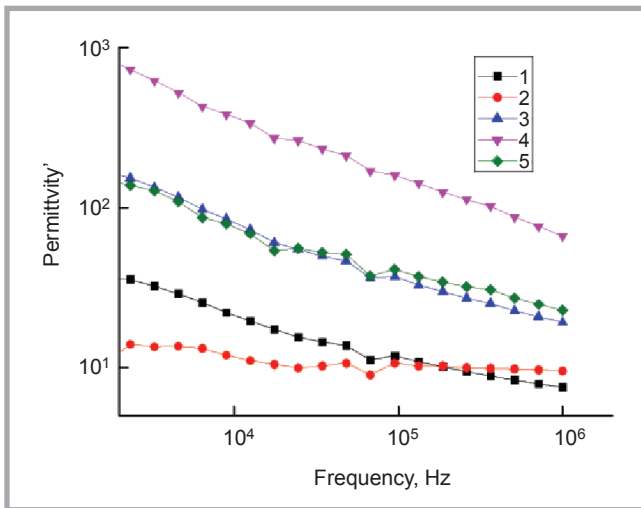


Figure 4. Influence of pyrrole concentration on the real part of the dielectric constant.

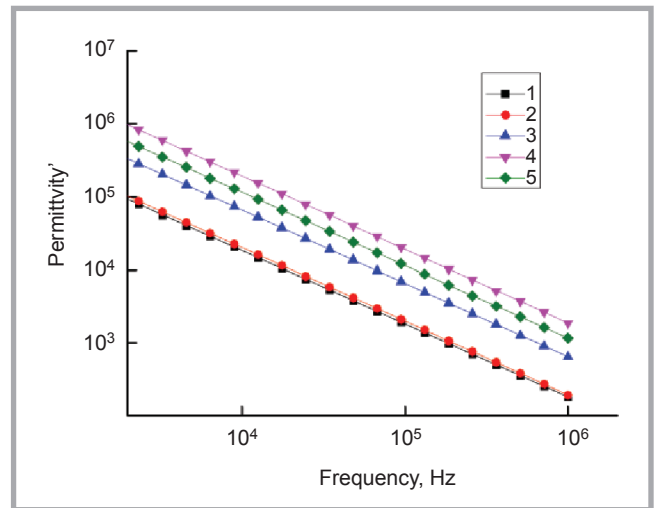


Figure 5. Influence of pyrrole concentration on the imaginary part of the dielectric constant.

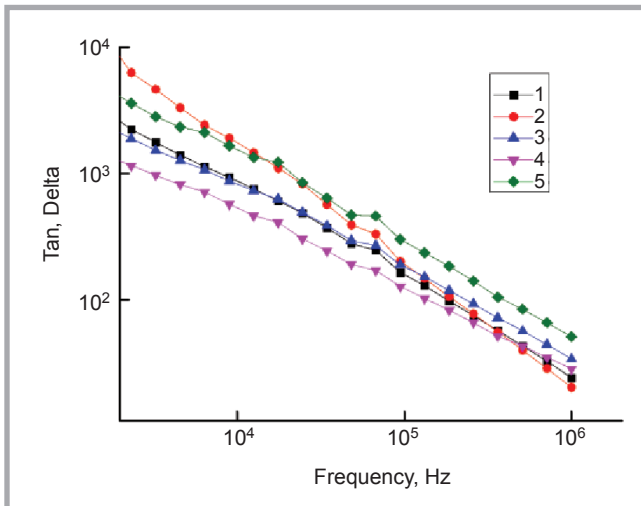


Figure 6. Influence of pyrrole concentration on the loss tangent.

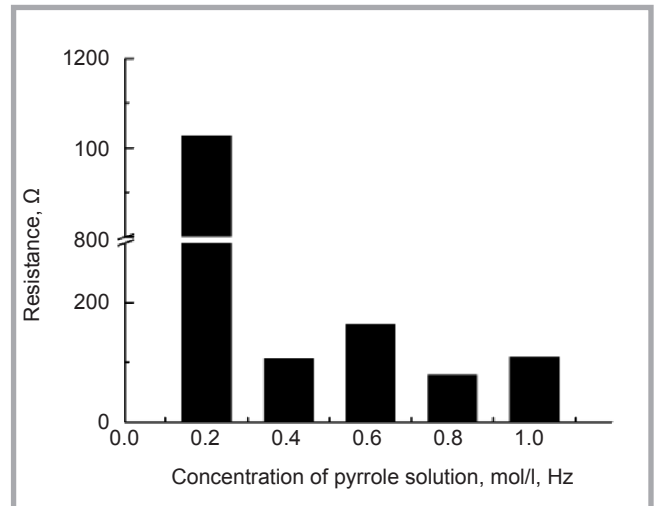


Figure 7. Influence of pyrrole concentration on resistance.

is oxidised to a cation radical as it loses an electron; subsequently, the cation radicals generate di-cations, and then the di-cation generates an electrically neutral pyrrole dimer by disproportionation. Then, the dimer is oxidised again, and this is followed by combination with cation radicals, thus generating a trimer by disproportionation [27-31]. The process ends as catenulated polypyrrole molecules are generated with a degree of polymerisation. **Figures 4 and 5** show that in the 0-10⁶ Hz frequency range, values of both the real and imaginary parts of the dielectric constant of the composites produced using different pyrrole concentrations decrease with an increase in frequency, and that the values of the real and imaginary parts of the dielectric constant of the 0.8 mol/l group are both at their largest, with the values of the real and imaginary parts of the dielectric constant of the 1.0 mol/l and 0.6 mol/l

groups taking second place. The dielectric constant is a function of the frequency of the electric field. The real part indicates the degree of polarisation of the composite under the action of an applied electric field; the greater this value, the greater the ability of the composite to undergo polarisation. The imaginary part is a measure of the energy loss due to the electrical dipole moment of the material, which causes rearrangement under the action of an applied electric field. The greater this value, the greater the ability to absorb electromagnetic waves. The ability of polarisation and loss of the 0.8 mol/l group are both at their greatest. **Figure 6** shows that the value of the loss tangent of each sample in the 0-10⁶ Hz frequency range decreases with an increase in frequency; and the value for the 1.0 mol/l experimental group is at its largest. The loss tangent illustrates the attenuation ability of an absorbing

material; the greater this value, the better the absorbing properties.

Figure 7 shows that the value of the surface resistance of the 0.8 mol/l group is at its smallest, and the value of the surface resistance of the 0.2 mol/l group is at its largest, which is 12 times that of the 0.8 mol/l group. This may be because when there is a low polypyrrole concentration produced, it tends to gather on the polyester fibres, but without forming a uniform and continuous film. Thus, the resistance value is larger and the composite shows poor electrical conductivity.

Electron microscopy (SEM) examination of polypyrrole/polyester fibre composites

From **Figure 8**, we can observe that there is an increased gathering of polypyrrole on the polyester fibre surface with

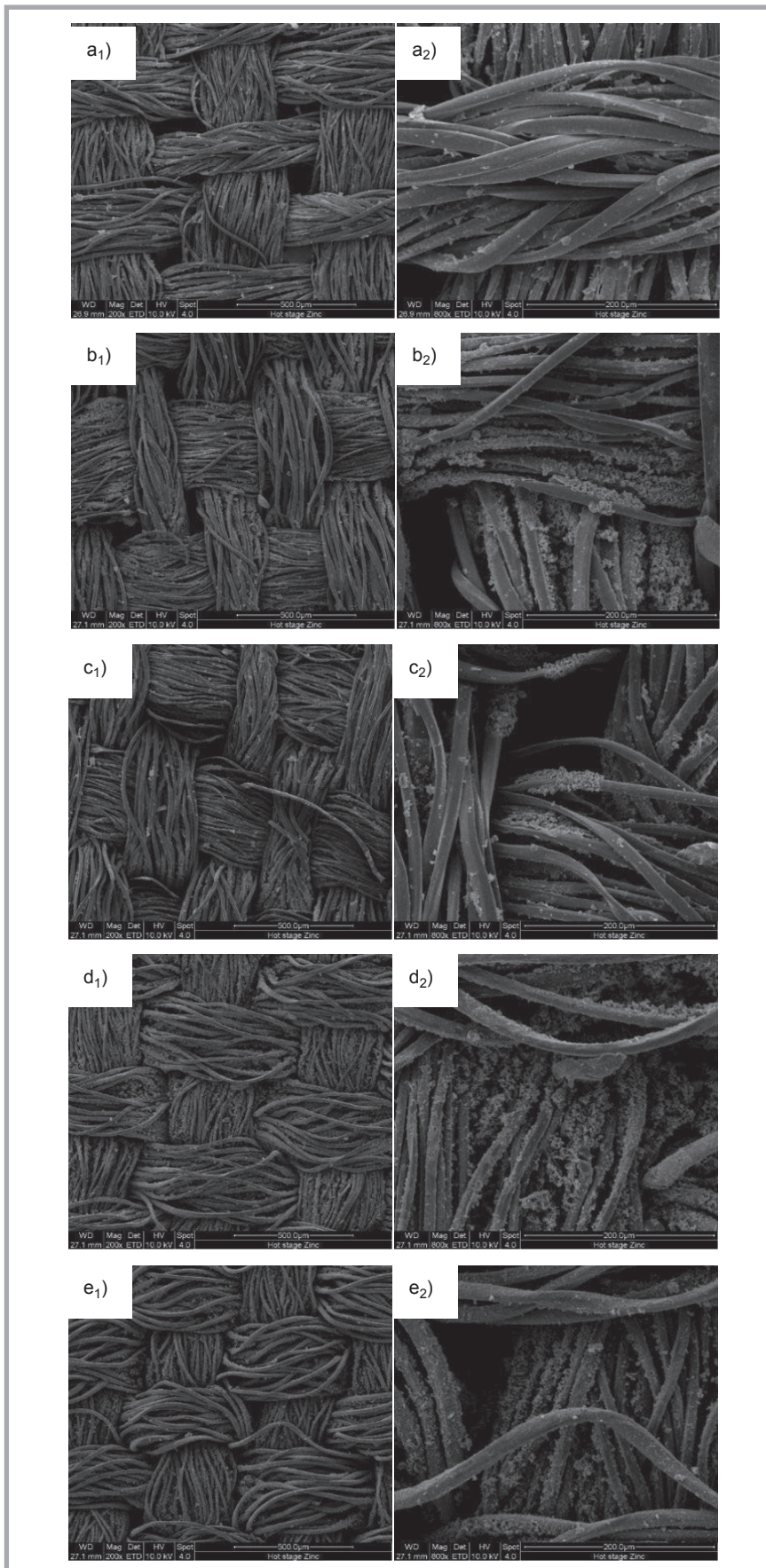


Figure 8. SEM images of polypyrrole coated fabrics composites: a₁, a₂) electron microscope images of pyrrole concentration 0.2 mol/l; b₁, b₂) electron microscope images of pyrrole concentration 0.4 mol/l; c₁, c₂) electron microscope images of pyrrole concentration 0.6 mol/l; d₁, d₂) electron microscope images of pyrrole concentration 0.8 mol/l; e₁, e₂) electron microscope images of pyrrole concentration 1.0 mol/l.

an increase in pyrrole concentration; polypyrrole with a scaly appearance adheres to the surface of fibres when the pyrrole concentration is low; with an increase in pyrrole concentration, a microporous aggregate with a 'cauliflower-like' appearance begins to appear, and with a continuous increase in pyrrole concentration, polypyrrole essentially covers the polyester fibre surface completely, and there is a porous 'cauliflower-like' structure which accumulates.

Influence of the temperature on the dielectric properties and resistance of polypyrrole/polyester fibre composites

To explore the influence of the temperature on the dielectric properties of the polypyrrole/polyester fibre composites, the four groups of samples produced were tested according to the process prescription given in *Table 2*.

Figure 9 shows that the values of the real part of the dielectric constant for each experimental group decrease with an increase in frequency, that the value for the experimental group produced at ambient temperature is at its largest, and that the ability of polarisation is at its strongest. *Figure 10* shows that the value of the imaginary part for the experimental group produced at ambient temperature is at its largest and the ability of loss is at its strongest, with the value of the 30 °C group taking second place. *Figure 11* shows that the loss tangent for each experimental group decreases with an increase in frequency, and that the value for the experimental group produced at ambient temperature is at its largest, which is clearly superior to the other groups.

Figure 12 shows that the value of the surface resistance for the experimental group produced at ambient temperature is at its smallest and that the electrical conductivity σ is at its strongest; the higher the temperature, the larger the value of the resistance. It may be that at a lower temperature of polymerisation, the chains of polypyrrole grow more slowly in the polymerisation process, and the content of defective structures in the polymer decreases, thus improving the regularity of the polymer structure; and hence the polypyrrole shows higher electrical conductivity. When the polymerisation temperature is higher, the process of polymerisation is too fast, which is not conducive to an orderly development of the

molecular chains of polypyrrole. Thus, the molecular chains of polypyrrole are shorter and the defects increase, which leads to the disruption of the conjugated π -electron structure. Consequently, the transfer of carriers between polymer molecular chains is unfavourable compared with migration along them, which leads to a larger resistance of polypyrrole composites and poor electrical conductivity.

Influence of the reaction time on the dielectric properties and resistance of polypyrrole/polyester fibre composites

To explore the influence of the reaction time on the dielectric properties of polypyrrole coated fabrics composites, the four groups of samples produced were tested according to the process prescription given in **Table 3**.

Table 2. Technological parameters. *Note:* No. 0 is untreated fabric. Reaction time is 90 min. Ambient temperature is 10 °C.

No.	Dosage of dopant (Hydrochloric acid), mol/l	Mole ratio of oxidant (Iron (III) chloride) to pyrrole	Pyrrole concentration, mol/l	Reaction temperature, °C
1	0.6	1:2	0.8	Ambient temperature
2	0.6	1:2	0.8	30
3	0.6	1:2	0.8	50
4	0.6	1:2	0.8	70

Table 3. Technological parameters. *Note:* No. 0 is untreated fabric. Reaction temperature is ambient temperature. Ambient temperature is 10 °C.

No.	Dosage of dopant (Hydrochloric acid), mol/l	Mole ratio of oxidant (Iron (III) chloride) to pyrrole	Pyrrole concentration, mol/l	Reaction time, min
1	0.6	1:2	1.0	30
2	0.6	1:2	1.0	60
3	0.6	1:2	1.0	90
4	0.6	1:2	1.0	120
5	0.6	1:2	1.0	150

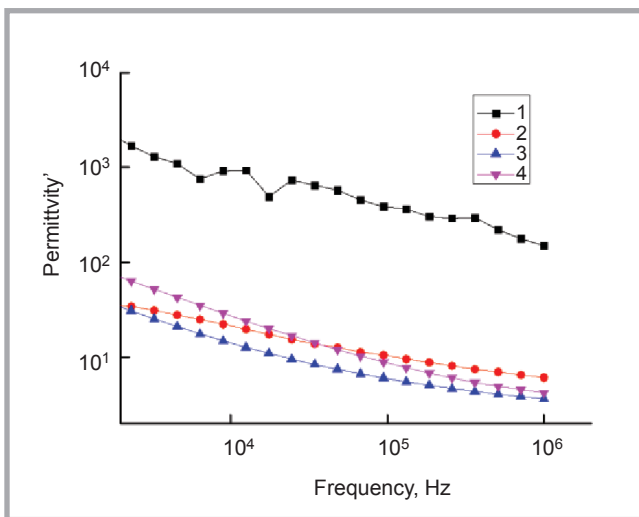


Figure 9. Influence of the reaction temperature on the real part of the dielectric constant.

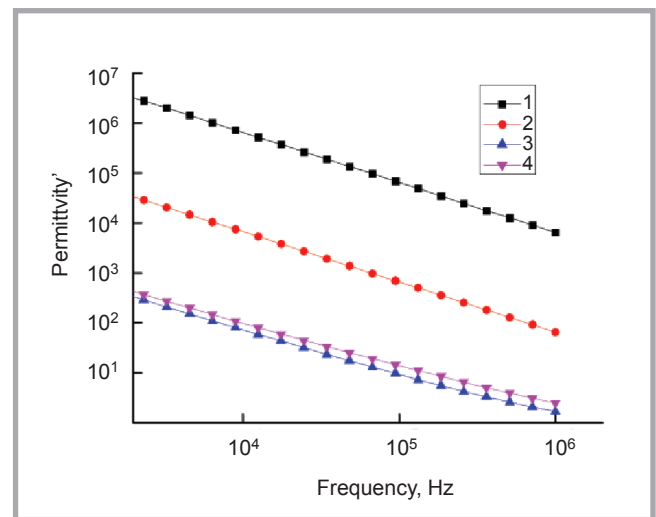


Figure 10. Influence of the reaction temperature on the imaginary part of the dielectric constant.

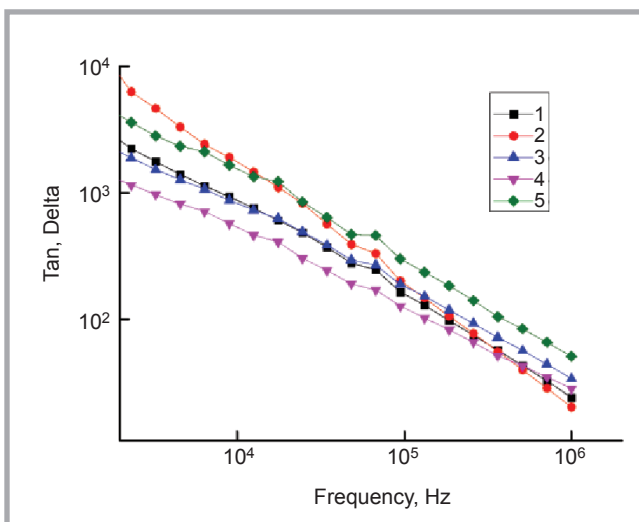


Figure 11. Influence of the reaction temperature on the loss tangent.

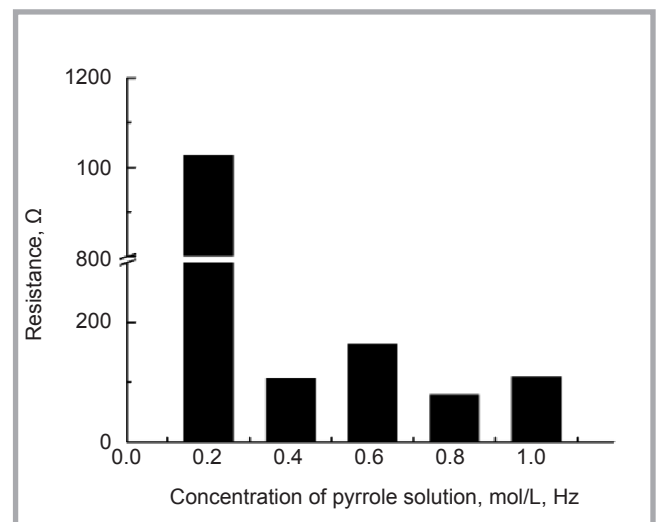


Figure 12. Influence of the reaction temperature on resistance.

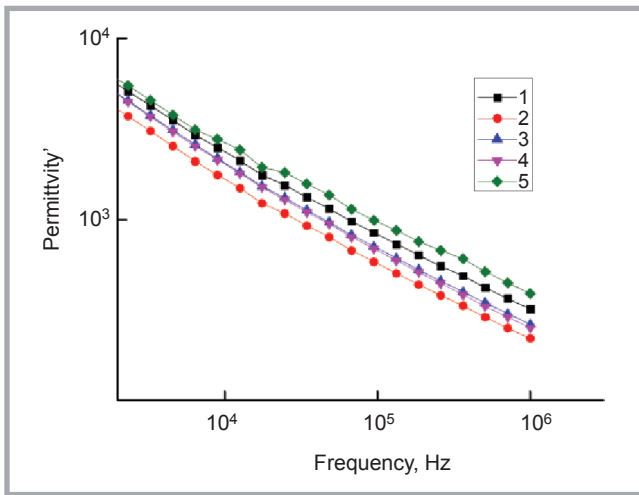


Figure 13. Influence of the reaction time on the real part of the dielectric constant.

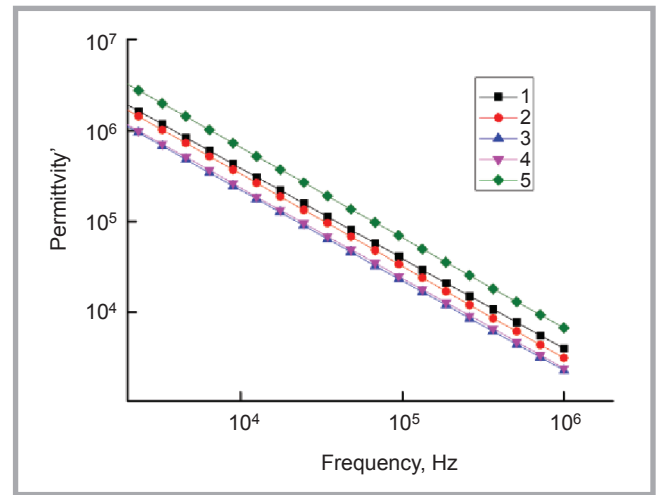


Figure 14. Influence of the reaction time on the imaginary part of the dielectric constant.

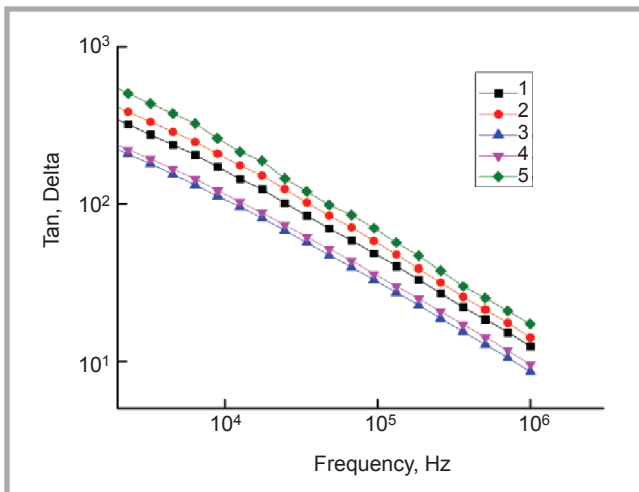


Figure 15. Influence of the reaction time on the loss tangent.

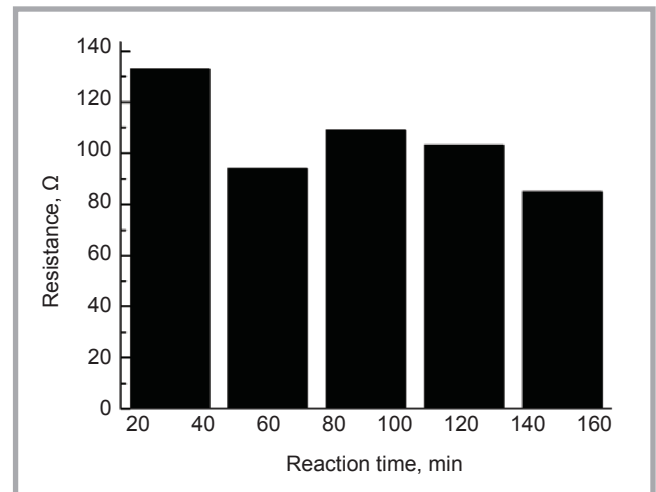


Figure 16. Influence of the reaction time on the resistance.

From **Figures 13 to 15**, it is clear that the values of the real and imaginary parts of the dielectric constant and the loss tangent of each group decrease with an increase in frequency. Various dielectric properties of the group produced using a reaction time of 150 min are better than for the other groups. This may be due to the smooth surface of polyester fibres, which were not treated by reducing the dosage of alkali before the reaction, and thus a longer reaction time was needed.

Figure 16 shows that the value of the resistance of the 150 min group is at its smallest, that the electrical conductivity is at its best, that the resistance of the 30 min group is at its largest and the electrical conductivity is at its worst.

Conclusions

In the 0-10⁶ Hz frequency range, the values of the real and imaginary parts of

the dielectric constant of the composites produced using different pyrrole concentrations decrease with an increase in frequency; the values of the real and imaginary parts of the dielectric constant of the 0.8 mol/l group are both at their largest. The value for the 1.0 mol/l experimental group is at its largest, while the value of the surface resistance of the 0.8 mol/l group is at its smallest, and the value of the surface resistance of the 0.2 mol/l group is at its largest, which is 12 times that given by the 0.8 mol/l group.

In the 0-10⁶ Hz frequency range, the values of the real and imaginary parts of the dielectric constant and the loss tangent for the experimental group produced by polymerisation at ambient temperature are at their largest, which is superior to other groups. The value of the surface resistance for the experimental group produced at ambient temperature is at its smallest and the electrical conductivity

is at its strongest; the higher the reaction temperature, the larger the value of the resistance. The various dielectric properties of the 150 min group are better than for the other groups; the value of the resistance is at its smallest and the conductivity is at its best; the value of the resistance of the 30 min group is at its largest and the conductivity is at its worst.

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