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# Preparation of Polypyrrole/Polyurethane Foam Composite Material

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## Abstract

Firstly, the paper focused on the polyurethane foam soaking process with pyrrole solution, and discuss the estimated electro-mechanical properties of the modified PU foam. Secondly, scanning electron microscopy (SEM) micrographs were collected to understand the polypyrrole distribution inside the foam. The results show that the chemical polymerisation parameters needed to realise this amount of polypyrrole in the foam were 0.1 mol/L of pyrrole, a mole ratio of 1:2.25, an oxidation temperature of  $12 \pm 3$  °C, and an oxidation time of 2 hours. SEM images of the samples prepared with the modified approach showed a continuous layer of about 10-15  $\mu\text{m}$  thickness of the polypyrrole attached to the surface of the PU foam.

**Key words:** pyrrole; polypyrrole, polyurethane foam, mechanical properties.

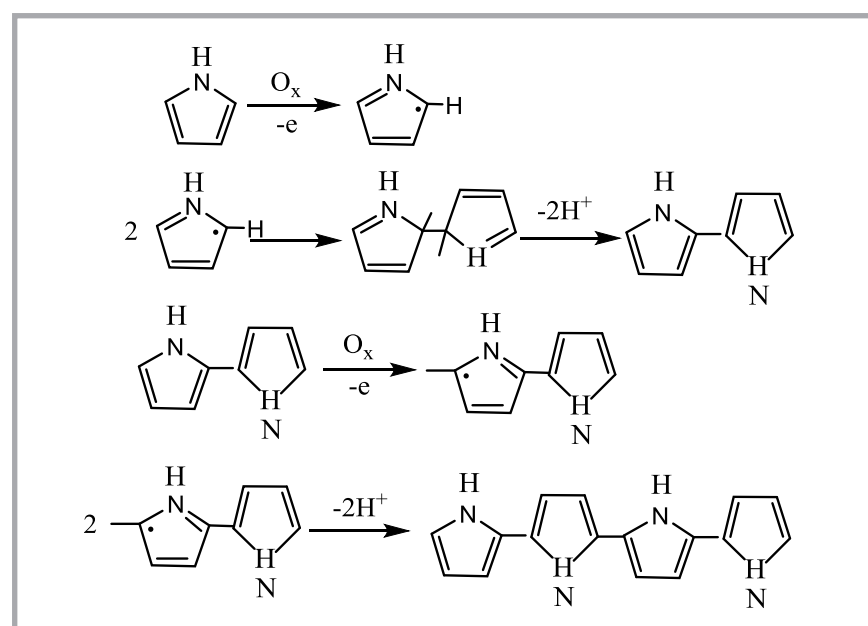
the process of preparing polypyrrole using the method of in situ polymerisation, when pyrrole monomers are oxidised to form bonds, some of its molecular chains will form defects of free radicals with positive charges due to the oxidised doping; at this time, the conjugate structure of single bonds and double bonds arranged alternatively is interrupted by these defects, and new energy gaps are produced respectively in the band gaps. When molecular chains form positive charges due to the oxidised doping, pairs of positive ion-free radicals, called polarons, can be formed. The higher the polaron number, the better the conductivity [10-13]. When the oxidation degree increases, free radicals of adjacent polarons can combine to produce new bonds, and consume the number of free radicals. The molecular chain does not have a lot of free radicals at this moment, most of

which are pairs of positive-positive ions, known as double polarons. The more the double polarons, the better the conductivity of polypyrrole [14-18].

In the first initiation step, the monomer is oxidised by  $\text{FeCl}_3$  to form a radical cation. Subsequently, this radical cation monomer reacts with the neutral pyrrole monomer. The product is then oxidised and deprotonated to form a neutral dimer, which is instantly oxidised to form a dimeric radical cation. Another monomer is then attacked by the dimeric radical cation formed, yielding a trimer. The chain then constantly grows via constant oxidation of the products formed and subsequent attacks on neutral monomers, yielding first oligomers and finally the desired polymer [18-21]. The basic principle of the polymerisation is shown in **Figure 1** and explained below.

## Introduction

The pyrrole formula is five yuan heterocyclic containing N. Polypyrrole is a linear macromolecule connected through the coupling of 2 and 5 pyrrole rings. Polypyrrole molecules have a conjugate structure of bonds of carbon and double bonds of  $\text{C}=\text{C}$  arranged alternately. The electron transfer of conjugated conducting polymers can be explained by the band theory [1-4]. Its double bonds of  $\text{C}=\text{C}$  are composed of  $\sigma$  electrons and  $\pi$  electrons, where  $\sigma$  electrons are fixed and unable to move, forming covalent bonds between carbon atoms [5]. The two  $\pi$  electrons in conjugated double bonds are not localised on a carbon atom; they can transfer from one carbon-carbon bond to another; namely, they have a tendency of extending in the entire molecular chain, that is to say, the intramolecular electron clouds overlap to produce an energy band possessed by the whole molecule. In this sense,  $\pi$  electrons are similar to free electrons in the metal conductor [6-9]. When combined with an electric field,  $\pi$  electrons can move quickly along the chain, making the polypyrrole conductive. In



**Figure 1.** Process of generating polypyrrole from pyrrole.

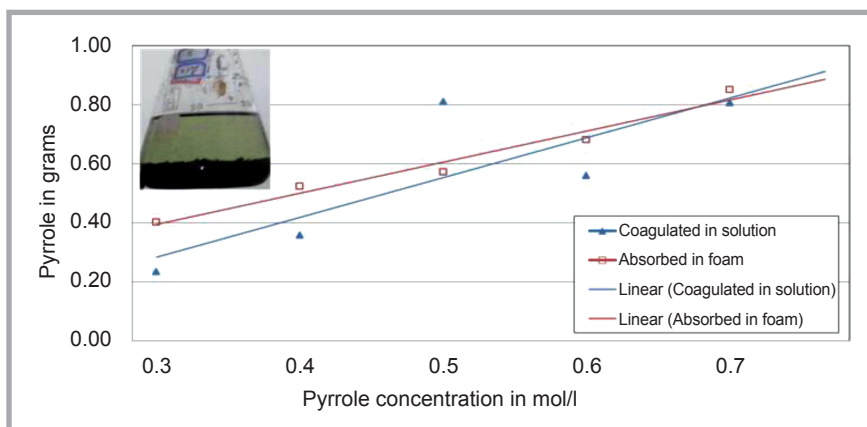


Figure 2. Polypyrrole absorbed in the foam vs. coagulated polypyrrole in the solution.

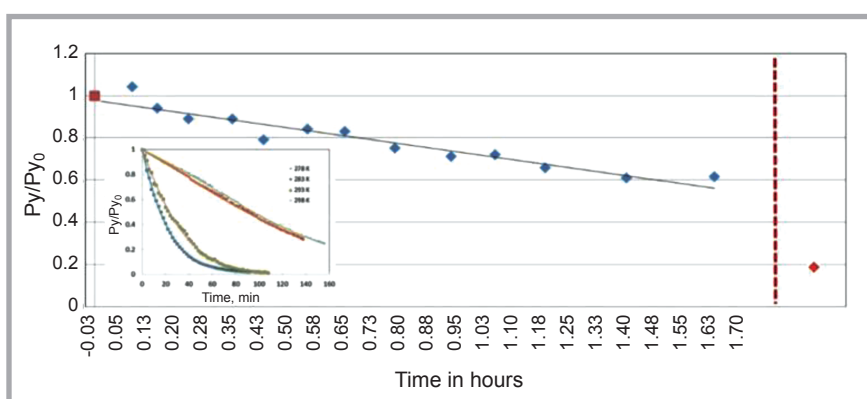


Figure 3. Pyrrole decline during the modified polymerisation approach.

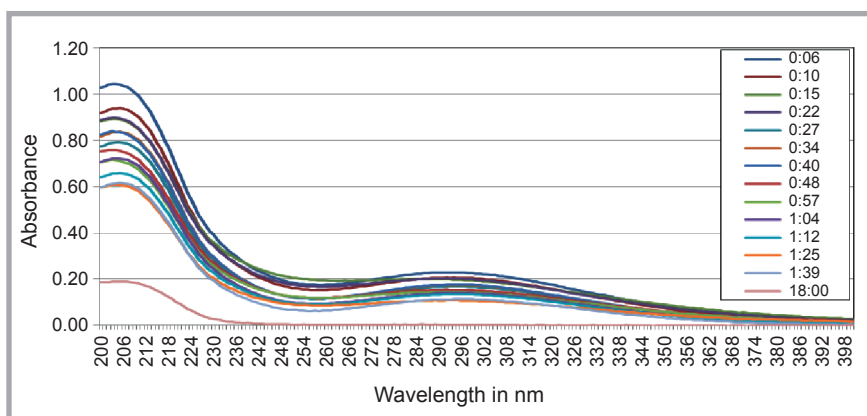


Figure 4. Absorbance spectrum from 200-400 nm.

The paper first focused on the obtaining of composite foams by soaking PU foam with pyrrole, which was then polymerised by the oxidative process, and subsequently the empirical electro-mechanical properties of the modified PU foam were discussed. Chemical oxidation was used here for the polymerisation of polypyrrole. Iron Chloride ( $\text{FeCl}_3$ ) served as the oxidant and deionised water as the solvent.

## Experiment

### Main materials and reagents

Material: the polyurethane foam (tensile strength: 1.0 Mpa, resilient rate: 30%, density:  $19 \text{ kg}\cdot\text{m}^{-3}$ ), produced by Zhejiang Hangzhou Rongsheng Chemical Fibre Co., LTD.

Ferric chloride, analytically pure, produced by Tianjin Fengchuan Chemical Reagent Technology Co., LTD.

### Main experimental instruments

An S-4800 type ice emission scanning electron microscope (sem), produced by the Hitachi company, Japan. A 3369 Type universal strength tester, produced by the INSTRON company, USA. An LFY-216C type fabric moisture transmission test instrument, produced by the Shandong Textile Science Instruments Institute.

### Materials and sample preparation

A liquid pyrrole monomer was dissolved in deionised water and the foam sample added. The pyrrole-foam mix was rotated for two hours prior to treatment with an oxidant solution in an infrared machine (AHIBA NUANCE ECO) at  $36 \text{ rpm}$  to ensure complete penetration of the pyrrole into the foam. A pyrrole to deionised water mixing ratio of 1:2.25 was used. In experiments with an oxidation temperature of  $25 \text{ }^\circ\text{C}$ , the foam-pyrrole-oxidant solution was constantly kept in motion during the oxidation by means of an infrared dyeing machine from AHIBA. In later experiments with an oxidation temperature of  $12 \text{ }^\circ\text{C}$ , the foam-pyrrole-oxidant solution was stirred manually due to the fact that the infrared dyeing machine could not be programmed to a temperature lower than the ambient temperature. Flasks containing the reagents were placed in a water bath, which was constantly cooled using crushed ice, ensuring an appropriate oxidation environment of  $12 \text{ }^\circ\text{C}$ .

## Results and discussion

### Initial polymerisation procedure

The mole ratio of pyrrole to  $\text{FeCl}_3$  was set to 2:1, the oxidation temperature was  $25 \pm 3 \text{ }^\circ\text{C}$ , and the oxidation time was 2 hours. Figure 2 shows the pyrrole concentration in the solution on the x-axis versus the amount of polypyrrole which either coagulated in the solution (blue line) or was absorbed by the foam (red line).

The flask pictured in the top left of the illustration shows the coagulated polypyrrole after the chemical polymerisation. The amount of polypyrrole absorbed in the foam is higher compared to that of the coagulated polypyrrole for lower pyrrole concentrations; however, this is not true for higher concentrations. The quantity of coagulated and polypyrrole absorbed at a pyrrole concentration of  $0.3 \text{ mol/l}$  is  $0.23 \text{ g}$  and  $0.4 \text{ g}$ ,

respectively. The foam absorbed 74% more polypyrrole than was coagulated in the solution. On the other hand, at a pyrrole concentration of 0.7 mol/l, only 0.80 g of polypyrrole was absorbed and 0.85 g coagulated in the solution. Here, 6% less polypyrrole was absorbed than was coagulated in the solution.

### Modified polymerisation procedure

The modified polymerisation process was verified by measuring the decline in pyrrole during the chemical oxidation, the results of which are shown in **Figure 3**. The graph shows time on the x-axis versus pyrrole decline on the y-axis. The decrease in pyrrole is linear for the whole reaction. After 1 hour of oxidation about 30% of the initial pyrrole concentration was polymerised, and after 1.7 hours almost 40% had reacted. A measurement after 18 hours showed a remaining pyrrole concentration of slightly less than 20%.

The absorbance spectrum from 200-400 nm shows not only a continuous decrease in pyrrole at a wavelength of 205 nm but also the presence of pyrrole oligomers in the range 250-350 nm. The last measurement, after 18 hours, does not show any light absorbance in this range anymore, which implies complete depletion of the oligomers.

A comparison of the initial and modified polymerisation processes shows an increase in the pyrrole absorbed per cm<sup>3</sup> of polyurethane for the modified approach, while at the same time only a fraction of the pyrrole is required (**Table 1**). For the initial approach, a pyrrole concentration of 0.50 mol/l is necessary to absorb 0.019 g of pyrrole per cm<sup>3</sup> of foam. For the modified approach, an absorption amount of 0.025 g can be achieved for half of the pyrrole concentration.

### Electro-mechanical properties

The electro-mechanical properties were then measured. The results for samples with different pyrrole concentrations compounded using the modified polymerisation approach are shown in **Figures 5 and 6**.

For each of the groups a linear decrease in resistance was observed for a displacement from 20% to 70%. Resistance values for a displacement from 0 to 20% and 70 to 100% did not yield reasonable resistance values, which is why they are

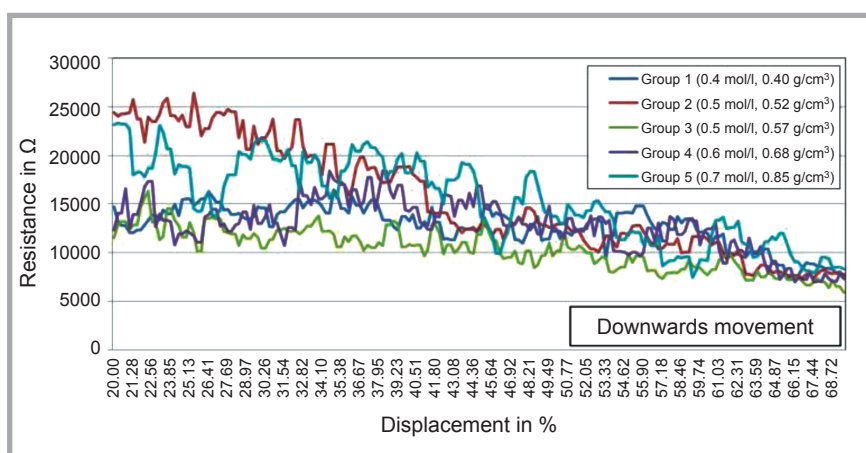


Figure 5. Resistance versus displacement while squeezing.

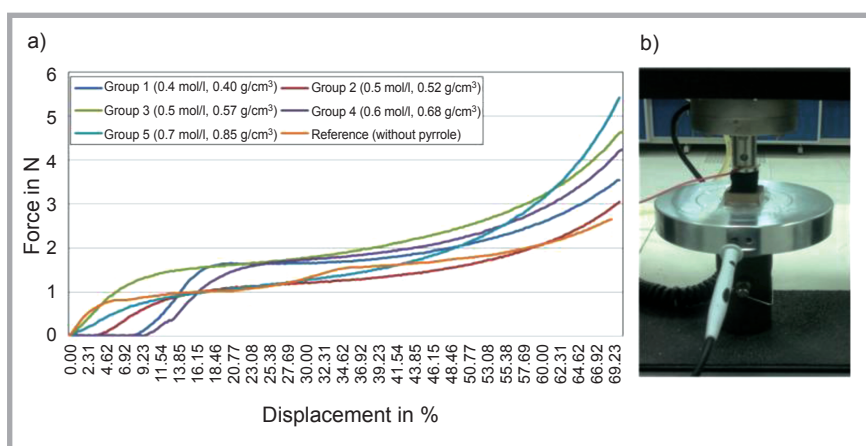


Figure 6. a) force versus displacement while squeezing, and b) electro-mechanical measurement device with sample.

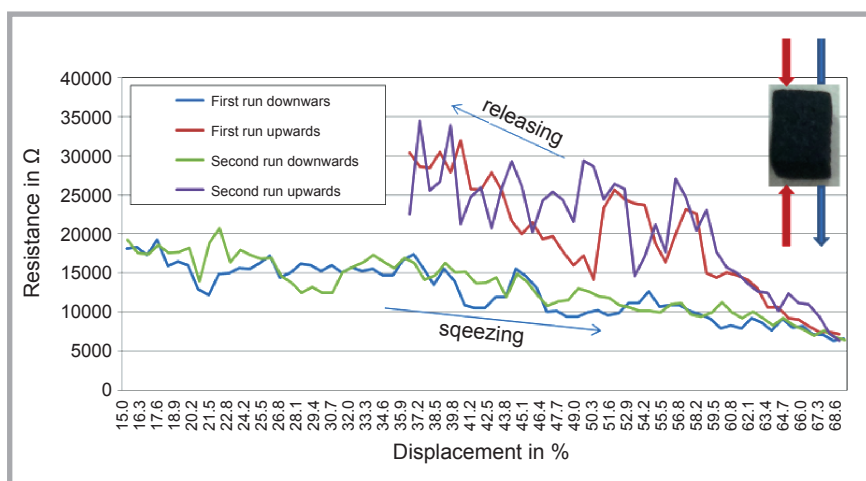
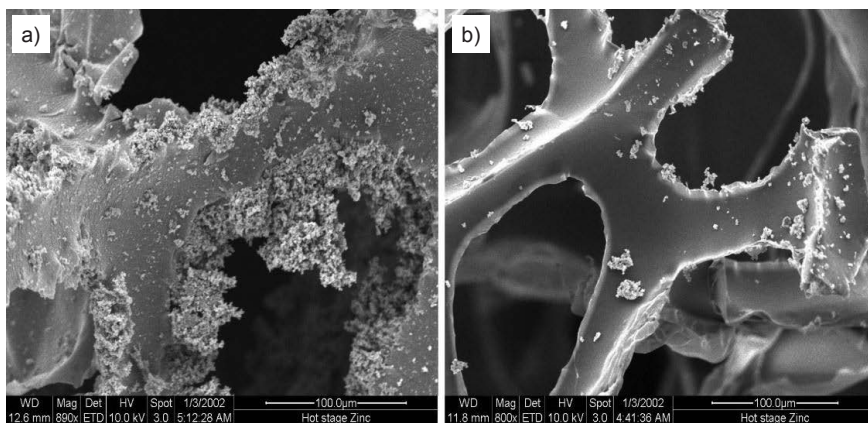


Figure 7. Hysteresis of polypyrrole modified PU foam samples.

Table 1. Comparison of the polymerisation approaches.

	Original polymerisation process									
Pyrrole conc., mol/l	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
Abs. pyrrole, g/cm <sup>3</sup>	0.001	0.003	0.005	0.007	0.009	0.009	0.012	0.013	0.016	0.019
	Modified polymerisation process									
Pyrrole conc., mol/l	0.05		0.10		0.15		0.25			
Abs. pyrrole, g/cm <sup>3</sup>	0.006		0.016		0.022		0.025			



**Figure 8.** SEM images at relatively high magnification. Comparison between the reference sample (b) and the sample with polypyrrole (a).

not considered in this report. Initial resistance values ranged from about 12000  $\Omega$  up to 25000  $\Omega$ . A relation between the polypyrrole absorbed and the initial resistance at 20% displacement could not be observed. All samples showed resistance values between 7500 and 5000  $\Omega$ , regardless of the amount of polypyrrole absorbed. On the other hand, **Figure 6** shows the increase in force needed to squeeze the sample from 20% to 70% with an increasing amount of polypyrrole per  $\text{cm}^3$  of foam. Higher stiffness at higher absorption rates was also already palpable by squeezing the sample manually in the hand. Furthermore, it should be mentioned that samples with higher absorption rates could not reach their initial height after squeezing.

The polypyrrole modified PU-foam samples exhibited a hysteresis, regardless of the amount of polypyrrole absorbed.

During the process of squeezing, a steady decrease in the resistance was observed. In contrast, releasing the samples from high to lower displacements always resulted in a much more rapid increase in the resistance, as shown in **Figure 7**. For a displacement of 40%, resistance values of about 1300  $\Omega$  and 2600  $\Omega$  were measured for squeezing and releasing, respectively. Repetition of the measurement yielded comparable resistance values for same displacements.

#### Scanning electron microscopy (SEM)

SEM images were collected to understand the polypyrrole distribution inside the foam.

**Figure 8** shows the internal structure of two foam samples with and without polypyrrole. The illustration on the

left shows a continuous layer of about 10-15  $\mu\text{m}$  thickness of the polypyrrole attached to the surface of the polyurethane. In contrast, the image on the right shows a structure of the PU foam with only minor impurities attached to the surface.

#### Conclusions

The chemical polymerisation parameters needed to deposit a polypyrrole layer of about 10-15  $\mu\text{m}$  in the pores of polyurethane foam were found to be 0.1 mol/l of pyrrole, a mole ratio of 1:2.25, an oxidation temperature of  $12 \pm 3$   $^\circ\text{C}$  and an oxidation time of 2 hours. It should also be noted that when manually squeezing the samples, irrespective of the amount of polypyrrole absorbed, a black cloud of fine polypyrrole disseminates out of the dry sample; for higher amounts of polypyrrole absorbed, this effect is more obvious. Photometric measurements at a wavelength of 205 nm for the initial and modified polymerisation process support the stoichiometric mole ratio stated. The result of the modification of the polymerisation process was, therefore, not only a significant increase in the amount of polypyrrole absorbed but also a more efficient utilisation of pyrrole; crucially, this decreases the remaining pyrrole concentration after the polymerisation. SEM images of samples prepared with the modified approach showed a continuous polypyrrole layer of about 10-15  $\mu\text{m}$  thickness on the surface of the polyurethane foam.

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