

# Supercritical Impregnation and in-situ Polymerization Electrically Conductive Fibres

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## Abstract

This work shows studies on solubility of monomers and oxidants in scCO<sub>2</sub>, on mass transport into important engineering polymers, and on in-situ polymerization. By supercritical impregnation and subsequent in-situ polymerization blends are obtained in a thermally gentle manner. Finally obtained data allow developing ecologically and economically justified - green - processes yielding polymeric blends with otherwise unattainable electrical properties such as tuneable electrical conductivity for electrostatic discharge control.

On the way to functional textile fabrics three independent process steps were investigated separately in detail: 1) solubility of monomers and oxidants in scCO<sub>2</sub>; 2) sorption of CO<sub>2</sub> into polymers / supercritical impregnation into polymers; 3) in-situ polymerization induced by oxidants (soluble ferric oxidants, iodine).

Solubility studies were conducted to approach homogeneous impregnation. In case of the more volatile liquid monomers the synthetic method was applied. The solubility of pyrrole and thiophene in scCO<sub>2</sub> follows 'type I' behaviour for binary systems, increasing steadily with density and temperature in the range of some weight-%.

Many [0]amorphous and certain semi-crystalline polymers (like PET and PA6 in this study), absorb considerable amounts of CO<sub>2</sub> in the supercritical state and are thus swollen. The polymer chains become more flexible and the glass transition temperature is depressed. By this lubricating effect and additionally by the high diffusivity and zero vapour pressure of supercritical fluids mass transport is significantly increased. Higher mass transport rates lead to more homogeneous solute distribution before equilibrium. Polymers are subjected to the experiments in form of fabrics or fibres. In-situ polymerization speed depends mostly on concentrations of oxidant and dopant as well as on thermodynamic conditions. The composite polypyrrole coated fabrics are characterized by optical- and electron microscopy (with EDS elemental analysis), Wide angle X-ray diffraction, thermo gravimetric analysis and via micro-ATR FT-IR.

## 1. Introduction

The aim of this research is to obtain electrically slightly conductive PA6 fibres, i.e. with a surface resistance measured from a fibre coil by substantially large electrodes in the range from 10<sup>6</sup>-10<sup>8</sup> Ohm. Possible applications are numerous, e.g. for electrostatic discharge control. It is known and proved again here that pyrrole or thiophene impregnated polymers can yield high conductivities when soaked in oxidant/dopant solution [1-4].

To achieve conductive fibres without using any liquid oxidant/dopant solution but instead running both impregnation and polymerization in scCO<sub>2</sub> would avoid waste in large scale. Upon expansion the solutes precipitate from CO<sub>2</sub> and can therefore be recollected and used again. Another possible benefit is time reduction for polymerization due to increased mass transfer in scCO<sub>2</sub> swollen polymer fibres. This makes the sc polymerization fundamental for the development of ecologically and economically justified – green – processes. The principle has already been proven feasible with polyester fabrics as substrate [5].

On the way to functional textile fabrics some independent process steps were investigated separately in detail: 1) solubility of monomers pyrrole (Py) and thiophene (Th), and oxidants in scCO<sub>2</sub>; 2) sorption of CO<sub>2</sub> and scCO<sub>2</sub> aided impregnation into polymers; 3) in-situ polymerization induced by oxidants (ferric triflate, iodine).

## 2. Experimental

### 2.1 Apparatus

Solubility studies were conducted in a variable volume (5-31mL) view cell applying the synthetic method, i.e. the overall composition was known. The equipment is explained in [6] and is similar to the one described in detail in [7].

Impregnation studies were conducted both in the 31mL view cell and in a 350mL autoclave with a magnetic stirring facility on the bottom. Monomers or oxidants were put onto the bottom of the autoclave. Teflon internals separated monomer/oxidant and PA6 coil. Temperature of the autoclave was set constant to 60°C with continuous flow of heated oil. Temperature calibration had been made previously in-situ with water as the heated medium and is therefore regarded to be very exact.

T<sub>m</sub> and T<sub>g</sub> of PA6 fibres were taken by a TA Instruments DSC2920.

### 2.2 Materials

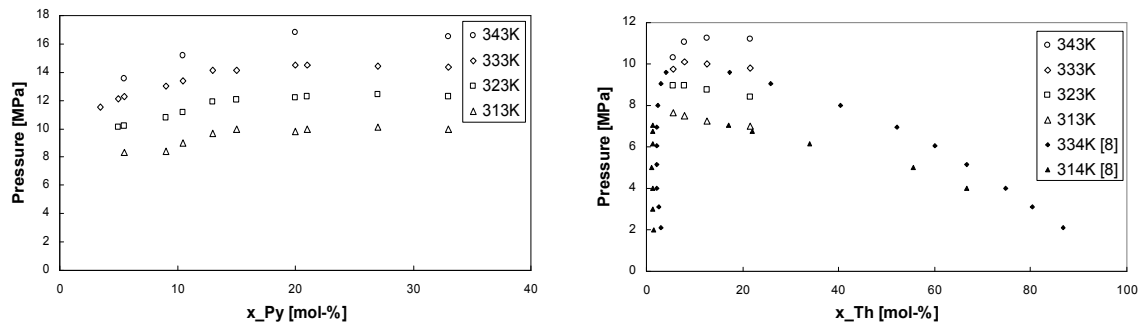
Technical grade CO<sub>2</sub> was supplied by Woikoski Oy. Pyrrole and thiophene were purchased from Acros Organics. Pyrrole was distilled and stored at + 4°C prior to use. Thiophene was delivered with a purity of min 99% and stored at + 4°C prior to use. Technical grade ethanol was used, supplied by Primalco with a purity of min 99.5%. The PA6 fibres had a fineness of 22dtex and were further investigated in this work. Ferric Triflate was donated by Klaus F. Meyer GmbH, Germany. It was dried in vacuum and stored in a desiccator prior to use; its melting point could not be determined under 150°C.

## 3 Results and Discussion

### 3.1 Solubility of Monomers and Oxidants in scCO<sub>2</sub>

The here presented solubility data is taken from previously done work [6]. Phase equilibria of the binary systems Thiophene – CO<sub>2</sub> and Pyrrole – CO<sub>2</sub> were measured at 313, 323, 333 and 343K for compositions in the range of 5.5-21.5mol% and 3.5-33mol%, respectively and shown in Figure 1. Obtained solubility for thiophene proved to be a satisfying complement to literature data [8]. Solubility of Pyrrole in scCO<sub>2</sub> is as expected a bit lower than thiophene. At relatively low pressures complete miscibility is reached for both solutes. Critical mixture points in the range from 313 to 343K taken in this work allow the guess that both binary systems Th–CO<sub>2</sub> and Py–CO<sub>2</sub> follow ordinary ‘type-1’ phase behaviour. The solubility ranges of both pyrrole and thiophene monomers proved to be high enough for impregnation studies.

**Figure 1: Solubility of Py and Th in P-x at 313- 343 K from this work ( $\Delta$ ,  $\square$ ,  $\diamond$ ,  $\circ$ ) and [8] ( $\blacktriangle$ ,  $\blacklozenge$ )**



The solubility of ferric triflate is given in literature for pure [1] and for ethanol aided dissolution [2]. In this work the ethanol aided dissolution of ferric triflate could not be established yet probably due to insufficient mixing.

The solubility of iodine is given in literature [3-4].

### 3.2 Supercritical Impregnation into Polymers

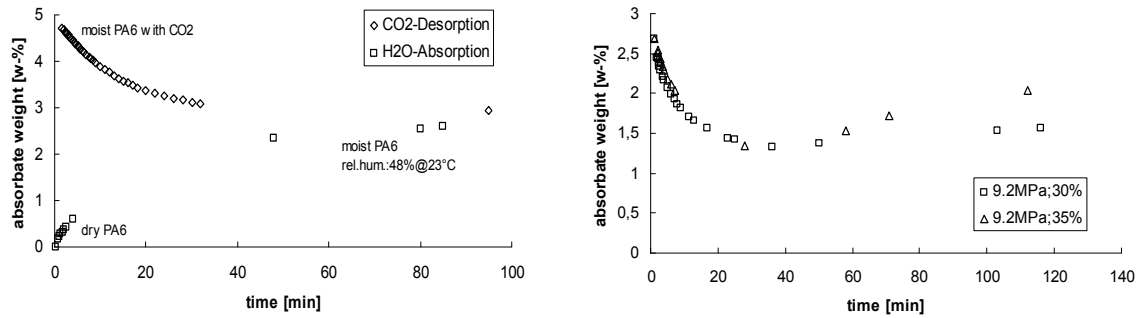
To determine the amount of impregnated monomer, H<sub>2</sub>O absorption and CO<sub>2</sub> desorption had to be investigated first.

DSC gave further insights into the PA6 fibre. The glass transition temperature was determined to 45°C; the crystalline melting temperature was 213°C. A crystallization enthalpy of 75.57J/g led to a crystallinity of 40%. At experimental conditions the amorphous fraction of 60w-% is in the rubbery state; this is where impregnation is supposed to occur. With a density of 1.14g/cm<sup>3</sup> the fineness of the fibre of 22dtex results in an outer diameter of 50µm.

#### H<sub>2</sub>O Absorption / CO<sub>2</sub> Desorption

An almost linear relationship between fibre water mass fraction [w-%] and relative air humidity at 23°C [%] was detected, the partition factor being 0.0769; zero humidity was assumed after 2 days in a 50°C vacuum oven. Air humidity varied with time but was constantly recorded. Due to the high affinity of water to PA6 and the low affinity to scCO<sub>2</sub>, the water content of the PA6 fibres does not vary significantly during the impregnation step and is regarded as constant; only a negligible amount of water will desorb from the fibres and dissolve in the surrounding sc-phase. This has been concluded from the comparison of CO<sub>2</sub> desorption experiments from moist and dried fibres. The weight of moist fibres decreased monotonously; the weight of dried fibres first decreased rapidly due to faster desorption of CO<sub>2</sub> than absorption of H<sub>2</sub>O and then after some time H<sub>2</sub>O absorbs faster than the CO<sub>2</sub> desorbs and the total weight increased slightly. In both cases upon longer exposure to ambience the water content gradually approached equilibrium with air humidity (compare Figure 2). The CO<sub>2</sub> content during the impregnation step rises quickly and is found to be constant after about 30min.

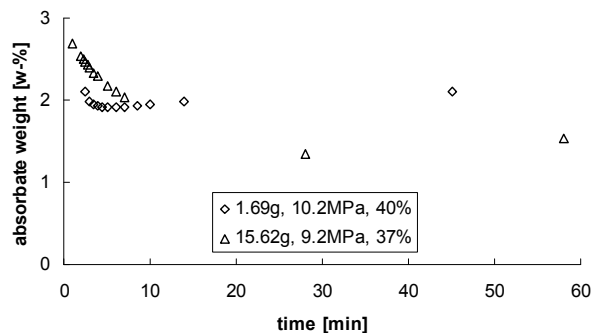
**Figure 2: CO<sub>2</sub> desorption from moist (left) and pre-dried (right) PA6 fibres**



The higher the CO<sub>2</sub> pressure was during the experiment, the higher was the absorbed mass of CO<sub>2</sub> in the fibre. Extrapolation of data points from the balance is complicated by different reasons: during depressurization and opening of the autoclave the CO<sub>2</sub> partial pressure is changing; furthermore, in order to avoid sublimation of CO<sub>2</sub> the expansion rate is thermodynamically restricted for higher pressures. Therefore only minimum absorption mass fraction can be presented: at 60°C the CO<sub>2</sub> uptake was over 2.1w-% for 5.9MPa, over 3.5w-% for 10.5MPa whereas at 16.1MPa it was more than 13w-%.

The CO<sub>2</sub> diffusivity in the PA6 fibre can not be determined from larger samples because of a time dependent bulk CO<sub>2</sub> concentration in the surrounding air. A small sample of ~1.5g reaches equilibrium with the surrounding atmosphere much faster than a sample of ~15g, as shown in Figure 3.

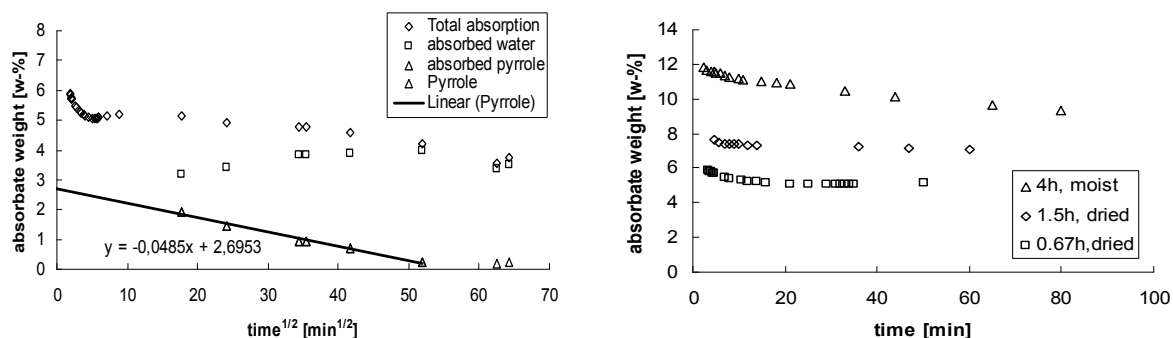
**Figure 3: Effective diffusivity dependence on coil size**



### **Pyrrole Sorption/Desorption**

All experiments were run at 60°C and around 10-11MPa, conditions at which the partition of pyrrole on PA6 was shown to be advantageous and the solubility sufficient. The pyrrole desorption is rather slow compared to the kinetic of water absorption or CO<sub>2</sub> desorption. Therefore, the uptake of pyrrole can be calculated when the sample weight is recorded for many hours. As the diffusion of pyrrole is slow the bulk concentration surrounding the coil can be regarded as constantly low so that extrapolation according to Fick's law of diffusion gives information about the initial content. The sample weight curve was extrapolated to the moment of exposure to air disregarding the influence of CO<sub>2</sub> desorption and H<sub>2</sub>O absorption on sample weight. The determination is shown in Figure 4 (left). The initial pyrrole content had only been around 2.7w-% due to short impregnation time of 40min. Longer impregnation times at same conditions led to about 5,5w-% pyrrole after 1.5h and up to 8w-% after 4h, see Figure 4 (right).

Figure 4: Pyrrole mass uptake determination (left) and influence of impregn. time (right); 60°C , 10.5MPa

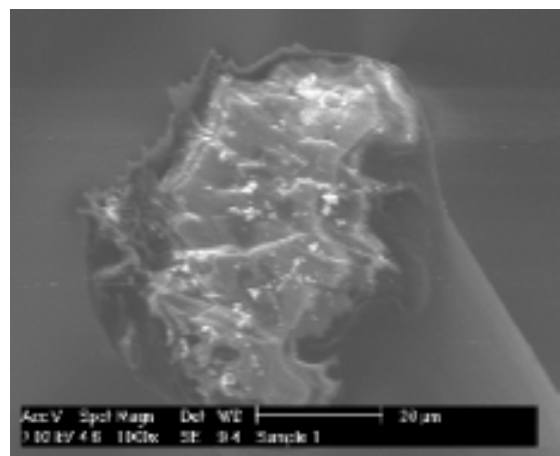


This knowledge allows letting the pyrrole exposed to air (for e.g. cleaning the autoclave, drying residual pyrrole from the sample) for some time without significant alteration of the experimental results of the subsequent polymerization step (see 3.3). Even in case of an excess amount pyrrole and precipitation upon expansion drying of the sample allows continuing the procedure.

### 3.3 In-situ Polymerization Induced by Oxidants

#### Polymerization in Liquid Solution

The time necessary for pyrrole impregnation can also be determined by putting the impregnated PA6 into a ferric triflate solution (in water or ethanol). Nearly independent of the impregnation time and solution, the PA6 fibres showed a surface resistance in the order of  $10^4$ - $10^5$  Ohm after the polymerization. Even when impregnation and polymerization lasted as short as 20min the reached conductivity exceeded the desired level. After 4h impregnation subsequent exposure to air for 5h did not reduce the pyrrole content significantly and resulted in a successful polymerization showing conductivity higher than required.



The pyrrole impregnation step is therefore shown to be as requested. The conductive part of the fibre is the outer layer as can be seen in the SEM- photograph (90min impregnation, 15min exposure to air, and 50min polymerization in ferric triflate solution). The limiting factor is the impregnation speed of the oxidant/dopant.

#### Polymerization in scCO<sub>2</sub> Solution

In scCO<sub>2</sub>+ ethanol+ ferric-triflate a satisfying polymerization of previously impregnated pyrrole has not been established yet. Only in one experiment, with a durance of one day, enough ferric triflate had been dissolved to at least blacken the fibres slightly. Still, there was no increase in conductivity. When the experiments were conducted in the opposite order, i.e. first ferric triflate and than pyrrole, the fibres remained white, too. It was therefore concluded that the problem was the dissolution of ferric triflate. It requires strong stirring that our stirring system can not perform. The polypyrrole coated the stirring bar, made its surface rough and stopped the stirring due to friction. Therefore in another experiment almost no dissolution had occurred within 3 days with 1.4vol% ethanol as cosolvent. The limiting factor

is therefore the dissolution of the oxidant in scCO<sub>2</sub>. Nevertheless, it had been reported in literature to be possible [6]. Even the whole process of supercritical impregnation and subsequent polymerization had been conducted successfully in a previous work on PET fabrics [5].

### Conclusions

Knowledge of CO<sub>2</sub> mass uptake of PA6 fibres supports the assumption that mass transport for impregnation is enhanced in supercritical compared to ambient or vacuum impregnation. It has been shown in two different ways that the supercritical impregnation of pyrrole is an unproblematic step. Pyrrole impregnation is fast and durable even without immediate subsequent polymerization. SEM-photograph showed that the polypyrrole from polymerization in liquid solution is exclusively located in an outer layer of the fibre. The polymerization, however, could not be conducted supercritically yet. The dissolution of the oxidant remains the decisive point. To overcome this problem, ferric triflate could be dissolved in scCO<sub>2</sub> (+cosolvent) in a previous step and then just brought into direct contact with the pyrrole impregnated fibre. Additionally, the stirring system must be improved. Further research will therefore be directed to the oxidant, its dissolution in scCO<sub>2</sub> and its partition between CO<sub>2</sub> and the impregnated fibre.

### Acknowledgements

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