

GOING FROM POLYMER TO APPLICATION: SOLVENT ELECTROSPINNING OF OPTICAL NANOFIBROUS SENSORS

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ABSTRACT (10 pt)

Optical nanofibrous sensors show potential in many application areas, including biomedicine, as they provide ultra-sensitivity combined with versatility, flexibility and user-friendliness. In our work stimuli-sensitive dyes are incorporated in a polymeric nanofibrous matrix by the process of solvent electrospinning. An important challenge that is tackled here is dye-immobilization as to design a stable sensor. In addition, an ecological friendly production process is aimed for resulting in the use of “green” solvents such as water and ethanol. However, the use of hydrophilic polymers poses some challenges with regard to the solvent electrospinning process, which are addressed in this work as well.

Key Words: SOLVENT ELECTROSPINNING, NANOFIBERS, OPTICAL SENSORS

1. INTRODUCTION

The development of so-called smart materials, *i.e.*, materials that are able to sense and respond to changes in their environment, is a hot topic in today’s research. Stimuli-responsive dyes show high potential within this field as environmental changes such as pH or the presence of a specific substance are visualized by a fast and simple change in optical properties, *i.e.*, color or fluorescence. A smart optical sensor can be fabricated by incorporating such dyes into a suitable matrix material (Figure 1), resulting in a custom, user-friendly product, providing clear information in a non-destructive way. Polymer nanofibers are a very well suited matrix material since nanofibrous nonwovens are characterized by a high specific surface area, small pore size, high pore volume and high absorbance capacity, making them ideal candidates for advanced, fast-responding sensor applications. However, many challenges are still to be faced.[1]

Dye-immobilization is currently a major challenge in nanofibrous sensor design as dye-doped solvent electrospinning, *i.e.*, the most commonly applied processing technique, suffers from leaching of the dye from the nanofibrous network. Our research focuses on dye-immobilization through covalent dye-modification, where the polymer backbone is modified with the dye before electrospinning, providing a covalent linkage between dye and polymer. This technique is of particular interest for the application of natural (bio)polymers, *e.g.*, chitosan.[2,3]

Another important challenge for the electrospinning field is that of environmental awareness. Although electrospinning is a well-known, already industrially available technique, its large breakthrough is limited by the use of deleterious solvent systems needed to solubilize the commonly applied hydrophobic polymers. Thermoresponsive polymers showing LCST (lower critical solution temperature) behavior might clear the way for so-called green electrospinning from ecological friendly solvent systems. These type of polymers show excellent aqueous solubility below their LCST but are stable above this threshold temperature. This indeed means that polymers with an appropriate LCST can be electrospun from aqueous solvent systems at room temperature, yet are stable at a specific application temperature. In our work we show that electrospinning from aqueous solvent systems requires special care as the control of ambient parameters such as temperature and relative humidity play a crucial role in the stability of the electrospinning process and the final nanofiber morphology.[4]

By facing these challenges our research aims to contribute to the knowledge on the design of optical nanofibrous sensors produced by an ecological friendly process, which might be of great interest to various fields of application including biomedicine.

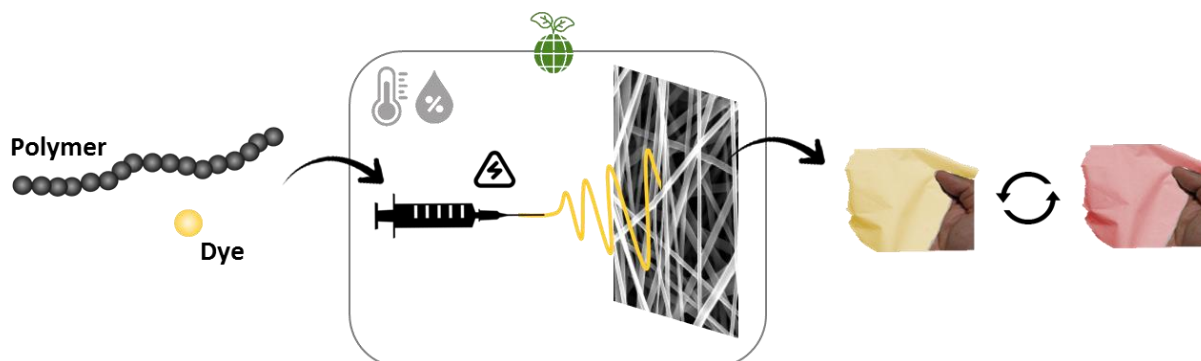


Figure 1. A polymer solution is functionalized with a stimuli-sensitive dye and subsequently electrospun in an ecological friendly way resulting in a nanofibrous membrane capable of changing its color upon external stimuli.

2. RESULTS AND DISCUSSION

Dye-immobilization for stable sensor design[1,3]

Covalent dye-modification is presented as an attractive alternative strategy to the commonly applied dye-doping technique for the production of colorimetric nanofibrous sensors, as dye-doped samples frequently suffer from dye-leaching. Here, the introduction of halochromism into nanofibers was successfully executed by the covalent modification of chitosan with two halochromic dyes from commonly used dye-classes, *i.e.* azo-dyes and xanthene-dyes, before blend electrospinning with poly(ϵ -caprolactone) (Figure 2).

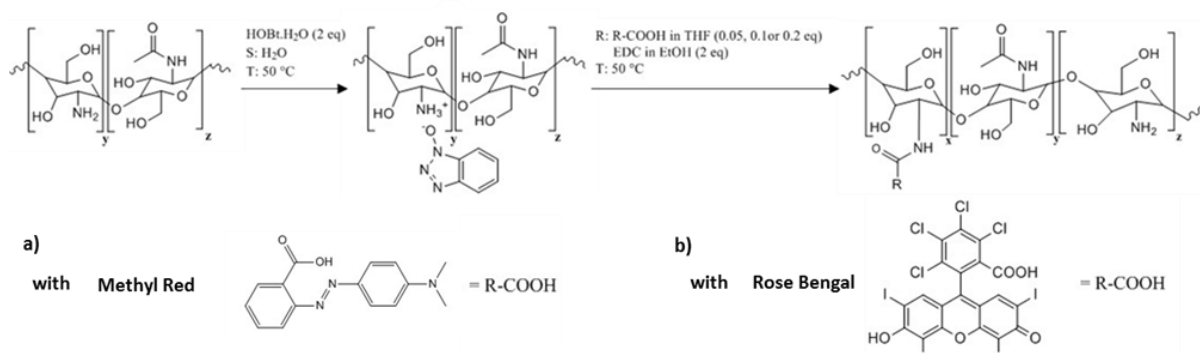


Figure 2. Modification of chitosan with a) Methyl Red and b) Rose Bengal resulting in red and pink colored powders, respectively, with brightness depending on dye-concentration.

Albeit with electrospinnability depending on the dye, biocompatible, fast responding, halochromic nanofibers were fabricated that instantaneously respond to pH-changes in both aqueous solution and when exposed to acidic or basic gases (Figure 3). In addition, covalent dye-modification was proven to be a viable dye-immobilization strategy, since the dyes were fully immobilized in the biomedical relevant pH-region, with only minor changes in their halochromic properties (Figure 4).

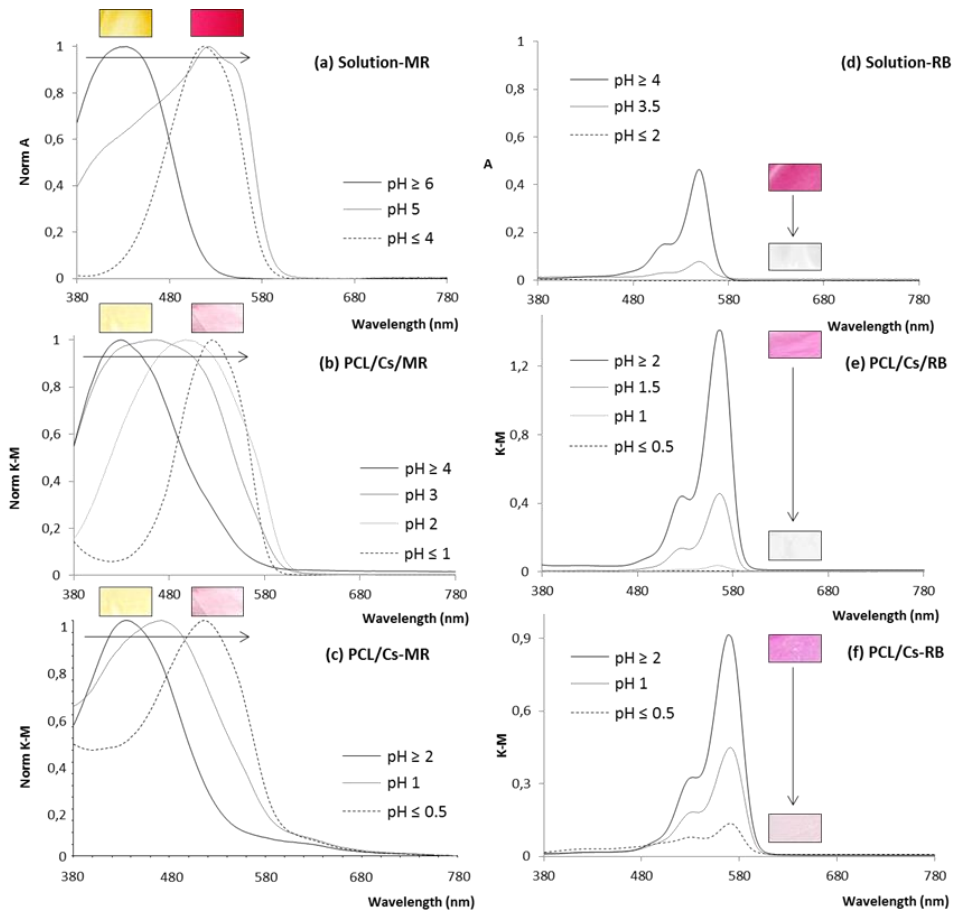


Figure 3. UV-Vis spectra show similar halochromic behavior of dye-doped and dye-modified nanofibers as the dyes in solution, except for a decrease in dynamic pH-range due to the presence of the polymer structure. The covalent modification, thus, leaves the halochromic behavior of the dyes intact.

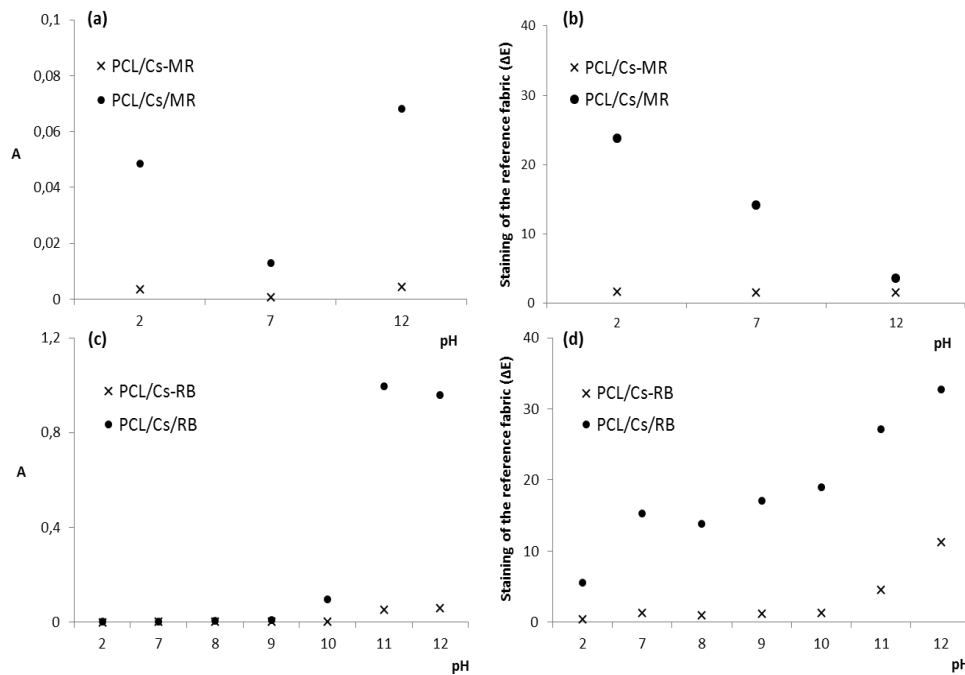


Figure 4. Comparison of leaching towards water baths (left) and migration towards reference fabrics (right) between dye-doped and dye-modified nanofibers, indicates efficient impediment of dye-release when the dye is covalently coupled to the polymer backbone.

Stable halochromic nanofibers show potential in many fields such as protective clothing, agriculture and biomedicine. For the latter, and wound management in particular, future research will include a broadening of the selection of suitable dye-matrix combinations towards color changes in the pH-range within the neutral to alkaline pH-region, as this is the pH-range accompanied with wound healing. The results given here already paved the road for covalent dye-modification combined with blend electrospinning, which has major potential, particularly, in the area of natural (bio)polymers, as it provides a universal method for versatile dye-functionalization of large area nanofibrous membranes, accompanied with proper dye-immobilization.

Green electrospinning of thermoresponsive polymers [4]

With increasing toxicity and environmental concerns, electrospinning from water, *i.e.*, waterborne or green electrospinning, is crucial to further exploit the resulting nanofiber potential. Most water-soluble polymers have the inherent limitation of resulting in water-soluble nanofibers and a tedious chemical cross-linking step is required to reach stable nanofibers. An interesting alternative route is the use of thermoresponsive polymers, such as poly(N-isopropyl acrylamide) (PNIPAM). PNIPAM is a well-known and commonly applied polymer in biomedical applications as its Lower Critical Solution Temperature (LCST) of *ca.* 30-35 °C in water is beneficial for use in drug delivery and cell culture. Below the LCST, hydrogen bonds are present between water molecules and the hydrophilic regions of the polymer chains, resulting in excellent water-solubility of PNIPAM. Yet, if the temperature is raised above the LCST, it becomes thermodynamically more favorable for the hydrating water molecules to go back to the bulk water, which is an entropic effect. As a result, the partially dehydrated PNIPAM chains become water insoluble and agglomerate (Figure 5).

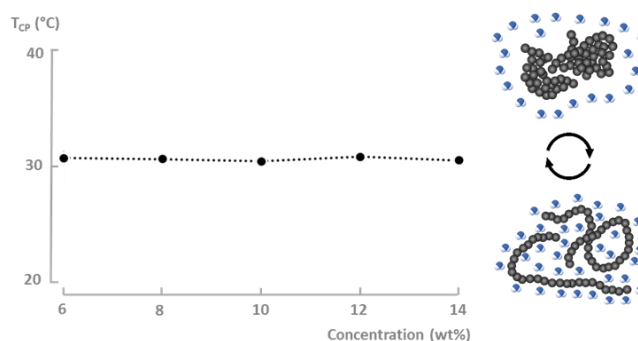


Figure 5. Cloud point temperature of PNIPAM in water as function of concentration determined by turbidimetry confirms the LCST of PNIPAM of *ca.* 31 °C.

This thermoresponsive behavior of PNIPAM allows low temperature electrospinning while the obtained nanofibers are water-stable above the LCST. Based on dedicated turbidity and rheological measurements, optimal combinations of polymer concentration, environmental temperature and relative humidity can be identified allowing, for the first time, the production of continuous, bead-free PNIPAM nanofibers electrospun from water. More specifically, PNIPAM gelation was found to occur well below its cloud point temperatures at higher polymer concentrations leading to a temperature regime where the viscosity significantly increases without compromising the polymer solubility. For concentrations around 8 wt% for instance, PNIPAM shows gelation at significantly lower temperatures than the LCST, resulting in a clear, transparent gel-like structure. This phenomenon proved to be crucial for PNIPAM's electrospinnability as it provides a concentration-dependent temperature range around the gelation temperature, wherein good solubility is combined with an increased viscosity that is suited for stable electrospinning from water (Figure 6).

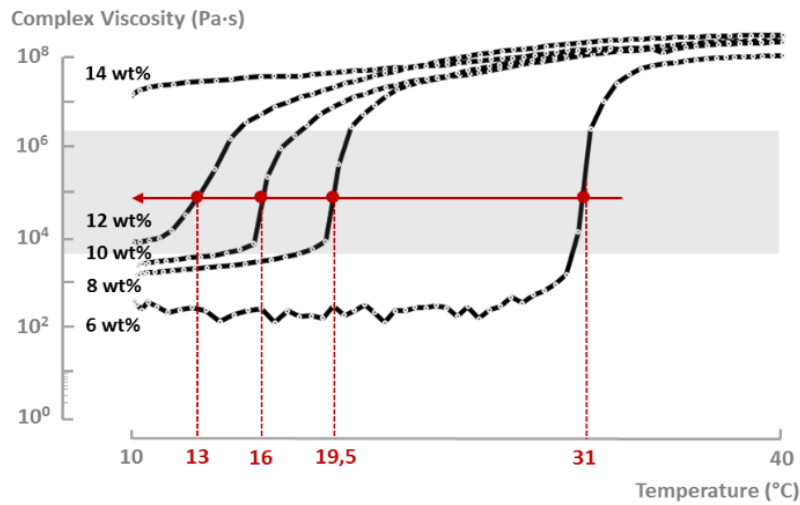


Figure 6. Complex viscosity (log scale) as a function of temperature based on rheological experiments; gelation: at lower temperatures for higher PNIPAM concentrations and determining the ideal viscosity range for electrospinning (highlighted in grey).

Although majorly overlooked in literature today, it is therefore crucial to adjust and control the environmental temperature as such. Moreover, also the relative humidity proved to play a crucial role, as a lower relative humidity (25 % RH) allows for a sufficiently fast water evaporation, required to form uniform nanofibers (Figure 7).

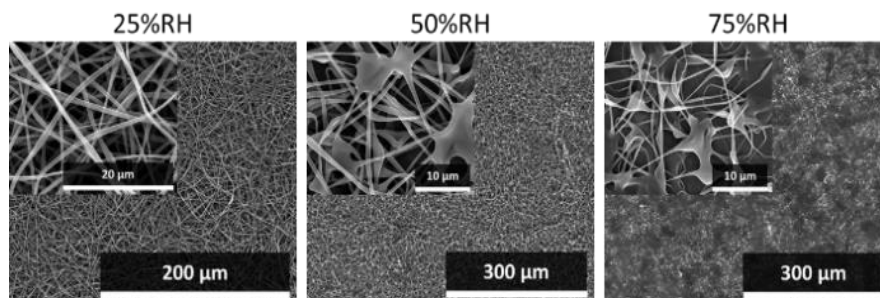


Figure 7. SEM images of 8 wt% PNIPAM nanofibers after electrospinning at different relative humidity, clearly showing non-uniformity and beads at increasing relative humidity. Temperature was kept constant at 20 °C based on the rheological results in Figure 6.

It can be expected that these insights will not only apply to the electrospinning of PNIPAM but also to the electrospinnability of its related copolymers and other thermoresponsive (co)polymers. This hypothesis as well as the investigation of different molecular weights and the influence of salts, which are known to influence the LCST behavior of PNIPAM, will be the focus of future research. Nevertheless, the current results already provide important insights in the rheological behavior of the thermoresponsive polymer PNIPAM and its ecological electrospinnability from water, showing major potential to many applications in biomedicine, including drug delivery and cell culture.

3. ACKNOWLEDGEMENTS

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