Influence of non-thermal plasma treatement on the adsorption of a stimuli-responsive nanogel onto polyethylene terephthalate fabric

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ABSTRACT

This paper presents an in-depth study of the surface modification of polyethylene terephthalate fabric (PET) with non-thermal plasma and temperature- and pH-responsive nanogel (PNCS) to impart smart thermoregulation properties. To increase the adsorption of the PNCS nanogel onto the PET, ammonia and oxygen plasma and a combination of both plasma gases were used. Chemical changes caused by the plasma treatment were investigated using X-ray photoelectron spectroscopy (XPS), morphological changes were determined using scanning electron microscopy (SEM) and the swelling and de-swelling ability was determined by measuring the moisture content at 20 and 40 °C. The greatest deposition of the PNCS nanogel, with unimpaired swelling ability, was found on the oxygen-plasma-treated samples, as they had the highest O/C ratio. Meanwhile, the least promising results were found for the samples treated with a combination of oxygen and ammonia plasma, where the highest concentration of nitrogen was present on the fibre surface. Since the treatment with oxygen plasma proved to be the most effective method, different exposure times to the oxygen plasma, namely, 10, 30 and 60 s, were studied in the second part of this study. The optimal oxygen plasma treatment time was found to be 30 s, where the greatest deposition and unhindered swelling/de-swelling ability of the PNCS nanogel on the PET fabric was achieved.

1. Introduction

Adaptive textile materials for increased comfort during wearing, can be tailored with the use of smart coatings, which provide active thermoregulation and adaptation to a variety of microclimates by switchable insulation. In warm conditions, the human body produces sweat, which needs to be able to transmit through the textile to make the wearer feel dry. Therefore, the textile material must be porous and breathable. Conversely, at lower temperatures, vapour transmittance should be blocked to obtain a microclimate next to the skin. Stimuli-responsive hydrogels in the form of micro- or nanogels, represent an important group of smart coatings, as they can affect the porosity of the textile material by the changes in their volume, which occurs as an outcome of the presence of a certain stimulus, such as temperature and pH, being the most important ones from the physiological point of view [1–3]. A hydrogel based on poly-(N-isopropylacrylamide) (poly-Ni-PAAm) and the biopolymer chitosan (PNCS) can provide these double

responsive characteristics. Temperature responsiveness is provided by poly-NiPAAm, with transition point at a lower critical solution temperature (LCST) equal to 32 °C, while chitosan governs the pH sensitivity of the PNCS hydrogel, having pKa of 6.5. This means that PNCS hydrogel exist in its fully swollen and hydrophilic phase at temperatures below 32 °C and pH below 6.5, but collapses and becomes hydrophobic at higher temperatures and pH [3–7].

In textiles, polyesters, such as polyethylene terephthalate (PET), are one of the most important synthetic fibres, distinguished by their low production costs, high chemical stability and mechanical stress resistance. Therefore, they serve as a suitable substrate for surface functionalisation; however, their inert surface, with the absence of active functional groups in the polymer chain, represents an obstacle to the adhesion of the functional finish. Surface modification of PET fibres can be achieved by plasma treatment [8], as plasma can cause hydrogen to separate from the polymer backbone, resulting in the creation of free radicals, which subsequently interact with oxygen or nitrogen from the

air and create new functional groups on the polymer surface. Depending on the gas used, different active groups can be attached to the polymer surface on the places where C−C and C−H bonds were broken [1]. Etching of the fibre surface leads to roughness and therefore increased specific surface area of the fibres. It is achieved with a longer treatment time and greater discharge power [9–12].

In previous studies, suitability of plasma treatment of various textile substrates before their functionalisation by PNCS hydrogel was proven [7,13–15]. To achieve greater stability of the PNCS hydrogel, Tourrette [7] used oxygen, nitrogen and argon low-temperature plasma to activate the surface of cotton fibres. Aside to increased number of functional groups on the surface of the fibres, the beneficial effect of plasma treatment was also shown in increased roughness of the fibres by etching, which resulted in greater contact between the fibres and microgel particles and thus in greater adsorption of the PNCS hydrogel. To perform graft polymerization of NIPAAm, followed by *in situ* hydrogel formation [14] and subsequent chitosan incorporation into the textile-hydrogel composite [15], argon plasma was used for the treatment of PET and polypropylene (PP) nonwoven fabrics. In both cases, argon plasma provided better wettability and larger graft density for the graft polymerisation.

In this study, non-thermal plasma treatment for the application of the PNCS nanogel on PET fibres was researched, with the intention of reaching the greatest deposition of PNCS nanogel onto the fabric while preserving its stimuli responsiveness. For this purpose, oxygen and ammonium plasma were chosen. Oxygen plasma is commonly used when the surface energy of the polymer should be increased and is known to greatly influence the hydrophilicity, therefore, achieving greater coating deposition on various polymer materials [16–18]. On the other side, ammonia plasma forms NH_2 and NH radicals as well as hydrogen and nitrogen atoms, which cause the functionalisation of the polymer with amino groups [19] as well as weak etching. It is suitable for treatment of oxygen-rich polymers, as the latter is partially replaced with nitrogen. Accordingly, hydroxyl and amine groups were found to increase on the PET fibres treated with ammonia [20,21]. Both ammonia and oxygen plasma increase the hydrophilicity of the otherwise hydrophobic PET fibre [10,22]. Therefore, it was expected that exposing the PET fabric to oxygen or ammonia plasma or a combination of both plasma gases could manifest in a greater concentration of the PNCS nanogel on the fibre surface while preserving the stimuli responsiveness of the coating. Furthermore, bearing in mind that the size of the hydrogel particles greatly influences their responsive characteristics, whereas a decrease in the hydrogel particle size cuts down response times [23,24], a PNCS nanogel, with a hydrogel particle diameter less than 100 nm when in its shrunken state, was synthesized and used in this study.

The research was divided in two parts, which gave the opportunity to systematically achieve the set goal. The first part of the study was focused on determining the most appropriate plasma gas or combination of gases that enable the unimpeded swelling and de-swelling of the applied nanogel. In the second part of the research, our focus switched to determining the optimum functionalisation time for the chosen plasma, followed by an in-depth characterization of the morphological changes and the temperature and pH responsiveness of the functionalised samples.

2. Experimental

2.1. Materials

In this study, 100% PET with a 182 g/m^2 mass area (warp density: 24 threads/cm; weft density: 21 threads/cm) provided by Luma d.o.o, Slovenia was used. For the preparation of the PNCS nanogel, chitosan (Chitoclear, Primex, Iceland; DD = 95%; η = 159 mPa), glacial acetic acid (Sigma Aldrich), N-isopropylacrylamide (NiPAAm) (Sigma Aldrich), N,N-methylenebisacrylamide (MBA) (Sigma Aldrich),

ammonium persulfate (APS) (Sigma Aldrich), N,N,N',N'-tetramethylethylenediamine (TEMED) (Sigma Aldrich) and sodium dodecyl sulphate (SDS) with high purity (GE Healthcare Life Sciences) were used.

2.2. Synthesis of the PNCS nanogel

Free radical polymerisation was used to synthesize the PNCS nanogel. First, 0.32 g of APS and 0.1 g of TEMED were dissolved in 60 mL of distilled water. The mixture was put in a flask, heated to 70 °C and degassed with nitrogen for 30 min with constant stirring (420 rpm). Monomer solutions were prepared as follows: 4 g of NiPAAm, 0.08 g of MBA and 1.58 g of 10% SDS solution was dissolved in 100 mL of distilled water. Chitosan (0.57 g) was dissolved in a 171 mL 0.6 w/w% solution of glacial acetic acid and stirred for 24 h prior to use. The monomer solutions were added into the polymerisation mixture dropwise at 2 h intervals. Polymerisation proceeded for 4 h at 70 °C, in a nitrogen atmosphere at constant stirring. Subsequently, the reaction mixture was dialysed against bi-distilled water using a Spectra/Por 4 membrane (Fisher Scientific) for 10 days to remove impurities and unreacted monomers. The water was changed daily. In this manner, PNCS nanogel with the concentration of dispersion of 8.8 g/L was prepared.

2.3. Characterization of the PNCS nanogel particle size

The nanogels morphology was inspected by transmission electron microscopy (TEM, JEOL-ARM200CF) at 80 kV. The nanogel dispersion in water was drop casted on a carbon coated Cu grid. The Cu grid was then dried overnight at room temperature in a low vacuum environment.

The hydrodynamic particle size of the dispersed nanogel, in correspondence with the changes in temperature and pH and the polydispersity index (PDI) were determined with dynamic light scattering (DLS) analysis on a Zetasizer Nano S (Malvern, UK) equipped with a 4 mW He-Ne laser operating at wavelength of 633 nm and an avalanche photodiode detector. Scattering light was detected at an angle of 173°. The nanogel was diluted 50 times, and the average hydrodynamic particle size was determined at a pH 6.5 with a temperature variation from 20 to 40 °C as well as at 20 °C and with pH values 3, 6.5 and 10. For each measurement, 60 μL of the sample was used, and the results represent an average of 3 measurements. The composition of the buffer solutions is presented in Table 1.

2.4. Plasma functionalisation

The PET samples with the size of 15 × 15 cm and weight of 4 g were functionalised with non-thermal low-pressure inductively coupled radiofrequency (IC-RF) plasma. An RF generator of adjustable power up to about 3 kW and a frequency of 27.12 MHz was connected to a coil of 10 turns. The coil was wrapped onto the discharge tube and connected

Table 1
The composition of buffer solutions for 100 mL of solutions with pH values of 3, 6.5 and 10.

pH	Composition
3	Potassium phthalate (0.1 M) − 50 mL HCl (1.0 M) − 22.3 mL Bidistilled water − 22.7 mL
6.5	Potassium dihydrogen phosphate (1.0 M) − 50 mL NaOH (1.0 M) − 13.1 mL Bidistilled water − 36.1 mL
10	Sodium tetraborate (borax) (0.025 M) − 50 mL NaOH (0.1 M) − 18.3 mL Bidistilled water − 36.1 mL