SPIN-COATED CHITOSAN ON COPOLYESTER SUBSTRATES

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Abstract

In this work, uniform thin chitosan coatings were spin coated onto copolyester substrate. The use of high concentration acetic acid (50 wt.%) as the chitosan solvent increased the protonation of chitosan amino groups, allowing for greater interactions between the solution and the surface of the substrate. Further, surface oxidation was used to incorporate additional functional groups in the copolyester surface, facilitating solution/substrate interactions. The interfacial interactions between the chitosan solution and copolyester substrate were evaluated by the contact angle measurements.

Key words
spin-coating process, chitosan coating, interfacial interactions, polyester substrate

1. Introduction

Spin-coating (SC) is a process used to create an uniform thin polymer films (with thickness down to the nanoscale) onto a flat substrate, primarily metal or ceramic [1],[2]. However, when using this method to create a polymer coating on another polymer substrate, some difficulties might appear [3]. The reason is that, the surface tension of the polymer substrate/polymer coating solution (solid/liquid) interface exceed the surface tension of the polymer substrate/air (solid/air) interface. In a consequence, the poor wetting occurs, indicating week intermolecular forces (both short-range and long-range) between the solution and substrate [4].

Chitosan, a natural polysaccharide, is a widely used material for coatings aimed at improving hydrophilicity, biocompatibility, and microbial resistance [5],[6]. However, because it dissolves only in aqueous acidic solutions with polar character, it is difficult to make high quality coatings on hydrophobic or nonpolar polymer surfaces.

PET-DLA copolymer is an aliphatic-aromatic polyester of poly(ethylene terephthalate) (PET) hard segments and ethylene dilinoleate (DLA) soft segments, with good physico-chemical properties at high content of hard segments (above 50 wt%) characteristic for implantable materials (like polyurethanes and polyamides), being a good representative substrate of biomaterials group. PET-DLA copolymer consists of polar ethylene terephthalate sequences (50 wt.%) and nonpolar long aliphatic chains of fatty acid dimers, which determine hydrophobic character of the PET-DLA surface. Such a hydrophobic surface leads to low wettability and hinders the formation of a chitosan coating from aqueous solution.

The aim of our work was to develop thin, uniform chitosan coatings on PET-DLA copolyester surfaces, using spin-coating. To achieve this goal, chitosan solutions, as well as polymeric substrate surfaces, were modified in order to improve their interfacial interactions. One of the method to increase the surface attractiveness in a case of PET homopolymer is a surface chemical treatment through hydrolysis, oxidation, reduction or amination reactions [7]–[11]. The ester groups occurring on the surface undergoing the treatment can break down and form extra carboxyl and/or hydroxyl groups. These groups are highly demanded because they can provide the additional interactions with chitosan solutions by electrostatic interactions and hydrogen bonding with amine groups of chitosan [12],[13]. However, the most common treatment – the hydrolysis of PET and its copolymers – causes surface erosion and may lead to high weight loss, as well as pore formation [13]. Therefore, in order to minimize the damage and enrich the surface with carboxylic groups we chose surface oxidation, treating the PET-DLA substrates with 30% hydrogen peroxide for 30 minutes [14],[15].

2. Materials and Methods
2.1. Substrate material

Polymeric discs used as a substrates were made of poly(aliphatic/aromatic-ester) multiblock copolymer, containing poly(ethylene terephthalate) (PET) hard

segments and butylene dilinoleate (DLA) as soft segments (50/50 wt%). The synthesis method of the copolymer, involving two-step process, transesterification and polycondensation from the melt, has been described elsewhere [16]. PET-DLA copolymer films with a thickness of 1 mm were obtained by melt process at 210-230ºC for 5 minutes. Next, disc shaped samples with diameter 20 mm were cut.

2.1.1. Treatment of polymeric substrates

To incorporate hydroxyl and carboxylic groups on the polyester surface, PET-DLA discs were treated with 30% hydrogen peroxide at 60ºC for 0.5 hour, then washed with methanol and water, and dried under reduced pressure also at 60ºC.

2.2. Coating formation *via* spin-coating

Spin-coated chitosan films on polyester substrate were prepared from chitosan (CH) solutions using chitosan ChitoClear® 43040 – hqg1600 Primex ehf Iceland Company (with deacetylation degree 95%) and acetic acid (AA) purchased from POCh, Gliwice. All solutions were prepared as fallowed: chitosan (from 0.25 to 2.5 wt.%) was dissolved in 50 ml of acetic acid solution, at concentration 1 and 50 wt.% in water. The chitosan was allowed to dissolve for 24 hours with continuous stirring at room temperature. The viscosity of chitosan solutions in 50% of AA was determined by Ares Rheometer, at room temperature.

A total of 1 mL of chitosan solution was spread on a PET-DLA disc and spin coated in 4 steps, as specified in Table 1, with a maximum speed of 1500 rpm for 30 sec. In order to facilitate microscopic visualization of chitosan, chitosan solutions were stained with 0.05 wt.% of Orange II dye (Sigma Aldrich).

2.3. Structure characterization

The chemical structure of PET-DLA copolymer was assessed by Fourier transform infrared-attenuated total reflection spectroscopy (FTIR-ATR) on Bruker ALPHA FT-IR ATR spectrometer. Prior to analysis, test samples were dried at 60°C under vacuum for 24 hours. For each sample, 32 scans were averaged across the spectral range of 400-4000 cm^{-1}.

2.4. Contact angle

The interaction between coating solution and substrate surface was described in terms of wettability of the substrate surface, as determined by the contact angle (CA) measurements. The CA analysis was performed by sessile drop shape analysis using a goniometer, Krüss DSA 100 Drop Shape Analyser, equipped with a camera and recording system.

Measurements were performed for combinations of treated and untreated PET-DLA substrates and wetting solutions including water and 1% wt. of chitosan in 1% and 50% of AA. Contact angle values were recorded after 10 seconds and averaged from 1-3 measurements.

2.5. Thickness measurement – Calotest

The thickness of the spin-coated chitosan coatings was measured by spherical abrasion test method using the Calotest apparatus from CSM INSTRUMENTS. Briefly, a rotating sphere (2500 rpm), with a 30 mm diameter (*R*) was pressed on the coating surface at 45° angle for 90-120 seconds. The addition of the abrasive slurry to the contact zone ('Calotest Hi-Quality (0.5-1 µm)', the water diamond solution) abraded a depression with the shape of a spherical cap into both the coating and the substrate. Optical microscopy (OM, Nikon Microscope) was used to determine parameters *x* and *y*, as shown in the Fig. 1, and the thickness of the coatings *s* was calculated:

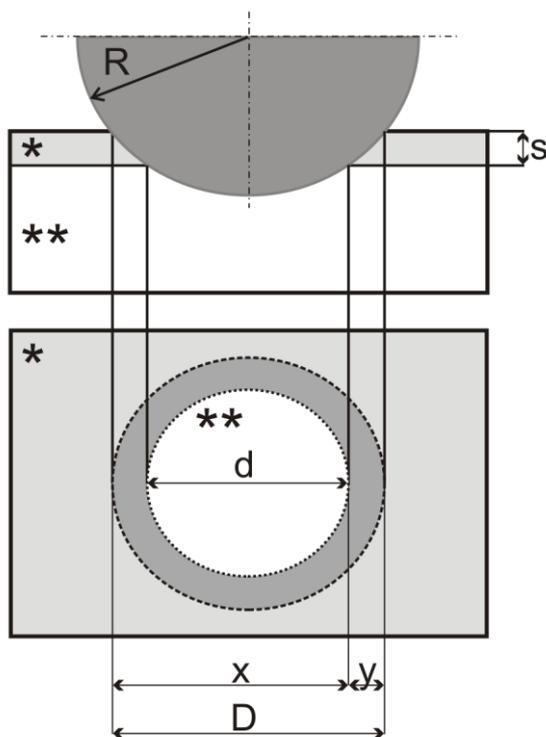$$s = \frac{1}{2}\left(\sqrt{4R^2 - d^2} - \sqrt{4R^2 - D^2}\right)$$

Figure 1. Designation of the ball/plane thickness model [17].

3. Results and discussion

3.1. Spin-coating process

The SC process consisted of four main steps (see Table 1 and Fig. 2), beginning with the deposition of chitosan solution on a PET-DLA disc (Fig 2A).

Next, the disc started to rotate, reaching a high angular velocity (spin speed) (Fig. 2B). The adhesion forces at the solution/substrate interface and the centrifugal forces result in strong sheering of the liquid, causing a radial flow and the rapid ejection of the chitosan solution from the substrate (Fig. 2C). This process, combined with subsequent evaporation, result in the decrease of the film thickness. The evaporation process causes the polymer concentration and viscosity to increase and, after evaporation, a uniform solid polymer film is formed (Fig. 2D).
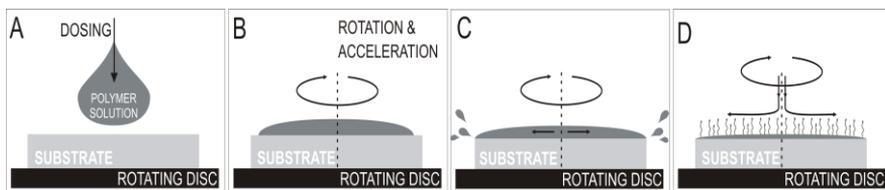

Figure 2. Scheme of four-step spin-coating process.

One advantage of the SC process is the ability to control the thickness of the coating by changing the maximal spin speed applied to the substrate. In our work, we used a four-step spin-coating program with maximal speed of 1500 rpm (see Table 1).

Table 1. Spin-coating program

STEP	TIME [s]	SPIN SPEED [rpm]	ACCELERATION [rpm/s]
1	5	250	50
2	30	1000	100
3	30	1500	200
4	30	250	50

Other parameters, beside the process parameters, that influence thickness and quality of the coating include the properties of the polymer solution, such as viscosity, drying rate, or surface tension, and the properties of the substrate surface [18]. These parameters influence coating thickness and quality by direct effects on the interfacial interaction between a coating solution and a substrate.

3.2. Physicochemical properties of PET-DLA substrate

Analyzing the structure of the PET-DLA copolymer based on infrared spectrum (see Fig. 3), the high band intensity of absorption at 2922 and 2852 cm^{-1} is noticeable and correlates with symmetric and asymmetric stretching vibration of C-H bonds, originating mainly from aliphatic chains of DLA. The next intensive bands at 1719 cm^{-1} and also at 1242, 1165 and 1095 cm^{-1} are the C-O

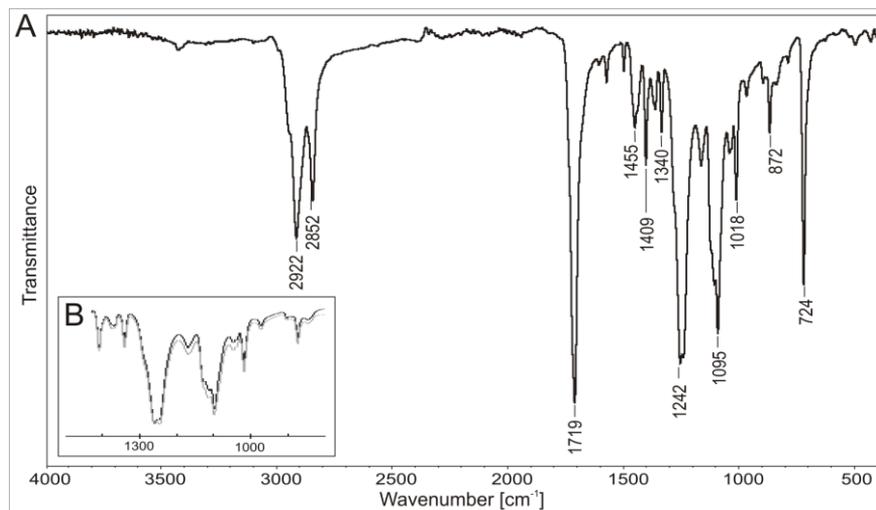stretching bands determined by the presence of ester groups of copolymer.

Figure 3. IR spectrum of PET-DLA copolymer in a full range (A) and the comparison of PET-DLA copolymer untreated (black curve) and oxidized (grey curve) in range from 1500 to 900 cm^{-1} (B).
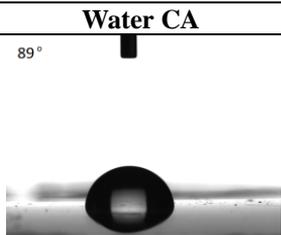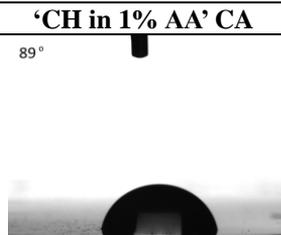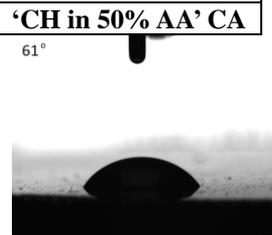
Following surface oxidation of PET-DLA sample, there is slight increase in absorption within the region of 1320-1000 cm^{-1} (corresponding to C-O stretching bands) of the IR spectrum (Fig. 3 B, grey curve), arising from the presence of new carboxylic groups on the surface. Despite the fact that the difference between the IR spectra of treated and untreated substrate is low, the effectiveness of the surface treatment was sufficient.

3.3. Interfacial interactions

To evaluate the interfacial interactions of PET-DLA substrate and chitosan solution, the contact angle measurements were conducted. The water contact angles of untreated and oxidized PET-DLA surface were the same and ranged around 89°. Also similar results were observed when 1 wt.% of chitosan solution in 1 wt% of acetic acid was used as the wetting solution (see Table 2). No change in the value of contact angle with the change of the wetting solution proves low interactions between these pair, with the consequence in a lack of the good quality of coating, as it is shown on microscopic picture in Fig. 5A. The cohesion forces in the chitosan solution are much stronger than the adhesion to the substrate. The low interactions between additional polar groups introduced to the surface and chitosan amino groups can arise from insufficient protonation of macromolecules of chitosan dissolved in the low concentrated acid solvent (1 % AA). The increase of the acetic acid concentration increases the degree of amino

groups' protonation and also enhances a net charge density of the chitosan solution and decreases the surface tension [18]. Therefore, to obtain higher protonation degree and thus create electrostatic interactions and potentially hydrogen bonding, another chitosan coating solution from 50% AA was prepared. The higher concentrated acetic acid was not used, due to the risk of the disintegration of glucosidic bonds of chitosan under the acid hydrolysis reaction occurring in concentrated acid solutions [19],[20].

Table 2. Contact angle (CA) of untreated and treated PET-DLA substrates and wetting solutions including water and 1% wt. of chitosan in 1% and 50% of AA.

UNTREATED PET-DLA SUBSTRATE		
Water CA	'CH in 1% AA' CA	'CH in 50% AA' CA
89°	89°	61°
OXIDIZED PET-DLA SUBSTRATE		
Water CA	'CH in 1% AA' CA	'CH in 50% AA' CA
89°	89°	50°
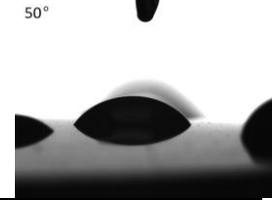
Contact angle of 1% chitosan solution in 50 % acetic acid was 61°and thereby much lower than for chitosan in 1% AA. This proves the better surface wettability especially for oxidized surface where the contact angle was 50°. This is the result of increased interactions between created carboxylic groups of oxidized substrate surface and protonated amino (but also hydroxyl) groups of chitosan solutions. The scheme of electrostatic interactions and hydrogen bonding is shown in Fig. 4.
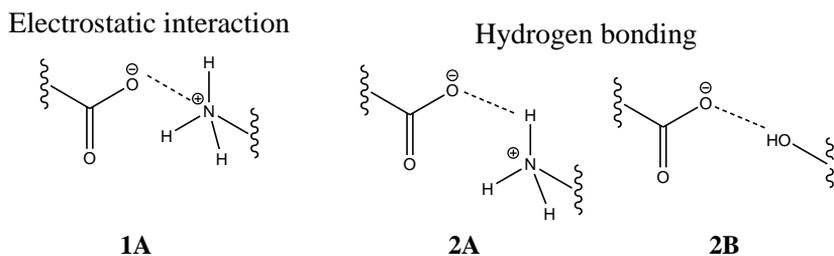
Electrostatic interaction   Hydrogen bonding

1A   **2A**   **2B**

Figure 4. Scheme of interactions occurring between chitosan solution and PET-DLA surface: A – between carboxylic substrate group and amino group of chitosan, B- between carboxylic substrate group and hydroxyl group of chitosan.

The concentrated acetic acid combined with surface oxidation process allowed to obtain the spin-coated chitosan layer covering the whole area of the PET-DLA surface (Fig. 5 B-C). The additional factor influenced the quality of a coating was viscosity of the solution. Therefore, in our work we examined solutions of different concentrations (viscosity) from 0.25 to 2.5 wt.% of chitosan. Higher concentration of chitosan in the solution resulted in better quality of the coating, with the best result for 2 wt.% of chitosan and the determined thickness of this coating was 5±2 μm. The 2.5% chitosan solution was too viscous to be applied in a spin-coating process. The viscosity results are summarized in the Table 3.

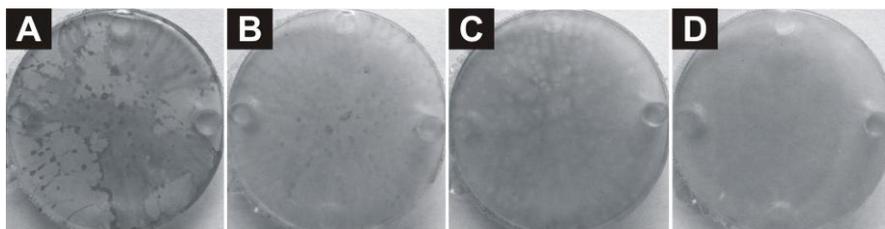**A**   **B**   **C**   **D**

Figure 5. Macroscopic pictures of coating created on oxidized PET-DLA substrate from: A – 1 wt.% of chitosan in 1 wt.% AA, B – 1 wt.% of chitosan in 50 wt.% AA, C – 1.5 and D – 2 wt.%

Table 3. The viscosity of chitosan solutions in 50% of acetic acid.

Chitosan concentration [wt.%]	0.25	0.5	1.0	1.25	1.5	2.0	2.5
Viscosity [Pas]	0.069 ±0.012	0.274 ±0.018	0.921 ±0.030	3.119 ±0.104	4.821 ±0.081	5.567 ±0.041	21.759 ±0.324

4. Conclusions

We demonstrated that spin-coating technique was successfully applied to prepare thin, uniform (5 microns) chitosan coatings on polyester surface. Several parameters were found to be critical in achieving this goal. First of all, incorporation of additional functional groups on polyester surface played an important role in increasing interfacial interactions between polar chitosan and non-polar polyester. Moreover, sufficiently high concentration of acetic acid (50%) increased the degree of amino groups' protonation and thus enhanced a net charge density of the chitosan solution and decreased the surface tension, what collectively provided sufficient polymer (polyester substrate)-polymer(chitosan coating) interactions.

5. Acknowledgements

6. References

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