FUNCTIONALISATION OF POLYAMIDE NANOFIBRES BY TANNIN FROM OAK BARK EXTRACT AND TESTING OF ITS pH DEPENDENT STABILITY

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Abstract

A new nanofibrous membrane with iremarkable chemical and strength properties was prepared through an interaction between polyamide nanofibres and oak bark extract, which is rich in the content of hydrolysable tannins.

The aim of this study was to verify the bond strength of tannins and polyamide nanofibres depending on the different pH of the aqueous medium.

Keywords: polyamide, nanofibres, oak bark, tannin, tannic acid, stability, pH.

1. INTRODUCTION

It is well known that strong bonds are created between tannins and some synthetic polymers, such as polyvinyl pyrrolidone (PVP) or polyethylene glycol (PEG). These polymers contain in the strand the oxygen molecules with which polyphenols form hydrogen bridges [1]. Tannins also have a high affinity to polyamide, wherein the hydrogen bondings are applied between tannin and peptide (amide) groups. The strong affinity of tannins to polyamide is used e.g. for the purification of plant extracts (tannins removal) by polyamide sorption [2] and in the food industry to modify fruit juices (removal of tannins eliminates their astringency) [3].

In Central Europe, the oak bark is a readily available material that is obtained as a waste in logging. It is a rich source of tannins (water soluble polyphenols), especially tannic acid (Figure 1) and its derivatives. The oak bark contains not only hydrolysable tannins (gallotannin, tannic acid, ellagitannins) [4] but also condensed tannins (proanthocyanidins) [5] [6], catechin, epicatechin [7], and other substances such as cellulose, hemicellulose, lignin and others [8].

Hence, we came up with an idea of immobilizing tannins from a solution on the surface of fibres based on their natural affinity to some fibres. We used an water extract from oak bark as a source of tannins. This extract was exposed to interaction with the surface of polyamide nanofibres. The binding between tannin and polyamide should be stable and independent of the pH over a relatively wide pH range from 2 to 8 [9]. The phenol groups are already ionised at strong alkaline pH, so that there are fewer hydrogen bonds and the fixation of tannins on the peptides quickly fades.

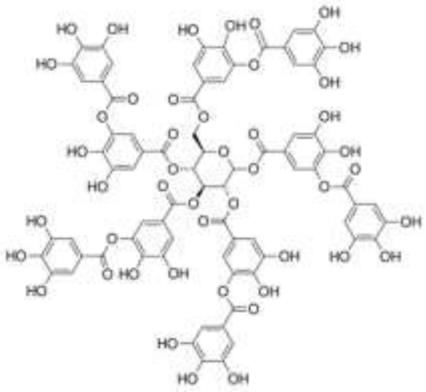

Fig. 1 Tannic acid

2. EXPERIMENTAL PART

2.1 Material

Nanofibrous layer of polyamide 6 (area weight 1.5 g / m^2 and diameter of fibres about 100 nm)
Extract from the oak bark (*Quercus robur* and *Quercus petraea*)
Folin-Ciocalteu reagens (Penta) and 0.5 M Na_2CO_3 (Lach-Ner)
Tannic acid as the standard (Sigma-Aldrich)
Buffers of pH of 4.0 – 5.9 - 6.8 – 8.2 and 10.5 (Penta)

2.2 Devices

VIS spectrophotometer Helios Epsilon (Thermo Scientific)
Electron microscope UHR SEM Ultra Plus (Carl Zeiss)

2.3 Methods

2.3.1 Extraction of tannins from oak bark and determination of their content

Tannins were extracted from the oak bark in water boiling for 60 minutes, at solution concentration of 70 g of dried oak bark per 1 litre of distilled water. The amount of extracted tannins was spectrophotometrically quantified using the analysis of phenol groups in Folin-Ciocalteu reagent. The interaction of phenol groups with the Folin-Ciocalteu reagent in alkaline medium creates a blue solution with the maximum absorbance at 736 nm and its colour intensity is directly proportional to the concentration of phenols in the mixture [10]. The content of tannins and total polyphenols is expressed by use of the standard (tannic acid).

2.3.2 Preparation of nanofibrous polyamide membrane coated with tannin (PA/T)

Thin nanofibrous polyamide layer (PA 6) of the area of 200 cm^2 and weight of 0.03 g were fixed to the grid of reinforced fabric from glass and polyester fibres, and subsequently immersed into the hot oak bark extract (85 °C) for 3 minutes. During this time tannins from the extract covered the surface of polyamide nanofibres. This was followed by rinse in distilled water and drying for 30 minutes at 50 °C.

2.3.3 Stability of the PA/T membrane at various pH

The stability of tannins adsorbed on the polyamide nanofibres was determined using solutions (buffers) of different pH, into which were inserted PA/T membranes of the same surface. Samples of these solutions were taken at regular intervals and in them the content of released tannins was determined by use of Folin-Ciocalteu reagent.

2.3.4 SEM analysis

The electron microscope UHR SEM Ultra Plus (Carl Zeiss) was used for displaying the polyamide nanofibres coated with tannin and for analysis of tannin desorption.

2.4 Results and discussion

2.4.1 The content of polyphenols in the extract and preparation of the PA/T membrane

The calibration line of the absorbance at 736 nm dependent on the polyphenols concentration was created using Folin-Ciocalteu reagent and standard (tannic acid). The amount of tannins (generally: polyphenols) extracted from the oak bark by boiling was calculated: extract contained approximately 2 g / L of tannin when extracting 70 g of dry and crushed oak bark with 1 litre of water for 60 minutes. This corresponds to about 30 g of tannic acid extracted at this liquor ratio from 1 kg of dried material. The PA layer doubled its weight after interaction with the hot extract, followed by rinsing and drying. This weight corresponds to the amount of tannin that coated nanofibres. Figure 2 shows the original polyamide nanofibres and Figure 3 shows nanofibres coated with tannin.

Fig.2 Polyamide 6 nanofibres
(10 000x)

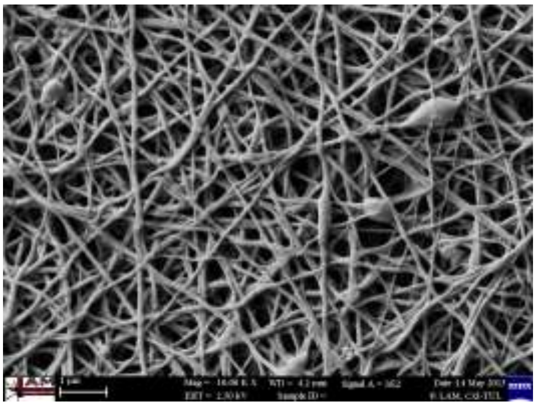

Fig.3 Polyamide nanofibres coated with tannin
(10 000x)

2.4.2 Stability of PA/T membrane at different pH

40 ml of buffers (pH of 4 – 5.9 - 6.8 - 8.2 and 10.5) was dosed into five jars and 25 cm^2 of PA/T membrane was inserted into each solution. Samples for measurement of desorbed polyphenols were collected at different times. The content of tannin desorbed from the PA/T membrane was analysed spectrophotometrically using the Folin reagent. As expected, the tannins desorbed from fibres under alkaline conditions very quickly, compare to acidic environment where their binding to polyamide fibres was relatively stable.

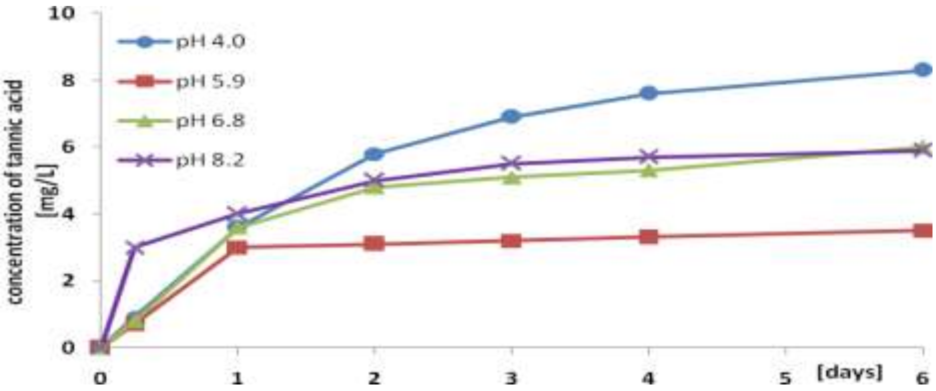

Fig.4 Tannin desorption of PA/T at pH from 4.0 to 8.2

It seems that desorption of tannin from fibres is not greater only in a strongly alkaline environment, but also in a more acidic environment at pH of 4 (Figure 4), although this instability is very relative. The total amount of tannin released from fibres at pH of 4 in 6 days corresponds to amount of tannin released from fibres at pH of 10.5 during the first hour alone.

It is possible to consider pH of 8.2 as still relatively favourable environment for the stability of PA/T membrane, because the comparable amount of tannin released from nanofibres into the solution at pH of 8.2 during 2 days (7.5 mg of tannic acid / L) correspond to desorption of tannins at first 10 minutes in pH of 10.5.

Table 1 contains an overview of kinetics of polyphenols released from polyamide nanofibres in differently acidic pH: c_{max} ...maximum concentration of released polyphenols (after 10 days when the desorption approaches the equilibrium), $t_{1/2}$ ....half-life of polyphenols desorption from fibres, k ....rate constant of this desorption at a given pH and room temperature, calculated from equation (1), *tan α …* slope of the linear part of the graph, *α* … angle that the linear part of the graph forms with the x-axis and whose size is a good indicator of the rate of desorption of tannin.

$$k=\left(\frac{\ln(2)}{t_{1/2}}\right) \tag{1}$$

.**Table 1** An overview of kinetics of polyphenols released from polyamide nanofibres in differently acidic pH

	pH 4	**pH 5.9**	**pH 6.8**	**pH 8.2**	**pH 10.5**
$\mathbf{c_{max}}$ [mg / L]	8.5	4.0	7.0	9.5	14.0
$\mathbf{t_{1/2}}$ [hours]	9.0	16.0	22.0	25.0	0.5
k [hours $^{-1}$]	0.077	0.043	0.032	0.028	1.386
tan α	3.60	3.02	3.63	12.00	31.70
α [degrees]	74.48	71.65	74.6	85.24	88.35

Based on graphs from Figure 4 and values from Table 1, it appears that the most stable binding of tannins to the polyamide is at pH about 5.9. The more acidic environment increases slightly desorption and this bond quickly weakens at pH higher than 8.0 due to the dissociation of phenol groups.

The graph in Figure 5 shows how fast polyphenols desorb from surface of polyamide in a strong alkaline environment. Decrease of actually measured values of phenol concentration released during three days in fact related more to their conversion to phenolates (or phenoxides). If we approximate the values of polyphenols desorbed from fibres at pH of 10.5 in the first 4 hours using logarithmic function with correlation coefficient R^2=0.95 (2),

$$y=1.528\ln(x)+7.809 \tag{2}$$

where *y* is the concentration of polyphenols released to solution (mg / L), *x* is the time (hours), it is possible to extrapolate the hypothetical values of tannin desorbed from polyamide nanofibres.

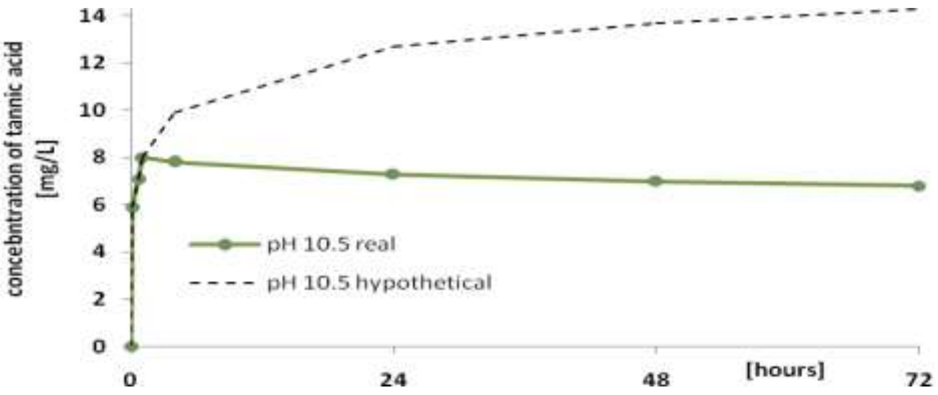

Fig.5 Tannin desorption of PA/T at pH 10.5 (actually measured and extrapolated)

The affinity of tannin to the polyamide is so strong that a solid monolithic layer of adsorbed tannins that completely seals spaces between nanofibres is created with use of higher concentration of tannins, higher temperature and longer time (Figure 6). This is undesirable because we use nanofibres just to obtain high surface area coated with tannin. Therefore it is necessary to optimize the reaction conditions and stop the reaction on time. Figure 7 shows how the nanofibres are again partly uncovered due to desorption of tannin in a strongly alkaline environment (pH of 10.5).

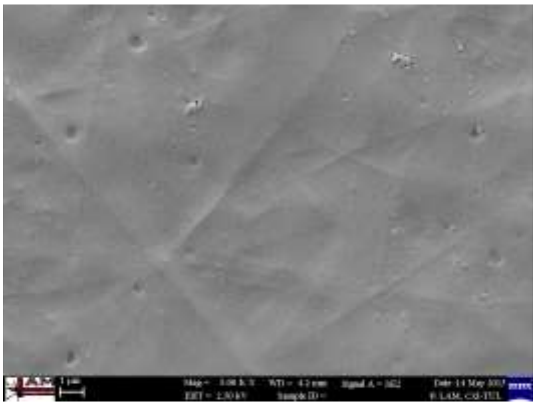

Fig.6 Nanofibrous PA with thick layer of adsorbed tannin (after interaction with tannic acid, 3 g / L, 5 min., 90 °C), (5 000x)

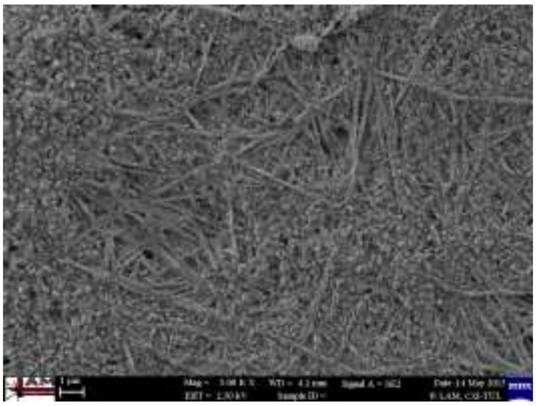

Fig.7 The same layer as in Fig.6 with partly desorbed tannin after 10 days in pH of 10.5 (5 000x)

2.4.3 Changes of the strength of PA nanofibrous layer

Adsorbed tannin also changes the strength characteristics of this nanofibre layer: preliminary strength tests suggest that PA/T membrane reduced elongation at break and tensile strength, however the Young's modulus significantly increased due to adsorbed tannin. It became considerably more rigid, which greatly improves and facilitates handling of the membrane. (Mechanical properties of PA/T membrane will be described in another publication).

3. CONCLUSION

We created a polyamide nanofibre membrane with unique properties that resulted from the immobilisation of vegetable tannin from oak bark on the surface of nanofibres. Due to the great specific surface of nanofibres and high affinity of tannin to the polyamide the membrane was able to immobilize a large amount of tannin (PA/T membrane doubled their mass). It was proven that this binding is stable until pH of 8.2. At the same time there was a change in strength characteristics of resulting nanofibrous layers: PA/T membrane obtained higher rigidity, which allowed an excellent handling of the nanofibre layer under dry or wet conditions and also increased its lifespan.

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