INFLUENCE OF THE LAYER-BY-LAYER MODIFICATION ONTO THERMAL PROPERTIES OF POLYPROPYLENE TEXTILES

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ABSTRACT

Polypropylene nonwovens were modified by using layer-by-layer method. This is quite new method, and relatively rarely used for textile products. As a modifiers were used different polyelectrolytes such as: PAA – poly(acrylic acid), PDMAEMA – poly(N,N-dimethylaminoethylmethacrylate), PAH - poly(allylamine hydrochloride). Polypropylene nonwovens modified by layer-by-layer method are the subject of controlled thermal degradation procedure. The whole sample weight consist mostly of the main object – weight of external, deposited layers is in comparison to main object, very small. That means that the thermogravimetric curve contains weight loss associated with thermal degradation of the polypropylene material. All changes in TG curve are connected with the influence of deposited layers onto the character of PP degradation.

Key Words: POLIPROPYLENE NONWOVEN, LAYER-BY-LAYER MODIFICATION, THERMAL PROPERTIES, THERMOOXIDATION

1. INTRODUCTION

For many years, the number of introduced new types of polymers systematically decreased. Currently, about 50% of textiles in the world are produced from cotton, the rest is mainly based on polyesters and polyamides; this is accompanied by small amounts of other materials, especially polyolefins [1, 2], but some analyzes predict that in a few years almost all relevant textile materials will be based on cotton, polyesters and polyolefins [2].

In parallel with the reduction in the number of polymer types used, the number of potential applications to which textile products can be used increases significantly. In particular, the technical product market shows impressive growth parameters, both quantitative and qualitative. The pressure on the creation of new materials or products with improved properties is systematically increasing. New products must therefore be made from available polymeric materials. For this reason, surface modifications of fibers, significantly increasing the application range of textiles, and are an important research field of study in textile science.

One of the most important modification techniques of recent years is the technology based on applying a modifier from colloidal solutions (sol) [2].

However, the most-promising technique of modification is currently the layer-by-layer method (lbl - layer by layer). In general, it consists on applying oppositely charged layers of polyelectrolytes, which are related to each other by electrostatic attraction forces. It allows to change the construction of the surface in a simple, effective and cheap way. Initially, it was used successfully for other types of materials than textiles, but now the process of its implementation in textiles takes place. It should be remembered that textiles are characterized by a surface difficult to modify and control, so often a simple transfer of the methodology effective to the surface of the film, or films does not work in the case of textile products, such as textiles, knitwear or nonwovens.

In this work, the lbl method was chosen for modification due to the advantages described above, as well as due to the new possible to obtain properties, which should open new, numerous application perspectives for modified products.

Typically it is to be expected that making external layer modifications affects surface properties such as: hydrophilicity (moisture sorption, capillacity, wettability and water uptake), dyeability, roughness or good touch. In this paper it is taken into account influence of lbl modification onto thermal properties.

2. EXPERIMENTAL

2.1 Materials

A polypropylene nonwoven was prepared by meltblown method (Cenaro-Lodz, Poland) with a surface weight of 27.9 g/m^2 and an average filament diameter of 9.65 μm. Nonwovens were produced using low-viscosity polypropylene granulates completely free from additives (HL604FB) produced by Borealis AG, Austria.

Poly(acrylic acid) (PAA) was prepared by polymerization of acrylic acid (AA) in toluene initiated with azobisisobutyronitrile (AIBN). The polymer was rinsed several times with toluene and dried under vacuum. Its average molecular weight (Mw=145 000 g/mol) was determined by gel chromatography.

Poly(allylamine hydrochloride) (PAH), commercial product from Fluka (Mw=70 000 and 15 000 g/mol) was used without purification.

Poly(dimethyl aminoethyl methacrylate) (PDAMA) was prepared by polymerization of dimethyl aminoethyl methacrylate initiated with AIBN. The average molecular weight (Mw= 63 000 g/mol) was determined by gel chromatography.

2.2 Sample modification

The nonwoven was activated heating in a solution of ammonium persulfate (20 g/dm^3, t=30min, T=80^{o}C, saturated with nitrogen), thoroughly rinsing with water, and grafted with concentrated AA (52 g/dm^3 , t=60 min, T=80^{o}C, saturated with nitrogen).

After grafting, the samples were immersed in an aqueous solution of appropriate polyelectrolyte (10^{-2} mol/dm^3). Before every such operation, samples were rinsed with distilled water.

Finally obtained structure was as follows:

Table 1. Composition of deposited layers

Composition	Layer number			
	Grafting	Deposition		
	1	2	3	4
1	PAA	PAH 70 000	PAA	PAH 70 000
2	PAA	PAH 15 000	PAA	PAH 15 000
3	PAA	PDAMA	PAA	PDAMA

2.3 Thermogravimetric analysis

The thermal analysis of all samples was carried out with a Perkin Elmer TGA 7 thermal analyser in a platinum measur¬ing cell, with the use of Pyris program for data handling.

Measurements were performed in a air atmosphere mainly with the heating rate 15 °C min^{-1}. The samples were heated up to 650 °C, starting from room temperature. All measurements were repeated at least three times. For each course, temperature of 50% degradation ($T_{50\%}$) was determined and after than average value calculated.

3. RESULTS AND DISCUSSION

The model of modification using lbl method was made in previous papers published by the author of that paper and his team [3-6]. In paper 3 was shown the phenomenon of obtaining of thermal effect after polyelectrolyte deposition on the surface. In presented paper this topic is continually developed and deeper analyzed.

The surface structure of the product modified by the lbl method can be divided into three zones [7] (Figure 1).

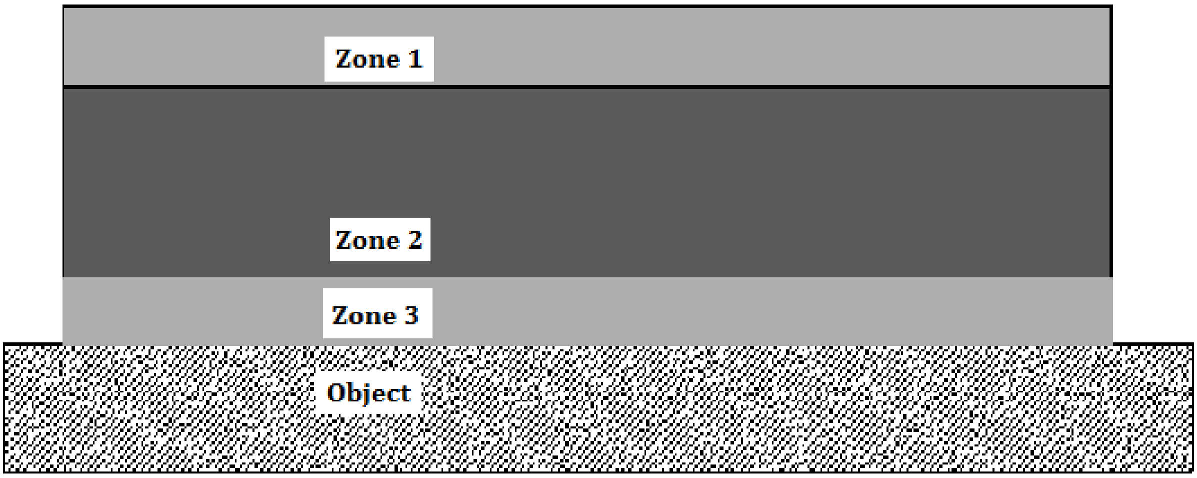

Figure 1. The model of zones formed after the application of polyelectrolyte layers to the object of modification according to Decher [37]

Zone 1 is the closest to the surface of the modified object. It consists from one to several layers. In this area of the multilayer it is largely dependent on the surface structure of the modified object. All layers that are between zones 1 and 3 are the zone of zone 2. In contrast, zone 3 also consists of one to several layers. Surface impacts with air or solution have the greatest influence on it. Areas of zones differ slightly in structure and chemical structure. Zone 2 is the most electrically neutral, the remaining zones are characterized by a higher charge. Depending on the charge density of the substrate and its roughness, variable, rather small amounts of counterions may be in zone 1. In zone 3, however, the counterions are in a greater amount. This results both from theoretical assumptions and measurements of surface potential. Unbalanced excess of charge on the surface must be compensated by small counter-ions.

The boundaries between the zones are of course rather fluid. It is also not possible to accurately determine the number of layers belonging to a given zone. It depends on the type of surface being modified, the type of layers applied and process conditions. The situation may additionally be complicated by the use of the non-stoichiometric polyelectrolyte system, which increases the number of uncharged charges. In the case of applying a small number of layers, only zones 1 and 3 can occur, without the creation of a separate zone 2. The thickness of this zone is, to a large extent, dependent on on the number of layers applied, as shown in Figure 2.

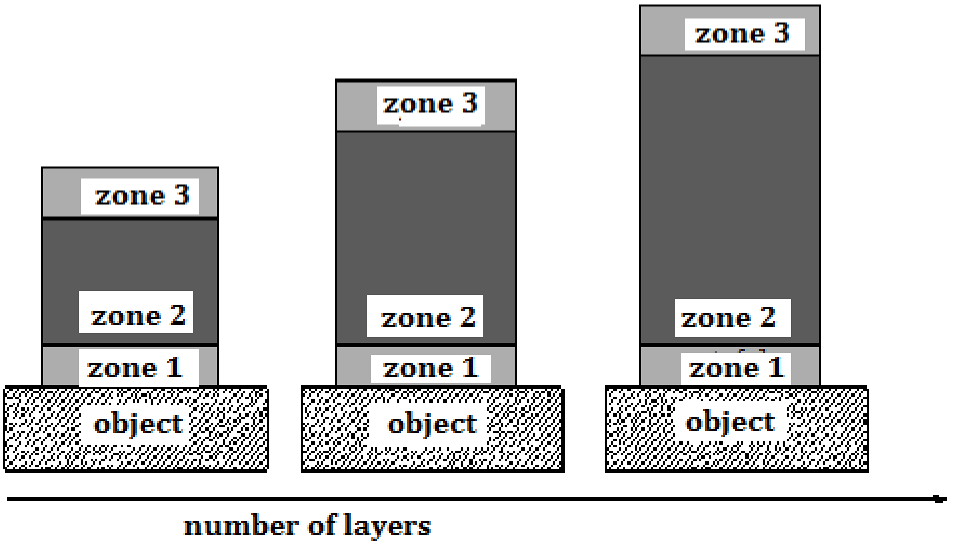

Figure 2. Size of zone 2 depending on the number of layers applied

The mechanism of the thermal destruction of the material with modified surface is very interesting. From our previous [3] it is clear that the character of the thermogram is quite similar – so it is always the same thermogram connected only with decomposition of main polypropylene material. Deposited layers can have influence only onto the temperature (or time) of destruction. On the Table 2 you can see, that temperature of 50% decomposition depends strongly on the number of layers.

Table 2. Temperatures (°C) of 50% decomposition for all samples (unmodified PP – 300,2°C)

Composition	Layer number			
	Grafting	Deposition		
	1	2	3	4
1	312.8	320.9	326.8	337.0
2		332.7	339.0	340.0
3		313.8	330.9	332.1

First step of modification was the same for all samples – grafting and its gives increase in 12.6 degrees. After deposition of next layers we have always delay, but in different level. For the samples with two layers thermal effect is better for PALL than for PDAMA, and surprisingly polymers with lower average molecular weight offers better effect. Third PAA layer moves temperatures for the same step – about 6 degrees. Finally, next deposition of polyamine electrolytes (4th layer) makes similar effect as the second layer.

Figure 3 presents the delay effect in graphical form.

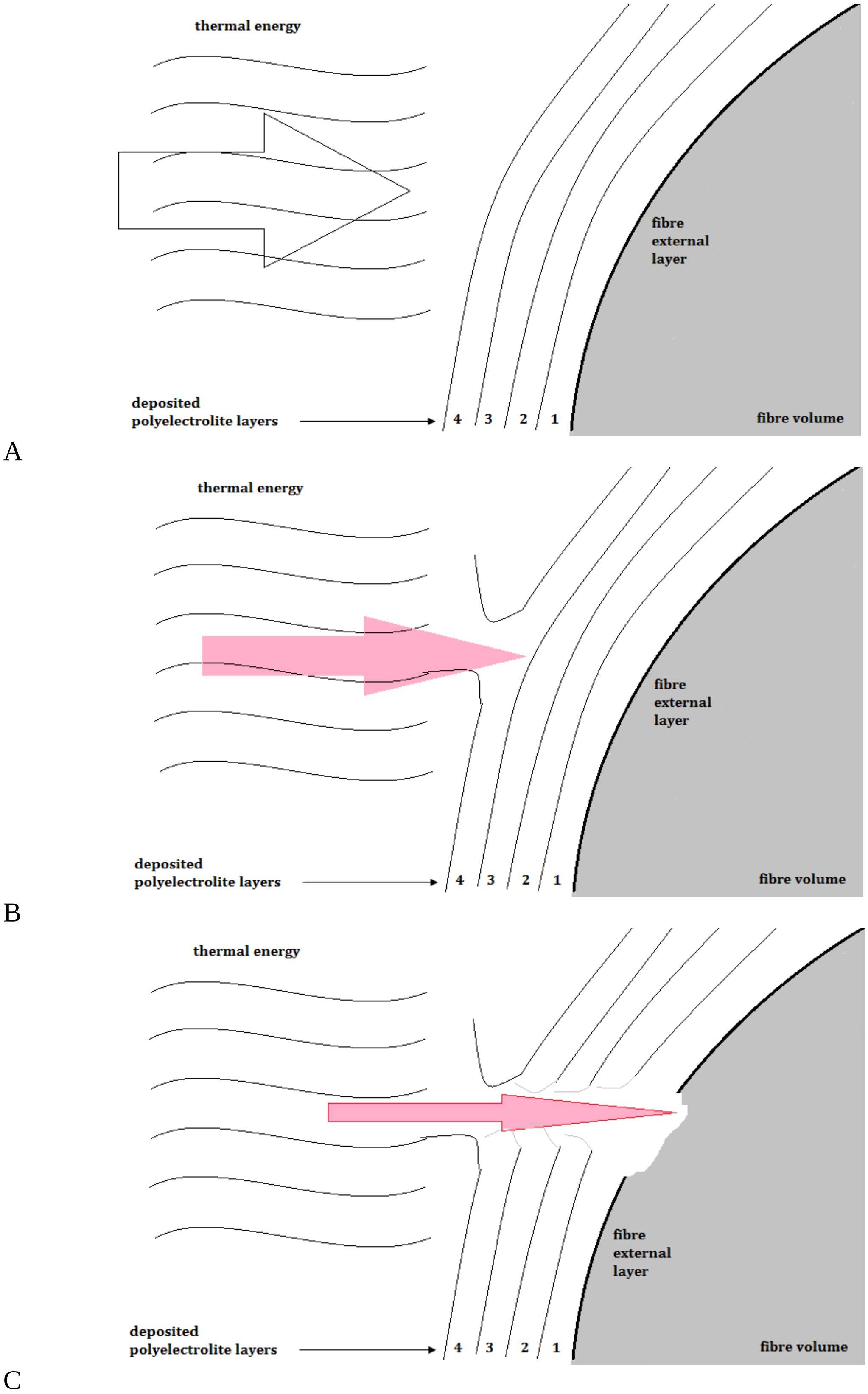

Figure 3. Scheme of steps of the thermal decompostion of PP fibre modified with polylectrolite layers: A – beginning, B – progress, C - advanced progress

4. CONCLUSIONS

The deposition of polyelectrolyte layers by the lbl method considerably changes the thermal resistance of the modified material. It means that modification of the external layer can influenced also volumetric properties. Presented delay in thermal decomposition is an effect of insulation made by deposited layers. This effect depends strongly on the number of layers, type of layers and sizes of the zones.

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