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Thermogravimetric Measurements of Poly(Propylene) Nonwovens Containing Deposited Layers of Polyelectrolytes and Colloidal Particles of Noble Metals

Abstract

The layer-by-layer method was used as a convenient way for depositing colloidal particles of silver, gold or platinum on textiles. After modifications the samples were tested using thermogravimetric analysis. It was found that the incorporation of metal particles onto a poly(propylene) nonwoven surface significantly increases thermal resistance. In the work herein presented it is proved that a significant increase in thermal resistance is observed when hydrogen saturated colloidal platinum has been incorporated.

Key words: thermogravimetric analysis (TGA), poly(propylene) PP, nanolayers, nonwovens.

obtained by the reduction of chloroauric or chloroplatinic acid, respectively [2]. Colloidal solutions of silver are commercially available [5].

Such sols are mostly unstable and they coagulate with time. They can be stabilized with protective colloids such as proteins, starch, poly(vinyl alcohol) or carboxymethyl cellulose [1, 2]. An important feature of colloidal systems is the charge observed in the particles of the dispersed phase. In the case of silver sols obtained by the above mentioned method, their Zeta potential has been found to be negative [1].

We have found, and described in our previous papers that layers of polymeric complexes can be deposited on textiles by the layer-by-layer method, successfully used to prepare modified polymeric films [6, 7]. Depending on their chemical structure such layers have a positive or negative electrostatic charge. In the present work, the presence of charges on metal sol particles and the oppositely charged polymer layer will be used to deposit nanoparticles of noble metal on fibers. The deposition of silver on textiles has been described by Jiang et al. [3].

The effect of incorporated silver on the improvement in the thermal properties of polymer has been observed in the case of poly(vinyl alcohol) film (PVA)[8]. It has been found that PVA containing incorporated silver particles shows a higher glass transition temperature by more than 20 degrees, even with a low addition of Ag (about 0.73%). Thermal analysis showed a considerable increase in thermal stability. In addition, a great

difference was found in the residues over 500 °C from 15% at silver content of 0.19% to 40% at Ag 0.73%. The authors explain that these results are due to the change in PVA chain mobility on the surface of nanoparticles. Such a high residue indicates that the course of degradation processes is different in the case of composites.

Similar behavior of other polymeric films and other metal nanoparticles has been reported in the literature [9, 10]. The authors [9] describe a process of preparation of poly(methyl methacrylate) (PMM) with palladium by incorporating palladium acetate during polymerization, followed by thermal reduction at a temperature of 120 °C. TGA and DTG analyses performed in air and nitrogen have shown that low quantities of incorporated palladium nanoparticles (from 0.001% to 0.1% by wt.) increase the thermal resistance of PMM in air very quickly. The temperature difference in weight loss by 50% ($T_{50\%}$) amounts to 50 °C. Moreover, the authors have found that the glass transition temperature of PMM within the examined range of incorporated palladium decreases from 130.1 to 121.7 °C. The dimensions of palladium particles ranged from 2 to 3 nm.

The authors of paper [10] have examined the effect of colloidal palladium particles on the thermal stability of poly(propylene) (PP), poly(ethylene terephthalate) (PET), polyamide 6 (PA) and polystyrene (PS). The metal particles were incorporated into a polymeric film by the sublimation of palladium acetate followed by reduction at a temperature of 180 °C. It was found in a previous

■ Introduction

The deposition of nanoparticles of noble metals on polymers, including textiles, is intended to modify their properties, for instance, to impart catalytic or bactericidal properties, etc. to these products. The colloidal particles of noble metals, of the currently most required size within nanometer range, can be incorporated into polymers in the form of nanopowder, mostly into polymer melts or solutions during product formation or they can be deposited on the surface of film, microsphere or fiber. This paper will consider the second case.

The first stage of colloidal particle deposition includes the formation of more or less stable sol. The preparation of sols of noble metals such as silver, gold or platinum has been studied since the end of the 19th century; nevertheless reports on this subject are continually published [1 - 4].

Silver sols are prepared mostly from Ag_2SO_4 and AgNO_3 by reduction with hydrogen, NaBH_4 , tannin or sodium citrate [1]; gold or platinum sols can be

study that under these conditions palladium penetrates the film about 100 μm in depth. The thermogravimetric analysis under nitrogen has shown that decomposition temperatures of PP and PS are increased, while those of PA 6 and PET are decreased. The authors believe that this is connected with suppressing the mobility of the polymer chains. It is worth noticing that in the case of PP very low quantities of metal (0.27%, 0.37% and 0.57%) change $T_{50\%}$ by about 10 °C. It is also of interest that this effect does not change significantly with an alteration in palladium content, at least within the range from 0.27 to 0.57%.

The present work concerns the deposition of noble metal particles on the surface of textiles from colloidal systems in order to examine the effect of the deposited layers on the course of thermal decomposition.

Experimental

Materials and methods

PP nonwoven with a surface weight of 20 g/m^2 was obtained by the melt-blown method at the Textile Research Institute (Łódź, Poland). Polyelectrolyte layers were deposited as described previously [6]. After grafting with acrylic acid, the nonwovens were immersed in aqueous solutions of appropriate electrolytes PAA – poly(acrylic acid), PDAMA – poly(dimethyl aminoethyl methacrylate), PAH - poly(allylamine hydrochloride) with a concentration of 10^{-2} mol/L. Prior to every such operation the samples were rinsed with distilled water.

Silver sol was prepared as in [1]. To 100 ml of AgNO_3 solution with a concentration of 10^{-2} mol/L heated to 95 °C, 3 ml of a 0.24 M solution of sodium citrate was added and the sol was left to cool.

Using a particle charge detector (Mütek PCD 03, Germany), it was found that the sol had a negative charge. Titration with a 10^{-3} C/L (coulomb per liter) solution of poly(allylamine hydrochloride) showed that the sol charge was 4.1×10^{-3} C/L.

This solution was used for padding nonwoven samples with deposited layers.

Preparation of gold sol

100 ml of chloroauric acid was neutralized with K_2CO_3 to pH 8, heated to boiling point and several drops

of freshly prepared 1% tannin solution were added and left to cool. The resultant dark red sol had a negative charge. The titration of charge with a 10^{-2} mol/L solution of poly(allylamine hydrochloride) showed that the concentration of charges in the sol was 1.8×10^{-3} C/L.

Preparation of platinum sol

46 ml of a 0.1% solution of chloroplatinic acid was neutralized to pH 8 with K_2CO_3 . The solution was heated to boiling point and several drops of freshly prepared 1% tannin solution were added and left to cool. The resultant dark green sol showed a negative charge. The titration with a 10^{-2} mol/L solution of poly(allylamine hydrochloride) showed that the concentration of charges was 3.4×10^{-3} C/L.

A PP nonwoven sample with deposited colloidal platinum particles was placed in a tube, through which hydrogen was passed. Next, it was left in the hydrogen atmosphere for 24 h and then stored under ambient conditions.

TG analysis

The thermal analysis of all samples was carried out with a Perkin Elmer TGA 7 thermal analyser in a platinum measuring cell, with the use of Pyris program for data handling. Measurements were performed in a nitrogen and air atmosphere mainly with the heating rate $15 \text{ }^\circ\text{C min}^{-1}$. The samples were heated up to 650 °C, starting from room temperature. All measurements were repeated at least three times. For each course $T_{50\%}$ was determined and after that the average value was calculated.

Results and discussion

Silver was deposited on PP nonwoven using the previously described method of sorption from silver sol [6] (method A), or by ion exchange between silver acetate and poly(acrylic acid) contained in the layer followed by a reduction with sodium citrate as in [11] (method B). PP nonwoven samples were immersed in a 5 mM/L solution of silver acetate for 24 h, rinsed and dried in air. Then, they were flooded with a hot (about 90 °C) 0.24 mol/L solution of sodium citrate.

The compositions of samples are listed in Table 1.

Table 1. Composition of samples for thermogravimetric analysis.

Sample No.	Nanolayers	Silver deposition method
1	PAA; PAH; PAA; PDAMA	A
2	PAA; PAH; PAA; PAH	A
3	PAA; PAH	A
4	PAA, PAH; PAA	B

Colloidal particles of gold and platinum were deposited from sols in a similar way as silver.

Electron microscope images of samples with deposited metal particles are presented in Figure 1.

The results of thermogravimetric measurements in air for samples from Table 1 with and without deposited silver are given in Table 2 and illustrated in Figure 2.

Comparing the results of thermogravimetric analysis of samples 3 and 2, with two and four layers, respectively,

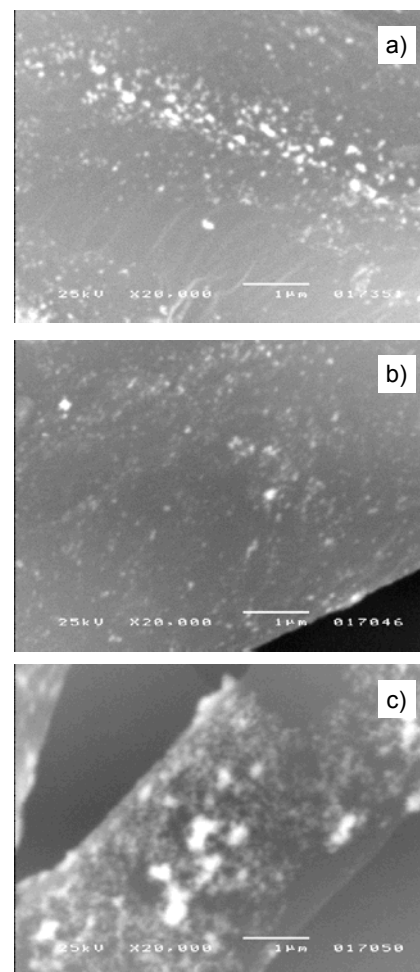


Figure 1. Electron microscope images of sample 1 (Table 1) with a) Ag, b) Au, and c) Pt.

but without deposited silver (Table 2), one can see that the number of nanolayers does not significantly influence the temperatures of the 50% decomposition ($T_{50\%}$). Also, the number of layers does not significantly affect the total thermal effect of samples containing deposited silver. On the other hand, the replacement of PAH in the external layer with PDAMA slightly decreases the thermal effect in both the samples with and without silver.

From the comparison of thermograms of samples 2 and 4 it follows that within the examined range the quantity of deposited silver (0.58 – 4.14%) does not significantly influence the thermal effect obtained.

The comparison of test results carried out under the atmosphere of air and nitrogen is shown in Table 3.

From the data in Table 3 it follows that the effect of increased thermal resistance

Table 3. Thermal effects of sample 1 with deposited nanolayers containing silver heated in air and under nitrogen; * in relation to $T_{50\%}$ of unmodified PP nonwoven.

Gas	Summarised $\Delta T_{50\%}$ *, °C
air	33.3
nitrogen	8.7

under nitrogen is several times lower than that in air. Similar observations have been noted by Lee et al. [10] after the deposition of palladium particles on polystyrene and poly(propylene) films, and also by Aymonier et al. [9] in the case of nanocomposites of poly(methyl methacrylate) with palladium.

Table 2. Thermogravimetric parameters of samples with deposited nanolayers without silver and after deposition of silver tested in air in relation to unmodified PP nonwoven reference; * in relation to $T_{50\%}$ of unmodified PP nonwoven, amounting to 346.1 °C, ** calculated from the differences in the solid residue quantity at 600 °C between a sample with nanolayers and that with nanolayers containing silver.

Sample	$T_{50\%}$ of sample with nanolayers, °C	$T_{50\%}$ of sample with Ag, °C	Summarised $\Delta T_{50\%}$ *, °C	percent of silver**, %
1	362.5	379.9	33.3	0.69
2	386.4	394.2	48.1	0.58
3	386.7	399.9	53.8	0.46
4	379.8	392.1	46.0	4.14

Table 4. Thermogravimetric parameters of sample 1 with deposited nanolayers containing gold, platinum and platinum after saturation with hydrogen in relation to unmodified PP nonwoven, taken in air; * in relation to $T_{50\%}$ of unmodified PP nonwoven, amounting to 346.1 °C, ** calculated from the differences in the quantity of solid residue at 600 °C between the sample with nanolayers and that with nanolayers containing metal.

Metal	$T_{50\%}$ of sample with metal, °C	Summarised $\Delta T_{50\%}$ *, °C	Metal percent**, %
gold	374.4	28.3	2.37
platinum	373.7	27.6	1.83
platinum with H ₂	417.6	71.5	1.83

The thermogravimetric results of sample 1 (Table 1) with deposited particles of gold, platinum and after the saturation of platinum with hydrogen are given in Table 4 and illustrated in Figures 3 and 4.

As is seen from the above data presenting the effect of deposited gold and platinum on the combustion process, both metals, similarly as with silver, bring about an increase in $T_{50\%}$ by about 30 °C. On the other hand, the incorporation of hydrogen into platinum considerably increases the thermal resistance ($T_{50\%}$ increases by more than 70 degrees).

PP nonwoven samples with deposited platinum and with platinum saturated with hydrogen were also tested in an atmosphere of nitrogen. The course of thermograms confirms the previous observation that the increase in thermal sta-

bility by metal deposition is considerably lower than that in air. On the other hand, the effect of platinum hydrogenation is vestigial in an atmosphere of nitrogen.

Conclusions

Based on the results presented one can state that the layer-by-layer method is a convenient way of depositing colloidal particles of silver, gold or platinum on textiles. Colloidal particles possessing a negative potential are adsorbed on external layers deposited on fibers possessing a positive potential, e.g. poly(allyl amine) or poly(dimethylamino ethylene methacrylate). It has been found that the colloidal particles are not aggregated, but are distributed at random.

It has been found that the deposition of silver, gold or platinum particles on the

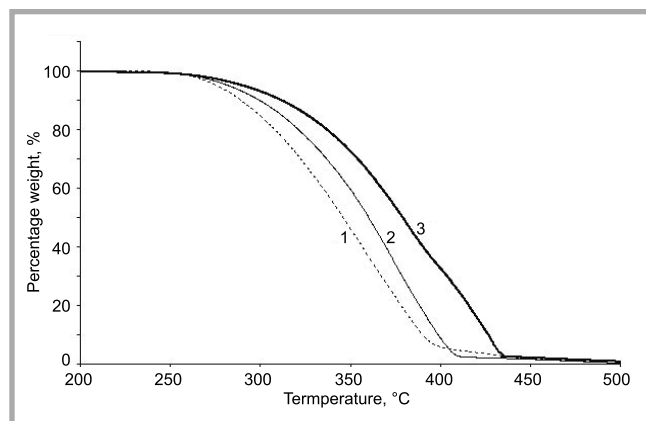


Figure 2. Thermogravimetric curves taken in air for: 1) PP nonwoven without deposited layers; 2) sample 1 (Table 1) without silver and 3) sample 1 with deposited silver.

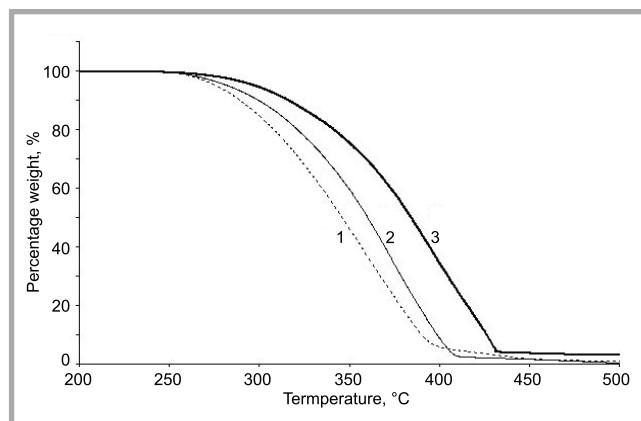


Figure 3. Thermogravimetric curves taken in air for: 1) PP nonwoven without deposited layers; 2) sample 1 (Table 1) without metal and 3) sample 1 with deposited gold.

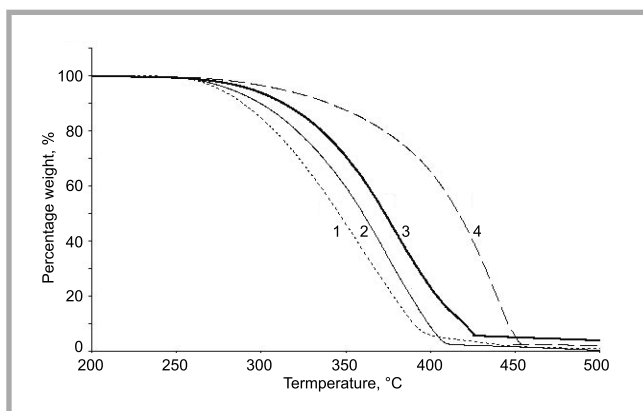


Figure 4. Thermo-gravimetric curves taken in air for: 1) PP nonwoven without deposited layers; 2) sample 1 (Table 1) without metal; 3) sample 1 after the deposition of platinum and 4) after the saturation of platinum with hydrogen.

surface of poly(propylene) nonwoven clearly increases the thermal stability of poly(propylene). As shown, the temperature of polymer decomposition up to 50% rises by about 30 - 50 °C just after depositing about 0.5% by wt. of metal. This is consistent with earlier reports [8], in which their authors have suggested that the increased thermal stability is due to the suppressing of polymer chain mobility during the thermal decomposition process.

It has been shown in the present study that an increase in thermal stability is

particularly high in the case of depositing colloidal platinum saturated with hydrogen. In such circumstances $T_{50\%}$ increases as much as by 71 °C. It seems that such a great change is connected not only with the previously suggested change in polymer segment mobility, but also with a change in the pyrolysis mechanism, and especially with the hydrogenation of unsaturated decomposition products. Such an interpretation is confirmed by comparing the behavior of samples in air and nitrogen.

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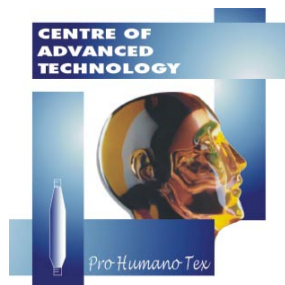
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