Acta Chimica Slovaca, Vol.2, No.1, 2009, 70 - 76

Coating of TiO_2 nanoparticles on the plasma activated polypropylene fibers

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Abstract

Polypropylene nonwoven were pretreated by coplanar diffuse surface barrier discharge operated at atmospheric pressure in nitrogen before coating them by TiO_2 nanoparticles. The plasma treatment induced chemical and topographical changes on the polypropylene surface were studied. Results indicate that incorporation of oxygen atoms in polypropylene surface and increasing of surface roughness are the main factors in TiO_2 adhesion enhancement.

Keywords: polypropylene nonwoven, TiO_2 nanoparticles, polypropylene surface

Introduction

For the success of polymer applications such as protective coatings the special surface properties with regard to chemical composition, hydrophilicity, roughness, crystallinity, etc. are required. Common surface modification techniques include treatments by flame, corona, plasmas, photons, electron beams, X-rays. These treatments have been applied to achieve the following purposes: produce special functional groups at the surface for specific interactions with other functional groups, increase surface energy, hydrophobicity or hydrophilicity, improve chemical inertness, modify surface morphology, increase surface electrical conductivity and improve dyeability.

Plasma treatment has become an important industrial process for modifying polymer surfaces (Corn et al., 1991, Inoue et al., 1990). Different types of gases such as argon, oxygen, nitrogen, fluorine, carbon dioxide and water can produce the unique surface properties required by various applications. The success of these techniques is related to their ability to change the surface properties of a material by physical and chemical modification of its most external layers (about 100 nm) without modifying its bulk characteristics. In this way, reengineering of surface chemistry can open completely new fields of application to conventional polymers (Marcandalli and Riccardi, 2007).

Plasma surface activation is usually understood as a plasma treatment under non polymerizing conditions. The chemical surface modification is initiated by radical reactions of the plasma or by plasma generated UV radiation. In atmospheric pressure plasmas, the surface activation typically takes places with oxygen-containing gas mixtures such as air. Surfaces with low functionality become more reactive by enhancing the concentration of oxygen-containing or other polar groups at the surface (Stegmaier et al., 2007). After plasma activation in air a great variety of different oxygen-containing functional groups, such as -OH, -C=O, -COOH will be introduced onto the surface of the material. Activation can also mean the increased wettability of surfaces whose surface energy is increased by the polar surface groups.

In the present work polypropylene nonwoven (PPNW) were activated using a novel type of atmospheric-pressure plasma reactor, which can generate „cold“ diffuse plasma with extremely high concentration of chemically active species at atmospheric pressure in any gases without using helium. The reactor is based on the so-called coplanar diffuse surface barrier discharge (CDSBD) (Šimor et al., 2002) here a macroscopically homogenous plasma layer with a high power density on the order of 100 W/cm^3 was generated in nitrogen or air.

Methods

In our research polypropylene nonwoven (PPNW) with surface area 50 $g.m^{-2}$ produced by Pegas, a.s. Brno was used. PPNW surface was activated by an atmospheric-pressure plasma treatment in N_2 using surface barrier discharge. Time of samples activation was 5 seconds. Activated samples were cut into size 3x3 cm and then were weighted.

Nanoscaled titanium dioxide in water dispersion was used for coating of activated samples. Water dispersion was prepared in three concentrations 0,5 g/l, 0,75 g/l and 1 g/l. In order to prevent creation of the nanoparticle aggregates during the mixing in distilled water, the modification of PPNW with TiO_2 water dispersion were carried out in ultrasound at 40°C for 30 minutes. The samples were dried in the air and weighted again. After that the samples of PPNW with TiO_2 coating were washed in distilled water in ultrasound to remove unlinked TiO_2 from the PPNW surface. Air-dried samples after washing were weighted again.

For characterisation of plasma activated surfaces of PPNW and PPNW with TiO_2 particles atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used.

Results and Discussion

In order to coat titanium oxide nanoparticles onto the polypropylene surface, the plasma activated samples were immersed into a water dispersion of TiO_2. Fig. 1 illustrates the comparison of the bonded TiO_2 content to PPNW and also the content of bonded TiO_2 nanoparticles after washing in distilled water in ultrasound during 30 minutes for removing unstably attached particles.

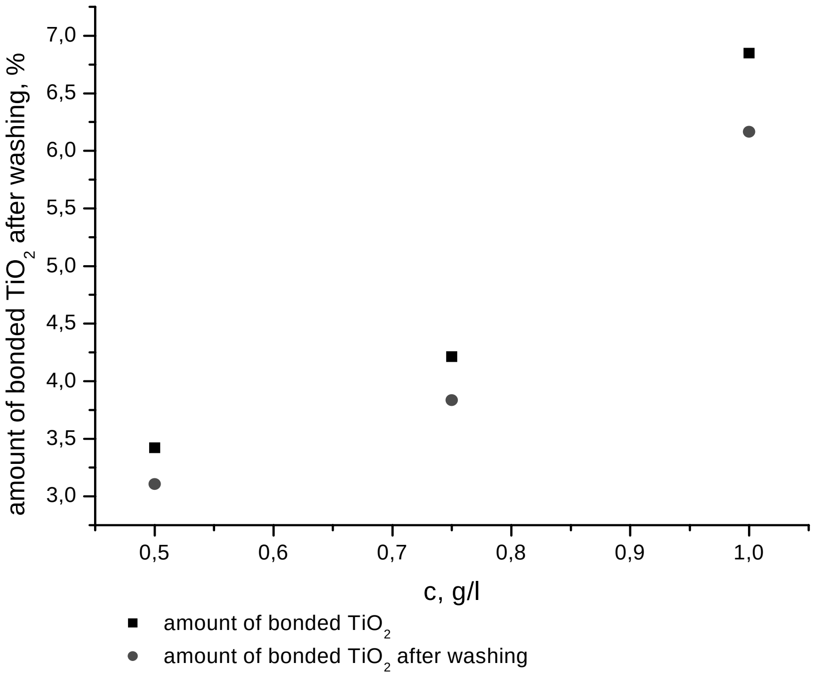
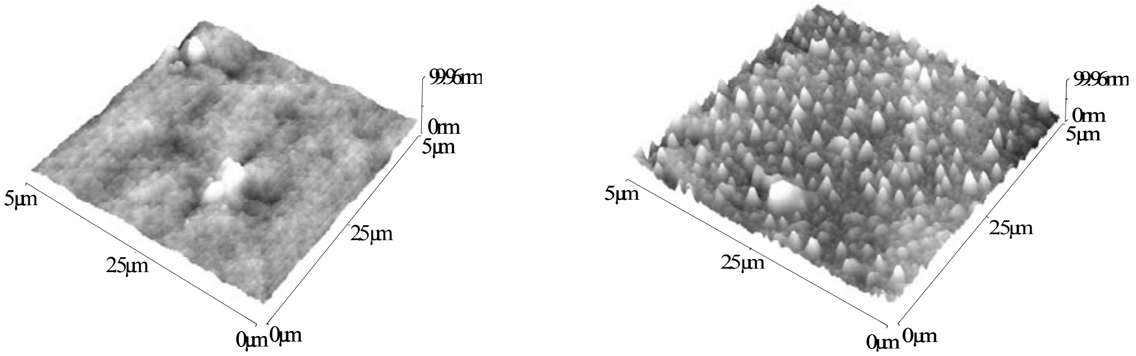


Fig. 1 Content of TiO_2 particles bonded to plasma activated PP NW independence on the concentration of TiO_2 water dispersion

The content of TiO_2 is increasing in dependence on the concentration of TiO_2 water dispersion. The values of linked TiO_2 nanoparticles varied from 3,4 % to 6,9 %. After washing about 9% of initially bonded TiO_2 nanoparticles were washed out in distilled water under sonication. Modified PPNW surface properties by an air dielectric barrier discharge have been studied using atomic force microscopy. This method allows material surface analyses without any pre-treatment. It is also suitable for study of topography, roughness determination and deformation of material surfaces. Fig. 2 shows noticeable differences between polypropylene nonwoven with and without surface modification. By plasma treatment the PPNW surface has become rough therefore the surface area increased.



PP NW

PP NW after plasma activation in nitrogen

Fig. 2 AFM image of PPNW unmodified surface and PPNW surface after plasma activation

Alternative method of polymer surface studying is scanning electron microscopy. SEM was used to compare the samples of PPNW surface coated with TiO_2 nanoparticles in chitosan dispersion (Fig. 3, 5) and samples coated in water dispersion (Fig. 4, 6). From pictures it is evident the big difference between that two. SEM images from the microscope showed us complete differences on the polypropylene fibers surfaces with TiO_2 nanoparticles coated from water and chitosan dispersion. At direct bonding of water dispersion of TiO_2 nanoparticles was the surface rough in contrast to chitosan dispersion, when the surface was smooth. In the Fig. 3 and 5 are presented the images of samples coated with TiO_2 nanoparticles in chitosan dispersion. It is visible that the layer of chitosan with TiO_2 nanoparticles creates relatively smooth surface on the fibre. At the higher magnification (Fig. 5) it can be seen on the surface attached particles with size of less than 100 nm, but the most part of particles are attached to the surface as clusters. The completely different morphology has a fibber coated with TiO_2 nanoparticles in water dispersion (Fig. 4 and 6). The polypropylene nonwoven surface is rough and the TiO_2 nanoparticles are attached on each other.

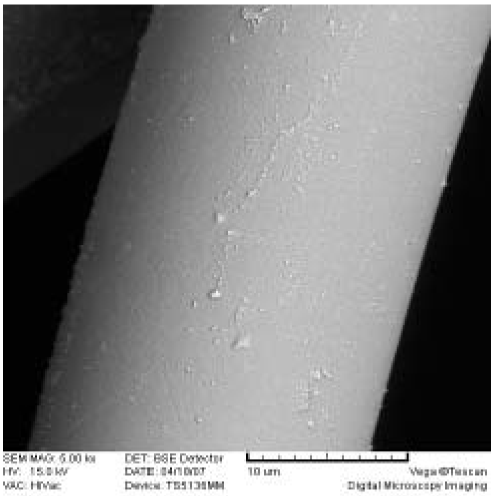


Fig. 3 PP fibber coated with TiO_2 in chitosan dispersion

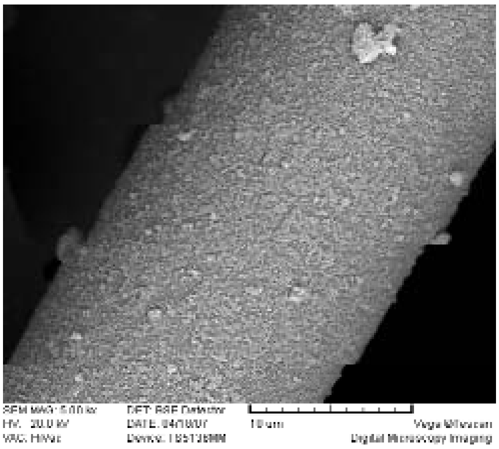


Fig. 4 PP fibber coated with TiO_2 in water dispersion

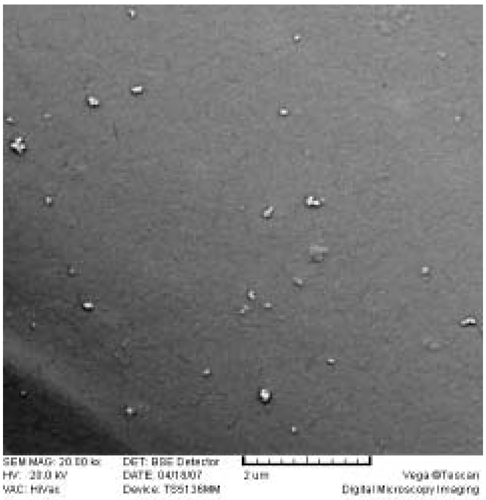


Fig. 5 PP fibber coated with TiO_2 in chitosan dispersion after washing

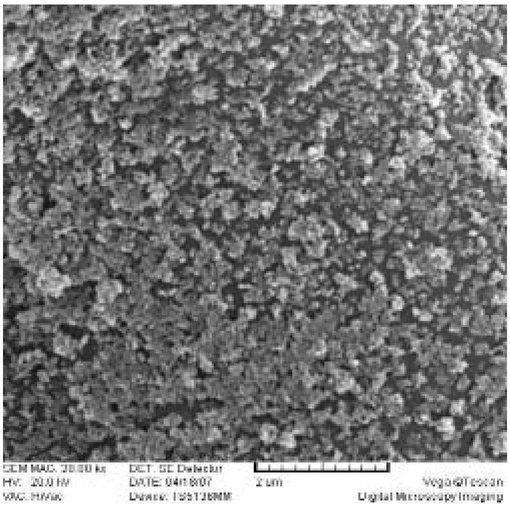


Fig.6 PP fibber coated with TiO_2 in water dispersion after washing

To analyse the changes of chemical composition on the polypropylene surface after activation by DCSBD and coating of TiO_2 particles, the X-ray photoelectron spectroscopy were used.

Four major emissions peaks can be observed at 285 eV for C1s, 533 eV for O1s, 400eV for N1s and 460eV for Ti2p, respectively (Fig. 7). Binding energy of 285 eV representing hydrocarbon type C-H bond. In plasma activated samples new C1s peaks occurs at the binding energy 276,1 eV and 274,8 eV respectively. These peaks corresponds to chemical bonding C-O or –C=O. Completely new peak was detected at binding energy 265,7 eV on the TiO_2 coated samples.

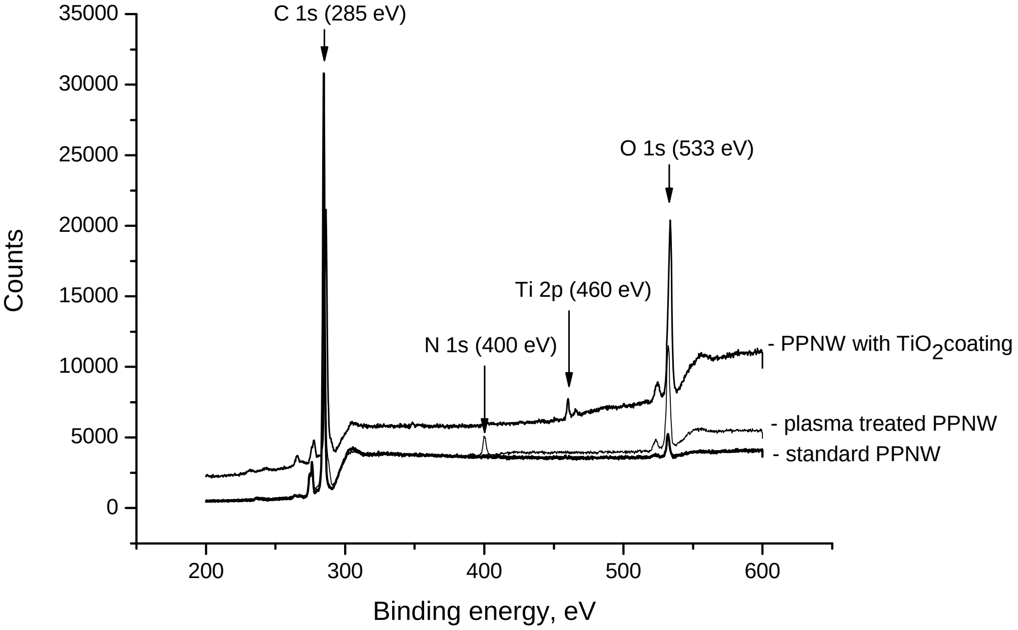


Fig. 7 XPS spectrum of unmodified PPNW surface, PPNW after plasma modification and PPNW coated with TiO_2

XPS O1s peaks shown in Fig.7 confirm that PP fibers are partially oxidized at the surface after plasma activation even though if it was carried out in nitrogen plasma. This is related to the fact that some oxygen is adsorbed also in untreated PPNW surface and some oxygen is built in PP surface after taking off the samples from plasma to air. Nitrogen N1s peak (400 eV) on the plasma activated samples shows that nitrogen atoms are incorporated on the surface of PP fibers after plasma activation as well.The appearance of Ti2p peaks located at a binding energy within the range from 458 eV to 460 eV confirms the existence of TiO_2 particles on the polypropylene fibers surface. Based on the above results it can be concluded that TiO_2 particles have sufficient binding strength with fiber surfaces. Even though it was suggested that dispersive forces are mainly responsible for the increased interfacial adhesion, the improvement in adhesion can be related to individual surface modification such as chemical composition or surface roughness or a combination of these effects. According some authors (Mittal 2007) the chemical modification of the surface after plasma activation is more influential than surface topography for high bond strengths.

For explanation of adhesive forces between titanium oxide and polypropylene fiber surface further investigation are needed. It is supposed that TiO_2 nanoparticles formed complexes with oxygen atoms built in polypropylene surface after plasma activation. It have been reported that TiO_2 can adsorb on polymers with -COOH groups in two different ways (Li et all., 2009). One is that TiO2 can be bound with two oxygen atoms by a bidentate coordination to Ti4+ cation. Another is to form H-bond between carbonyl group at the polymer surface and the surface hydroxyl group of TiO_2.

Conclusion

Polypropylene nonwoven were activated by coplanar diffuse surface barrier discharge at atmospheric pressure in nitrogen. The physical and chemical changes on polypropylene surfaces induced by plasma were studied. Surface analysis shows incorporation of both oxygen and nitrogen atoms into the polypropylene surface as well as topographical changes on the surface with an increase of surface roughness. This type of surface modification allows adsorbing of TiO_2 nanopatricles on the polypropylene surface from water dispersion. The most part of TiO_2 are attached to the fibers surface as clusters.

Acknowledgement

This work was supported by Grant Agency of Slovak Republic VEGA 1/4095/07 and Grant Agency of Czech Republic KAN 101630651

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