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Original Research Paper

Time dependence of the surface chemistry of the plasma treated polypropylene powder

Jindřich Matoušek *, Nicol Bendlová, Zdeňka Kolská, Pavla Čapková, Jaroslav Pavlík, Martin Kormunda

University of J.E. Purkyně in Ústí nad Labem, Faculty of Science, Department of Physics, České mládeže 8, 40096 Ústí nad Labem, Czech Republic

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ABSTRACT

The polypropylene (PP) powder is used for various purposes. However, its good mechanical properties are accompanied by poor wettability. The PP powder was therefore modified by air plasma in fluidized bed reactor (FBR). Several techniques were employed to characterize the treated samples – XPS for the surface chemistry, electrokinetic analysis for zeta potential determination, contact angle measurement for the wettability characterization and SEM for morphology observations. The wettability was enhanced by the plasma treatment and the contact angle of water decreased from 139° to 83° after the plasma treatment. The XPS showed over 20% of oxygen on the surface after the plasma modification. SEM confirmed that only chemistry is responsible for the wettability improvement. No morphological changes were induced by the plasma. The wettability measurements were done also with polyethylene (PE) powder and some similarities between PP and PE were observed.

1. Introduction

The polypropylene (PP) powder is widely used as a precursor in various industrial processes. It is often used due to its lightweight, mechanical properties and chemical resistance. However, its wettability is poor which is common for the polyolefin polymers like PE or PP. The wettability is governed mainly by surface energy of the powder and in consequence by presence of the polar functional groups on the surface [1]. For this purpose various treatments can be used, e.g. wet chemical processes, photon irradiation or flame treatment. Use of the plasma modification is also very popular because the plasma modification is usually solvent free single step process and allows one to create a wide range of chemistry on the surface of almost any material. Various types of plasma reactors can be used including low pressure plasmas; DC discharges, RF or MW plasma; and also atmospheric pressure plasmas can be used [2–8]. In case of this study, the fluidized bed reactor (FBR) was selected for the plasma treatment as it is capable of powder modification.

The industrial processes usually follow immediately one after another, but the material must be often stored for extended time period. Therefore the ageing of the treated powder and stability of the modified surface should be studied too. Although some works [9,10] were considering PP modification in the fluidized bed reactor, the ageing was not studied extensively (according to the author's best knowledge). Some studies of flat PP samples addressed long term (9 months) ageing in an oxidative solution [11] or natural ageing in atmosphere with or without light irradiation [12]. Short term (10 days) ageing of PP powder treated by argon RF plasma was investigated using contact angle measurement only [4]. In this work the ageing was done mainly by XPS and the measurements covered time period of 60 days. The SEM measurements were performed to study the possible morphology changes on the powder surface and electrokinetic analysis of freshly treated powder was done for characterization of surface polarity and chemistry and to support the XPS measurements. The study of wettability of the powder was carried out by the contact angle measurements where two approaches were used – measurements with double sided carbon tape covered by powder and powder pressed into pellets. Some wettability measurements with PE powder were carried out too as PE is a polymer of the same class as PP and some similarities in behavior of the plasma treated PP and PE were found.

2. Materials and methods

2.1. FBR apparatus

The PP powder was supplied by Unipetrol RPA and it was sieved to 355 μm grain size. The fluidized bed reactor was built using

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* Corresponding author.
E-mail address: jindrich.matousek@ujep.cz (J. Matoušek).

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80 cm long quartz glass tube with DN25 ISO KF flanges at both ends. The laboratory air was flown up through the porous membrane located at the bottom of the reactor. The blowing air mixed and fluidized the powder sitting on the membrane. At the end of the experiment most of the powder landed back to the porous membrane and was collected for analysis. The working gas was the laboratory air fed by a mass flow controller (MKS). The humidity of the laboratory air ranged between 30% and 38% as measured before each experiment. The RF power from generator Dressler Cesar 133 was delivered through the matching network and two outer ring electrodes that were 1 cm apart from each other. The optimal conditions for powder fluidizing were found at 120 sccm gas feed and pressure 560 Pa. For this flow and pressure the modification time dependence was investigated for 20 W plasma discharge. The plasma modification times ranged from 2 s to 960 s. Several experiments using 50 W were done too. The treatment time ranged from 2 s to 20 s in this case. The air was used as a working gas because it contains oxygen and humidity which should result in the presence of polar groups on the surface after the modification. As a consequence the wettability should be significantly higher after the modification. For the polar groups detection (oxygen containing groups respectively) the XPS technique was used.

2.2. XPS measurements

The XPS technique was used for revealing the surface chemistry of the samples and for the polar groups detection as these functionalities influence the surface energy as described in literature [1,13]. The PP powder was put onto the double sided carbon tape that is being used for conductive attachment of the samples on the sample holder. The spectrum of the pure carbon tape was recorded too, to avoid misinterpretation of the spectral features. This measurement confirmed that the powder covered whole tape area so there was no need for any additional corrections. The spectra were recorded using hemispherical analyser Phoibos 100 from Specs operated in FAT mode. Non-monochromatized X-ray beam of Al anode at 200 W with Al Kα photon energy 1486.6 eV was used. The survey spectra for binding energies from 1300 eV to 0 eV were recorded with pass energy 40 eV, energy step 0.5 eV and dwell time 0.1 s. For the C1s and O1s high resolution spectra pass energy 10 eV was used and the scan was repeated 10 times. The XPS is not equipped with electron gun for charge compensation, so the spectra were referenced to the peak of aliphatic C— H bonds at 285 eV. Quantification was done from survey spectra using relative sensitivity factors $RSF_{C1s} = 1$ and $RSF_{O1s} = 2.93$. Software CasaXPS was used for the spectra processing. Error of the oxygen (and carbon) content estimation is about several units of atomic percent.

2.3. Wettability measurements

The experiments described in this work are batch process and the amount of the powder from one experiment is about 0.3 g. Therefore it was not possible to use e.g. Washburn method for the wettability estimation. This was solved by using double sided carbon tape – the tape was sticked to a flat surface and its upper side was completely covered by the PP powder. Then the contact angle of distilled water was measured by sessile drop method. 3 μl droplet was used and measured by See system (Advex Instruments). This measurement can be strongly influenced by the roughness of such surface so 3 measurements were averaged to obtain final value. The standard deviation of these data was lower than 1.5° so the influence of the varying roughness was probably minor.

Another possibility for powder wettability estimation is to create pellets. The manual hydraulic press (H-62 from Trystom s.r.o.) was used and the pressing force was varied from 10 kN to 60 kN. The contact angle of water changed with the pressing force as described later.

2.4. SEM measurements

Several grains of the powder were poured on the double sided carbon tape and covered by 15 nm of gold to prevent charging during measurement. Then the samples were measured by SEM Tescan Vega LSU. The Acceleration voltage was 20 kV, magnification 5000× was used. Higher magnifications did not bring any additional information.

2.5. Electrokinetic analysis

Determination of zeta potential (ζ potential) of all samples (unmodified and plasma modified) was accomplished on SurPASS Instrument (Anton Paar, Austria). Samples were studied inside the cylindrical cell in contact with the electrolyte (0.001 mol d m^{-3} KCl) at room temperature. For each measurement the same amount of powder (0.50 g) was put into the cell. All samples were measured four times at constant pH (pH = 6.3) with a relative error of 5%. For determination of the zeta potential the streaming potential method was used and the Fairbrother–Mastins equation was applied to calculate zeta potential [14].

3. Results and discussion

3.1. XPS results

For all samples, the first XPS measurement was done immediately after modification, i.e. the samples were introduced in less than 5 min after modification into the load-lock chamber of the XPS apparatus and the chamber was evacuated to enable the measurement. Other measurements followed after approximately two weeks and 1 month. Last measurements were done after 2 months of ageing. Fresh (i.e. modified and aged but not measured previously) powder was used for each XPS measurement.

The XPS quantifications are given in Fig. 1. The survey spectrum of untreated PP powder shows small amount of oxygen (3% atomic) on its surface. Also the high resolution C1s peak of pristine powder in Fig. 2 shows presence of small amount (6%) of oxygen containing groups bonded to carbon (components at 286.7 and 287.9 eV) which can be result of the PP powder fabrication process or surface oxygen or water contamination.

The modification in air plasma gives rise to the oxygen content. Even 2 s short exposure at 20 W creates about 9% of oxygen on the powder surface. As the modification time at 20 W prolongs, the amount of O rises up to 17% for 960 s long treatment. Higher power plasma (50 W) results in higher O content which rises from 15% (2 s) up to 22% for 20 s treatment.

The high resolution spectra of C 1s peak revealed the bond character between C and O. The nitrogen was not observed on the surface of any sample in amount detectable by XPS, neither auger N KLL was observed. Therefore the carbon – nitrogen bonds were excluded from C 1s deconvolutions. The deconvolutions of the C1s high resolution spectra were done for 3 types of carbon – oxygen bonds. The components were restricted to be at 285.0 eV (C—C), 286.7 eV (C—O), 287.9 eV (C═O) and 289.2 (O—C—O) according to the literatures [15,16].

The carbon—oxygen bonds amounts derived from C1s deconvolutions are shown in Fig. 3. The changes show no clear trend during ageing, but it is possible to see, that the 50 W treatment results usually in higher amount of carbon oxygen bonds. Especially the O═C—O bonds amount is significantly higher than in case of the