

# Surface Properties of Plasma-Modified Poly(1-butene)

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**Abstract:** Surface properties of poly(1-butene) films has been modified by a radio frequency plasma treatment. To minimize degradation and ageing effects it is necessary adjusted the gas composition and the plasma conditions on the polymer type. For this purpose plasma containing five various gasses or their mixtures: air, argon, argon then allylamine, argon wearing ammonia and argon with octafluorocyclobutane, were used. Changes in the surface hydrophilicity, roughness and the chemical composition of modified poly(1-butene) films were investigated by contact angle measurements, atomic force microscopy and X-ray photoelectron spectroscopy. All types of plasma treatment expect fluorocarbon plasma cause increase of polar functional groups on the surfaces and their hydrophilicity. On the other hand, fluorocarbon plasmas cause increase of contact angle and hydrophobicity.

**Key-Words:** isotactic poly(1-butene), plasma treatment, contact angle, AFM, XPS, surface

## 1 Introduction

Isotactic poly(1-butene) (PB-1) is one of the semi-crystalline polymers which exhibits pronounced polymorphism and morphologies depending on thermal treatment and mechanical handling. Analogous to the other polyolefins with asymmetrical monomer units PB-1 also exhibits polymorphic crystallization behavior. Five different crystalline modifications, designed as I, II, III, I' and II', have been reported. Natta et al. discovered that PB-1 assumes a 113 helical conformation with a tetragonal unit cell when crystallizing from the melt [1]. This crystalline structure is known as a form II and upon ageing at room temperature is gradually transformed into the trigonal form I. This transformation takes about one week under normal conditions and is reflected in important changes in the physical-mechanical properties. During the transformation, density, crystallinity, hardness, rigidity, stiffness and tensile strength increase to values characteristic of the form I. Beníček et al. intensively studied thermal-induced transformation of PB-1 structure and properties [2].

Poly(1-butene) and other polyolefins, like polypropylene or polyethylene, have numerous applications in many fields of industry because of their outstanding resistance to creep, good mechanical properties, chemical resistivity, easy processing, low manufacturing costs and easy recycling.

On the other hand, these polymers are known as non-polar, hydrophobic materials with a low surface energy, poor adhesion and wettability, resulting in significant problems when applying surface coating, printing or sticking. So that, many applications of these polyolefins require improving of their surface and adhesive

properties. In this context, a lot of methods have been devised and commercially used to modify the surface. Among them, plasma treatment is a very effective way to enhance the hydrophilicity of polymer surface. Plasma can interact with the polymers through the formation of cross-linkages between adjacent polymer chains or by chain scission. The improving of surface hydrophilicity is induced by forming of new oxygen containing groups on the surface, such as carbonyl, carboxyl or hydroxyl [3–5]. On the other hand, some applications e.g., diffusion barrier or corrosion protection, require hydrophobic character of polymer surface. For these purposes fluorocarbon plasmas is an efficient tool to increase CA and improve hydrophobicity.

Plasma processing of polymers is a common procedure. Many studies have been focused on the plasma treatment of polypropylene, polyethylene, poly(ethylene terephthalate), polycarbonate, polystyrene, poly(methyl methacrylate) [6–8]. Nevertheless, the published studies dealing with plasma modified poly(1-butene) are very scarce, Shen et al. used RF plasma polymerization for the improvement of interfacial adhesion between glass fibers and poly(1-butene) [9].

Recent paper reports experimental results concerning poly(1-butene) surface properties modified by plasma treatment. To improve the surface properties to the best advantage and simultaneously minimize degradation and ageing effects it is necessary adjusted the gas composition and the plasma conditions on the polymer type. For this purpose plasma containing 5 various gasses or their mixtures were used. According our knowledge, the plasma treatment of PB-1 is presented here for the first time. The surface hydrophilicity was

measured by contact angle (CA). Surface topographic analyses were carried out by atomic force microscopy (AFM) and the chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS).

## 2 Experimental Section

### 2.1 Materials

In this study, two commercially-available grades of isotactic poly(1-butene) produced by LyondellBasell Louvain la Neuve, Belgium were used, a homopolymer PB 0300M (PB), characterized by melt flow index of 4 g/10 min (190 °C/2.16 kg) and density of 0.915 g.cm<sup>-3</sup>, and a random copolymer of butene-1 and ethylene, PB 8640M (coPB) with melt flow index 1 g/10 min and density 0.906 g.cm<sup>-3</sup>.

PB-1 sheets, approx. 1 mm thick, were prepared by compression molding. Prior to any deposition, rectangular samples with dimension of 80 × 10 mm were cut out, washed in acetone, denaturated alcohol, distilled water and then dried at temperature of 40 °C for 20 min.

### 2.2 Methods

Plasma treatment was performed at RF reactor FEMTO, Diener, Germany. The reactor, set up on a chamber used for the sample introduction, was a cylinder of 320 mm length and 150 mm diameter. The processing conditions were selected: excitation frequency 13.56 MHz, the generator power 50 W, gas flow 5 cm<sup>3</sup>.min<sup>-1</sup> and time of plasma treatment 60 s. The following processing gasses were used: air, argon (Ar), argon and thereafter 3 hours in allylamine vapor (Ar/C<sub>3</sub>H<sub>5</sub>NH<sub>2</sub>), argon bubbled through ammonia (Ar/NH<sub>4</sub>) and mixture of 50 % argon and 50 % octafluorocyclobutane (Ar/C<sub>4</sub>F<sub>8</sub>).

The contact angle measurement characterized by Surface Energy Evaluation System (See System), Advex Instruments, Brno, Czech Republic, was performed at room temperature to evaluate the hydrophilicity/hydrophobicity of the samples. There was used so-called "sessile drop" technique in this study. Water after reverse osmosis was utilized in all experiments. The drop volume was 4 µl. Ten separated readings of contact angle were averaged to obtain one representative value for each substrate and standard deviations were evaluated. Contact angle of pure PB-1 and plasma treated PB-1 at different time (from 10 min to 14 days) after plasma treatment were measured.

The surface topography of untreated and plasma modified PB-1 plates were studied on a nanometer scale using atomic force microscopy. Different areas were studied on each sample in order to obtain representative information. The AFM images were recorded by

Nanosurf, EasyScan2, Switzerland. Scan rate 1 line / 1.5 s, scanned area 50 × 50 µm and 5 × 5 µm.

Surface composition was analyzed with an XPS instrument TFA XPS Physical Electronics. The base pressure in the chamber was about 6 × 10<sup>-8</sup> Pa. The samples were excited with X-rays over a 400-µm spot area with a monochromatic Al K $\alpha_{1,2}$  radiation at 1486.6 eV.

## 3 Results and Discussion

The extent of hydrophilic/hydrophobic modification of the plasma treated PB-1 sheets was investigated by CA measurement. Figure 1 shows the variation in the CA of pure and plasma modified PB-1 specimens. The contact angle of untreated PB sheet reaches 99° and in the case of coPB specimen 104°. PB-1 and other polyolefins as polypropylene are strongly hydrophobic due to the lack of polar function groups on their polymer chains. However, plasma treatment causes change of surface properties and CA. In most cases, expect of Ar/C<sub>4</sub>F<sub>8</sub> plasma, decrease of CA can be seen. The most obvious decrease of CA was observed in the case of the sample PB after air plasma treatment (65°) and PB after Ar/NH<sub>4</sub> plasma (67°). On the other hand, the minimum decrease of CA was achieved in the samples treated by Ar/C<sub>3</sub>H<sub>5</sub>NH<sub>2</sub> plasma (PB ~ 86° and coPB ~ 84°). This decrease of CA can be ascribed to the formation of hydrophilic groups on the plasma treated polymer film surfaces. The plasma creates radical species on the polymer surface, mainly through polymer chain scission or hydrogen abstraction by bombardment of plasma particles. These species can combine with oxygen from air, and thus also contribute to increase of the amount of polar groups such as -OH, C=O, COOH and COO- on the plasma treated polymer surfaces. Hence these polar groups cause that the plasma treated polymer surfaces become more hydrophilic compared to the untreated polymer surface [10]. As can be seen, the contact angles of PB homopolymer are in the most cases slightly lower than that of coPB random copolymer, independent on the time after plasma treatment. The concentration of such polar groups on the surface of the plasma treated polymer depends on the physicochemical characteristics of the polymer surface. However, situation is absolutely different in the case of Ar/C<sub>4</sub>F<sub>8</sub> plasma where increase of CA was observed (PB ~ 111° and ~ 113°). Fluorocarbon plasmas cause increase of CA and hydrophobicity. During first 24 hours after plasma treatment, values of CA do not change significantly. Nevertheless, over time slow increase of CA can be observed. This process of hydrophobic recovery of the plasma treated PB-1 surface results from the tendency to reduce polymer surface energy, respectively increase its contact angle to be more resemble its environment. The thermodynamic

preferences influence the time dependent polar functional groups rearrangement in the direction of the polymer bulk, as well as the diffusion of low-molecular additives, or oligomers towards the surface of PB-1 [11]. Moreover, polymer ageing as well as chemical reactions may contribute to the surface changes. Again, an opposite trend can be seen in the case of fluorocarbon plasma where decrease of CA appears.

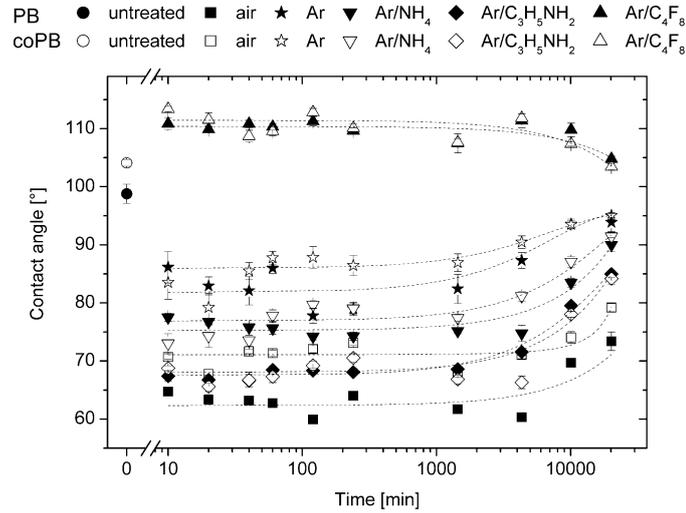


Fig.1 Contact angle variation of plasma treated PB and coPB specimens as a function of time.

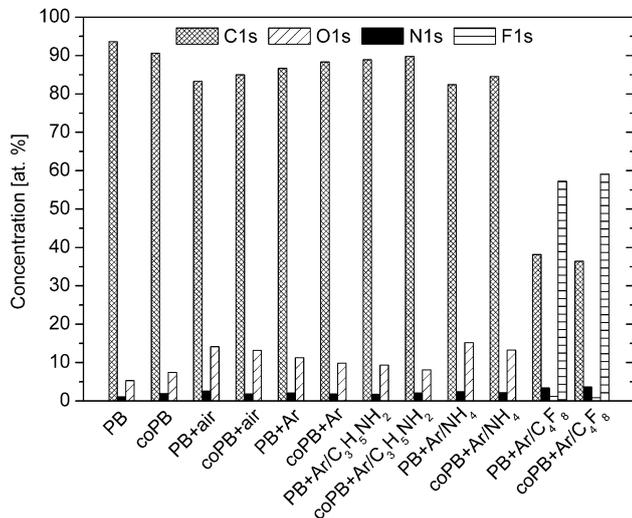


Fig.2 Comparison of surface composition of PB and coPB samples.

The surface chemical composition of neat and plasma treated PB-1 samples was investigated using XPS. Comparison of the surface composition of PB and coPB samples is presented in Fig. 2. Virgin PB and coPB samples contain predominantly carbon (approx. 94 and 91 at.%), oxygen (5 and 7 at.%) and neglectable amount of impurities like N, Si and Cl. As can be seen, plasma-treated samples (except the ones modified with Ar/C<sub>4</sub>F<sub>8</sub>)

have very similar surface composition: nitrogen concentration up to 2.6 at.% and oxygen concentration up to 15 at.%. On some samples surface impurities like F, Si, Na, Ca and Cl were found. Since nitrogen is found already on untreated samples, we can conclude that only little additional nitrogen is incorporated into the surface during treatment in Ar/C<sub>3</sub>H<sub>5</sub>NH<sub>2</sub> or Ar/NH<sub>4</sub>. Chemical composition is considerably different in the case of the Ar/C<sub>4</sub>F<sub>8</sub> treated samples where 57-59 at.% of F was detected at the surface. Furthermore, higher content of nitrogen on the surface up to 3.6 at.% and some oxygen – about 1 at.% can be found.

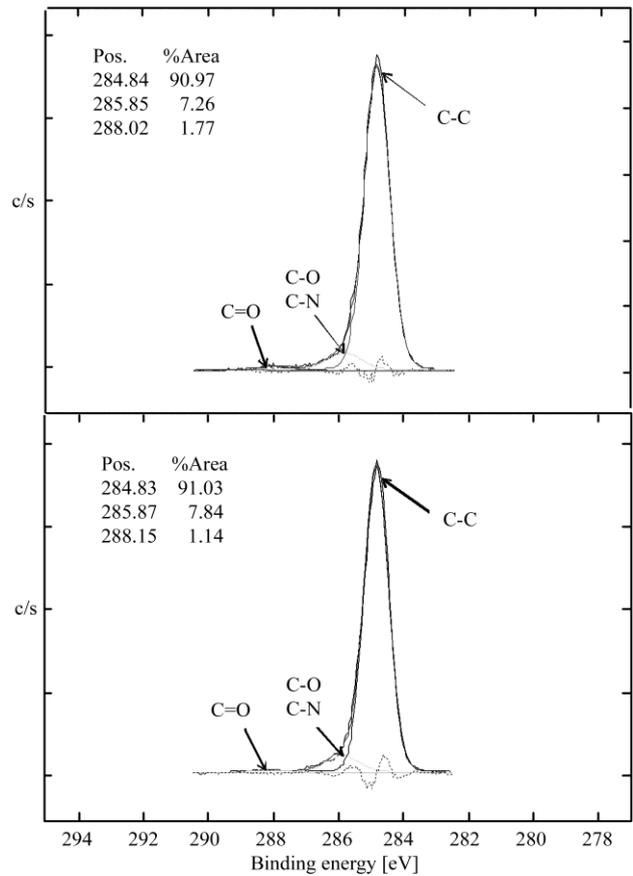


Fig.3 Carbon C1s peak of untreated PB (up) and coPB (down) samples.

A more detail analysis of the XPS spectra of the carbon C1s region of the untreated PB and coPB samples revealed the formation of different functional groups as can be seen in Fig.3. The prevailing component of the C1s peak located approx. at 284.8 eV indicates the existence of hydrocarbon components (C–C and/or C–H bonds). A weak shoulder is consistent with the levels of oxygen and carbon detected in the survey scans and was fitted with two peaks corresponding to carbon singly bonded to oxygen and to nitrogen (C–O/C–N) at approx. 285.9 eV, and to carbon doubly bonded to oxygen (C=O) at approx. 288.0 eV [12,13]. In some components, like C–O and C–N, the binding energies of the C1s peak are

very close, making it almost impossible to identify unambiguously the component.

As expected, according to the surface composition shown in Fig. 2, carbon peaks of PB and coPB samples treated by air, Ar, Ar/C<sub>3</sub>H<sub>5</sub>NH<sub>2</sub> and Ar/NH<sub>4</sub> plasma looks quite similar indicating that there are only small differences between the samples. Fig. 4 shows XPS spectra of the carbon C1s region of the PB sample treated by Ar/NH<sub>4</sub> plasma. The majority of carbon atoms can be found in C–C bonds (binding energy 284.6 eV) and minority in C–O/C–N bonds (286.5/286.3 eV), C=O bonds (287.9 eV) and O=C–O bonds (289.2 eV). Similar spectra have been also observed for the other treated samples which are not shown. The C1s peaks of all surface-treated samples show significantly stronger contributions at the higher binding energy side of the C–C peak, arising from the creation of oxygen-containing functional groups at the surface.

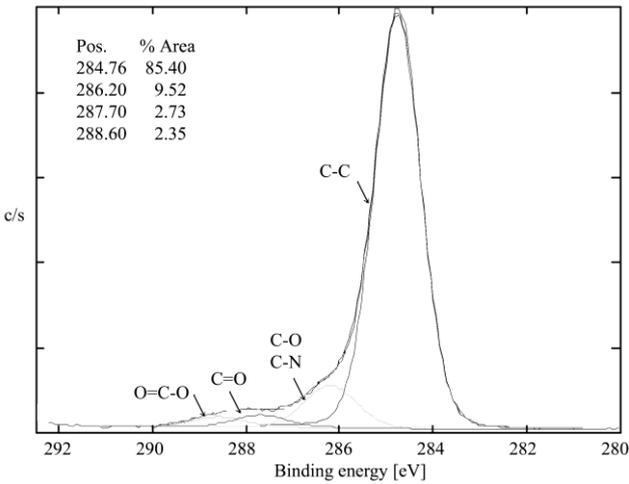


Fig.4 Curve fitting of carbon peak of sample PB+Ar/NH<sub>4</sub>.

Curve fitting of carbon C1s peaks of PB and coPB samples treated by Ar/C<sub>4</sub>F<sub>8</sub> plasma are shown in Fig. 5. Very broad spectrum indicates formation of various different carbon–fluorine bonds at the higher binding energies. The majority of carbon atoms can be attributed to CF<sub>3</sub> and CF<sub>2</sub> bonds located at approx. 293.8 and 291.8 eV and minority to C–C/H bonds (285.1 eV). In the case of coPB results apparent increase of CF and CF<sub>2</sub> bonds at the expense of C–C/H bonds can be observed.

AFM images of untreated and plasma treated PB and coPB samples have been reproduced in order to evaluate the effect of the modification on the surface morphology. Surfaces were scanned with a resolution of 50 × 50 μm with the corresponding Z range of 200 nm and 5 × 5 μm with Z range of 50 nm. From the AFM measurements we can conclude that plasma treatment independently on used gas does not change markedly surface morphology or roughness of modified poly(1-butene) samples.

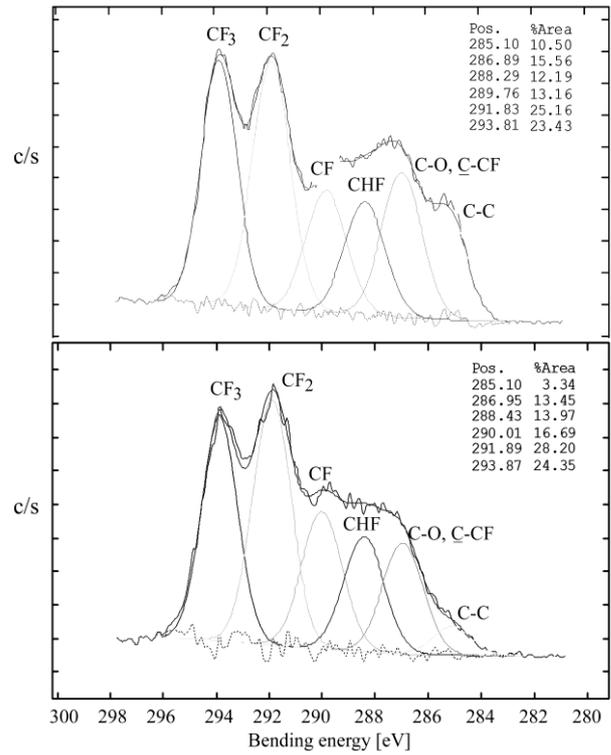


Fig.5 Curve fittings of carbon peak of PB (up) and coPB (down) samples treated by Ar/C<sub>4</sub>F<sub>8</sub> plasma.

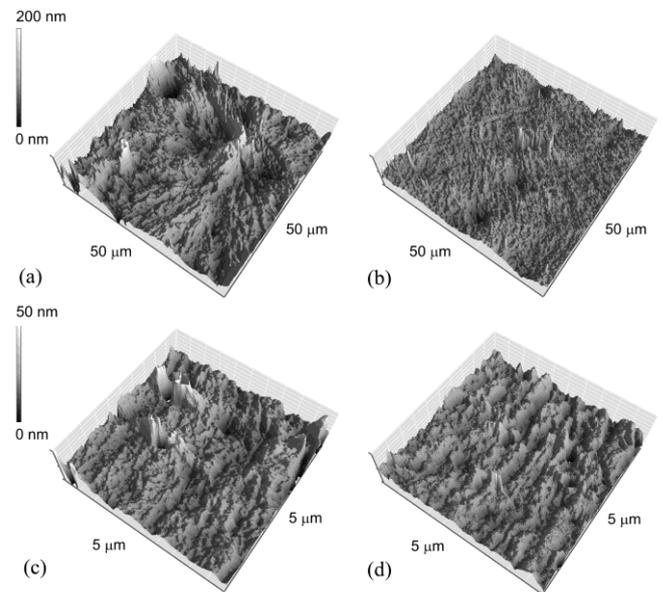


Fig.6 AFM topographic representation of (a) untreated, (b) plasma treated sample with an analyzed area of 50 × 50 μm and (c) untreated, (d) plasma treated sample with an analyzed area of 5 × 5 μm.

An example of AFM images of PB sample before and after air-plasma treatment is presented in Fig.6. It can be seen on the 50 μm scale that the surface becomes smoother after the plasma treatment (Fig.6b). However, on the 5 μm scale (Fig.6c,d) it is evident that the roughness of the surfaces is nearly similar, unchanged.

## 4 Conclusion

The experimental study has been focused on modification of the poly(1-butene) surface using RF plasma. The influence of various processing gasses was investigated. The plasma treatment can greatly change the surface chemistry. The polar functional groups generated due to almost all used types of plasma treatment on the surface of PB-1 sheets causes decrease in contact angle and increase of hydrophilicity. Contradictory effect can be observed in the case of fluorocarbon plasma which causes increase of contact angle and increase of hydrophobicity. Plasma treatment is an interesting and environmentally efficient method to modify the polymer surface for technical applications.

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