

Influence of oxygen and nitrogen plasma treatment on polypropylene (PP) bumper surface

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ABSTRACT

Purpose: The advantage of plasma treatment is that it modifies only the top few nm of the surface, the modification is uniform and it leaves the bulk properties of the material unchanged. Plasma treatment with oxygen or nitrogen plasma provides polar functional groups on the surface, which alters the surface energy of polymer.

Design/methodology/approach: Surface activation was made by two different plasma gases at different treatment times. In this work, surface activation of polypropylene (PP) based bumper materials by O₂ or N₂ plasma was carried out and material surface characteristics after plasma treatment were investigated. The plasma treated surface was studied by contact angle measurements.

Originality/value: Plasma activation has many advantages over traditional wet-chemical and physical activation procedures. Surface activation by plasma treatment is exceedingly fast, effective, economical, and environmentally friendly. When the plasma comes into contact with the PP surface it transfers the additional energy from the plasma to allow for subsequent reactions to take place on the material surface.

Keywords: Plasma treatment; Activation; PP; Plasma gases

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MANUFACTURING AND PROCESSING

1. Introduction

Polypropylene (PP) is low in cost but has outstanding mechanical properties and moldability, it accounts for more than half of all the plastic materials used in automobiles. PP compounds are used for a variety of parts, including

bumper facias, instrumental panels and door trims [1-3]. The increasing use of polypropylene materials in automotive sector, has forced the need to overcome some of their some limitations by means of innovative processing. In the automobile industry a complex and critical process is used in order to enhance both wettability

and paintability properties of PP bumper surfaces. Plasma treatment represents an efficient, environmental friendly and economic alternative to activate nonpolar PP surfaces [4,5].

PP exhibits low surface free energy values (28-30 mN/m), which are due in essence to its inherent hydrophobicity. This low surface energy affects all technical processes where wettability and improved adhesion are required. Printability, lamination, and paintability properties, as well as the processability, convertibility of the final materials depend strongly on the possibility of enhancing the polypropylene substrate's surface properties. Consequently, enhancing the surface activation of polypropylene has attracted (and still does) worldwide interest both in academia and in industrial research.

Physical surface activation methods, however, are the most extensively used because they allow the provision of more precise surface modification without requiring rigorous process control, and because, involving no chemical reagents and therefore no disposal of waste liquids, they are environmentally safe and clean processes. Among the theme of physical methods [6-13] currently available for the surface modification of plastics (flame, corona discharge, UV, gamma-ray, electron beam, ion beam, plasma, and laser treatments), flame treatment and corona discharge are the most widespread, especially in particular sectors such as packaging and automotive, which has primarily been ascribed to the lower cost and higher effective of these methods [14,15].

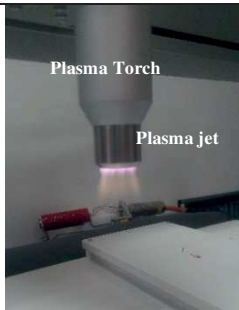
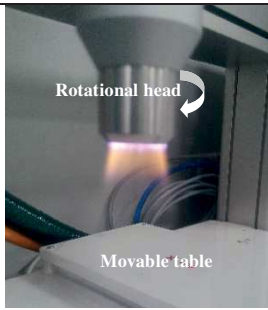
Flame surface common activation treatment is a traditional industrial bumper paint shop process used to improve wetting and adhesion properties of Polypropylene based components, such as automobile body parts (bumpers, dashboards, headlights, etc.). Main limitations are respectively: a) air to gas ratio (excess of air) is the most critical variable, b) distance: influence on temperature and on oxido/redox property flame, c) uniformity with which flame will contact the area to be treated [15,16]. An alternative effective method is a plasma treatment. Plasma surface treatments have been used in the many industries for a few decades now and latterly in the automotive sector by Audi, Ford and BMW for example. There are two types of plasma treatment available, vacuum and atmospheric. The vacuum type of plasma process requires the parts to be treated under low vacuum pressure in a chamber. A bleed gas is then introduced and ionised. A number of gases have been used, including, oxygen and, nitrogen, helium and air. The gas ions bombard the surface of the component causing chemical and topographical changes in the near surface region (100-150 nm depth). The chemical changes

are complex but involve removing atoms or breaking bonds which results in free radical evolution and cross linking. Bumper moulders and paint manufacturers have been seeking procedures via which the inert bumper surface is changed to a more polar and subsequently more wettable one. This is more challenging with process engineers developing 'dry treatment', because bumpers should be treated continuously, and the surface of the moulding should be uniformly modified in spite of the complicated shape [17]. In plasma surface treatment process has many parameters which is control the plasma activation efficiency. One of the important parameter is a plasma gas type or composition. Ionized plasma gases determine the plasma energy. This high density plasma bombard the surface and break the unstable weak surface C-H or C-OH bonds. Ionized oxygen and/or nitrogen atoms joint to free surface carbon atoms and occur C-O or C-N compounds in plasma atmosphere [18]. In this study the alteration of PP surface characteristics after plasma treatment with two different gases (O_2 and N_2) is discussed with the results obtained by observation with FTIR analysis and the measurement of the contact angle.

2. Material and method

Before testing or plasma treatment, all PP bumper samples (180 x 80 mm) were cleaned with IPA (isopropylealcohol) then dried with dry air. PP samples were plasma treated using the PlasmaTreat GMBH atmospheric plasma activation unit for 120 mm/sec. per side between 5-15 mm distance from the plasma torch (Table 1). Plasma conditions were optimized according to the manufacturer's instructions (300 V, 18.2 A, 21 kHz).

Table 1.
Experimental details of atmospheric plasma treatment

O_2 Plasma	N_2 Plasma
	
Standoff distance: 5-10-15 mm, Torch velocity: 120 mm/s	

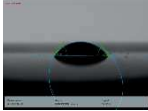

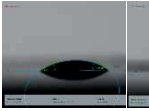

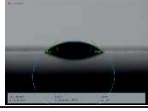

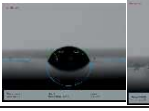
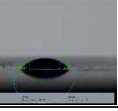
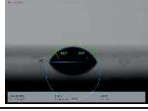



Contact angles were measured with Kruss DSA 30S contact angle measurement device and were determined by the Kruss Advanced software, using only the steady-state portion of the force position curve during the advancing and receding stages. The surface energy and its polar and dispersive components were calculated from the advancing contact angles in water and diiodomethane. Free surface energy was determined with Laplace Young Method. Surface chemical change analysed with ATR-FTIR. Microscopic investigations were realized with stereo microscope (Zeiss).

3. Results and discussion

3.1. Surface free energy and wettability

Plasma treatments were applied at different torch-surface distances. The wettability of PP was significantly improved by plasma treatment. As a result of measurement can be seen with regard to PP, its base (untreated) surface energy is approximately of 28-30 mN/m (contact angle 95-105°). Contact angle and surface energy measurements were given in Table 2. after the plasma treated with N₂ and O₂.

Table 2. surface energy and contact angle measurement results for O₂ and N₂ plasma

Distance	N ₂ Plasma		O ₂ Plasma	
	Water	Diiodomethane	Water	Diiodomethane
5 mm				
	Water: 42.9° Diiodomethane: 124.5° γ = 63.48 mN/m		Water: 36.6° Diiodomethane: 60.13° γ = 60.93 mN/m	
10 mm				
	Water: 42.15° Diiodomethane: 62.3° γ = 57.08 mN/m		Water: 71.3° Diiodomethane: 52.9° γ = 41.9 mN/m	
15 mm				
	Water: 64.2° Diiodomethane: 67.9° γ = 40.87 mN/m		Water: 69.2° Diiodomethane: 66.3° γ = 38.19 mN/m	

In comparison between N₂ and O₂ plasma: At all distances; N₂ plasma is more effective than the O₂ plasma. But N₂ plasma usage usually is not feasible for industrial applications. It was reported that the increase of surface energy after plasma activation could be interpreted also as a consequence of closer distance to surface. At higher distances of 20 mm, plasma is ineffective. We have found a strong dependence of the plasma treatment effect on the distance between the sample and the plasma torch. The general trend, increase in distance leads to decrease in surface energy. Highest surface energy (63±2 mN/m) has been obtained at 5 mm with N₂ Plasma. At 15mm distance; this value decreases to 40±2 mN/m.

3.2. Surface morphology

Plasma treatment of polymers is commonly associated with the changes of morphology and roughness of treated surfaces. In Figure 1 the comparison of the surface morphology is given for plasma untreated and plasma treated PP samples at different plasma treat distances.

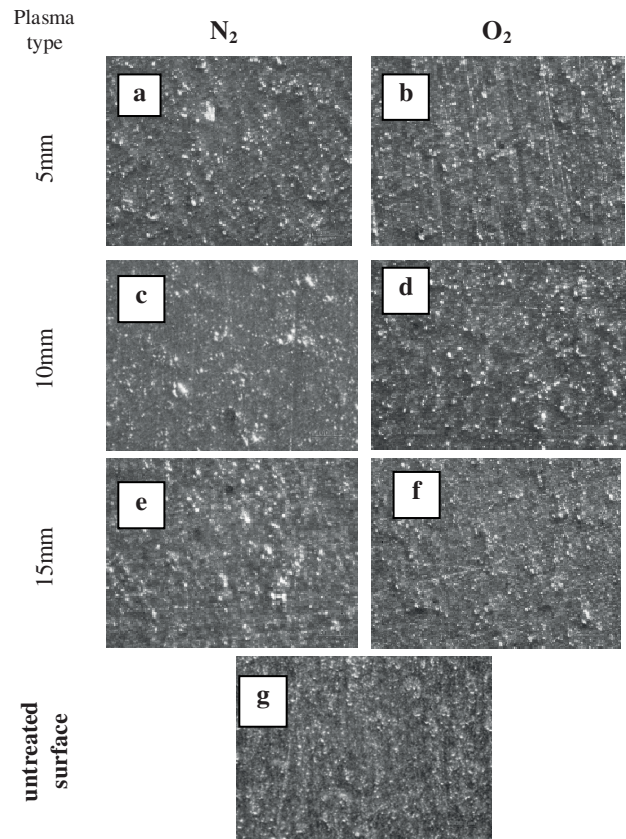


Fig. 1. Surface Micrographs after O₂ and N₂ plasma treatment at different standoff distances between 5mm and 15 mm

The surface of plasma untreated PP samples exhibit high surface unhomogeneity and roughness and the plasma treatment does not macro affect the surface morphology significantly (Fig 1g). But micron or nanoscale of surface morphology changed depend on plasma type. N₂ Plasma has high energy density, for this reason surface roughness is lower than the O₂ plasma. When the O₂ gas is ionized, surface is bombarded with oxygen atoms. Due to the higher molecular size of oxygen atoms, this leads more rough surface.

3.3. ATR-FTIR analysis

Plasma surface modifications are confined only to a few nanometers below the surface. FTIR spectroscopy in Attenuated Total Reflection (ATR) mode is one of the methods used to bring out the finer surface information. The surface functionalities were also detected by ATR-FTIR spectroscopy. When the untreated PP spectrum is compared with the nitrogen treated PP spectrum it is seen that a broad band occurs, which correspond to the hydroxyl group (-OH). Figure 2 shows the influence of N₂ plasma discharge on chemical composition of surface of polypropylene. There are some small surface changes of PP surface at different distances, before (green line) and after plasma treatment, in the region of carbonyl and carboxyl groups (1510-1740 cm⁻¹). It confirms creation of small amount of polar functional groups (-NH at 1545 cm⁻¹)

on the surface. Carbonyl (C=O) groups are observed at 1647 cm⁻¹. Wang, K. et al has also observed similar kind of group (C-O, C-N, C=O, C-O-C, O-C=O, O-CO-O) attachment on the surface on polyethylene samples treated with nitrogen plasmas [19,20]. At 3183 and 3357 cm⁻¹ peaks may be OH, NH and NH₂. By N₂ Plasma activation on PP at different distances showed that shorter plasma-surface distance (5 mm, bottom blue line), plasma activation effect is increased.

It is well known that an oxygen plasma can react with the polymer surface to produce a variety of atomic oxygen functional groups, including C-O, C=O, O-C=O and CO₃ at the surface. In an oxygen plasma, two processes occur simultaneously: etching of the polymer surface through the reaction of atomic oxygen with the surface carbon atom, giving volatile reaction products and the other one is the formation of oxygen functional groups at the PP surface through the interaction between the active species from the plasma and the surface atom.

FTIR analysis results for O₂ plasma treatment at different standoff distances are given in Fig. 3. Untreated surfaces spectrum is green line. Peaks in 3650-3300 cm⁻¹ region are -OH bonds. Between 1830 and 1580 cm⁻¹ region at 1738 cm⁻¹ peak is C=O bonds. Oxidized C-C bonds change to C-O and C=O bonds by the plasma treatment. Plasma treatment oxidizes thin surface layer. Depth of oxidation is 5-20 nm. Highest C-O bond peak appeared at 5 mm distance (blue line).

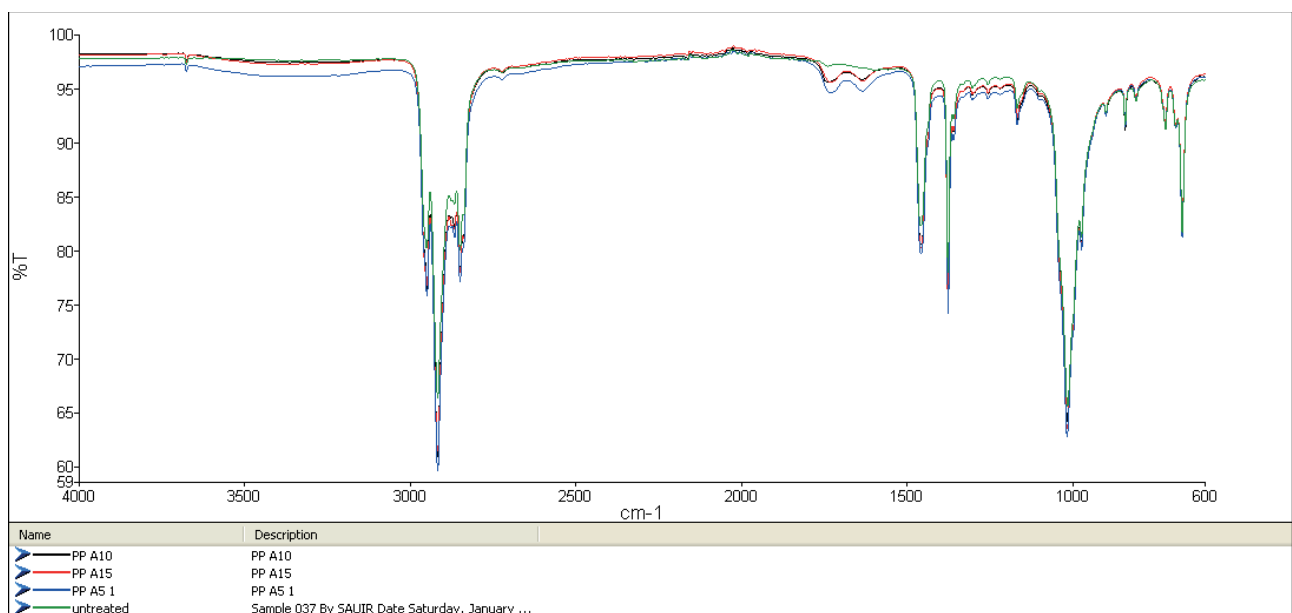


Fig. 2. FTIR analysis for N₂ Plasma activated PP surfaces at 5, 10 and 15 mm distances

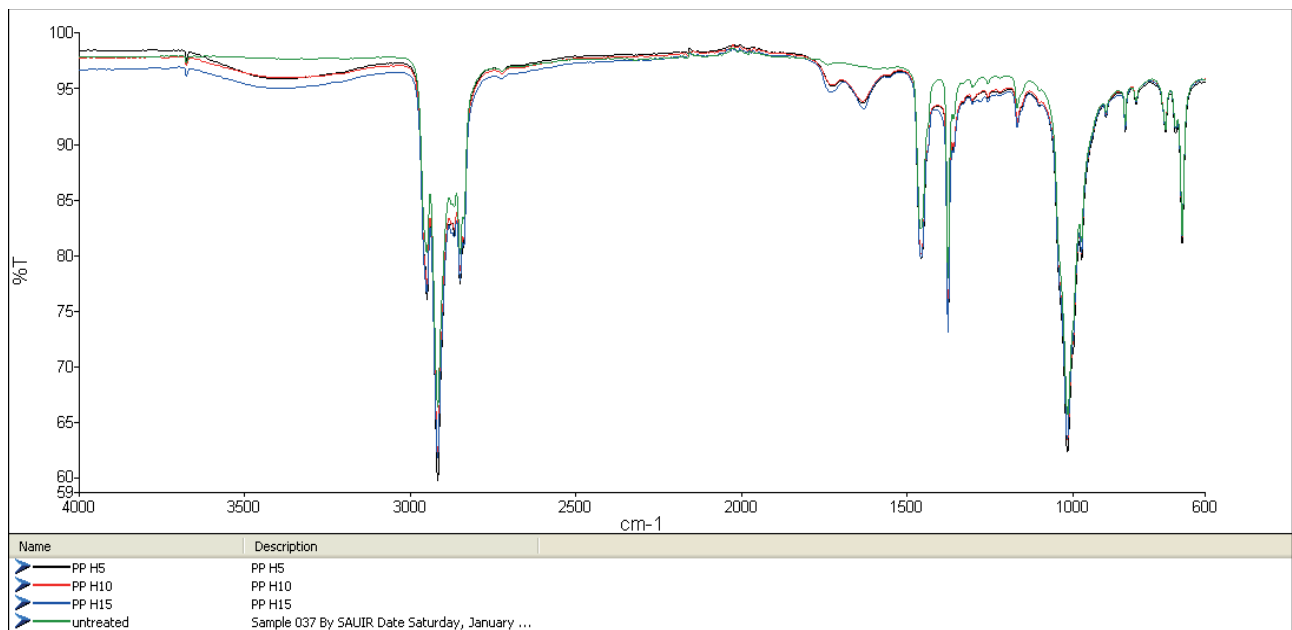


Fig. 3. FTIR analysis for O₂ Plasma activated PP surfaces at 5, 10 and 15 mm distances

4. Conclusions

Plasma activation has many advantages over traditional wet-chemical and physical activation procedures. Surface activation by plasma treatment is exceedingly fast, effective, economical, and environmentally friendly. When the plasma comes into contact with the PP surface it transfers the additional energy from the plasma to allow for subsequent reactions to take place on the material surface. The altered surface properties on most polymers. Plasma treatment of low-surface-energy polymers has been shown to increase the surface energy and improve the wetting characteristics. This wetting improvement leads to a concurrent, significant improvement in adhesion to these polymer surfaces, allowing bonding and painting characteristics. With oxygen or nitrogen added to the plasma activation process, polymers receive new surface functionalities. After plasma activation, high surface tension spread on the activated surface, showing very small contact angles. The changes in surface energy and the increases in adhesion are primarily due to the chemical changes at the surface induced by exposure to the plasma. The chemical interaction of oxygen based plasma systems also create strong covalent carbon-oxygen bonds which are of greater polarity than the initial carbon-hydrogen bonds. Surface energy is higher in the N₂ plasma than in the O₂ plasma at same process conditions. Surface energy was

increased from 28±2 mN/m to 63±2 mN/m by plasma treatment.

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