Innovative Food Science and Emerging Technologies 30 (2015) 119–126

Contents lists available at ScienceDirect

Innovative Food Science and Emerging Technologies

journal homepage: www.elsevier.com/locate/ifset

Effect of mechanical, barrier and adhesion properties on oxygen plasma surface modified PP

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ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 30 March 2015
Accepted 18 May 2015
Available online 30 May 2015

Keywords:
Polypropylene
Oxygen plasma treatment
Contact angle
FTIR
AFM
XRD
Tensile strength
OTR
WVTR

ABSTRACT

In this work, the Polypropylene (PP) film was surface modified by Oxygen plasma treatment and the effect of mechanical, barrier and adhesion properties was studied. The PP film was plasma treated with various RF power settings of 7.2 W, 10.2 W and 29.6 W in various time intervals of 60 s, 120 s, 180 s, 240 s and 300 s. To characterize the wettability, the contact angle was measured and the surface energy values were estimated with different test liquids. The generation of oxygen functional groups on the surface of plasma modified PP and the surface change characterization were observed by attenuated total reflection-Fourier transform infrared spectroscope (ATR-FTIR) and they resulted in wettability improvement. The roughness of the PP film and the surface morphology were analyzed by Atomic Force Microscopy (AFM). It was found that the roughness value increased from 1.491 nm to 7.26 nm because of the increase of treatment time and RF power. The PP crystallinity structure of the untreated and treated PP was evaluated by X-ray diffraction analysis (XRD). The bond strength of the untreated and surface modified films were measured by T-peel test method. For the untreated and oxygen plasma treated sample, the mechanical properties like Tensile Strength and the barrier properties like oxygen transmission rate (OTR), Water vapor transmission rate (WVTR) were also calculated. From the results, the tensile strength reduced from 6 MPa to 1.350 MPa because of polypropylene etching and degradation. The OTR increased from 1851.2 to 2248.92 cc/m^2/24 h and the Water vapor transmission rate increased from 9.6 to 14.24 g/m^2/24 h.
Industrial Relevance: Plasma technology applied to packaging and printing industry is a dry, environmentally- and worker-friendly method to achieve surface alteration without modifying the bulk properties of different materials. In particular, atmospheric non-thermal plasmas are suited because most are heat sensitive polymers and applicable in continuous process. In the last years plasma technology has become a very active, high growth research field, assuming a great importance among all available material surface modifications in packaging industry.

1. Introduction

Polymers like PE, PP, PS and PET are the mostly used packaging materials because these are available in large quantities at low costs (Pankaj et al., 2013). In industry, PP films are used in many packaging applications. It has good mechanical, physical, barrier and chemical resistance properties. These polymers are having low surface energy and therefore it have poor adhesive properties (Shin et al., 2002). For a particular application, if the polymer surface does not have the desired properties, it leads to material failure and the system or device containing it (Hoffman, 1995). For good adhesion between polymer and coating the polymer surface must be activated (Vesel & Mozetic, 2012). This can be done by the plasma treatment. By this technique, the surface properties of the polymers can be modified without affecting the bulk properties. The lack of adhesion can be owed without surface modification (Shin et al., 2002). For modifying the surface properties of polymers, a number of techniques have been developed such as mechanical, thermal, chemical and plasma treatments. For packaging, the use of plasma treatment seems to be suitable and to attain important change in the properties governed by surface characteristics (Wei, Gao, Hou, & Wang, 2005). The plasma refers to a partly or entirely ionized gas that consisted essentially of ions, photons and free electrons. The atoms in the excited or fundamental states are holding a net neutral charge (Liu, Cui, Brown, & Meenan, 2005). To attain the surface modification characteristics of polymeric materials, the effective technology is the plasma treatment (Cireli, Kutlu, & Mutlu, 2007). The surface phenomena such as crosslinking, etching and activation are done by the interactions between surface molecules of polymers and plasma (Riccardi et al., 2003). Over the conventional process, these plasma treatments offer many benefits because these are normally a dry process and they cannot generate chemical waste (Yang, Chen, Guo, & Zhang, 2009). Dependent on the conditions and the plasma species, the polymer surface properties such as hydrophobicity, morphology and the adhesion can be altered (Kauling et al., 2009). They can give impact on the barrier, mechanical and adhesion properties of the polymers. The reactive

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http://dx.doi.org/10.1016/j.ifset.2015.05.007
1466-8564/

functional group and the surface roughness can be introduced and also improved in the polymer surface by the plasma (Kirk et al., 2010). By this the mechanical performance and the adhesion property can also be improved. This was done due to the mechanical interlocking mechanism and also by the chemical interaction (Shin et al., 2002).

In this present study, the surface of the polypropylene was modified by RF oxygen plasma. This oxygen plasma promoted the surface modification by surface activation and slight etching. The contact angle and the polypropylene surface morphology were analyzed by goniometer and AFM. The surface energy studies were carried out and the bonding strength was also calculated. The mechanical and the barrier properties of untreated and the oxygen plasma treated polypropylene samples were carried out and the influence of surface modification on these properties was analyzed.

2. Materials and methods

2.1. Materials

In this study, the commercial polypropylene film was used and it was purchased from Jayanthi Plastics, Erode, India. It has the thickness of 0.048 ± 003 mm and density of 0.92 g/cm^3. Double distilled water and Formamide were used for contact angle measurements as test liquids. Ethanol and acetone were obtained from Sigma Aldrich, India.

2.2. Preparation of sample

For oxygen plasma treatment the samples were prepared in the dimension of 20 × 20 cm. The samples were cut into various dimensions for different studies. The films were washed with ethanol and then with acetone and they were kept dried under vacuum for 24 h.

2.3. Oxygen plasma treatment

The Harrick plasma equipment was used to carry out the oxygen plasma treatment. In this equipment, the principle is under suitable low pressure when a gas is passed, it is imperiled to a high frequency oscillating magnetic field and with the gas molecules the accelerated ions in the gas strike with them and ionizing them resulting in forming plasma. In the reaction chamber, the sample should be placed. At a pressure of 200–600 mtorr and the flow rates of 5–10 SCFH the gas was processed. Within the chamber, the plasma was created at RF electromagnetic radiation at 8–12 MHz near the ambient temperature. The minimum pump speed of vacuum pump is 1.4 m^3/h and the minimum total pressure is 200 mtorr. It was functioned at RF power settings of low, medium and high with 7.2 W, 10.2 W, 29.6 W.

2.4. Contact angle measurements and surface energy estimation

The static contact angle measurements were carried out at room temperature (23 ± 2 °C) by sessile drop method on a KSV CAM 200 goniometer (KSV Instruments, Helsinki, Finland) equipped with the DIGIDROP Image analysis software. The samples were dried in a vacuum oven for 24 h at 50 °C before the measurement. The test liquids were double distilled water and formamide. 10 μL of MilliQ grade water drop and formamide were placed with a micro syringe on the sample and the contact angle was measured within 5 s. At six different locations, the contact angle measurements were obtained and the average values on each polymer film were calculated and the experimental uncertainty was within ±1°.

From the contact angle values the surface energy was estimated. To calculate the surface energy of the untreated and oxygen plasma treated PP film, the test liquids water and the formamide with known dispersive component γ^d and the polar component γ^p were used and they were represented in Table 1.

Table 1
Polar, dispersion and surface energy of test liquids.

Liquid	γ_l^d (mJ/m^2)	γ_l^p (mJ/m^2)	γ_1 (mJ/m^2)
Distilled water	21.7	51.0	72.7
Formamide	39.5	18.6	58.1

By the Fowkes equation, the polar and dispersive components of the surface energy of the film surface were calculated.

$$\gamma_1(1+\cos\theta) = 2\left(\gamma_1^d\gamma_s^d\right)^{1/2} + 2\left(\gamma_1^p\gamma_s^p\right)^{1/2} \quad (1)$$

In Eq. (1), θ is the measured contact angle of the liquid with the solid surface, γ_1 is the surface tension of the liquid, γ_l^d and γ_l^p are the polar and dispersive components of test liquids. The total surface tension of the liquids γ_1 and their polar and dispersion components were summarized in Table 1. Finally, the total surface energy γ_s was estimated by the following Eq. (2)

$$\gamma_{s=}\gamma_s^p + \gamma_s^d \quad (2)$$

2.5. Surface morphology analysis

By using the non-contact mode of AFM, a Dualscope–Rasterscope C26 (Denmark) was used to analyze the morphology and the surface roughness of the untreated and oxygen plasma treated polypropylene film in an ambient atmosphere at room temperature. For sample imaging, the tapping mode was used and the scanning range was 5 μm × 5 μm. The silicon tip probes were used with a spring constant of 20–80 N/m. The resonance frequencies were in the range of 250–300 kHz and the Nanoscope image processing software was used to analyze the images.

2.6. Surface chemical composition analysis

To obtain the surface chemical changes made by the oxygen plasma treatment on the untreated and oxygen treated polypropylene films were performed on total reflection – Fourier transform infrared spectroscope (Perkin-Elmer SL, Spain). The spectra were investigated in the wavenumber range of 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1} with 16 scans.

2.7. X-ray diffraction analysis

Wide angle X-ray diffraction was obtained using Bruker AXS D8 advance X-ray diffractometer utilizing nickel filtered CuKα radiation having the wavelength of 1.54056 Å. The current and the voltage were 40 mA and 40 kV. The countings were carried out at 10 steps per degree.

2.8. Bonding strength analysis

The standard T-peel test method of ASTM D 1876-72 was used to analyze the bonding strength of the untreated and the plasma treated PP samples. In this, the commercially available adhesive tape was used. The test was carried out at room temperature by Universal Testing Machine (UTM, H10KS, Tinius Olsen, UK) machine at a rate of 10 mm/min. The adhesive tape was pasted over a length of 15 cm with a width of 5 cm. The test was carried out by fixing the sample in one of the holder and the tape in turn adhered to the piece of paper is fixed in another holder. The peel strength was carried for three specimens for every treatment time and the mean value was calculated.