STUDY OF THE HELIUM PLASMA-POLYPROPYLENE INTERACTIONS. EFFECT ON THE STABILITY OF THE WETTABILITY, ADHESION AND MECHANICAL PROPERTIES OF THE POLYMER

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ABSTRACT

The purpose of this work was to minimize the ageing phenomenon observed on a NH_3 treated polypropylene (PP), by stabilizing the surface layer via crosslinking using an inert gas discharge. The stability of the wettability, adhesion and mechanical properties of treated PP is investigated by a comparative study of two different plasma treatments (i.e. a NH_3 plasma and a He plasma pretreatment carried out before the NH_3 plasma). Results of aluminium/polypropylene (Al-PP) interface analyses by Auger spectroscopy are presented.

1. INTRODUCTION

Polyolefins are a class of polymers which possess inert surfaces and this greatly limits their range of applications. Plasma polymer interactions have been actively studied because of their unique ability to modify the polymer surface properties without affecting their bulk properties [1, 2]. However, it is well known that the surface modification efficiency introduced by the plasma treatment decays with time, which is very important from the view point of industrial applications such as adhesion. The contact angle measurement of a drop of liquid deposited on the plasma treated surface is a well suited method to study such reorganization. However, as we know, the plasma treatment can induce the surface crosslinking of the polymers [3, 4]. In this contribution, we report how the helium plasma pretreatment (He plasma is well known to crosslink polymer surfaces [5]) stabilizes the cohesive and mechanical properties of polymers. The role of the two plasma treatments (i.e. a NH_3 plasma and a He plasma pretreatment carried out before the NH_3 plasma) to strengthen the topmost layers at the surface has been thus evidenced thanks to the elongation at break measurements as well as the tensile strength. We demonstrated that the elongation properties of He treated PP remained relatively unchanged with treatment time (this phenomenon was not observed in the case of a NH_3 treated PP). Finally, Auger Electron Spectroscopy (AES) was used to identify chemicals bond at the Al-PP interface and to reveal the behaviour of the aluminium thin film with respect to the plasma modified layer of the polymer film.

2. EXPERIMENTAL

The bell jar-type reactor used for the treatment and the in-situ metallization of polypropylene films had an asymmetrical configuration of electrodes consisting of a high voltage hollow electrode-grounded cylinder (diameter = 0.07 m) and has been described elsewhere [6]. The operating pressure was maintained at 100 Pa by a 2012 AC chemical pump. The industrial 800 W excitation source had a frequency of 70 kHz. Typical powers of 5 - 50 W and total flow rate of 100 sccm were maintained during the experiments.

Auger electron spectroscopy (AES) was performed from nonderivative spectra collected in the EN (E) mode. They were quantitatively exploited by the use of the peak to background ratio (P/B), hereafter referred to as Auger ratio. For the Auger sputter profiling (ASP), a low energy ion gun (Electrostatic Reflex Ion Source; ERIS) has been developed in order to reduce the knock-on spreading effect; it delivered a 100 eV-50 mA Ar^+ ion beam in a 7 mm diameter spot [7, 8].

3. RESULTS AND DISCUSSION

3.1. Role of the helium pretreatment on the stability of the wettability

The surface properties of the treated polypropylene films were obtained from measurement of the advancing contact angle (sessile drop) of bidistilled water droplets using an image processing system. In the case of a NH_3 plasma treated PP, the variation in the advancing contact angle with ageing time depicts an increase of about 40 % between a freshly treated PP and an aged sample, and a plateau is obtained after 10 days (figure 1).

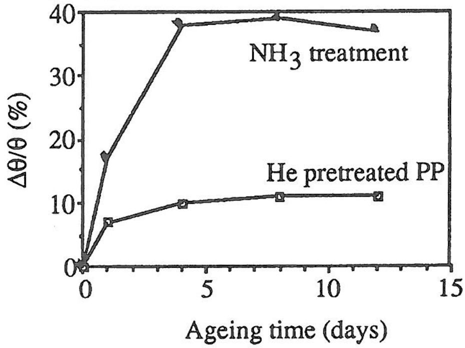


Figure 1:

Variation in the advancing contact angle with ageing time in function of the treatment gas.

NH_3 treatment: (P_w = 50 W; P = 100 Pa; gas flow = 100 sccm; t = 1 s)

He pretreatment: P_w = 5 W; P = 100 Pa; gas flow = 100 sccm; t = 30 s)

These results show that there is an evolution in the chemical composition of the PP surface since the surface characteristics shift from hydrophilic to hydrophobic. With an additional helium pretreatment carried out before the ammonia treatment, the surface energy remained relatively unchanged, and the contact angle of water in figure 1, increased very slowly in 4 days (less than 10 %), and then remained constant for longer periods. Such a difference can be explained by the lower mobility of the surface polar groups after the He plasma pretreatment has crosslinked the polymeric surface i.e. the mobility of the polymer segments at the surface depends on its crosslink density. Moreover, the low molecular weight (LMW) fragments may be formed not only on the surface but deeper in the polymer, by vaccuum ultraviolet radiation from the plasma. These LMW fragments can migrate to the surface and reduce in this way the wettability. The diffusion will be prohibited by the He crosslinked layer.

3.2. Adhesion measurement

The apparatus and the experimental conditions which allowed to peel the aluminium film have been described elsewhere [6]. The bar graph presented in Fig.2 displays, for both treatments, the same optimum treatment time (t = 1 s), above which the adhesion starts to decline.

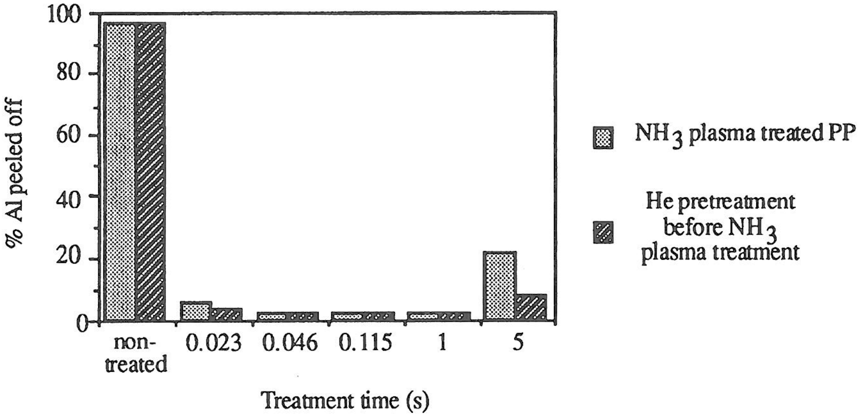


Figure 2: Evolution of the amount of aluminium peeled off as a function of the NH3 plasma treatment time: role of the He pretreatment on the stability of the adhesion properties.

In the case of an overtreated PP by a NH3 plasma (t = 5s), the degradation of adhesion occured since the Al removed on peeling increased from 2-3 % (for t = 1s) to 20-25 % (for t = 5 s). The LMW material formed due to the scission of the polymer forms a weak boundary layer (WBL) that leads to a degradation of the adhesion properties of the plasma treated PP. This WBL is probably composed of small molecular weight fragments on the surface.

With a 30 s helium plasma pretreatment,the percentage of aluminium peeled off increased much slowlier as it increased from 2-3 % to only 8-10 %. As the polymeric surface is now crosslinked, the scission effect due to a plasma overtreatment (t = 5 s) is considerably less, limiting in this way the formation of a weak boundary layer responsible for the adhesion degradation of Al-PP. Mass spectrometric analysis of the effluent gases during He pretreatment of polypropylene showed that only hydrogen was generated; very few gaseous hydrocarbons were detected. This result is consistent with the fact that the surface of the polymer is crosslinked during the He pretreatment, since the active sites are created on the surface by a dehydrogenation process.

3.2. Mechanical properties:

The mechanical properties of treated nonmetallized polymers in NH3- and He- plasmas were studied. The samples were stretched in air at room temperature, until the fracture occured. In a recent paper [9], we have confirmed by the measure of the tensile strength, that the plasma treatment induced only small changes in the bulk properties, since the stress-strain behaviour of the polymer was not modified. The initial modulus, for example, showed no significant variation from untreated polypropylene, and was the same for the different plasma treatments. Fig.3 shows the stress-strain characteristics of polypropylene treated by different plasma gases.

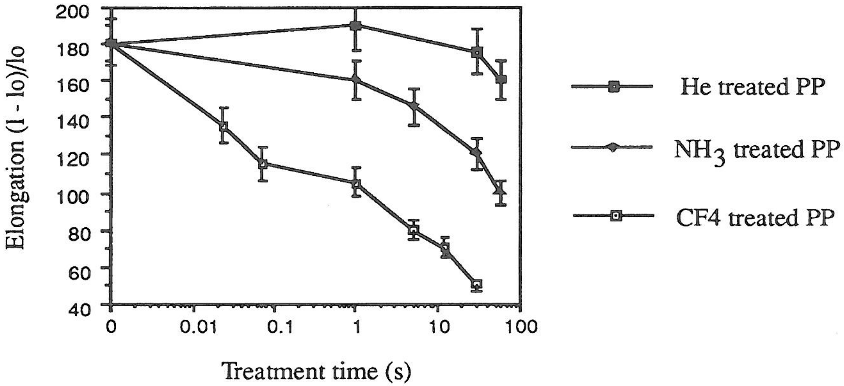
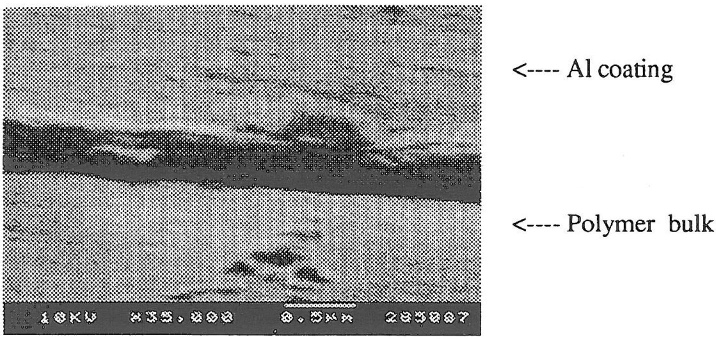


Figure 3: The effect of He, NH_3 and CF_4 plasma on the stress-strain behavior of polypropylene films.

In the case of a NH_3 treated PP, the elongation at break decreases from 180 % to 160 % for the first treatment time (t = 1s), and reaches 145 % for an overtreated sample (t = 5s). Nevertheless, the elongation properties of helium treated PP remain relatively unchanged with treatment time, which supports the hypothesis of a cohesive strengthening of the polymeric surface by the formation of a thin crosslinked layer.
Now, if one compares a CF_4 plasma which is widely used for the fluorination and etching of polymers, with the treatments mentioned above, the alteration of the mechanical properties of polypropylene are more pronounced ; this may be ascribed to the diffusion of fluorine through the surface layer, as detected by RBS [10]. The CF_4 plasma caused a loss of tensile strength at the break point. In this case, the fracture path of a metallized CF_4 treated PP, started by crack extension at the weakest point, i. e. at the fragmented surface, and propagated perpendicularly in the polymer bulk , as revealed by SEM analyses (penetration depth is around 0.3 μm)(picture 1).



Picture 1: SEM analysis of a peeled metallized-CF_4 overtreated PP
(Experimental conditions: Pw = 20 W; P = 100 Pa; t = 5 s)

3.3. Study of the Al-PP interface

Auger profiles of the metallized polypropylene films have been studied in detail [6]. In this paper, we have analyzed the interface region in the case of the two differently treated PP films. Fig. 4 shows the peak to background ratio (P/B) of Al_{ox} LVV (52 eV), Al_{met} LVV (63.5 eV), O_{KLL} (503 eV) and C_{KLL} (263 eV) in depth profiling versus Ar^+ sputter dose for both treatments. In both cases the oxygen and the Al_{ox} signals increase as we get close to the polymer surface due to the oxidized interface.

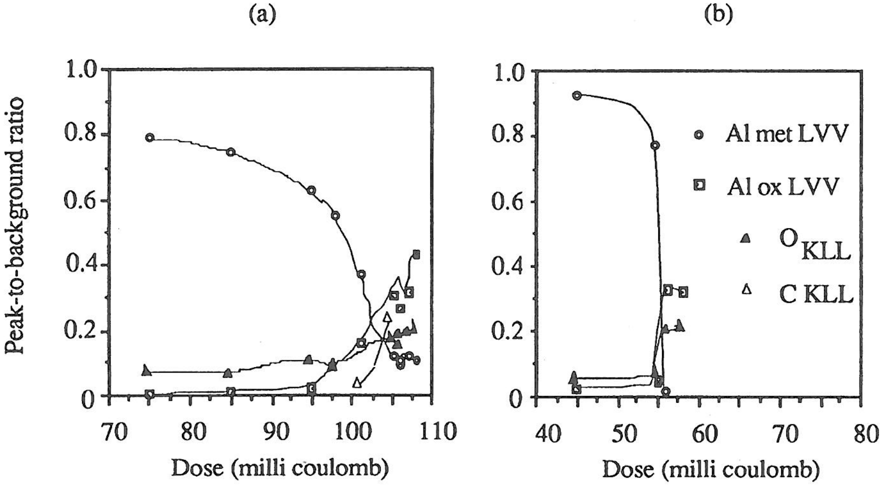


Figure 4: Auger analyses of the Al-PP interface.
(a): NH_3 treated PP ; (b): He pretreatment before NH_3 plasma treatment

In the case of an ammonia plasma treatment with a helium pretreatment (fig. 4.b), AES shows a sharp interface whereas without a He treatment, the interface is broad (fig. 4.a) . In the case of the former, a drastic decrease of the Al_{met} peak ratio is observed as soon as we get into the polymer, for a slight increase of the ion dose near the interface (2 mc). In the vicinity of the polymer substrate, charge effects appear which prevent measurement of the carbon : we reach an aluminium free insulating zone. No intermixing of Al with carbon has been observed in the reinforced polymer film. In this case, interfacial slippage does not occur as expected for sharp interfaces, since the intermolecular forces lead to a mechanically strong interface.
On the contrary, in the case of the NH_3 treated PP, a broader interface is observed over a wide range of ion dose, showing in this way the intermixing of Al with the overtreated NH_3 polymer. The presence of Al through the interface allows to measure carbon. This intermixing of Al in the polymeric zone is not sufficient to achieve good adhesion since the interface is mechanically weak.
If we look at the trend of the Al/CF_4 plasma treated-PP interface (figure 5), we obtain a very large interface with a considerable diffusion of Al in the fragmented polymeric zone. In this case, the polypropylene undergoes degradation. This could explain the adhesion test results of Al-PP system [9], since the mode of failure was cohesive in the PP film (photo 1) and contributed to a poor Al/PP adhesion.

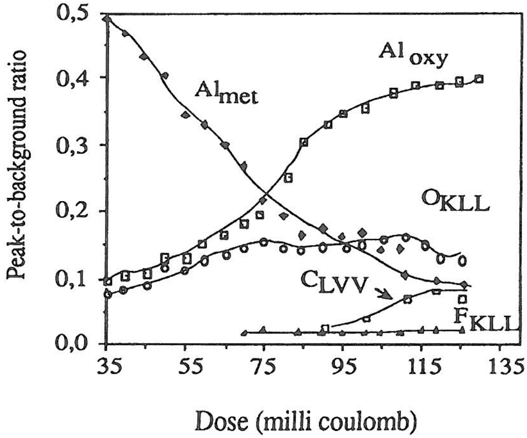


Figure 5:

Auger analyses of the Al-PP interface.

CF_4 treatment of PP (Pw = 20 W; P = 100 Pa; t = 5 s)

4. CONCLUSION

The study of the ageing phenomenon of polypropylene treated in NH_3 plasma showed a change in the surface properties with time, leading to a decrease of the wettability and degradation of the adhesion properties with respect to aluminium. That is why an additional He plasma pretreatment was carried out before NH_3 treatment. For such treated samples, the surface energy remained almost stable. This was explained by a more crosslinked surface induced by the short wavelength photons and the He metastable species. Moreover, in such treated samples, AES showed sharp interfaces revealing no intermixing of Al with the crosslinked surface of the polymer substrate. Even though in all plasma gases there is a competition between the crosslinking process and degradation, it has been pointed out that the He plasma is well adapted to mechanically stabilize the surface and therefore to limit ageing of the surface properties.

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