

PLASMA TREATMENTS OF POLYMERS FOR REDUCING AGEING

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Abstract

Water contact angle and electron spectroscopy for chemical analysis measurements have been utilized to understand the effects of different plasma treatments (O₂, NH₃) and pre-treatments (H₂) on the hydrophobic recovery of conventional polymers, with the aim of limiting their ageing. Our results are expressed according to a model developed by Chatelier *et al.* [1-3], in terms of fractions of the various classes of grafted groups onto the polymer surface: *mobile polar groups*, *immobile polar groups*, and *apolar groups*.

Introduction

Grafting chemical groups and/or crosslinking by means of plasma treatments can deeply change the chemical characteristics and surface energy of polymers at high rate and throughputs, in a very wide range. Mostly plasma treatments are utilized to "activate" the surface of a polymer to optimize its interaction with other materials, molecules, or biological systems. Polar groups (*e.g.*, -NH₂, -OH, etc.) can be conveniently grafted, for example, to increase the wettability of conventional polymers in biomedical applications or, in food packaging, to improve the adhesion of evaporated/sputtered Al layers at the surface of polyester films. An important issue in this context, often crucial for industrial applications, is the *ageing* of plasma treated surfaces. In fact, when polar groups are covalently bound to the surface chains of a hydrophobic polymer (down to 0-20 Å from the interface), a dynamic polymer/air interface is created, which experiences, at different extents, the *hydrophobic recovery* of the original moieties of the polymer at its surface. In the case of treated polymers stored in air, in fact, rotational and translational motions, when permitted, allow the original hydrophobic moieties of the polymer to emerge at the interface to minimize the interfacial energy, while polar groups are moved immediately below. As a consequence, the Water Contact Angle (WCA) value increases back toward the original value of the untreated polymer. Starting from Cassie equation [4], Chatelier *et al.* [1-3] derived a time-dependent model to describe these surface restructuring processes in polymers in terms of the fractions of mobile and immobile polar grafted groups, and of apolar surface groups, based on measurements of WCA trends as a function of time. The fractions of different groups can be calculated by fitting the equilibrium WCA data with an iterative procedure, assuming an exponential decay for the fraction of mobile grafted polar groups. We have used this model to evaluate the capability of different plasma treatments and pre-treatments to reduce the *hydrophobic recovery* of plasma-treated polymers.

Experimental

Plasma treatments were carried out in a parallel plate tubular pyrex reactor, with the upper electrode connected to the RF (13.56 MHz) generator and the lower one (sample holder) grounded. The treatments were carried out on polyethyleneterephthalate (PET), and polytetrafluoroethylene (PTFE), two polymers of high industrial relevance, with O₂ or NH₃ gas feeds. H₂ plasma pre-treatments, aimed to limit the hydrophobic recovery of the polymers, have been also investigated. The process parameters are summarized in Table I.

Plasma treated polymer samples were stored in air. Advancing and receding WCA values were measured at room temperature with a contact angle goniometer (Ramé-Hart, model 100-00) using the sessile drop method [5], and were utilized to calculate the equilibrium WCA values [1-3]. Such WCA values were plotted as a function of the ageing time, and best-fitted with the mathematical model. Figure 1 show these trends for NH₃ and O₂ plasma-treated PET.

Table I: Process Conditions

	Treatment	Pre-treatment
Gas feed	NH ₃ , O ₂	H ₂
RF Power	100 W (PET); 100 and 20 W (PTFE)	40 W
Pressure	200 mtorr	200 mtorr
Flow Rate	10 sccm	10 sccm
Time	1 min	1 min

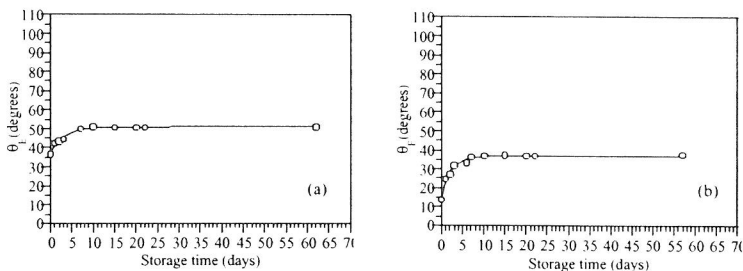


Fig.1 Best fit of the equilibrium WCA as a function of storage time for (a) NH₃ and (b) O₂ plasma treated PET.

It can be seen that, soon after the modification, O₂ plasma treatments of PET lead to lower WCA values respect to NH₃. Further, O₂ treatments, in our conditions (see Table I; 1 min of treatment) result in more hydrophilic, stable PET surfaces respect to NH₃, after more than 50 days of ageing. It must be said, however, that treatment time plays probably a mayor role in distinguishing NH₃ from O₂ treatments. NH₃ treatments at very short times (ms), for example, revealed to be much more effective than O₂ ones in grafting suitable Lewis basic groups at the surface of PET [6] for improving the adhesion of sputtered Al layers.

Surface restructuring parameters have been calculated and it has been found that the fraction of polar immobile grafted groups onto PET is almost double in the case of O₂ plasma treatments (about 60% of grafted groups), which result in more hydrophilic stable surfaces. In the case of PTFE, O₂ plasma treatments performed in our conditions are not effective at all

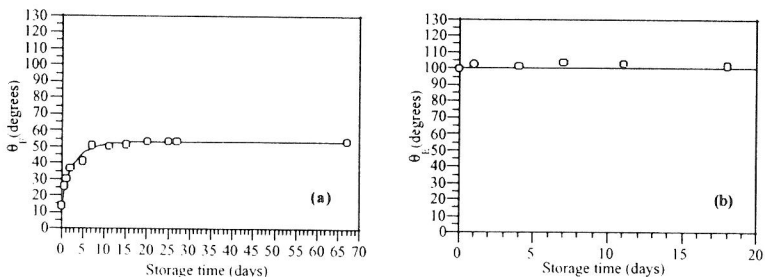


Fig.2 Best fits of the equilibrium WCA as a function of storage time for (a) NH₃ and (b) O₂ plasma treated PTFE.

in conferring a good hydrophilic character, as shown in Figure 2 (b); stable hydrophilic PTFE surfaces, instead, are obtained after NH₃ plasma treatments, characterized by about 70% of grafted immobile polar groups. This difference is probably due to the presence of H atoms in the ammonia plasma; H atoms can, in fact, abstract F atoms from PTFE and graft on its surface, thus activating it toward the grafting of N-containing polar species.

H₂ plasma pre treatments in different conditions have been carried on PET and PTFE before O₂ and NH₃ treatments, in order to check their capability in limiting the ageing of the treated surfaces. H₂ plasmas should be effective for this task also due to their efficacy in cross linking polymer materials by means of UV radiations, that would result in an additional reduced rate of the chain/group restructuring motions at the polymer/air interface.

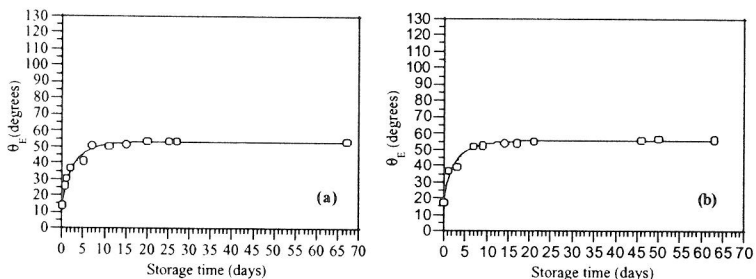


Fig. 3 Best fits of water contact angles as a function of storage time, for NH₃ plasma (100 Watt) treated PTFE surface, without (a) and with (b), H₂ plasma pre-treatment.

Observing figure 3 it can be deduced that hydrogen pre-treatment of PTFE surface has no effect on its ageing. In this case, the effectiveness of the pre-treatment has been verified by XPS measurements of fluorine atomic concentration, which is much lower than the one of the untreated polymer.

Probably the ammonia treatment is too energetic and this hides changes induced on sample surface by hydrogen pre-treatment, leading to the same results in both of the experiments discussed.

In order to demonstrate the last hypothesis, experiments have been repeated at a lower RF power input of ammonia plasma.

Here we report the results obtained at 20 Watt, keeping all the other process parameters as the previous one.

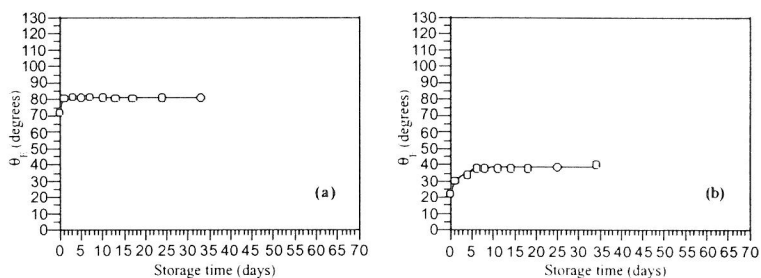


Fig. 4 Best fits of water contact angles as a function of storage time, for NH_3 plasma (20 Watt) treated PTFE surface, without (a) and with (b), H_2 plasma pre-treatment.

In this case it is evident how a milder ammonia plasma treatment, together with hydrogen pre-treatment, makes the water contact angle value, at zero storage time, fall down to about twenty degrees. Moreover surface restructuring, in experiment 4(b), is slow quite enough to have a final water contact angle value of only 45° , much lower than 115° typical of untreated PTFE.

These findings allow us to conclude that low power NH_3 treatments, preceded by H_2 pre-treatments, are very effective for producing stable and hydrophobic surfaces onto PTFE.

Conclusions

A mathematical model describing the phenomenon of the *hydrophobic recovery* of plasma treated polymers has been utilized for a quantitative evaluation of the capability of O_2 and NH_3 plasma treatments, and of H_2 plasma pre treatments, in obtaining stable wettable polymer surfaces with limited ageing and long shelf life.

For PET it has been demonstrated that O_2 treatments are very effective while, in the case of PTFE, O_2 fails in producing significant effects and ammonia treatment permits to decrease hydrophobicity.

In particular, for this polymer, excellent results have been reached by combining hydrogen plasma pre-treatment with ammonia treatment at low RF power input (20W).

References

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