STUDY OF THE EFFECT OF AN AMMONIA OR OXYGEN PLASMAS ON THE PHYSICOCHEMICAL MODIFICATIONS OF PP SURFACES

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Abstract

The physicochemical properties of NH_3 and O_2 treated polypropylene (PP) surfaces were studied using different analytical techniques. The acid-base properties of surfaces were characterized using contact angle titration method and XPS in conjunction with Lewis acidic (chloroform) and basic (dimethylsulfoxide) probes. The effect of treatment time of these two plasma atmospheres on the fragmentation of the polymeric chains at the surfaces were analyzed and discussed.

I- Intoduction

The intermolecular interactions have been classified for a long time as "polar" or "non polar" as a result of the remarkable achievements in the understanding of the nature of the attractive forces in gases. Afterwards, it became customery to discuss the dipole-dipole interactions and dipole- induced dipole interactions for molecules in condensed phases[1]. In the modern theory of acid-base interactions Fowkes and coworkers have shown that in liquid and solid states there is no evidence for any measurable dipole interaction energies of cohesion and adhesion[1]. Instead, the importance of acid-base interactions between the so-called "polar" groups is now well recognised and it was concluded that dipole-dipole interactions, in those cases, are negligibly small compared to acid-base and dispersive force interactions. However, to validate this concept it is necessary to characterise such properties by adequate techniques and methods[2]. The purpose of this work is to characterise and compare the physicochemical properties of O_2 or NH_3 treated PP surfaces. For this, different techniques having different degrees of surface sensivity were used.The acid-base properties of the treated surfaces were especially characterized by the contact angle titration method and XPS in conjunction with molecular probe technique.Capillary Electrophoresis Ion Analysis permits us to identify the exisiting ionic organic species on the treated surfaces. ATR-IR and SSIMS were used as complementary surface diagnostic techniques.

II- Plasmas treatments

A low pressure plasma reactor with non symmetrical configuration of electrodes (High Voltage hollow electrode-earthed cylinder) was used in this study[3]. The discharge was established with the help of 70 kHz excitation source. Gases were introduced through MKS mass flow controllers and the pressure was monitored with an MKS capacitive gauge.Two types of plasma atmospheres were chosen for the treatment, namely O_2 as an oxidizing gas and NH_3 as a reducing one.

III- Characterization of the acid-base properties of treated surfaces

III-1. Contact angle titration method

This method employs the classical contact angle technique , but instead of pure water, aqueous acidic and basic solutions with pH values ranging from 1 to 14 are used[4,5]. From these measurements , the work of adhesion is defined as a function of pH and the shape of the curve shows the acidic or basic property of the treated surfaces [4]:

$$W_{sl}=\gamma_l\ (1+\cos\theta) \qquad (1)$$

III-2. X-Ray Photoelectron Spectroscopy

XPS permits to determine the acid-base properties of polymers by monitoring the concentration and the chemical shifts experienced by a lewis acid or base sorbed in the host polymer [6].The detection of a residual amount of solute shows the formation of polymer-solute acid-base interactions. In this work, we make use of chloroform to characterize the basicity of polymers and dimethyl sulfoxide (DMSO) for the very first time as a molecular probe to investigate the surface acidity of oxygen plasma treated PP [3,7]. Cl2p and S2p are the target core hole of which the relative intensity and chemical shift will be related to the surface treatment.

IV. Capillary Electrophoresis Ion Analysis (CIA) of the soluble low molecular fragments.

This technique permits to analyze small ionic species. Separations are performed by applying an electrical field to the sample in a capillary filled with an electrolyte. The droplets of very pure water (V=20µl, pH=5) deposited on the surfaces were analyzed by CIA. Since the application of this technique to surface treatment is very recent, the main problem is the identification of ionic species which vary with the nature of the plasma gas and the surface to study.

V- Complementary Analysis

ATR-IR spectroscopy and ToF-SIMS (Time-of flight ion mass spectrometry) on a Charles Evans & Associates equipment [8], were carried out on the untreated and treated surfaces.

VI-Results and discussion

The contact angle of unbuffered aqueous solutions at the surface were measured immediately after treatments. Fig. 1a &1b show the variation of the total work of adhesion as a function of pH, of NH_3 and O_2 treated PP for different treatment times[3]. Fig. 1a shows the acidic character of the O_2 treated PP surfaces. That is the total work of adhesion increases when one passes from acidic test liquids to basic ones. This difference is enhanced with treatment times due to an increase of the grafted acidic groups at the surfaces[3]. However, the same study carried out for PP films treated in a reducing atmosphere shows completely different results: for treatment times of the order of 0.7-1 s, the surface shows a basic character, i.e an increase of the total work of adhesion from basic test liquids to acidic ones. However, an amphoteric character revealed by the same total work of adhesion for the strongly basic and acidic aqueous solutions, has been observed for longer treatment times. The NH_3 plasma treatment leads to the chemical modification of the PP surface by grafting nitrogen and/or oxygen namely identified by an increase of N/C and O/C ratio around 12% and 5% respectively.

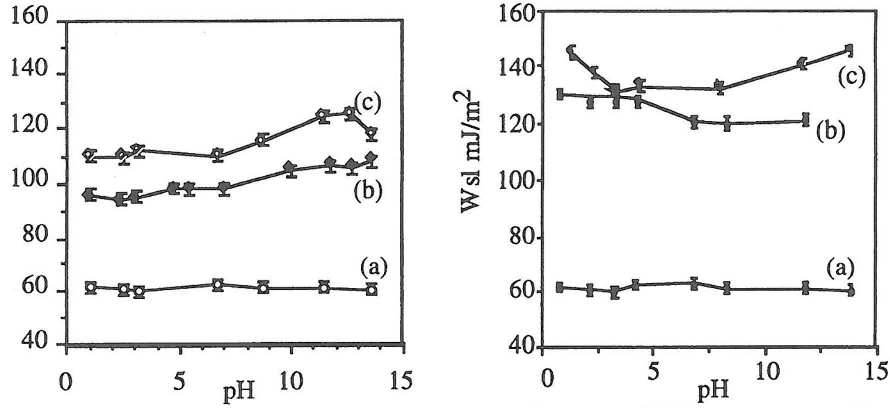


Figure 1a. Case of O_2 treatments: (a) untreatred PP; (b) t=1s; (c)t=30s.

Figure 1b. Case of NH_3 treatments: (a) untreated PP; (b) t=1 s; (c) t= 30s.

Figure1. Variation of the total work of adhesion with different test liquids for different treatment times.Treatment conditions: O_2 plasma: P=150-200 Pa; Q=100 sccm; P_W= 30 W. NH_3 plasma : P=150 Pa; Q= 150 sccm; P_W= 70 W.

These results were confirmed with XPS in conjunction with the molecular probe which is sensitive to all of the grafted functional groups over a thickness of 5 nm[7]. After the exposure of O_2 treated PP to DMSO (Lewis base) and NH_3 treated surfaces to chloroform (Lewis acid) vapours, samples were analyzed by XPS. The detection of S2p and Cl2p signals after treatments gives evidence on the formation of acid-base interactions between molecular probe and acidic or basic groups grafted after treatments. The molar ratio of DMSO and chloroform per polymer repeat unit (%S) is evaluated in Fig. 2a & 2b respectively. In the case of O_2 treated surfaces %S increases with treatment time and reaches its maximum value, i.e. 1.17% after 15 s [7]. On the contrary, in the case of NH_3 treated surfaces, for treatment times shorter than 1s, the %S has its upper value (5%) and then it decreases sharply (0.7s) for a treatment time equal to 30s[7]. These results parallel well those obtained from contact angle measurements, i.e. the reinforcement of acidic character of O_2 treated PP with treatment times and the disappearance of the basic character of NH_3 treated PP for long treatment times.

To have more information about the nature of soluble functional groups in water and the degradation effect of these different plasmas, the droplets of very pure water deposited on the surfaces were analyzed by CIA[9]. In each case the ionic species were identified with standard solutions of known conductivity (i.e. known migration times)[9]. Only anionic species were detected for both NH_3 and O_2 treated surfaces.

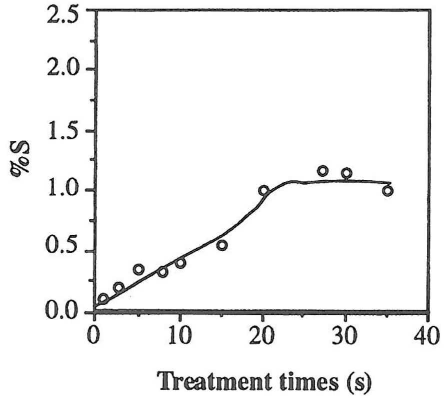


Figure 2a. Case of O_2 treatments : the DMSO to oxygen atom ratio (in %) vs treatment time.

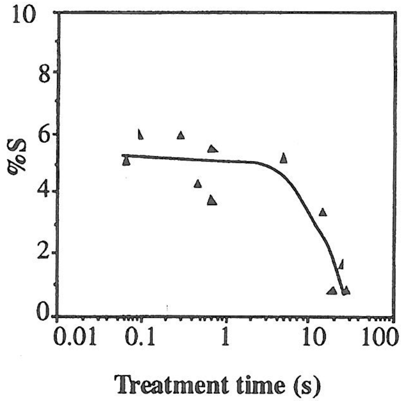
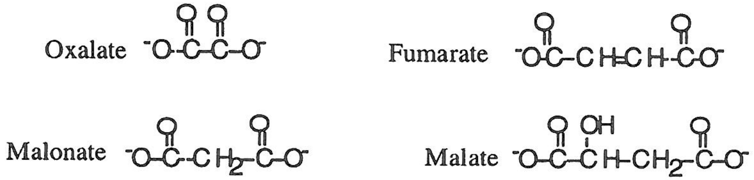


Figure 2b. Case of NH_3 treatments : the chloroform to nitrogen atom ratio (%S) vs treatment time.

The O_2 treated surfaces show the presence of oxalate, fumarate and malonate species, whereas, NH_3 treated films are rather enriched with malate and fumarate species. Their chemical structures are displayed in Fig 3.



Oxalate ${}^{-}O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O^{-}$

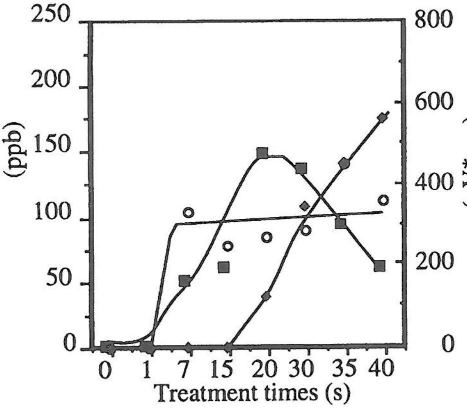
Fumarate ${}^{-}O-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-O^{-}$

Malonate ${}^{-}O-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O^{-}$

Malate ${}^{-}O-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-O^{-}$

Figure 3. Structure of organic acids present at the surface of PP treated films

It should be noted that in the case of NH_3 treated surfaces two peaks appear for short treatment times probably due to the presence of fumaric and malic acids. These peaks form a single broad one for longer treatment times due to their high concentration. The migration times of these two organic acids being very close, the deconvolution of the broad peak obtained for long treatment time is very difficult. Fig 5b. shows the evolution of these species with treatment times. Their concentration are in the order of ppm whereas in the case of O_2 treated PP the concentration of all of the present species (fumaric, oxalic and malonic) don't go beyond 300 ppb (Fig. 5a), i.e. 3 orders of magnitude lower than NH_3 treatments. It is well known that O_2 plasma brings about degradation leading to low molecular weight fragments and volatilization of the latter by decarboxylation, explaining the low concentration of polymeric fragments on the surface compared to an NH_3 treated one. Actually, these organic acids mentioned above are formed by oxidative cleavage of PP chains and it seems that for longer treatment times, in both cases, the surface is enriched with stable structures having conjugated double bonds, i.e. presence of fumarate on NH_3 treatments and oxalate and fumarate on O_2 plasma treatments. These results could explain the increase of the surface conductivity with treatment time [10]. Moreover, It seems that these structures could favor the formation of cyclic compounds in the case of O_2 treated surfaces [8]. One should note that for both treatments the organic acids are observed for a treatment time of 5 s which has shown to be an over treatment leading to the degradation of the adhesion properties of PP to aluminium layers [7].



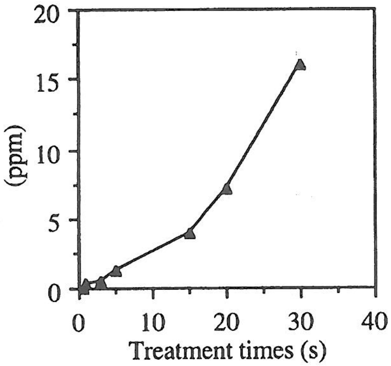


Figure 5a.Case of O_2 treated surfaces:
○ oxalate (ppb), ◇ fumarate (ppb),
■ malonate (uV*sec)

Figure 5b. Case of NH_3 treated surfaces: ▲ fumarate and malate

Figure 5. Variation of ionized organic acids at surfaces with plasma treatment times.

We have used ATR-IR to complement our study which probes a depth of about 10^3 nm. Adsorption at 1650 cm^{-1} due to the presence of amine, amide and ketones was detected in the case of the NH_3 treated surfaces. The spectra of O_2 treated PP show the presence of (carboxylic acids, esters) at 1715 cm^{-1} and aldehydes and ketones at 1640 cm^{-1} [9]. After washing surfaces with a basic solution (pH=13) in order to reveal the presence of organic acids, new peaks centered at 1520 and 1425 cm^{-1} appear [8] for both treatments. In fact the latter is almost totally due to $RCOO^-$, the signal of which appears at 1520 and 1425 cm^{-1} corresponding to the antisymmetrical and symmetrical vibrations af carboxylate anions respectively [9]. The intensity of these vibrational peaks increase with the O_2 plasma treatment time. These results confirm the acidic character of an O_2 plasma whileas in the case of the NH_3 treatment with increasing treatment time the $RCOO^-$ groups have not been detected when washed with basic solution. The latter could be due to the non accessibility of acidic groups either enlaced in a branched structure or eliminated by washing. One should however emphasize that these peaks have not been detected when washed with neutral or acid solutions.

Preliminary ToF-SIMS results were obtained on O_2 and NH_3 plasma modified PP samples as a function of treatment time (from 0.5 to 30 s)[11]. These results exhibit clear differences between both plasma treatments : the oxygen content (as measured by the O^-/CH^- ratio) is higher for the O_2 plasma treated samples. The normalized intensities (the total intensity minus $H^{+/-}$ and contaminants intensities) of oxygenated positive and negative ions are also higher. The other significative difference for the NH_3 plasma treated samples is the higher normalized intensities of ions that could be related to amine and amide compounds. The latter one is very interesting to be studied: it is totally absent for the O_2 plasma treatment samples but it is also the only one for which a significative variation is revealed as a function of treatment times for the NH_3 plasma treatment: there is a decrease for treatment times higher than 1 s. It could be related to the loss of the basic character of these samples for the same treatment times. No significative variation is revealed as a function of the treatment time for the O_2 plasma treated PP samples . Further comparison with similar studies as a function of the treatment time are needed in order to obtain more precise information from these ToF-SIMS results.

VII-Conclusion

The physicochemical properties of O_2 and NH_3 modified PP surfaces were compared in this paper. The acid-base properties of treated surfaces were characterized by contact angle measurements and XPS using acidic (chloroform) and basic (DMSO) probes. The adsorption of molecular probe at the surfaces were interpreted in terms of acid-base interactions.CIA analysis was used to quantify the degradation phenomena on the treated surfaces. Oxygen plasma gives an acidic character to the surface and favors bond cleavage followed by decarboxylation and a probable cyclisation of polymeric fragments for long treatment times. In the case of an NH_3 treatment short treatment times (1s) gives a basic character to the surface with no degradation. This property is replaced by the appearance of low molecular fragments with a global amphoteric character leading to a weak adhesion to Al for long treatment times (5s)[7].

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