Improved Surface Energy Analysis for Plasma Treated PET Films

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Wetting experiments in PET/polar liquid systems performed at 25 °C in air have shown that the values of contact angle measured one day after PET treatment with He and He/O_2 plasmas decrease significantly compared to the untreated PET. Higher oxygen content in the He plasma improves wetting, whereas the substrate bias and total gas pressure (500 and 750 mTorr) are of minor importance. The calculated absolute values of the surface energy of plasma treated PET films combined to XPS measurements proved that the surface modification enhances their polar component while the dispersive one remains practically unaffected. Moreover, the results have shown that only a part of the polar interactions contribute to the wettability performance assuming that all the dispersive components interact at the solid/liquid interface.

Introduction

The demand for polymeric materials with improved properties for applications in the automotive, aerospace, microelectronics, biomedical, and food industries is endless. Particularly, there is a growing interest in polymers with specifically improved surface properties like wettability, printability, and biocompatibility.[1–6] In this direction, plasma processing presents some major advantages: i.e., it is a dry, clean, and very fast process, having a very low specific consumption of chemicals and energy, while it affects only the surface and not the bulk material. Low pressure and atmospheric discharges of inert and reactive gases like He, Ar, O_2, N_2, NH_3, and H_2O have been proposed for this purpose. The use of inert gas discharges results in chain scission of the outermost layer of the polymer followed by cross-linking, a process known as CASING (cross-linking via inert gas activated species). Furthermore, the use of reactive gases (O_2, N_2, NH_3, and H_2O) may additionally lead in grafting of new functional groups on the treated surface. The former process has the advantage of simplicity while in some cases it can improve the surface wettability as effectively as reactive gas discharges.

Various methods are used to characterize the polymer surfaces and evaluate their wettability performance of the polymers before and after plasma treatment. The most common among them utilizes liquid–solid contact angle measurements. The aim of the present work is to calculate the energy of interaction (work of adhesion) in systems consisting of untreated and plasma-treated PET in contact with different polar liquids. We will further examine the nature and magnitude of PET's surface energy components acting in the wettability performance and their dependence on treatment conditions and time. These studies are carried out on samples treated under carefully chosen conditions. An effort is made to evaluate the effects of biasing the polymer substrate with a DC voltage together with the effects of pressure in pure He and in He/O_2 discharges, thus modifying both the mechanism and the rate of surface etching.

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Finally, PET thin films were examined with XPS, 1 and 45 days after treatment with He and He/O_2 plasma.

Experimental Part

The discharge chamber 160 mm in diameter, described in detail elsewhere,[7] has the shape of an asymmetrical cross equipped with four quartz windows suitable for optical diagnostics, and two parallel 55 mm round electrodes with a constant interelectrode distance of 25 mm for this series of experiments. One of the two electrodes is powered by a 13.56 MHz RF generator while the other electrode, where the polymer film is attached, is either grounded or biased by a DC generator. The voltage and current signals on the RF electrode are recorded, using special probes, in a digital storage oscilloscope and then transferred to a computer for Fourier analysis. The exact method used for the determination of the real power consumed in the discharge is described in ref.[8] High purity gases helium (99.9995%) and O_2 (99.9998%) were used as received. The PET films had a thickness of 100 μm and were washed in alcohol and dried in a nitrogen flow before the introduction in the chamber where they remained at room temperature till the pressure was 10^{-6} Torr or better. The conditions of the PET surface treatment are summarized in Table 1.

The liquids used for the wetting experiments were: water (H_2O, triply distilled), commercial normal saline (NS, 0.85% NaCl), simulated body fluid (SBF, Tris-buffered at pH = 7.25, Kokubo's SBF [9]), ethylenglycol (EG), and methyleniodide (MI). The total surface energy, γ_{lv}, of these liquids as well as their dispersive, γ_{lv}^{d}, and polar, γ_{lv}^{p}, components are summarized in Table 2.

All wetting experiments were carried out in atmospheric pressure at $T = 25\,°C$. The volume of the liquid drops was approximately 8×10^{-3} cm^3. The drops were released gently onto the solid substrate from the tip of a micropipette, each experiment lasting for about 3 min. Neglecting the influence of gravity forces the drop had the form of a spherical segment thus allowing for the calculation of the contact angle θ.

Table 1. Samples nomenclature and the corresponding experimental conditions for the PET surface treatment (gas composition, total gas pressure, and applied substrate bias).

Sample	Gas	Pressure	Substrate bias
		mTorr	V
PET1	He	750	0
PET2	He	750	−30
PET3	He	750	30
PET4	1% O_2 in He	500	0
PET5	2.5% O_2 in He	500	0
PET6	5% O_2 in He	500	0
PET7	He	500	30
PET8	He	500	−30
PET9	He	500	0

Table 2. Liquid surface energy, γ_{lv}, and its despersive, γ_{lv}^{d}, and polar, γ_{lv}^{p}, components in (mJ · m^{-2}).

Liquid	γ_{lv}	γ_{lv}^{d}	γ_{lv}^{p}	Reference
H_2O	72.4	21.7	50.7	[10]
NS	71.3	23.8	47.5	[10]
SBF	69.6	24.5	45.1	[10]
EG	47.7	30.1	17.6	[11]
MI	50.8	48.5	2.3	[12]

Results and Discussion

In all the PET/liquid systems examined, there were no observable changes of the contact angles during the experiments, showing that an equilibrium is established at the solid–liquid interface from the beginning.

Table 3 shows the mean values of the experimentally measured contact angles of the liquids with a standard deviation of ±3° for the untreated as well as the plasma treated PET surfaces, 1 day (PET1–6) and 1, 5, and 10 days (PET7–9) after the treatment, under different bias and plasma pressure conditions.

For the untreated PET/water system, the measured contact angle (72.4°) is in the range of values found in the literature (76°,[13,14] 70°,[11] 76.5°,[15] and 78°[16]). The value of 29.6° measured for the PET/MI system lies also in the range of values given by Owens and Wendt.[13]

A significant decrease of the contact angle of all the liquids in contact with the plasma treated surfaces of PET is observed. For the PET surfaces treated with the 750 mTorr helium plasma (PET1–3), the results show that in these cases there is no significant difference due to the variation of the substrate bias. The water contact angles (32.3°–38.5°) are comparable to those found in the literature.[14] Lower angles are obtained with He/O_2 plasmas (PET4–6). In this case, the contact angles decrease with increasing O_2 percentage in the gas mixture. The value of 24.8° obtained for the PET6/water system after treatment with a 5% O_2 in He plasma, is almost identical with the value of 24.4° for PET treated with oxygen plasma.[11] The time dependent measurements (PET7–9) showing an increase of the contact angle with time after the treatment equivalent to an decrease of the surface energy toward the properties of the untreated surface. In fact, measurements on PET samples treated under various plasma conditions have shown that 60 days after the treatment the treated samples exhibit water contact angles equal to 70% of the untreated PET. The decrease of the He pressure from 750 to 500 mTorr does not seem to induce any significant difference.

These results can be used for the calculation of the work of adhesion as follows: The general equation, correlating

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Table 3. Measured contact angle θ in (deg.), in different PET/liquid systems at room temperature.

Sample	Days after treatment	H_2O	NS	SBF	EG	MI
PET (untreated)		72.4	73.2	68.8	48.4	29.6
PET1	1	38.5	35.7	36.2	19.1	21.5
PET2	1	35.9	37.1	35.5	14.1	22.6
PET3	1	32.3	37.5	35.5	15.9	19.6
PET4	1	28.7	33.8	33.4	19.7	15.1
PET5	1	26.9	27.7	25.0	12.3	15.5
PET6	1	24.8	25.3	24.3	11.2	14.5
PET7	1	37.1	36.9	33.7	20.0	20.6
PET8	5	42.2	43.9	38.4	25.1	21.2
PET9	10	43.5	45.0	42.7	27.1	21.5

the wetting and bonding behaviors at the interface of a solid–liquid vapor system in thermodynamic equilibrium, is

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \tag{1}$$

where the work of adhesion W_a, which represents the energy of interaction between the liquid and the solid phases per unit area, is related to the surface energies of the solid γ_{sv} and the liquid γ_{lv}, respectively, combined with the interfacial solid–liquid energy γ_{sl}.

For a sessile drop of a liquid lying on a solid substrate Young's equation holds

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv}\cos\theta \tag{2}$$

where, θ is the contact angle. By combining Equation (1) and (2) results in

$$W_a = \gamma_{lv}(1 + \cos\theta) \tag{3}$$

The surface energy γ of solids and liquids results from the additive contributions of a variety of intermolecular forces.[12] For polar solids or liquids the total surface energy is a sum of the always existing London dispersion forces (γ^d) with intermolecular interactions that depend on the chemical nature of the material, compiled as polar forces (γ^p)

$$\gamma = \gamma^d + \gamma^p \tag{4}$$

If one assumes that at the interface between the two phases, only similar components of the respective surface energies interact, then their contribution to the total interfacial energy, γ_{sl}, can be written as[13]

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\left[(\gamma^d_{sv}\gamma^d_{lv})^{\frac{1}{2}} + (\gamma^p_{sv}\gamma^p_{lv})^{\frac{1}{2}}\right] \tag{5}$$

and therefore

$$W_a = W^d_a + W^p_a = 2\left[(\gamma^d_{sv}\gamma^d_{lv})^{\frac{1}{2}} + (\gamma^p_{sv}\gamma^p_{lv})^{\frac{1}{2}}\right] \tag{6}$$

Combining Equations (3) and (6) gives

$$\cos\theta = -1 + 2\left[\frac{(\gamma^d_{sv}\gamma^d_{lv})^{\frac{1}{2}}}{\gamma_{lv}} + \frac{(\gamma^p_{sv}\gamma^p_{lv})^{\frac{1}{2}}}{\gamma_{lv}}\right] \tag{7}$$

In Figure 1, we show the variation of the work of adhesion, W_a, at the interface of the PET/liquid systems calculated according Equation (3). The strongest effects are observed

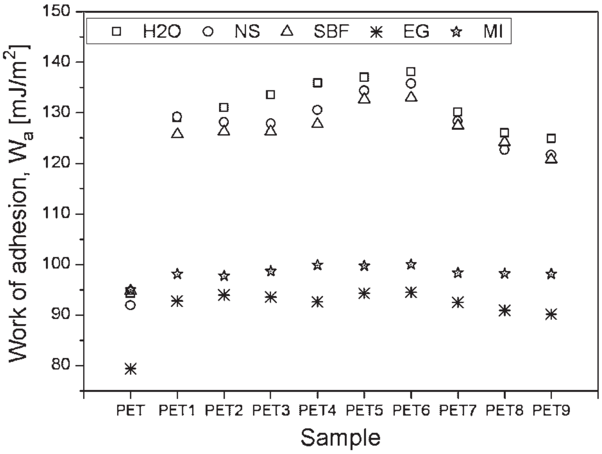

Figure 1. Work of adhesion of plasma treated PET, under different conditions (Table 1), in contact with different polar liquids at room temperature.

in the cases were the treated surfaces are in contact with strongly polar liquids (H_2O, NS, SBF). On the other hand, the work of adhesion for MI ($\gamma^{p}_{lv} = 2.3$ mJ $\cdot$ m^{-2}) is almost the same with the untreated PET. From this observation one can conclude that the treatment of the PET surface under various plasma conditions affects almost exclusively the surface energy due to polar forces (γ^{p}_{sv}). This is in line with the observed reduction of W_a with time (PET8 and 9).

From the results presented above (Table 2 and 3) it is possible to estimate adequately the dispersive component of the PET surface energy, γ^{d}_{sv}, in accordance with literature.[12,17,18] This can be done by plotting cosθ against $\frac{\sqrt{\gamma^{d}_{lv}}}{\gamma_{lv}}$ [Equation (7)]. The value of γ^{d}_{sv} is then estimated from the slope ($= 2\sqrt{\gamma^{d}_{sv}}$) of the line connecting the origin (cos$\theta = -1$) with the intercept of the straight line of cosθ against $\frac{\sqrt{\gamma^{d}_{lv}}}{\gamma_{lv}}$ at cos$\theta = 1$ (Figure 2).

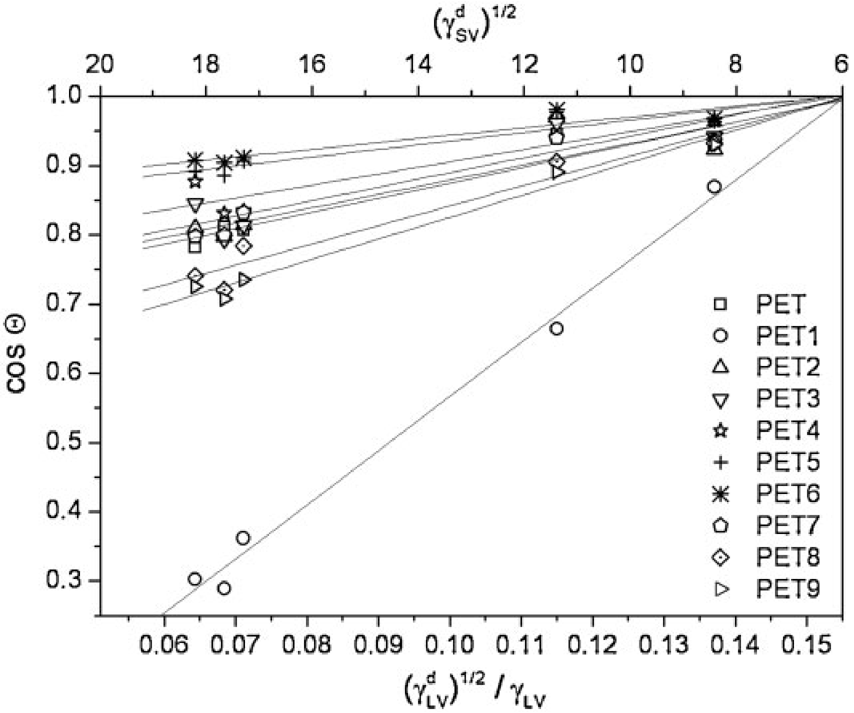

Figure 2. Plot of cosθ vs. $\frac{\sqrt{\gamma^{d}_{lv}}}{\gamma_{lv}}$ for plasma treated PET films in contact with different polar liquids.

Assuming that all the dispersive forces, either of the liquid or the solid, are actively contributing in the wettability performance, it is possible to calculate the dispersive component of the work of adhesion $W^{d}_{a} = 2(\gamma^{d}_{sv}\gamma^{d}_{lv})^{1/2}$. Then from the difference $W^{p}_{a} = W_a - W^{d}_{a} = 2(\gamma^{p}_{sv}\gamma^{p}_{lv})^{1/2}$ the work of adhesion due to polar forces can be estimated. The slope of the plot of $(\gamma^{p}_{sv}\gamma^{p}_{lv})^{1/2}$ versus $\sqrt{\gamma^{p}_{lv}}$ gives the value of γ^{p}_{sv}. Table 4 presents the calculated values of γ_{sv}, γ^{d}_{sv} and γ^{p}_{sv} of the untreated and plasma treated samples. The values obtained for the untreated PET are in the range of the values that can be found in literature.[11,13,14,16,19] The results show that the surface energy of PET that is due to dispersive forces does not change with surface treatment or with time after treatment, having a mean value of 41.7 ± 0.7 mJ $\cdot$ m^{-2} which is practically identical to the value of the untreated PET (41.4 mJ $\cdot$ m^{-2}). On the other hand, the part of the surface energy owed to polar forces increases significantly with plasma treatment. The samples treated with helium under different pressure and bias conditions (PET1–3 and 7) present γ^{p}_{sv} values between 32 and 34 mJ $\cdot$ m^{-2}. Helium/oxygen treated samples (PET4–6) present higher values ranging between 35 and 40 mJ $\cdot$ m^{-2}, increasing with the oxygen content, in accordance with literature data taken for PET treated in Ar + O_2 plasma.[19] The γ^{p}_{sv} values for the PET8 and 9 samples decrease with the after treatment whereas the respective dispersive components are constant.

Finally, the calculated values of the work of adhesion calculated according to Equation (6) are higher than those calculated directly from the contact angles [Equation (3)], under the assumption that the whole amounts of γ^{p}_{lv} and γ^{p}_{sv} are active at the solid–liquid interface. This indicates that, in the wettability performance, only a part of the total γ^{p}_{lv} and γ^{p}_{sv} interact with each other, contributing to the total energy of interaction at the solid–liquid interface.

He and He/O_2 plasma treated PET thin films were examined with XPS, 1 and 45 days after the treatment, in

Table 4. Solid surface energy,γ_{sv} and its dispersive, γ^{d}_{sv} and polar, γ^{p}_{sv} components in (mJ/m²)

Sample	γ_{sv}	γ^{d}_{sv}	γ^{p}_{lv}
PET (untreated)	48.4	41.4	7.0
PET1	72.6	40.6	32.0
PET2	74.3	41.4	32.9
PET3	76.6	42.9	33.7
PET4	76.9	41.8	35.1
PET5	81.2	42.3	38.9
PET6	82.2	42.3	39.9
PET7	73.8	41.1	32.7
PET8	69.8	41.4	28.4
PET9	68.0	41.3	26.7

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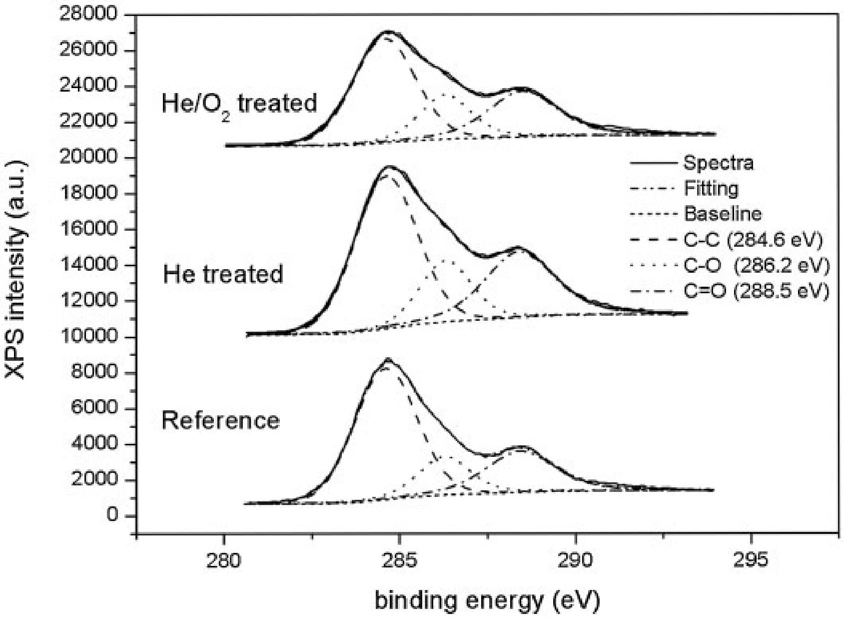

Figure 3. C1s XPS spectra of the topmost layer (angle 15°) for (a) untreated PET films, (b) PET1 (He treated at 750 mTorr) and (c) PET6 (5% O_2/He treated at 500 mTorr).

order to follow the effects of O_2 addition on the discharge, the surface properties and the ageing process. Figure 3 presents the C1s XPS spectra of PET1 and PET6 thin films. The spectrum of an untreated PET (a) is also included for reference. The spectra of modified and untreated PET surfaces exhibit two characteristic peaks located at 284.7 and 288.7 eV, corresponding to C–C and O=C–O bonds, respectively.[20] It can be clearly observed that PET treated with either He or He/O_2 discharges present a larger number of O=C–O relative to C–C compared to untreated PET and this is in agreement with the smaller contact angle measurements and the corresponding higher hydrophilicity of these solid surfaces. The O=C–O/C–C ratio was estimated by integrating the peak located at 288.7 eV to the integral of the peak located at 284.7 eV, following deconvolution of the spectra. The deconvolution procedure has shown that a much better fitting of the experimental spectra is achieved when a third peak located at 286.4 eV is considered. This peak is attributed to isolated C–O bonds[21] and was included in our calculations.

Table 5 summarizes the results of this procedure. The surfaces treated with He/O_2 discharges have a larger number of C–O bonds compared to the ones treated with pure He, while the number of C=O bonds is about the same for the treatment with either He or He/O_2 discharges. In fact, both pure He and He/O_2 plasmas seem to affect, through hydrogen abstraction, CH_2 groups or phenyl rings rather than ester groups. In the case of O_2 containing plasmas, part of the removed hydrogen atoms is replaced

Table 5. Ratio of O=C–O, C–O peaks to = C–C from C1s XPS spectra for PET1 (He treated at 750 mTorr) and PET6 (5% O_2/He treated at 500 mTorr), after 1 and 45 days.

Sample	**Days after treatment**	**O=C–O/C–C**	**C–O/C–C**	**FWHM**		
				cm^{-1}		
				C–C	**C–O**	**C=O**
PET (untreated)	–	0.40	0.28	2	1.8	1.6
PET1	1	0.55	0.34	1.8	2.1	1.5
PET1	45	0.48	0.30	1.8	1.9	1.6
PET6	1	0.55	0.40	1.9	1.5	2.1
PET6	45	0.50	0.36	1.9	1.5	1.8

by O atoms. This can explain the enhancement of the peak at 286.4 eV which corresponds to C–O, CH–O, or CH_2–O groups. On the other hand, in the case of pure He plasmas the abstraction of H atoms is not followed by O grafting, the most probable mechanism of further surface modification being chain-scission and formation of small hydrocarbons and carbon dioxide.[22] The modified surface has a larger ratio of ester groups to carbon atoms compared to PET and this explains the observed relative enhancement of the peak at 288.7 eV.

The ageing effect is observed for the surfaces treated with either He or He/O_2 discharges, as a reduction of the number of O=C–O and C–O bonds for the measurements performed after 45 days. This change is related to the thermal motion of the hydrophilic groups from the topmost layer to the inside of the film,[21–23] which in turn is reflected as a relative drop of the peaks at 286.4 and 288.7 eV compared to the peak at 284.7 eV.

Conclusion

From the wetting experiments in systems of untreated and plasma treated PET under very different plasma conditions, in contact with different polar liquids we have calculated the work of adhesion as well as the absolute values of the established surface energy of solid PET, given as a sum of dispersion and polar interactions.

The results have shown that the dispersive term does not depend on the plasma conditions whereas the polar term increases significantly after treatment. However, the influence of either substrate bias or pressure in He discharges is minor. On the contrary, a strong increase of the polar term is observed with the addition of oxygen. XPS measurements have shown that this enhancement is due to the higher C–O and O=C–O content in relation to the C–C bonds.

In addition, it has been shown that only a part the surface energy due to the polar forces of solid PET is actively contributing to the total energy of interaction at the solid–liquid interface. Furthermore, the γ_{sv}^{p} values decrease with time after treatment whereas the respective dispersive components are constant. This decrease is also related to the C–O, O=C–O/C–C ratio (Table 5), which is reduced with time.

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