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Surface modification and adhesion improvement of polyester films

Research Article

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Abstract: Facile surface modification of polyester films was performed *via* chemical solutions treatment. Surface hydrolysis was carried out by means of sodium hydroxide solutions, leading to the formation of carboxylate groups. Three commercial polyester films of 100 μm in thickness were used in this work: AryLite™, Mylar™, and Teonex™, hydrolysis time being the main modification parameter. FTIR-ATR analysis, topography and contact angle (CA) measurements, surface free energy (SFE) and T-Peel adhesion tests were carried out to characterize the modified films. A quantitative estimate of the carboxylates surface coverage as a function of treatment time was obtained through a supramolecular approach, i.e. the ionic self-assembly of a tetracationic porphyrin chromophore onto the film surface. The surface free energy and critical surface tension of the hydrolyzed polyesters was evaluated by means of Zisman, Saito, Berthelot and Owens-Wendt methods. It was shown that NaOH solution treatment increases roughness, polarity and surface free energy of polymers. As a result, T-Peel strengths for modified Mylar™ and Teonex™ films were respectively 2.2 and 1.8 times higher than that for the unmodified films, whereas AryLite™ adhesion test failed.

Keywords: *Surface modification • Polymeric substrate • AryLiteTM • Self-assembly • Porphyrins*

1. Introduction

Polyesters, both amorphous and semicrystalline, are a promising class of commercial polymers for optoelectronic applications primarily by virtue of their good mechanical, chemical, thermal and optical stability [1,2]. The major potential advantages of using organic substrates in future applications lie in low production costs, easy processing, reduction of weight (30%) and thickness (50%) of the devices as compared to glass, and improved flexibility and mechanical robustness [1].

Many challenging applications can be attained by using polymeric materials, such as development of Organic Light Emitting Diode (OLED) displays, all these advantages encouraging the replacement of glass with polymeric materials [1].

Flexible OLEDs usually embed several organic/inorganic layered architectures into a single device, thus the detailed knowledge of the thermal properties and mechanical response of each single layer, as well as of the adhesion strength between the various interfaces are of significant importance [3]. The modification of polymer surfaces is a research field that has received much attention because specific surface characteristics are needed in a number of applications, such as adhesives [4], biomaterials [5], protective coatings [6] and organic optoelectronic devices.

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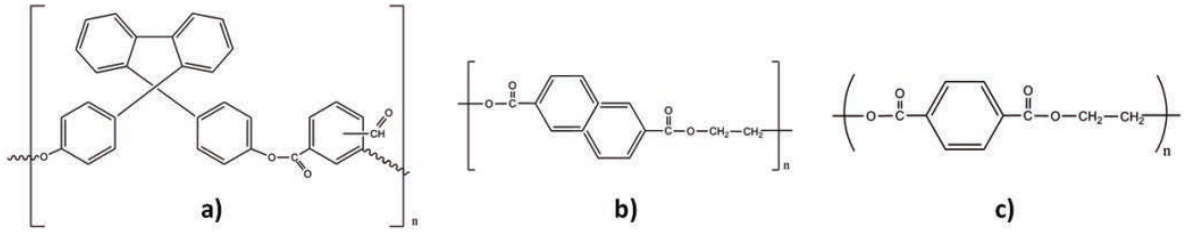


Figure 1. Chemical structures of a) AryLite™, b) Teonex™ and c) Mylar™.

The aim of this study is to modify the polymer surface to improve the adhesion properties. The adhesive bonding of solids has been associated with their surface energies and an improvement of adhesion usually involves ways to increase surface energy, one of the most effective ways being to chemically change the functional groups at the polymer surface [7]. This latter can be modified by means of various physical and/or chemical processes, the most common techniques including plasma treatment [7], electric discharge [7], surface grafting [8], flame treatment [9], UV irradiation [10-13] and wet chemical reaction [7], and often these chemical changes are accompanied by the modification of surface or the elimination of impurities.

In a wet chemical approach to surface modification a material is treated with liquid reagents to generate reactive functional groups on the surface, and this well-established method does not require specialized equipment being carried out in most laboratories. Alkaline hydrolysis is one of the most rapid methods to modify the chemical and physical characteristics of a polyester [14]: the nucleophilic attack of a base on the electron-deficient carbonyl carbon of the ester linkage causes chain breaking along the polyesters chain, producing carboxylate and hydroxy polar end-groups. The increased surface polarity leads to better wettability.

In the present paper, the surface modification of three commercial polyester films *via* hydrolysis reaction in sodium hydroxide solution has been reported. The modified surfaces has been characterized using FTIR-ATR spectroscopic analysis, roughness and contact angle measurements, surface free energy calculation and T-peel test measurements. A quantitative determination of the surface density of carboxylate groups vs. hydrolysis time has been obtained *via* a non-covalent approach, consisting in the self-assembly of a tetracationic porphyrin derivative onto the negatively charged surface of a Mylar™ film which has been chosen as a model system.

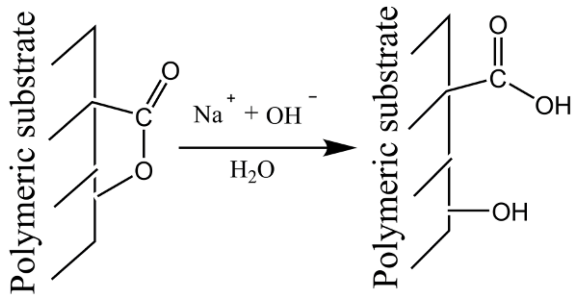
2. Experimental procedure

2.1. Materials

Commercial polyester films of 100 μm in thickness were selected. AryLite™, supplied by Ferrania Imaging Technologies S.p.A., is an amorphous aromatic polyester [15] characterised by very high glass transition temperature. Mylar™ (Polyethylene Terephthalate, PET) and Teonex™ (Polyethylene Naphthalate, PEN), both supplied by DuPont, were selected for their good properties such as mechanical strength, toughness, fatigue resistance at elevated temperatures, and a high crystalline melting temperature (>250°C). Moreover, these selected materials are recyclable and their intrinsic low surface energy makes them ideal candidates for chemical surface modification. Tetra(N-methylpyridinium-4-yl)porphyrin p-toluenesulfonate salt, NaH_2PO_4, NaOH, and CuO (Sigma Aldrich) were of the highest purity available and were used as received. Tetra(N-methylpyridinium-4-yl)porphyrinato copper(II) was prepared through a heterogeneous reaction previously reported in the literature [16]. Porphyrins stock solutions were prepared from the solid in Millipore purified water and stored in the dark. Solution concentrations were determined from known molar extinction coefficient at the absorption maximum (λ_{max} = 426 nm; $\varepsilon = 2.31\times10^5$ M cm^{-1}) [17].

2.2. Mechanical properties

Young's modulus (E), yield strength (σy) and elongation at break (εr) properties were investigated according to UNI-EN-ISO 527-3 on rectangular specimens with 150 mm length, 25 mm width and 0.1 mm thickness using a SANS mod. 4023 mechanical dynamometer with a 30 kN loading cell and a traverse speed of 20 mm min^{-1}. The modulus has been calculated from the slope of the linear part of the curve. Each sample was measured five times at room temperature and the values of the mechanical tests were averaged.



Scheme 1. Scheme of nucleophilic substitution of the hydroxide ion to the carbonyl group.

2.3. Thermal properties

The thermal properties of the substrates under investigation were evaluated in order to determine both melting point (T_m) and glass transition (T_g) temperatures by using a TA Instruments mod. Q1000 differential scanning calorimeter, at 10°C min^{-1} scanning rate in N_2 purging flow. The initial degradation temperatures (T_{id}) were measured by using a TA Instruments mod. 2950 thermogravimetric analyser, at 10°C min^{-1} scanning rate in N_2 purging flow. T_{id} is associated to 3% weight loss.

2.4. Surface treatments

The polymer films were immersed in an alcohol/water (1/1, v/v) solution for 2 h in order to clean their surface, rinsed with a large amount of distilled water, and dried under reduced pressure for 12 h at 25°C. For hydrolysis reaction the films were immersed in an aqueous solution of 4.5 M NaOH at 75°C. It's well known that the hydrolysis reaction produce alcohol functionality *via* nucleophilic substitution of an hydroxide ion (OH^-) to the carbonyl group (C=O) [7] (Scheme 1). After treatment the films were thoroughly rinsed with distilled water and then dried under reduced pressure at 25°C overnight.

2.5. Characterization of modified surfaces

2.5.1. Attenuated Total Reflectance

Infrared spectroscopic analyses were performed by Nicolet Nexus mod. 670 FTIR equipped with attenuated total reflection (ATR) smart ARK HATR accessory. In ATR, the sample is placed in optical contact against a zinc selenide (ZnSe) crystal with a high refraction index (2.43). The IR beam penetrate a short distance into the sample. This penetration is termed the evanescent wave. The sample interacts with the evanescent wave, resulting in the absorption of radiation by the sample, which closely resembles the transmission spectrum for the same sample. However, the ATR spectrum will depend upon several parameters, including the angle of incidence (θ) for the incoming radiation, the wavelength of the radiation (λ), and the refractive indices of the sample (n_2) and the ATR crystal (n_1). The penetration depth (d_p) of the evanescent wave, is defined by Eq. 1:

$$d_p = \frac{\lambda}{2\pi(n_1^2 sen^2\theta - n_2^2)^{\frac{1}{2}}} \quad (1)$$

In the investigated wavenumber range (400 – 4800 cm^{-1}), d_p generally varies from 5 μm to 15 μm for polyesters substrates. After hydrolysis treatment of the polyester films FTIR-ATR provided information on the formation of hydroxy groups on the polymer surfaces.

2.5.2. Topography measurements

Topography (roughness) measurements on polyester films were performed with a Micro Materials Ltd. mod. NanoTest™ Platform, which monitors and records the load and displacement of an indenter tip, being able to achieve sub-nanometric depth resolution in the horizontal plane. A diamond three-sided pyramidal indenter with a curvature radius of about 100 nm was used, and a constant load of 10 μN was applied. Scans (200 μm) were made both with the tip in contact with the surface and with the tip in close proximity to (but not contacting) it. The topography changes after surface treatment could be measured through roughness values, providing valuable information on contribution of surface roughness to adhesion strength. Two specimens of each film were randomly selected to record 20 measurements per sample, at room temperature, after microscopic inspection to avoid defects. Average surface root means squared roughness [17] (R_{RMS}) was calculated from Eq. 2:

$$R_{RMS} = \sqrt{\frac{\int_0^L (x_n - \bar{x})^2 dy}{L}} \quad (2)$$

where x_n is the height of a random location on the scanned profile, $\bar{x}$ is the mean height of all measured heights and L is the sampling scan length.

2.5.3. Contact angle measurements

The surface wettability was evaluated by contact angle measurements [18-20] using the sessile drop method that considers the shape of the small liquid test drop to be a truncated sphere. The sessile drop contact angle was measured by a Dataphysics mod. OCA 20 using 1 μL volume sampling. Liquid drop contact angles were used both to assess the efficiency of surface modification experienced by the polymer films and for critical surface energy calculations. Each solid sample was measured ten times with liquids at room temperature and the values of the contact angles were averaged.

2.5.4. Evaluation of surface free energy

In order to achieve meaningful results for the surface free energy (SFE) of the polymer surfaces three liquids

Table 1. Solvent surface tension components at 20°C (mJ m^{-2}).

Liquid	γ_d	γ_p	γ_T
Water	22.1	50.7	72.8
Ethylene glycol	30.1	17.6	47.7
Diiodomethane	44.1	6.7	50.8

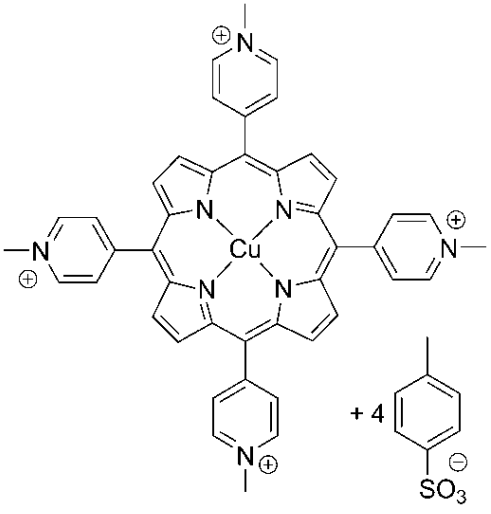


Figure 2. Molecular structure of tetra(N-methyl-pyridinium-4-yl) porphyrinato copper(II) (CuT_4).

of known surface tension were used [19]: distilled water, ethylene glycol and diiodomethane. The liquids, supplied by Aldrich, were used without further purification. Surface tension components of liquids are reported in Table 1. Critical surface tension and SFE of the polymer substrates were calculated using the methods proposed by Zisman, Saito [19], Berthelot [21] and Owens-Wendt [20]. Zisman, Owens-Wendt and Saito's methods allows the calculation of the surface tension using at least two liquids, while Berthelot method allows the calculation of surface free energy using only one liquid. The results obtained with one, two or three liquids were combined using different approaches according to the requirements of each method.

2.5.5. T-peel test of adhesion

T-Peel tests were carried out jointing the samples with a polyurethane thermoset adhesive composed by Polurene FP38B and Polurene FP38CS1 used as hardener agent, both supplied by S.A.P.I.C.I. S.p.A. The polyurethane adhesive was selected as a probe to test the effect of the change in SFE of the polymeric substrates, since isocyanate moieties can react with the hydroxy groups of the treated films, and lead to an improvement in the adhesion strength. The T-peel tests of adhesion [23] were carried out on the untreated and treated substrates using SANS mod. 4023 universal testing machine with a load cell of 30 kN and a peel speed of 10 mm min^{-1} according to ASTM D 1876-01 on rectangular specimens with 100 mm length, 25 mm width and 0.1 mm thickness. Polyurethane (about 100 µm in thickness), have been applied uniformly on both substrates. A static load was applied on substrate joints for seven days at room temperature. The T-Peel strength was determined from the average of five specimens.

2.5.6. Determination of the carboxylate surface density on hydrolyzed films

UV/Vis spectra were obtained on a Hewlett-Packard mod. 8453 diode-array spectrophotometer. Several Mylar™ samples of standard size (l × h = 1×3 cm), previously treated with NaOH for different times, were each immersed for 6 h at 24°C into 3.5 mL of a 5 mM phosphate buffer solution (pH ~9) containing 1.3 µM tetra(N-methyl-pyridinium-4-yl)porphyrinato copper(II) (CuT_4) (Fig. 2). The UV/Vis absorption spectra of all the CuT_4 solutions were recorded in 1 cm optical path length cells, before and after Mylar™ soaking, to determine the dye loading on each polymeric film and, from that value, the carboxylate density of the film surface. After immersion in the buffered porphyrin solution, the various films were thoroughly rinsed to remove any CuT_4 excess, placed in a water-containing cell, and their UV/Vis extinction (absorption + scattering) spectra recorded.

3. Results and discussion

The use of polymer substrates in microelectronic applications implies issues as: optical, thermal, mechanical and morphological properties, good wettability and a high compatibility with different materials that will be deposited. Polymer substrates used in microelectronic applications are thermoplastic polyesters: amorphous (AryLite™) and semicrystalline (Teonex™, Mylar™).

Numerous studies have looked at surface properties such as roughness, polarity, chemical composition and surface free energy to describe and explain adhesion phenomena at a surface or interface.

3.1. Mechanical properties

Young's modulus (E), yield strength (σ_y) and elongation at break (ε_r) properties were investigated according to UNI-EN-ISO 527-3, the tests being performed at room temperature (under glass transition temperature).

The nominal stress–strain curves for each film were obtained by averaging the results of five experiments, and the Young's modulus was calculated according

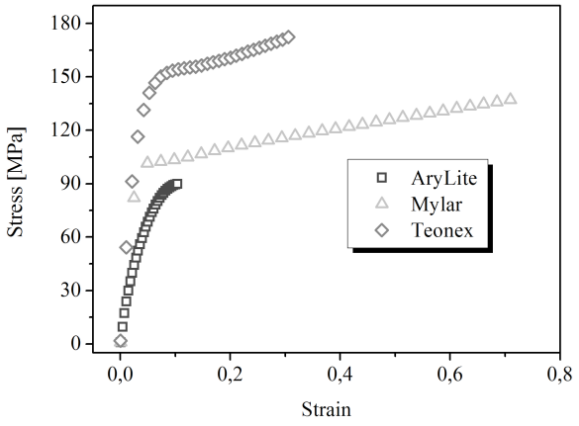


Figure 3. Stress-Strain curves of polyester substrates.

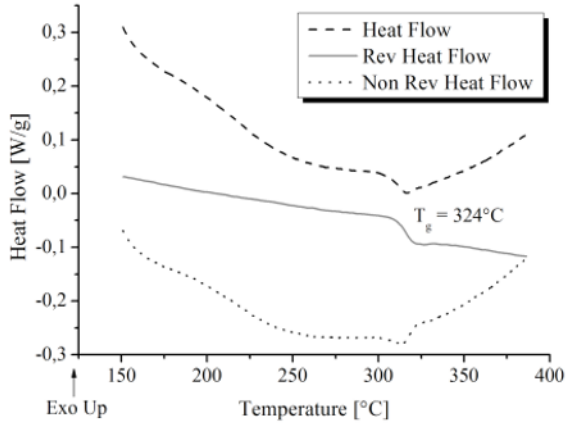


Figure 4. Modulated Differential Scanning Calorimetry of AryLite™.

to UNI-EN-ISO 527-3 from the slope of the linear part of the curve and values are listed in Table 2, while Fig. 3 shows the nominal stress–strain curve of each film. It can be seen that Teonex™ have the highest Young's modulus (6.3 GPa), while the Mylar™ have the highest elongation at break (72%).

The observed elastic and ultimate properties can be related to molecular backbone structure reported in Fig. 1. The rigid molecular backbone of AryLite™ is responsible for reduced elongation at break, and the lack of crystalline reinforcement results in poor elastic and ultimate properties. On the other hand, the presence of reinforcing crystalline structure improves the elastic properties of semiflexible Mylar™ and Teonex™ samples, still preserving ductile behavior due to structural rearrangements and yielding of amorphous phase.

3.2. Thermal properties

The differential scanning calorimetry (DSC) thermal analysis technique measures heat flows and phase changes on a sample under thermal cycles. The T_g of AryLite™ is overlaid by an enthalpic relaxation phenomenon. Therefore, deeper investigations were performed with Modulated DSC. In the latter case, samples were heated from 150°C to 400°C, at heating rate of 2.5°C min^{-1}, with a modulated temperature amplitude of 0.5°C and a frequency of 60 s under nitrogen flow.

Reversing Heat Flow signal is purified by influence of enthalpic phenomenon, which affects only Non Reversing Heat Flow signal, and reveals a glass transition temperature of 324°C (Fig. 4).

Thermal properties of the various polyester samples are reported in Table 3. Noticeably, AryLite is completely amorphous and have the highest T_g. The presence of aromatic and rigid moieties in the molecular skeleton prevents conformational rearrangements required for the obtainment of sterically ordered crystalline structure.

Table 2. Mechanical properties of Arylite™, Teonex™ and Mylar™.

	AryLite™	Mylar™	Teonex™
E [GPa]	2.42±0.24	4.49±0.54	6.26±1.10
σ_y [MPa]	-	102±7.65	153±15.61
ε_r [%]	10.24±2.56	72.50±7.32	31.32±5.68

Table 3. Thermal properties of Arylite™, Teonex™ and Mylar™.

	AryLite™	Mylar™	Teonex™
T_g [°C]	324	79	122
T_m [°C]	-	248	153
T_{id} [°C]	488	410	398

3.3. Attenuated Total Reflectance

In order to study the chemical changes of the polyester films during immersion in NaOH solution, the surfaces of polyester before and after exposure were characterized with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), the results being displayed in Fig. 5.

Several bands characteristic of polyesters are observed for all samples. The peak centered at 1730 cm^{-1} is attributed to C=O stretching of the ester groups [24].

In order to make a comparison between treated and untreated samples the intensity of each peak was normalized [25] against the absorbance of the band at 1500 cm^{-1}. This peak is attributed to C-H in-plane bending of the benzene ring, and is not affected by the hydrolysis reaction.

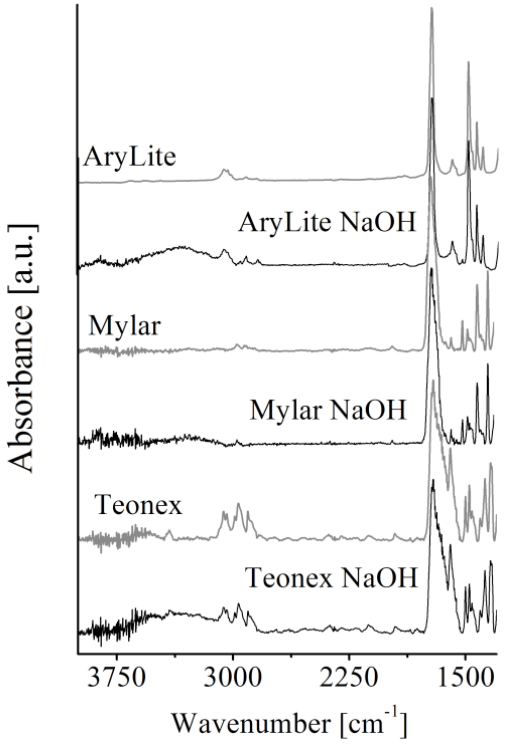


Figure 5. FTIR–ATR spectra of treated and untreated polyester films in the range 4000–1300cm^{-1}.

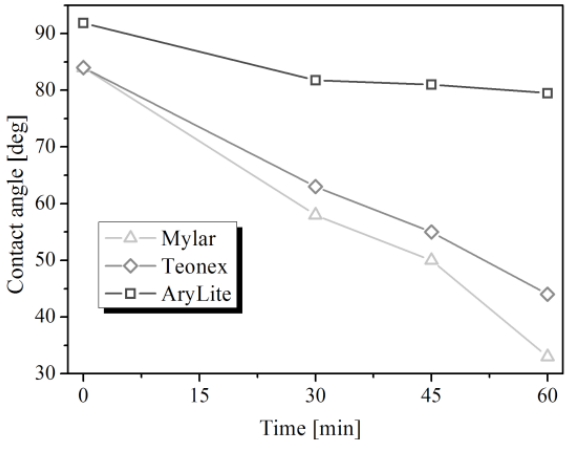


Figure 6. Water Contact Angle of Mylar™, Teonex™, and AryLite™ treated with NaOH solution for different times.

After NaOH hydrolysis, the spectra of AryLite™ and Mylar™ show bands typically observed in treated samples, namely a signal increasing around 1540 cm^{-1} which can be attributed to the asymmetric -COOH stretching vibrations, and a decrease of C=O ester linkage at 1726 cm^{-1}. After 30 minutes of hydrolysis in NaOH solution, all polyesters display also a strong absorption band in the broad 3200–3500 cm^{-1} region, which is characteristic for hydrogen-bonded –OH stretching.

All this spectroscopic evidence indicates that the nucleophilic attack of the hydroxide ion (OH^-) to the carbonyl group have indeed led to new carboxyl moieties on the surfaces of the exposed samples.

3.4. Topography measurements

The topography scan technique was used to measure the roughness of samples before and after the hydrolysis treatments, since these changes might provide a contribution to substrates adhesion strength. Treated and untreated samples exhibit a root means squared roughness (R_{RMS}) lower than 20 nm (Table 4), then according to Bénard *et al.* [27] all these films can be considered as totally flat from a topographical point of view.

Table 4 shows that, predictably, the surface roughness of the treated polymers was higher than the untreated polyesters and untreated AryLite™ films have shown the lowest roughness value (about 2.64 nm).

3.5. Contact angle

For an ideal solid surface, *i.e.*, one that is flat, rigid, perfectly smooth (roughness <0.5 μm) and chemically homogeneous [27,28], only one contact angle (CA) exists, that is the true equilibrium CA. CA measurements are not reliable for surfaces with a roughness higher than 0.5 μm [17], which is by far larger than the values reported in Table 4 for our samples.

According to the liquid surface tension theory [29], the largest CAs are measured for water, while the smallest ones correspond to diiodomethane.

Fig. 6 shows the water CA changes (with an error of ± 2%) for untreated and hydrolyzed polymer films as a function of NaOH treatment times. Teonex™ and Mylar™ films exhibit a similar behaviour after exposure for 60 minutes at 75°C in NaOH, with a decrease in water CA from 84° to 44° and from 81° to 34°, respectively, while the same treatment induces a smaller effect for AryLite™, that shows a low surface energy and a chemical inertia.

Since in all cases NaOH treatment longer than 30 minutes resulted in severe damage of substrate surfaces with reduction of gloss and optical transparency, a treatment time of 30 minutes has been selected for all the other tests. Under these conditions, the surfaces have the lowest CA, and no significant weight loss and transparency reduction could be detected.

The wettability of polymer films can be examined by using two solvents as a reference in order to compare the interactions of polar and non-polar liquids with the substrates surface. A comparison between CA values for water and diiodomethane (polar and non-polar liquids,

Table 4. Roughness and contact angles of unmodified and treated polyester substrates.

		RMS [nm]	CA [°] Water	CA [°] Diiodomethane
AryLite™	*Untreated*	2.64±0.57	92±1	24±1
	Treated	5.63±1.97	82±2	44±2
Mylar™	*Untreated*	5.78±1.52	80±1	40±2
	Treated	15.75±5.20	61±3	39±2
Teonex™	*Untreated*	7.15±1.06	84±3	38±1
	Treated	9.86±2.44	63±2	39±3

respectively) shows that surface modification increase the polyester surface polarity: after hydrolysis, the CA of water decreases whereas that of diiodomethane increases (Table 4), pointing to an increased hydrophilicity of all samples.

3.6. Surface Free Energy

In the present study, further characterization of surface wettability has been performed by calculating surface tension components using CA measurements for three different fluids whose surface tensions components data are given in Table 1.

When a drop of a liquid rests on a solid surface, it forms an angle θ with the surface, called contact angle. In thermo-dynamical equilibrium conditions, Young showed that

$$\gamma_L \cos\Theta = \gamma_S + \gamma_{SL} \quad (3)$$

where γ_S is the surface energy solid/air, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_L is the surface tension liquid/air. Many different methods have been proposed to evaluate γ_S using values of contact angles formed by drops of different liquids with known surface tensions.

The experimental values of the CA at room temperature by drops of water, diiodomethane and ethylene glycol have been used to evaluate the SFE *via* the above mentioned methods of Zisman, Saito, Berthelot and Owens-Wendt.

Berthelot approximation is based on work of adhesion for a solid–liquid interface by a geometric mean and obtained from Young's equation:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_L}} \quad (4)$$

This Equation is a very simple tool to calculate the SFE of a solid, since it requires one data obtained from one liquid. However, use of one liquid data may not be reliable and this equation over-estimates the pair interaction between unlike molecules, therefore largely deviating values are obtained when different liquids are used.

Zisman's method shows that the cosines of CA (θ) formed by drop of homologous liquids on a solid surface vary linearly with their surface tension. The critical surface tension can then be found by extrapolating the linear function to $\cos\theta = 1$, indicating complete wetting ($\theta = 0°$).

Saito shows that $\log(1+\cos\theta)$ for different liquids vary linearly with $\log(\gamma_L)$ (where γ_L is the surface tension of the liquid). The critical SFE of the material is found from the point where θ is zero as in the Zisman plot.

The critical surface tension of the solid is conceptually related to the SFE but is not necessarily the same value. Shimizu *et al.* [20] show that surface free energy of polypropylene and polystyrene corroborate reasonably well the critical surface tensions calculated with the Zisman's and the Saito's methods. Table 5 shows values of SFE for pristine samples and for those after treatment with NaOH solution for 30 minutes. The critical surface energy values delivered by the Zisman method are lower than that determined with all other methods; it was defined that use of a pair of liquids in which one is highly polar and the other is almost non-polar gave better results in the calculations [20]. It can be assumed that water–diiodomethane pair gave the most accurate value, since the polarity difference is high when compared with other pairs.

AryLite™, Mylar™, and Teonex™ SFE calculated by Saito's method is higher than that determined with all other methods.

Berthelot method depends on the used liquid [22,23]. Polar liquids (water, ethylene glycol) lead to the higher deviation from the average SFE value. For this reason diiodomethane CAs have been used for Berthelot SFE evaluation.

The largest increase in mean SFE by NaOH solution treatment (Table 5) is induced for Mylar™ and Teonex™, while the lowest one is measured for AryLite™, going from 29.97 mJ m^{-2} to 32.54 mJ m^{-2}.

Fowkes approach focuses on the interactions between phases across interfaces, and it is based on the hypothesis that the types of forces working between the molecules act independently of each other. He divided the total surface free energy in 2 parts: dispersive part and non-dispersive (or polar) part. Owens and Wendt [22] method use the Fowkes equation and they combine the dispersion and polar force components:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^p \gamma_L^p} \quad (5)$$

Table 5. SFE and polarity of polyester substrates, unmodified and treated for 30 minutes with NaOH solution.

[mJ m^{-2}]	Owens–Wendt				Zisman	Saito	Berthelot	Mean[a]
	γ_s^p	γ_s^d	γ_s	P_s	γ_s	γ_s	γ_s	γ_s
AryLite™	1.67	30.39	32.06	0.05	23.89	36.04	29.99	29.97
AryLite™ NaOH	5.58	28.78	34.36	0.16	27.42	36.82	33.39	32.54
Mylar™	4.41	35.41	39.82	0.11	31.53	38.92	34.39	34.95
Mylar™ NaOH	17.25	27.18	44.43	0.39	38.58	41.97	40.71	40.42
Teonex™	2.30	39.23	41.53	0.06	32.29	41.41	32.54	35.41
Teonex™ NaOH	15.80	27.54	43.34	0.36	39.94	43.90	39.43	41.09

[a] *averaged values between Zisman, Saito and Berthelot's method*

Table 6. T-Peel strength of unmodified and treated polyester substrates.

T-Peel strength [kN m^{-1}]	AryLite™	Mylar™	Teonex™
Untreated	-	0.69±0.12	0.87±0.07
NaOH Solution[a]	-	1.51±0.44	1.53±0.23

[a] *treatment of 30 minutes*

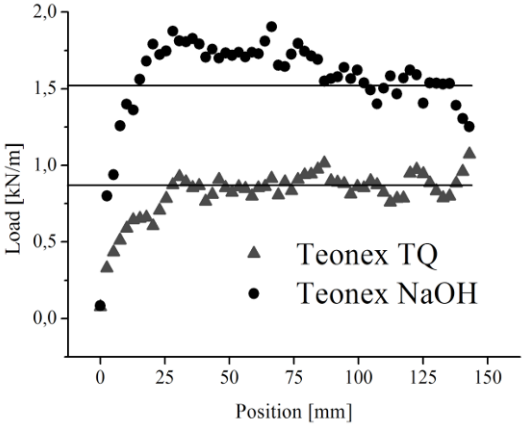


Figure 7. T-Peel test curve of Teonex™ sample.

Dispersion force and polar components are indicated respectively by superscript d and p. From the Young equation it follows that:

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (6)$$

In order to obtain γ_s^d and γ_s^p of a solid, CA data for a minimum of two known liquids are required (polar and non-polar).

The analysis revealed that a reduction of water CA and an increase of diiodomethane CA was accompanied by an increase in the γ_s^p components; consequently, after NaOH treatment the SFE of the solid increases (Table 5).

It has been also observed that the hydrolysis treatment increases the polarity (P_s) of all polyesters (Table 5):

$$P_S = \frac{\gamma_S^p}{\gamma_S} \quad (7)$$

Mylar™ exhibits the greatest polarity increase after surface modification attributable to the formation of a higher number of polar OH groups.

3.7. T-peel test of adhesion

To test the effect of surface treatment of the polymeric substrates a T-Peel test of adhesion has been carried out by using polyurethane adhesive as a probe: the N=C=O group of Polurene is highly reactive with the OH group of treated polyesters with the formation of an urethane linkage, therefore an increase of adhesion strength using this thermoset material should imply an increase in the amount of surface OH groups.

T-Peel values are recorded in force per unit of width [kN m^{-1}] of the bonded specimen. They tend to fluctuate more than any other adhesive test result because of the extremely small area at which the stress is localized during loading. A load curve of the T-peel test for treated and untreated Teonex™ samples are shown in Fig. 7. T-Peel strength is taken as the average value of the centre portion of the curve.

Table 6 shows the average values of T-peel strength [kN m^{-1}].

It was not possible to measure the T-Peel strength of AryLite™ film because ethyl acetate is present into the polyurethane adhesive. Even if ethyl acetate is a weak solvent for the amorphous AryLite™, the substrates are slightly deformed when they are glued and, as a consequence, AryLite™ samples break during the test of adhesion.

The T-Peel strengths for Teonex™ and Mylar™ modified by NaOH treatment are respectively 2.2 and 1.8 times higher than that for the unmodified films.

These comparisons show that the surface modification of the polyester films with the hydrolysis

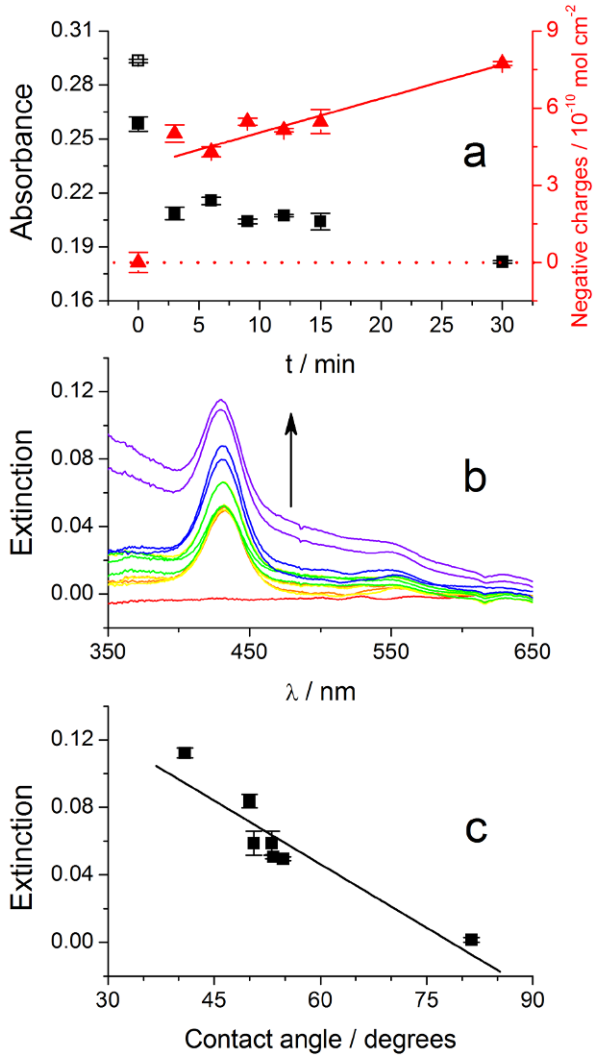


Figure 8. (a) UV/vis absorption at 425 nm of buffered CuT_4 solutions after Mylar™ soaking vs. Mylar™ hydrolysis time (filled squares, left Y axis; empty square: absorption of the reference solution), and the corresponding values of carboxylate densities expressed as moles of negative charges per unit surface (triangles, right Y axis) slope = (3.7 +/- 0.3)×10^{10} mol cm^{-2} min^{-1}; intercept = (1.3 +/- 0.1)×10^{11} mol cm^{-2}; R^2 = 0.95 (b) UV/Vis extinction spectra of the Mylar™ films after soaking in the porphyrin solutions, the arrow indicating the increase in Mylar™ hydrolysis time. (c) Corrected UV/vis extinction at 429 nm of Mylar™ films after soaking in CuT_4 solutions vs. films contact angle; slope = (-2.51 +/- 0.4)×10^3 deg^{-1}; intercept = (0.20 +/- 0.02); R^2 = 0.84.

reactions is effective in improving the adhesion between polyurethane and polyester.

3.8. Determination of carboxylate surface density

To obtain an estimate of the efficacy of hydrolysis as wet chemical treatment to change the functional groups at the surface of the polyester films, a supramolecular approach has been selected for its simplicity and sensitivity. The general idea consists of soaking a treated polyester film, Mylar™ having been chosen as a model system, in a solution of a suitable dye able to interact non-covalently with the hydrolyzed surface and to yield a new observable for determining the amount of carboxy functions formed upon NaOH treatment.

In this framework, the porphyrin derivative tetra(N-methyl-pyridinium-4-yl)porphyrinato copper(II) (CuT_4, Fig. 2) has been chosen as a dye probe to report the surface density of carboxylate groups through light absorption in the visible range. The UV/Vis spectrum of CuT_4 solutions in water presents a very strong absorption band around 426 nm, having an extinction coefficient of around 10^5 M^{-1} cm^{-1}, accompanied by two weaker features at longer wavelengths.

Besides that for its good photophysical properties, CuT_4 has been selected because its four pH-independent positive charges make it suitable for the ionic self-assembly with the negatively charged groups formed at the surface of the polyesters films upon hydrolysis. As well, the presence of the coordinated copper(II) ion prevents any pH dependent protonation of the N atoms at the macrocycle core, reducing the number of interferences in the spectroscopic data and allowing to fully exploit the good photophysical properties of this dye, leading to a method of high sensitivity.

This method works under the assumption that (i) at a pH ~ 9 every carboxy groups at the film surface is deprotonated, *i.e.*, it is negatively charged, and (ii) all the negative charges at surface will be saturated by the positive ones belonging to the porphyrins that spontaneously absorb onto the polymeric film.

This approach has been applied to various Mylar™ samples previously treated with NaOH, to verify the possibility to exert a control on the extent of surface functionalization simply by changing the hydrolysis time. On comparing the absorbance of the starting CuT_4 solution (Fig. 8a, empty square; λ = 426 nm) to that of the aliquots where the hydrolyzed films have been soaked in (Fig. 8a, filled squares; λ = 426 nm), it is possible to notice that the longer the chemical treatment on a given film, the smaller the absorbance of the corresponding aliquot. The amount of dye absorbed on the various films due to ionic self-assembly can then be calculated from these differences, after eliminating the contribution to the surface binding of CuT_4 given by nonspecific interaction, which in turn, can be determined from the porphyrin solutions where untreated Mylar™ samples had been immersed (Fig. 8a, data at t=0 s). Once the volume of each aliquot (3.5 mL) and the surface of each polyester sample (6 cm^2) has been taken into account, the surface density of carboxylate groups can be calculated obtaining a linear increase of this value

upon increasing the hydrolysis time, up to a value of 8×10^{-10} moles of negative charges per unit surface (Fig. 8a, triangles).

In agreement with the above-reported results, the UV/Vis absorption spectra of the hydrolyzed films after immersion into the CuT_4 solutions for several hours (and subsequent thorough rinsing) show features typical of the chromophore in use (Fig. 8b). The main band is centered at 430 nm and it is slightly red-shifted ($\Delta\lambda$ = + 4 nm) as compared to its position in solution, pointing to the presence of an interaction between dye and surface that does not cause any distortion to the porphyrin molecular structure [30]. As well, the intensity of this band, namely the dye loading on the polymeric surface, increases upon increasing the time of chemical treatment applied to the various Mylar™ samples. In agreement with the proposed model, the dye loading of the polyester films shows a linear dependence with respect to their water contact angle (Fig. 8c), confirming that the increase in hydrophilicity of the samples can be directly linked to the increase in the density of hydrolyzed ester groups at surface.

4. Conclusions

Different polyester films have been treated with strong alkali solutions to enhance their adhesion characteristics, the best experimental conditions being 75°C and 30 minutes immersion in 4.5 M NaOH. Under these conditions the surfaces have shown the lowest water contact angle, as well as no significant weight loss or damage of their optical properties, even though some additional experiments should be carried out to overcome the chemical resistance of some target polymers, as in the case of Arylite™ which have displayed only slight surface modification upon hydrolysis.

The presence of carboxy and hydroxy groups introduced on surface by hydrolysis has been detected by FTIR-ATR analysis, with a significant increase of surface polarity for Mylar and Teonex substrates as confirmed through contact angle measurements. Topography measurements have confirmed an increase in roughness after chemical treatment of the samples surfaces. T-Peel data obtained by means of a polyurethane adhesive show an increase of adhesion strength after NaOH treatment, and the improvement of adhesion with this probe thermoset can be attributed to both the increased polarity and to an increase in surface roughness due to the surface modification. Finally, a quantitative estimate of the surface density of the carboxylate groups has been obtained though a supramolecular approach consisting in the ionic self-assembly of a cationic porphyrin chromophore on the negatively-charged surface of the hydrolyzed polyester films.

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