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Effect of the corona treatment and of the 1,4-cyclohexanedimethanol on the surface characteristics of the Poly(ethylene terephthalate) film

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SUMMARY: Several techniques have been applied for the characterization of three PET films surfaces: homopolymer PET film, corona treated PET film and a poly(ethylene terephthalate-co-1,4-cyclohexanedimethanol) film. The objective of this work is to investigate and to apply precise and mutually complementary techniques which give detailled information about theses surfaces, as there are few papers with global and conclusive results. The film surfaces were investigated to support the development of new products and envisage new apllications to the existent films.

Scanning electron micrographs, attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR) and multiple internal reflection Fourier transform infrared spectroscopy (FTIR-MIR) spectra show that the chemical composition, topography and surface roughness of the films are different. The corona-treated PET film shows high surface tension value due to the major contribution on the polar groups and oxidation level acquired. The copolyester film is much less crystalline than the other films analyzed, as demonstrated by refractive index measurements and X-ray photoelectron spectroscopy (XPS). The amorphous structures obtained and the high tension level of the corona-treated films provide a better understanding of the adhesion phenomena.

In view of results obtained, one can assume that corona treated films owing to its higher surface tension and films with CHDM owing to its surface amorphization should provide manufacturing industries better processing conditions than films without surface treatment and also higher levels of adhesion to paints and coatings.

Introduction

The annual PET films word production is approximately 1 million tons. This huge amount is due to the great diversity of their different uses which include magnetic films, capacitors, printed circuits, photographic films and flexible packagings. Among these films there are PET homopolymer surfaces, copolymers surfaces and surfaces which receive treatments to modify their superficial characteristics $^{1)}$. PET films have a high rupture resistance, good dimensional stability, high transparency level, flexibility, excelent electric properties and a good retention of physical properties in the range between 70 to 150°C.

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The PET film without surface treatment makes the printing process very difficult due to the low number of polar groups which take part in the necessary links in the adhesion of the coating and its high crystallinity which hinders the penetration of the ink in the polymeric surface. According to Sapieha e. a. [2)], Owens e. a. [3)], Briggs e. a. [4)] and Leclercq e. a [5)] plasma treatment in surface films, contribute to the adhesion phenomena, enhancing the concentration of superficial polar groups. Therefore, the films should to be submitted to treatments such as, the corona treatment, one of the most used plasma treatments and can also be coextruded with other polymers capable to reduce the crystallinity [1,6)].

In the present study three types of PET films with 12 μm thickness and different surface characteristics were analyzed. The techniques were choosen in order to characterize the main physical and chemical properties, based on suggestions given by several authors: to analyze the chemical composition of the surfaces of the different films, FTIR-ATR [7,8)], FTIR-MIR [9)] and XPS [10)] were used. To evaluate the morphologic state and the degree of molecular orientation, refractometry [11)] was choosen; to analyse the surface topography, SEM [12)] and friction factor determination were used. Wettability [13)] of the film surfaces was evaluated by contact angles using conventional liquids.

Experimental

Materials

All the analysed PET films were made by Terphane Ltda (Cabo-Pernambuco,Brazil). The film production process basically consisted of dry extrusion, quenching, biaxially drawn, winding and cutting. The A film has no superficial treatment and the B film has one of its faces treated by eletric corona discharge with a normalized energy of 20 J/cm^2. The superficial treatment was done immediately after the drawing process and directly before winding. The C film was obtained by coextrusion and has a 11.6 μm layer of PET homopolyester and a second layer of 0.4 μm of poly(ethylene-co-cyclohexanedimethanol terephthalate). The compositon of this copolymer layer is 84.6 % T monomer and 15.4 % C comonomer random inserted in the PET chain:

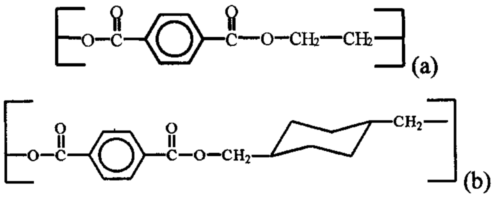

Figure 1. Chemical structures of C film: (a) T monomer; (b) C comonomer.

Methods

FTIR-ATR equipment used to identify the functional groups on the film surfaces was Brukker, model IFS66. The accessory to measure the total attenuated reflexion was a ZnSe crystal with the refractive index = 2.4 and the 45° incidence angle of radiation in relation to the sample. Each sample measured 1.4 cm corresponding to the size of the crystal. At these experimental conditions, the analysed superficial depth was in the range of 4 μm to 700 cm^{-1} and 0.9 μm to 3000 cm^{-1}. For comparative reasons, FTIR-MIR analysis was performed with a Perkin-Elmer spectrometer model 1720. The X-ray photoelectron spectroscopy (XPS) analysis were made with a Kratos Analytical equipment, XSAM HS model, under ultra high vacuum (in the range from 5.10^{-7} to 10^{-6} Pa) and a magnesium Kα radiation with $h\nu$ = 1253.6 ev and the power of 150 W (emission of 10 mA and 15 kV).

The refractive index data were obtained using an Abbe digital refractometer made by Leica, Mark/Reichert Jung. The analysis were made in the x, y, z directions. From each film (A, B, C) six probes were taken and the methodology defined by one of us 14) followed.

The contact angle analysis is based on *sessile drop method* described by Garbassi e. a.15). A Ramé-Hart goniometer model 100-00 was equiped with a 100-15 accessory for plastic films. The liquids employed were α-bromonaphthalene as the apolar liquid and distilled and deionized water as the polar liquid. The data of the respective liquids are listed in Table 1:

Table 1: Dispersive and polar components of water and α-bromonaphthalene.

Properties / liquids	γ_L^d/(mN/m)	γ_L^p/(mN/m)
α-bromonaphthalene	44.6	0
water	21.6	51

The drop volume was mantained constant at 4 µL to eliminate gravitational effects 16) and the measurement time less than 30 s in order to reach equilibrium 17) and avoid evaporation 18). The room temperature was mantained in the range from 23 to 26°C. From each film type two samples with the dimensions 10.10 cm were taken. For each liquid and each sample, the measurement was repeated ten times. The base inclination angle for measures of advance and retreat angles was 50°.

The surface tension of a solid γ_s is defined by the contact angles (θ_1 and θ_2) for two different liquids, as defined by the Young equations used by Fowkes 19) and Good 20), where γ_{L1} and γ_{L2} are the surface tensions of liquid 1 and 2 while γ_s^d and γ_s^p the dispersive and polar components respectively:

$$\gamma_{L1}\,(1 + \cos\theta_1) = 2\,(\gamma_s{}^d\gamma_{L1}{}^d)^{1/2} + 2\,(\gamma_s{}^p\gamma_{L1}{}^p)^{1/2} \quad (1)$$

$$\gamma_{L2}\,(1 + \cos\theta_2) = 2\,(\gamma_s{}^d\gamma_{L2}{}^d)^{1/2} + 2\,(\gamma_s{}^p\gamma_{L2}{}^p)^{1/2} \quad (2)$$

$$\gamma_s = \gamma_s^d + \gamma_s{}^p \quad (3)$$

For micrographs a scanning electron microscope was used (JEOL model JSM-T200), with the magnification from 200 to 15000 times 21).

Results and discussion

Spectrograms obtained lead to the identification of the chemical composition of the film surfaces investigated. This is extremely important for the understanding of phenomena of adhesion to paints and coatings, as these groups participate in interactions between such materials. Figure 2 shows spectrograms obtained by FTIR-ATR of the films with and without treatment. The spectrograms are typical for PET and they present its main characteristics: C-H bonds (848 cm^{-1}), ether (1095 cm^{-1}), ester (1240 cm^{-1}) and ketone (1716 cm^{-1}). Besides these, we have also detected the reference band of PET (1410 cm^{-1}), that is assigned to the C-H aromatic ring vibration. The crystallinity band in PET can be identified at 1340 cm^{-1},which is associated both with a *trans* conformation of oxygen atoms in the glycol segment ($-O-CH_2-CH_2-O-$) and a *trans* planar conformation of the terephthalate residue of the polymer repeat unit 22). The *trans* isomer is found in the fully extended polymeric chain and it is related to the crystalline state. It may be present also in amorphous state.

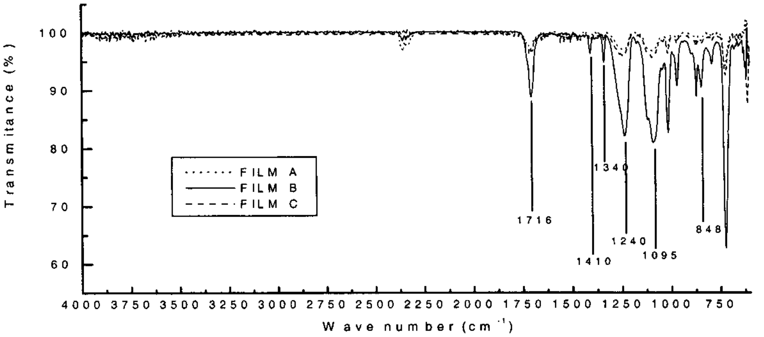

Figure 2 : Spectrograms by FTIR-ATR of A, B and C films.

Carbonyls of ester (O=C-O-) and ether (-CH_2-O-) found in the spectrograms of films under analysis were present in the typical structures of these ethers; they may be caused by oxydation process of the free radical type [4]. A and C films always produced the same spectrograms while spectrograms of B film exhibit 5 cm^{-1} deviations which, although falling within the accepted range, still constitute oscillation of bands in relation to film A. Our spectrograms are different from those found by Briggs e. a. [4] but similar to the results of ATR obtained by Chen & Carthy [8]. The latter confirm that chemically treated PET films produce spectrograms equal to those of films without treatment.

Spectrograms found by MIR from our films are similar to those observed by FTIR-ATR. In the case of C film, a new attribute was discovered at 1452 cm^{-1} related to CHDM: the inclusion of this group in the homopolymer produces an ester that increases the amorphous state of the surface [14].

From the XPS spectrograms of A, B and C films with high resolution in energy, we have calculated the atomic ratios O/C, which are listed in Table 3. It may be inferred from the Table 3 that the atomic ratios of A and B films are similar; the differences between them are below 5 %, similar to those reported by Strobel and coworkers [23]. Moreover, one finds that the C film was the lowest concentration of oxygen among the three films (O/C = 0.36); this confirms the inclusion of CHDM, a group formed only by C and H; see Figure 3.

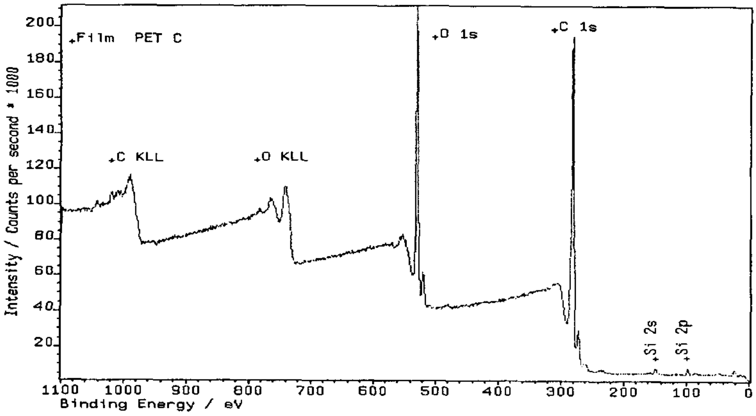

Figure 3: Spectrogram by XPS of C film

Results achieved from experiments with the B film are similar to those reported by Turner e. a. [24)]. According to them, PET films irradiated by excimer laser contain aromatic carbons (present in benzenic rings) and also carbons present in ether bonds. This increases the surface tension and enhances their wettability. O/C atomic ratios found by Wallace e. a. [10)] turned out to be quite similar to ours.

Our results agree with those at Briggs [4)] and Strobel [23)] who reported an increase of oxydation of corona-treated films by their of O/C atomic ratios. They detected a substantial aging process in corona-treated PET films over a period of one month. We infer that the oxydation losses occurred may be a result of the migration of oxydation functions to regions beyond the area shown by XPS towards the interior of the film.The individual and averages refraction indices plus the crystallinity of A, B and C films are listed in Table 2.

Table 2: Refractive indices and other characteristics of A, B and C films.

Parameters	Film A	film B	film C
n_1	1.6694 ± 0.0003	1.6692 ± 0.0017	1.4978 ±0.0004
n_2	1.6508 ± 0.0008	1.6494 ± 0.0017	1.4990 ± 0.0006
n_3	1.4984 ± 0.0005	1.4978 ± 0.0003	1.4982 ±0.0008
N	1.6062	1.6054	1.4983
X / (%)	47.19	45.93	-

According to Table 2, in C film the three refraction indices are identical, what proves the absence of preferencial orientations and the amorphous nature of the copolyester. The amorphous nature and the low viscosity of the layer at sealing temperatures are the most influential variables in the production of highly resistant joints. Moreover, the adhesion of paints used in printing is greatly benefitted by amorphous surfaces with a large accessible volume and reduced if any crystallization velocity 25).

Also according to Table 2, A and B films present n_1 values exceeding those of n_2 and n_3, indicating a higher orientation in the final stretching of the film (transverse direction). On the other hand, the n_3 values of the three films are virtually identical. The least value of N (the average refractive index) of the C film indicates the lowest level of orientation among the three films.

Table 2 also shows the crystallinity X of A, B and C films calculated from Eq. (4) assigning to the PET film N_a=1.5769 and N_c=1.6319 26):

$$X\,(\%) = (1820\,N - 2870) \qquad (4)$$

The crystallinity obtained from the refractive indices must be treated with some care. With regard to the morphology, taking into account the crystallinity values, we find that the C film is less crystalline than the A and B films; this may be explained by the presence of the CHDM groups in the copolyester. The result is an amorphous composition of the external layer of the C film. It was also found that the corona-treated B film is less crystalline than the A film; the explanation lies in the assumption that it is similar to the amorphization created by an excimer laser 21,27). These studies based is spectroscopy in reflexion absorption infrared (IRRAS) and in XPS indicate that the radiation converts a large fraction of crystalline regions in the film into amorphous ones.

Taking into account the contact angle measured at the equilibrium point between A, B and C films and the reference liquids α-bromonaphthalene (θ_2) and destilled deionized water (θ_1), also considering smooth, homogeneous, perfectly flat and non-deformable films, calculations were made using Eqs. (5) and (6) of the dispersive γ_s^d and polar γ_s^p constituents of the surface tension. By adding the dispersive and polar factors one arrives at the total surface tension γ_s^T of each film:

$$\gamma_{L1}\,(1 + \cos\theta_1) = 2\,(\gamma_s^d\gamma_{L1}^d)^{1/2} + 2\,(\gamma_s^p\gamma_{L1}^p)^{1/2} \qquad (5)$$

$$\gamma_{L2}\,(1 + \cos\theta_2) = 2\,(\gamma_s^d\gamma_{L2}^d)^{1/2} + 2\,(\gamma_s^p\gamma_{L2}^p)^{1/2} \qquad (6)$$

The results are listed in Table 3.

Table 3: Partial and total values of surface tension of A, B and C films.

films	γ_s^p/(mN/m)	γ_s^d/(mN/m)	γ_s^T/(mN/m)
film A	5.97 ± 0.15	43.87 ± 0.06	49.84 ± 0.06
film B	9.07 ± 0.74	43.90 ± 0.06	52.97 ± 0.71
film C	6.27 ± 0.21	43.83 ± 0.06	50.10 ± 0.12

Each value listed above corresponds to the average of 30 experiments. Among the films analyzed, the B film presents the highest value of the total surface tension. We infer that the corona treatment introduces hydrophylic specimens (carbonyls and carboxyls, for example) which cause alteration in the polar component 5).

From the differences between the angles of advance and retreat (Table 4), one can assume that the corona treatment causes lowering of these angles, enhancing at the same time the differences between them and therefore amplifying the histeresis. Moreover, the corona treatment causes roughening of heteregeneous surfaces; the advance and retreat angles differ substantially between themselves and their values are lower than those for films without treatment 23). Furthermore, one should take into account that the reduction of the retreat angle of the B film enhances the wettability and hence the adhesion to the surface. This justifies, therefore, the use of the corona treatment for surfaces of polymeric films used in printing.

Table 4: Advance and retreat angles of A and B films.

films	Advance water angle/(°)	Retreat water angle/(°)	Histeresis
film A	69.35 ± 0.88	67.70 ± 0.59	1.65
film B	61.67 ± 2.72	59.68 ± 2.72	1.99

The SEM results which we show in Figures 4 to 6 exhibit differences among the three films under analysis. The film that received the corona treatment presents a slight increase in the surface roughness as compared to the film without treatment; the corona treatment leads to the formation of pores and holes 5). These results also agree with those of Strobel e. a. 12) who asserted that the corona treatment increases substantially the roughness of the polymer in high relative humidity (> 50%) and for energies above 1,7 J/cm^2. However, this change in the topography does not produce any increase of the film wettability; the latter depends on the introduction of polar specimens.

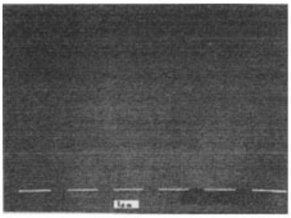

Figure 4: Scanning electron micrograph of A film

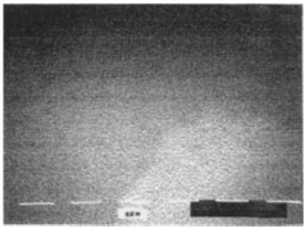

Figure 5: Scanning electron micrograph of B film

Micrographs of A, B and C films enlarged 200 times, show the existence of nearly spherical particles of the mineral filler (SiO_2) used in the production of films; this was confirmed by XPS.

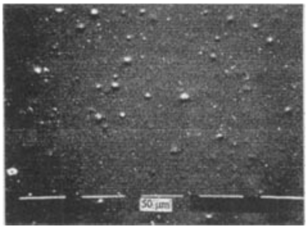

Figure 6: Scanning electron micrograph of C film

Static and dynamic friction coefficients (COF) of A, B and C films can be found in Table 5. In the case of the B film, the highest values of both kinds of COFs found are due to a higher concentration of polar groups in the surface of the film; this leads to dipolar type interactions between the slipping surfaces.

Table 5: Static and dynamic coefficients of A, B and C films.

	film A	film B	film C
static COF	0.525 ± 0.022	0.561 ± 0.034	0.517 ± 0.023
dynamic COF	0.386 ± 0.018	0.404 ± 0.021	0.390 ± 0.019

Conclusion

Results suggests that the film with copolymer is less oxydized than the other ones and it has the lowest crystalline state. From others results, we can conclude that the corona-treated film is less crystalline than the film without treatment, more heterogeneous, and has the highest roughness and surface tension. In view of the described results, we conclude that treated films should provide better physical and chemical conditions of adhesion to paints and coatings.

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