Pretreatment of Polypropylene Films for the Creation of Thin Polymer Layers, Part 1: The Use of Chemical, Electrochemical, and UV Methods

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ABSTRACT: The surface of a polypropylene (PP) film was activated with chemical, electrochemical, and physical methods, and the effectiveness of these methods was compared. The effects of PP activation were assessed with attenuated total reflection IR spectroscopy (ATR-IR), SEM microscopy, and an analysis, based on the liquid contact angle, of the free energy components of the surface. The activation of the PP surface, which was dependent on the oxidizing medium, increased the energy of the PP surface layer and formed new chemical (carbonyl) groups, which were identified by IR (ATR) absorption spectroscopy and confirmed by selective surface dyeing. The treatments were ranked in the following order of increasing effectiveness: UV irradiation $<$ 3M nitric acid $<$ 30% hydrogen peroxide $<$ silver nitrate (electrochemical method) $<$ chromic mixture. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2071–2080, 2011

Key words: polypropylene; films; electrochemistry; UV irradiation; chemical activation

INTRODUCTION

Polypropylene (PP) materials are increasingly common substrates in the manufacture of new functional products. They are elastic, light, high-performance, and chemically resistant substrates[1] on which one can deposit thin organic or inorganic functional layers with, for example, optical, electroconductive, hydrophilic, and oleophobic properties. During deposition, layers begin to form at nucleation centers on the substrate surface where active chemical groups (e.g., polar groups and radicals) are located. However, pure PP substrates have no polar groups because of their chemical structure.[1] Polar groups can be formed before deposition during surface pretreatment. This step typically consists of oxidizing the top polymer layer.[2] This process is performed with oxidizers in chemical[3–7] and electrochemical[8] methods or in a plasma medium.[9–14] The UV component of sunlight can also oxidize polymers.[15–18] The extensive variety of pretreatment methods ensures the selection and adaptation of an appropriate procedure for the specific form of deposition (chemical,[19,20] electrochemical,[21,22] and plasma[23,24] methods).

A substantial amount of research has focused on PP surface activation, but few comparative studies have been conducted to inform the selection of effective and suitable pretreatment methods for certain deposition processes.

The objective of this research was to compare chemical, electrochemical, and physical methods for stimulating the formation of active centers in the PP top layer. The active centers formed by the pretreatment processes were examined with IR-TR absorption spectroscopy and selective surface dyeing. Changes, caused by the active centers, in the free energy of the PP surface and its polar and dispersive components were assessed on the basis of contact angle measurements and the use of test liquids.

The tests were performed for two PP films with different physical microstructures: a noncrystalline, nonorientated film and a crystalline, bidirectionally oriented film.

Part 1 presents the results of the PP surface pretreatments with chemical, electrochemical and UV irradiation methods. Part 2 will describe the results of the pretreatment with a low-temperature RF plasma medium.

EXPERIMENTAL

Materials

Two commercially available, transparent PP films with no antiphotooxidation additives (Petrochemia

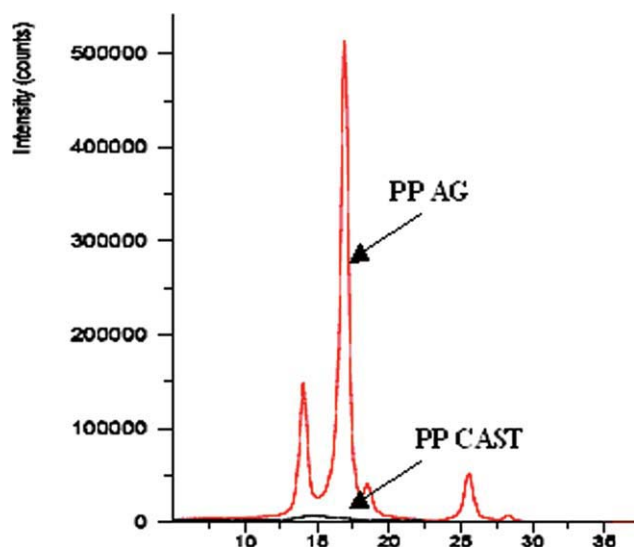*Correspondence to:* W. Urbaniak-Domagala (wurbando@p. lodz.pl).

Figure 1 X-ray diffraction diagram of commercial PP films before oxidation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Płock S.A.) were used: (1) a nonoriented PP film (CAST), with a nominal thickness of 30 μm, a density of 0.89 g/cm^3, a softening point of 152°C, and birefringence coefficients of $\Delta n_\alpha = 0$ and $\Delta n_\beta = 0$ and (2) a bidirectionally oriented PP film (AG), with no weldable layers and a nominal thickness of 30 μm, a density of 0.91 g/cm^3, a softening point of 166°C, and birefringence coefficients of $\Delta n_\alpha = 0.151$ and $\Delta n_\beta = -0.0145$. The PP AG films had a higher percentage of the crystalline phase ($x = 45\%$) than did the PP CAST film ($x = 0\%$; Figure 1). The PP samples were preliminarily purified by methanol extraction.

The following reagents were used: analytically pure (a.p.) potassium dichromate [Polskie Odczynniki Chemiczne S.A. (POCh S.A.)], a.p. sulfuric acid (POCh S.A.), a.p. nitric acid (POCh S.A.), hydrogen peroxide (POCh. S.A.), a.p. silver nitrate (POCh S.A.), methylene iodide (Fluka Chemika), and α-bromonaphthalene (Fluka Chemika).

Modification of PP film

Chemical modification

Chemical modification of the PP films was performed by strong oxidizing compounds, such as 3M nitric acid, 30% hydrogen peroxide, and a saturated solution of potassium dichromate in 70% sulfuric acid ($K_2Cr_2O_7 + H_2SO_4$) without preliminary activation with unsaturated oil.[7] The padding method was used to treat PP under various conditions of time and temperature. PP modification with nitric acid was performed at room temperature for 0.5, 1, or 24 h, while modification with the $K_2Cr_2O_7 + H_2SO_4$ solution was conducted at 20 and 70°C for 1, 3, or 5 min. PP modi-

fication with the 30% aqueous solution of hydrogen peroxide was conducted at room temperature for 0.5 and 1 h. Modified samples were rinsed repeatedly with distilled water to remove residues of the oxidizing solution and oxidation products.

Electrochemical modification

Figure 2 shows the system in which PP was electrochemically modified. An electrolyzer with two 100-mL chambers separated by a membrane was constructed (Figure 2). In the chambers, platinum electrode plates with dimensions of 3×5 cm^2 were positioned. The anolyte was $AgNO_3$ solution (0.5 mol/dm^3) in nitric acid with a concentration of 3 mol/dm^3, and the catholyte was nitric acid with the same concentration.[8] A PP film spread on a Teflon frame was placed in the anolyte near the anode. Electrolysis was conducted under controlled voltage and intensity conditions using a Unitra supply unit. To optimize PP treatment, the intensity of the current in relation to the electrode area was changed from 50 to 100 mA/cm^2, and the time of the anolyte-sample interaction was increased from 5 to 30 min.

Physical method

To physically modify the PP, a film sample was irradiated under specified conditions of temperature and relative air humidity (RH) using a Xenotest 450 apparatus (Original Hanau Heraeus GmbH). To simulate sunlight-induced aging, a light with spectral characteristics consistent with standardized global solar radiation in the range from 310 to 800 nm was used.[25] PP film samples were irradiated at an ambient temperature of 20°C and a RH of 75% for 20 to 170 h.

Test methods

Examination of the PP crystalline phase

The super molecular structures of the PP films were investigated with the wide angle X-ray scattering
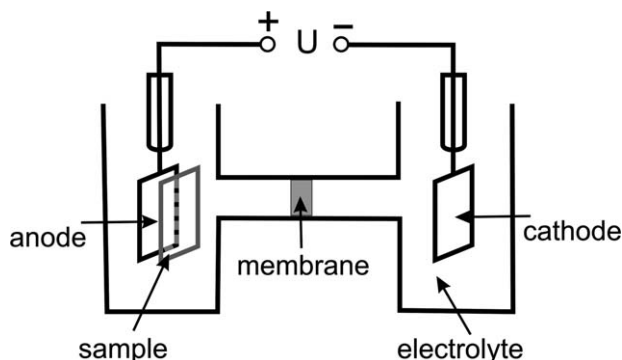

Figure 2 System for electrochemical treatment of polymers.

method, using an X'Pert PRO diffractometer (PANalytical; CuKα, λ = 0.154 nm). The working parameters of the X-ray tube were U = 40 kV and I_A = 30 mA.

The diffraction patterns enabled estimation of the degree of crystallinity (X_C; i.e., the prevalence of the crystalline phase in the films). The WAXSFIT software,[26] which is based on the Hindeleh–Johnson method, was used to determine the degree of crystallinity according to the following formula: $X_C = A_C/(A_a + A_C)$, where A_C is the field of identified peaks in the diffraction pattern of the crystalline substance, and A_a is the field of the surface of the amorphous background.

Examination of the chemical structure of the PP surface with ATR-IR spectroscopy

The PP film surface was analyzed with the ATR-IR technique, using a KRS-5 crystal and an FTIR-8300 spectrophotometer. IR spectra were recorded as a function of absorbance in the range from 400 to 4000 cm^{-1}.

Electron microscopic examination of PP film surface

The film surface was observed with a JSM-5200 LV electron microscope (JEOL, Japan), using a secondary electron detector. Before observation, a JFC-1200 JEOL magnetron duster was used to dust the film surfaces with gold. Samples were tested in a vacuum using an accelerating voltage of 15–25 kV.

Changes in the free energy of the PP film surface

The surface tension of the PP film, as measured by the free energy of the surface, was determined on the basis of the advancing angle, Θ, of the liquid deposited on the film surface. Liquids with specified surface tension properties (dispersive component, γ_d, and polar component, γ_p^2) were used. The test mixture was composed of distilled water (γ_d = 21.8 mN/m^2 and γ_p = 51.0 mN/m^2), α-bromonaphthalene (γ_d = 44.4 mN/m^2 and γ_p = 0), and methylene iodide (γ_d = 49.5 mN/m^2 and γ_p = 1.3 mN/m^2).

The advancing angle was tested with the sessile drop method. Liquid drops with a constant volume of 1 µL were deposited on the sample surface with a microsyringe. Drop images were recorded with a CCD camera with PAL resolution (768 × 576 pixels) equipped with a panchromatic 2.5× lens. The images from the CCD camera were sent as a CVBS signal to a PC (IndeoFast Y/C) and analyzed with the MultiScanBase software. Based on the image of the drop meniscus, the advancing angle was determined numerically.[27] Using the advancing angle values of the polar and dispersive liquids, the dis-

persive, γ_d^f, and polar, γ_p^f, free energy components of the surface were calculated according to the Owens-Wendt procedure[28] (eqs. (1) and (2)):

$$\gamma^{c_1} \cdot (1 + \cos\theta_1) = 2 \cdot \sqrt{\gamma_p^f} \cdot \gamma_p^{c_1} + 2 \cdot \sqrt{\gamma_d^f} \cdot \gamma_d^{c_1} \quad (1)$$

$$\gamma^{c_2} \cdot (1 + \cos\theta_2) = 2 \cdot \sqrt{\gamma_p^f} \cdot \gamma_p^{c_2} + 2 \cdot \sqrt{\gamma_d^f} \cdot \gamma_d^{c_2} \quad (2)$$

where γ_d^{c1} and γ_d^{c2} are the surface tensions of liquids 1 and 2, respectively; γ_d^f and γ_p^f are the dispersive and polar components of the surface free energy of the film; γ_d^c and γ_p^c are the dispersive and polar components of the surface tension of the liquid; and θ_1 and θ_2 are the contact angles of liquids 1 and 2, respectively.

Testing the density of active centers on the film surface

The prevalence of active centers on the film surface was tested by selective dyeing.[29] A cationic dye, Astrazon-Blue-BG (Bayer) known as C.I. Basic-Blue-3, was used. Samples were dyed in a 0.1% dye solution for 20 min at room temperature and a pH of $\sim$ 7. Dyed samples were carefully rinsed with distilled water, and dye was extracted from the samples with acetone until the color had disappeared. The dye content was determined with the photometric method using a Specol 2000 apparatus. Assuming that the dye combined exclusively with the active centers on the film surface, the number of moles of combined dye was used as a quantitative index of the centers. Assuming uniform distribution of dye molecules on the film surface, the density of active centers, G, was calculated according to G = (number of dye moles × N)/2S (n/nm^2), where n is the number of centers, S is the sample surface area, and N is Avogadro's number.

RESULTS AND DISCUSSION

The methods of PP surface modification were optimized to achieve a high density of active centers on the film surface. The effects of treatment time and oxidation energy on the PP surface were considered in this process.

Morphology study

SEM observations indicated virtually no substantial differences in the surface topography of the amorphous and oriented PP films (Figure 3). Oxidation with 3M nitric acid, 30% hydrogen peroxide (chemical methods), silver nitrate (electrochemical method), and UV irradiation did not change the topography of the PP surface. The development of the PP surface
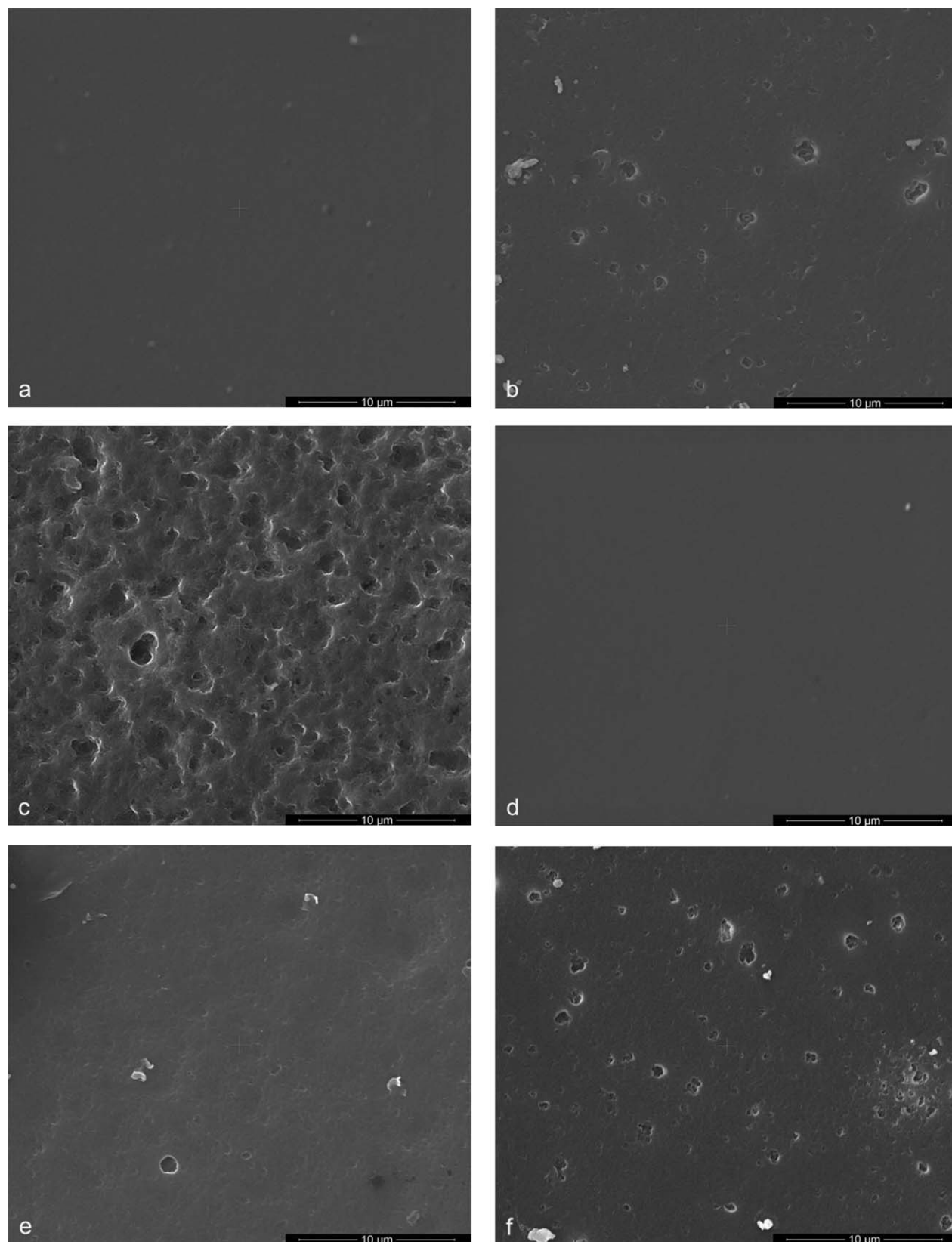
Figure 3 SEM images of an untreated PP surface and modified by the chromic mixture for 3 min. Sample (a) is the untreated PP Cast. Sample (d) is the untreated PP AG. Samples (b)-(c) are PP Cast modified at 70°C (Sample b), at 100°C (Sample (c). Samples (e)-(f) are PP AG modified at 70°C (Sample e), at 100°C (Sample f).

was affected only by the saturated solution of potassium dichromate in 70% sulfuric acid ($K_2Cr_2O_7$ + H_2SO_4). The degree of PP surface development, as determined in the study, increased with increases in the solution temperature and the time of treatment. Figure 3 compares the effects of PP surface modifications performed at 70 and 100°C for 3 min. Chemical etching of the PP surface began at a temperature of 70°C and progressed as the temperature increased. Progression was particularly rapid in the amorphous polymer. Thus, this form of modification should be conducted at temperatures of less than 70°C.

SEM images show that chemical etching of the PP film surface occurred selectively and that pits were formed by local degradation of the polymer. These pits, incidental at the beginning, indicated removal of polymer molecules with a low chemical resistance (considerably amorphous). Unetched areas, which were more resistant to the chromic acid mixture, seemed to have been formed by flexural macromolecules to create defected lamellae. The etching was anisotropic, occurring faster inside the surface layer than on the layer plane. This could have been related to the location of lamellae in the film surface layer. The fragments of macromolecules protruding from the defected lamellae were etched faster than those contained in the oriented lamellae in the film surface layer.[30]

Surface ATR-IR spectra

The selective absorption of IR radiation in the surface layers of the PP film indicated that the oxidizing agents had a significant effect on the chemical structure of the amorphous polymer (CAST PP). In the surface layer of the PP CAST film, a new type of absorption was observed in the range from 1730 to 1680 cm^{-1} (Figure 4). The absorption maximum was slightly shifted in different oxidizing media. For the PP activated with hydrogen peroxide or nitric acid, the maximum absorption occurred at 1700 cm^{-1} (λ = 5.88 μm). The PP activated with nitric acid had a maximum at 1700 cm^{-1} (λ = 5.88 μm), and activation with the chromic mixture or irradiation in the Xenotest produced a maximum at 1702 cm^{-1} (λ = 5.87 μm). The PP surface modified by the electrochemical method did not reveal any new type of absorption. IR absorption from 1730 to 1680 cm^{-1} indicated a newly formed carbonyl group.[31] Many studies have reported that carbonyl group formation in alkanes under the influence of oxidizers is a process of nucleophilic substitution on the tertiary carbon atom. The susceptibility of nucleophilic substitution depends on the carbon order, and the ratio of the susceptibility of tertiary, secondary, and primary carbon is 7000 : 1100 : 1.[32] During intermediate stages of PP oxidation,[32] products were found con-
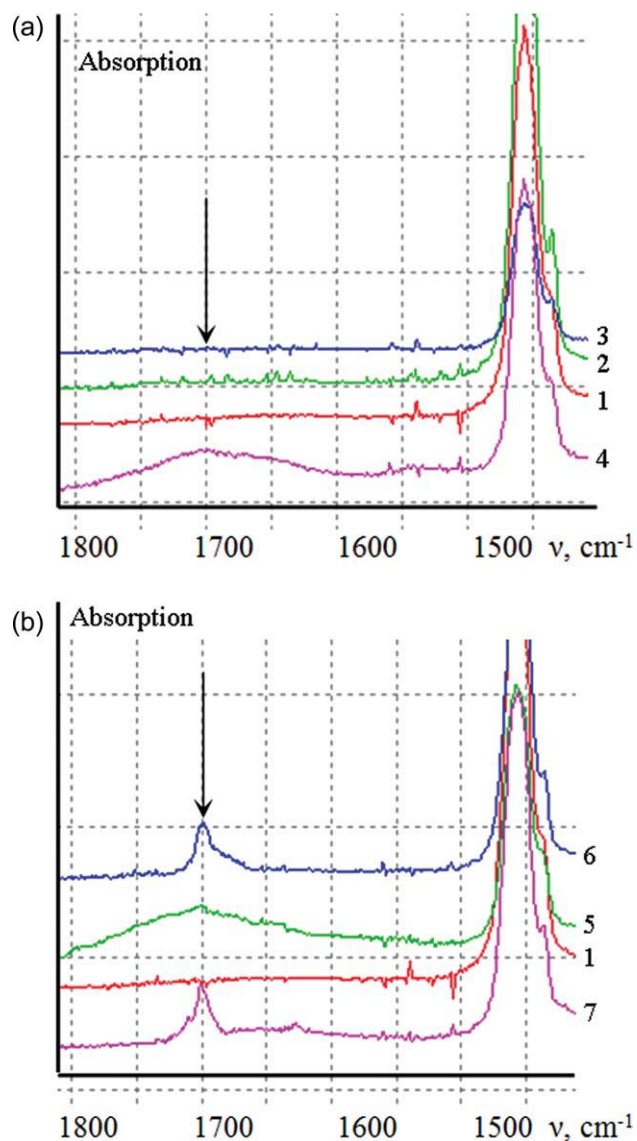

Figure 4 ATR-IR spectra of commercial PP films (a) before and (b) after oxidation. Sample 1 is the untreated PP CAST. Sample 2 is the untreated PP AG. Samples 3–7 are PP CASTs modified with the electrochemical method at a current intensity of 100 mA/cm^2 for 30 min (Sample 3), the Xenotest UV treatment for 170 h (Sample 4), $K_2Cr_2O_7$ + H_2SO_4 solution at 70°C for 3 min (Sample 5), 3M nitric acid at 20°C for 24 h (Sample 6), and 30% hydrogen peroxide at 20°C for 1 h (Sample 7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

taining carbonyl groups in the form of aldehydes and ketones, which show selective absorption in the following bands[33,34]: 1700 cm^{-1} absorption ($>$C = CH—CO—OH), λ = 5.88 μm; 1710 cm^{-1} absorption (—CO—OH), λ = 5.85 μm; 1715 cm^{-1} absorption ($>$C = O), λ = 5.84 μm; 1718 cm^{-1} absorption (—CCH$_3$—CH$_2$—CO—CH$_2$—CH$_3$), λ = 5.82 μm; and 1726 cm^{-1} absorption (—CCH$_3$—CH$_2$—CO—CH$_3$), λ = 5.79 μm. The absorption band in the modified PP surfaces was substantially wide, which could
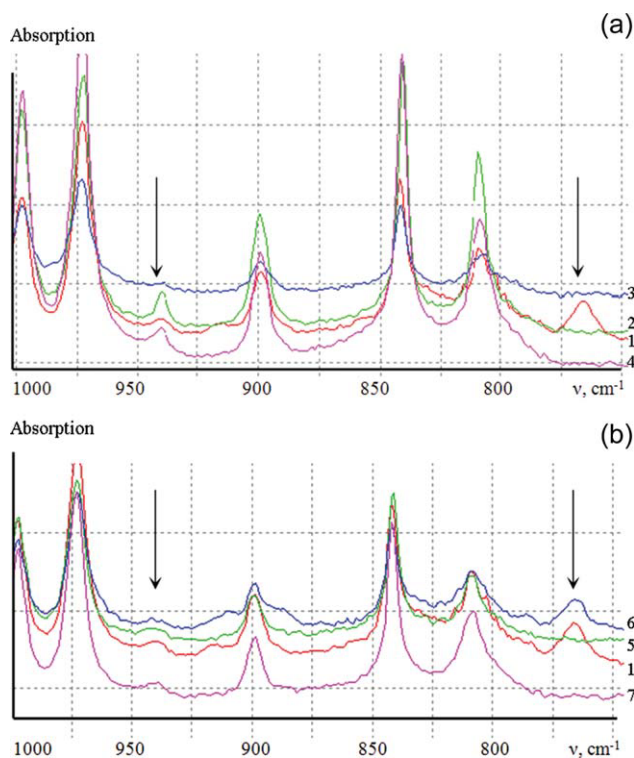
Figure 5 ATR-IR spectra of commercial PP films (a) before and (b) after oxidation. Sample 1 is the untreated PP CAST. Sample 2 is the untreated PP AG. Samples 3–7 are PP CASTs modified with the electrochemical method at a current intensity of 100 mA/cm^2 for 30 min (Sample 3), the Xenotest UV treatment for 170 h (Sample 4), $K_2Cr_2O_7$ + H_2SO_4 solution at 70°C for 3 min (Sample 5), 3M nitric acid at 20°C for 24 h (Sample 6), and 30% hydrogen peroxide at 20°C for 1 h (Sample 7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicate the superposition of the aforementioned bands of chemical groups formed during oxidation.

In addition to the 1700 cm^{-1} band, two other bands were noticeable: one at 940 cm^{-1} (λ = 10.64 µm) and one at 765 cm^{-1} (λ = 13.07 µm; Figure 5). The absorption band at 940 cm^{-1} (λ = 10.64 mm) indicated skeleton vibration of mer links with a relative phase shift of 2/3; this is mainly characteristic of the crystalline phase.[35] This band had a high intensity in the PP AG film and a decreased intensity in PP CAST film, and after oxidation, the surfaces ceased to absorb radiation at this wavelength. The PP seemed to become completely amorphous in the surface layer.

The second absorption band at 765 cm^{-1} (λ = 13.07 µm) indicated deformation (oscillatory) vibration of a methylene group ($-CH_2-$).[31] This absorption was found on the surface of the amorphous PP film and was caused by the presence of a $-CH_2-$ group in the surface layer. After oxidation, the PP surface ceased to absorb radiation at this wavelength. This could have been caused by a reduction in the

number of methylene groups following polymer degradation in the surface layer. This absorption does not appear in crystalline PP because of spherical restrictions caused by the long-range order.

Because of the molecular order and crystallinity of PP AG, no absorption band for the carbonyl group was found with the ATR-IR method. The ATR-IR method was assumed to have a low sensitivity when the concentration of active centers was low.

Active centers

Table I lists the densities of active centers as measured by carbonyl groups on the PP AG and PP CAST surfaces modified by various oxidizing media.

In the selective dyeing, cationic dye was used as a quantitative index of carbonyl groups. These groups can appear in an oxidized form of PP as aldehydic, ketonic, and carboxylic groups. The list of the densities of groups indicates that the susceptibility of PP to oxidation depends on the supermolecular structure of PP, the type of oxidizing medium, and the process conditions. In the chemical oxidation method, the most effective medium was the saturated solution of potassium dichromate in sulfuric acid. The effectiveness of the process increased as the temperature of the medium was increased from 20 to 70°C for a period of up to 3 min. Raising the temperature above 70°C and prolonging oxidation for more than 3 min decreased the number of active centers on the PP surface and fogged the film, indicating the initiation of secondary polymer crystallization. Under optimal process conditions, the density of active centers was found to be ~ 4.6 n/nm^2 on the PP CAST surface and 2.5 n/nm^2 on the PP AG surface.

In the 30% aqueous solution of hydrogen peroxide, optimal active group generation was reached within 0.5 h. Active centers at densities of ~ 1.5 and 1.2 n/nm^2 were observed on the PP CAST and PP AG surfaces, respectively. The immersion of PP in 3M nitric acid produced similar active center densities.

In the electrolytic method, the active oxidizing agent is silver ions which are formed during the electrolysis process.[8] In this process, PP films were placed near the anode with the highest observed concentration of ions. The treatment of PP with the electrolyte lasted from 5 to 30 min, and the current intensity ranged from 50 to 100 mA/cm^2. The amorphous PP film (CAST) was more susceptible to the oxidizing action of the electrolyte than the crystalline film (CAST). The effectiveness of various conditions increased as the density of the electrolysis current and the exposure time were increased. After 30 min at a current density of 100 mA/cm^2, active centers were generated with densities of ~ 3.1 and 2.4 n/nm^2 on the PP CAST and PP AG surfaces, respectively.

TABLE I
Densities of Carbonyl Groups on the PP Film Surface

			Density of active centers (number of groups/nm^2)	
Type of treatment			PP Cast	PP AG
Untreated sample			0.0	0.0
Chemical treatment	HNO$_3$	0.5 h	0.8	0.5
		1 h	1.0	1.0
		24 h	1.5	1.0
	K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (20°C)	1 min	1.9	1.2
		3 min	2.9	1.9
	K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (70°C)	1 min	1.8	1.5
		3 min	4.6	2.5
	H$_2$O$_2$	0.5 h	1.5	1.2
		1 h	1.5	1.2
Electrochemical treatment		50 mA/cm^2, 5 min	1.4	1.0
		50 mA/cm^2, 10 min	1.8	1.5
		50 mA/cm^2, 15 min	2.1	1.8
		50 mA/cm^2, 30 min	2.0	1.8
		100 mA/cm^2, 15 min	1.9	1.5
		100 mA/cm^2, 30 min	3.1	2.4
UV treatment (Xenotest)		170 h	0.5	0.3

The irradiation of PP for a period of up to 170 h in the Xenotest apparatus produced slight changes in the chemical structure of PP and in the formation of new active centers.

The modification methods generated carbonyl groups on the PP film surface at densities of 0.5 to 4.6 n/nm^2. These values can be interpreted using the scale of elementary cells of ordered PP. Assuming an isotactic PP in the polymorphic form α, the macromolecules of which have a helical conformation and a helix pitch of three mers, with a long-order crystal lattice, the elementary cell in the monoclinic system is determined by four PP chains. Accounting for the geometrical cell dimensions described by Natta, Turner-Jones, and Mencik,[36–38] the maximum density of centers formed by the oxidation of —CH$_3$ groups

was from 3 to 14 n/nm^2 depending on the location of the PP macromolecules in the film surface layer. The number of groups can be increased if successive side groups are oxidized. These relationships are different on the surface of amorphous polymers in which the accessibility of tertiary carbon in PP macromolecules to oxidizing media is increased.

Wettability

Figures 6–9 show changes in the contact angle of polar liquids (water) and nonpolar liquids (alfa-bromonaphthalene) with the PP film surface before and after oxidation. Based on the angle values, the polar and dispersive components of the PP surface tension were determined (Table II).
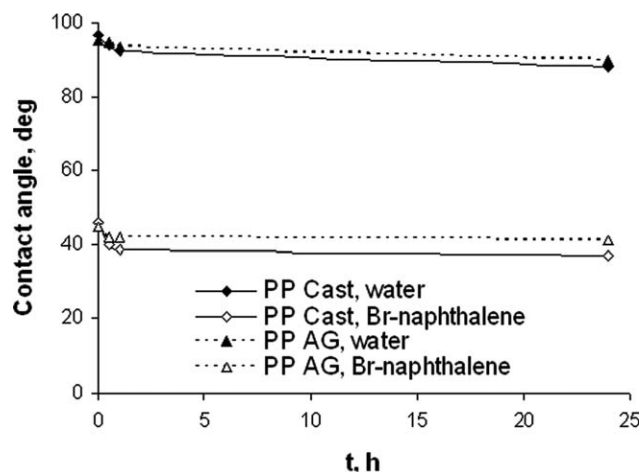

Figure 6 Changes in the liquids contact angles with the modified PP film surface with treatment time for the nitric acid.
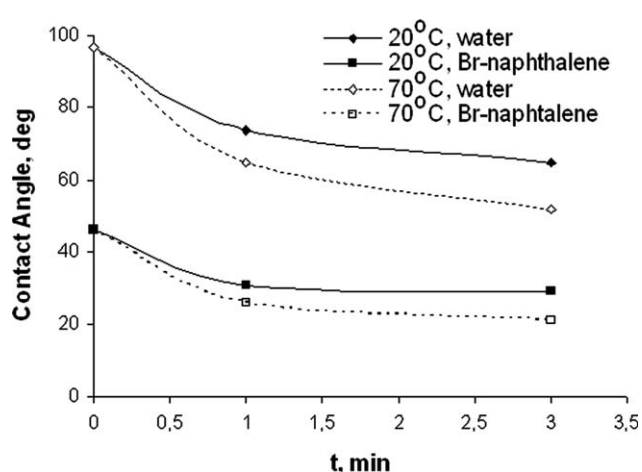

Figure 7 Changes in the liquids contact angles with the modified PP CAST film surface with treatment time for the chromic mixture.
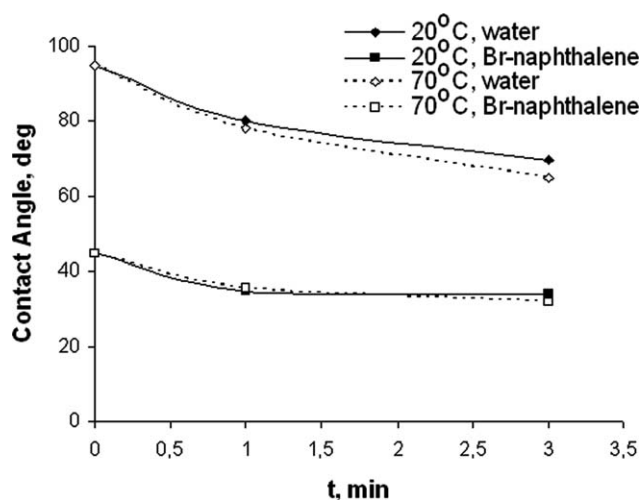
Figure 8 Changes in the liquids contact angles with the modified PP AG surface with treatment time for the chromic mixture.

Figure 9 Changes in the liquids contact angles with the modified PP film surface with treatment time for the silver nitrate electrochemical method (current intensity = 50 mA/cm^2 and temperature = 70°C).

On the surfaces of the modified PP films, drops of water and alfa-bromonaphthalene were formed with lower contact angles than those formed before modification. Thus, the wettability of the PP films increased as a result of modification. The immersion of PP in hydrogen peroxide or nitric acid decreased contact angles by an average of 7°. Substantial increases in wettability at 20° (PP CAST) and 15° (PP AG) were observed after oxidation with the chromic mixture (chemical method) and with silver nitrate (electrochemical method). Based on the IR-ATR measurements and selective PP dyeing, the increased wettability of the PP film surface was caused by the formation of polar carbonyl groups in the top layer
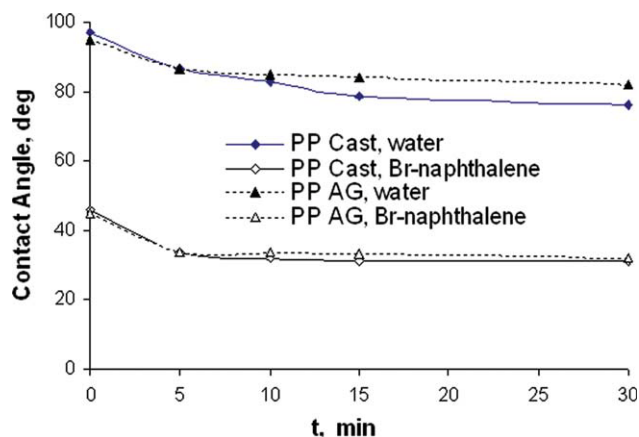
of the film. This is in agreement with the calculation results of the polar component of the surface energy of the film (Table II). The film surface before activation had a small polar component because of the low number of polar groups in the PP surface. The increase was caused by an increase in the polar and dispersive components of the surface energy (Table II). Assuming the maximum uncertainty of the calculated surface free energy components was ±1.5 mJ/m^2 (the maximum uncertainty of the contact angle measurements was ±3°), the increments of surface free energy observed in the modified surfaces, especially those with longer treatment times, were statistically significant (Table II).

TABLE II
Surface Free Energy (mJ/m^2)

			Surface			Free energy (mJ/m^2)		
			PP Cast			PP AG		
Type of treatment			γ_p	γ_d	$\gamma_p + \gamma_d$	γ_p	γ_d	$\gamma_p + \gamma_d$
Untreated sample			0.8	31.6	32.4	0.9	32.0	32.9
Chemical treatment	HNO$_3$	0.5 h	0.9	34.3	35.2	0.9	33.4	34.3
		1 h	1.1	35.2	36.3	1.1	33.4	34.5
		24 h	1.9	35.6	37.5	1.9	33.9	35.8
	K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (20°C)	1 min	6.5	38.3	44.8	4.2	36.4	40.6
		3 min	10.6	38.7	49.3	8.7	36.8	45.5
	K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (70°C)	1 min	10.2	40.0	50.2	5.3	36.4	41.7
		3 min	16.7	41.4	58.1	11.0	37.6	48.7
	H$_2$O$_2$	0.5 h	2.0	33.0	35.0	1.5	33.0	35.5
		1 h	5.0	34.3	39.3	4.0	33.0	37.0
Electrochemical treatment		50 mA/cm^2, 5 min	2.2	37.2	39.4	2.2	37.2	39.4
		50 mA/cm^2, 10 min	3.3	37.6	40.9	2.7	37.2	39.9
		50 mA/cm^2, 15 min	4.6	37.9	42.5	2.7	37.2	39.9
		50 mA/cm^2, 30 min	5.3	37.9	43.2	3.3	37.5	40.8
		100 mA/cm^2, 15 min	4.2	37.9	42.1	3.2	37.9	41.1
		100 mA/cm^2, 30 min	6.1	38.3	44.4	5.0	37.0	42.0
UV treatment (Xenotest)		170 h	1.0	34.0	35.0	1.0	33.0	34.0

The observed increase in the dispersive component of the modified surfaces was associated with the elimination of surface impurities and with polymer degradation in the surface layer, which increased the number of low molecular weight macromolecules with nonpolar groups. The relative increase in the dispersive component was particularly noticeable after modification with the Xenotest. This was attributed to cross-linking of the PP surface by UV radiation.

Effect of the super molecular structure of the PP film

The PP films used in this study, with different molecular orientation degrees and crystallinities, reacted differently during oxidation. Nitric acid interacted with the crystalline and amorphous PP films similarly. A similar increase was observed in the polar component of the total free energy of the surface. The surface of the amorphous film had a higher density of newly formed active centers in the potassium dichromate and sulfuric acid solution (70°C for 3 min) and a greater increase in surface wettability; the contact angle decreased by $\sim 22°$ on the PP CAST film and by $\sim 15°$ on the PP AG film. For both films, the oxidation process resulted in the formation of new polar groups and an increased number of polar and dispersive components, which increased the free energy of the surface. Further, 70°C and 3 min were the optimal operating conditions. The electrochemical modification of PP was sensitive to the physical microstructure of the film surface under a high current density and a long treatment time. For samples treated at a current density of 100 mA/cm^2 for 30 min, the changes observed in the physical and physicochemical properties of the PP CAST surface were more significant than those in the PP AG film. The results showed a considerable decrease in contact angles (to 21°) and a higher density of active centers (up to 3.1 n/nm^2) compared with the oriented and crystalline film. It was concluded that the media actively modified both the amorphous and crystalline PP CAST films.

CONCLUSIONS

1. The surface of a PP film was activated to prepare it for the deposition of thin organic layers. To ensure adhesion of layers to the PP substrate, new chemically active centers in the PP surface layer were formed in a pretreatment process with various oxidizing media and methods, including 3M nitric acid, 30% hydrogen peroxide, a saturated solution of potassium dichromate in 70% sulfuric acid ($K_2Cr_2O_7 + H_2SO_4$; chemical methods), silver nitrate (electrochemical method), and UV irradiation. The oxidizing media formed active carbonyl groups in the surface layer of the PP film, and this was confirmed by selective surface dyeing and IR-ATR measurements. The treatments were arranged in the following order of increasing effectiveness: UV irradiation < 3M nitric acid < 30% hydrogen peroxide < silver nitrate < chromic mixture. Oxidation of the PP film by the chromic mixture at a temperature of 70°C for 3 min formed the most active groups; 4.6 were formed on 1 nm^2 of the nonoriented and amorphous PP film, and 2.5 were formed on 1 nm^2 of the oriented, crystalline PP film.

2. PP oxidation increased the prevalence of polar and dispersive components and, thus, increased the free energy of the PP surface. The effectiveness of this increase was limited by the oxidizing medium. The treatments were arranged in the following order of increasing effectiveness: UV irradiation < 3M nitric acid < 30% hydrogen peroxide < silver nitrate < chromic mixture.

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