Characterization of Metallized Biaxially Oriented Polypropylene Film

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ABSTRACT: The effect of corona unit energy applied for retreatment of metallized biaxially oriented polypropylene film surfaces before the lamination process was studied using optical, scanning electron, and atomic force microscopies. Increased surface roughness and polarity due to oxygen groups were detected, and these changes became more evident with the increase of corona treatment intensity. The number and size of spots on the surface, possibly deriving from processing aids incorporated as additives into the polymer, increase with corona treatment. The response of specimens in accelerated aging was also studied for evaluation of the outdoor stability of these composite structures. Specimens were exposed to the combined action of UV-radiation, humidity, and heat, and the stability of yellow, orange-yellow, orange, green, and bordeaux colors was determined as a function of the exposure time. Minor color changes were recorded for exposure up to 100 h, which became more significant for longer exposure intervals depending on the type of color. Finally, a 40% decrease in tensile strength was observed after 216 h of ageing, accompanied with a decrease of 15% of modulus and an increase of 160% in the elongation at break, possibly because of the plasticizing effect taking place during the ageing process. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1713–1722, 2007

Key words: films; corona; adhesion; ageing; mechanical properties

INTRODUCTION

Biaxially oriented polypropylene (BOPP) film, produced either by tubular or tenter process, has been widely used in packaging. The BOPP film studied in this work was produced by the tenter process, which is the following: the PP sheet is extruded through a flat die and cooled under controlled conditions in a subsequent stage. This film is reheated to be treated for orientation. First, the film passes over a system of rolls running at different speeds so that orientation in the ''Machine Direction (MD)'' takes place. Then, the film is enclosed in a hot air oven for orientation in the ''Transverse Direction (TD)'' by a system of chain-mounted clips.[1]

An additional option that can greatly enhance the barrier properties of BOPP film is vacuum deposition of aluminum on its surface. Metallized films and/or structures using metallized films, like all other films, must have functional properties such as printability, heat sealability, and machinability. On the other hand, packaging end-users can take advantage of one or more of the following properties:[2]

Visual impact
Light filtering and blocking
Gas barrier
Water vapor barrier

Finally, metallized-BOPP (met-BOPP) films offer excellent gas and water vapor impermeability, making it an exceptional value as barrier packaging material. Their primary applications have been in laminated structures.[3]

Due to the low surface energy of many plastic films, especially those who lack functional groups, problems are often encountered in industrial applications, such as printing with inks, lamination to other films, and similar coating applications, where adhesion to plastic films is required.

In the above cases, a treatment of the polymer film is necessary to alter its surface properties and promote adhesion. The basic concept of these technologies is the incorporation of functional groups and the increase of surface energy. Improved adhesion to other layers is mostly because of pure physical interactions or to the formation of weak bonding such as hydrogen bond, Van der waals forces, or dipolar interactions.[4]

Although surface modification of polymers can be accomplished either by chemical or physical methods, the latter offer some advantages. Physical methods provide more precise surface modification without the need of rigorous process control; they are environmentally safe and clean procedures because no chemical solution is involved and therefore they

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do not produce any waste liquids. Physical surface modification methods range from simple flame and corona treatments to more complicated and advanced techniques such as UV, γ-radiation, electron beam radiations, ion beam, plasma, and laser treatments.[5]

Among them, corona discharge treatment (CDT) is widely used to enhance the surface energy of plastic films and therefore to improve their wettability and adhesion properties. In principle, corona treatment involves the ionization of the air between two electrodes across which a high voltage and a high frequency power is applied. The generated charged particles collide with the surface of plastic material, which is placed in between the electrodes, resulting in its modification by raising its surface energy.

As reported by O'Hare et al.,[6] CDT incorporates hydroxyl, carbonyl, peroxy, ester, carboxylic acid, and carbonate functional groups on the surface of the films. These groups are present in varying relative concentrations, depending on the energy of the corona utilized. In addition, the above authors observed a transformation of the fibrillar crystalline structure into globular morphology because of a low-molecular-weight product (LMWOM) created by CDT via oxidation.[6,7]

The disadvantage of CDT is the deterioration of properties on the oxidized surface layer with time. This effect is stronger in polyolefins because polar groups on the oxidized surface layer have a high surface energy that generates a driving force to reshape the material into a hydrophobic and thermodynamically more stable structure.[5]

Kullberg and Mueller[3] made a comparative study between flame and air corona treatment on BOPP film. They came to the conclusion that flame treatment produces a higher surface functionalization and treatment stability, which lead to enhancement of metal adhesion. This fact provides improved barrier integrity after lamination and package formation.

Atomic force microscopy (AFM) is a powerful tool for the study of morphological features of polymer films. The application of AFM on isotactic PP films produced by cast-film extrusion by Vancso et al.[8] revealed a branched fibrillar structure. Corona treatment of the PP films resulted in the formation of 400–500 nm large ''droplet-like'' spots on the surface. During metallization, 20–40 nm diameter A1 particles were deposited.

For better machineability of the films, various additives are normally formulated, prominent among them being slip and antistatic agents together with lubricants. Most commonly, these are low molecular weight materials that are not compatible with the base polymer at room temperature.

Polyolefin films typically have a tacky surface and exhibit high coefficient of friction (COF). To reduce COF and make the films easier to handle, slip additives are blended into the polymer prior to extrusion. Once the film solidifies, the additives migrate to the surface over time and modify the surface properties.[9]

The wettability of a film's surface is affected adversely, especially by the slip additives that are commonly used to provide the required friction characteristics for polyethylene and polypropylene films. These slip additives migrate to the film surface and reduce its wettability. Many converters restore the wettability and adhesion of the film surface by increasing the surface energy with an additional in-line corona treatment. The improved wettability is achieved by the creation of additional polar groups on the film surface. The retreatment also ''cleans'' the film surface by removing the slip additives that have migrated to the surface. Adelsky[10] made a quantitative study of the effects of retreatment power and time on surface energy and friction characteristics of different oriented polypropylene (OPP) films. According to the author, in some cases retreatment resulted in minor improvements or even deterioration of surface characteristics of the OPP films.[10]

In this work, the effect of corona retreatment of met-BOPP film was studied using different corona unit energies. Optical microscopy, scanning electron microscopy (SEM), and AFM were used to study the changes in film's surface topography. Laminated structures of met-BOPP/printed BOPP were periodically exposed to UV-radiation, humidity, and heat for periods up to 216 h. The stability of yellow, orange-yellow, orange, green, and bordeaux colors was examined in CIE LAB color system as a function of the exposure time. Evaluation of the tensile properties in untreated and treated specimens was also performed.

EXPERIMENTAL

Materials

The film used in this study was a 20-μm thick transparent BOPP (DIAXON SA, Greece) produced by the tenter process and then metallized under vacuum (met-BOPP) and laminated with dry-offest printed BOPP film.

Surface treatment

The metallized BOPP film samples were treated using a typical corona-discharge device GX30R Corona Treater manufactured by Sherman Treaters (Thame, Oxon).

The discharge gap was 2 ± 0.2 mm and the length of the electrode 400 mm.

TABLE I
The Unit Energy and the Related Corona Discharge Power Using a Film Speed in the Gap of 200 m/min

P (KW)	0.00	1.50	4.50	7.50
E (KJ/m^2)	0.00	1.14	3.41	5.68

The speed of the treatment roll was 200 m/min. Film surfaces were treated to different levels of surface energy by varying the power output of the corona treater.

The unit energy (E) of the corona treatment was determined from the following equation:

$$E = \frac{P}{uL} \quad (1)$$

where P is the corona discharge power (kJ/s), u is the linear speed of the film in the gap (m/s), L is the length of the discharge electrode (m).

The corona treatment of met-BOPP film was carried out using three different levels of electric power (Table I).

Optical microscopy

Observation of metallized BOPP surfaces was made by the use of an optical microscope (Leitz Aristomet). Untreated met-BOPP film and specimens of corona-treated samples at energy levels of 1.14, 3.41, and 5.68 kJ/m^2 were examined.

Image analysis of the collected pictures was performed using the appropriate software (Image pro plus) on three different selected areas with dimensions 360 × 360 μm^2 for each examined sample of met-BOPP film.

Scanning electron microscopy

SEM was used to better examine the surface of untreated and treated met-BOPP surfaces using the equipment Quanta 200, FEI (Hillsboro, OR) in environmental mode function. Elemental analysis was also performed using X-ray energy dispersion spectroscopy (X-ray EDS).

Atomic force microscopy

The observations of metallized BOPP film with AFM were performed by the MultiMode Nanoscope III (Digital Instruments, Santa Barbara, CA). AFM images were obtained in tapping mode experiments to gain both topographic and phase imaging using rectangular NanoSensor Si cantilever probes of 122-μm length and 10–15 μm width. The spot size for the collected AFM images was 1 × 1 μm^2 using a scanning rate of 3.05 Hz (μm/s). Three different spots were examined for each of the examined samples.

Accelerated ageing process

Laminated met-BOPP/BOPP films were exposed to accelerated ageing conditions using the appropriate chamber type QUV-Weathering Testers (Q-Panel, Lab Products).

The ageing tests were run according to ASTM D 4587-01[11] and ASTM D 4329-99.[12] Specimens were exposed to repeated cycles of 4 h each, where exposure to UV-radiation and damp heating took place. The UV-radiation was produced using a lamp type UVB-313. Water in the bottom of the test chamber was heated, filling the chamber with hot vapor, and creating 100% humidity at 40–50°C.

The conditions of the accelerated ageing procedure performed in this work were:

i. UV-radiation with a power of 0.77 W/(m^2 nm) at (50 ± 2.5)°C and
ii. Water-condensate at (40 ± 2.5)°C.

During the accelerated aging process, specimens were removed after 103, 144, and 216 h of exposure. Color change, infrared spectroscopy, and tensile tests were performed to evaluate the effect of accelerated ageing on the properties of treated films.

Color test

Color changes (ΔE) were examined with a micro-color tristimulus colorimeter (Micromatch plus, Sheen Instruments). This instrument is designated to determine color characteristics in the CIE LAB color system according to ASTM D 2244-68.[13] The system is an approximately uniform color space using three parameters (L, a, b) to define color, where (L) measures the light-dark character, (a) the red-green character, and (b) the yellow-blue character. Color change can be calculated from the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a_L)^2 + (\Delta b_L)^2} \quad (2)$$

Tensile properties

Tensile tests were carried out according to ASTM D 882-75b[14] specification. Ten specimens from each sample were tested in an Instron (model 4466) tensometer, equipped with a load cell of maximum capacity of 10 kN and operating at grip separation speed of 50 mm/min. The dimensions of specimen were: length 12 cm, width 1.5 cm, and thickness

20 μm. The tensile properties were examined along the MD of the film.

Attenuated reflectance infrared spectroscopy

For spectroscopic measurements (Nicolet FTIR spectrometer, model Magna IR 750; DTGS detector; Nichrome source; beamsplitter; KBr), a total of 100 scans were applied with a resolution up to 4 cm^{-1}. Spectra were obtained at the attenuated total reflectance (ATR) mode using a standard ZnSe 45° flat plate Contact Sampler (12 reflections; Spectra-Tech) on which samples of laminated BOPP films were placed (100 μL). Spectroscopic data were treated using the standard software (OMNIC 3.1, Nicolet).

All spectra were smoothed using the ''automatic smooth'' function of the above software, which uses the Savitsky-Golay algorithm (5-point moving second-degree polynomial). After the above procedure, the baseline was corrected using the ''automatic baseline correct'' function.

X-ray diffraction

X-ray diffraction (XRD) data between 5° and 35° were obtained using a Siemens D5000 X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm) operating at 40 kV and 30 mA.

RESULTS AND DISCUSSION

Corona retreatment of met-BOPP film

Metallized BOPP film was treated with CDT using different levels of energy to evaluate the improvement of its surface adhesion properties during the laminating process with printed transparent BOPP film. The optical microscopy used to examine the effect of the above treatment on the treated surfaces showed black spots on the surface of the met-BOPP film, as can be seen on Figure 1(b).

By image analysis using the appropriate software for processing the collected pictures, it was observed that concentration and dimensions of these spots increased by increasing the energy of the applied corona treatment. These results are presented in Table II.

To elucidate the effect of corona treatment on the met-BOPP surfaces, further study was performed using SEM. As it can be seen in Figure 2(a), the untreated met-BOPP surface is rather smooth with two types of irregularities: microcraters and white spots. The number of these irregularities is increased as the energy of the applied corona treatment increases [Fig. 2(b)]. Microcraters are most probably created as a result of the corona discharge. The observed white spots essentially consist of additives

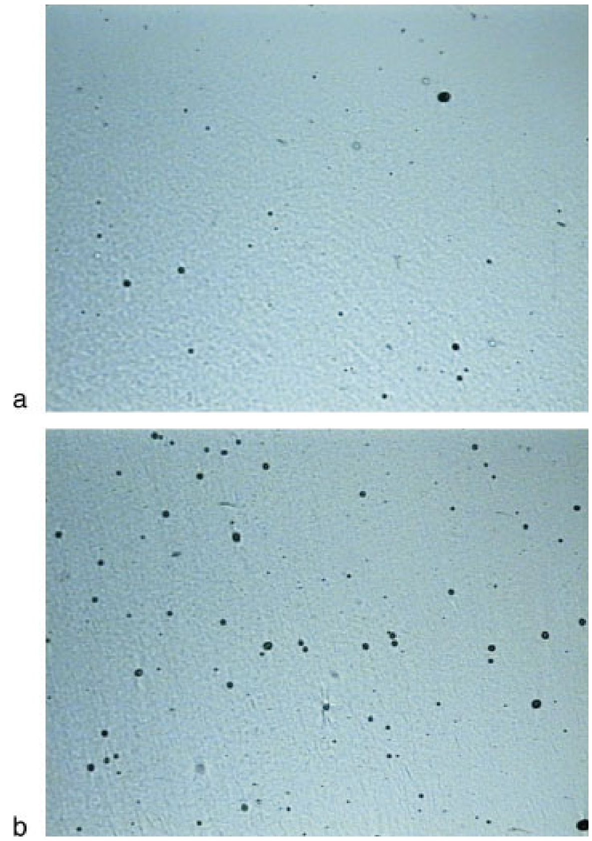

Figure 1 Optical microscope images of met-BOPP film: (a) untreated and (b) corona-treated with unit energy 5.68 kJ/m^2 (magnification ×200). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

incorporated into the polymer to facilitate processing or to improve the final properties of BOPP film. Particles of these additives or their aggregates are brought on the surface as a result of etching of the polymer surface layers because of corona retreatment. Probably, a parallel mechanism to the above procedure would be the migration of some of these additives to the polymer surface.

Further investigation of the chemical composition of these areas was carried out using X-ray EDS analysis (Fig. 3). As expected, carbon and aluminum were the main elements found on the surface of met-BOPP film. Silica, a compound used in antiblocking

TABLE II
Image Analysis of the Black Spots on the Surface of Treated Met-BOPP Film Using Different Levels of Energy

E (KJ/m^2)	Number of black spots (%)	Diameter of black spots (μm)
0.00	1.060 ± 0.0150	5.1618 ± 0.1054
1.14	2.590 ± 0.035	5.3000 ± 0.3790
3.41	2.785 ± 0.030	5.3075 ± 0.0070
5.68	3.305 ± 0.023	5.5480 ± 0.2064

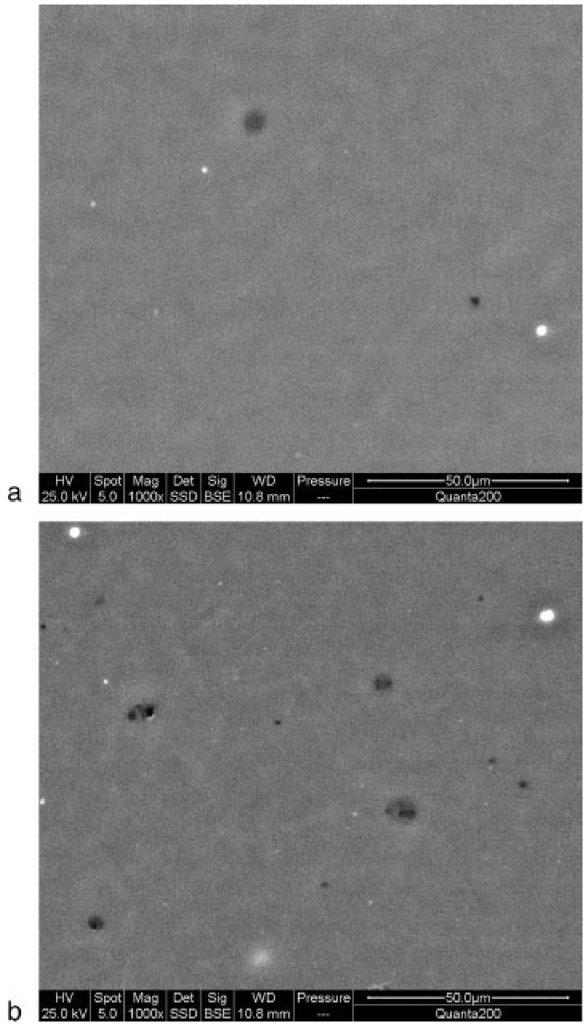

Figure 2 SEM microimages of met-BOPP film: (a) untreated and (b) corona-treated with unit energy 5.68 kJ/m^2 (magnification $\times$1000).

additives, was essentially the basic constituent of white spots. Oxygen was also found at the surface of the corona treated samples, most probably because of oxidation taking place during corona discharge.

Analysis in many microcraters revealed that the composition of these areas is the same as that of the main substrate and, therefore, these configurations obviously resulted from surface roughening without any change in the chemical composition of the polymer.

AFM is a technique that can detect the variation in height or topography of a sample surface. Samples of untreated and treated met-BOPP films were observed using the AFM method. The topographic images (Fig. 4) showed that the metallization thickness is not uniform over the whole film surface.

In our samples, the texture of the metallized surface is affected by the topography of the PP surface layer on which deposition of the thin aluminum layer takes place. The metal layer is formed according to the topography of the polymer surface. During the production of BOPP film, its surface is treated with corona to ensure efficient adhesion between metal and polymer in the subsequent vacuum-metallization stage. An additional stage of corona-treatment was applied on the metallized surface to promote adhesive bonding during the laminating process. In most packaging applications, metallized BOPP film is used as a multilayer structure in combination with other types of films made during the lamination process. This additional treatment is expected to create stronger bonding between the layers of the laminated film, which gives better barrier properties. It should be noted that the study of adhesive bonding and surface energy of the film as a function of the operating parameters of the system during corona treatment seems very important for the interpretation of experimental results, as well as for the prediction of the end use properties of metallized BOPP films. However, in our work we

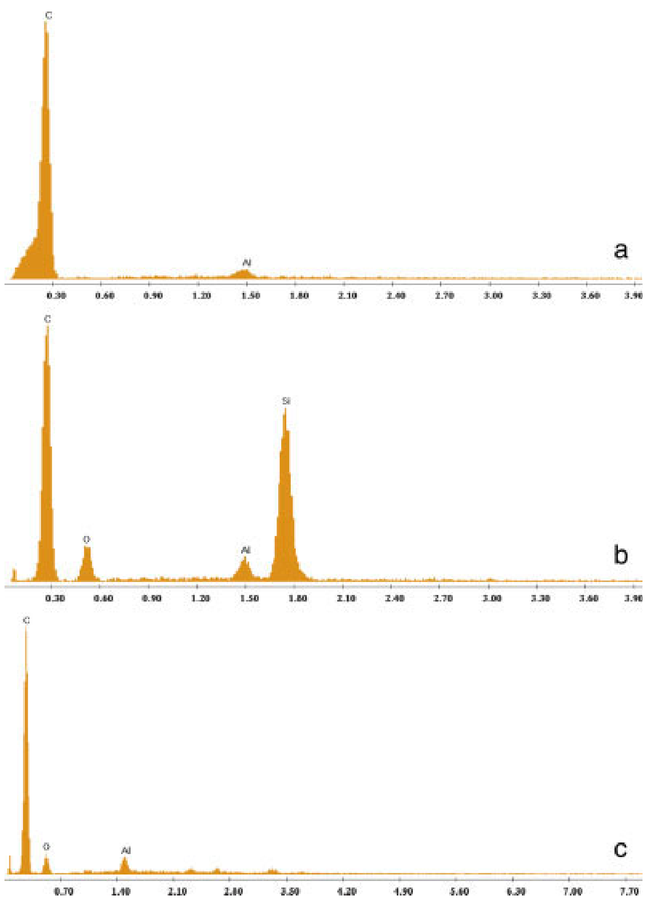

Figure 3 X-ray EDS analysis on met-BOPP film (a) untreated surface, (b) on white spots of corona treated surface, and (c) on microcraters of corona treated surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

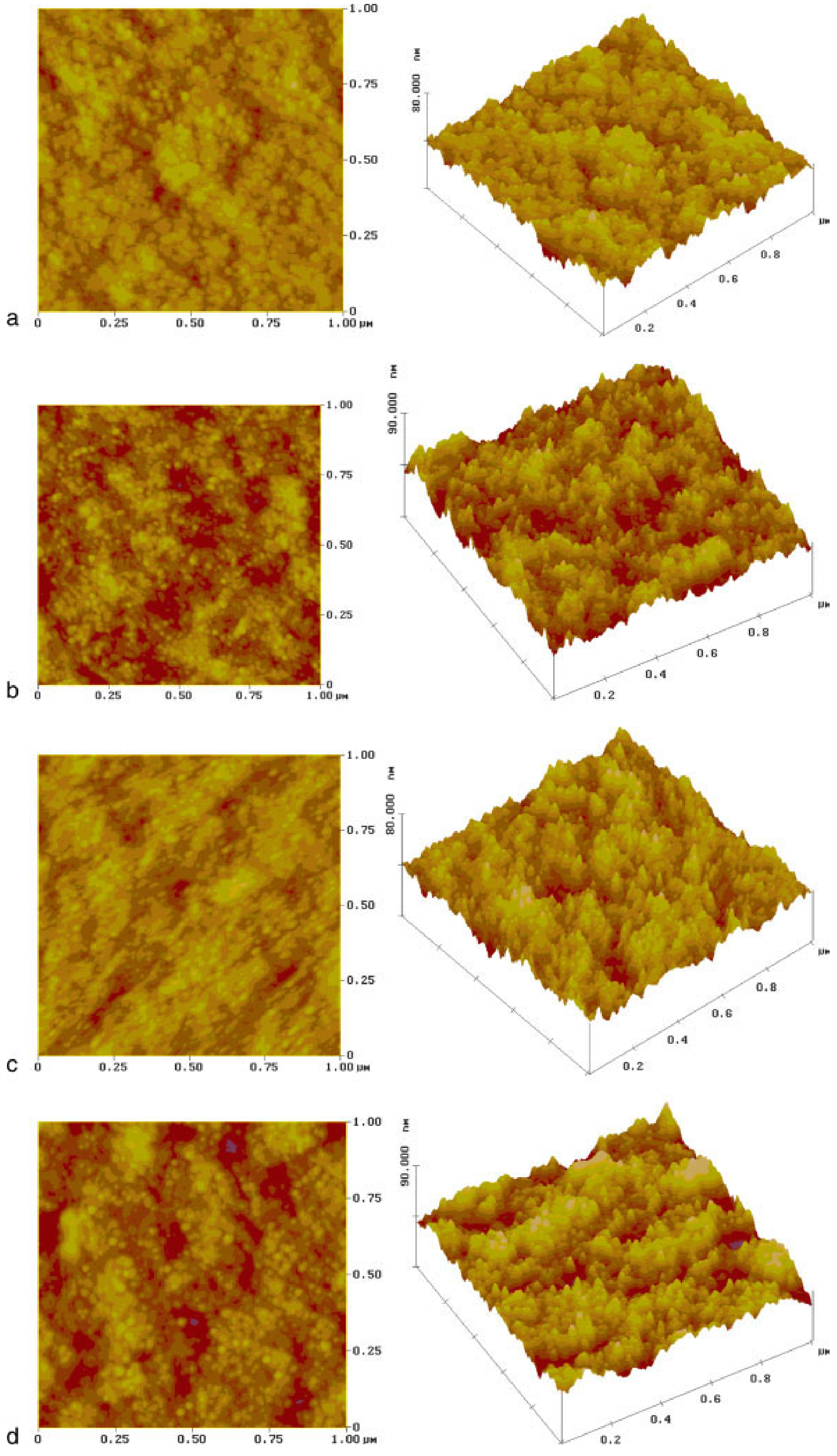

Figure 4 Tapping-mode AFM images of metallized BOPP films (a) untreated and corona-treated with unit energy (b) 1.14 kJ/m^2, (c) 3.41 kJ/m^2, (d) 5.68 kJ/m^2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Main Surface Roughness of Corona-Treated Met-BOPP Films Using Different Levels of Energy

E (KJ/m^2)	Main surface roughness R_a (nm)
0.00	2905
1.14	3008
3.41	3271
5.68	3062

were not able to run the appropriate tests because we used films supplied directly from the production line of the converter company, where a standard industrial process is applied, and which does not provide the necessary experimental versatility for changing the corona treatment parameters. On the other hand, even a single measurement of surface energy or adhesive bonding of the as-received films was not feasible because these characteristics show a strong dependence on the time after treatment and therefore, we could not obtain reliable data from such measurements.

The dark areas shown in the obtained AFM images correspond to planar and smooth areas of the BOPP film surface, whereas areas with light color correspond to rough spots. From Figure 4(a) it is observed that the peaks of the untreated met-BOPP have more regular shapes and smaller dimensions in comparison with the samples of the corona-treated met-BOPP surfaces. This additional treatment increases surface roughness and gives increased irregularity in the shape of peaks, as can be seen in Figure 4(b–d).

The surface roughness can be estimated by the R_a, which is the arithmetic mean of the absolute values of the profile height deviations. In all experiments, a roughness average was calculated taking into account measurements from a number of sections across the scan area, and the obtained R_a values are presented in Table III. A tendency for increased surface roughness by increasing the corona unit energy can be observed for the treatment. The increased surface roughness is expected to cause improved mechanical interlocking and therefore strong adhesive bonding when lamination with other substrates take place. However, this effect has some limitations.

Żenkiewicz,[15] using different levels of corona unit energy up to 5.0 kJ/m^2, studied the effect on the surface properties of BOPP film by measuring the contact angle of various liquids, the extent of surface oxidation by X-ray photoelectron spectroscopy, and the adhesion strength with acrylic adhesive using the 180°-peel test. The free energy of the film surface shows a fast increase as the unit energy increases up to 1.2 kJ/m^2, and then it continues to increase with treatment energy at lower rate. The extent of oxidation of the surface layer and the adhesion strength between the BOPP film and the acrylic adhesive increase almost linearly with the unit energy applied in the corona treatment. These results suggest that further increase in the unit energy leads to a saturation of oxidation sites in the outer layers, and the progress of this reaction in deeper layers does not neither contribute to further increase of the surface free energy of the film nor to the adhesive bonding.

The type of slip agents incorporated into the polymer influences the configuration of surface topography of the film. Using different types of slip agents, Ramírez et al. studied the effect of the surface topography on the obtained values of COF. The above authors came to the conclusion that large, soft and plate-like crystals may smear more readily and provide less physical resistance to sliding motion and therefore reduce the COF. In most commercial BOPP films, to ensure strong adhesive bonding between polymer surface and aluminum layer, the incorporation of slip additives is restricted in the exterior polypropylene layer.

Accelerated ageing of laminate met-BOPP/printed BOPP film

Exposure of met-BOPP film laminated with printed BOPP film samples to accelerated ageing conditions for 216 h seems to have an essential effect on the properties of the composite film structure. To explore this interaction, the following properties were tested as a function of time:

i. Color stability of different printing inks,
ii. Chemical composition of the film surface, and
iii. Tensile properties.

The examined colors were yellow, orange-yellow, orange, green, and bordeaux, deriving using basic dry-offset inks, according to the compositions showed in Table IV.

It was found that periodic exposure to the combined action of UV-radiation, heat, and moisture results in significant changes in the L, a, and b values of the printing colors.

TABLE IV
Composition of Printings Colors Using Basic Process Colors

	Inks (%)					
Color	Yellow	Magenta	Blue	Black	Fire-red	Lacquer
Yellow	55	–	–	–	–	45
Orange-yellow	98	–	–	–	2	–
Orange	79	–	–	–	21	–
Green	85	–	13	2	–	–
Bordeaux	36	57	–	7	–	–

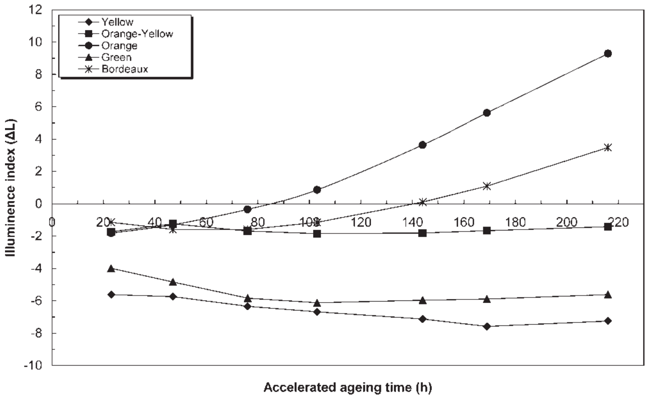

Figure 5 The change of illuminence index (ΔL) during accelerated ageing of different printed colors on BOPP film.

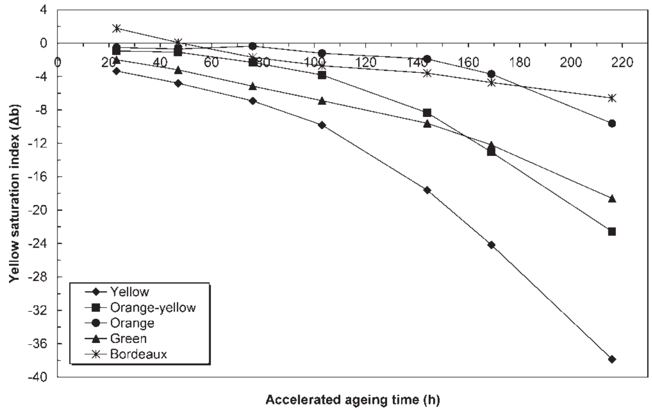

Figure 7 The change of yellow saturation index (Δb) during accelerated ageing of different printed colors on BOPP film.

The index L values for the yellow, yellow-orange, and green colors as a function of exposure time remains almost constant. On the other hand, orange and bordeaux demonstrate significant changes in L values, especially after 100 h of exposure (Fig. 5).

The red saturation index a, which corresponds to the red-green character of a color, shows some decrease with time, which is more evident for the bordeaux and orange colors (Fig. 6).

Finally, the yellow saturation index b decreases and this effect becomes more evident for the yellow color after 100 h of exposure (Fig. 7).

The total color change ΔE was calculated using eq. (1), and the obtained results are presented in Figure 8. It can be seen that maximum variations in ΔE value correspond to yellow and orange. For exposure in accelerated ageing conditions longer than 100 h, the color change proceeds at higher rates.

The exposure in accelerated ageing does not only affect the color stability of the composite structure of BOPP film, but also attacks the polyolefins and initiates the auto-oxidation reactions of these polymers. This process is responsible for the formation of oxidation products and chain scission, which results in a decrease in molecular weight of the polymer. The above-mentioned effects become more significant under the combined action of UV-radiation, humidity, and high temperature. Taking into consideration that BOPP film structures are used in packaging applications, the investigation of their response in accelerated ageing should be of importance for practice.

An additional effect of the accelerated ageing on the properties of the film is that on mechanical properties. For this reason, the tensile properties of samples of printed BOPP film laminated with met-BOPP film as function of exposure time were studied.

The elongation curve of untreated specimens, shown in Figure 9, consists of three distinct areas: in the first linear part elastic deformation of the specimen is observed, followed after the yield point by cold drawing deformation where the orientation of polymer molecules results in further increase of tensile strength before rupture. In the case of specimens

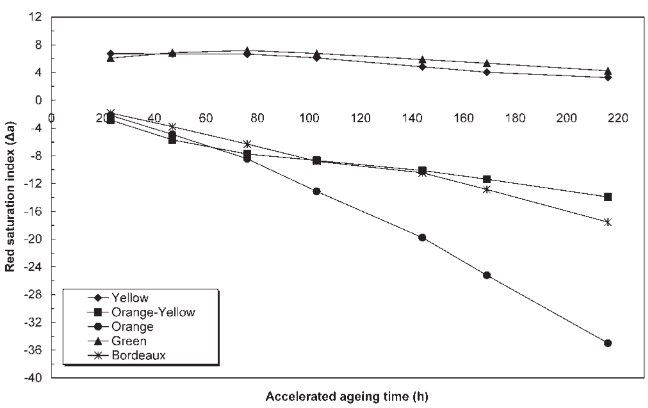

Figure 6 The change of red saturation index (Δa) during accelerated ageing of different printed colors on BOPP film.

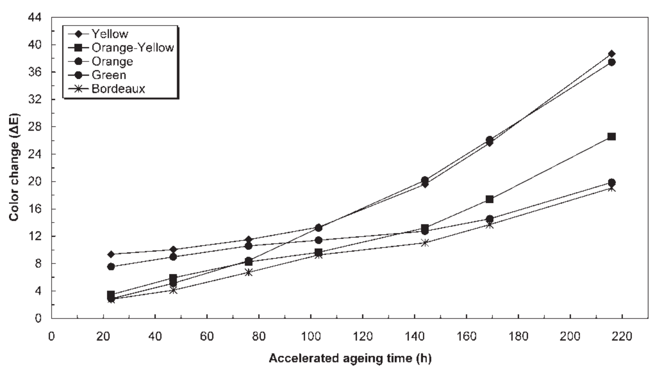

Figure 8 The color change (ΔE) during accelerated ageing of different printed colors on BOPP film.

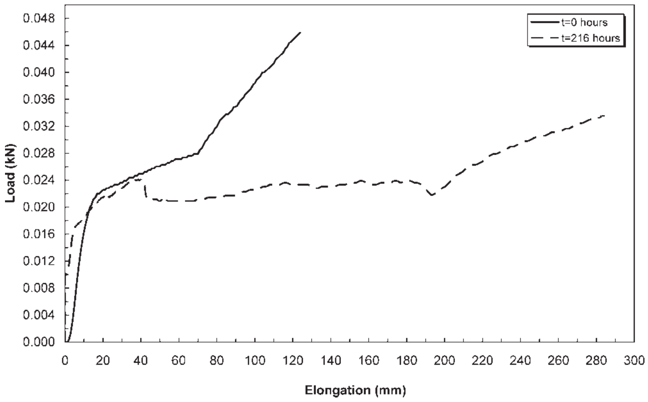

Figure 9 Typical load-elongation curves during tensile test of laminated met-BOPP/BOPP film.

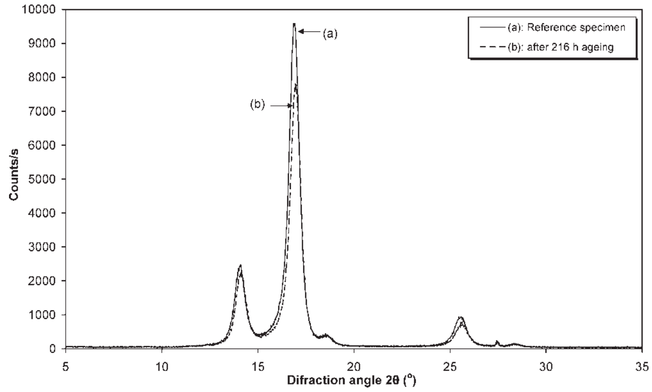

Figure 10 X-ray diffraction patterns of laminated met-BOPP/BOPP film, (a) reference specimen and (b) after 216 h exposure in accelerated ageing conditions.

exposed to accelerated ageing, the load-elongation curve shows significant changes in shape. In fact, the ductile character of the film seems to be enhanced, as with further deformation the load remains almost constant and the tensile strength increases before break.

As a result of the above mechanical response of the aged film, elongation at break increases with exposure time, as can be seen in Table V. The exposure in UV radiation in combination with heating and high humidity leads to a decrease of tensile strength up to 40% after 216 h. This behavioral result can be attributed to oxidation and chain scission of PP due to ageing. As already reported by other researchers,[16,17] these reactions are likely to reduce crystallinity of PP and therefore, lead to a product with lower rigidity. The above interpretation can be further supported by the fact that crystallinity of the PP film exposed to UV radiation shows a clear reduction in comparison with that of the as-received film, as estimated from the graphs obtained by XRD. In fact, the diffraction patterns shown in Figure 10 show typical reflections at $2\theta = 14.2°$, $17°$, and $18.8°$. Clearly, the reflection peaks corresponding to UV-exposed specimens are lower than those of the pure polymer. The tensile modulus presents a modest decrease reaching 15%, after 216 h of exposure. The BOPP film produced by the tenter technology is subjected to strong biaxial orientation, i.e., in both MD and TD. Therefore the effect of accelerated ageing does not contribute significantly to this behavior.

TABLE V
Tensile Test Results in Laminated BOPP//Met-BOPP as a Function of the Accelerating Ageing Exposure Time

Time (h)	Tensile strength (MPa)	Modulus of elasticity (MPa)	Elongation at break (mm)
0	92.9 ± 9.9	2325.1 ± 106.7	53.9 ± 3.2
103	85.6 ± 9.1	2203.6 ± 155.4	90.3 ± 12.8
144	75.6 ± 16.7	2090.2 ± 103.5	118.6 ± 26.7
216	55.9 ± 2.9	1979.4 ± 161.2	140.2 ± 10.7

Visual observation of the broken specimens with an optical microscope reveals that failure occurs through delamination of the film layer of the composite.

The diffuse reflectance FTIR spectra of the original laminated BOPP/met-BOPP film, as well as of the specimens exposed for 216 h to accelerated ageing are illustrated in Figure 11. The same peaks are present in the patterns of the obtained spectra. The peaks at 1376 and 1456 cm^{-1} are attributed to bending of the C—H bonds from the CH_2 and CH_3 groups. The peaks in the area 2837–2953 cm^{-1} correspond to stretching of the aliphatic C—H bonds, whereas the absorption zone below 1300 cm^{-1} wavelength corresponds to the isotactic-PP fingerprint. This was confirmed by comparing the above spectra with the reference spectrum of isotactic PP.

The only difference detected using ATR spectroscopy is the area of the collected peaks. In particular, the area of the peaks of the treated spectrum is lower compared with that corresponding to the untreated specimens. This difference can be attributed to already mentioned decrease of molecular weight of treated specimens.

CONCLUSIONS

Laminated structures of metallized and transparent BOPP films offer unique properties as barrier materials in packaging applications. Retreatment of metallized BOPP film by corona discharge is a simple and effective method applied before laminating process in an attempt to increase the surface free energy and consequently the adhesion properties with other films. Increased adhesion results in improved barrier properties of the prepared composite structure. The use of optical microscopy

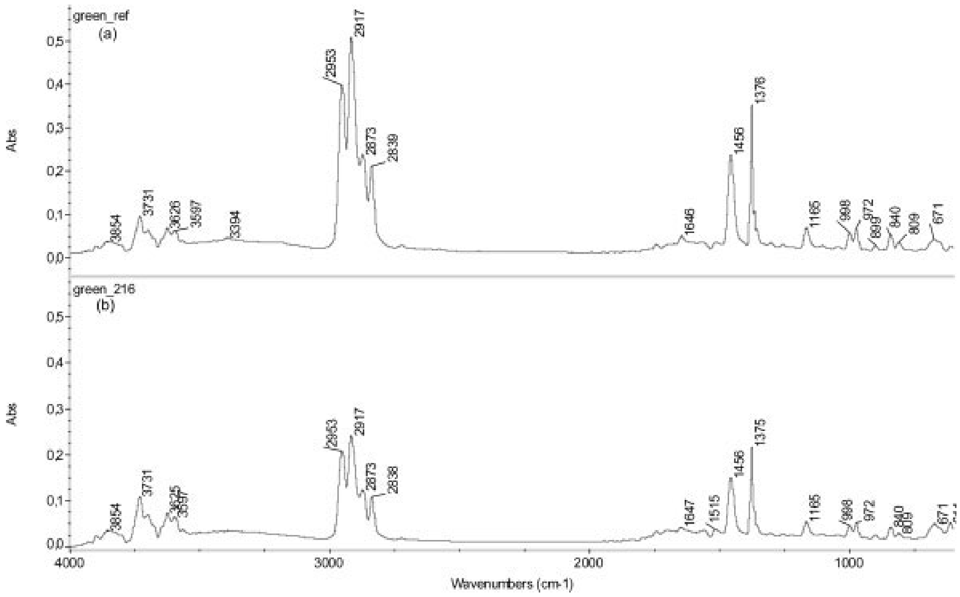

Figure 11 ATR spectra of laminated met-BOPP/BOPP film, (a) reference specimen and (b) after 216 h exposure in accelerated ageing conditions.

revealed that the black spots observed in the treated met-BOPP surfaces are more dense and large in size compared with those found in the untreated samples. Microcraters and white spots were observed using SEM for the study of the smooth met-BOPP film surface. Elemental analysis of the white spots by X-ray EDS confirms the presence of Si deriving from antiblocking agents incorporated into the polymer. The same analysis focusing on microcraters confirmed their almost similar composition with the main met-BOPP film substrate. These spots resulted from the corona treatment and they increase the surface roughness of the film. The increase of surface roughness with the increase of corona unit energy and change in the surface texture were confirmed with AFM.

Another critical requirement for these laminated structures of met-BOPP/printed BOPP films is their stability to environmental conditions. To simulate this effect, periodic exposure to UV-radiation, increased humidity, and temperature for a total period 216 h was performed. Yellow, orange-yellow, orange, green, and bordeaux were the examined colors using L, a, b scale. The total color change (ΔE) became significant after 100 h of exposure for all the examined colors. Yellow and orange are the more sensitive colors in the exposure to accelerated aging conditions.

After 216 h of accelerated aging, a decrease of 40% in tensile strength was recorded, whereas a decrease of 15% was found for the modulus of elasticity. The significant increase in elongation at break (160%) was attributed to the reduction of crystallinity of the polymer, which lead to a material with increased ductility.

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