Surface properties and printability of polypropylene film treated by an air dielectric barrier discharge plasma

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Keywords

Dielectric barrier discharge plasma, polypropylene, surface energy, adhesion, print quality

Summaries

Surface properties and printability of polypropylene film treated by an air dielectric barrier discharge plasma

The effect of air dielectric barrier discharge plasma treatment on the chemical structure and morphology of polypropylene (PP) film was studied using UV-VIS (ultraviolet-visible), FT-IR, (Fourier transform infrared), SEM (scanning electron microscopy) and AFM (atomic force microscopy). Polypropylene samples were printed using solvent-based gravure ink. An evaluation of the print quality criteria of the treated PP films included measurement of print density and print gloss. SEM investigated the ink laydown on the modified PP film. The results showed that after a few seconds of plasma treatment, both the surface energy and the surface roughness of the treated PP film increased. There was an increase in the absorbance at the almost-visible range, and C=C and C=O bands were found after the air discharge plasma treatment. A short plasma treatment of 15 seconds was found to bring about a dramatic increase in the print density readings, but a decrease in print gloss. The time of the air discharge plasma treatment was found to have no effect on the print density or print gloss at a high ink film thickness. The results showed that air dielectric barrier discharge plasma treatment, for a few seconds, is effective in printing and is economical for industrial use (this will be studied in detail in future work).

Propriétés de surface et imprimabilité de films polypropylène traités par plasma d'air obtenu par décharge à barrière diélectrique

On a étudié l'effet du traitement par plasma d'air obtenu par décharge à barrière diélectrique sur la structure chimique et sur la morphologie de films polypropylène (PP) grâce à l'ultraviolet visible (UV-VIS), à l'infrarouge par transformée de Fourier (FT-IR), à la microscopie électronique à balayage (SEM) et à la microscopie à force atomique (AFM). Des échantillons de polypropylène ont été imprimés en utilisant de l'encre de gravure au solvant. Une évaluation des critères pour la qualité d'impression des films PP traités comprenait la mesure de la densité de l'encre aussi bien que celle du brillant de l'impression. La déposition de l'encre sur le film modifié a été investiguée par SEM. Les résultats ont montré, qu'après quelques secondes de traitement par le plasma, l'énergie de surface, aussi bien que la rugosité de la surface du film PP traité, ont augmenté. L'absorbance a augmenté dans la gamme presque visible et des bandes C=C et C=O ont été trouvées après le traitement par le plasma d'air obtenu par décharge à barrière diélectrique. On a trouvé qu'un court traitement, de 15 secondes, par le plasma a augmenté d'une manière dramatique les mesures de la densité de l'encre mais a diminué le brillant de l'impression. On a trouvé que la durée du traitement par plasma d'air obtenu par décharge à barrière diélectrique n'avait ni d'effet sur la densité de l'impression ni d'effet sur le brillant de l'impression quand le film d'encre était d'une épaisseur élevée. Les résultats ont montré que le traitement par le plasma d'air obtenu par décharge à barrière diélectrique, quand il s'agit d'une durée de quelques secondes, est efficace pour ce qui est de l'impression et rentable pour ce qui est de son usage commercial. (Ce dernier sera étudié minutieusement dans une œuvre future.)

Die Oberflächeneigenschaften und Druckeignung eines Polypropylenfilmes, der mit Luft-dielektrisch behinderten barrierenentladenem Plasma behandelt wurde

Der Effekt einer Luft-dielektrisch behinderten barrierenentladenem Plasmabehandlung ("Plasma-Printing") auf die chemische Struktur und Morphologie eines Polypropylenfilms (PP) wurde mittels UV-Sichtbar Spektroskopie (UV-VIS), FT-IR Spektroskopie, Scan-Elektron-Mikroskopie (SEM) und Rasterkraft-Mikroskopie (AFM) erforscht. Die Druckeignung der behandelten PP-Filme wurde bewertet, insbesondere die Druckdichte und der Glanz sowie – mittels SEM – die Tintenniederlegung. Die Ergebnisse – bei Verwendung von lösungsmittelhaltigen Gravurtinten - zeigten, daß ein paar Sekunden Plasmabehandlung sowohl die Oberflächenenergie als auch die Obverflächenrauheit des behandelten Filmes erhöhte. Die Plasmabehandlung erhöhte die Absorptionskraft des Filmes im fast-sichtbaren Bereich sowie in der C=C und C=O Breite. Eine kurze Plasmabehandlung von 15 Sekunden erzielte einen dramatischen Anstieg der Druckdichte, aber eine Verringerung des Glanzes. Bei dicken Tintenfilmen hatte die Länge der Plasmabehandlung keinen Einfluß mehr auf die Druckdichte und den Glanz. Die Ergebnisse zeigten aber daß eine kurze Plasmabehandlung von ein paar Sekunden eine effektive Druckmethode ist und in der Industrie kostengünstig angewendet warden kann (eine weitere Arbeit wird sich mit dieser Frage eingehender beschäftigen).

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Introduction

Untreated polyolefin-based polymers have a number of undesirable characteristics including poor wettability, poor printability, and poor adhesion to secondary phases. These properties are associated with the low surface energy of polyolefin-based polymers and their high resistance to most chemicals and solvents.[1] Raising the surface energy of plastic substrates to more than 42mNm^{-1} at the printing press is necessary for adequate ink adhesion.[2,3] There are several pretreatment methods available. Chemical, flame, corona, plasma and ultraviolet (UV) treatments are among the most frequently used methods which enhance the ink receptivity of the polyolefin substrates.[4,5] Plasma treatment significantly influences wettability which is directly related to adhesion.[6] Excited species created during the plasma discharge react with the film surface, which is modified chemically and morphologically. Hydroxyl, carbonyl or carboxyl groups are the most likely groups to be formed.[7,8]

To-date, thorough research on the effect of plasma treatment on polyolefin-based polymers has been carried out.[4–8] However, the fundamental understanding of the effect of plasma treatment on the print quality of plastic films appears still to be inadequate.

The growing trend toward the utilisation of plastic film labels has led to the development of new production methods such as the production of a certain film with a top coating suitable for use with dot matrix printers designed for printing computer imprintable variable information as bar codes. Because of its low cost, clarity, as well as moisture, chemical, and scratch resistance, polypropylene is preferred for use in prime labels. Biaxial-oriented polypropylene is gaining a market share largely as a result of the increased production of recyclable plastic bottles and plastic containers.[9,10] Also, film costs have fallen because of a reduction in film thickness and the use of cheaper, lower-density resins such as polypropylene/polyethylene blends.[11,12]

For ink to wet a substrate, its surface tension should be at least 10mNm^{-1} lower than the surface energy of the substrate. If the surface energy of the liquid is higher than that of the substrate, the surface will be poorly wetted, the lay of the ink will be poor, and it may even exhibit reticulation.[13]

The subjective definition of print quality is the degree to which the appearance characteristics of the print approach those of the desired result. Good print quality can be determined by a regular, evenly-covered appearance, even print density, sharp-edged half-tones, low half-tone dot enlargement, high print contrast, high print gloss, good ink take-up, constant substrate inking and brightness, with little set-off and smudging, high rub resistance, and little penetration of ink through the substrate.[14,15]

The present work is devoted to study the effect of an air dielectric barrier discharge (ADBD) on some surface properties, namely the wettability and the morphology of polypropylene films, and to investigate the effect of these changes on ink lay-down and print quality.

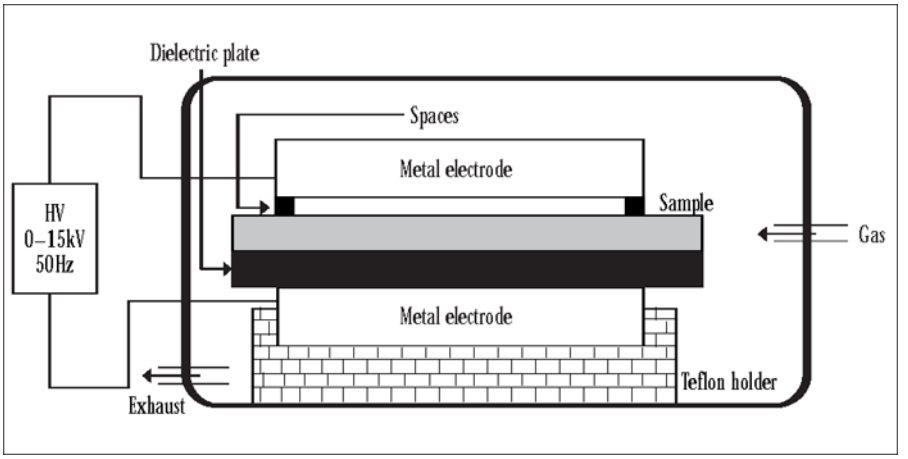


Figure 1: A schematic diagram of the air dielectric barrier discharge plasma system

Experimental

Plasma treatment of PP film

Biaxial-oriented 40μm PP film, with a density of 0.9g/m^3, was used in the current work, supplied by Technopack Co, Cairo, Egypt.

The surface treatment was carried out using an in-house-built air dielectric barrier discharge (ADBD). Figure 1 represents a schematic diagram of the instrument. The system used to produce the ADBD consisted of two stainless steel plates, each measuring 4 x 13cm^2. The lower plate was covered with a glass plate with a thickness of 1mm as an insulator. The untreated PP film was cut into pieces 4.5 x 13.5cm^2. Each piece was placed on the surface of the glass plate and separated from the upper electrode with a poly-tetrafluoro ethylene (DuPont) spacer of 2mm thickness. The system was housed in a rectangular Pyrex glass enclosure into which the working gas (air) was introduced, passing through the gap between the electrodes. The exhaust gas was carried via plastic tubing to the fume cupboard. The electrodes were connected to an AC source with a 50Hz frequency, and an output voltage of up to 15kV. In the present investigation, 8kV were used throughout the whole work.

Surface characterisation

Surface energy measurement

The surface energy of the treated PP film was measured using the ASTM D2578-94 method.[16] In this method, drops of a series of mixtures of formamide ($HCONH_2$) and ethylene glycol monoethyl ether (ethyl cellosolve: $CH_3CH_2OCH_2CH_2OH$) of gradually increasing surface tension are applied to the surface of the PP film. Each mixture is spread on an area measuring 650mm^2 of the PP surface by wetting the tip of a cotton applicator, starting from the lower surface energy ones. When the mixture breaks into drops in about two seconds, the test is stopped. The surface energy of the polypropylene film surface is approximated by the surface tension of this particular mixture.

Chemical structure

The chemical structure of the untreated and modified PP films was investigated. Ultraviolet- visible (UV-VIS) spectroscopy was carried out with a Schimadzu UV-160A. Infrared measurements were performed with a Nicolet Nexus 670 reflection Fourier transform infrared (FT-IR) spectrometer.

Surface morphology

A Philips XL-30 scanning electron microscope, attached to an energy depressive x-ray (EDX) unit, was used to study the surface structure of untreated and ADBD plasma-treated PP samples. A magnification of 2000x, with an acceleration voltage of 5.0KV was selected in this study.

Surface roughness measurements

Atomic force microscopy (AFM) was used to identify the topography of the PP films before and after the ADBD plasma treatment. The AFM used was supplied by Park Scientific Instruments, USA. The morphology of the films was measured at room temperature by using Auto Probe CP Research features ProScan for data acquisition. Data analysis is accomplished using IP2.0 image processing software. The imaging area is ≥ 90 x 90μ^2 (micrometres^2), the z displacement allowed was ≥ 6μm.

Printing of PP films

Simple solvent-based gravure ink (supplied by Packin Co, Egypt) was used for printing the test samples (see Table 1). For the grinding process, an Eiger 'MINI' Motor mill (England), was used and the dispersion fineness was measured by using an Ault and Wiborg grinding gauge. The viscosity of the prepared ink was adjusted at 20 seconds using a standard Ford B4 flow cup at 25°C directly after preparation and measured again after 24 hours.

Table 1: Ink formula

Raw materials	*% content*
Carbon black	12
Nitrocellulose	10
Ethyl acetate	75
Titanium acetyl-acetonate	3
Total	100

Carbon black Printex3, supplied by Degussa Co, US, was used. It has a specific gravity of 1.687g/cm^3 and an oil absorption of 125ml/100g pigment.

The RK printing proofer (UK) was the laboratory apparatus used for preparing the printed samples. Ink is transferred directly onto the substrate from an electronically engraved printing plate (halftone), which contains four engraving cell depths: 28, 32, 36 and 40μm. A steel doctor blade is set at an angle of 45°. The substrate is attached to a rubber-covered impression roller. Both the doctor blade and the impression roller are adjusted by micrometers. The printing speed was 0.55ms^{-1}, and the distance between the impression roller and the printing plate was 3.7mm.

Print evaluation

The following criteria were used for print evaluation:

Adhesion test

Adhesion is the joining of two surfaces with an adhesive. The adhesion test corresponded to ISO 2409,[17] which gives a qualitative evaluation related to the adhesion of inorganic and organic coatings to a substrate by covering the coating area with an adhesive tape and pulling it strongly. The sample will pass the test if the coating film resists the pull, which means that the coating remains anchored to the substrate.

Print density measurement

The reflection densitometer measures the percentage of light reflected from photographs and printed sheets in one or more colours.[18] Reflectance is usually expressed as the percentage of incident light reflected from a surface:

$$\text{Density} = \log\frac{1}{R}$$

where R = percentage of the reflected light.

For print density measurements in this work, the RCP portable colour reflection densitometer was used, with an accuracy of ± 0.02 density units. Before using the densitometer, it was zero-adjusted and calibrated. All the measurements were carried out 24 hours after printing.

Print gloss measurement

Print gloss is defined as the property of a printed surface to reflect light in a specular direction. The gloss meter Pro-Gloss3 was used at an angle of 60°. Following the ASTM D2457–97 standard method,[19] a black matt paper sheet was placed under the printed samples during measurement. All the print gloss measurements were also carried out 24 hours after printing.

Surface examination of printed PP films

The same scanning electron microscope, as described previously, with an acceleration voltage of 10 to 20KV, was used to study the surface of the printed PP samples. For this experiment, the selected magnifications were 350x and 5000x.

Results and Discussion

Surface characterisation results

Figure 2 shows that the surface energy was remarkably affected after a few seconds of ADBD plasma treatment. It rose from 31mNm^{-1} for the untreated film to 46mNm^{-1} after 15 seconds of treatment. A further increase in the treatment time caused a gradual increase in the surface energy until it reached 72mNm^{-1} after a treatment time of 20 minutes. It is thought that the surface energy increased due to oxygen moieties and/or radicals produced on the plasma-treated PP surface.[7]

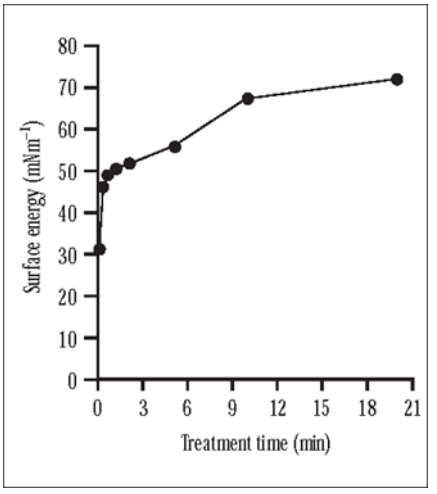


Figure 2: Effect of ADBD plasma treatment time on surface energy of PP film, 40μm

Figure 3 shows the effect of ageing on ADBD plasma-treated PP film after a treatment time of ten minutes. It was found that the surface energy declined over a period of about 45 hours to settle at a level of about 64mNm^{-1}.

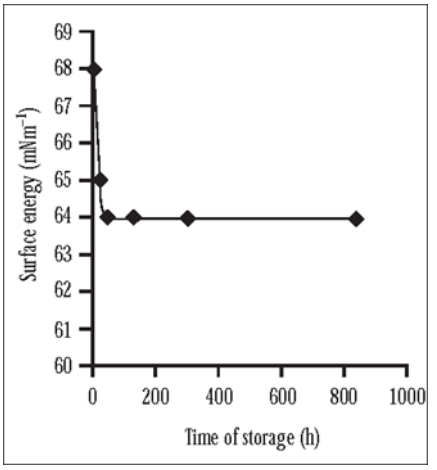


Figure 3: The ageing effect of ADBD plasma treatment on polypropylene film at a treatment time of 10 minutes

Figure 4 shows that there was an increase in the absorbance at the almost-visible range with the ADBD plasma treatment. The increase in absorbance may be attributed to bond cleavage and reconstruction induced by the plasma.[20]

Figure 5 shows that the symmetric and asymmetric stretching, scissors or bending, and wagging of $-CH_3$ and $-CH_2$ frequencies were observed in the untreated as well as the ADBD plasma-treated

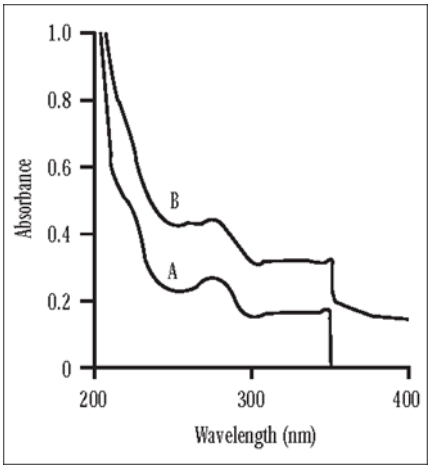


Figure 4: UV-VIS absorption spectra of (A) untreated PP film and (B) 10 minutes ADBD plasma-treated PP film

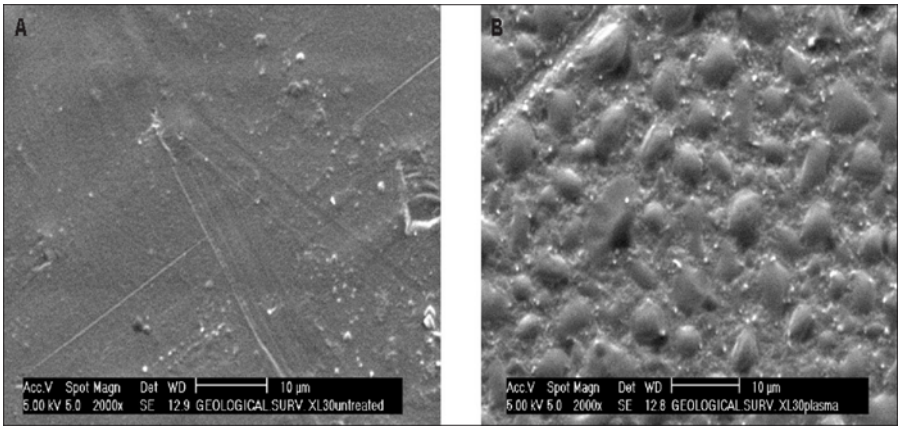


Figure 6: SEM micrograph of PP film (A) untreated and (B) ADBD plasma-treated for 10 minutes, 2000x

PP films. A characteristic peak was observed at 2875cm^{-1} and 2840cm^{-1}, which can be attributed to the $-CH_3$ symmetric-stretching vibration. The peak positions in the untreated and the ADBD plasma-treated PP films remained almost constant, indicating that the structure of the film was not destroyed due to plasma treatment.[21,22] After the ADBD plasma treatment, bands of C=C (at 1635cm^{-1}) and C=O (at 1725cm^{-1}) appeared. The increase of carbonyl bond formation was the result of the reaction of a carbon radical with an oxygen molecule, whereas the vinylic bond creation was the result of the recombination of two adjacent carbon radicals. The untreated PP spectra also showed the presence of the two weak C=C (at 1635cm^{-1}) and C=O (at 1725cm^{-1}) bands due to low-level intrinsic oxidation or surface contamination.[23,24] These two bands appeared greater after plasma treatment as shown in Figure 5.

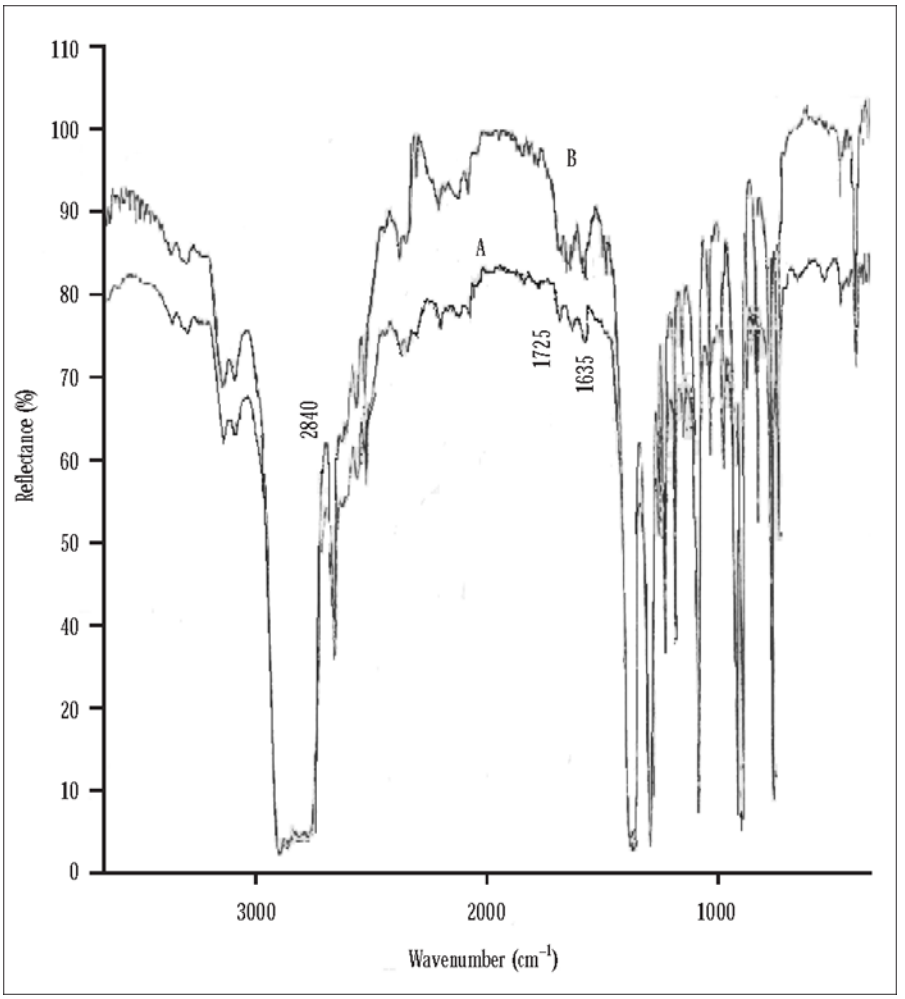


Figure 5: FTIR spectra of (A) untreated PP film and (B) 10 minutes ADBD plasma-treated PP film

Figure 6 shows a scanning electron micrograph of untreated and ADBD-treated PP films (after an exposure time of ten minutes), respectively. ADBD plasma treatment led to the formation of randomly-shaped protrusions on the surface of the PP film.

Figure 7 shows the topography of the PP sample associated with the ADBD plasma treatment. Both the two images are 100µm x 100µm, with the corresponding z ranges and R_q roughness given below the individual images. Figure 7a shows the untreated sample with a smoother surface than the treated sample, while protrusions were found on the surface of the ten-minute treated sample causing an increase in surface roughness.

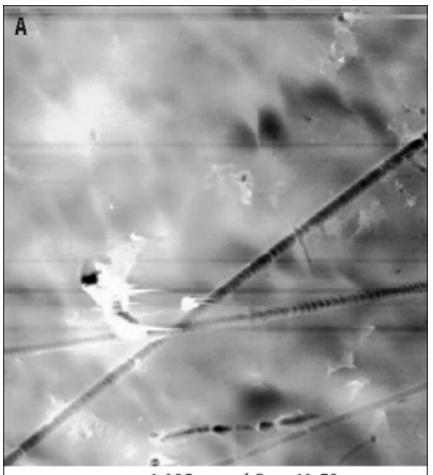
Print evaluation results

Print adhesion

The untreated PP film completely failed in resisting the pull, while the plasma-treated film showed excellent resistance.

Print density results

A short ADBD plasma treatment of 15 seconds caused a substantial increase in the print density readings at the cell depth of 32µm (see Figure 8). This may be attributed to the fact that as the plasma treatment increased, the surface roughness and the surface energy also increased. The sites at the surface which bonded with the ink increased and the film became more ink-receptive.[7] It is postulated that the splitting of the non-immobilised ink was closer to the surface of the substrate than to that of the printing plate because the micro-roughness of its surface provided nucleation sites for cavitations. However, the plasma treatment time was found to have no significant effect on the print density



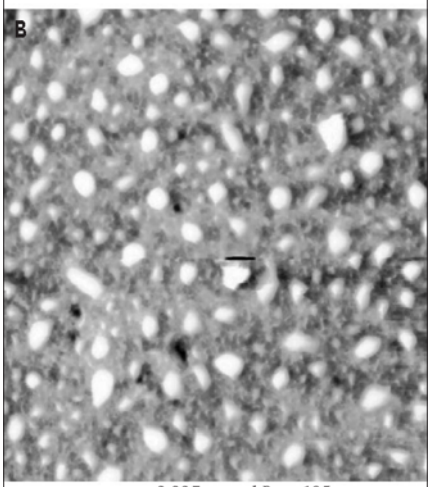


Figure 7: AFM image of PP film (A) untreated and (B) 10 minutes ADBD plasma-treated. the image size is 100μ x 100μ. the z variation and roughness are shown below the images

value with increasing the ink film thickness at cell depths of 32, 36 and 40μm because the ink transfer was independent of the surface free energy.[25]

Print gloss results

Untreated PP film has a print gloss higher than that of ADBD plasma-treated PP films at cell depths of 28 and 32μm, as shown in Figure 9. An increase in the atmospheric plasma treatment time caused a decrease in the print gloss readings only at the cell depth of 28μm. This may be attributed to the increase of ink film thickness at the substrate surface (detected by increasing the print density readings) with an increase of ADBD plasma treatment time. As the ink film thickness increased, a smaller portion of light was reflected from the thicker ink film, and then the print gloss was decreased.[26] The plasma treatment had no effect on the print gloss at a high ink film thickness, at cell depths of 38 and 40μm.

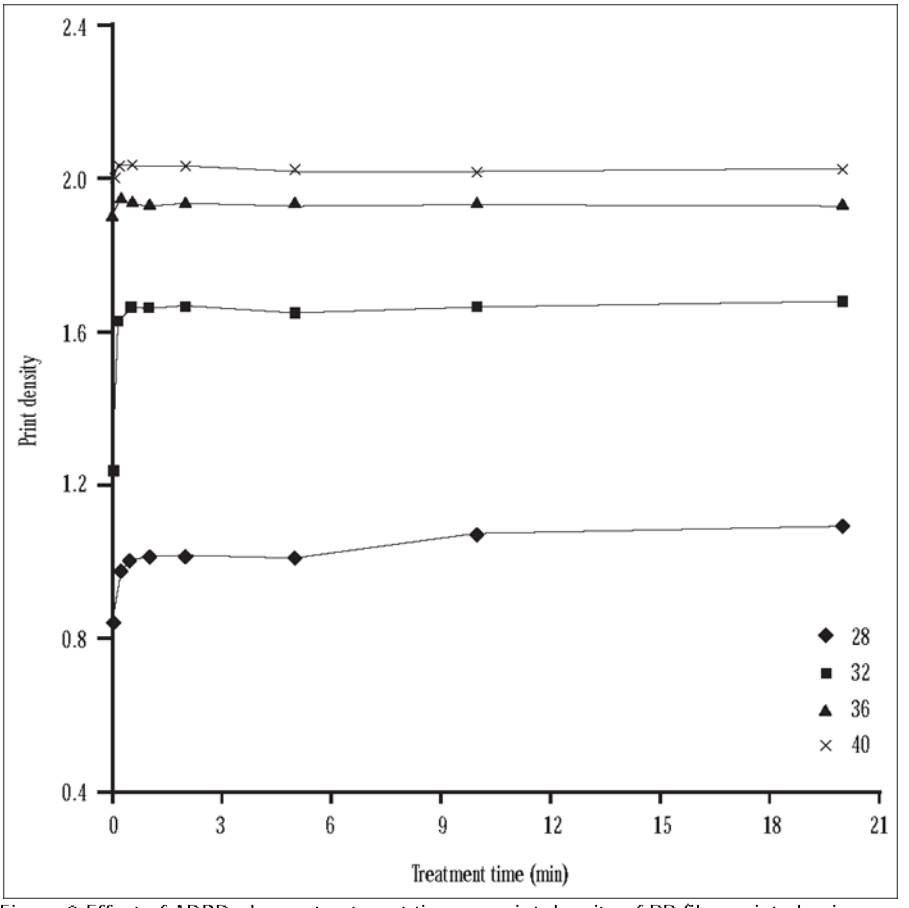


Figure 8:Effect of ADBD plasma treatment time on print density of PP film, printed using solvent-based ink, at cell depths 28, 32, 36 and 40μm

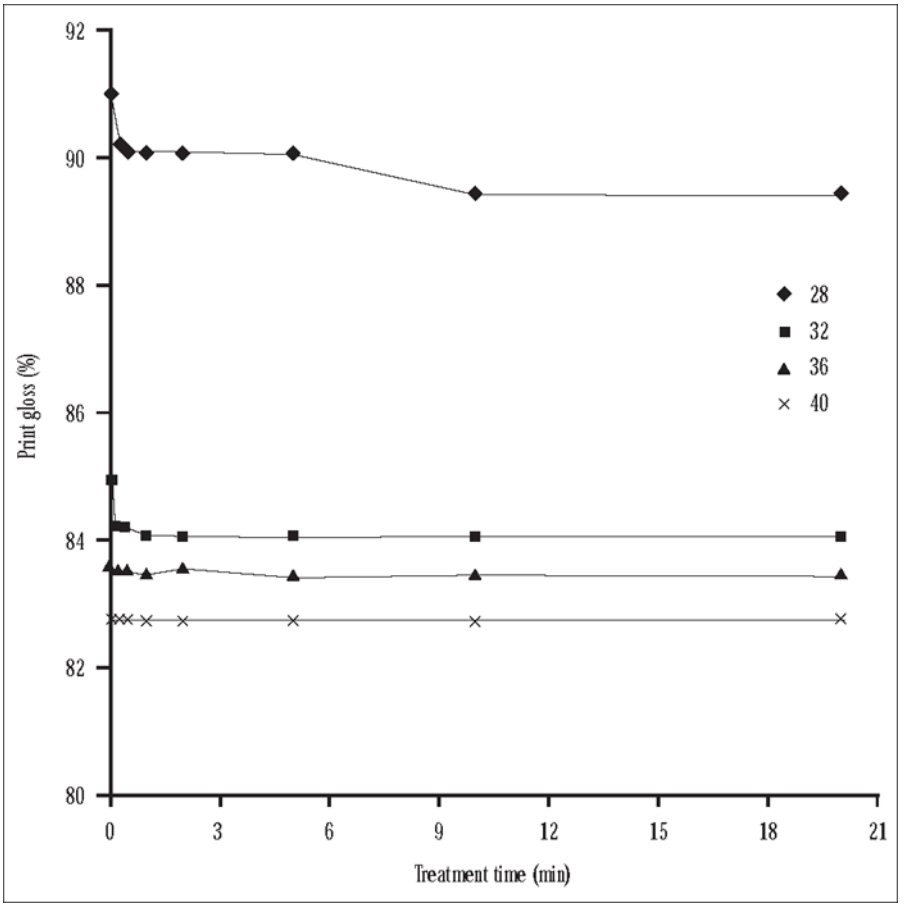


Figure 9: Effect of ADBD plasma treatment time on print gloss % of PP film, printed using solvent-based ink, at cell depths 28, 32, 36 and 40μm

Figure 10 shows a scanning electron micrograph of printed untreated and printed ADBD plasma-treated PP film (at ten minutes of exposure time), at a cell depth of 28μm and magnification of 350x. Figure 10b shows that the contour of ink cells of ADBD plasma-treated film had more regular features than the untreated PP film. The ink formed hair-like lines that were thinner in width in the case of the untreated PP film. This explains the lower values of print density in this case.

Figure 11 shows a scanning electron micrograph of an untreated and ten-minute plasma-treated PP film at a magnification of 5000x, and a cell depth of 28μm. It is shown that the ink lay-down was affected by surface roughness. In the case of the untreated PP film, the surface was smooth and the ink particles formed a continuous and regular film, while the ink film was rough and irregular on the ten-minute-treated PP film. This effect caused a decrease in specular light reflection, which explains the decrease in print gloss values of the ADBD plasma-treated PP film.

Conclusions

The application of ADBD for surface treatment brought about significant changes within the surface physico-chemical and printing properties of the polypropylene films. The plasma treatment resulted in a remarkable increase on the surface energy after a few seconds of treatment. Thus, plasma treatment increased surface roughness, which was observed by SEM and AFM micrographs, showing the formation of randomly-shaped protrusions on the surface of the treated PP film. UV-VIS spectra of plasma-treated films revealed an increase in absorbance in the nearly-visible range, indicating a probable bond cleavage and reconstruction induced by the plasma. FT-IR spectra proved the presence of two bands, namely C=C (at 1635cm^{-1}) and C=O (at 1725cm^{-1}). The surface structure of the film was not destroyed after ADBD plasma treatment. The induced changes caused increased adhesion and printability of the PP film. The effect of plasma treatment on print density and print gloss was more pronounced at a low ink film thickness (28 and 32μm) and for a short plasma treatment time (15 seconds). The time of plasma treatment had no effect on print quality at high ink film thickness. The results proved that ADBD plasma treatment for a few seconds is effective in printing and is economical for industrial use.

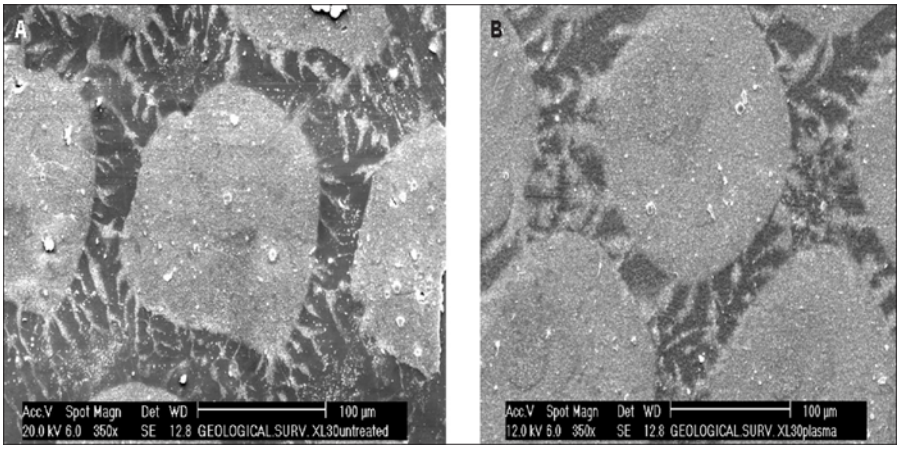


Figure 10: SEM micrograph of printed PP film (A) untreated film and (B) 10 minute ADBD plasma-treated film, at 350x

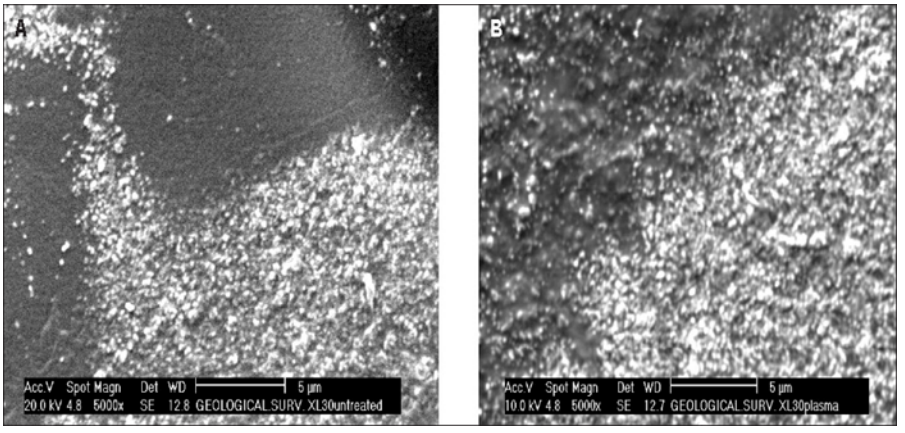


Figure 11: SEM micrograph of printed PP film (A) untreated film and (B) 10 minute ADBD plasma-treated film, at 5000x

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