Applied Surface Science 314 (2014) 331–340

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Practical approach in surface modification of biaxially oriented polypropylene films for gravure printability

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ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form 22 May 2014
Accepted 5 June 2014
Available online 11 July 2014

Keywords:
BOPP
Corona treatment
Surface free energy
Ink

ABSTRACT

Biaxially oriented polypropylene (BOPP) film is one of the most popularly used materials for the gravure printing process in flexible packaging industry. The skin layers of BOPP film were associated with 3–6 weight % of propylene–ethylene copolymer. These films were completely biaxial-oriented by sequential stretching process after which the film surfaces were subjected to corona treatment integrated in the production line. The FT-IR results exhibited that polar functional groups as carbonyl molecules were established on the corona-treated BOPP film. The contact angles of these BOPP films were measured; the surface free energies (SFE) were then calculated. AFM topographical images also agreed well with the SFE which increased as the contents of propylene–ethylene copolymer increased. An approximated 20% increased SFE was obtained for the BOPP film that was associated with 6% propylene–ethylene copolymer. The printing quality on BOPP films was tested by light microscope which confirmed that the chromatic resolution of the printed images improved down to even more smaller groove sizes, 10 or 5 dot%. This improvement was also examined and found to correspond well with the interfacial tensions and work of adhesion between the inks and the modified BOPP films.

1. Introduction

Biaxially-oriented polypropylene (BOPP) film is an extruded polypropylene sheet that was subjected to the two stretching orientations, i.e. machine- and transverse-machine directions. This film is widely known for its universal applications including food packaging, protective coating, pressure sensitive tape, label, printing, metallizing, and decorative products [1–3]. The popular use of BOPP film is provided by its possession of excellent optical, electric, and mechanical properties. It also has light weight and is considered a reliable gas- and water-proof material [4]. Despite these advantages, BOPP film naturally gives one main limitation for its usage—low adhesive interaction—due to the non-polar surface property. One of the most common problems according to this non-polarity is the difficulty to print objects such as liquid inks on the BOPP surface that might have surface free energy (SFE) as low as 22 mJ/m^2 [5]. For decades, the methods to raise the adhesive property of BOPP film had been extensively developed; most techniques involved the different approaches of surface treatments. Chemical [6,7], UV [8], plasma [9,10], flame and corona discharge [11,12] treatments are among most methods employed to increase surface properties. The corona treatment is an effective one by means of industrial applicability because it can be used to improve SFE, hydrophilicity, and hence printability of the substrates with no requirement of running expensive costs [4]. The other advantage is that the corona treatment refers to the ease of handlings and feasibility to be integrated with the film production process. This corona method is based on the electrical discharging in air, and as a result, ions, radicals, photons, and ozone are generated within the gap discharged between the film and the corona treater. The surface of the film is then activated by ions and photons to give alkyl radicals, which subsequently react with the surrounding gaseous species, mainly oxygen and water vapor in air, leading to the major formation of oxygen based functional compounds, such as alcohol, ether, ketone, acid, or ester [13–16]. However, since PP molecular chain is structured by the isopropyl repeating unit, its tertiary radicals mainly formed under corona discharging are so unstable that they rather undergo β-scission or disproportionation when compared to

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http://dx.doi.org/10.1016/j.apsusc.2014.06.032
0169-4332/

the case of primary and secondary radicals [11,17,18]—such species found in PE chain.

The seeking of chemical and physical alternatives to improve hydrophilicity of the non-polar PP film has been continued unabated. Żenkiewicz [19] reported the comparative study of corona treatment upon LDPE and BOPP films which indicated that, under low corona energy treatment, oxygenated molecules were more formed on LDPE than on BOPP. This report was also similar to the results in experiment carried out later by Guimond and co-workers [20]. Recently, the study in modification of PP for adhesion and surface properties has been inclusively presented by Novák et al. [21]. The interest has also been extended to other potential substances; for examples, Dilsiz et al. [22] polymerized trimethyl borate monomer/N_2 gas mixture on the BOPP surface to increase its hydrophilicity and flame retardancy. Wu et al. [2] grafted keratin molecules from its solution onto PP films using air plasma to increase the surface wettability readily for printing. Kalapat et al. [23] studied the modification of BOPP surface using acrylic acid vapor under corona treatment to find that the wettability of the film increased practically with the change in chemical compositions and corona energy. Other hybrid materials to be formed successfully as thin films mentioned in these works may require multitude of efforts carried out to meet qualitative appreciation. The stability of such modified films in long term as well may be questionable. In fact, the use of polyolefin PE or its copolymer, the similar class with BOPP should be re-determined for their great values. It is inexpensive and mutual compatibility in most preparation condition. Ethylene–propylene copolymer (PEco) employed in metallizing BOPP film was previously disclosed by All and Duncan [24]. However, the scientific explanation of its systematic usage in gaining surface affinity specifically via corona treatment for printing technology is not well-known, especially by means of fundamental knowledge involving the surface interaction between substrate and printing ink. The optimum setting of methods which all important ingredients of the process are taken into account needs to be refreshed for each different application.

Gravure printing process is considered a coating technique to create a film on a moving substrate that wipes a proportion of ink or liquid trapped in the cell of a gravure roller [25]. This type of printer was developed for mass production owing to the high speed roll-to-roll printing method which is useful for newspaper, wallpaper, package, and label printings. The pattern of the cell is usually obtained by mechanical engraving or chemical etching [26] typically made in three different complex patterns, i.e. quadrangular, trihelical, and pyramidal [24]. Even though gravure printing is cost-effective and has the ability to produce high quality images using its aforementioned complex grooves, the resolution of the printed quality is affected by the factors such as substrate properties and ink properties. These two properties are relevant to the ink transfer efficiency which can be possibly adjusted by the modification of BOPP film surface via corona treatment and change of chemical compositions.

In this report, we propose an applicable approach to improve the gravure printability on BOPP film using corona treatment and appropriated content of PEco. The original and modified BOPP film are subjected to characterizations including contact angle analysis, infrared spectroscopy, and atomic force microscopy, which indicated that the low-molecular-weight oxidized materials (LMWOM) of the PEco-associated BOPP might be formed mainly due to ester and aldehyde. The results of contact angles, SFE, and coefficient of friction (COF) are also determined with the printability tested from the two different inks, magenta and cyan. Their printed qualities in terms of cell or groove size are closely investigated with the obtained interfacial tensions between the inks and the treated surface. These are also found to correlate with the calculated work of adhesion (W) and spreading coefficient (S) which are the comprehensible terms for most of adhesive, coating, and printing technology.

Table 1
List of BOPP film samples.

Sample code	Corona treatment	Skin layer (%)		Major layer (%)		
		PP	PEco	PP	AS	SA
I	No	100	–	100	–	–
II	Yes	100	–	100	–	–
III		–	100	100	–	–
IV		100	–	99.5	0.5	–
V		97	3	99.5	0.5	–
VI		94	6	99.5	0.5	–
VII		100	–	99	0.5	0.5
VIII		97	3	99	0.5	0.5
IX		94	6	99	0.5	0.5

2. Experimental

2.1. Materials

Polypropylene (PP) homopolymer (HP525J grade) was purchased from HMC Polymer Co., Ltd. Propylene–ethylene copolymer (PEco) (FS5612L grade) was obtained from the Polyolefin Company (Singapore) Pte., Ltd. Antistatic masterbatch from 33% amides, coco, N,N-bis (hydroxyethyl) and slip agent masterbatch from 6% erucamide both in polypropylene homopolymer were obtained from Amphacet (Thailand) Co., Ltd. Water used in contact angle measurement was a double-distilled water from Merck KGaA. Diiodomethane from Merck Schuchardt OHG was used without further purification. Magenta (M17) and Cyan (C39) ink colors were supplied by Toyo Ink (Thailand) Co., Ltd.

2.2. Preparation of BOPP film

The BOPP film was produced at an industrial scale by extrusion casting of a primary film from a slot die, which was then biaxial-oriented by stretching via two-stage drawing process. The 3-layers co-extruder (Bruckner Group, 1327AJP) was used for preparing the BOPP samples containing three layers by which each component was extruded through the top, core, and bottom dies namely as skin (1 μm), major (18 μm), and inner (1 μm) layers, respectively. The skin component was varied from pristine PP, PEco, and blended PEco/PP. The major layer may contain antistatic or slip agent master batch. The inner layer was just the PP only. The weight percent compositions of skin and major layers for BOPP films are presented in Table 1. The corona-discharge treatment was applied for sample **II** to **IX**.

2.3. Corona treatment

The corona treatment was carried out on a corona station (Softal) immediately after the BOPP film was produced and just passed through the stretching process in transverse direction. The treater was the three electrodes system where a ground roll electrode was allowed to face with the film within a distance of 2 mm corona gap. A constant corona energy of 34 W min/m^2 or 2.04 kJ/m^2 was delivered to the film at a 450 m/min speed line.

2.4. Contact angle measurement and surface free energy calculation

Contact angles of pure water and diiodomethane on the non-corona-treated (NCT) and corona-treated (CT) BOPP film were measured on a Kyowa instrument (DM500) by which ten drops