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Aluminum oxide barrier coatings on polymer films for food packaging applications☆

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ABSTRACT

In the field of packaging, barrier layers are functional films, which can be applied to polymeric substrates with the objective of enhancing their end-use properties. For food packaging applications, the packaging material is required to preserve packaged food stuffs and protect them from a variety of environmental influences, particularly moisture and oxygen ingress and UV radiation. Aluminum metallized films are widely used for this purpose. More recently, transparent barrier coatings based on aluminum oxide or silicon oxide have been introduced in order to fulfill requirements such as product visibility, microwaveability or retortability. With the demand for transparent barrier films for low-cost packaging applications growing, the use of high-speed vacuum deposition techniques, such as roll-to-roll metallizers, has become a favorable and powerful tool. In this study, aluminum oxide barrier coatings have been deposited onto biaxially oriented polypropylene and polyethylene terephthalate film substrates via reactive evaporation using an industrial 'boat-type' roll-to-roll metallizer. The coated films have been investigated and compared to uncoated films in terms of barrier properties, surface topography, roughness and surface energy using scanning electron microscopy, atomic force microscopy and contact angle measurement. Coating to substrate adhesion and coating thickness have been examined via peel tests and transmission electron microscopy, respectively.

1. Introduction

Polymer films vacuum coated with a thin layer of evaporated aluminum are a standard component in the composite structure of flexible packaging materials for a variety of food stuffs. These thin coatings with a thickness of a few tens of nanometers [1] are produced on industrial roll-to-roll vacuum web coaters, generally referred to as metallizers. The machines predominantly use resistively heated evaporation boats and can coat films of a width of 4.45 m at speeds up to 1000 m/min [2,3]. The main purpose of applying these thin layers is to confer barrier properties to the polymer films, which on their own generally do not act as good barriers, and thus create a functional packaging material. The impermeability of the packaging material to vapors and gases such as water, oxygen, carbon dioxide and aromas (either going into or coming from the product) is an essential design consideration for the longevity of the packaged food product and hence key to successful food packaging. In recent years, transparent barrier coatings, such as aluminum oxide or silicon oxide (usually referred to as AlO_x and SiO_x as the exact stoichiometry is not generally measured) have been gaining interest. When applied onto polymer films, these barrier coatings bring additional advantages over opaque metallized films in that they offer product visibility, microwaveability/retortability and are also suitable for passing through metal detectors, whilst still providing the barrier levels required. With the transparent barrier flexible packaging market growing worldwide at a rate of 10 to 15% per year [2], the use of vacuum deposition techniques to produce transparent barrier layers has become very attractive. Products such as ethylene vinyl alcohol copolymer (EVOH) coated and coextruded barrier films and polyvinylidene chloride (PVdC) atmospheric coated polymer films conventionally tend to dominate this market [4]. However, vacuum deposited thin barrier coatings only require a small fraction of the thickness of these polymer based barrier layers, i.e. their thickness is three orders of magnitude less, whilst still producing similar barrier properties. This can potentially provide vast economic and environmental benefits in terms of raw material consumption and the associated costs. Using and modifying a standard 'boat type' roll-to-roll metallizer to deposit transparent barrier coatings has been an aspiration for many years [5–10]. The injection of oxygen into the aluminum vapor stream in the evaporation zone results in the deposition of a transparent aluminum oxide layer, which can give good barrier properties, when the process and its conditions are controlled appropriately. When using polyethylene terephthalate (PET) base film, this process produces consistent barrier performance with the reactively

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evaporated aluminum oxide. However, considering the low profit margins within the packaging market, the associated cost of the base substrate also plays a major part and commodity biaxially oriented polypropylene (BOPP) films still remain at a lower cost level than PET. The barrier levels of aluminum oxide coated BOPP, though, are heavily affected by the plain film surface characteristics and thus the growth conditions created for the depositing thin film. As will be shown, the surface characteristics of standard packaging grade BOPP films can vary significantly. Therefore, this paper reports the characterization of plain film surface properties, such as surface energy, roughness and topography and relates the findings to the barrier levels obtained after AlO_x coating. Additionally, coating adhesion and coating surface energy, important parameters for further conversion of vacuum coated films, and coating thickness have been assessed using peel tests, contact angle measurement and transmission electron microscopy, respectively.

2. Experimental

2.1. Substrate materials

Various packaging grade BOPP films and a PET base film (all corona treated in-house by the film producers), as well as a BOPP film coextruded with a special high surface energy polymer as a skin layer ('UHB', produced by Brückner Maschinenbau GmbH & Co. KG, Siegsdorf, Germany) were coated with an aluminum oxide barrier layer. The coatings were applied to the corona treated side of each film and the high surface energy polymer skin layer, respectively. All standard packaging grade BOPP films used consist of a three layer coextruded structure with a homopolymer core and either co- or terpolymer skin layers on each side in order to obtain a heat-sealable film. These skin layers also contain additives such as antiblock particles (up to several μm in diameter, typically consisting of silica), which ensure good film processing and converting characteristics. However, they are also known to negatively impact the barrier properties of vacuum deposited coatings. In contrast to the standard packaging grade BOPP films, the BOPP film with the special polymer skin layer consists of a five layer coextruded structure, with no antiblock particles added to the high surface energy polymer skin layer [11]. The PET film coated as a reference material is a monolayer film, with antiblock particles dispersed throughout the single layer. Furthermore, all films contain a variety of additives to stabilize the polymer film and guarantee optimized film handling and end-use properties. Exact film compositions are, however, commercially sensitive information not made available by the individual film producers.

2.2. Coating process

The polymer films were coated via reactive thermal evaporation using a Bobst Manchester Ltd. (formerly General Vacuum Equipment Ltd.) General K4000 vacuum metallizer with an AlO_x coating system installed. The K4000 roll-to-roll metallizer can handle webs up to 2450 mm wide and the AlO_x coating process was performed at web speeds up to 840 m/min. For the films coated here, the web width varied between 1000 mm and 1650 mm and samples were generally taken from the center of the web. The vacuum coater has a deposition source consisting of resistively heated evaporation boats (standard intermetallic composite) onto which aluminum is continuously fed in the form of a wire. Oxygen is introduced into the aluminum vapor stream in order to produce a transparent aluminum oxide coating and a special optical monitor beam and closed loop control system is used to achieve consistent optical properties of the coated film across the web width and length. The pressure during aluminum oxide deposition is of the order of 0.05 Pa. For development purposes, in-line plasma pre- and post-treatments were performed using a plasma source with magnetically enhanced water cooled electrodes. The pressure at the plasma treatment units is kept between 2 and 4 Pa, in order to minimize unintended sputtering from the electrodes. The plasma treatment was performed using power settings and gas recipes previously optimized at Bobst. For this study, other than the plasma treatment conditions, all coating parameters were kept constant to ensure coatings of comparable thickness and stoichiometry.

2.3. Analytical techniques

Barrier properties, in terms of oxygen and water vapor transmission rates (OTR/WVTR), were determined in accordance with ASTM F 1927 and ASTM F 1249/ISO 15106-3 using a Mocon Oxtran 2/20 and Systech Illinois 8001 for oxygen permeation and a Mocon Permatran-W 3/33 and Systech Illinois 7001 for water vapor permeation. Test conditions for OTR were 23 °C and 50% relative humidity (RH), whilst WVTR is stated for 37.8 °C and a gradient of 90% RH.

Furthermore, a Zeiss Supra 40VP field emission gun scanning electron microscope (SEM) was used to acquire images of the uncoated and aluminum oxide coated film surfaces at an acceleration voltage of 0.4/0.5 kV. In order to avoid masking any surface detail, no conductive layer was applied to these insulating samples prior to analysis.

The plain film and coating surfaces were additionally analyzed with a WiTec alpha500 and a Veeco DI CP II atomic force microscope (AFM). Pulsed force mode and tapping mode, respectively, were used to acquire roughness data and topography images. All images were corrected by first order line-wise leveling. Root mean square (RMS) and roughness average (R_A) values were calculated from $5 \times 5\ \mu m^2$ size scans. Therefore, several scans were performed from different areas that did not exhibit antiblock particles in order to obtain an average value and the standard deviation.

The coating to substrate adhesion was assessed using a peel test, as described in further detail in Ref. [12,13]. This industrial based test is normally applied to examine the adhesion of aluminum metallized films. For this test, an ethylene acrylic acid (EAA) film is bonded to the coated surface of the polymer film and, after conditioning, the EAA/coating is peeled off at a peel-off angle of 180°.

The surface energy of the uncoated films and the AlO_x coating surface energy were investigated by means of contact angle measurement via the sessile drop method. Contact angles for three different test fluids (water, diiodomethane and ethylene glycol) were measured with a Krüss MobileDrop system and DSAII software. When curve fitting and measurement of contact angles were not possible with the Krüss system, the acquired images were analyzed using a drop shape analysis plugin for ImageJ [14]. These angles were then used to calculate the surface energies according to the Owens–Wendt–Rabel–Kaelble approach [15–17]. Throughout this investigation, sample swatches were stored under ambient conditions.

A FEI Tecnai 12 Biotwin transmission electron microscope (TEM) at a 100 kV acceleration voltage was used to acquire images of the AlO_x layer for coating thickness evaluation after embedding and ultra-microtome sectioning.

3. Results and discussion

3.1. Barrier performance

The barrier performance obtained for the plain BOPP films and the AlO_x coated films is summarized in Table 1. Also listed in this table are the results for a PET reference film and the results following different plasma treatments. These values were used to determine the barrier improvement factor (BIF) for each transmission rate (i.e. transmission rate ratio of uncoated to coated film), which is a quality indicator commonly used to characterize the effect of vacuum deposited barrier coatings. The results presented in Table 1 allow the BOPP films to be rated with respect to their barrier performance after AlO_x coating:

- BOPP A — poor performing polymer
- BOPP B — standard performing polymer