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Investigation of aluminium thin layer microstructure on BOPP polymer substrate

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Abstract In this work, 40 µm biaxially oriented polypropylene (BOPP) polymer substrate is coated in a roll coater system. The single- and double-coated aluminium thin layers are analyzed by XRD, SEM, TEM, AFM and optical light microscopy. The size and density of pinholes are investigated by using TEM, the size of the pinholes are in the range of 0.8–8 µm, it is shown that with increasing sample thickness, the dimension of pinholes decreases. SEM and AFM are applied to study the surface morphology. The results show that the surface roughness of double-coated film is better than the single-coated one and the size of pinholes is smaller. The transmittance through the samples is measured on the UV–Vis range. The results show that double-coated film has significantly low transmittance (almost zero transmittance) in UV–Vis region.

Introduction

The vapour deposition of the metal aluminium on the polymer substrate has been used in the very wide range of industrial systems. Metalized polymer films are useful in decorative industry and capacitors. Because of their very good barrier property, it is very useful in packaging industry and for economical reasons it is replaced with the aluminium foil. In spite of the widespread of its uses, only a few results about microstructures properties exist in the literature [1–6]. The paper written by Jamieson et al. [1] evaluates the structure of the aluminium film formed on commercially metalized polyester film substrates. They found that the deposited aluminium layers on polyester films are similar to aluminium layers deposited on glass and other inorganic substrates with the diameter of aluminium crystals approximately the same as the thickness of the layer, but the crystal diameter depends on the vacuum level during the deposition. Weiss et al. [2] analyzed optical density and the effect of the coating conditions and the layer thickness on the structure, the grain size and the morphology of the aluminium layer on the polyester and polypropylene substrate. Haidara et al. [3] investigated the relationship between structural properties of vapour-deposited metallic films on polymer and their related adhesive properties. Vassiliadi et al. [4] studied the effect of corona unit energy applied for retreatment of metalized biaxially oriented polypropylene (BOPP) film surfaces before the lamination process. They showed that increasing in the adhesion improves the barrier properties of the prepared composite structure. They also emphasized that with increasing corona unit energy, the surface roughness increases and the surface texture changes.

Coating of aluminium thin film on the polymer substrate not only changes the optical and electrical properties, but also changes its permeability to the water vapour, oxygen, other gasses and the light. Diffusion of gasses in solids is influenced by many factors such as crystallization of solids, defects, polarity of gas as well as possible chemical interaction between them [7]. The existence of the pinhole defects in the coated aluminium thin layer determines the permeability of these films to gasses. The defect in the layers reduces the barrier properties.

In this article, the microstructure of vapour-deposited aluminium thin layer on the BOPP polymer substrate is

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analyzed through XRD, EDX, TEM, AFM and SEM methods. Our results are compared with the results of coated aluminium thin layer on the polyester substrate [1].

Experimental procedures

Materials

The thin film used in this work was a 40-µm thick transparent BOPP (PUSHINE Co, Iran), the purity of coated aluminium metal was more than 99.99%.

Vacuum metallization

Metallized samples used in this study were produced in a roll to roll machine, the process sequence includes the following steps: loading a roll of uncoated web, pumping down to necessary vacuum for processing, preconditioning of coating source, deposition of one or more layers, venting and unloading of coated web. A simplified schematic of vacuum web is shown in Fig. 1.

The coating of the polymer substrate was done at the speed of 2 m/s with molten aluminium which is held above heated boats. The thickness of coated layer can be controlled by the speed of rolling. To have a thinner metallized layer we must increase the speed of the rolling cylinder in the coating systems. In our experiment, we used the same speed of rolling for both coating. The working pressure of vacuum chamber was approximately 10^{-3} Torr.

Scanning electron microscopy (SEM)

The crystal grain size and morphology of aluminium layer are determined by SEM of model 'Philips XL 30'. X-ray energy dispersion spectroscopy (X-ray EDS or EDX) were used for element analysis.

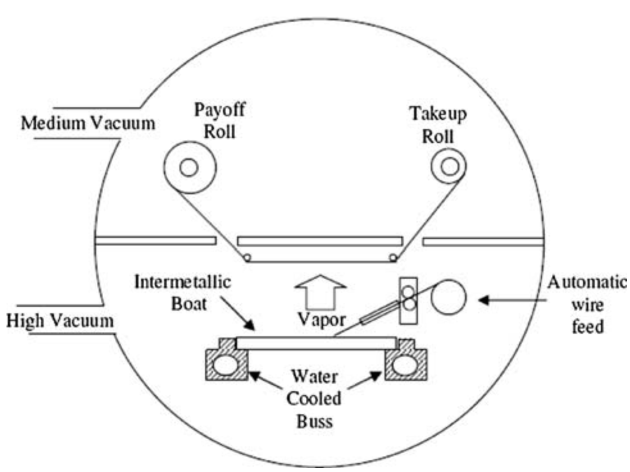

Fig. 1 Simplified scheme of a vacuum roll coater

Transmission electron microscopy

Metalized BOPP pieces of 2 × 2 cm were cut out for face on microscopy. The samples are prepared by dissolving the BOPP substrate with xylene solution for 10 min at 35 °C and scratching the aluminium layer with a copper grid.

Transmission electron microscopy investigations were performed by 'Philips EM 208 S' electron microscopy.

Optical microscopy

Optical microscopy by 'Lights' model was used for observations of metalized BOPP surfaces and pinholes.

Atomic force microscopy (AFM)

AFM provides a real space, three dimensional (3D) image of a surface through the detection of an interaction between a sharp mechanical tip and the surface.

Our AFM study was performed by the 'Dual Scope C-21 DME'. The AFM images were obtained in a tapping mode experiment to gain both topographic and phase imaging using a rectangular Nanosensor Si cantilever probes of 445-µm length and 45-µm width. The radius of tip was 10 nm and the scanning rate was 5 µm/s. The spot size for the collected AFM images was 5 × 5 μm^2. Three different spots were examined for each of the examined samples.

Result and discussion

Our XRD results show that the aluminium thin layer has a preferred orientation with [111] an aligning normal to the plain of the film as in Ref. [1]. The same results were also observed for the aluminium layer with a glass substrate [8]. The XRD broadening made use of Scherrer formula which relates the film thickness to the half-width of the diffraction peak [9]. The thickness of the prepared thin layer aluminium samples ranged from 20 to 60 nm. The same thickness values were obtained by using electrical resistivity method.

The SEM image of aluminium thin layer with BOPP substrate is shown in Fig. 2. It is seen that the aluminium layer has a homogeneous structure and the structure of layer is polycrystalline and crystalline grain having boundary between them. The size of crystal grain is about 20–70 nm, the same order of the sample thickness. Vapour water and gasses diffuse to metallized layer through this boundary layer.

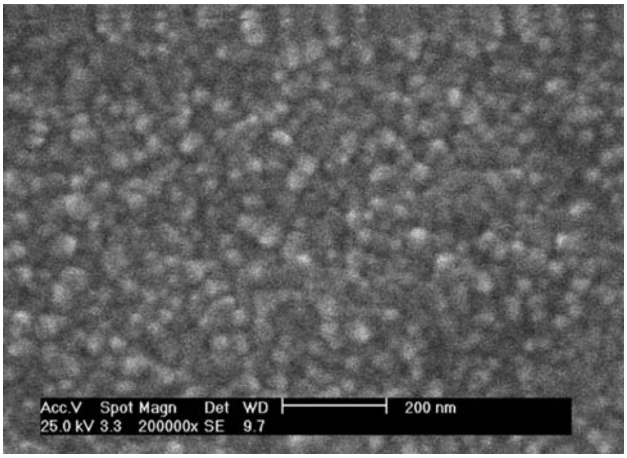

Fig. 2 SEM microimage of metallized BOPP film, it is seen that the aluminium layer has a homogeneous structure and the structure layer is polycrystalline, the size of the crystal grain is about 20–70 nm

The EDX results are shown in Fig. 3a, b for a single-coated and a double-coated sample, respectively. Double-coated sample has approximately two times thickness than the single-coated sample. As expected, carbon and aluminium are the main elements found on the surface of metallized BOPP film. As it can be seen, a small percentage of oxygen atoms are also found at the surface of the samples. The existence of oxygen atom shows the presence of Al_2O_3 on the aluminium layer. This indicates that the oxidation has taken place during corona discharge and deposition process [1, 4]. The Al_2O_3 is an excellent barrier because of its high electrical resistivity which restricts the supply of electrons at the surface necessary for the reaction $O_2 \rightarrow 2O^{2-}$ [1].

AFM is one of the useful techniques that can detect the topography of a sample surface. Surface of single- and double-coated samples are observed using the AFM method. The topographic images (Fig. 4) showed that for both films the metallization thickness is not uniform over the whole film surface. Despite of this, the roughness of the surface on the double-coated sample is better than the single-coated one. We are not sure this roughness is related to the thickness or the double-coated processes. Figure 5a shows the TEM image of a single-coated aluminium thin layer. It is seen that the crystal grain are near to each other and have different sizes (some of them are small and some are big). The black colour of some grains is due to the diffraction of electrons. The continuity of thin aluminium layer is very effective in modifying barrier property. There is some intrinsic defect which could not be completely removed and the most important of them is the existence of the pinholes in the layer. The water vapour and gasses can diffuse through these pinholes to the packaging and spoil the food.

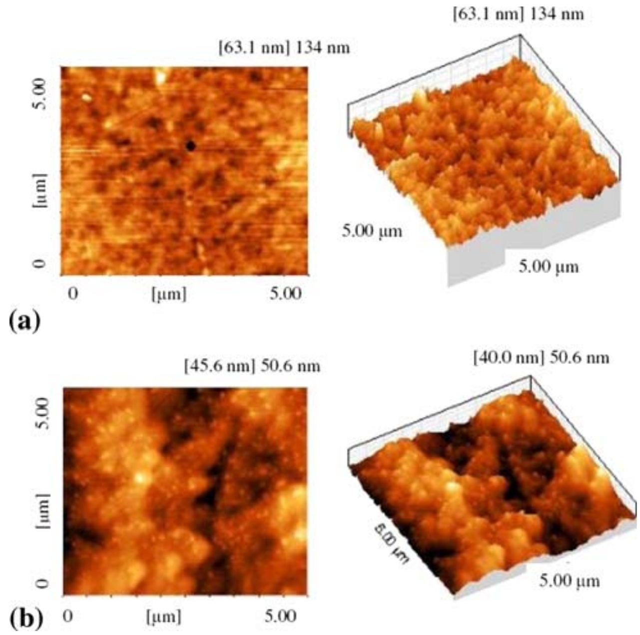

Fig. 4 Tapping mode AFM images of metalized BOPP **a** single-coated films and **b** double-coated films. The topographic images show that for both of the films the metallization thickness is not uniform over the whole film surface. For double-coated film, roughness of the surface is better that of the single-coated one

The reason for the formation of such pinholes has been discussed in the literature [10, 11]. Dust on the substrate is the main factors on the formation of these pinholes, which prohibits the formation of aluminium layer on these locations. One of the methods for blocking pinholes formation due to dust is to clean the polymer layer before coating. In this work, we used corona discharge method for treatment of surface of polymer substrate. Figure 5b, c shows the

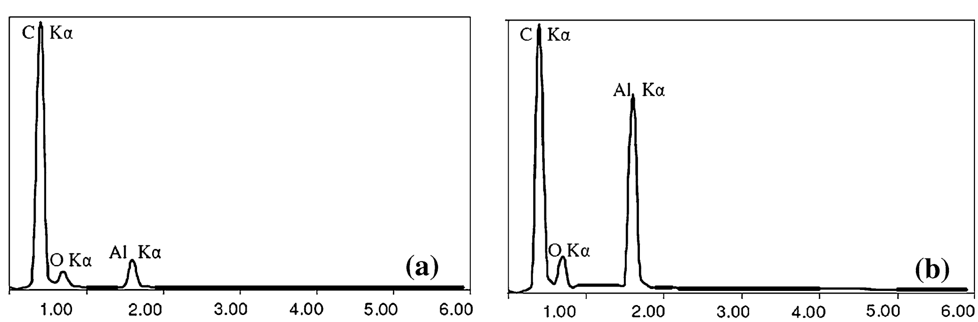

Fig. 3 The EDX result for **a** single-coated and **b** double-coated sample

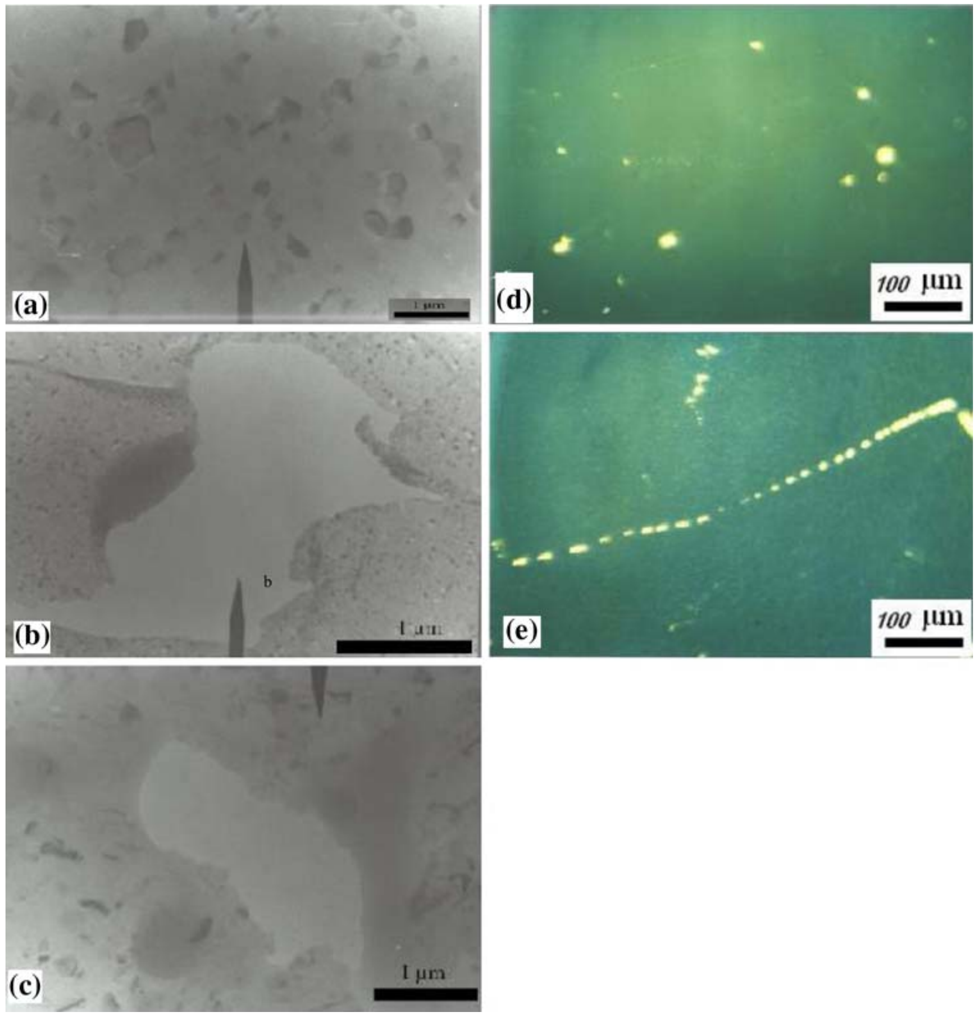

Fig. 5 TEM image of single-coated thin aluminium layer with BOPP substrate, it is seen that the crystal grains are near to each other and have different sizes (**a**). The TEM picture of pinhole for two samples single coated (**b**) and double coated (**c**). The size of the pinholes are in the range of 0.8–8 μm. It is seen that with increasing of sample thickness the dimension of holes decreases. The transmitted light micrograph of pinholes, due to the dust (**d**) and due to the folding or stretching which causes scratches to the surface of BOPP film prior to coating (**e**)

TEM picture of pinholes formation on the single- (Fig. 5b) and double-coated (Fig. 5c) samples. The size of the pinholes are in the range of 0.8–8 μm, which are less than the average size reported by Jemison et al. [1] and their density is 20–30 mm^{-2} which is same as Jemison. It is seen that with increasing of sample thickness the dimension of the holes decreases. The pinholes are also observable by the transmitted light microscope. Figure 5d, e shows two different types of pinholes on the single-coated aluminium thin layer. In Fig. 5d the pinholes are scattered points due to the dusts, but in Fig. 5e pinholes are in the straight line, which can be related to folding and stretching of polymer film in the rolling and unrolling process which causes scratches to the surface of BOPP film prior to coating.

The formation of pinhole due to the folding and stretching (as a mechanical defect) can be controlled by regulating the speed of rolling cylinders. The transmittance of the single- and double-coated samples is compared with uncoated BOPP substrate. Figure 6 shows the transmittance of uncoated BOPP with 40-μm thickness (solid line), single-coated (dashed) and double-coated (dotted) samples

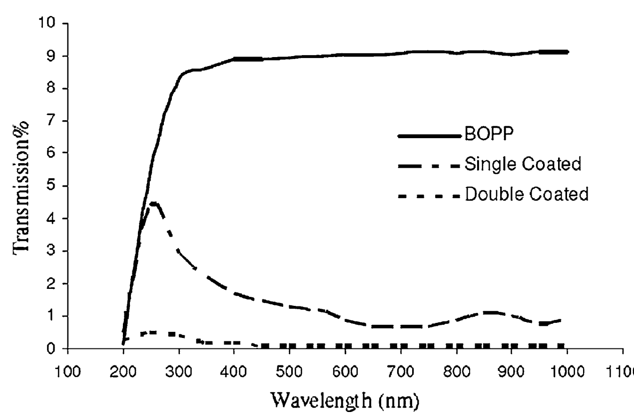

Fig. 6 Transmittance of uncoated BOPP with 40-μm thickness (*solid line*), single coated (*dashed line*) and double coated (*dotted line*). The transmittance is reduced significantly, so that the double-coated sample has zero transmission. The transmittance of uncoated BOPP is divided to 10

on UV–Vis region. In order to present a clear comparison among these three samples, we have divided the transmittance of uncoated BOPP to 10.

As it is seen, by coating of the BOPP by aluminium, the transmittance is reduced significantly, so that the double-coated sample has zero transmission. Measurements were done by using of photospectrometer (model CE20041).

Conclusion

In this work, the aluminium thin layer BOPP polymer substrate is investigated. The results of XRD, SEM, TEM, AFM and optical light microscopy are presented. XRD results show that thin aluminium layer with polymer substrate is crystalline and the grain growth is in the [111] direction. SEM pictures shows that the layer surface is mono grain and structure of layers is polycrystalline with a boundary between them. The EDX results show that a small percentage of the oxygen atoms exist on the coated layers. The TEM results present the formation of different types of pinholes. The micrographs of optical light microscopy also show the formation of the pinholes. These pinholes can be due to dust and the folding or the stretching of the substrate film. It was shown that the surface roughness of double-coated film is less than the single-coated one. The size of pinholes for the double-coated sample is smaller than the single-coated sample and double-coated sample has superiority to single-coated one, such that the double-coated sample has lower roughness and significantly lower transmittance (almost zero transmittance) in the UV–Vis region. The size of the pinholes was determined to be in the range of 0.8–8 μm, which are less than the average size reported by Jemison. It was shown that with increasing the sample thickness, the dimension of pinholes decreases.

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