

Characterization of vapor deposited aluminum coatings on oriented polypropylene films

Martin J. Fay and Thomas D. Allston

ABSTRACT: *The structure of vapor deposited aluminum on corona-treated polypropylene can be examined by a number of analytical techniques. Among these techniques are scanning electron microscopy, atomic force microscopy, transmission electron microscopy, and electron spectroscopy for chemical analysis.*

KEYWORDS: *Aluminum, analysis, barrier properties, coatings, corona discharge, measurement, metalized film, polypropylene, surface structure, surface treatment, vacuum deposition, vapor barriers.*

Metalized polymer films are widely used for a variety of packaging applications. The metal coating provides an effective light barrier, which is important for foods that experience accelerated spoilage when exposed to light (i.e., foods with high fat content). Metalization can also significantly enhance a film's barrier to oxygen and water transmission (1). This is critical for extending the shelf life of packaged foods.

Generally, aluminum is the metal of choice for metalized packaging films due to its low cost, good appearance, and resistance to corrosion. The most common method of

coating is physical vapor deposition under a moderate vacuum. Rolls of film are placed in a metalizer, and the metalizer is pumped down to pressures of 10^{-3} – 10^{-4} torr. Aluminum is heated to temperatures high enough to vaporize it. The film is coated by passing it over the vaporized aluminum. Reducing the metalization pressure increases the mean free path of the vaporized aluminum and minimizes oxidation of the aluminum vapor by ambient oxygen and water vapor (2).

The increasing importance of enhanced oxygen and water barriers for packaging applications has generated considerable interest in the

structure of aluminum-coated polymer films. In theory, a defect-free coating of aluminum should provide an almost complete barrier to oxygen and water transmission. In practice, however, poorly metalized films can show only moderately better barriers than unmetalized films. This discrepancy suggests that a significant number of defects can exist in the aluminum coating.

The following discussion examines the structure of vapor deposited aluminum on corona-treated polypropylene by a number of analytical techniques. The goal of these measurements is to gain a better understanding about the structure of the aluminum coating and how this structure might affect its barrier properties.

Experimental

Film preparation

The base film was biaxially-oriented polypropylene homopolymer. The metalized surface was corona-treated prior to metalization. The level of treatment was relatively high, yielding a surface energy of approximately 56 dynes/cm. The optical density of the metalized film was 2.3.

Metalization resulted in considerable barrier enhancement relative to the base film. The water vapor

Fay and Allston are senior research chemists with Mobil Chemical, Films Division, 729 Pittsford-Palmyra Rd., Macedon, NY 14502.

Metalized Film Coating

transmission (WVTR) and oxygen transmission (OTR) rates of the base film and the metalized film are given in Table I.

Scanning Electron Microscopy (SEM) measurements

The metalized films were lightly coated with gold prior to measurement (the gold coating was approximately 100 Å thick). This was done to increase the conductivity of the film surface, which improves the quality of the SEM images. This coating of gold is not observable at the magnifications of the SEM images presented in this report. SEM images of the metalized film cross-sections were obtained by imbedding the film in epoxy and microtoming the imbedded film at a 30° bias. The microtomed blocks of the imbedded films were then coated with gold prior to examination.

Atomic Force Microscopy (AFM) measurements

The atomic force measurements were made with the Digital Nanoscope III. The film samples were mounted with double-sided tape and measured directly under ambient conditions.

Transmission Electron Microscopy (TEM) measurements

The aluminum coating was removed from the film substrate prior to examination. This was done by dissolving the polymer substrate in hot trichlorobenzene (approximately 100°C). The remaining aluminum coating was placed on a TEM grid for measurement. The TEM cross-section images were taken from thin sections microtomed from the metalized film embedded in epoxy.

Electron Spectroscopy for Chemical Analysis (ESCA) measurements

The metalized films were mounted on double-sided tape and placed directly in the ESCA spectrometer.

During the ESCA measurements, the metal coating was sputtered (eroded) with a beam of 3 KeV Ar⁺ ions. The size of the sputter crater was 3 mm x 3 mm, and the ESCA analysis spot was a 1 mm x 1 mm region centered in the sputter crater. The sputter rate of the Ar⁺ ions was 50 Å/min for SiO₂.

Results and discussion

SEM images of aluminum coated film

SEM micrographs were taken of the metalized film surface to gain information about the topology of the metalized coatings. The images shown in Figs. 1 and 2 were taken at magnifications of 10,000X and 50,000X. The SEM images from the metalized surface show a topology characterized by large "mounds" several thousand angstroms in diameter. These mounds reflect the surface topology of the base film (not the metal coating). These "mounds" are the result of corona treatment, which alters the morphology of the polypropylene surface considerably. No evidence for fractures or voids in the aluminum coating is apparent. At the highest magnification (50,000X), the "grains" of the Al coatings become evident as small "spheres" on the film surface.

A cross-section image of the metalized film is shown in Fig. 3. The image is from the film imbedded in a block of epoxy and microtomed. This image provides a direct measurement of the aluminum coating thickness which is indicated on the micrograph. The thickness of the metal coating is approximately 40 nm (400 Å). This aluminum coating thickness corresponds to an optical density of 2.3.

AFM images of aluminum coated film

AFM is similar to SEM in that it provides information about the surface topology. However, AFM is capable of much higher magnification and can be measured under ambient

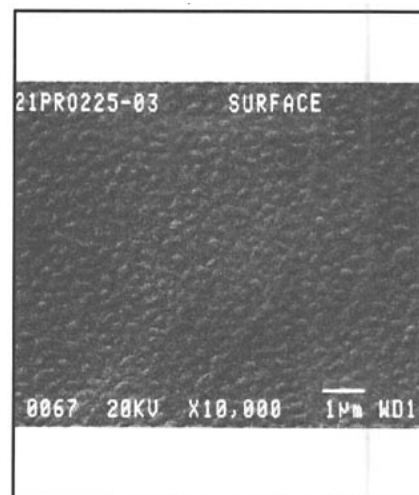
I. Water vapor transmission rates and oxygen transmission rates of base film and metalized film

Film	WVTR ^a	OTR ^b
Corona treated polypropylene	0.339	114.9
Metalized film	0.105	4.97

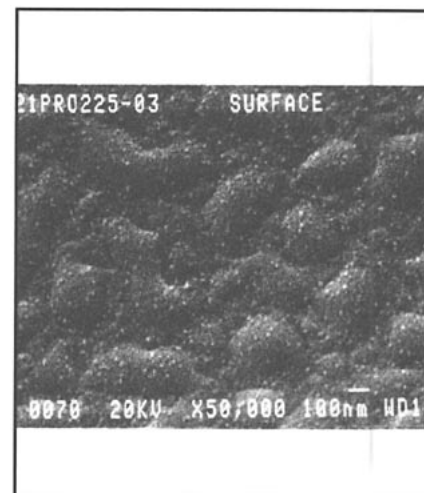
^a WVTR units = g/100 in.²/24 hr at 98°F and 90% relative humidity

^b OTR units = cc/100 in.²/24 hr at 73°F and 0% relative humidity

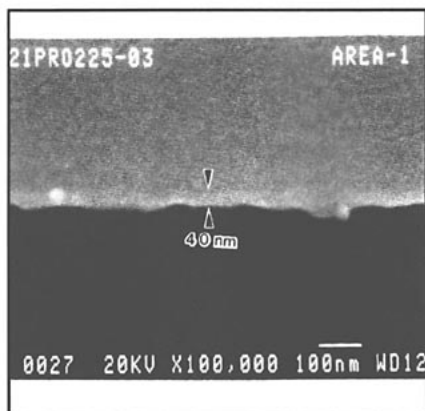
1. SEM image of metalized film surface (magnification 10,000X)



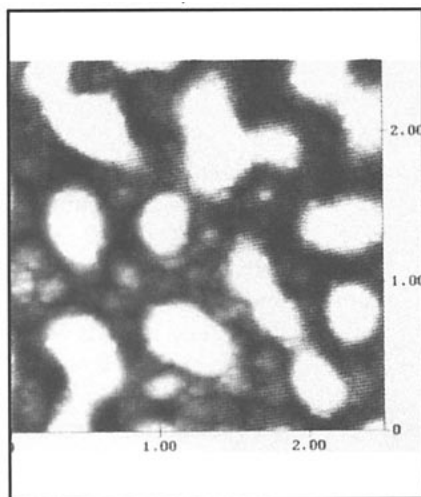
2. SEM image of metalized film surface (magnification 50,000X)



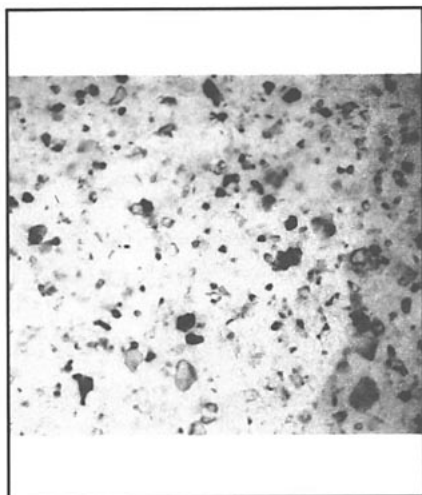
3. SEM image of metalized film cross section (magnification 100,000X)



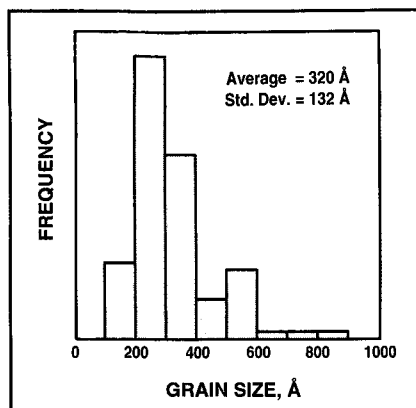
4. AFM image of metalized film surface (magnification 93,000X)



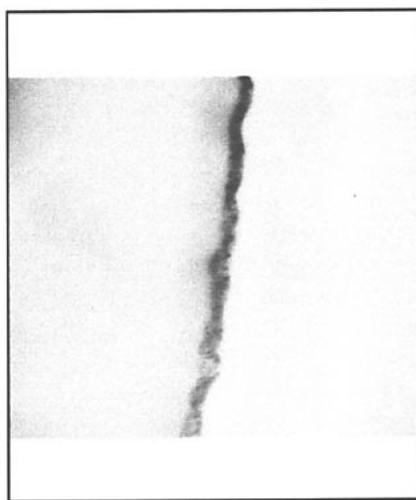
5. TEM image of aluminum coating (magnification 182,000X, 1 cm = 0.055 μ m)



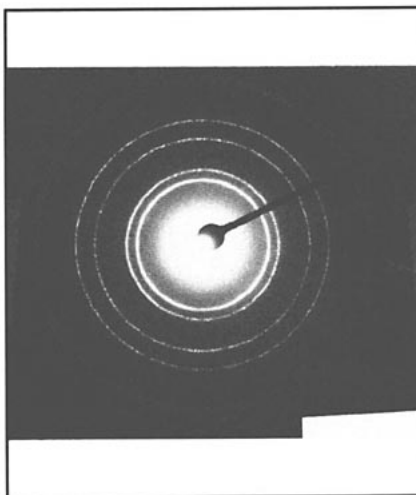
6. Grain size distribution from the TEM image



7. TEM cross section of aluminum coating (magnification 91,000X, 1 cm = 0.11 μ m)



8. TEM electron diffraction pattern from aluminum coating



conditions with a minimum of sample preparation (no coating is required). An AFM image from the surface of the metalized film is shown in Fig. 4; magnification is approximately 93,000X. The large mounds can be attributed to the base sheet topology noticed in the SEM images. The metalized coating is apparent as small spheres on the film surface. These spheres reflect the individual grains of the aluminum coating. These spheres can be measured to determine the grain size distribution of the aluminum coating.

TEM images of aluminum coating

Transmission electron microscopy was used to provide information about the grain structure (size and distribution) of the aluminum coatings. Since TEM measures the transmission of electrons through the aluminum coating, it was necessary to remove the polymer substrate. Typically, this has been done by dissolving the polymer from the aluminum coating in hot trichlorobenzene. Initially, this preparation procedure raised concerns that the temperature of the trichlorobenzene could be altering the morphology of the aluminum coating. These concerns prompted us to carry out the procedure at a variety of solution temperatures. From these preparations, it was found that temperatures as high as 130°C had no observable effect on the aluminum morphology. Ultimately, a solution temperature of 100°C was chosen for dissolving the polymer film from the aluminum coating.

A TEM image from the aluminum coating is shown in Fig. 5. At the magnification of 182,000X, the individual grains of aluminum are clearly observed. It is also noticed that no "holes" are apparent in the aluminum coating. The darker regions represent individual grains that strongly diffract the electron beam of the TEM. The size of the grains can be easily measured to gain information about the grain size distribution of

Metalized Film Coating

the aluminum coating. This was done by manually measuring the darkest grains. The grain size distribution from the TEM image is shown in Fig. 6.

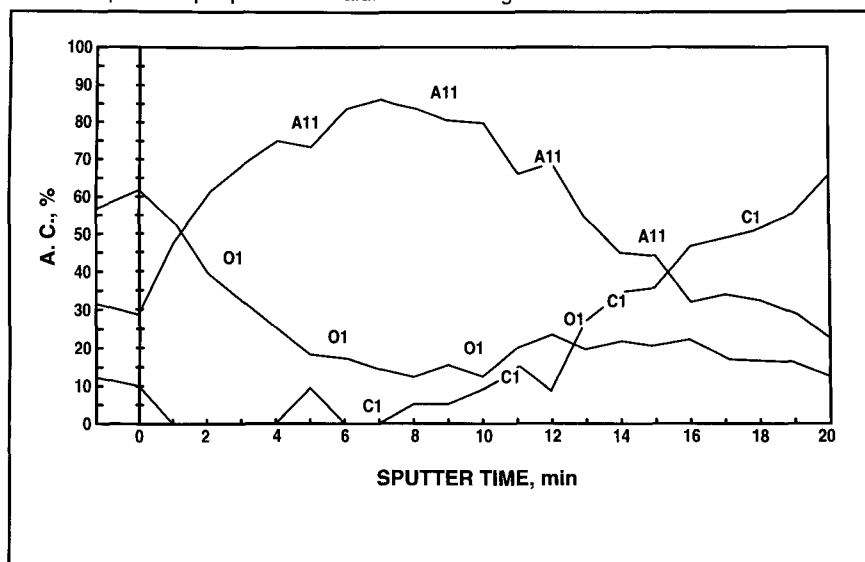
Figure 7 shows the TEM image of the metal coating cross section. This cross section was prepared by microtoming thin sections from the metalized film imbedded in epoxy. The average aluminum coating thickness measured by TEM is 940 Å with a standard deviation of 200 Å. This coating thickness from TEM is considerably greater than the coating thickness measured by SEM (approximately 400 Å). One explanation for this discrepancy is that microtoming the thin sections results in some smearing of the aluminum coating. The SEM measurement was made on film imbedded in the block of epoxy. Possibly, the block of epoxy reduces the smearing of aluminum coating to a greater extent than in the thin sections cut for TEM measurement. The SEM thickness measurements are better supported by measurements of the coating thickness by other techniques, such as Rutherford backscattering and X-ray fluorescence.

TEM can also provide information about the crystal structure of the aluminum coating. The electron diffraction pattern from the aluminum coating is shown in Fig. 8. The location of the diffraction rings is characteristic for the crystal structure of aluminum metal. The fact that the diffraction pattern is a series of concentric rings indicates a random orientation of the aluminum crystallites (grains). If there was some degree of crystal orientation, then a pattern other than rings would be expected.

ESCA depth profile of aluminum coating

ESCA depth profiles of the metalized film were carried out to gain information about the aluminum/polymer interface. The ESCA depth profile procedure involves simulta-

9. ESCA sputter depth profile from aluminum coating



neous measurement of the film surface by ESCA while the surface is being eroded (sputtered) with a beam of energetic Ar^+ ions. This procedure has a number of well documented artifacts, such as preferential (uneven) sputtering, chemical effects, and scrambling of surface atoms (3). Given these potential artifacts, sputter depth profiling can still provide useful information relatively quickly and simply.

Figure 9 shows the ESCA depth profile results from the metalized polypropylene film. The depth profile presents the atomic concentrations of carbon, oxygen, and aluminum versus sputtering time. The aluminum concentration increases initially and then decreases. Conversely, the oxygen and carbon concentrations initially decrease and then gradually increase at longer sputtering times. This behavior indicates that an aluminum oxide layer exists at the outer surface of the aluminum coating. In addition, there is a layer of carbonaceous material at the outer surface of the aluminum coating. As the carbon overlayer and the aluminum oxide are sputtered from the surface, pure aluminum metal is exposed. Further sputtering begins to expose the aluminum/polymer interface, resulting in an

increase in the carbon concentration and oxygen concentration (from aluminum oxide at the aluminum/polymer interface). Evidence for a layer of aluminum oxide at the aluminum/polymer interface has also been observed in Rutherford backscattering measurements.

The initial ESCA measurements (prior to sputtering) show a carbon concentration of 15.0% on the outer surface of the aluminum coating. This indicates a significant amount of carbonaceous material is present on the surface of the aluminum coating. Evidence is also found for carbon/oxygen species in the C 1s photoelectron spectrum. The origin of this relatively thick carbonaceous layer is unknown, but its presence could explain the difficulty often experienced when printing on the surface of metalized films.

Summary

The characterization results about the morphology of the aluminum coating are:

1. The aluminum coating is approximately 400 Å for an optical density of 2.3. No obvious defects such as holes were observed in the aluminum coating.

2. The average aluminum grain size is 320 Å. The distribution of grain sizes is broad, with a standard deviation of 132 Å.

3. The aluminum grains have a random crystal orientation.

4. The outer surface of the aluminum coating consists of a thin layer of Al_2O_3 . A layer of Al_2O_3 also exists at the aluminum/polymer interface.

5. The surface of the aluminum coating is covered with a layer of carbonaceous material. 

Literature cited

1. Kiang, W. W., and Hormozi, H., *Plastics Eng.*, C-42(6):31(1986).
2. Hill, R. J., *Physical Vapor Deposition*, Temescal, Berkeley, CA, 1986.
3. Hoffmann, S., in *Practical Surface Analysis* (D. Briggs and M. P. Seah, Eds.), John Wiley & Sons, Chichester, 1990, p. 161–173.

The author would like to acknowledge the contributions of T.J. Hagenbaugh of Mobil Chemical, Macedon, NY.

Received July 12, 1993.

Accepted Sept. 16, 1993.

Presented at the TAPPI 1993 Polymers, Laminations and Coatings Conference.