The Effect of Coatings on the Surface Precipitation of Oligomeric Crystals in Poly(ethylene Terephthalate) Films

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Synopsis

Crystalline particles of cyclic oligomers are formed on the surface of poly(ethylene terephthalate) (PET) films during heat treatment or exposure to solvent vapor. The formation of crystals of oligomers due to heat treatment can be prevented by depositing onto the PET films morphologically continuous coatings of various elements. The critical thickness of the coating which effectively stops nucleation of these crystals depends on the element deposited under given experimental conditions. In the case of solvent (methylene chloride) exposure, the most important factor preventing oligomer crystallization was the chemical nature of the element used as a coating.

INTRODUCTION

Metallized polymer films are used in many technological applications, such as the packaging and electrophotography industries.[1,2] The majority of commercially metallized films consist of aluminum deposited on polyester, cellulose, or even paper as the base. The aluminum coating is exceedingly thin (a few tenths of nanometer is typical) and has a profound influence on the optical and electrical properties of the film.

Significant changes in the electrical properties of polymer films owing to crystallization of small molecules during heat treatment or solvent exposure can impose limitations on their uses in the technological applications. There is a need to understand the phenomenon of crystallization of small molecules and develop techniques to prevent their crystallization.

Polyethylene terephthalate (PET) films known under the trade name of Mylar (DuPont Co.) were used in this study. During the heat treatment or solvent exposure, precipitation of ethylene terephthalate oligomers occurs on the film surface of Mylar.[3-6] The oligomers could be linear or cyclic. The concentration of linear oligomers varies with the heat treatment while the concentration of cyclic oligomers, predominately trimers, is nearly constant, about 1–1.5 wt %. By heat treatment at temperatures between 200°C and 250°C this concentration can be reduced to 0.5 wt % but not further than that. Thus, the presence of oligomers in Mylar is inevitable and cannot be prevented by any chemical or physical treatment.[7] The presence of these oligomer crystals causes an increase in surface resistivity under high humidity conditions while, in the case of aluminized Mylar films, a decrease in the surface electrical conductivity of the aluminum coating has been observed. To the best of our knowledge, there has not been any study of the effect of thin metal films on the surface crystallization in Mylar.

The effect of coatings on the surface precipitation of oligomers in Mylar films was studied. This paper focuses on the morphological structure observed in scanning electron microscope of Mylar films coated with a thin layer of metal or metal oxide.

Experimental

The samples of Mylar (125 μm in thickness) films used in this study were obtained from DuPont Co. The prewashed Mylar films were coated by vacuum deposition with aluminum, chromium, gold–palladium, and carbon of different thicknesses (ranging from 5 to 20 nm). Three commercially coated samples were also studied: aluminum coated Mylar from DuPont, gold coated (trade name, Intrex G) and indium-tin oxide coated (trade name Intrex K) Mylar films from Sierracin Co. All samples were either heat-treated at 165°C for 2 h in an oven or exposed to the vapor of methylene chloride for 1 h at room temperature. The treated samples were examined in a Philips-505 Scanning Electron Microscope.

Heat-Treated Samples

The crystallization of ethylene terephthalate cyclic oligomers on the surface of heat-treated Mylar film is shown in Figure 1(a) by the presence of polyhedral crystals of ca. 3 μm in size. A few hexagonal platelike crystals of ca. 8 μm are also evident. Figure 1(b) shows an example of heat-treated commercial aluminized Mylar (of typical aluminum coating of 10 nm in thickness). Again oligomeric crystals, a few microns in size, are visible. The distribution is uneven, most of the surface being free of the particles. Small, submicron size features seen in the micrographs are the roughness structures of the commercial Mylar film.

In order to study the effect of the thickness of aluminum coating (which can be varied) on Mylar films, we have examined samples with controlled thicknesses of 4 nm and 10 nm. Figure 2(a) shows the sample of Mylar film
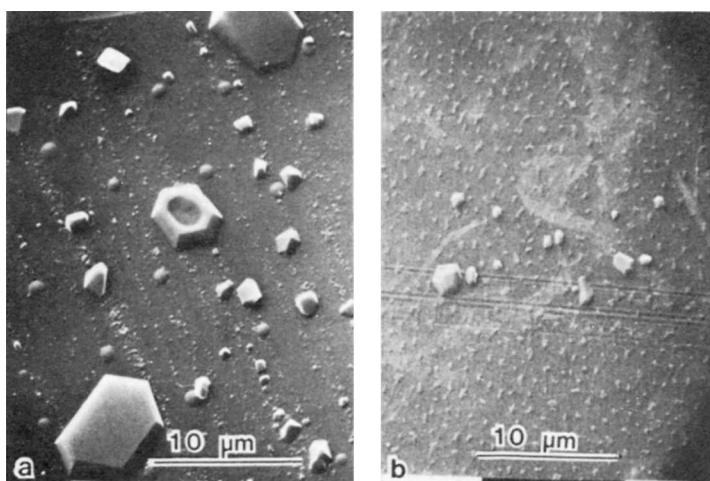

Fig. 1.   (a) Scanning electron micrograph of Mylar, heat-treated at 165°C for 2 h; (b) scanning electron micrographs of commercial aluminized Mylar, heat-treated at 165°C for 2 h.
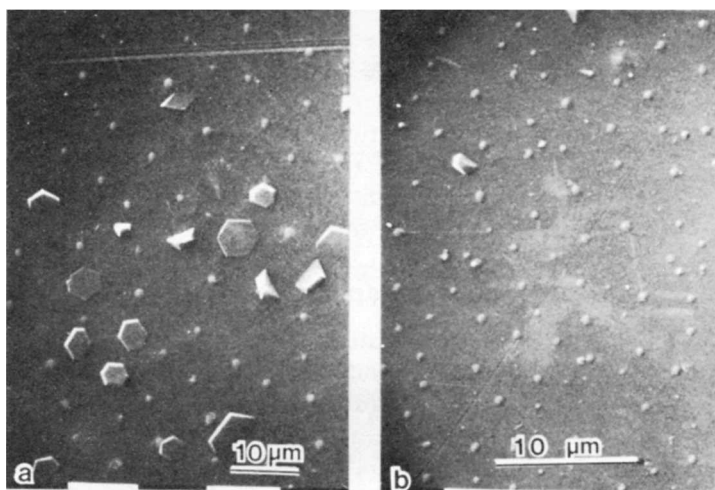
Fig. 2. (a) Scanning electron micrograph of Mylar coated with 5 nm thick aluminum film, heat-treated at 165° for 2 h; (b) scanning electron micrograph of Mylar coated with 10 nm thick aluminum film, heat-treated at 165°C for 2 h.

coated with aluminum of 4 nm thickness and heat-treated at 165°C for 2 h. Hexagonal and polyhedral particles are evenly distributed over the surface. However, when the aluminum coating is increased to 10 nm, hardly any oligomeric crystals are formed on annealing, as seen in Figure 2(b). Small spherical structures seen everywhere on the film are the topographic structures of Mylar film. Figures 3(a) and 3(b) show electron micrographs of heat-treated Mylar coated with chromium films of thicknesses 5 and 10 nm, respectively, and heat-treated. Oligomeric crystals are present although they appear to be grouped together rather than being evenly distributed over the surface [Fig. 3(a)]. Mylar films with a 10 nm thick chromium coating
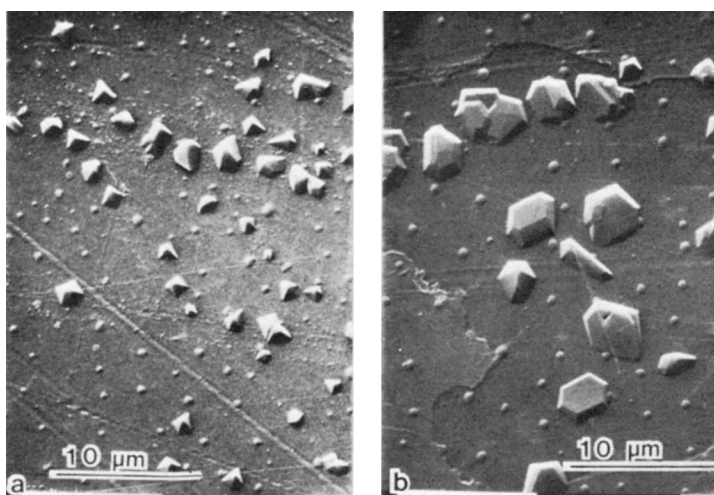

Fig. 3. (a) Scanning electron micrograph of Mylar coated with 5 nm thick chromium film, heat-treated at 165°C for 2 h; (b) scanning electron micrograph of Mylar coated with 10 nm thick chromium film, heat-treated at 165°C for 2 h.

also show some crystals precipitating upon annealing, mostly in areas where the chromium film has been disrupted [Fig. 3(b)]. It was found that when Mylar was coated with chromium of 20 nm in thickness, no oligomer crystals were formed.

The effect of a gold/palladium coating (20 nm thick) on oligomer precipitation was similar, with a total absence of oligomeric crystals. Similar effects were observed with Mylar films coated with carbon, gold (Intrex G) and indium-tin oxide (Intrex K) of a thickness greater than 20 nm.

Samples Exposed to the Vapor of Methylene Chloride

Figure 4 shows a sample of uncoated Mylar film following solvent exposure. Many evenly distributed cylindrical particles as well as needle like particles are seen on the surface. Figure 5(a) is a scanning electron micrograph of Mylar film coated with 5 nm chromium film. It is interesting to note that oligomeric crystals form only at locations where cracks in the coatings appear. Figure 5(b) shows the result of solvent exposure for Mylar film coated with a 20 nm thick layer of chromium. Again, crack formation and oligomer precipitation at these locations were observed.

Oligomeric crystals were observed with aluminum coatings of 5 nm and 10 nm thickness as well as with commercially aluminized Mylar. Mylar films coated with gold (Intrex G) and indium–tin oxide (Intrex K) when exposed to methylene chloride vapor did not exhibit any precipitation of oligomeric crystals.

All results presented above are summarized in Table I.

DISCUSSION

The experimental results presented above on the precipitation of oligomer crystals on Mylar surfaces during heat treatment where a thin coating has been deposited prior to heat treatment, and their absence in the case of a thick coating can be understood in the light of the morphological characteristics of deposited coatings. It is well known[8-10] that, during vacuum
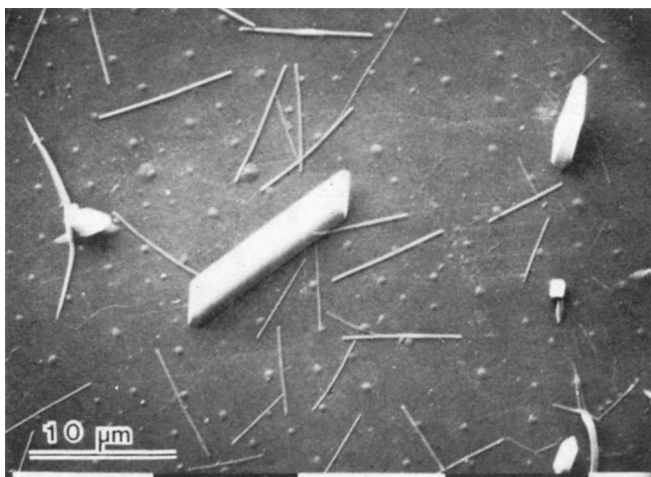

Fig. 4.   Scanning electron micrograph of Mylar, exposed to vapor of methylene chloride for 1 h.
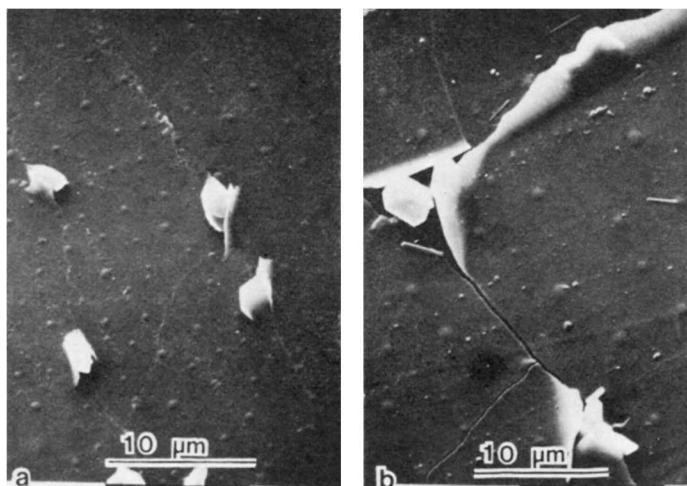
Fig. 5. (a) Scanning electron micrograph of Mylar coated with 5 nm thick chromium film, exposed to vapor of methylene chloride for 1 h; (b) scanning electron micrograph of Mylar coated with 10 nm thick chromium film, exposed to vapor of methylene chloride for 1 h.

deposition of thin metal films, the characteristic sequential growth stages are the following:

1. Randomly distributed, 3-dimensional nuclei are first formed and rapidly approach a saturation density with a small amount of deposit. These nuclei then grow to form islands whose shapes are determined by interfacial energies and deposition conditions. The growth is diffusion-controlled; that is, adatoms and subcritical clusters diffuse over the substrate surface and are captured by the stable islands.

2. As islands increase in size by further deposition and come closer to-

TABLE I
Summary of Results Obtained with Heat Treatment and Solvent Exposure

Coating	Thickness of the coated film (nm)	Precipitation of oligomeric crystals
Heat treatment		
Commercial Al	Unknown	Uneven distribution of particles
Al	5	Even distribution of particles
Al	10	Particles scarcely observed
Cr	5	Uneven distribution of particles
Cr	10	Particles scarcely observed
Cr	20	No particles
Au/Pd	> 20	No particles
C	> 20	No particles
Au	> 20	No particles
In-Sb-Oxide	> 20	No particles
Solvent exposure		
Commercial Al	Unknown	Particles scarcely observed
Al	5	Even distribution of particles
Al	10	Particles scarcely observed
Cr	5	Uneven distribution of particles
Cr	20	Uneven distribution of particles
Au	20	No particles
In-Sb-Oxide	20	No particles

gether, the larger ones appear to grow by coalescence of the smaller ones. Island density decreases monotonically at a rate determined by the deposition conditions. This stage, coalescence I, involves considerable mass transfer by diffusion between the islands.

3. When the island distribution reaches a "critical" state, a rapid large-scale coalescence of the islands results in a connected network structure and the islands are flattened to increase surface coverage. This coalescence II is very rapid initially but slows down considerably on formation of the network. The network contains a large number of empty channels.

4. The final stage of growth is a slow process of filling the empty channels which requires a considerable amount of deposit.

Figure 6 demonstrates a sequence of different morphologies developed during the growth of an indium film.[11] Most of our experimental observations can be therefore explained by the presence or absence of continuous deposited film on the Mylar surface; the presence of a continuous coating prevents the cyclic oligomer molecules from migrating to the surface and forming crystals. It is clearly demonstrated that for coatings less than 10 nm in thickness (presumably being of channellike morphology), the precipitation of oligomers is possible while for continuous deposited coatings of thickness >10 nm the formation of oligomers is prevented.

The solvent-exposure experiments showed the presence of oligomeric crystals on coated Mylar surfaces regardless of coating thickness in most cases. However, the formation of oligomeric crystals seems to be related to the
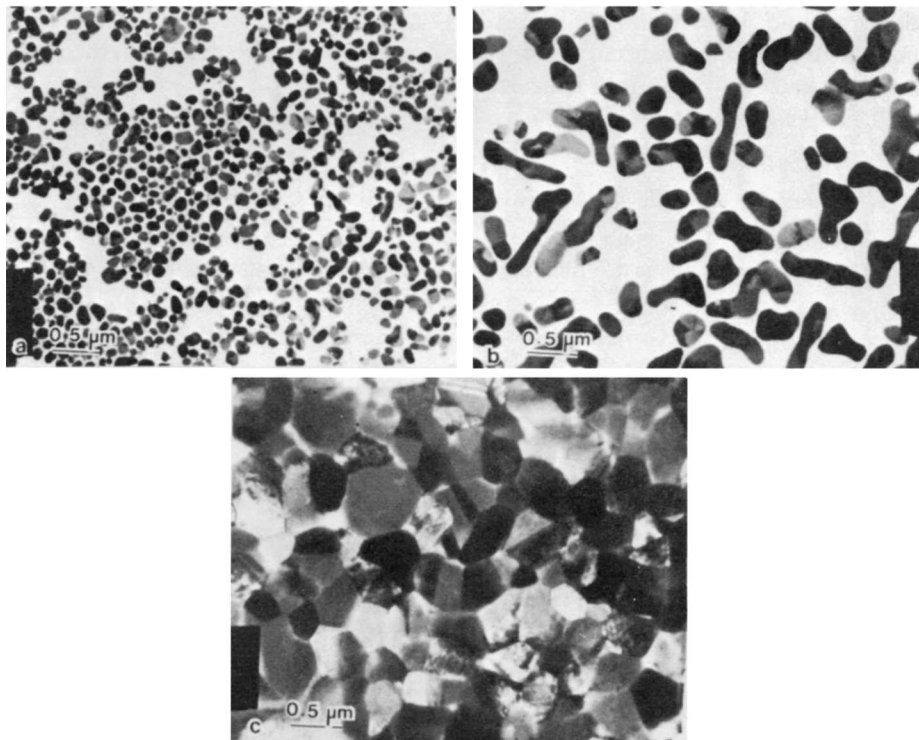

Fig. 6. Transmission electron micrographs of indium film of thicknesses: (a) 13.5 nm; (b) 35 nm; (c) 60 nm.

chemical nature of the coating. That is, under exposure of methylene chloride vapor, chromium and aluminum coatings developed cracks on the surface while gold and indium–tin oxide coated Mylar films did not exhibit cracks. The absence of oligomeric crystals during exposure of methylene chloride of gold and indium–tin oxide coatings is probably due to their chemical resistance and permeability to the solvent vapor. In the case of chromium and aluminum coatings exposed to methylene chloride vapor, oligomer molecules emerge and precipitate on the surface at the cracks ("exits") as revealed by the electron micrographs. The precipitation is localized at the points of "exits" because the molecules do not have enough thermal energy at room temperature to diffuse along the surface.

CONCLUSIONS

Mylar films coated with different elements of various thicknesses, when exposed to heat treatment, showed no precipitation of oligomeric crystals on its surface only in cases where the coating thickness was greater than some critical value, presumably a thickness at which a continuous film is formed. With coatings less than that critical thickness, extensive oligomer precipitation was observed. Thus, the crystallization of ethylene terephthalate oligmers due to heat treatment may be prevented by vacuum deposition of a coating on the Mylar film, provided that the coating exceeds the critical thickness for the particular element deposited.

On exposure of Mylar films to the vapour of methylene chloride, precipitation was observed in most cases, regardless of the coating thickness. A strong interaction between the solvent vapor and the deposited coating (surface etching) was noted. In the case of gold and indium–tin oxide coatings, no crystallization of oligomers was observed, due to their good chemical resistivity and permeability. The oligomer crystals on Mylar surface could be controlled by the chemical nature and thickness of deposited coatings.

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