Multilayer Low T_g Inorganic Glass/Polymer Barrier Films

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ABSTRACT

Conventional high barrier films are produced by coating or laminating inorganic materials to polymeric substrates. While successful at lowering the permeability of the films, several unit operations are required to introduce multiple inorganic barrier layers. Here, we detail a new approach for making films comprised of as many as thousands of alternating layers of inorganic and polymeric materials using a single processing step to coextrude low T_g glass with polymers. The resulting composite structures exhibit extremely low moisture vapor permeability and show promise for applications ranging from flexible electronics to food packaging.

Keywords: polymer, composite, glass, barrier, film

1 INTRODUCTION

Lightweight, thin barrier films are commercially important materials for a variety of industrial and consumer applications. Poymers such as EVOH, PVdC, and PCTFE are commonly used to limit the diffusion of small molecules through these films. While effective at limiting the migration of certain permeants, a given polymer generally does not provide barrier against a broad range of diffusing molecules. For instance, non-polar HDPE provides excellent barrier to polar molecules but poor barrier to non-polar molecules. Even though highly crystalline, polymers such as HDPE contain a significant amorphous fraction through which permeants can absorb and diffuse.

Current food and pharmaceutical product packaging is frequently comprised of complex layered assemblies of different polymeric materials that are selected to maintain the microbiological, organoleptic and compositional qualities of the packaged contents. To preserve product safety and efficacy, it is common to dedicate multilayer sub-assemblies to limiting the diffusion rate of small molecules like oxygen and water through the package wall. Polymers with low permeability to specific molecules are often favored for industrial production because of the ability to easily melt and shape the materials through established extrusion processes.

However, the most demanding applications rely upon inorganic materials with extremely low free volume to control diffusion. Techniques such as chemical vapor deposition and atomic layer deposition enable the creation of organic/inorganic composites, but several manufacturing steps are needed to convert the coated structures into a finished film, and the ability to use those techniques for creating complex geometries is limited [1].

This paper presents a new method for making films composed of alternating layers of inorganic and organic materials from which many barrier layers can be formed in a single unit operation. The process relies on layer multiplication of coextruded melts containing low T_g inorganic glasses. While traditional silica-based glasses become workable at temperatures greater than 1000 °C, tin fluorophosphate (TFP) glasses flow at temperatures close to 100 °C, which allows them to be processed within the operating window of several polymers [2]. Like other inorganic glasses, TFP glasses are brittle at room temperature but becomes flexible when made into thin fibers or sheets.

The layer multiplication process employed in the present work is an extension of traditional polymer coextrusion that has been used to produce a variety of layered polymer composites [3]. The technique involves splitting a layered melt vertically and redirecting the flow such that the two halves are recombined one on top of the other. This process doubles the number of layers in the melt stream while halving their thicknesses. Several multiplier dies can be arranged sequentially to form films having as many as thousands of layers with thicknesses as low as several nanometers [4].

2 METHODS

2.1 Materials

A glass having a nominal composition of 20 mol% SnO/50 mol% SnF_2/30 mol% P_2O_5 was prepared from SnF_2, SnO, and $NH_4H_2PO_4$, which were mixed and heated in a crucible to 450 °C for 15 min. The melt was quenched and milled to a particle size of 1 mm or finer.

Skygreen™ S2008, a glycol-modified polyethylene terepthalate copolymer (PETG), was obtained from SK Chemicals. A polyamide 6 (PA6) polymer, Ultramid® B36, was obtained from BASF. The low density polyethylene (LDPE) 640I was obtained from Dow Chemical Company and used as a skin material in coextruded films.

2.2 Sample Preparation

Films were produced on an extrusion line consisting of three, 1.25" single screw extruders equipped with melt pumps. Two extruders fed an ABA feedblock in-line with 5 layer multiplier dies. The third extruder formed skins on the layered extrudate before the combined melt stream exited a

14" wide flat die. The melt curtain was cooled with a chill roll, slit in-line, and wound on a fiber core. For each run, the extruder and die heater temperatures were set to 230 °C.

For comparative experiments, a high vacuum thermal evaporator equipped with an Inficon deposition controller was used to deposit a thin film of TFP glass onto six, 100 mm diameter circles of PET substrates. Glass was placed in a tungsten evaporation boat 5/8" in diameter and 1/8" deep (R.D. Mathis). The chamber was pumped below 100 mTorr and a 55 A current was supplied to heat the boat and evaporate the glass for 50 minutes.

2.3 Microscopy

Film morphology and layer distribution were analyzed with a JEOL JSM-6010PLUS SEM operated at 10 kV. Images were collected with a backscatter detector to highlight the contrast between TFP glass and adjacent polymer layers. Cross-sections were prepared by cryogenically freezing a clamped specimen and cutting the cold film with a microtome blade.

Atomic force microscopy of sputtered and extruded glass was performed with an AsylumResearch MFP-3D-Bio AFM to probe the topological features of each sample.

2.4 Moisture Vapor Transmission Rate

Moisture vapor transmission rate (MVTR) of films was measured with a MOCON AQUATRON Model 1 operating at 38 °C and 90% RH.

3 RESULTS AND DISCUSSION

Two structures were produced by coextrusion: LDPE/(PA6/TFP glass)$_{65}$/LDPE and LDPE/(PETG/TFP glass)$_{65}$/LDPE. Film containing PA6 was nominally 30 μm thick while film containing PETG had a nominal thickness of 50 μm. Both films were optically transparent and exhibited a high degree of flexibility. A representative roll of multilayer film produced by coextrusion and layer multiplication of TFP glass and polymer is depicted in Figure 1.

Figure 1. Flexible film consisting of 65 alternating layers of PA6 and TFP glass.

A cross section of PA6/TFP film is shown in Figure 2 The higher electron density of the TFP glass is highlighted by the ligher color of glass layers in the image relative to the darker polymer layers. Each of the 65 layers formed by multiplication of the melt stream can be discerned. Notably, the layers are discrete and show a high level of uniformity, with each layer measuring ~ 50 nm in thickness.
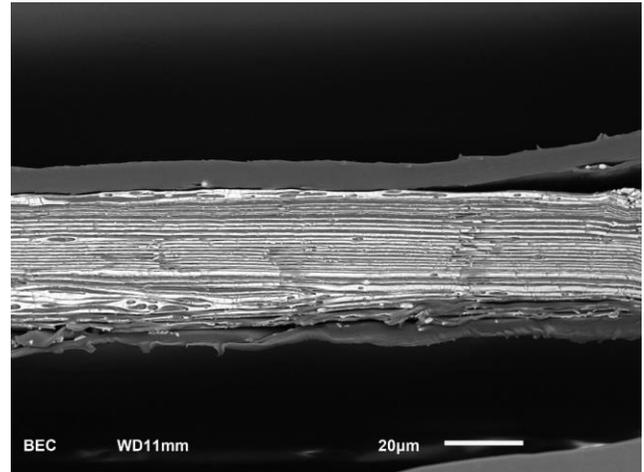

Figure 2. Cross section of PA6/TFP glass film.

Coextrusion of PETG and TFP glass also produced discrete and continuous layers, as evidenced by the cross section provided in Figure 3. The background in this image is an epoxy used to mount the sample. PETG and TFP glass layers comprising the core of the structure were measured to be ~ 60 nm thick.
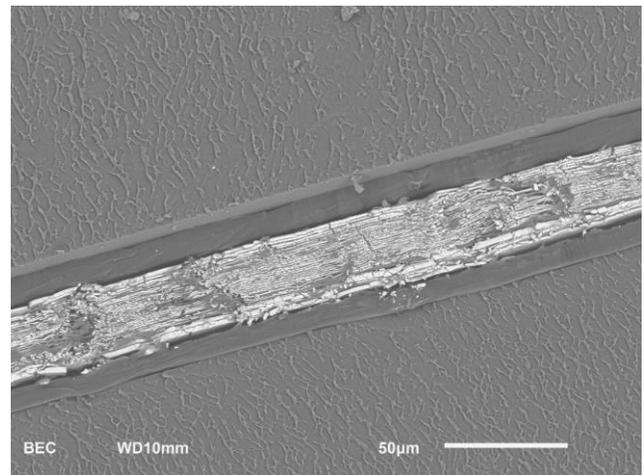

Figure 3. Cross section of PETG/TFP glass film.

The extreme flexibility of the laminate without pervasive cracking of the glasss is postulated to occur because of several effects. The layers of glass are very thin. Because the strength of brittle materials is highly dependent on defects, reducing the dimensions of the glass layers excludes larger cracks from existing. Furthermore, the insulating properties of molten polymers around the cooling

glass layers is thought to allow the glass to aneal during processing, even at relatively high throughput rates.

Exposed glass layers were observed to have very smooth topologies through electron microscopy. Smooth surfaces free of stress-raising defects would also facilitate the creation of strong glass capable of sustaining high elastic strains without breaking. To investigate the smoothness of glass layers formed through coextrusion, AFM was employed to examine the surface of glass exposed by the removal of LDPE skins from a coextruded laminate as well as the surface of glass that had been sputter coated onto an OPET film via thermal evaporation.
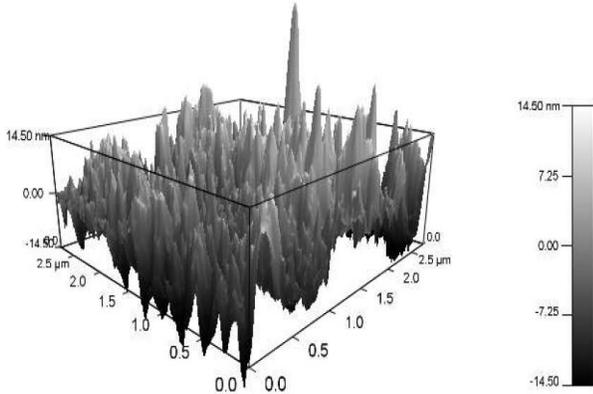

Figure 4. AFM images of a 2.5 x 2.5 µm area of OPET sputtered with TFP glass.

Representative surface topologies of the sputtered glass and exposed coextruded glass surfaces are given in Figures 4 and 5, respectively. The sputtered glass is significantly rougher than the coextruded glass. The RMS roughness of each of these samples and that of the OPET substrate upon which the sputtered glass was deposited were calculated and summarized in Table 1.
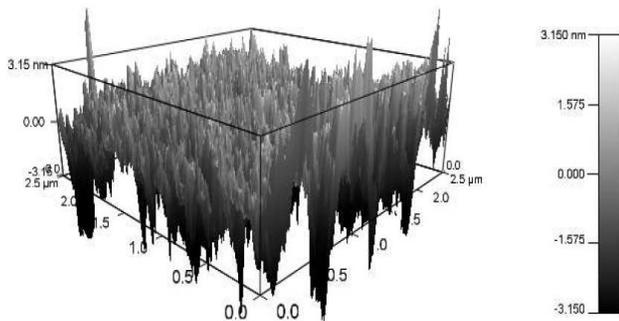

Figure 5. AFM images of a 2.5 x 2.5 µm area of coextruded TFP glass.

The sputtered glass exhibited a lower root mean square average profile height deviation than the OPET film it was sputtered onto. The relatively high roughness of the substrate could have contributed to the roughness of the glass observed post-sputtering. Regardless, the coextruded

glass roughness was found to be very low, which may in part explain the flexibility observed.

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Table 1. A comparison of the RMS roughness of sputtered and extruded TFP glass

Sample	RMS Roughness (nm)
OPET control	7.36
Sputter coated	2.52
Extruded	1.57

The barrier properties of the multilayer glass/polymer composties were evaluated by measuring the transmission rates of water vapor through the films. LDPE/(PA6/TFP glass)$_{65}$/LDPE films were measured to have an MVTR of 0.022 g/m^2/day. A higher transmission rate of 0.70 g/m^2/day was measured for LDPE/(PETG/TFP glass)$_{65}$/LDPE films. It is hypothesized that some layers of glass cracked, allowing measurable permeation of water through the films. However, the tortuous path formed by having several layers present in the film structure may have enabled the excellent overall laminate moisture barrier even with the use of PETG and PA6, which do not have particularly low MVTRs individually.

4 CONCLUSION

Polymer/glass layered composites having excellent moisture barrier were produced with conventional thermoplastic processing equipment. Thin film coextrusions that alternated sub-micron-thick glass and thermoplastic layers displayed good layer continuity and uniformity Additionally, the glass layers showed exceptional resiliency to cracking upon bending.

By leveraging established multilayer coextrusion processing technologies, an article with many alternating inorganic/organic barrier layers can be produced in a single unit operation, a feat not possible with CVD or ALD. The ability to leverage the scale and design flexibility of thermoplastic extrusion processes in the production of glass/polymer composites offers a new set of possibilities for barrier product design for food and pharmaceutical packaging, flexible electronics, and beyond.

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