A Review of Transparent Barrier Coatings.

B.M. Henry, J. Topping, H. E. Assender, and C.R.M. Grovenor

Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH UK

Abstract

The transparent barrier films presently available on the market all have their strengths and weaknesses. At the same time there is consideration to use more plastic-based materials for different applications, e.g. displays and insulation panels. This situation has stimulated the industry to provide new, more efficient barrier solutions. Some of the innovations go along the following lines: nanocomposite materials; Ormocers®; hybrid PECVD coatings; PML structures; and ‘super sapphire’ sputtered layers. This extended abstract presents an overview of some of the different approaches, outlining the basic principle behind each barrier technology, its performance and the companies developing and producing the materials.

Introduction

The barrier properties of transparent metal oxide layers deposited on flexible plastic substrates are of interest to many markets including packaging and the display industry. For over two decades numerous methods have been used to manufacture transparent barrier coatings with varying degrees of success. In this paper an overview is presented of transparent coatings fabricated by a wide range of techniques as reported in the literature. To reflect the current trend, emphasises is placed on films which exhibit very high gas barrier properties.

Barrier Technologies:

Transparent coatings of modest barrier properties can be deposited by conventional PVD techniques such as sputtering [1–3], evaporation [4–6], and by CVD techniques [7, 8]. Whereas sensitive food products can be protected with a single polymer film coated with one inorganic layer produced by any of the techniques outlined above, display applications, however, require barriers of higher performance to prevent the devices from degradation. In this section a brief overview is given of some of the different strategies that have been adopted to fabricate transparent barrier films.

Nanocomposite Coatings

The term nanocomposite in this case refers to polymers filled with small inorganic particles with a high aspect ratio. An improvement in barrier properties is obtained by increasing the tortuosity of the diffusion path which is strongly dependent on the morphology. The use of small particles, typically in the nano-size scale, and low loading means that the resulting material in most cases remains transparent.
InMat® Inc., has produced Nanolok™ which is an aqueous suspension of nanodispersed silicates in a polymer matrix. The suspension is applied by a roll coating process onto a substrate which when dried produces a coating of micron-scale thickness. The layer is transparent and contains hundreds of nanodispersed platelets which forms a tortuous path for permeating molecules such as oxygen which can be 100’s of times less permeable than the uncoated substrate.

**Ormocers®**
This technology, developed by the Fraunhofer Institute in Wurzburg, is inorganic organic hybrid polymers known as Ormocers®. These materials are produced through sol–gel chemistry and deposited as transparent coatings or adhesive layers with a thickness in the micrometer range. They can be used independently to obtain a moderate barrier improvement or in combination with a metal oxide, in which case very high-barrier materials are obtained. Table 1 gives barrier data for some Ormocer® materials.

**Table 1: Oxygen transmission and water vapour transmission rates of Ormocers® materials.**

<table>
<thead>
<tr>
<th>Description</th>
<th>$O_2$ [cm$^3$/m$^2$·d]</th>
<th>$H_2O$ [g/m$^2$·d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>single layer: PET/SiOx/inorganic organic hybrid polymers (Ormocers®)</td>
<td>$3\cdot10^{-2}$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>two layers: PET/[SiOx/inorganic organic hybrid polymers (Ormocers®)] x 2</td>
<td>$5\cdot10^{-4}$</td>
<td>$4\cdot10^{-3}$</td>
</tr>
</tbody>
</table>

**Hybrid PECVD Coatings**
General Electric has recently developed a graded hybrid PECVD barrier structure based on SiO$_x$N$_y$ and SiO$_x$C$_y$ alternate layers. The individual layers are approximately 5nm thick and show good interfacial adhesion properties. For graded hybrid structures on polycarbonate, ultra high barrier films are formed with WVTR of $4 \times 10^{-6}$ g/m day measured at 23°C and 50%RH [9].

**PML based Barrier Films**
Significant improvement in permeation-barrier performance can be achieved by using multilayered structures based on successive deposition of polymer/inorganic layers. The polymer multilayer (PML) process was first developed by GE for capacitors when it was observed that the number of pinholes in the inorganic layers was significantly reduced [10]. The reduced pinhole density was related to the flat polymer layer. The smoothing effect of the polyacrylate occurs due to the deposition process in which the flash evaporated acrylate monomer first condenses on the substrate surface and then is subsequently cured by either UV rays or an electron beam [11], [12]. By repeating the alternating process to deposit multiple layers, the polymer films “decouple” any defects in the inorganic layers, thereby preventing propagation of defects through the PML structure. Vitex has reported barrier structures that achieve WVTR as low as $2 \times 10^{-6}$ g/m day [13], however, due to time lag issues this rate may not be representative of steady state values.
Ion Assisted Sputtering

General Atomics has recently developed a high barrier film called ‘super sapphire’ based on an ion assisted PVD process [14]. Prior to the deposition of an inorganic layer the polymer surface is pretreated with ion-gun enhanced plasma in the presence of oxygen. A dense barrier coating is deposited using ion-assisted sputtering with an argon ion gun. The alumina coating is transparent and amorphous. A single layer of ‘super sapphire’ on a PET substrate has a WVTR of $5 \times 10^{-5}$ g/m$^2$/day at 38°C and 100%RH.

Summary

A brief overview has been shown of some the techniques that have been used to fabricate high performance barrier films. Many of the methods incorporate a multilayered configuration with WVTR values as low as $10^{-6}$ g/m$^2$/day being reported.

References


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