TRANSPARENT BARRIER LAYERS ON POLYMER FOILS BY PROCESS COMBINATION

HERING Wolfgang[1], KEIL Doreen[1], HOMUTH Marion[1], GRÜNLER Bernd[1], SPANGE Stefan[2]

[1]Innovent e.V., Jena, Germany, EU, wh1@innovent-jena.de

[2]TU Chemnitz, Faculty of Natural Sciences, Chemnitz, Germany, EU

Abstract

Gas and migration barrier coatings which are flexible and transparent can be generated on polymer films by combining Combustion Chemical Vapor Deposition (CCVD) and Sol-Gel Technology.

The CCVD (especially the Pyrosil® method) allows the formation of highly compact oxide layers based on siloxanes under atmospheric pressure. In order to make them more flexible and to reduce the permeability, the use of the Sol-Gel technique is suitable. In this case, hybrid Si and / or Al oxide layers with an inorganic and an organic network can be deposited.

The Oxygen Transmission Rate (OTR) and the Water Vapor Transmission Rate (WVTR) are mainly used as an indicator for gas barrier effect (GBE). GBE can be significantly improved by synergistic combination of different coating techniques wherein stacked layer systems are formed.

These systems are only a few hundred nm thick. Hence, they appear optically transparent. This property is very important for usability in the packaging and electronics industry. Topography of the layers was investigated by AFM. Chemical composition was studied by FTIR and layer thicknesses were determined by Profilometry and/or Ellipsometry.

Furthermore, the overall permeability to certain permeates can be adjusted by the property of each single layer. This allows the generation of semipermeable membranes and therefore the use in filtration technology.

Keywords: Chemical Vapor Deposition, Sol-Gel technology, barrier coatings, packaging, filtration

1. INTRODUCTION

Because untreated polymer films usually exhibit poor barrier properties, they are not suitable for certain fields of application (e.g. food packaging and electronic industry). In order to protect the food or electronic components from oxidation or degradation, semipermeable coatings can be deposited on such packages or used for encapsulation.

For this purpose, a multilayer system consisting of Pyrosil® and Sol-Gel layers, which has a high barrier effect against oxygen and water vapor, is generated. The Sol-Gel technique can also be used to introduce additional functionalities into the layer composite. For example, fluorescent, photocatalytic or antibacterial properties can be achieved.

2. THEORETICAL FOUNDATIONS

The gas transfer from one phase through a solid to another phase is called permeation. The particle migration through a film takes place over four partial steps. First, the gas particles from the phase with the higher concentration adhere to the surface of the film (adsorption). These particles are absorbed (absorption) by the film and migrate through it (diffusion). On the backside, the particles enter the phase with the lower concentration (desorption) [1].

Corresponding to the permeation coefficient *P*, which results from the product of solubility coefficient *S* and diffusion coefficient *D*, the steps of adsorption and diffusion can be mainly influenced by layer deposition:

$$P = -\frac{F \cdot d}{\Delta p} = D \cdot S \;, \qquad (1)$$

with *F* - diffusion flow of the permeating substance, *d* - thickness of the material and Δp - Partial pressure difference

Accordingly, compact layers with high flexibility adapted to the substrate films must be applied. These criteria can usually not achieved sufficiently by use of a single layer. Therefore multi-layer systems were deposited. As a result, the advantages of the individual coatings can be utilized whereas their disadvantages can be circumvented.

In this study dense Pyrosil® layers, showing a high barrier effect, were combined with relatively flexible and smooth Sol-Gel layers. Unfortunately, the Pyrosil® layers become rough and brittle with increasing layer thickness. Due to releasing solvent during drying, the coating procedures often induce pores formation in the Sol-Gel layers. That reduces their barrier effect. As a result of the stacking, more impermeable, smoother and more flexible layer systems are obtained whose surface can be analyzed by AFM (**Figure 1**).

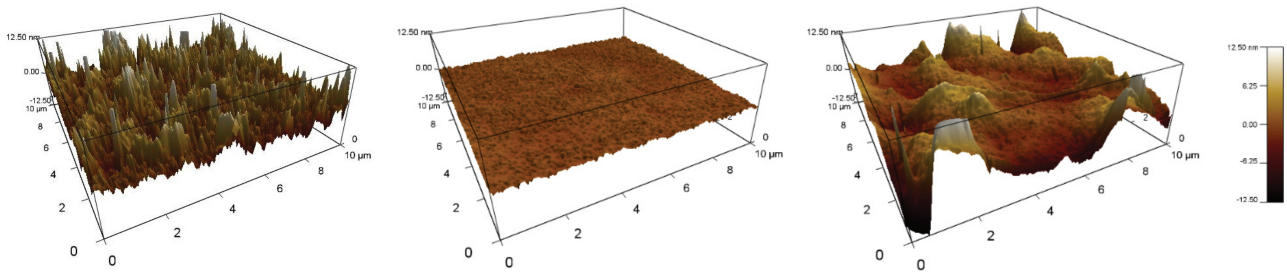


Figure 1 AFM images of a Pyrosil® layer (left), Sol-Gel layer (middle) and a combination of both on PET

The layer composite can be kept substantially more stable which allows stacking of up to five individual layers. Hereby the transparency of the film is only slightly reduced since the layer thickness of the system of transparent individual layers can be kept below 400 nm.

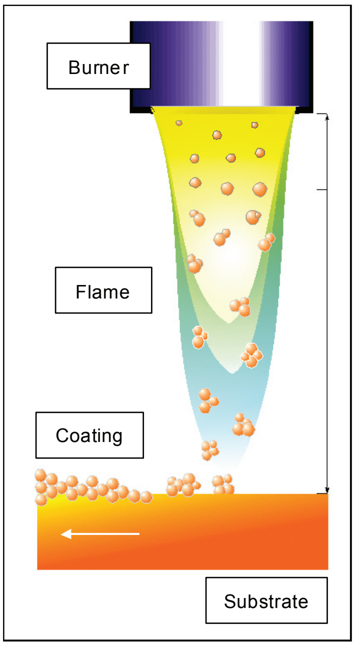
3. EXPERIMENTAL METHODS

A brief overview of the methods used is given below. This is the CCVD (especially the Pyrosil® method) and the Sol-Gel process. A combination of both methods was used to coat PET films (Hostaphan® from MITSUBISHI POLYESTER FILM, thickness 12 μm). The compositions of the used Sols were optimized by means of design of experiments (DoE), which was evaluated by the program Statgraphics® from STATCON.

As precursor for the pyrosil process served mainly hexamethyldisiloxane (HMDSO). In the sols, aminopropyl-triethoxysilane (AMEO), 4,4'-methylenebis (N, N-diglycidylaniline) (MDGA) and aluminum tri-sec-butoxide (ABO) were used as reagents.

3.1. CCVD (Pyrosil® technique)

The Combustion Chemical Vapor Deposition (CCVD) is a special case of chemical vapor deposition. This is done by flame-pyrolytic decomposition of reactive precursors [2]. If a silane is used as precursor, it is called Pyrosil method® (**Figure 2**).



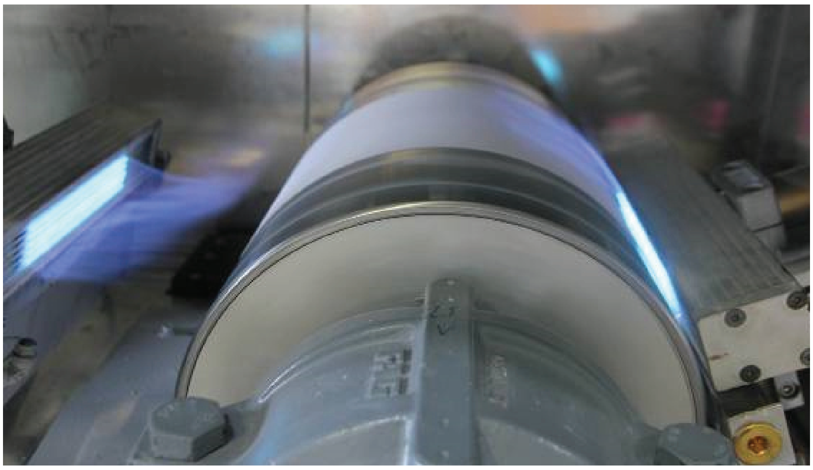


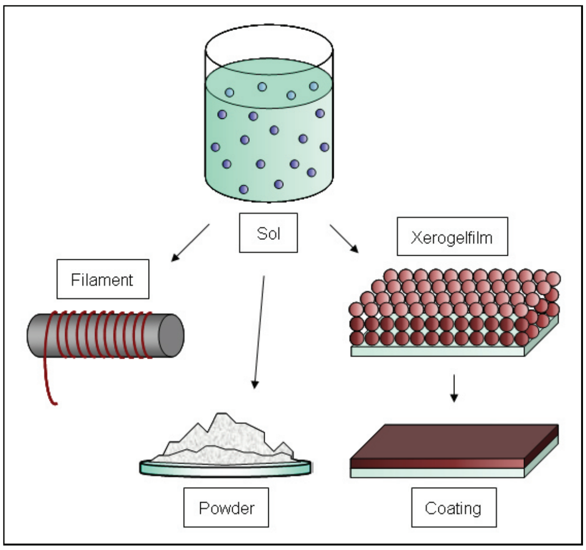
Figure 2 Scheme of the Pyrosil process (left) and practical implementation from roll-to-roll (right)

These compounds decompose in the reducing part of the burner flame to reactive silicon, which reacts in the oxidizing part to form silicates they can agglomerate. If a substrate is moved through the oxidizing area, the impinging agglomerates will form a three-dimensional network on its surface.

Via CCVD, highly compact oxide layers based on silicon can also be produced on polymer films by adapting the process parameters. The processing can also be performed from roll-to-roll (R2R), which allows a high throughput, whereby it becomes economically lucrative.

3.2. Sol-Gel coating

In order to make the layer composite more flexible and to reduce its permeability additionally, the inclusion of the sol-gel technique is suitable. In this case, hybrid Si and / or Al oxide layers can be generated which have an inorganic and an organic network portion.



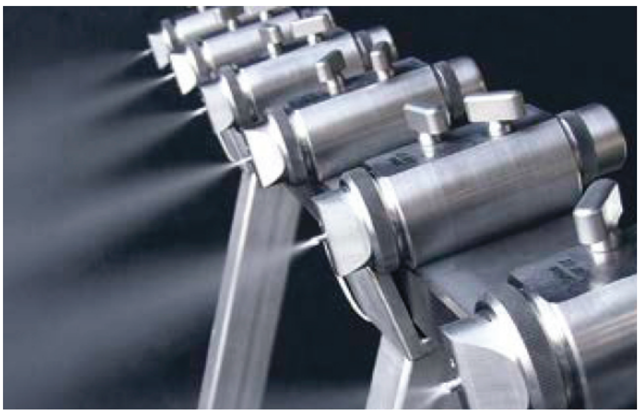


Figure 3 Processing possibilities during the sol gel process (left) and application by spray nozzle (right) [4]

In the sol gel process, a sol is formed from a dissolved precursor substance after addition of water as second reactant. The sol is finally formed by progressive hydrolysis and condensation reactions, optionally in the presence of an acid or base as catalyst [3]. As precursors, alcoholates of metals or non-metals can be used. Alkoxysilane compounds are generally more stable against hydrolyses than aluminium alcoholates. This fact requires a carefully adjusting of the reaction conditions when both compounds are used in combination.

In addition, a hybrid network with inorganic and organic content can be generated by substitution of alcoholate groups by both polymerizable and crosslinkable organic moieties. A gel is formed as a result of three-dimensional crosslinking reactions in the sol, which increases its viscosity. By removing the solvent, the gel can then be converted into a stable oxide film or a powder (**Figure 3**).

Sol-Gel layers can in principle be applied analogously to lacquers, for example by dip, spray or doctor blade coating. The processing can be carried out R2R in accordance with the CCVD method with special coating equipment at INNOVENT by means of slot die or spray nozzle.

4. RESULTS AND DISCUSSION

The parameters Oxygen Transmission Rate (OTR) and Water Vapor Transmission Rate (WVTR) are mainly used as an indicator of the barrier effect against gases on polymer films. These rates can be significantly influenced by both Pyrosil and Sol-Gel layers. Nevertheless, the individual layers are still not sufficient to meet industry standards.

In the food packaging industry, OTR values of about 1 $cm^3 / (m^2 \text{ d bar})$ and WVTR values of 1 $g / (m^2 \text{ d})$ are given [5]. These can only be achieved with a combination of both coating methods. In order to reduce the water vapor permeation to this value, five layers had to be applied in an alternating sequence using a conventional sol (**Figure 4**).

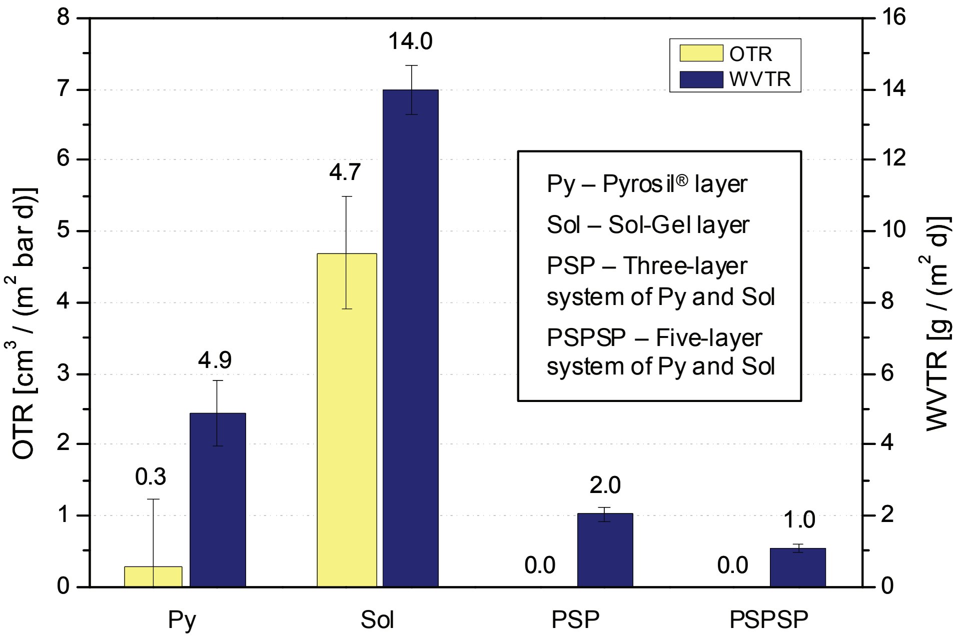


Figure 4 Permeation rates of individual Pyrosil and Sol-Gel layers as well as combination layers

The introduction of aluminium-containing and epoxy components allows a further reduction in the permeation rates of the whole system. The optimization of their contents as well as the general composition of the sols was achieved by design of experiments (DoE). The desirability function serves as a basis for the adaptation of the corresponding input variables (**Figure 5**).

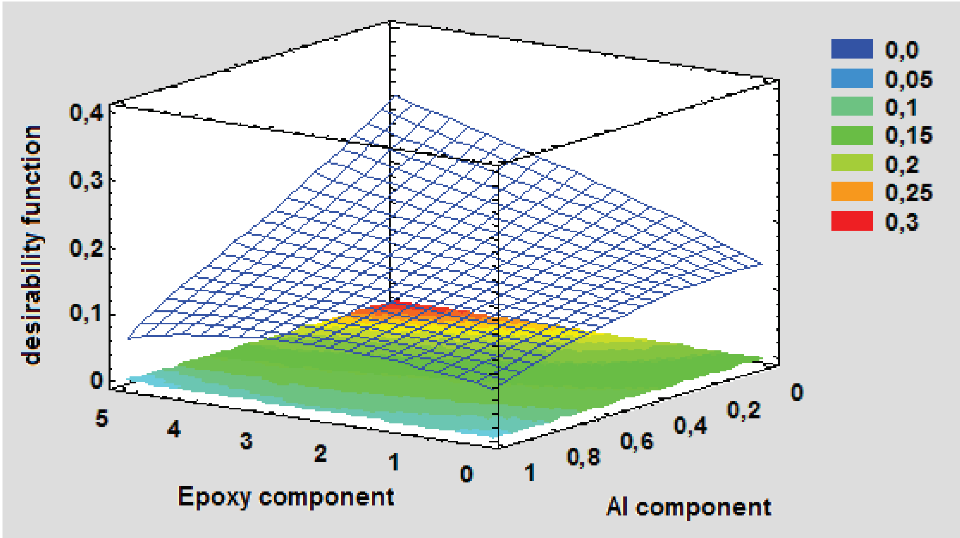


Figure 5 Desirability function depending on the epoxy and aluminium content in the sol

According to this, the epoxide content should be as high as possible and the alumina content should be as low as possible. However, since both the minimization of the WVTR and the layer thickness were prioritized, the optimum epoxide content was about 1.25 wt% and for alumina 0.15 wt%.

By use of this sol composition, a three-layer system formation was already sufficient to meet the industrial requirements. The total layer thickness of this coating was about 300 nm and it is highly transparent as well as flexible.

The permeability of the layer system can be precisely adjusted by the properties of the individual layer components. Thus, semipermeable coatings may also have to be produced. These could then be used, for example, in the filtration technology or corrosion protection.

However, further studies are necessary in this field of application. Notably, first results promise further improvements with regard to the adjustment of the permeability of ions.

5. CONCLUSION

The use of CCVD in combination with the Sol-Gel technique allows the production of thin layer systems with high barrier properties against gases such as oxygen and water vapor. By varying the reactant composition of the sol, their efficiency can be additionally increased, which allows an industry-compatible layer composite with a total layer thickness of approximately 300 nm.

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