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Development of Passive and Active Barrier Coatings on the Basis of Inorganic–Organic Polymers[#]

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Summary. With a new kind of barrier coating material, namely inorganic–organic polymers, it is possible to obtain excellent barrier properties against oxygen, water vapor, and flavor permeation. These hybrid polymers can be synthesized by the sol–gel technique. If extremely low permeation values are needed, the combination of hybrid polymer coatings with thin inorganic oxidic layers (SiO_x, AlO_x) is very effective and leads to permeation values for oxygen and water vapor below $10^{-3}\,cm^3/m^2 \cdot d \cdot bar$ or $g/m^2 \cdot d$. These passive barrier layers can be further improved by the combination with active oxygen barrier layers which have been developed for the food packaging industry. This approach makes these multilayer laminates promising candidates for special applications in the food packaging industry as well as for sophisticated applications in technical areas: the encapsulation of sensitive organic devices like solar cells, organic light emitting diodes, or polymer electronic systems.

Keywords. Hybrid polymers; Barrier coatings; Active barrier layers; Oxygen scavengers; Barrier laminates.

Introduction

In the food packaging industry an ever increasing demand for flexible and transparent polymeric materials is to be noted because of their light weight, good handling properties and, most important, low cost. Due to their relatively high permeability for various substances, such as gases or water vapor, polymers are not applicable for purposes where this feature is a handicap. To achieve the necessary improvements in barrier properties of polymers, additional barrier layers or polymer multilayers have to be used.

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[#] Dedicated to Prof. Dr. *Ulrich Schubert* on occasion of his 60th birthday

The quality and shelf-life of foods is in most cases reduced by the influence of oxygen. A wide range of food is susceptible to oxidative damages of flavor and color. General consequences are nutrient and flavor losses, browning, or bleaching. More typical for fatty foods is the development of rancidity. Aerobic microbial growth can be a problem in meat, prepared dishes, and juices.

Already very small amounts of oxygen, *i.e.* in the range of 1–200 ppm (mg/kg), may cause a substantial quality loss of food. The levels of residual oxygen in most packaging systems are much higher, *e.g.* between 0.1% in vacuum packs and 2% in gas flushed packaging processes. Therefore, not only avoiding the access of oxygen to the filled goods is an important task in packaging, but also the reduction of levels already present at the time of packing. Important access paths for oxygen to filled goods are the inherent permeability of the packaging material, and defects in the package. Suitable materials which can be used for these sensible areas in food packaging combine passive barrier layers with active barrier layers, *e.g.* oxygen consuming layers (“oxygen scavengers”).

At present, several methods exist that allow the incorporation of “oxygen scavengers” into the packaging, in most cases as separate elements (sachets, tablets) [1]. Since these methods are not allowed in all countries and may also make the consumers unsettled, new concepts are needed in order to ensure significantly higher barrier properties and to incorporate the oxygen scavengers homogeneously into the whole area of the packaging films. The barrier properties of the laminates available on the market are sufficient for standard packaging applications. However, for very sensitive contents, *e.g.* pharmaceuticals, drugs, cosmetics, and for many technical applications these barrier properties are insufficient (see Fig. 1) [2].

Industrial applicants deal with this problem by using complicated laminated films, consisting of eight or more components in order to fulfill the high barrier requirements against different permeants [3]. The final aim is to move from complicated multilayer laminates towards simpler film constructions which is necessary for both environmental and cost reasons. This work focusses on the improvement of the oxygen barrier properties by developing active oxygen barrier layers.

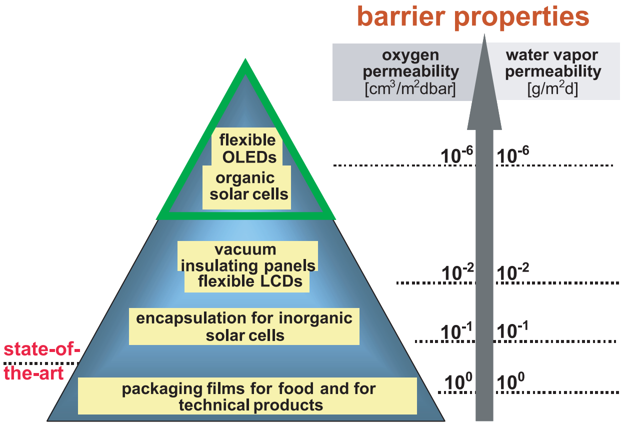


Fig. 1. Barrier layer technology; products on top have the highest requirements

Results and Discussions

Passive Barrier Layers

A new class of barrier coating materials, inorganic–organic nano-composites, were shown to provide very good barrier properties with respect to the permeation rates of oxygen, water vapor, and volatile organic compounds [4]. In combination with inorganic oxide layers (*i.e.* AlO_x, SiO_x, see Fig. 2) high and ultra-high barrier properties can be realized (see Fig. 3) [3].

The results in Fig. 3 show the barrier properties obtained through the combination of the hybrid polymers with inorganic barrier layers, in this case Al_2O_3 sputtered layers and SiO_x layers which were applied by physical vapor deposition.

Inorganic–organic hybrid polymers (ORMOCER®s, trademark of the Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., Germany) combine the

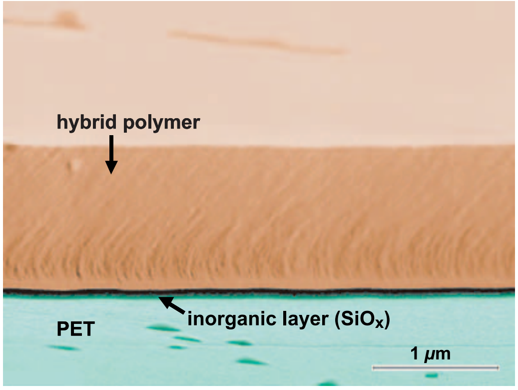
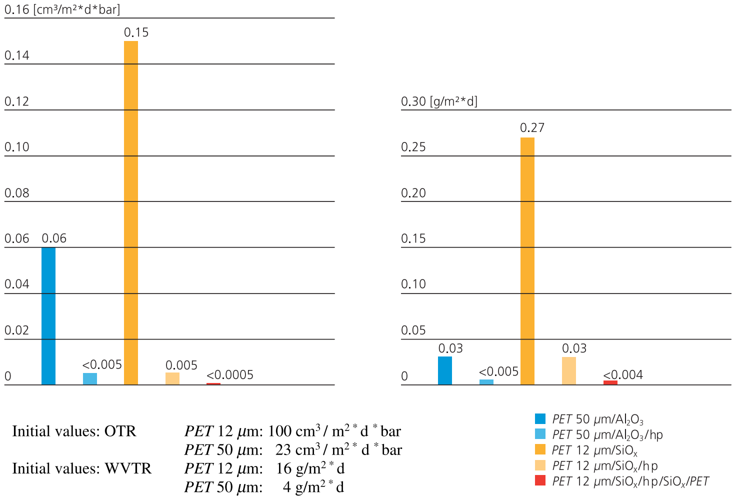


Fig. 2. Scanning electron micrograph of a thin hybrid polymer coating on SiO_x deposited on a flexible *PET* film



Initial values: OTR	*PET* 12 μm:	100 cm^3 / m^2 * d * bar
	PET 50 μm:	23 cm^3 / m^2 * d * bar
Initial values: WVTR	*PET* 12 μm:	16 g/m^2 * d
	PET 50 μm:	4 g/m^2 * d

Fig. 3. Oxygen (OTRs, left) and water vapor (WVTRs, right) transmission rates of *PET* films with inorganic layers (*PET*/Al_2O_3 sputtered layer and *PET*/SiO_x PVD layer) and hybrid polymer based coatings (hp)

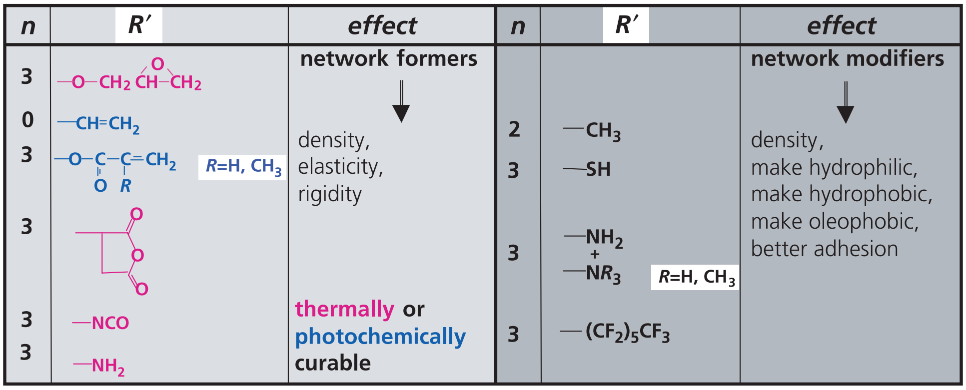


Fig. 4. Bifunctional silanes $R'(CH_2)_nSi(OR)_3$; examples for functional organic groups R' for formation of an organic network and for functionalization of the matrix

properties of organic polymers with those of silicones and glass-like materials. Such nano-composites have strong covalent or ionic-covalent bonds between the inorganic and the organic phases [5]. These materials combine the key properties of their constituents: high transparency, hardness, chemical and thermal stability (glass-like), low processing temperatures, functionalization, toughness (polymer-like), and flexibility (silicone-like). The nano-composites are synthesized *via* the sol–gel process [6]. Organoalkoxysilanes are used as starting materials (see Fig. 4).

Active Oxygen Barrier Layers

The functional principle of the newly developed oxygen scavenger system is based on a photo-initiated, metal catalyzed oxidation of a cyclo-olefin bonded chemically to a silicate backbone. This concept permits the activation of the scavenging process by UV light and prevents the formation of low-molecular oxidation products which may decrease the quality of the packaged goods or may be toxic. A similar strategy is followed by Chevron Chemical Company and Cryovac Inc., a subsidiary of Sealed Air Corporation [7, 8]. In their patents they describe the production of a terpolymer with oxygen scavenging properties *via* partial transesterification of an ethylene/methacrylate copolymer with an alcohol comprising a cyclic olefin compound by means of reactive extrusion. The major difference between the Chevron concept and the system described here is the backbone to which the cyclic olefin groups are linked. While the ethylenic backbone of the Chevron scavenger system is preformed and subsequently modified in order to introduce functional groups, the silica-based system is formed in a one-step synthesis by hydrolysis of the corresponding alkoxysilanes. In addition, the resulting sol can be applied to any suitable film substrates by common coating techniques, whereas the terpolymer-based scavenger system is extruded to films which in turn have to be incorporated into laminates.

Spectroscopic evidences regarding the formation of the oxidation products shown below (see Fig. 5) could be obtained through *Raman* spectra (see Fig. 6) of a layer of scavenger system A (see Experimental).

As can be seen in Fig. 6 the intensity of the C=C-bond signal at 1665 cm^{-1} clearly declines during two days after UV activation. Interestingly, the spectrum of the partially oxidized polymer allows for the differentiation of the two double-bond

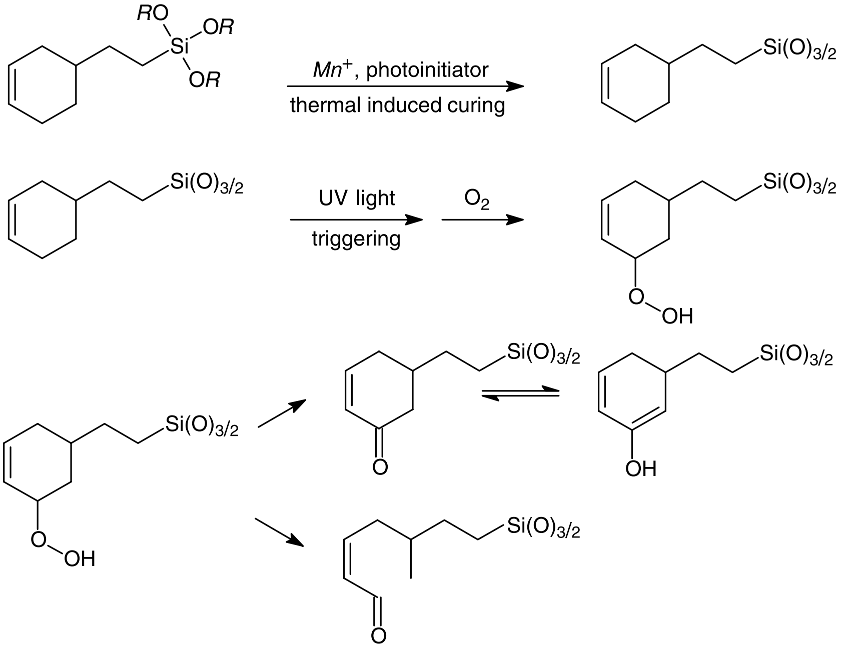


Fig. 5. Proposed mechanism of the transition metal catalyzed oxidation of the silylated cyclic olefin compound

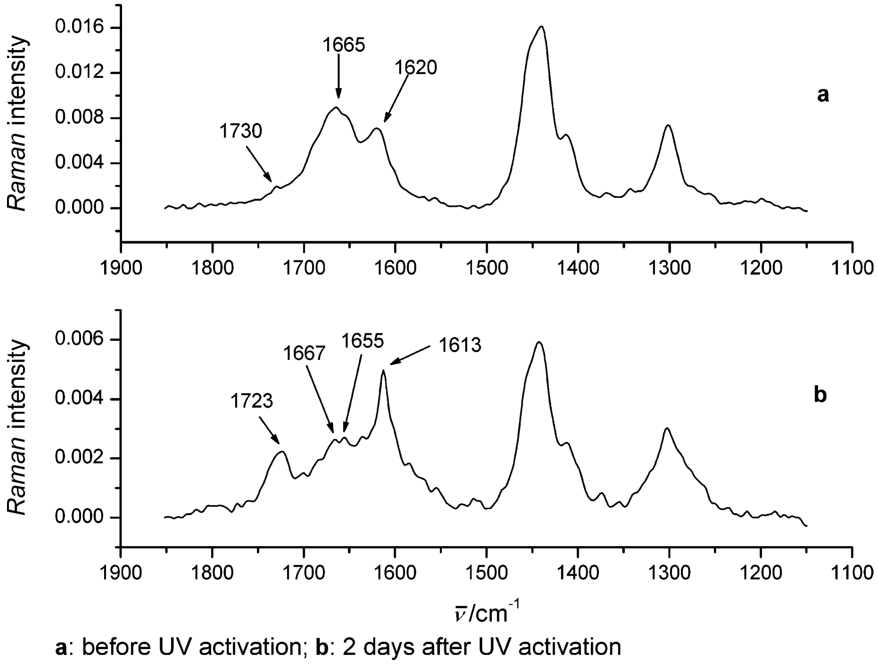


Fig. 6. Solid state FT-*Raman* spectra of scavenger system A before UV activation and two days after UV activation

isomers of 2-cyclohexenylethyltriethoxysilane (*CHEO*, 1667 cm^{-1} and 1655 cm^{-1}). At the same time, one can see the formation of a new intensive band at 1613 cm^{-1}, which is in good accordance with the data found in the literature for C=C-bonds of

α,β-unsaturated carbonyl compounds [9]. The simultaneous formation of a broad band centered at 1723 cm^{-1} indicates that to a minor extend also saturated carbonyl compounds are generated [9].

The scavenger system A was applied on a *PET* film by the spiral applicator method and subsequently cured thermally. The coated films were UV activated and then evaluated with regard to their oxygen consumption. One fraction of the samples was directly put into the measurement cells after UV activation. A second fraction of the samples was stored for one day in the dark at room temperature in atmospheric conditions. Afterwards, the samples were activated and put into the measurement cells. The last fraction of the samples was stored for three days under the conditions described before, and then activated and put into the measurement cells. The samples evaluated directly after UV activation showed an oxygen consumption of 77 cm^3 $\mathrm{O_2/g}$ layer. This value corresponds approximately to a 100% theoretical oxidation rate according to Fig. 5 if one takes into consideration that the measuring inaccuracies of the oxygen scavenging measurement method adds up to about 10 cm^3 $\mathrm{O_2/g}$ layer. Samples which were activated and measured after one or three days had significantly lower oxygen consumptions: 38 and 3 cm^3 $\mathrm{O_2/g}$ layer (see Fig. 7). These results demonstrate that the scavenger layer A cannot be stored under air without substantial loss of scavenging performance.

Raman and IR spectra (IR spectra are not shown here) indicate that already before UV activation a minor part of the double bonds is oxidized without activation of the educts. However, when storing the scavenger system A in nitrogen atmosphere (*e.g.* for four days, in daylight) and doing the UV activation afterwards,

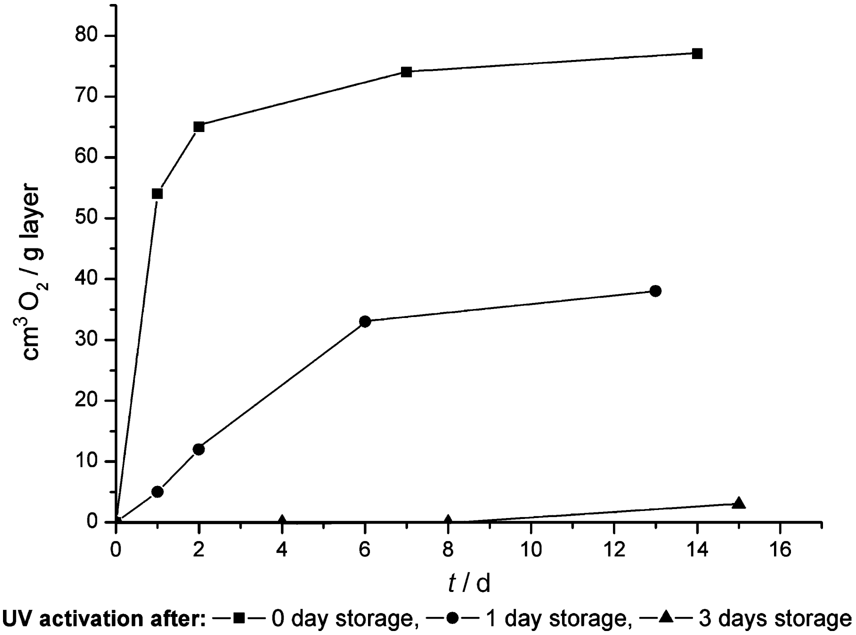


Fig. 7. Dependance of the scavenging activity on the storage time of scavenger system A (scavenger layer on *PET* film)

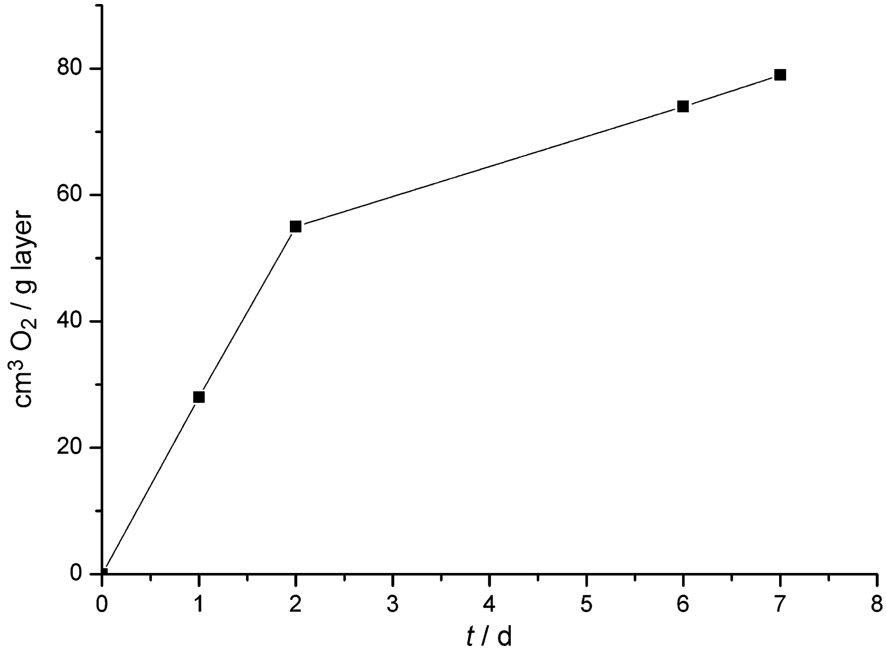


Fig. 8. Scavenging activity of scavenger system A after four days of storage in nitrogen atmosphere and subsequent UV activation

the oxygen capacity of the freshly activated system can be reproduced (see Fig. 8). This result shows that the daylight had no influence on the oxygen uptake of the stored samples. For practical applications the shelf life of the active coatings had to

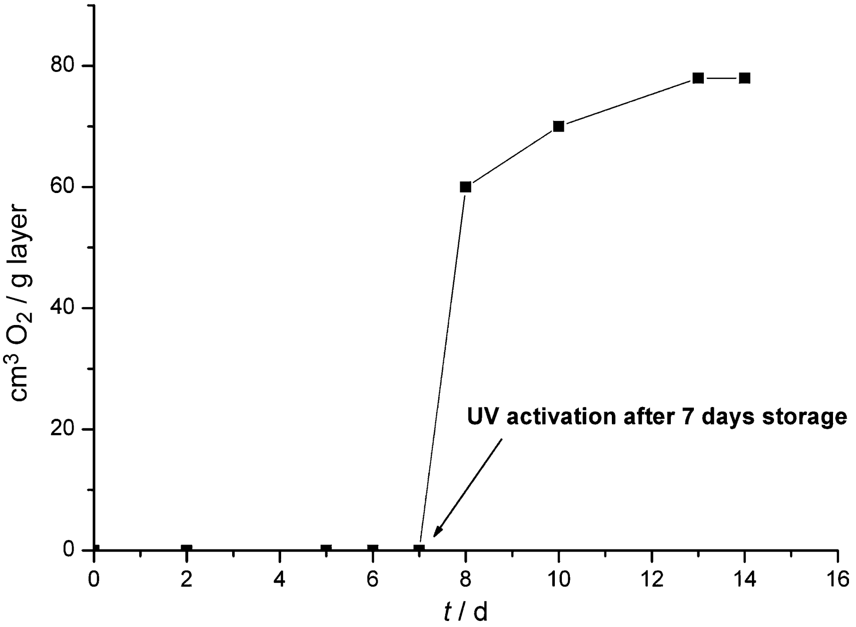


Fig. 9. Scavenging activity of scavenger system B after 7 days of storage under air and subsequent UV activation

be improved. It is very important that the coated films can be stored under air exposure for some time.

In the course of further development steps on the basis of scavenging system A, a new scavenging composition containing an antioxidant (vitamin E) could be found. The antioxidant is used in very low concentrations ($\leq 1\%$ by weight) and shows no detectable oxygen consumption. This newly designed scavenging system B exhibits an oxidation rate comparable to that obtained with system A (see Fig. 9).

Unlike system A this new system shows a good shelf life with regard to storage under air and subsequent UV activation combined with an excellent oxygen capacity (see Fig. 9). In addition, the maximum oxygen uptake is reached 6 days after UV activation, meaning that the kinetics of the oxidation process is very fast. Rapid oxygen consumption by the scavenger is a matter of high importance especially in food and pharmaceuticals packaging where remaining oxygen in the headspace may be detrimental to product quality within a short period of time.

Conclusion and Outlook

Active oxygen barrier layers were produced *via* sol–gel transformation of a resin consisting of oxidizable organoalkoxysilanes, a UV initiator, and a transition metal catalyst. Upon UV activation, these layers act as oxygen scavengers and provide both high oxygen uptake and fast oxidation kinetics. Thus, these active oxygen barrier layers are particularly suitable for food packagings.

By combining passive barrier layers with the newly developed active oxygen barrier layers it may also be possible to make these barrier films available for new fields of applications (see Fig. 10). The ambitious target for future research projects is to create new "zero transmission" laminates, *e.g*. for flexible OLEDs and organic solar cells. Regarding the oxygen barrier properties first promising results could be obtained. New concepts for a further significant improvement of the water vapor barrier properties are also necessary and will be focussed on in the near future.

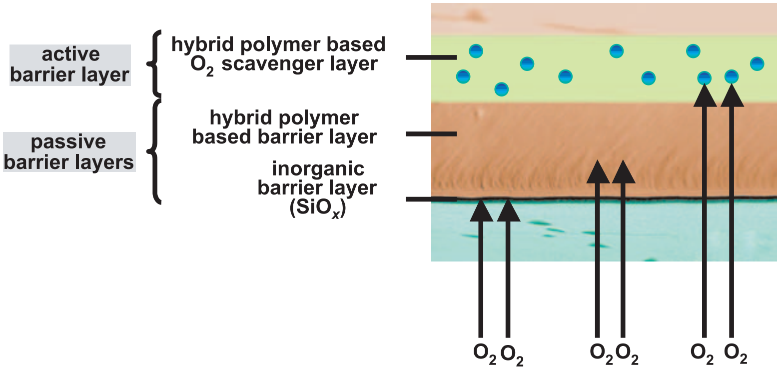


Fig. 10. Combination of passive barrier layers with an active oxygen barrier layer to create "zero oxygen transmission" laminates (schematic representation)

Experimental

FT-*Raman* spectroscopic investigations were carried out on a Bruker spectrometer model RFS 100 (laser power on the samples 500 mW, spectral resolution 4 cm^{-1}) with a Nd-YAG laser as excitation light source with an emission wavelength of 1064 nm. Infrared spectra of samples were performed on a Nicolet Magna 750 FT-IR spectrometer (spectral resolution 4 cm^{-1}).

The activation of oxygen scavenger systems was carried out on a Beltron 22/III with a UV-perfomance of 8.2 J/cm^2 (2 UV-lamps, each 1200 W, throughput speed of 0.4 m/min and exposure time of 30 sec).

Syntheses

Matrix system: A solution of 44 mmol 2-cyclohexenylethyltriethoxysilane and 44 mmol *n*-octyltriethoxysilane in 2-butoxyethanol was placed in a three-necked flask and cooled in an ice bath. After hydrolysis with 50% of the stoichiometric amount of H_2O (in the form of 1 *N* HCl) with respect to the hydrolyzable alkoxy groups the mixture was stirred at room temperature for 2 h. To this mixture a solution prepared by mixing of Zr-*n*-propoxide (12 mmol) and ethyl acetoacetate (molar ratio metal alkoxide/complexing agent = 1/2) was added. The completion of the hydrolysis reaction was controlled by *Raman* spectroscopy (solids content 33%).

Oxygen scavenger system A: To the obtained matrix, Co(II)-oleat ($\leq$2% by weight) and 1% by weight of the photoinitiator Lucirin® TPO (Ciba) were added. The mixture was stirred to give a clear solution. Curing conditions: 1 h at 130°C.

Oxygen scavenger system B: To the obtained matrix, Co(II)-oleat ($\leq$2% by weight), 1% by weight of the photoinitiator Lucirin® TPO, and vitamin E as antioxidant (1% by weight) were added. The mixture was stirred to give a clear solution. Curing conditions: 1 h at 130°C.

Application

The sols were applied with a spiral applicator, the coating thickness was 4 μm.

Measurements and Calculations Regarding Oxygen Capacity

The measurements of the O_2 consumption were performed on a WTW Clark-Elektrode CellOx 325 equipped with a measuring device Oxi 315i. The calibration of the measuring system was carried out under atmospheric conditions (20.7% O_2 content). The calculation of the oxygen capacity of the developed scavenger matrices is described elsewhere [10].

Acknowledgements

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