



## Barrier Properties of Inorganic-Organic Polymers: Influence of Starting Compounds, Curing Conditions and Storage-Scaling-Up to Industrial Application

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**Abstract.** With a new kind of barrier coating material, namely inorganic-organic polymers, it is possible to obtain high-barrier properties for oxygen, water vapor, and flavor permeation. These hybrid polymers can be synthesized by the sol-gel technique. Network forming reactions and degrees of condensation in the coating sols as well as in the cured coating materials were characterized using  $^{29}\text{Si}$ ,  $^{13}\text{C}$ -NMR and FT-Raman spectroscopy. The oxygen barrier properties of the hybrid polymers were found to be strongly influenced by the inorganic and also by the organic network density. In order to scale-up the excellent laboratory results to pilot plant and production dimensions additional efforts were necessary. For optimization of the barrier coating compositions the influence of the starting compounds on the resulting barrier properties had to be investigated. A constant quality of the coating sols during the industrial processing had to be guaranteed so as to obtain reproducible barrier properties. The influence of storage conditions on chemical reactions in the coating sols, indicated by changes of viscosity, was investigated. Since the curing times of the laboratory system were not transferable to the high speed of the production roll coating process more effective curing methods had to be found. The influence of the storage time of the cured coating materials on the oxygen barrier properties was investigated. Even by storing at ambient temperature further improvement of the oxygen barrier properties was obtained. Only by optimizing all of the above mentioned parameters can the excellent barrier properties result in marketable products.

**Keywords:** hybrid polymers, barrier materials, water vapor barrier, oxygen barrier, flavor barrier

### 1. Introduction

The possibility to use transparent barrier coatings for polymers is of great interest to the food and pharmaceutical packaging industry, as well as for technical applications. Since polymers are permeable to gases, water vapor and volatile organic compounds, special coating materials with combined barrier properties are necessary. Earlier research has shown that coating materials based on inorganic-organic polymers have excellent barrier properties for water vapor, oxygen and flavors [1, 2]. The hybrid polymers are synthesized via the sol-gel technique [3]. In order to reproduce the out-

standing laboratory barrier results on a production scale additional efforts were necessary. First the recipes were optimized and a constant quality of the coating sols during the processing and storage time had to be guaranteed. Secondly, due to the high speed of the production roll coating the curing conditions had to be adjusted. Finally the influence of storage of the cured coating materials on the oxygen transmission rates (OTRs) had to be determined.

### 2. Experimental

*Synthesis:* The oxygen barrier properties of a thermally curable sol-gel derived coating material 1 based on

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tetramethoxysilane (TMOS), (3-glycidoxy-propyl) trimethoxysilane (GLYMO), (3-aminopropyl)-triethoxysilane (AMEO) and Al-sec-butoxide (ethylacetoacetate complex) were investigated. The synthesis of this material is described elsewhere [3]. For the optimization work and quality control experiments, simpler compositions, 1a GLYMO/Al-sec-butoxide (ethylacetoacetate complex); 1b GLYMO/AMEO were synthesized.

**Preparation of the inorganic-organic polymer coatings:** The coating sols were applied with a spiral applicator on corona-treated polypropylene (PP) or polyethyleneterephthalate (PET) films (uncoated PP film: 50  $\mu\text{m}$ , OTR: 1800  $\text{cm}^3/\text{m}^2 \cdot \text{d} \cdot \text{bar}$ ). In order to exclude the synergistic effects through combination of vacuum deposited layers and inorganic-organic polymers [1] the coating materials were applied on these polymer films without any vacuum deposited layer. The sols were cured by an air circulation system (two hours at 100°C) and/or with IR-treatment (Beltron Belthrotherm, contact time: 3 minutes, 120°C), coating weight: 5  $\text{g}/\text{m}^2$ .

**Parameters employed for the production roll coating experiments:** Web speed: 50 m/min, thermal curing in a drying tunnel at 120°C, contact time: 10 seconds, coating weight: 2  $\text{g}/\text{m}^2$ .

**Characterization:** OTRs were measured with an OX-TRAN 100 TWIN (Mocon) in accordance with DIN 53380 (23°C and 50% r.h.). FT-Raman spectroscopic investigations: Bruker RFS 100 (laser power on the samples: 500 mW; spectral resolution: 4  $\text{cm}^{-1}$ ; laser line: 1064 nm). NMR measurements: Bruker DRX 300 NMR spectrometer and Bruker DSX 400 solid-state NMR spectrometer.

### 3. Results and Discussion

#### 3.1. Optimization and Quality Control of the Coating Sol Composition

##### 3.1.1. Influence of Increased Amounts of TMOS.

The TMOS-content of the barrier coating material 1 was varied from 0 up to 40 mol%. While increasing the amount of TMOS, the quantity of GLYMO was decreased simultaneously. All the coating materials were cured for two hours at 100°C. The carrier foil was PP. In Fig. 1 it can be seen that the OTRs decrease with increasing TMOS-content.

This result can be attributed to an increase of the inorganic network density, which hinders the oxygen

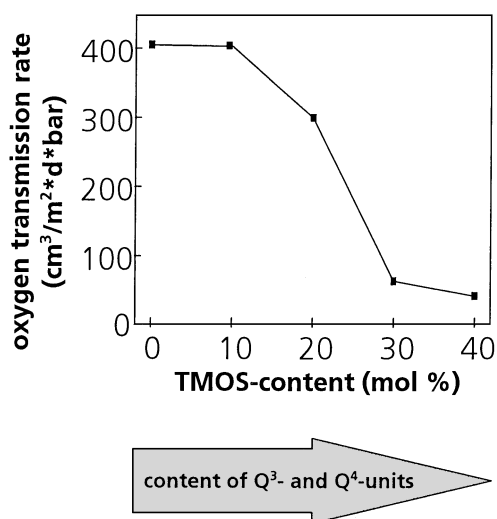


Figure 1. Dependence of the oxygen transmission rate on the TMOS-content of the barrier coating material (carrier foil: PP).

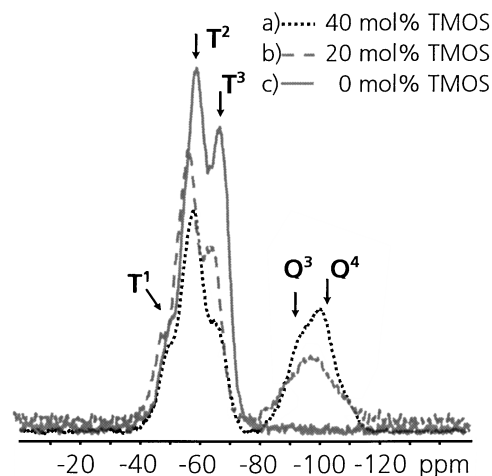


Figure 2. Solid-state  $^{29}\text{Si}$  CP-MAS NMR spectra of system 1 with different contents of TMOS.

molecules from permeating through the more dense and rigid hybrid polymer network as detected by NMR measurements. Figure 2 shows the solid-state  $^{29}\text{Si}$  CP-MAS NMR spectra of coating sols with different TMOS-contents.

The spectra demonstrate, that an increase of the TMOS-content leads to an increase of the  $\text{Q}^3$  and  $\text{Q}^4$ -groups resulting in a higher inorganic network density.

**3.1.2. Influence of Storage on the Coating Sols.** It was found that the resulting OTRs strongly depend on

the age and the storing conditions of the coating sols. An increase of the viscosity of aged coating sols (stored at room temperature) was observed. Therefore the ageing behaviour e.g. the continuation of organic and inorganic reactions of the coating sols was investigated.

*Organic reactions:* The epoxy functional group of GLYMO as the main compound of the coating sol 1 is expected to form the organic network in the cured material. In the sol three possible ring-opening reactions of the epoxy group have to be considered: I. reaction with alcohols, II. with water or III. with an epoxy group of another oxirane. Only this last reaction possibility is the desired one and results in the organic network consisting of oligo- or poly(ethyleneoxide) derivatives. The coating sol 1 contains an Al-butoxide complex and AMEO. Both are possible catalysts for the ring-opening reactions at elevated temperatures during the curing process [4]. In order to examine whether these compounds already start the ring-opening reactions at ambient temperature in the sols, their temporal effects on the simplified compositions 1a and 1b were investigated using FT-Raman spectroscopy. In composition 1b (GLYMO/AMEO) no decrease of the epoxy-content could be observed in the FT-Raman spectra (not shown here). The Al-butoxide complex however (composition 1a) significantly catalyzed the ring-opening reaction of GLYMO (s. Fig. 3).

Figure 3 illustrates the significant intensity decrease of the epoxy band at  $1256\text{ cm}^{-1}$  after storing

[5]. This indicates the continuation of ring-opening reactions. Due to the presence of high amounts of water and alcohols in the coating sol the epoxy ring-opening reactions lead mainly to diols and ether products as seen by  $^{13}\text{C}$ -NMR spectroscopy (not illustrated here). Their amount depends on the water-to-alcohol-ratio in the sols [6]. It can be concluded that the longer the storage period at ambient temperature the lower the epoxy-group concentration in the coating sol. Figure 4 shows the effect of different epoxide-contents of aged coating sols (s. Fig. 3) on the OTRs of the cured coating materials. Each of the sols (type 1a) was applied to PP films and cured at  $100^\circ\text{C}$  for two hours.

The lower OTRs can be explained by a higher amount of reactive epoxy groups which can form a higher organic network density in the resulting coating materials. By storing the coating sols at lower temperatures ( $\leq 10^\circ\text{C}$ ) the ring-opening reactions can be inhibited thus conserving the maximum epoxy concentration.

*Inorganic reactions:* To obtain information whether the storage time also has an influence on inorganic reactions the coating sols were investigated by  $^{29}\text{Si}$ -NMR spectroscopy (spectra not shown here). The comparison of a freshly synthesized coating sol (1a) with a sol stored for three days at ambient temperature showed that the inorganic crosslinking continued noticeably. The  $^{29}\text{Si}$ -NMR spectra showed a clear increase of the ratio of  $\text{T}^3$  to  $\text{T}^2$ -units. This result can also be confirmed in Fig. 3. With an extended

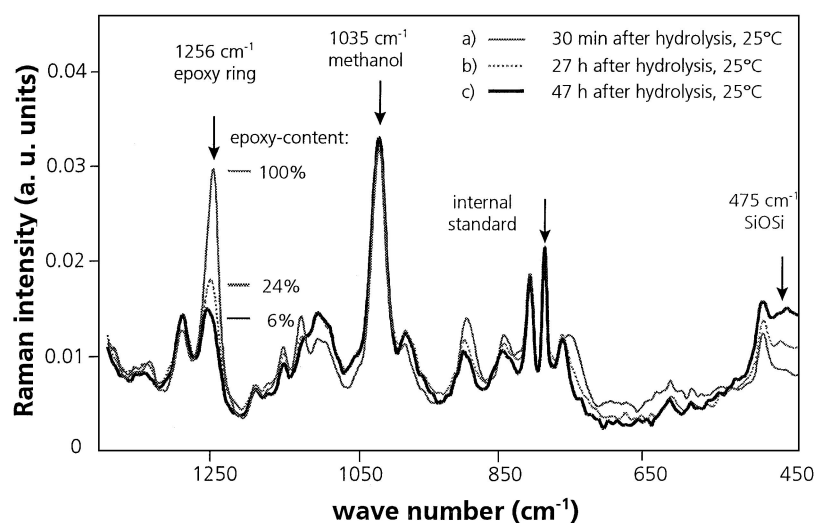


Figure 3. Raman-spectra of composition 1a, different storing times at ambient temperature.

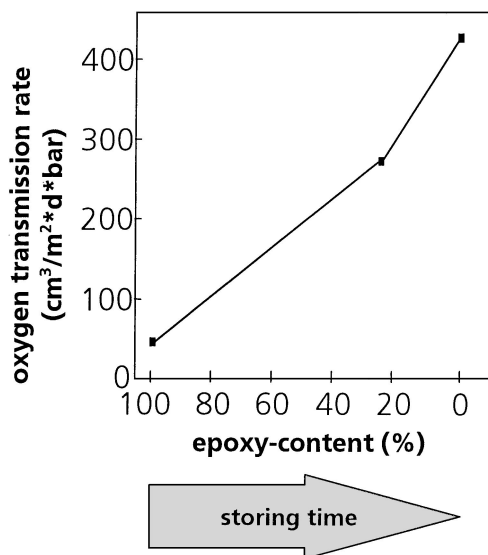


Figure 4. Dependence of the oxygen transmission rate on the epoxy-content of the type 1a coating sol (carrier foil: PP).

storage time, an increase of the intensity of the Raman signals below  $500\text{ cm}^{-1}$  can be observed. This can be an indication of an increased, more condensed, inorganic network and explains the enhancement of the coating sol viscosity. By storing the sols at temperatures below  $10^\circ\text{C}$  this undesired effect can be retarded.

### 3.2. Adjusting of the Curing Conditions to the High Speed Production Process

The best OTRs of hybrid polymers on PET films were found at a curing temperature of  $100^\circ\text{C}$  and a curing time of two hours. These laboratory conditions are not acceptable for production processes. The three solid-state  $^{29}\text{Si}$  CP-MAS NMR spectra in Fig. 5 show the ratios of the T-groups of samples (1a) which were cured under different conditions a) laboratory cured coating b) laboratory IR-cured coating, c) production cured sample.

Figure 5 demonstrates, that the degree of inorganic condensation, which is achieved by curing under industrial conditions does not reach the desired inorganic network density of the laboratory cured sample leading to very low OTRs. Since longer curing periods are not possible in the production process, modified curing procedures had to be found to guarantee comparable network densities. Figure 5 shows, that IR-curing already results

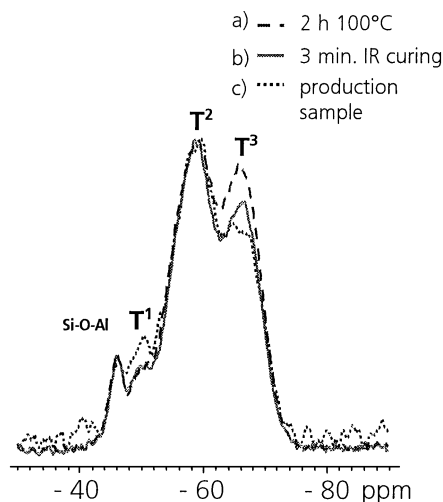


Figure 5. Solid-state  $^{29}\text{Si}$  CP-MAS NMR spectra of coatings cured under different conditions (Si—O—Al bonding [4]).

in a higher degree of inorganic crosslinking compared with the production process. The optimum degree of inorganic crosslinking for the production process can be achieved by combined curing (air circulation and IR). The first tests with such a combined curing procedure showed that coatings with very good barrier properties can be obtained.

### 3.3. Effect of Ageing on the OTRs of Cured Barrier Materials

Following the storing time of the already cured coating materials from a) simulated production process ( $120^\circ\text{C}$ , contact time: 10 seconds) and b) laboratory process further improvement in the OTRs was observed (s. Fig. 6).

Figure 6 shows that insufficient curing in a simulated production process can nearly be compensated by storing at ambient temperature. This is due to a further increase of mainly the inorganic network units (solid-state  $^{29}\text{Si}$ -NMR and  $^{13}\text{C}$ -NMR not shown here) which thus leads to better barrier results compared to the un-stored laboratory sample.

## 4. Conclusion

The use of inorganic-organic polymers as high barrier coating materials for a large scale application considerably depends on whether an optimum network density can be achieved under production conditions.

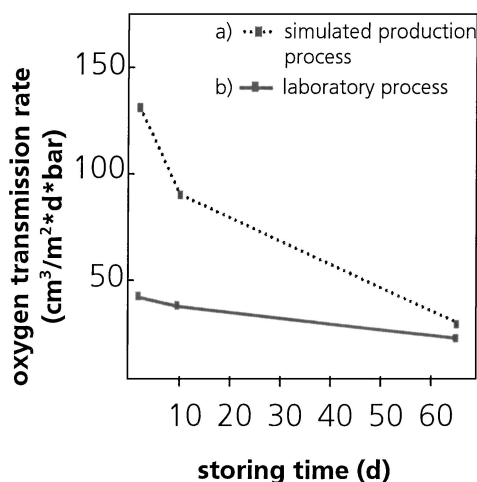


Figure 6. Oxygen transmission rates of coated PP films (simulated production and laboratory process) after storage at ambient temperature.

Constant quality and optimum OTRs can be guaranteed by the following measures:

- low temperatures for the coating sols during storage and processing,

- combined curing (air circulation and IR-curing),
- postcuring at room temperature.

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