Mechanical properties of the oxygen barrier dyad system of a pp-HMDSO and a silica-like thin film

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Abstract: To improve temperature durability for autoclaving of SiOₓ diffusion barrier coatings pp-HMDSO was applied as interlayer material. The influence of the O₂/HMDSO ratio on coating properties was investigated. Reducing the O₂/HMDSO ratio results in carbon-rich polymer-like coatings with low density, low internal stress, and excellent adhesive and cohesive properties at the expense of barrier performance.

Keywords: pp-HMDSO, multilayers, diffusion barrier, PECVD, (poly)propylene, autoclaving

1. Introduction

Silicon oxide (SiOₓ) coatings are extensively applied as gas diffusion barrier coatings on polymers. For packaging industry polypropylene (PP) is an interesting substrate material due to its inherent water vapor barrier, low density, high availability, and low cost.

Apart from its high oxygen permeability one major drawback of PP as substrate for the deposition of thin brittle oxide films is its high thermal expansion and low glass transition temperature. Therefore, brittle coatings tend to crack at elevated temperatures, as they occur e.g. during autoclaving. This may result in an almost total loss of barrier performance.

The combination of amorphous hydrogenated carbon nitrogen (a-C:N:H) and a-Si:C:N:H layers with SiOₓ diffusion barrier coatings in a multilayer approach was shown to be capable of efficiently improving temperature durability during autoclaving [1].

In this work, alternatively a single precursor approach is followed to obtain a good compromise between temperature durability and barrier performance. By variation of the oxygen to monomer ratio, properties of the resulting coating can be changed from polymeric to SiO₂-like [2]. Particularly the influence of the oxygen to monomer ratio on the barrier performance, the density, the internal stress, the cohesive and adhesive properties, and the chemical structure of the coatings is investigated.

2. Experimental

Coating of 30 μm thick cast poly(propylene) (PP) foil, provided by Profil Kunststoffe (Germany), was conducted in a cylindrical stainless steel PECVD apparatus on the powered electrode, which was capacitively coupled to a 13.56 MHz radio frequency (RF) generator via a matching network. The powered electrode was water-cooled to 25°C, while the reactor wall, representing the grounded electrode, was heated to 50°C. Oxygen (Pangas, 99.999%) and hexamethyldisiloxane (HMDSO, Sigma-Aldrich, 98.5%) flow rates were controlled by MKS mass flow controllers. Oxygen was introduced at the top of the reactor and HMDSO 150 mm above the substrate using annular distributors. The process pressure was kept constant at 0.1 mbar by a butterfly valve. Prior to coating circular PP samples were cleansed in an ultrasonic acetone bath. In order to keep the thermal load on the PP substrate low, intervals of 4 s plasma operation were followed by 10 s off-time.

The oxygen transmission rate (OTR) was measured by a permeability tester (Ox-Tran 100, Mocon Inc.) according to DIN 53380-3 at 25°C and 50% relative humidity.

To test the temperature durability, coating/PP composites were consecutively heated to 80, 100, 120, and 140°C in a hot air oven, maintained at the corresponding temperature for 30 min, cooled down to room temperature, and the OTR was determined after each step. Additionally, temperature durability was tested in an autoclave (121°C, steam, 2.1 bar) for 30 min and the OTR was measured before and after.

Deposition rates were determined on Si-wafers, which were centered on the substrate, with a variable angle spectroscopic ellipsometer (M-2000F, J.A. Woollam Inc.) at three angles of incidence (65°, 70°, and 75°) in the range of 371 to 995 nm. The wavelength dependence of the refractive index was approximated with a Cauchy model. Reference measurements were performed with a stylus profilometer (Tencor P10).

Mass density of the coatings was calculated from the measured coating thickness and the mass, which was determined on 50x50 mm² glass slides.

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The in-plane internal coating stress σ was deduced from the radius of curvature R of the substrate/coating composite applying Stoney’s equation [3]:

\[ \sigma = -\frac{E_s h_s^2}{6Rh_c} \] (1)
where $h_c$ and $h_s$ are the coating and the substrate thickness, respectively, and $E_s$ is the Young’s modulus of the PP substrate. For $E_s$ a value of 1.38 GPa was assumed (manufacturer information). $R$ was determined from the maximum deflection $d$ on the length $L$ according to $R = L^2/(8d)$. The accuracy is about ± 30%.

The fragmentation test method is a reliable technique to investigate the adhesive and cohesive properties of thin, brittle coatings on polymer substrates [4]. Fragmentation tests were carried out on a Rhoemetric Scientific Minimat tensile tester in situ in an optical microscope (Olympus BX 60) equipped with videoextensometry. Samples of 8x40 mm² were incrementally strained and crack patterns were analyzed in terms of crack density (CD) versus true strain. The thickness of all investigated coatings was 119 ± 6 nm. The crack onset strain (COS) is the critical strain at propagation onset of the first crack in the coating. It was derived by linear regression from the crack density vs. strain data at the beginning of fragmentation and is closely related to the cohesive properties of the coating. On the other hand, the crack density at saturation (CD sat), which is reached if the crack density remains constant at further elongation, is related to the adhesive properties of the coating. Further details regarding this technique are given elsewhere [4, 5].

Fourier transform infrared (FTIR) spectroscopy was performed on Si-wafers with a Perkin-Elmer Spectrum BX II FTIR system in the range of 600-4000 cm⁻¹ at 2 cm⁻¹ resolution. For each spectrum 64 scans were collected and averaged. The coating thickness was adjusted to 1039 ± 81 nm to achieve a high signal to noise ratio.

3. Results and Discussion

Dry heat and autoclaving test results of the pp-HMDSO/SiOₓ dyad barrier coating are shown in Fig.1 and compared to results of a single SiOₓ coating and coatings with SiOₓNy or a-C:N:H and a-Si:C:N:H as interlayer material between PP and the SiOₓ barrier layer. Process parameters of the pp-HMDSO/SiOₓ dyad coating are summarized in Table 1. With regard to the high OTR of the PP substrate, excellent barrier performance is obtained with all tested single and multilayered coatings. Up to 100°C all coatings retain their barrier performance. After 30 min of exposure to 120°C, the SiOₓ coating without interlayer shows beginning deterioration of barrier properties. Exposure to 140°C results in severe loss of barrier performance of the single SiOₓ coatings and the formation of cracks in the coating is evidenced. A pp-HMDSO interlayer prevents the SiOₓ coating from cracking and exposure of the pp-HMDSO/SiOₓ dyad coating to 140°C results only in a minor increase of the OTR to 20 cm² m⁻² d⁻¹ bar⁻¹. Alternatively, a-C:N:H and a-Si:C:N:H or SiOₓNy or can be applied as interlayer material as previously shown [1]. Comparison of results shows similar behavior for all multilayer coatings with only slightly lower OTRs of the pp-HMDSO/SiOₓ dyad coating. Autoclaving at 121°C in 2.1 bar of steam affects the SiOₓ coating less than exposure to 140°C at dry conditions. For the investigated multilayer coatings comparable low OTRs are obtained after autoclaving and after exposure to 140°C.

Applying pp-HMDSO as interlayer material has the advantage that only a single precursor needs to be employed. In order to change from conditions for the interlayer (layer 1) to the barrier layer (layer 2) in principle only oxygen needs to be added, while other process parameters are kept constant. Therefore, the influence of the O₂/HMDSO ratio on the coating properties is investigated in the following.

In Fig.2 the influence of the O₂/HMDSO ratio on the OTR and the deposition rate is shown for constant RF power, HMDSO flow rate, process pressure, and coating thickness of 100 W, 2 sccm, 0.1 mbar, and approximately 120 nm, respectively. A critical O₂/HMDSO ratio, which is around 10 at these conditions, needs to be overcome in order to obtain good barrier performance. Similar trends in OTR are reported in literature [6-8].

Table 1. Deposition conditions of the pp-HMDSO/SiOₓ dyad coating.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pp-HMDSO</th>
<th>SiOₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power [W]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>HMDSO flow rate [sccm]</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>O₂/HMDSO flow rate ratio [-]</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>Pressure [mbar]</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Deposition Time [s]</td>
<td>3x4</td>
<td>15x4</td>
</tr>
<tr>
<td>Thickness [nm]</td>
<td>132</td>
<td>184</td>
</tr>
</tbody>
</table>

Fig.1 OTR of single and multilayered coatings on PP after deposition, after 30 min at 80, 100, 120, 140°C, and after 30 min autoclaving at 121°C and 2.1 bar of steam. Deposition conditions and coating thicknesses of the pp-HMDSO/SiOₓ dyad coating are summarized in Table 1.
The deposition rate decreases strongly with increasing O₂/HMDSO ratio up to a ratio of 15. Further increase of the O₂/HMDSO results only in a minor decrease of the deposition rate. At conditions applied for the pp-HMDSO interlayer of the pp-HMDSO/SiOₓ dyad coating (10 sccm HMDSO) high deposition rates of 780 nm min⁻¹ are achieved.

The dependence of the internal stress and the mass density on the O₂/HMDSO ratio is reported in Fig. 3. The mass density increases from 1.3 to 2.1 g cm⁻³ as the O₂/HMDSO ratio is increased from 0 to 30. The density of SiOₓ obtained for O₂/HMDSO = 30 is close to that of fused silica (2.2 g cm⁻³) and compares well with densities obtained at similar conditions [7, 9]. The internal stress is of compressive nature (indicated by a negative algebraic sign) and rises as the O₂/HMDSO ratio is increased. In-ternal stresses in the same range were determined for SiOₓ deposited by a PVD method on PET [4].

Fragmentation tests results of coatings deposited with varying O₂/HMDSO ratio between 0 and 30 are given in Fig. 4 as the crack density versus the applied strain. For SiOₓ coatings with best barrier properties, i.e. for O₂/HMDSO = 30, crack onset strains of approximately 0.9% are measured on PP, which is comparable to values reported for SiOₓ on PET [4, 10]. Decreasing the O₂/HMDSO ratio results in a tremendous increase of the COS up to 18% for pp-HMDSO as applied in the pp-HMDSO/SiOₓ dyad coating. Accordingly, CDₘₐₓ is increased with decreasing O₂/HMDSO ratio. On the inset of Fig. 4 the crack density is shown as a function of the local strain at a highly strained position for pp-HMDSO, deposited from 10 sccm HMDSO. Extremely high saturation crack densities of 1300 mm⁻¹ are observed, being evidence of excellent adhesion of pp-HMDSO to the PP substrate. Properties of the investigated coatings are summarized in Table 2 and compared to the alternative interlayer materials SiOₓNy and a-C:N:H.

FTIR spectroscopy was employed to investigate the influence of the O₂/HMDSO ratio on the chemical structure of the coatings. FTIR spectra of coatings deposited with varying O₂/HMDSO ratio between 0 and 60 are depicted in Fig. 5. With increasing O₂/HMDSO ratio vibrations of carbon containing groups, such as C-H in CH₂ and CH₃ at 2880, 2900, and 2960 cm⁻¹ or in Si(CH₃)x at 810, 840, 880, and 1270 cm⁻¹, are reduced and diminish for O₂/HMDSO ≥ 30. Similar behavior is observed for the absorption at 2240 cm⁻¹, which is characteristic for Si-H in H-SiO₃. For pp-HMDSO, i.e. O₂/HMDSO = 0, the absorption of Si-H is down-shifted to 2140 cm⁻¹, indicating

![Fig. 2 OTR and deposition rate as a function of the O₂/HMDSO ratio. RF power = 100 W, HMDSO flow rate = 2 sccm (open symbols), HMDSO flow rate = 10 sccm (solid symbols).](image1)

![Fig. 3 Internal in-plane stress and mass density of SiOₓ coatings as a function of the O₂/HMDSO ratio. RF power = 100 W, HMDSO flow rate = 2 sccm (open symbols), HMDSO flow rate = 10 sccm (solid symbols).](image2)

![Fig. 4 Crack density as a function of the applied strain of SiOₓ coatings with varying O₂/HMDSO between 0 and 30. RF power = 100 W, HMDSO flow rate = 2 sccm (open symbols), HMDSO flow rate = 10 sccm (solid symbols). Inset: pp-HMDSO (10 sccm HMDSO) at a highly strained position.](image3)
that the Si is not linked in a dense Si-O-Si network. This is consistent with the proposed mechanism for the deposition of pp-HMDSO of low fragmentation and retention of large structures [2]. The intensity of the Si-O-Si stretching vibration at around 1065 cm\(^{-1}\) is increased and the peak position is shifted to higher wavenumbers as the O\(_2\)/HMDSO ratio is increased, indicating a densification of the Si-O-Si network. At 2340 cm\(^{-1}\) characteristic absorptions of CO\(_2\), which is incorporated in small voids of the network during deposition, are only evident for O\(_2\)/HMDSO ratios \(\geq 15\). This suggests that high fragmentation of monomer molecules and complete oxidation of methyl groups only occurs at high O\(_2\) dilution.

### 4. Conclusions

To improve temperature durability during autoclaving interlayers of pp-HMDSO proved to be efficient in preventing the SiO\(_x\) diffusion barrier layer from cracking as alternative to other possible interlayer materials. Advantages of pp-HMDSO are that only a single precursor is needed and high deposition rates are achieved. By reducing the O\(_2\)/HMDSO ratio coating properties are changed significantly. At high oxygen dilution brittle, SiO\(_2\)-like coatings with high mass and network density, high compressive stress and good barrier performance are obtained. Pure HMDSO feed to the discharge results in polymer-like coatings with high carbon content, low internal stress, low mass and network density (as a result of low monomer fragmentation), and excellent adhesive and cohesive properties at the expense of barrier properties. Thus, the combination of pp-HMDSO and SiO\(_x\) in a dyad or graded coating is a promising approach not only for packaging applications.

### Table 2. Summary and comparison of interlayer and barrier coating material properties.

<table>
<thead>
<tr>
<th>Material</th>
<th>pp-HMDSO</th>
<th>SiO(_x)</th>
<th>SiO(_x)N(_x)</th>
<th>a-C:N:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)/HMDSO ratio [-]</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>HMDSO flow rate [sccm]</td>
<td>100</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>RF power [W]</td>
<td>100</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>N(_2) flow rate [sccm]</td>
<td>100</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C(_2)H(_2) flow rate [sccm]</td>
<td>100</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Crack onset strain [%]</td>
<td>18.4</td>
<td>11.4</td>
<td>6.2</td>
<td>1.2</td>
</tr>
<tr>
<td>CD at saturation [mm(^{-1})]</td>
<td>1334</td>
<td>432</td>
<td>406</td>
<td>312</td>
</tr>
<tr>
<td>Mass density [g cm(^{-3})]</td>
<td>1.2</td>
<td>1.3</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Internal stress [MPa]</td>
<td>-35</td>
<td>-55</td>
<td>-108</td>
<td>-183</td>
</tr>
<tr>
<td>Deposition rate [nm min(^{-1})]</td>
<td>780</td>
<td>570</td>
<td>325</td>
<td>230</td>
</tr>
<tr>
<td>OTR [cm(^{-3}) m(^{-2}) d(^{-1}) bar(^{-1})]</td>
<td>&gt;2000</td>
<td>&gt;2000</td>
<td>1140</td>
<td>23</td>
</tr>
</tbody>
</table>

Fig. 5 FTIR spectra of SiO\(_x\) coatings with varying O\(_2\)/HMDSO ratio from 0 to 60. RF power = 100 W, HMDSO flow rate = 2 sccm.

### References


