Oxygen permeation, mechanical and structural properties of multilayer diffusion barrier coatings on polypropylene

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Oxygen permeation, mechanical and structural properties of multilayer diffusion barrier coatings on polypropylene

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Abstract
To improve temperature durability for autoclaving of SiOₓ diffusion barrier coatings on polypropylene, plasma polymerized hexamethyldisiloxane (pp-HMDSO) is applied by plasma enhanced chemical vapour deposition as interlayer material and compared with results obtained with amorphous hydrogenated carbon–nitrogen (a-C:N:H) and a-Si:C:O:N:H interlayers. The influence of the O₂/HMDSO ratio on the chemical structure and related mechanical and oxygen barrier properties is investigated by fragmentation tests, dilatometry, oxygen transmission rate, internal stress and mass density measurements as well as Fourier transform infrared and x-ray photoelectron spectroscopy. Carbon-rich, polymer-like coatings with low density, low internal stress and excellent adhesive and cohesive properties are found for pp-HMDSO at the expense of barrier performance. In the SiOₓ/pp-HMDSO coating a broad transition in chemical composition was observed, explaining improved mechanical properties responsible for good barrier performance after thermal cycling or autoclaving.

1. Introduction
Silicon oxide (SiOₓ) coatings are extensively explored and applied as gas diffusion barrier coatings on polymers such as for instance polyethylene terephthalate (PET). Even more than PET, though, polypropylene (PP) is an interesting substrate material for the packaging industry. This is because of its inherent water vapour barrier, low density, high availability and low cost. Apart from its high oxygen permeability, one major drawback of PP as a substrate for the deposition of thin brittle oxide films is its high thermal expansion and low glass transition temperature of 20 × 10⁻² K⁻¹ and −18°C, respectively [1, 2]. In direct radio frequency (RF) plasma aided deposition the temperature is well above the glass temperature of PP and polymer chains are in a rubber-like state. For food or pharmaceutical packaging applications, exposure to elevated temperatures is often inevitable, e.g. during autoclaving. Here brittle SiOₓ coatings tend to crack because of the thermal expansion mismatch with the consequence of a significant loss of barrier performance. For electron beam evaporated SiOₓ coatings, it was observed that exposure to 60°C is already sufficient to induce cracks and alter gas barrier performance [3]. In this regard, plasma enhanced chemical vapour deposition (PECVD) is superior to physical vapour deposition (PVD) methods due to the formation of an extended interphase with a gradient in composition between the substrate and the coating as a result of rival ablation and redeposition processes [4, 5]. Therefore, a smoother transition of material properties and good adhesion is achieved.

For further adhesion improvement and to adapt mechanical properties between the substrate and the coating,
Table 1. Deposition parameters and properties of a-C : N : H (A), a-Si : O : C : N : H (B), pp-HMDSO (C, D) and SiOx (E–G) single layer coatings.

<table>
<thead>
<tr>
<th>Layer</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2/HMDSO ratio (—)</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>HMDSO flow rate (scm)</td>
<td>2</td>
<td>2</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>N2 flow rate (scm)</td>
<td>52.5</td>
<td>55</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C2H2 flow rate (scm)</td>
<td>7.5</td>
<td>3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Deposition rate (nm min⁻¹)</td>
<td>94</td>
<td>207</td>
<td>713</td>
<td>543</td>
<td>307</td>
<td>198</td>
<td>177</td>
</tr>
<tr>
<td>OTRa (cm² m⁻² d⁻¹ atm⁻¹)</td>
<td>14</td>
<td>101</td>
<td>&gt;2000</td>
<td>&gt;2000</td>
<td>1142</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Atomic composition</td>
<td>C₁₀ : N₀.05</td>
<td>Si : O₁.2 : C₁.5 : N₀.2</td>
<td>Si : O₇.7 : C₁.7</td>
<td>—</td>
<td>Si : O₁₆ : C₀.4</td>
<td>Si : O₁₀.9 : C₀.2</td>
<td>Si : O₁₉ : C₀.03</td>
</tr>
<tr>
<td>Si 2p peak position (eV)</td>
<td>—</td>
<td>102.7</td>
<td>102.4</td>
<td>—</td>
<td>103.3</td>
<td>103.6</td>
<td>103.7</td>
</tr>
<tr>
<td>Si 2p fwhm (eV)</td>
<td>—</td>
<td>2.1</td>
<td>1.9</td>
<td>1.8</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Mass density (g cm⁻³)</td>
<td>—</td>
<td>—</td>
<td>1.2</td>
<td>1.3</td>
<td>1.8</td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Internal stressb (MPa)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CLTEc (10⁻⁶ K⁻¹)</td>
<td>—</td>
<td>—</td>
<td>18.0</td>
<td>—</td>
<td>4.6</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>E₀ (GPa)</td>
<td>—</td>
<td>—</td>
<td>4.4</td>
<td>—</td>
<td>7.4</td>
<td>32.8</td>
<td>80.0</td>
</tr>
<tr>
<td>νc (—)</td>
<td>—</td>
<td>—</td>
<td>0.30</td>
<td>—</td>
<td>0.18</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>Dundurs parameter α (—)</td>
<td>—</td>
<td>—</td>
<td>0.73</td>
<td>—</td>
<td>0.92</td>
<td>0.96</td>
<td>0.98</td>
</tr>
<tr>
<td>Normalized ERR g(—)</td>
<td>—</td>
<td>—</td>
<td>2.7</td>
<td>—</td>
<td>6.3</td>
<td>9.6</td>
<td>15.4</td>
</tr>
<tr>
<td>COSd (%)</td>
<td>2.7</td>
<td>3.8</td>
<td>18.4</td>
<td>11.4</td>
<td>6.2</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Toughness Gc (J m⁻²)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>77</td>
<td>9</td>
<td>20</td>
</tr>
<tr>
<td>CDfₑ (mm⁻¹)</td>
<td>210</td>
<td>265</td>
<td>1334</td>
<td>—</td>
<td>406</td>
<td>312</td>
<td>242</td>
</tr>
<tr>
<td>IFSS (MPa)</td>
<td>—</td>
<td>—</td>
<td>162</td>
<td>—</td>
<td>65</td>
<td>21</td>
<td>28</td>
</tr>
</tbody>
</table>

a For constant deposition time of 15 × 4 s (thickness according to deposition rate).
b Coating thickness ≈200 nm.
c Coating thickness ≈120 nm.
operation were followed by 10 s off-time. In addition, two multilayer coatings were produced, namely, SiO\textsubscript{x}/pp-HMDSO by combining a SiO\textsubscript{x} top layer (layer G, deposition time 15 × 4 s) with a pp-HMDSO interlayer (layer C, 3 × 4 s) and SiO\textsubscript{x}/a-Si : C : O : N : H by combining the same SiO\textsubscript{x} top layer with a a-Si : C : O : N : H (layer B, deposition time 3 × 4 s) and an a-C : N : H (layer A, deposition time 3 × 4 s) interlayer.

2.3. Oxygen transmission rate

The OTR was measured by a permeability tester (Ox-Tran 100, Mocon Inc.) according to DIN 53380 at 25 °C and 50% relative humidity with a measurement accuracy of approximately ±2%.

2.4. Temperature durability and autoclaving tests

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, separate samples were tested in an autoclave (121 °C, steam, 2.1 bar) for 30 min and the OTR was measured before and after.

2.5. Dilatometry analysis

Expansion and shrinkage behaviour of uncoated PP and 180 nm thick SiO\textsubscript{x}/PP samples of 8 × 40 mm\textsuperscript{2}, cut along and perpendicular to machine direction, was explored using a dynamic mechanical analyzer (DMA Q800, TA Instruments) in the temperature range 25–135 °C with a heating rate of 5 K min\textsuperscript{-1} applying a constant load of 1 mN. The change in length of the sample was measured as a function of temperature. The coefficients of linear thermal expansion (CLTE) were deduced from the initial linear part between 30 and 45 °C.

2.6. Deposition rates and mass density

Deposition rates were determined on Si wafers, which were centred 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 371–995 nm. The wavelength dependence of the refractive index was approximated with a Cauchy model [10]. Reference thickness measurements were performed with a stylus profilometer (Tencor P10).

Mass densities of the coatings were calculated from the measured coating thickness and the mass was determined on 50 × 50 mm\textsuperscript{2} glass slides.

2.7. Internal stress

The internal stress \(\sigma_i\) was deduced from the radius of curvature \(R\) of the substrate/coating composite applying the equation derived by Inoue and Kobatake [12] as also in [13]:

\[
\sigma_i = \frac{E_h h_c^2}{6 Rh_c \left(1 + mn\right)} \times \left\{1 + n(4m - 1) + n^2 \left[m + (1 - m)^2 \right]\right\},
\]

(1)

where \(m = E_c/E_s\) and \(n = h_c/h_s\) (\(E_c\), \(E_s\) and \(h_c\), \(h_s\) are the coating and the substrate Young’s moduli and thicknesses, respectively). \(E_s\) of the PP foil was determined by a Zwick/Roell Z005 tensile tester to 611 MPa on rectangular samples of 18 × 10 mm\textsuperscript{2} and for \(E_c\) estimates reported in table 1 were applied. The thickness of the coatings \(h_c\) was 200 nm for all investigated compositions. \(R\) was determined from the maximum deflection \(d\) of 80 × 15 mm\textsuperscript{2} rectangular samples placed on supports with spacing \(L\) according to \(r = L^2/(8d)\).

The influence of gravity on sample curvature was found to be negligible, which was checked by measuring the deflection of the same sample twice, first with coating upside and second with coating downside.

2.8. Fragmentation tests

The fragmentation test method is a reliable technique to investigate the adhesive and cohesive properties of thin, brittle coatings on polymer substrates [13]. Tests were carried out using a Rheometric Scientific Minimat tensile tester \textit{in situ} under an optical microscope (Olympus BX 60) equipped with videoextensometry with strain accuracy better than 10\textsuperscript{-3}. Rectangular samples of dimensions 8 × 40 mm\textsuperscript{2} were incrementally strained and crack patterns were analysed in terms of crack density (CD) versus true strain. The thickness of all investigated coatings was 119 ± 6 nm. The critical strain at the propagation onset of the first crack in the coating (also termed crack onset strain, COS) was derived by linear regression from the CD versus strain data at the beginning of fragmentation. The cohesive properties of the coating such as fracture toughness can be calculated from the COS and from the elastic properties of the coating. The crack density at saturation (CD\textsubscript{ss}), defined as the inverse fragment length, when an increase in strain does not result in further cracks, was also determined. This value is related to the adhesive properties of the coating. Further details regarding this technique are given elsewhere [13, 14].

The toughness of the layers, \(G_{ss}\), was calculated assuming that it is equal to the energy release rate (ERR) at COS, \(G_{ss}\), using the approach detailed in [15, 16]:

\[
G_{ss} = \frac{\pi}{2} \tilde{E}_c h_c e^2 g(\alpha, \beta),
\]

(2)

where

\[
\tilde{E}_c = \frac{E_c}{(1 - \nu_c^2)}
\]

(3)

is the plane strain modulus of the coating (\(E_c\) and \(\nu_c\) are Young’s modulus and Poisson’s ratio of the coating) and \(g(\alpha, \beta)\) is a function of the Dundurs parameters \(\alpha\) and \(\beta\), which describe
the elastic mismatch of the layer/substrate system. In the case of plane strain problems

\[ \alpha = \frac{\bar{E}_c - \bar{E}_s}{\bar{E}_c + \bar{E}_s}, \]

(4)

where

\[ \bar{E}_c = E_c/(1 - \nu_s^2) \]

(5)
is the plane strain modulus of the substrate (\( \nu_s \) is Poisson’s ratio of the substrate). In this work we used \( \beta = \alpha/4 \). \( E_c \) was estimated as a first approximation from \( E_{SiO_2} \) and CLTE\(_{SiO_2}\) values for PECVD SiO\(_2\) (80 GPa [14] and \( 1 \times 10^{-6} \) K\(^{-1}\) [17]) and the CLTE\(_c\) of the coatings as follows [18]:

\[ E_c = E_{SiO_2} \frac{CLTE_{SiO_2}}{CLTE_{c}}, \]

(6)

where CLTE\(_c\) was linearly interpolated from the values for SiO\(_2\) and pp-HMDSO (\( 18 \times 10^{-6} \) K\(^{-1}\)) using the C/Si atomic ratio, derived from XPS analysis, as the variable. The same was done with Poisson’s ratio, assuming that it is equal to 0.15 for SiO\(_2\) and 0.3 for pp-HMDSO (changing these values will marginally affect the final results).

The interfacial shear strength (IFSS), which characterizes the adhesion between the inorganic coatings and the PP substrate, was derived using the perfectly plastic Kelly–Tyson model [19]:

\[ \text{IFSS} = 1.337 \mu \text{H}_c \sigma_{\text{max,CD}} \text{sat}, \]

(7)

where \( \sigma_{\text{max}} \) is the coating strength taken equal to \( E_c \times \cos \theta \).

2.9. FTIR spectroscopy

FTIR spectroscopy was performed on Si wafers with a Perkin-Elmer Spectrum BX II FTIR system in the range 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 in order to obtain a high signal-to-noise ratio.

2.10. XPS analysis

XPS was performed with a Kratos Axis Nova (Kratos Analytical, Manchester, UK). The source was monochromatic Al K\( \alpha \) irradiation, run at 225 W (15 kV, 15 mA). The analysed area was 700 × 300 \( \mu \)m\(^2\) in general and reduced to a diameter of 110 \( \mu \)m for the depth profiles. The photoelectrons were detected with a hemispherical analyzer, operated in the fixed-analyzer-transmission mode with a pass energy of 40 eV for the detailed spectra and 80 eV for the survey spectra (full width at half-maximum (fwhm) for Ag 3d\(_{5/2}\) = 0.75 eV and 1.1 eV, respectively). The take-off angle was 90°. Charging of the samples was over-compensated with slow electrons from the neutralizer.

The sputtering was performed using argon ions accelerated with 3.8 kV. The extractor current was 100 \( \mu \)A. For sputter cleaning of the reference samples, an area of 3 × 3 mm\(^2\) was sputtered for 30 s. For sputter depth profiling, the sputtered area was 2.5 × 2.5 mm\(^2\), resulting in a sputter rate of 15 nm min\(^{-1}\) for a Ta\(_2\)O\(_3\) reference sample.

3. Results and discussion

3.1. Dry heat and autoclaving tests

In figure 1 OTR results of the dry heat and autoclaving tests of the SiO\(_2\)/pp-HMDSO/PP multilayer coating are shown and compared with results of a SiO\(_2\)/PP single layer coating and an SiO\(_2\)/a-Si:O:C:N:H/a-C:N:H/PP multilayer coating. With respect to the high OTR of the PP substrate of approximately 3100 cm\(^{-2}\) m\(^{-2}\) d\(^{-1}\) atm\(^{-1}\), an excellent barrier performance was obtained with all tested single and multilayer coatings with barrier improvement factors (BIF = OTR\(_{uncoated}\)/OTR) exceeding 500. Up to 100 °C all coatings retained their good barrier performance. After 30 min of exposure to 120 °C, the SiO\(_2\) coating without interlayer showed initial deterioration of barrier properties. Exposure to 140 °C resulted in severe loss of the barrier performance of the single SiO\(_2\) coating and the formation of cracks in the coating, perpendicular to the machine direction of the polymer, could be evidenced by optical microscopy [8, 22].
Exposure of the SiO$_x$/pp-HMDSO/PP coating to 140 °C leads only to a minor increase in the OTR to 18 cm$^2$ m$^{-2}$ d$^{-1}$ atm$^{-1}$ as the pp-HMDSO interlayer prevents the SiO$_x$ coating from cracking. Alternatively, a-C:N:H and a-Si:C:O:N:H can be applied as interlayer materials as shown previously. A comparison of the results shows very similar behaviour for the two multilayer coatings with only slightly superior barrier performances of the SiO$_x$/pp-HMDSO/PP coating. Autoclaving at 121 °C in 2.1 bar of steam for 30 min affected the coatings less than the exposure to 140 °C in dry conditions. Therefore, the temperature and the resulting thermal expansion mismatch seems to be the crucial reason for barrier performance deterioration rather than humidity. For the investigated multilayer coatings comparable low OTR values were obtained after autoclaving and after exposure to 140 °C.

3.2. Dilatometry analysis

The dilatation behaviour of PP and SiO$_x$/PP films during heating was investigated by means of DMA. The relative elongation of the films is shown in figure 2 over the temperature range 25–135 °C. The CLTE of the PP film was found to be equal to 20.0 × 10$^{-5}$ K$^{-1}$ in good agreement with the literature data [1,23], and that of SiO$_x$/PP was found to be 13.5 × 10$^{-5}$ K$^{-1}$.

With increasing temperature, the influence of the coating on the dilatation behaviour becomes more significant. The SiO$_x$ coating prevents expansion of the PP film to a considerable extent, which is evidence for good adhesion and cohesion of the coating. A similar deviation is also observed for PET and SiO$_x$/PET films above the glass transition temperature of PET, where the shrinkage is reduced by the coating [13]. Comparing the elongation for the different orientations of the PP substrate with respect to its machine direction shows remarkable anisotropic behaviour. In the machine direction a high elongation of several per cent is observed, while at high temperatures a slight shrinkage is noticed perpendicular to the machine direction. Therefore, a high thermal tensile stress is induced in the machine direction. This is the reason for the observed cracks, formed in the brittle SiO$_x$ coating perpendicular to the machine direction after extended exposure to 140 °C, compromising barrier performance as shown in figure 1.

Polymeric interlayers may act as buffer layers for the thermal expansion and, therefore, prevent the SiO$_x$ diffusion barrier layer from cracking. For pp-HMDSO a CLTE of 18 × 10$^{-6}$ K$^{-1}$ is reported [24]. This value is between the CLTE of the PP substrate and that of SiO$_2$ at (0.5–1) × 10$^{-6}$ K$^{-1}$ [17,25]. Applying pp-HMDSO as interlayer material between a brittle SiO$_x$ diffusion barrier layer and the PP substrate has the advantage that only a single precursor needs to be employed. In order to change conditions for the interlayer and the barrier layer, in principle only oxygen needs to be added to the process gas mixture, while other process parameters may remain constant. Therefore, the influence of the O$_2$/HMDSO ratio on the mechanical and chemical properties of the resulting coatings is investigated in detail in the following.

3.3. Influence of the O$_2$/HMDSO ratio

In figure 3(a), the influence of the O$_2$/HMDSO ratio on the OTR and the deposition rate is shown for constant RF power, HMDSO flow rate, process pressure and deposition time of 100 W, 2 sccm, 10 Pa and 15 × 4 s, respectively. A critical O$_2$/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 the literature [10,26,27].

The deposition rate decreases strongly with increasing O$_2$/HMDSO ratio up to a ratio of 15. Further increase in the O$_2$/HMDSO results only in a minor decrease in the deposition rate. At conditions applied for the pp-HMDSO interlayer of the SiO$_x$/pp-HMDSO coating (10 sccm HMDSO) high deposition rates of 710 nm min$^{-1}$ are achieved.

The dependence of the internal stress and the mass density on the O$_2$/HMDSO ratio is reported in figure 3(b). The mass density increases from 1.3 to 2.1 g cm$^{-3}$ as the O$_2$/HMDSO ratio is increased from 0 to 30. Densities typically range between 1 and 2 g cm$^{-3}$ depending on the deposition conditions [26]. The density of SiO$_x$ obtained for O$_2$/HMDSO = 30 is close to that of fused silica (2.2 g cm$^{-3}$) and compares well with densities obtained at similar conditions [10,28].

The internal in-plane stress is of a compressive nature in all coatings (indicated by a negative algebraic sign). Internal stresses of the same range were determined for SiO$_x$ deposited by PVD methods on PET [13,29]. The internal stress rises as the O$_2$/HMDSO ratio is increased and follows a similar trend as the mass density and the OTR. This can be ascribed to the higher fragmentation of HMDSO molecules at high O$_2$/HMDSO ratios due to the high abundance of atomic oxygen.

3.4. Adhesive and cohesive properties

Adhesive and cohesive properties of single layer coatings deposited with varying O$_2$/HMDSO ratio between 0 and 30 were determined from the measured CD with applied tensile strain (figure 4). For SiO$_x$ coatings with best barrier properties,
HMDSO flow rate

stress

reasonable and would correspond to a compressive thermal

In spite of rather crude approximations, the obtained values are

on PP, which is comparable to values reported for SiO

α

analyses [32]) would clearly be useful. The Dundurs parameter

(using for instance indentation techniques or thermal stress

i.e. for O2/HMDSO = 30, a COS of 0.9% is measured

on PP, which is comparable to values reported for SiOx

O2/HMDSO ratio. In the inset of figure 4, the CD is shown as

a tremendous increase in the COS up to 18% for pp-HMDSO as

increased from 0 to 5, 15 and 30. It is known that the Si–H

stretching frequency shifts towards higher frequencies with

excellent adhesion of pp-HMDSO to the PP substrate. Properties

ties of the investigated coatings are summarized in table 1

for O2/HMDSO ratio vibrations of carbon containing groups, such as C–H in

the position of the absorption

The IFSS increases with increasing carbon content as

reported in table 1. The IFSS of the SiOx layer on PP is found

to be equal to 28 MPa, which is almost three times higher than

the shear stress at yield τy of the PP substrate equal to 11 MPa.

This value was derived from the measured tensile yield stress

of the polymer, σy = 19 MPa, using the von Mises criterion:

Figures 3. Influence of the O2/HMDSO ratio on (a) OTR and

deposition rate at constant RF power = 100 W, and deposition time

= 15 × 4 s and (b) internal in-plane stress and mass density.

HMDSO flow rate = 2 sccm (open symbols), HMDSO flow rate

= 10 sccm (solid symbols).

HMDSO/PP interface is capable of strain hardening, and

the pp-HMDSO coating is fully elastic up to strains as high

as its COS equal to 18%. A very high IFSS implies that the

The IFSS of the pp-HMDSO coating is as high as 162 MPa, as

compared with the alternative interlayer materials a-C : N : H

and a-Si: C : O : N : H.

The IFSS increases with increasing carbon content as

reported in table 1. The IFSS of the SiOx layer on PP is found

to be equal to 28 MPa, which is almost three times higher than

the shear stress at yield τy of the PP substrate equal to 11 MPa.

This value was derived from the measured tensile yield stress

of the polymer, σy = 19 MPa, using the von Mises criterion:

τy = σy/\sqrt{3}.

(8)

The IFSS of the pp-HMDSO coating is as high as 162 MPa, as

compared with the tensile strength of the PP substrate, close

to 125 MPa. This IFSS value is likely to be overestimated,

essentially due to the calculation of σmax which assumes that

the pp-HMDSO coating is fully elastic up to strains as high

as its COS equal to 18%. A very high IFSS implies that the

pp-HMDSO/PP interface is capable of strain hardening, and

this is in fact visible in figure 4, where tensile failure of the

pp-HMDSO coating still operates at strain levels beyond 150%.

3.5. FTIR spectroscopy

FTIR spectra of coatings deposited from O2–HMDSO mixtures with varying O2/HMDSO ratio between 0 and 60 are depicted in figure 5(a). 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 disappear for O2/HMDSO ≥ 30. Similar behaviour is observed for the absorption at around 2250 cm\(^{-1}\), which is characteristic for the Si–H stretching vibration. The position of the absorption maximum is shifted towards higher wavenumbers from 2145 to 2241, 2258 and 2274 cm\(^{-1}\) as the O2/HMDSO ratio is increased from 0 to 5, 15 and 30. It is known that the Si–H stretching frequency shifts towards higher frequencies with
increasing sum of electronegativity of the atoms or groups bonded to the silicon [33, 34]. The stretching frequencies of the silicon monohydrates H–SiC\textsubscript{3}, H–SiOC\textsubscript{2}, H–SiO\textsubscript{2}C and H–SiO\textsubscript{3} were calculated to 2135 cm\textsuperscript{-1}, 2185 cm\textsuperscript{-1}, 2234 cm\textsuperscript{-1} and 2283 cm\textsuperscript{-1} with an error of ±13 cm\textsuperscript{-1}, respectively [34]. Therefore, the observed frequency shift can be ascribed to a change in the chemical environment of the silicon in pp-HMDSO from mainly the former two monohydrates to a change in the chemical environment of the silicon in coatings in the literature [37]. The intensity of the Si–O–Si stretching vibration at around 1065 cm\textsuperscript{-1} is increased and the peak position is shifted to higher wavenumbers (from 1041 to 1068 cm\textsuperscript{-1}) as the O\textsubscript{2}/HMDSO ratio is increased from 0 to 30, indicating a densification of the Si–O–Si network. Of the characteristic bands for CO\textsubscript{2} at 2340 and 2360 cm\textsuperscript{-1} and a similar shift was observed for HMDSO derived SiO\textsubscript{2} with the highest O\textsubscript{2}/HMDSO ratio and the thermal oxide reference sample (see table 1). In the literature, the Si 2p peak of polydimethylsiloxane (PDMS) was found at 102.1 eV while in quartz it was at 103.4 eV [39]. In PDMS the silicon is bound to two carbon atoms and two oxygen atoms (SiO\textsubscript{2}C\textsubscript{2} configuration), while in quartz silicon is bound to four oxygen atoms (SiO\textsubscript{4} configuration). A comparison of the Si 2p peak positions with these values suggests that in pp-HMDSO the PDMS-like SiO\textsubscript{2}C\textsubscript{2} and the SiO\textsubscript{4}C\textsubscript{2} configurations are prevailing, while for O\textsubscript{2}/HMDSO ratios ≥15 almost all the silicon is found in the highly oxidized SiO\textsubscript{4} configuration. The FWHM was 2.1 eV for the a-Si: C: O: N: H and pp-HMDSO coatings, decreased to 1.9–1.7 eV with increasing oxygen content in the process gas mixture and dropped to 1.5 eV for the oxidized silicon wafer reference sample. This supports the hypothesis that for the a-Si: C: O: N: H and pp-HMDSO coatings a mixture of Si–O and Si–C bindings is present and with increasing O\textsubscript{2}/HMDSO ratio the amount of Si–C bindings is decreased.

3.6. XPS analysis

Further insight into the chemical composition was gained by XPS analysis of single layer coatings and by depth profiling of the applied multilayer coatings. Figure 6 shows the detailed spectra of Si 2p, C 1s, O 1s and N 1s of the as-deposited films. Comparing spectra C–G shows a binding energy shift of the Si 2p peak from 102.4 eV for pp-HMDSO up to 103.7 eV for the SiO\textsubscript{2} with the highest O\textsubscript{2}/HMDSO ratio and the thermal oxide reference sample (see table 1). In the literature, the Si 2p peak of polydimethylsiloxane (PDMS) was found at 102.1 eV while in quartz it was at 103.4 eV [39]. In PDMS the silicon is bound to two carbon atoms and two oxygen atoms (SiO\textsubscript{2}C\textsubscript{2} configuration), while in quartz silicon is bound to four oxygen atoms (SiO\textsubscript{4} configuration). A comparison of the Si 2p peak positions with these values suggests that in pp-HMDSO the PDMS-like SiO\textsubscript{2}C\textsubscript{2} and the SiO\textsubscript{4}C\textsubscript{2} configurations are prevailing, while for O\textsubscript{2}/HMDSO ratios ≥15 almost all the silicon is found in the highly oxidized SiO\textsubscript{4} configuration. The FWHM was 2.1 eV for the a-Si: C: O: N: H and pp-HMDSO coatings, decreased to 1.9–1.7 eV with increasing oxygen content in the process gas mixture and dropped to 1.5 eV for the oxidized silicon wafer reference sample. This supports the hypothesis that for the a-Si: C: O: N: H and pp-HMDSO coatings a mixture of Si–O and Si–C bindings is present and with increasing O\textsubscript{2}/HMDSO ratio the amount of Si–C bindings is decreased.

![Figure 5. FTIR spectra of (a) SiO\textsubscript{2} coatings with varying O\textsubscript{2}/HMDSO ratio from 0 to 60 at constant RF power = 100 W and HMDSO flow rate = 2 sccm and (b) (A) a-Si: C: O: N: H, (B) a-Si: C: O: N: H.](image-url)
The binding energy of oxygen was 532.8 ± 0.1 eV for the a-Si:C,O:H, the pp-HMDSO and the a-C:N:H coating and 533.2 ± 0.1 eV for the SiO$_2$ coatings. These are typical values for oxygen bound to organic carbon and oxygen bound to silicon [40, 41]. The carbon signal exhibited peaks of three contributions, aliphatic carbon and carbon bound to silicon at 285.0 eV, a peak at 286.7 ± 0.2 eV due to carbon bound to oxygen or nitrogen and a peak at 288.5 ± 0.4 eV due to carbon bound to nitrogen, carbonates, esters or carboxylic groups. For the a-C:N:H and the a-Si:C,O:H layer, N 1s was found at 399.4 eV and at 399.7 eV, respectively, a binding energy typical for organic nitrogen [20, 42].

The Si 2p peak position of a-Si:C,O:H (spectrum B in figure 6) is very close to that of pp-HMDSO as shown in table 1. This supports the similarity in the chemical structure to pp-HMDSO observed by FTIR spectroscopy, but additionally carbon and nitrogen containing functionalities may be present within this material.

The influence of the O$_2$/HMDSO ratio on the C/Si and O/Si atomic ratios of the resulting pp-HMDSO and SiO$_2$ films is shown in figure 7 and compared with the atomic ratios of thermal oxide grown on a Si wafer. The as-deposited samples showed higher C/Si and O/Si ratios than the sputter-cleaned films. The O/Si and C/Si ratios of the thermal oxide are reduced with sputter cleaning from 2.13 and 0.11 to 2.01 and 0.00, respectively. The stoichiometric composition of SiO$_2$ after sputter-cleaning indicates that the sputtering procedure is adequate to remove organic surface contamination and that no selective sputtering takes place. For the PECVD deposited films the reduction in the C/Si and the O/Si atomic ratio by sputtering is more pronounced compared with the thermal oxide. This may be explained by post-deposition reactions of free radicals with hydrocarbons and residual water in the vacuum chamber of the PECVD process or the adsorption of oxygen and organic material from ambient conditions. For as-deposited pp-HMDSO a C/Si ratio of 2.2 and an O/Si ratio of 0.8 were determined. Similar ratios are reported in the literature [43]. The precursor HMDSO exhibits theoretically a C/Si ratio of 3 and an O/Si ratio of 0.5. The lower C/Si ratio compared with the monomer is related to the formation of a cross-linked hydrocarbon network by methyl group abstraction and the higher O/Si ratio to reactions of long-lived radicals in the plasma polymer with atmospheric or residual oxygen and water in the plasma chamber [43–45].

The addition of oxygen results even for a low O$_2$/HMDSO ratio of 5 in a significant decrease in the C/Si ratio and in an increase in the O/Si ratio. This effect is more pronounced for higher O$_2$/HMDSO ratios: for O$_2$/HMDSO = 30 films with almost no carbon and an O/Si ratio of 1.9 were obtained. The observed trend is consistent with the shift of the Si 2p peak position to higher binding energies with increasing O$_2$/HMDSO ratio and with results from FTIR spectroscopy, indicating an increase in the Si-O absorption in Si–O–Si at the expense of carbon containing species (C–H, Si(CH$_3$)$_3$).

XPS depth profiles of the SiO$_2$/pp-HMDSO/PP and the SiO$_2$/a-Si:C,O:H/a-C:N:H/PP multilayer coatings are shown in figures 8(a) and (b) and compared with a SiO$_2$/PP coating in figure 8(c). The top SiO$_2$ layer of the SiO$_2$/pp-HMDSO/PP multilayer coating was found to be approximately 60 nm in thickness as determined by ellipsometry of single layer films applying the same deposition parameters on Si wafers. In the bulk of the SiO$_2$ top layer,
properties from the organic pp-HMDSO layer to the inorganic gradual interphase provides a smooth transition of material and ascribed to rival etching/redeposition processes [5]. This deposited on a carbon-rich layer is reported in the literature constant atomic concentrations close to those of the sputter-cleaned pp-HMDSO reference sample. Higher sputter rates by a factor of 1.5 are reported for pp-HMDSO compared with SiO₂ in the literature [5]. This agrees well with the respective sputter times of the SiO₂ and the pp-HMDSO layer and the measured thickness of approximately 130 nm of the pp-HMDSO layer by means of ellipsometry and profilometry on a reference sample produced under the same conditions. At the pp-HMDSO/PP substrate transition a gradual change in composition is observed as well. The thickness of this interphase is related to the substrate roughness [28]. In this case the interphase is rather thin affirming that the surface of the PP foil is smooth ($S_z < 2$ nm). In figure 8(c) the XPS depth profile of SiOₓ/pp (layer G) deposited applying the same deposition time as in the SiOₓ/pp-HMDSO/PP coating is shown. Similar atomic concentrations are obtained as in the top layers of the multilayer coatings. Between the SiO₂ coating and the PP substrate a sharp transition in atomic composition is observed with a thin interphase comparable to the pp-HMDSO/PP substrate transition in SiOₓ/pp-HMDSO/PP.

For the depth profile of the SiOₓ/a-Si : C : O : N : H/a-C : N : H/PP multilayer coating, the original thickness of the SiOₓ barrier layer (layer G) of approximately 180 nm was applied. The a-C : N : H was kept as thin as possible due to the low deposition rate of a-C : N : H and its brownish appearance, which becomes noticeable for thick layers. As a consequence of the rival etching/redeposition processes, it is impossible to distinguish the thin a-C : N : H and a-Si : C : O : N : H layers of approximately 19 and 45 nm as would be expected for the applied deposition time of $3 \times 4$ s, respectively. Moreover, a gradual transition with steadily decreasing silicon, increasing carbon content and a maximum in nitrogen content of 7% is observed.

4. Conclusions

To improve temperature durability during autoclaving, a pp-HMDSO interlayer proved to be efficient in preventing the SiO₂ diffusion barrier layer from cracking as alternative to other interlayer materials. After exposure to 140°C only a minor loss of barrier performance from 5 to 18 cm³ m⁻² d⁻¹ atm⁻¹ is observed, while for the corresponding SiO₂ coating without interlayer this results in almost complete loss of barrier performance to 1040 cm³ m⁻² d⁻¹ atm⁻¹ due to the formation of cracks. These cracks are formed perpendicular to the machine direction of the PP substrate, for which the highest relative elongation of up to 7% at 130°C is observed by means of dilatometry analysis. The thermal expansion is significantly reduced by deposition of a SiO₂ coating, which is evidence for good adhesive and cohesive properties of the coating.

Plasma polymerized HMDSO is advantageous as interlayer over a-C : N : H and a-Si : C : O : N : H due to its much higher deposition rate of 710 nm min⁻¹. Furthermore, the SiOₓ/pp-HMDSO coating can be deposited with HMDSO as the only precursor at constant RF power by simply adding oxygen in a one-stage process. Reducing the O₂/HMDSO ratio changes the coating properties 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. For O$_2$/HMDSO = 30 an increase in the O$_2$/HMDSO ratio does not succeed in providing further improvement of barrier performance. Under these conditions the coating is virtually carbon free with an atomic composition of SiO$_1$. A high density of 2.1 g cm$^{-3}$ and a high compressive stress of ~487 MPa is determined under these conditions accompanying a low COS of only 0.9%.

Pure HMDSO feed to the discharge results in polymer-like coatings with a high carbon content showing an atomic composition of SiO$_2$-$\gamma$C$_{1.7}$. FTIR spectra revealed pronounced absorptions of CH$_x$, Si(CH$_3$)$_x$, and Si–H species, while the Si–O–Si peak intensity is drastically reduced and the peak position shifted towards lower wavenumbers, indicating low Si–O network density as a result of low monomer fragmentation. In pp-HMDSO a low internal stress is measured, accompanied by a low mass density of 1.2 g cm$^{-3}$. Fragmentation tests on pp-HMDSO coatings indicated a high COS of 18% and a high CD$_{sat}$ of 1300 mm$^2$. Estimates of the fracture toughness and IFSS are found to be close to 80 J m$^{-2}$ and 160 MPa, i.e. four and six times higher than the respective values for the SiO$_2$ coating. Therefore, the obtained pp-HMDSO coatings show excellent cohesive and adhesive properties. Unfortunately, these properties of pp-HMDSO are achieved at the expense of barrier performance. The XPS depth profile of the SiO$_2$/pp-HMDSO coating shows a broad gradual transition in chemical composition between pp-HMDSO and SiO$_2$ because of rival etching/redeposition processes and a not so broad transition between the PP substrate and pp-HMDSO due to the smooth substrate surface. This provides a gradual transition of material properties and good adhesion.

Therefore, pp-HMDSO and SiO$_2$, in a multilayer coating combine advantageous properties of both materials and present a promising approach for packaging applications, where coatings are subjected to thermal cycling.

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