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Plasma Deposition of Silicon-containing Layers on Polymer Substrates

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Abstract: Plasma-polymerized coatings have been deposited on polymer substrates using mixtures of silicon-containing monomers with O_2 and/or CF_4. With ternary gas mixtures, novel silicon oxyfluoride coatings were obtained. By oxygen plasma post-treatment, improvements in barrier properties of polymer substrates to gases were observed.

INTRODUCTION

Thin films deposited from plasma polymerization exhibit very interesting and sometimes unique properties (Ref. 1). On metal substrates, the preferred applications range from protective coatings to biocompatibility. On polymer substrates, the most interesting issues were barrier, biocompatibility, wear and friction, though other applications have been pursued, like membrane permselectivity, electrical insulation, moisture sensors and UV protection (Ref. 2 and references therein).

For improving barrier properties of polymer films against small molecules like oxygen, water and carbon dioxide, deposition of thin inorganic coatings was found advantageous mainly in food packaging applications (Ref. 3). While aluminium deposition is the preferred solution on industrial scale, the deposition of silica-like coatings was found interesting when transparent layers are preferred. Provided that the deposited coating is dense, free of defects and resistant to mechanical load (necessary for surviving in further processing, like lamination of a sealable film), an improvement of barrier properties comparable to that of obtained by aluminium metallization can be achieved (Refs. 3,4). However, the economics of the process is not yet well assessed because it is necessary to start from costly SiO, instead of SiO_2, which needs a very high evaporation temperature. Furthermore, whereas SiO, when evaporated in the presence of oxygen, gives rise to a dense and glassy SiO_x ($x = 1.5$-1.7) coating, SiO_2 forms a nanoporous layer permeable to small gas molecules (Ref. 4).

An alternative solution is the plasma deposition of siloxane monomers like hexamethyldisiloxane (HMDSO) (Ref. 5) and tetramethyldisiloxane (TMDSO) (Ref. 6). It was

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found that, in order to obtain a barrier improvement, some oxygen must be present in the plasma discharge atmosphere. In this way, the nature of polysiloxane deposited by plasma can be shifted from organic (silicone-like) to inorganic (silica-like) character by controlling the plasma parameters (Ref. 7). This work concerns the plasma deposition from siloxane monomers on polyolefin substrates, using some original experimental procedures like the presence of fluorinated monomers in the discharge gas feed, or post-deposition plasma treatment of polysiloxane coating.

RESULTS AND DISCUSSION

Plasma polymerization

A parallel-plate plasma reactor was used for deposition experiments. As substrates, several polymer plates or films have been used, made of high-density polyethylene, HDPE (1mm thick), linear low-density polyethylene, LLDPE (0.02 mm thick), biaxially oriented poly(ethylene terephthalate), PET (0.012 mm thick) and polyamide 6, PA-6 (0.012 mm thick). Hexamethyldisiloxane (HMDSO) and tetramethyldisiloxane (TMDSO), used as polymerizable monomers, were introduced into a glass vessel connected to the plasma reactor through a glass valve and a glass-metal joint. The temperature of the vessel was maintained at 30 °C. They were used alone or in the presence of other gases, like oxygen, CF_4 or their mixtures.

The deposition rate was monitored by a quartz crystal microbalance (Intellemetrics).

Characterization

Chemical composition of deposited layers was determined by X-ray photoelectron spectroscopy (XPS), using a PHI model 5500 XPS spectrometer. Layer thickness was measured by depth profiling carried out with combined XPS and ion bombardment. A sputter rate of 1.5 nm/min was adopted, as calibrated with a Ta_2O_5/Ta standard specimen.

Wettability was determined by contact angle measurements, using the sessile drop method and a Ramé-Hart goniometer. Each contact angle value is the average of at least five different measurements on the same sample sheet.

Permeability to oxygen was measured by a Lissy GPM-200 gas permeability fractometer. This instrument measures isostatic permeability, i.e., without substantial pressure differences on the two sides of the sample.

More details on experimental procedures can be found elsewhere (Ref.8).

Results

In order to determine the effect of experimental conditions and to optimize the application performance of deposited films, the following parameters were taken into account:

- nature of monomers or monomer mixtures, and their composition;
- plasma polymerization parameters, i.e., power, gas flow rate, time;
- nature of the substrate.

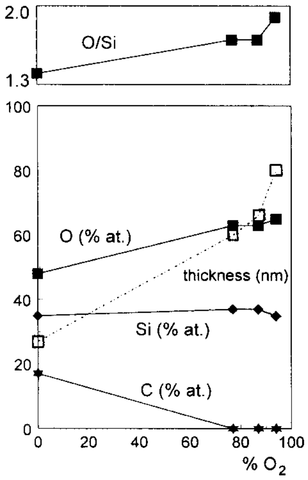

Fig. 1 Surface composition and thickness of plasma-deposited coatings from HMDSO/O_2 mixtures vs. O_2 amount.

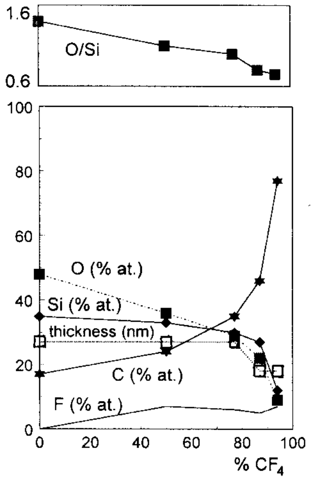

Fig. 2 Surface composition and thickness of plasma-deposited coatings from HMDSO/ CF_4 mixtures vs. CF_4 amount.

The results are presented in Figs. 1-9. Figure 1 shows the effect of the presence of increasing amounts of O_2 in the HMDSO plasma. The deposition rate, as suggested by the increased thickness of the coating, increases, while the chemical character of the surface is converted from partially organic to inorganic, as suggested by the complete elimination of carbon. The O/Si atomic ratio slightly increases with the increase in oxygen amount in the gas feed, reaching at the highest O_2 concentration a value near that expected for SiO_2, viz. 2. Such results are in agreement with previous literature (Refs. 9,10) and suggest a better efficiency of oxygen-rich mixtures in abstracting the organic portion of siloxane. Figure 2 reports the effect of an increasing amount of CF_4 in the HMDSO plasma. In this case, where CF_x radicals are formed in the plasma (Refs. 11,12), a coating containing a high amount of carbon is deposited. The carbon content increases with the CF_4 concentration in the gas feed. The coating thickness is always low and tends to decrease, due to the high probability of formation of volatile compounds. Some fluorine is introduced in the coating, thanks to the reaction of CF_x species with the polysiloxane chains. The O/Si ratio is always low, assuming a value around unity and showing some fair tendency to decrease.

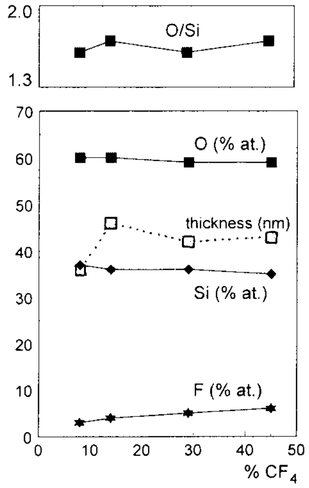

Fig. 3 Surface composition and thickness of plasma-deposited coatings from HMDSO/ O_2/CF_4 mixtures vs. CF_4 amount (HMDSO/ O_2 = 1/5).

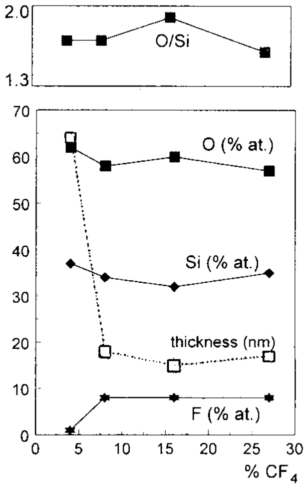

Fig. 4 Surface composition and thickness of plasma-deposited coatings from HMDSO/ O_2/CF_4 mixtures vs. CF_4 amount (HMDSO/ O_2 = 1/12.5).

In Figs. 3 and 4, the effects on coating properties of the presence of O_2/CF_4 gas mixtures at two different oxygen concentration levels are presented. Gas feed compositions were chosen in order to maintain always a relatively high oxygen concentration. In these conditions, in addition to abstracting the organic moiety from the coating as described above, also the formation of atomic fluorine in the discharge is favoured, as described in the literature (Refs. 11,12). In both cases, a silicon oxyfluoride coating not containing carbon residues is clearly formed, having O/Si atomic ratios around 1.7. F/Si ratios behave differently changing the oxygen concentration: at the lower level, F/Si shows a fair tendency to increase (from 0.08 to 0.17) with increasing CF_4, while at the higher level the ratio assumes a fairly constant value around 0.24, apart from an exception when the the O_2/CF_4 is very high (25). In the latter case, a F/Si of 0.03 was measured. Because in the same conditions, a rather high thickness of the deposited coating was observed relative to others, it is likely that in such conditions lower amounts of atomic fluorine are formed in the plasma. In the other cases, the low amounts of fluorine in the coating (relative to oxygen) is related both to the tendency of forming volatile compounds and the difficulty to accommodate fluorine atoms in the silica-like coating structure.

As expected, the thickness of coatings derived from ternary mixtures is always lower than that from binary HMDSO/O_2 mixtures because the presence of CF_4 leads to a higher tendency to etching and forming volatile compounds.

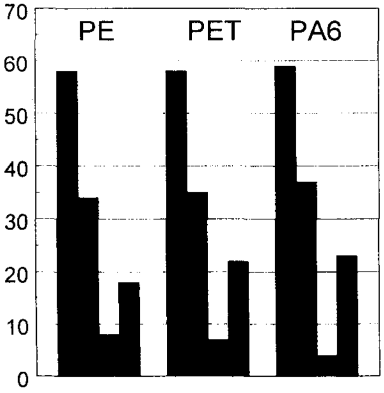

Fig. 5 Surface composition (% at.) and thickness (nm) of plasma-deposited coatings from HMDSO/O_2 /CF_4 mixtures on different substrates. Bars represent from left to right O, Si, F and thickness.

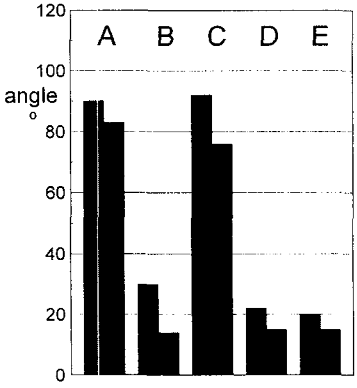

Fig. 6 Water advancing (left bars) and receding (right bars) contact angles for coatings deposited from plasma having following compositions (% of HDMSO, CF_4 and O_2, resp.): A 0,0,0; B 13, 87,0; C 50. 0, 50; D 14, 72, 14; E 7, 84, 7.

Figure 5 shows that, at least in the adopted experimental conditions (HMDSO/O_2/CF_4 4/50/4), the nature of the polymeric substrate has minor effect on the coating composition and thickness. Some preliminary contact angle measurements are reported in Fig. 6. Coatings obtained from HMDSO/CF_4 mixtures show low wettability, with contact angles similar to those of plain siloxane coatings (Ref. 13), while coatings from binary and ternary gas feed mixtures containing oxygen are all rather wettable.

Effects of discharge power on the deposition rate and surface composition of coatings are reported in Figs. 7 and 8, respectively. In these cases, the substrate polymer was HDPE. Figure 7 shows that the deposition rate depends directly on power discharge. Furthermore, it is also deeply affected by the nature of the polymerizable monomer. In fact, the deposition rate of HMDSO is always lower than that of TMDSO, the former being deposited only with a power

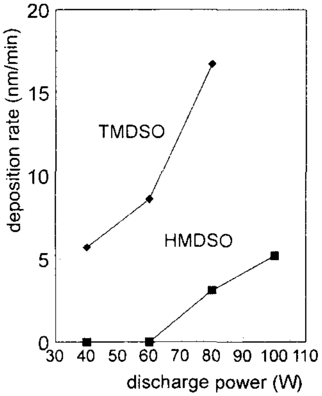

Fig. 7 Deposition rate of coatings from TMDSO and HMDSO on HDPE vs. discharge power.

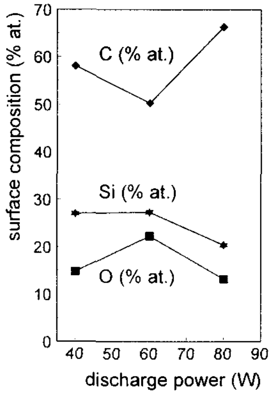

Fig. 8 Surface composition of coatings from TMDSO and HMDSO on HDPE vs. discharge power.

higher than 60 W. On the other hand, TMDSO produces, at high power (100 W), white flakes of some millimeters in diameter (Ref. 8). It is likely that such difference in reactivity depends on the fact that only in the TMDSO molecule hydrogen atoms are directly bonded to silicon atoms. Hydrogen atoms are mobile and thus easily abstracted from the disiloxane molecule, forming a reactive diradical (Ref. 14).

Surface composition of coatings obtained from TMDSO plasma polymerization at different discharge power values are reported in Fig. 8. At 40 W power, the experimental composition is very close to the theoretical (O 14.3% at., C 57.1% at., Si 28.6% at.). This result means that, in the adopted conditions, the TMDSO molecule does not undergo strong fragmentation (apart from hydrogen abstraction). At 60 W power, O/Si increases and C/Si decreases, in agreement with the expected increase in the inorganic character of the coating (Ref. 15). Finally, at 80 W, the opposite effect is observed, with an unexpected high carbon concentration. This result is interpreted considering that at high power (and, consequently, at high deposition rates), an inhomogeneous coating is deposited, with cracks through which the substrate remains exposed to the XPS analysis (Ref. 8).

The results of permeability measurements of HDPE coated by plasma polymerization of TMDSO are reported in Fig. 9. As expected, no effect on barrier properties against oxygen was observed, due to the organic character of the deposited layer. On the contrary, if the coating is subjected to post-treatment with O_2 plasma, capable of increasing its inorganic character, an

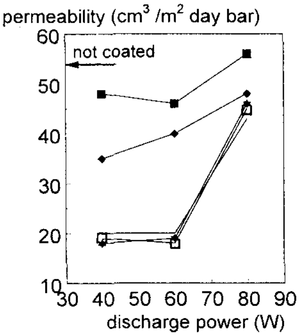

Fig. 9
Permeability to oxygen of TMDSO plasma-coated HDPE vs. discharge power after various post-treatment times with oxygen plasma.

(■ 0, ◆ 30, ∗ 60, □ 120, ◇ 600 min)

appreciable decrease in permeability was observed, at least for intermediate treatment power values (40-60 W), where the coating is sufficiently homogeneous (Ref. 8). Such a decrease is of the same order as that observed if oxygen was directly present in the gas feed (Ref. 16). The final result, however, is probably limited by the formation of cracks in the coating, due to the shrinkage of the molecular backbone (Ref. 8).

For coatings obtained with HMDSO/O_2/CF_4 mixtures, preliminary data show barrier properties similar to or better than those obtained with HMDSO/O_2. Also an improvement in wear resistance was observed, interesting for anti-scratch applications.

CONCLUSIONS

It was found that the inorganic/organic character of the deposited siloxane coatings has a great influence on the barrier properties. The occurrence of a SiO_2-like film free from defects and pinholes is essential for obtaining a good performance. This can be obtained both by adding oxygen in the plasma discharge or post-treating the deposited layer with oxygen plasma.

On the other hand, the use of ternary gas mixtures (siloxane/O_2/CF_4) allows to obtain deposited films with properties interesting both from the fundamental research and application points of view.

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