Barrier Coatings on Polymeric Foils for Food Packaging

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Abstract. Processing of polymeric materials by plasma technologies receives considerable attention in food packaging industry. The main objective is to improve barrier properties of polymeric foils by deposition of thin barrier layer. This study is focused on the deposition of a-C:H and SiOx films by means of plasma polymerization using either n-hexane or HMDSO as precursors. Barrier properties of produced films are presented alongside with their chemical structure and wettability.

Introduction

Nowadays, polymeric materials are widely used for food and beverage packaging. Typical examples of such materials are polypropylene (PP), polyethylene (PE), or polyethylene terephthalate (PET) [Silvestre et al., 2012, Kylian et al., 2013]. Though these polymers have numerous advantages over conventional packaging materials (glass, metals, paper) including high flexibility, strength, stiffness, mechanical resistance and optical transparency, their main drawback is relatively high oxygen, CO2 or water vapour transition rate. This may limit shelf-life of the packed foodstuff or have serious impact on its quality. Because of this different strategies were developed that enable to improve barrier properties of commonly used polymeric foils. One of the most often employed approaches is coating the polymeric foils by thin barrier films deposited by plasma based methods, which allows maintaining beneficial bulk characteristics of coated foils.

Different barrier coatings based on metal oxides (such as for instance aluminium, titanium or zinc oxides [Fahlteich et al., 2009]), hydrogenated carbon (a-C:H) [Abbas et al., 2005a, Vasquez-Borucki et al., 2000], silicon oxides [Coclite et al., 2010, Deilmann et al., 2009] and their nanocomposites [Abbas et al., 2005b] were successfully applied on packaging materials. Among them, the most examined and used layers for improving barrier properties are silicon oxide and a-C:H films. In case of silicon oxide deposits, they have, beside their good barrier properties, main advantage to be colourless or transparent that allows customers clear view of packed food or beverage. But use of SiOx layers is limited due to their relative high brittleness, which reduces their barrier performance [Gruniger et al., 2006, Deilmann et al., 2008, Hegemann et al., 1999]. Also a-C:H films have many advantageous properties. They are very hard, chemically inert and thermally stable. In addition, they are, in comparison with metal oxides and silicon oxides, more suitable for recycling process [Boutroy et al., 2006, Abbas et al., 2005a].

Basic techniques for deposition of barrier coatings are based on magnetron sputtering [Fahlteich et al., 2009] or low-pressure plasma-enhanced chemical vapour deposition (PECVD) [Ohring, 1992]. The later technique uses volatile precursors (e.g., hexamethyldisiloxane, tetramethoxysilane, divinyltetramethyldisiloxane, allyltrimethylsilane, acetylene or methane), which become excited and partially decomposed in the plasma. This leads to the production of molecules or radicals originally not presented in the initial gas or gas mixture, which in turn initiates complex cascade of plasma-chemical reactions that leads to the growth of a film on a substrate. The properties of deposited films depend strongly on the deposition conditions (e.g., used monomer, working gas, pressure, power etc.) and may be varied in a broad range.

![Figure 1](Image)

Figure 1. Chemical structures of (a) n-hexane and (b) hexamethyldisiloxane.
In this study, we present the first results related to deposition of a-C:H and SiOx films on PET foils by means of PECVD method employing n-hexane (C6H14) and hexamethyldisiloxane (HMDSO) organic precursors respectively, whose chemical structures are depicted in Figure 1. The main aim of this study is to compare properties of these two kinds of materials. The main attention is devoted to their barrier properties as well as to their wettability.

Experimental details
Deposition setup
Thin films of a-C:H were prepared by low pressure radio frequency (RF) plasma polymerization using argon/n-hexane gas mixture with n-hexane concentration 10%. A schematic drawing of deposition system is presented in Figure 2a. The working pressure in the deposition chamber was 2 Pa and total gas flow 15 sccm. The substrates were positioned on the powered electrode, which was capacitively coupled, via a matching network, to a RF power supply operated at frequency 13.56 MHz. This position of substrate allowed to control energy of ions reaching the growing a-C:H film, which is given by DC negative self-bias on the powered electrode, by applied RF power. The DC negative self-bias value of – 400 V on the powered electrode was selected on the basis of the previous study performed at our department, since it leads to high density and low water vapor and oxygen permeation rates of the coatings [Polonskyi et al., 2013].

For deposition of SiOx films was used experimental set-up that is shown in Figure 2b. RF power at 80 W was applied to circular, water cooled electrode. The substrate with PET foil was placed on a substrate holder, which was at distance of 7 cm from the powered electrode. A working gas mixture HMDSO/O2 with ratios from 1:30 to 1:60 was used. The working pressure was kept at 4 Pa and flow of HMDSO was kept constant and equal to 0.25 sccm.

Similar arrangement to the one presented in Figure 2b, was employed also for plasma treatment of deposited coatings. In this study following treatment conditions were used: argon/oxygen mixture 1:5, pressure 5 Pa, total gas flow 3 sccm and applied RF power of 50 W. The samples were placed on a substrate holder, which was located 50 mm from the powered RF electrode.

Both types of gas barrier coatings were deposited on 23 μm thick PET foils (Hostaphan RD23, Mitsubishi Polyester Film GmbH).

Permeability measurement setup
An original set-up of own construction was used for the evaluation of barrier properties of a-C:H films deposited on PET foils. This system, which is schematically presented in Figure 3, is based on measuring the temporal pressure rise in an ultra-high-vacuum (V1) chamber evacuated before the measurements to the base pressure of 3x10^-6 Pa and separated from the surrounding environment (V2) by the tested polymeric foil.

Figure 2. (a) Schematic setup for deposition of a-C:H films and (b) Schematic setup for deposition of SiOx films.
Before each measurement the UHV chamber (V1) was pumped by turbo-molecular pump to the base pressure. At the same time, the volume above the foil (V2) was pumped by scroll pump (SP) to pressure of 1 Pa. After this pumping stage, which was in all cases 24 hours in order to reach reproducible results, the volume V2 was filled by testing gas (water vapor in our case) and the pumping of UHV part was stopped. The rising pressure in the UHV chamber was measured by an ionization gauge (IG). The slope of the pressure rise is proportional to permeability coefficient of a tested gas through a polymeric foil. More details regarding the set-up and measuring protocol may be found in the previous study [Polonskiy et al., 2013].

Characterization of samples

The chemical composition of the films deposited on Si wafers was analyzed by X-Ray Photoelectron Spectroscopy (XPS, Phoibos 150, Specs) using an Al Kα X-ray source (1486.6 eV, Specs). The thickness of films was determined on Si wafers coated together with PET foil by means of spectroscopic ellipsometry using a variable angle spectroscopic ellipsometer (Woolam M-2000DI) in the wavelength range of \( \lambda = 192–1690 \text{ nm} \) at an angle of incidence AOI = 55–75° in air and at room temperature. Finally, the wettability was measured by means of a sessile drop method using a goniometer.

Results and discussion

The first studied material was a-C:H. The chemical structure of deposited films was investigated using XPS. It was found that according to XPS a-C:H films are contaminated by oxygen (atomic concentration of O atoms was around 11 %). The presence of oxygen is most likely due to the contamination from open air during transport of the samples from the deposition chamber to XPS.

The transition rates of water vapor through the PET foils with different thickness of a-C:H coatings were measured. The results are presented in Figure 4a. The significant improvement of barrier properties of PET foil was observed after their coating with a-C:H film having the thickness of about 12 nm (two order of magnitude enhancement of barrier properties was observed). Below this value the thickness of deposited a-C:H film is most likely not sufficient for formation of a continuous layer covering entire surface of PET foil. In contrast, further increase of the thickness of a-C:H film resulted in gradual decrease of barrier performance of the coatings. This behavior may be most likely attributed to the formation of micro-cracks in the a-C:H coatings, which is connected with mismatch of mechanical properties of a-C:H film and PET foil.
Water vapor permeability measurements of non-coated PET foils and PET foils coated by (a) a-C:H films and (b) SiOx films.

In case of SiOx coatings, they are composed from oxygen, silicon and carbon, as revealed by XPS. The content of carbon in the surface layer was found to decrease with increasing fraction of oxygen in the working gas mixture (it decreased from 6% for mixture 1:30 to 2% for mixture 1:60). Because of this, mixture HMDSO/O2 1:60 was used for further experiments.

Regarding barrier properties of SiOx coatings, qualitatively similar situation to the one of a-C:H films was observed: as can be seen in Figure 4b, after reaching the highest barrier character towards water vapors for thickness of SiOx coating about 40 nm, the significant increase of water vapor permeation through the foils was observed at 70 nm thickness. Although these results are still preliminary and further experiments are necessary to indicate optimal thickness of SiOx films in terms of their barrier properties, observed behavior indicates formation of micro-cracks also in SiOx coatings. The higher thickness, at which decrease of barrier properties occurred in case of SiOx coatings in comparison with a-C:H films, may be ascribed to differences in modulus of these two kinds of coatings.

To conclude this part, it was found out that although there are differences in optimal thickness of a-C:H and SiOx coatings leading to their highest barrier properties, both materials, if deposited as thin films, are capable to significantly decrease permeability of water vapors through PET foils (at least by one order of magnitude). Therefore, the applicability of these materials for food packaging will be influenced by other characteristics. One of them is wettability of coatings, i.e., parameter that is important for their good printability.

In spite of very good barrier properties of a-C:H coatings, their wettability is due to their chemical composition very low (75°, see Figure 5a) in comparison with SiOx films, that are highly hydrophilic (e.g., for the working mixture HDMSO/O2: 1:60 the water contact angle of deposited coatings was 11°). Because of this, we have tested a possibility to increase wettability of a-C:H films by additional plasma treatment in Ar/O2 mixture. As can be seen in Figure 5b, plasma treatment causes significant decrease of water contact angle that is for treatment time 5 minutes lower than 10° and comparable with wettability of SiOx coatings. Observed increase of wettability after plasma treatment may be attributed to the surface oxidation of a-C:H films, which is supported by high resolution XPS spectra of C 1s peak that showed increased surface density of C=O functional groups (see Figure 6).
Conclusion

In this study we have investigated properties of a-C:H and SiO$_x$ thin films deposited by plasma enhanced chemical vapour deposition using Ar/n-hexane and HMDSO/O$_2$ gas mixtures on PET foils. It was demonstrated that both materials are capable to significantly improve barrier properties of PET foils used for food packaging. Moreover, it was clearly shown that barrier properties of both a-C:H and SiO$_x$ coatings depend strongly on their thickness and that there exists an optimal thickness that leads to highest barrier improvement factor of PET foils. This effect was ascribed to the formation of micro-cracks due to the mismatch of mechanical properties of PET foils and barrier layer. However, it has to be noted that further experiments are needed to confirm this hypothesis.

In addition, wettability of a-C:H and SiO$_x$ coatings was determined. Related to this, the SiO$_x$ films exhibited much lower water contact angle as compared to a-C:H coatings. However, it was demonstrated that wettability of a-C:H coatings may be dramatically increased by additional plasma treatment.

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References


