Investigations of Surface-Waves Plasma Deposited SiOx Barrier Layer on Plastic For Food Packaging

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Abstract: In this paper we reported that nano-scale SiOx layers deposited on polyethylene terephthalate (PET) foils by microwave surface-wave plasma-enhanced chemical vapor deposition for purpose of improvement of their barrier properties. Oxygen (O_2) and hexamethyldisiloxane (HMDSO) were employed as oxide gas and precursor, respectively, in this work for SiOx deposition. Analysis by fourier transform infrared spectroscope (FTIR) for chemical structure and atomic force microscopy (AFM) for morphology of SiOx layers demonstrated that both chemical compounds and surface feature of coatings have a remarkable effect on the coating barrier properties. A permeation parameter of oxygen transmission rate (OTR) of 1.35 cc/m^2.day.atm for SiOx coated 12.5 μm PET foils, i.e. decreasing ca. 100 times compared to control sample (130 cc/m^2.day.atm) was achieved. The dependency of process parameters, such as the ratio gas mixture, input power, working pressure, and coating thickness on oxygen permeation through PET foil were explored in the whole process.

Keywords: Silicon oxide, Oxygen permeability, microwave surface-waves, PET

1. Introduction

Plastic packaging materials, such as poltyethylete terephthalate (PET), do not offer a barrier property against permeation of gases and moisture through the polymer. The gas and moisture permeation certainly leads to a reduced shelf-life of packed food and beverages [1-4]. In general, the homo-polymers only provide barrier properties towards particular vapors or gasses, and the combination of different polymers is able to fulfill high barrier requirements in a large part. Due to increasing commodity prices and high production costs for this kind of multi-layer packaging material, the research of barrier coatings for homo-polymers gains a great interest [5]. The nano-sized amorphous SiOx coatings received considerable attention in packaging industry due to their excellent diffusion barrier performance. As is well known, the main advantages of these coatings compared to metallic films are optical transparency, recyclability, and suitability for microwave heating [6]. Common deposition techniques for SiOx films are based on physical vapor deposition (PVD) or plasma-enhanced chemical vapor deposition (PECVD). The PVD processes comprise evaporation or sputtering of a solid precursor (Si, SiO, or SiO_2). In contrast, PECVD processes use volatile organo-silicon precursors, which are excited and partially dissociated in the plasma at low temperatures, is especially suitable for preparing the coatings on thermally sensitive and variform plastic substrates [4-9]. Transparent materials such as silicon oxide (SiO_x) prepared by PECVD then have been widely used as gas and moisture barrier layer on plastic substrates for decade years [10-14]. In this paper, SiOx coating on plastic PET prepared by microwave surface-wave PECVD deposition is explored. For SiO_x deposition the hexamethyldisiloxane (HMDSO) and oxygen are used as precursor and oxide gas, respectively,

where the pulsed low pressure plasma is employed to excite the precursor and generate the reactive species.

We focus on processing parameters during SiOx coating deposition affecting the oxygen permeability through PET. We achieved a low oxygen transmission rate (OTR) barrier performance after optimizing the processing parameters in the pulsed microwave plasma. Afterwards, the chemical compounds of the coating was analyzed by Fourier Transform infrared spectroscopy (FTIR), whereas their surface structure was characterized by atomic force microscopy (AFM). We present the cause of low OTR on SiOx coated PET after plasma functionization its surface.

2. Experiments

The experimental setup is schematically shown in Fig.1. It is composed of a vacuum chamber and a surface waveguide. In case of treating PET foils, a carrier (inner diameter=115 mm) is used which is located on the center around the plasmaline antenna. The reactor chamber can be evacuated to a base pressure of ~5 Pa. Microwave power is applied to the system by means of a plasmaline antenna. This antenna consists of a copper tube with surrounding inner and outer quartz tubes. For surface treatment argon (Ar) (99.99% in purity) was used as a discharge gas, whereas for the SiOx coating deposition liquid HMDSO (98%) and oxygen (O_2) (99.999%) were used as precursor and oxide gas, respectively. The chamber was pumped by a rotary pump to ~5 Pa after 15 minutes. Microwave power source provides microwave energy surface wave at f=2.45GHz.

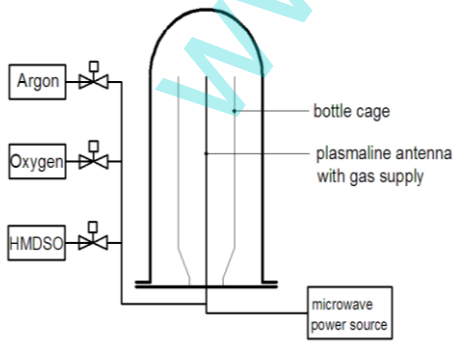


Fig.1 Schematic diagram of plasma experimental setup

PET bottles were used as substrate materials for the evaluation of the barrier properties of plasma deposited SiOx coating. The foil was 12.5 μm in thickness and characterized by OTR at 130 cc/m^2 .day. atm, where the oxygen permeation rate was determined by a MOCON OX-TRAN 2/21 using a test area of 50 cm^2 under T=23℃ and a relative humidity of 0%. All permeation rates of coated and uncoated foils were tested at these conditions.

The FTIR spectra were obtained by Thermo Scientific NICOLET 6700, USA, to measure the coating chemical composition and structure. The scanning range was from 400 cm^{-1} to 4000 cm^{-1} at the resolution of ± 4 cm^{-1}. A surface profilometer (Veeco Dektak 150, USA) was used to measure the coating thickness and calculate the growth rate. Surface topography of SiOx coatings was analyzed by atomic force microscope (SPM Probe CSPM-4000, China).

3. Results and discussion

For the deposition of barrier coatings, a pulsed plasma of O_2:HMDSO was ignited by the microwave surface wave plasma. Compared to continuous wave plasma, as known, pulsed plasmas offer many advantages concerning interdependencies of plasma parameters like gas flux, working pressure, input power and coating thickness for improvement of barrier properties.

3.1 Variation of gas flux

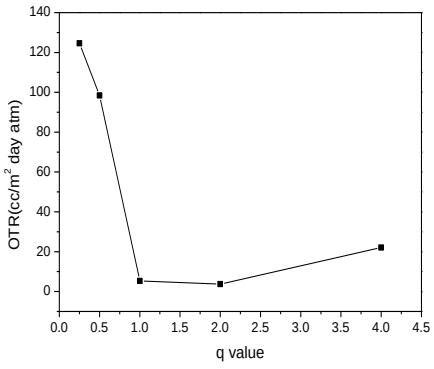


Fig. 2 OTR of about 60 nm thick SiOx coated PET (12.5 μm) for various ratio of gas fluxes at plasma condition of

p=20 Pa, P=1500 W, t_{on}=4 ms and t_{off}=40 ms

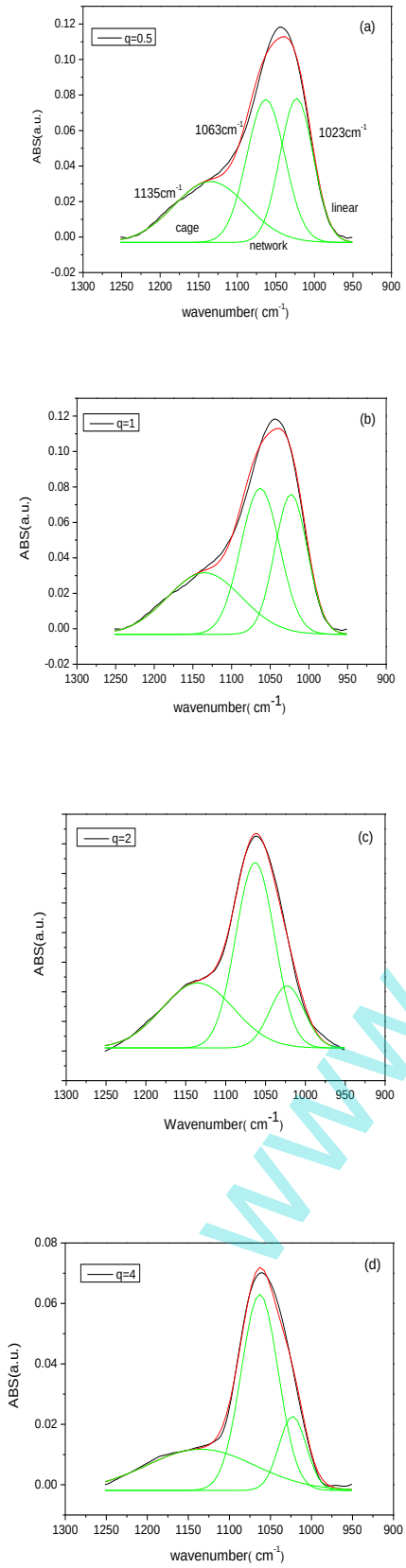


Fig.3 Deconvolution of Si-O-Si absorption peak by linear, network, and cage configurations at various oxygen to monomer ratio of q (a) q=0.5; (b)q=1; (c)q=2; (d)q=4

Table 1 The ratio of the cage, network and linear structure of the SiOx under the various value q (q=0.25-4) based on the deconvolution in Fig.3

q	Linear structure A1(1023 cm^{-1})	Network structure A2(1063 cm^{-1})	Cage structure A3(1135 cm^{-1})
0.25	0.48	0.35	0.17
0.5	0.33	0.37	0.30
1	0.31	0.38	0.31
2	0.15	0.51	0.34
4	0.14	0.53	0.33

Considering the role of O_2/HMDSO (q) ratio on the OTR value, we conducted the experiments to study the characteristics of SiOx coatings with various values of q. In Fig. 2 we notice that q value demonstrates a critical role on film properties. Fig. 2 shows the behavior of oxygen permeation rate through coated PET foils depending on the gas fluxes. For a lower q value, the barrier properties are only marginally improved. If q is higher, a strong reduction of OTR was obtained. However, when q is increased beyond 2, OTR demonstrates a little bit rising reversely which it might cause from brittleness and the degradation of coatings. According to Ref [3], the oxygen permeation rate was strongly influence by the hydrogen and carbon contents in the coating, and carbon was known taking a negative effect on the barrier properties. With the increase of O_2 proportion in mixture gases, the coating underwent a structure transformation from the organic ones with carbon and hydrogen contaminations to a highly pure inorganic, quartz-like coatings, the OTR values is then improved from the virgin PET 130 cc/m^2.day.atm to 3.69 cc/m^2.day.atm. Nevertheless the obtained low OTR values from microwave surface–wave PECVD SiOx coatings are reasonable for food barrier packaging applications.

As known, the different SiOx structures demonstrate different efficiencies in blocking the gas and moisture permeations [14,16]. Thus it shall be indispensable to analyse the deposited SiOx structure varying with the O_2 concentration and to explore this effect on barrier properties. As Fig. 2 shows, the main peaks of Si-O-Si asymmetric band were deconvoluted into three peaks centered at 1135, 1063 and 1023 cm^{-1}, respectively [14]. The peak centered at 1135 cm^{-1} is attributed to a larger angle Si-O-Si bonds in a cage structure with a bond angle of approximately 150°. The peak centered at 1063 cm^{-1} is attributed to the stretching of smaller angle Si-O-Si bonds in a network structure. The peak centered at 1023 cm^{-1} is attributed to the stretching of even smaller angle Si-O-Si bonds angle, such as might be a linear silicon suboxide. The ratios of the three peak areas were calculated and shown in Table 1. One can see that ratio of network and cage structure increases and the linear structure decreases along with O_2 concentration.

3.2 Variation of input power

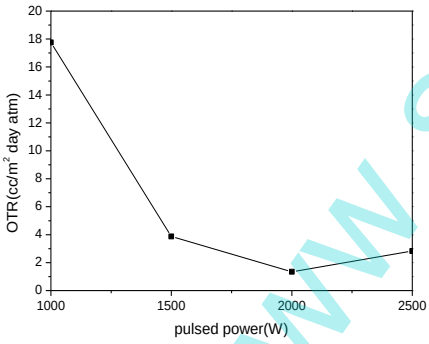
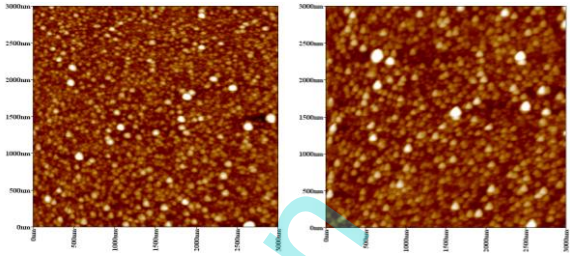


Fig.4 OTR of about 60nm thick SiOx coated PET (12.5um) for various input powers at plasma conditions of q=2, p=20 Pa, t_{on}=4 ms and t_{off}=40 ms.

Table 2 The ratio of the cage, network and linear structure in the SiOx coating for various input powers

input power(W)	Linear structure A1(1023 cm^{-1})	Network structure A2(1063 cm^{-1})	Cage structure A3(1135 cm^{-1})
1500	0.15	0.51	0.34
2000	0.18	0.65	0.17
2500	0.24	0.65	0.11



a b

Fig.5 AFM images of SiOx coatings on glass substrates with input power (a=1500 W, b=2000 W)

Besides the influence from the ratio of gas fluxes, the input power also determined the compounds and the barrier properties of the deposited barrier. Fig. 4 shows the behavior of oxygen permeation rate through coated PET foils depending on the pulsed power. With the increase of input power the OTR is dropped exponentially. In particular when the pulsed power P = 2000 W, OTR is lowest to 1.35 cc/m^2.day.atm. From Fig. 5 the AFM images, we find that the increase of pulsed power leads to a t dense coating formation rather than in the low input power. As known the increase of input power indicates an increase of plasma energy and density, which benefits to the pinhole-free film formation. Regardless of the pulsed power positive behavior, a good correlation of coating compounds with the barrier properties as described is also confirmed. The ratios of the three peak areas were calculated and shown in Table 2. One can see that ratio of network and linear structure were increased and the cage structure was decreased, when the input power was increased.

3.3 Variation of working pressure

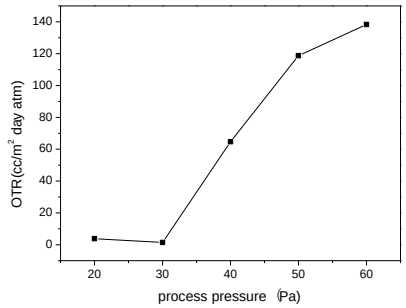


Fig.6 OTR of about 60 nm thick SiOx films coated PET (12.5um) for various working pressures at plasma conditions of q=2, P=1500 W, t_{on}=4 ms and t_{off}=40 ms.

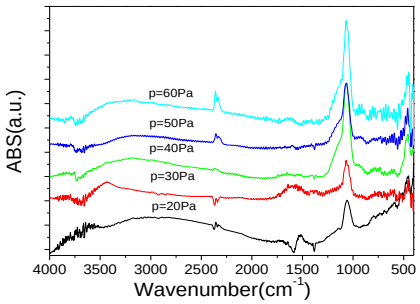


Fig.7 FTIR Spectrum of SiOx coatings at various working pressures (from 20 Pa to 60 Pa)

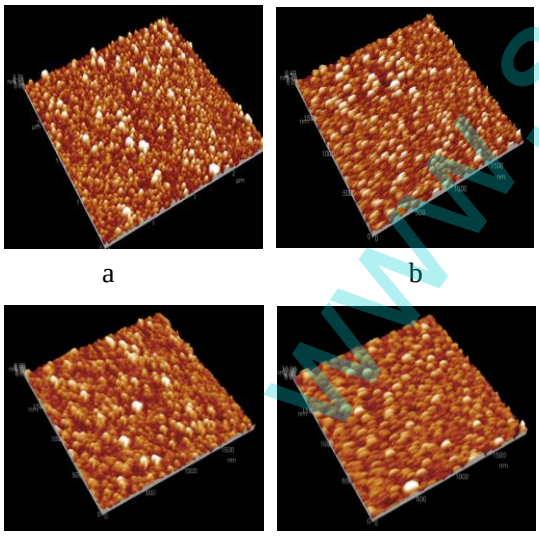


Fig.8 AFM images of SiOx coatings on glass substrates with varying processing pressures (a=30Pa, b=40Pa, c=50Pa, d=60Pa)

Fig. 6 shows the behavior of oxygen permeation through coated PET foils depending on the processing pressure from 20 Pa to 60 Pa. An increase of oxygen permeation rate is found for working pressure p>30Pa. When process pressure p≥50Pa the permeation rate is similar to uncoated PET. In particular, due to the etching the OTR of 60 Pa deposition SiOx coated PET was larger than that of the control one. From Fig.7, the FTIR analysis of the coatings deposited under different processing pressures shows not only concerning the peak intensity of Si-O-Si bond at ca. 1072cm^{-1} but also the location of the main peaks. For the 20 Pa deposited SiOx the Si-O-Si is located at 1059 cm^{-1}, whereas at the high pressure the Si-O-Si is moved to 1065 cm^{-1} and even at 1072 cm^{-1} when the pressure is 60 Pa. As well known, the intensity of the peak correlates to the thickness of coatings, where the intensity at 60 Pa is highest and has the thickest SiOx coating. So it implies that SiOx structure rather than the coating thickness dominates the oxygen permeation rate.

Besides, from Fig. 8 the AFM images, we find that in a low working pressure a significant densification coatings is formed because of an increase of electron temperature, which is revealed by a reduction of surface roughness. Examination of the morphology of the SiOx coatings deposited under various pressures clarifies the surface roughness is one of the main factors affecting the barrier property.

3.4 Influence of coating thickness

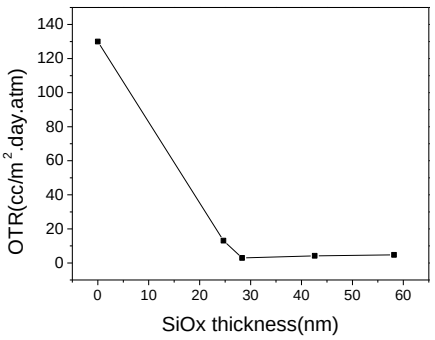


Fig.9 OTR of SiOx films coated PET for various films thicknesses at plasma conditions q=2, p=20 Pa, P=2000 W, t_{on}=4 ms and t_{off}=40 ms

Experiments also revealed that the coating thickness is one of the very important parameters dominating the barrier properties. Fig.7 shows the OTRs depending on coating thicknesses. A critical thickness, ca.d≈30nm is deduced from the curve, where the OTR is stabilized. A further increase of coating thickness does not enhance sustainably the barrier property. Hence, a micro-permeation through coating defects, like micro cracks, can be assumedly occurred.

4. Conclusions

The oxygen permeability of SiOx coating on plastic PET prepared by microwave surface wave plasma-enhanced chemical vapor deposition was investigated in the paper. The role of plasma parameters on the oxygen permeation rate was explored in detail. The significant improvement of barrier properties in the SiOx coating has been achieved as low as 1.35 cc/m^2.day.atm. The optimal parameter is was obtained based on the experimental data, where the q value was 2, the thickness of coatings was ~30nm, the input power was 2000 W, and the working pressure was ~30Pa. In this condition, the coatings were significantly dense. The smooth surface also plays a very important role on the improvement of barrier properties. Future research should be concentrated on the barrier mechanism. With the Surface topography of the optimization, oxygen permeation rate would be future decreased.

Acknowledgments

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