Investigation of Microwave Surface-Wave Plasma Deposited SiO$_x$ Coatings on Polymeric Substrates*

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Abstract In this paper, we reported nano-scale SiO$_x$ coatings deposited on polyethylene terephthalate (PET) webs by microwave surface-wave assisted plasma enhanced chemical vapor deposition for the purpose of improving their barrier properties. Oxygen (O$_2$) and hexamethyldisiloxane (HMDSO) were employed as oxidant gas and Si monomer during SiO$_x$ deposition, respectively. Analysis by Fourier transform infrared spectroscope (FTIR) for chemical structure and observation by atomic force microscopy (AFM) for surface morphology of SiO$_x$ coatings demonstrated that both chemical compounds and surface feature of coatings have a remarkable influence on the coating barrier properties. It is noted that the processing parameters play a critical role in the barrier properties of coatings. After optimization of the SiO$_x$ coatings deposition conditions, i.e. the discharge power of 1500 W, 2 : 1 of O$_2$: HMDSO ratio and working pressure of 20 Pa, a better barrier property was achieved in this work.

(Some figures may appear in colour only in the online journal)

1 Introduction

Plastic packaging materials, such as polyethylene (PE) and poltyethylete terephthalate (PET), do not own good barrier properties against gas and moisture permeations. The gas and moisture permeations certainly lead to a short shelf-life of packed food and beverages [1−4]. In general, the homo-polymers can only provide barrier properties towards particular vapors or gases, 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 these kinds of multi-layer packaging materials, the research of barrier coatings for homo-polymers gains a great interest [5]. In particular the nano-sized amorphous SiO$_x$ coatings receive considerable attention in packaging industry due to their excellent diffusion barrier performance and high transparent rate. The main advantages of these coatings compared to metallic films are optical transparency, recyclability, and suitability for microwave heating [6]. Common deposition techniques for SiO$_x$ films are based on physical vapor deposition (PVD) or plasma-enhanced chemical vapor deposition (PECVD). The PVD process is mainly performed by evaporation or sputtering of a solid source (SiO, or SiO$_2$). In contrast, PECVD process using volatile organo-silicon monomers, 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 layers on plastic substrates for decades [10−14].

Surface-wave assisted plasma (SWP) is one kind of high efficient plasma sources, producing super-dense plasmas sustained by fields of electromagnetic waves traveling along plasma–dielectric surface boundaries in the range of 10^{11} cm^{-3} to 10^{13} cm^{-3} by using 2.45 GHz microwaves at a low gas pressure. Compared with inductively coupled plasma (ICP), heliconwave plasma (HWP), and electron cyclotron resonance plasma (ECR), SWP source demonstrates a similar high density but with low electron temperature (a few electron volts).

In this paper, SiO$_x$ coatings on plastic PET prepared by microwave surface-wave assisted PECVD is explored. For SiO$_x$ deposition the hexamethyldisiloxane (HMDSO) and oxygen are used as monomer and oxidant gas, respectively, where the pulsed microwave surface wave sustained plasma is employed to excite the monomer and generate the reactive species. The (in)organic coatings consisting of silicon, oxygen as well as hydrocarbon compounds were deposited as barrier layers on the PET foils. The basic properties of the deposited siloxane coatings were characterized by the

Fourier transform infrared spectroscope (FTIR), the stylus profiler and the atomic force microscope (AFM).

2 Experiments

The experimental setup is schematically shown in Fig. 1. It composes of a vacuum chamber and a surface waveguide. In the case of deposition of SiO_x on PET foils, a carrier (inner diameter=115 mm) is used and located on the center around the plasmaline antenna. The reactor chamber can be evacuated to a base pressure of $\sim$5 Pa. Microwave power is applied to the system by means of a plasmaline antenna at f=2.45 GHz. This antenna consists of a copper with surrounding inner and outer quartz tubes. For surface treatment argon (Ar, 99.99% in purity) was used as a discharge gas, whereas HMDSO (99%) and oxygen (O_2, 99.999%) were used as monomer and oxidant for the SiO_x coatings deposition, respectively.

PET webs were used as substrates for the evaluation of the barrier properties of plasma deposited SiO_x coatings. The property of original foil with thickness of 12.5 μm was characterized by oxygen transmission rate (OTR) to be 130 cc/m²·day·atm, as given by MOCON OX-TRAN 2/21 on a test area of 50 cm² at T=23 °C and a relative humidity of 0%. All permeation rates of coated and uncoated foils were tested under these conditions.

The FTIR spectra were obtained by Thermo Scientific NICOLET 6700, USA, for the coating chemical composition and structure. The scanning range was from 400 cm^{-1} to 4000 cm^{-1} at the resolution of $\pm$ 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 SiO_x coatings was analyzed by atomic force microscope (SPM Probe CSPM-4000, China).
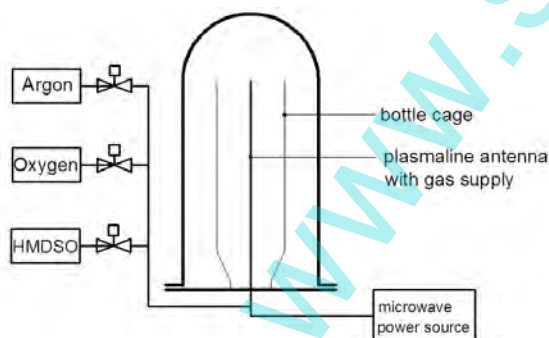

Fig.1 Schematic diagram of the plasma setup

3 Results and discussion

3.1 Chemical structure

Fig. 2 presents the results of FTIR spectrum of all SiO_x coatings prepared with various ratios of O_2 to HMDSO (denoted as q). The remarkable peak at 1034 cm^{-1}, corresponding to Si-O-Si asymmetric stretching vibration, is obvious in the spectrum, but it shifts to 1056 cm^{-1} along with the increase of proportion of O_2 in the mixture gases. The symmetric

bending vibration mode of Si-CH$_3$ bond at 1260 cm^{-1} indicates an incomplete oxidation reaction of O_2 with HMDSO and the existence of hydrocarbon radicals in the coatings. The peak decays consistently and then eventually vanishes from the spectra when q rises above 2. We then assume that the increase of O_2 proportion in the mixture gases alters the chemical structure from the organic ones with carbon, hydrogen contaminations to a highly pure inorganic, quartz-like coatings.
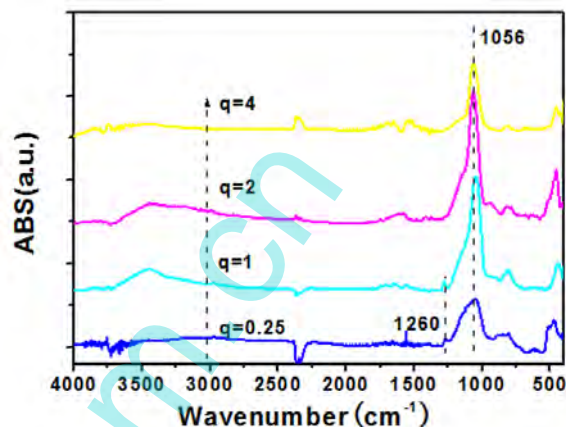

Fig.2 FTIR spectrum of as-deposited SiO_x coatings for various oxygen to monomer ratios

As known, the different SiO_2 structures exhibit different behaviors in blocking gas and moisture permeations [14-16]. Thus it shall be indispensable to analyze the deposited SiO_x structure by varying the O_2 concentration and to explore its relationship with barrier properties. In Fig. 3 the main peaks of Si-O-Si asymmetric band are then deconvoluted into three peaks centered at 1135 cm^{-1}, 1063 cm^{-1} 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; and the peak centered at 1023 cm^{-1} is the stretching of even smaller angle Si-O-Si bonds angle, it might be a linear silicon suboxide. The ratios of the three peak areas are then calculated and the results are shown in Table 1. One can see that the ratio of network to cage structures increases whereas the linear structure decreases along with O_2 concentration. Therefore in the processing of coating deposition, an appropriate q value should necessarily be selected for the purpose of controllable organic/inorganic content.

Table 1. The ratio of the cage, network and linear structure of the as-deposited SiO_x under various values of q (q = 0.25-4) based on the deconvolution data from Fig. 3

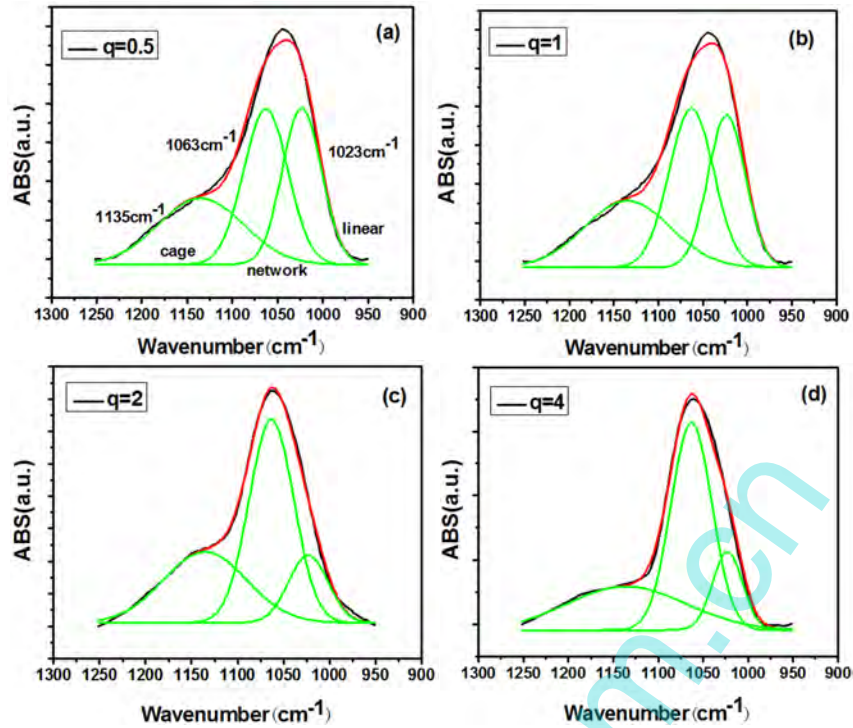| q	Linear structure A1(1023 cm^{-1})	Network structure A2(1063 cm^{-1})	Cage structure A3(1135 cm^{-1})
0.25	0.48	0.35	0.17
0.5	0.33	0.37	0.30
1	0.31	0.38	0.31
2	0.15	0.51	0.34
4	0.14	0.53	0.33

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

As known, the organic compound in SiO$_x$ coatings is beneficial to the flexibility of the coating, and the inorganic compounds are good for barrier properties. However, the inorganic network structure of Si-O-Si with fewer C, H elements will inevitably cause high internal stress and brittleness of the deposited coatings. So the appropriate q value for SiO$_x$ properties by PECVD is a balance between a sufficiently low organic content for flexibility and a high concentration of inorganic Si-O for good barrier performance.

3.2 Surface topography

From Fig. 4 we can conclude that the O$_2$ concentration in mixture gas not only influences the chemical composition, but also plays an essential role in surface morphology. The AFM images are obtained at different oxygen to monomer ratios. One can see that when the coating is prepared at q=1, the film surface is extremely smooth, the roughness is only about 2.03 nm as Table 2 shows, and the small aggregated nano-spherical particles with the size of ca. 46 nm were visual in the image; On the other hand, when the coating is formed at q=4, the abundant bigger spherical particles are grown, the surface roughness increases to ca. 4.34 nm and the average particle size is ca. 120 nm, i.e. the higher the oxygen concentration, the larger the grains. The bigger particle aggregation causes a bigger pore path for the gas and moisture to permeate, which might lead to poor barrier properties [17].

Table 2. The roughness of the SiO$_x$ coating under various values of q (q=1-4) derived from Fig. 4

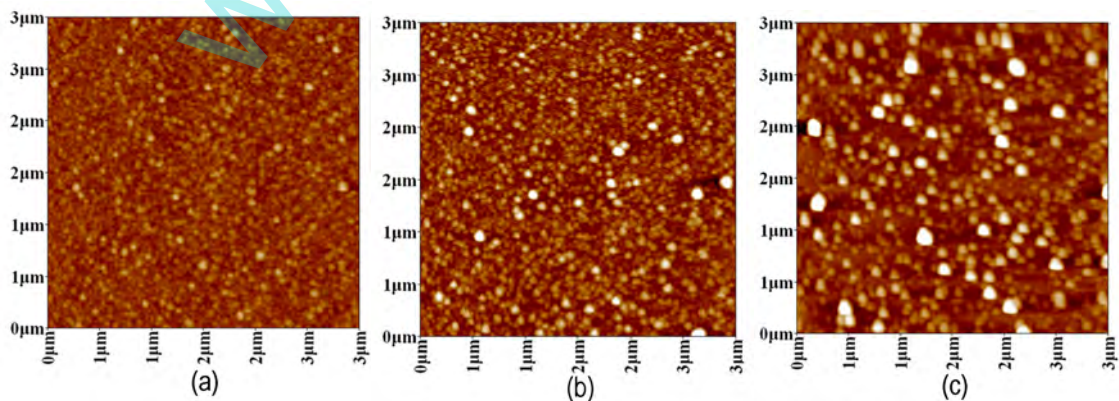| Sample	q=1	q=2	q=4
Ra (nm)	2.03	3.52	4.34

Fig.4 AFM images of SiO$_x$ coatings on Si substrates for various oxygen to monomer ratios. (a) q=1, (b) q=2, (c) q=4

3.3 Barrier properties

To study the effect of O_2/HMDSO ratio on OTR value, we conducted a series of trials to deposit SiO_x coatings with various values of q and measure the barrier properties accordingly. Fig. 5 confirms that the behavior of oxygen permeation rate through coated PET foils indeed depends on the ratio of mixture gases. The q value manifests a critical effect on film properties. For small q value, the barrier properties of coated PET are only marginally improved; On the other hand, when q is larger, a dramatic reduction of OTR is observed. As shown in Fig. 2 concerning the increase of O_2 proportion in mixture gases, the coatings underwent a structure transformation from the organic ones with carbon and hydrogen contaminations to highly pure inorganic, quartz-like films, which partially dominate the barrier property. Lastly we obtained a small OTR values of 3.69 cc/m^2·day·atm when the processing was optimized. According to Ref. [3] and the FTIR results in Fig. 2 we believe that the hydrogen and carbon contents in coatings decreased at a higher O_2 concentration because carbon manifests a negative effect on the barrier properties.
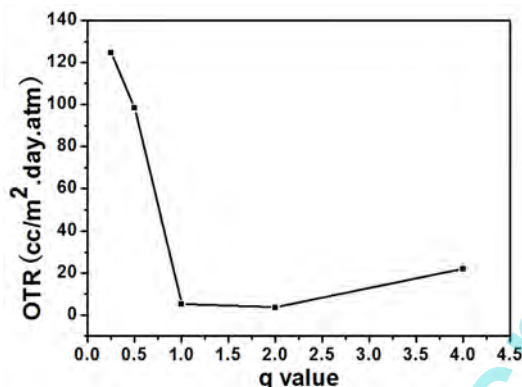

Fig.5 OTR of ca. 60 nm thick SiO_x coated PET (12.5 μm) versus oxygen to monomer ratio at deposition conditions of q=20 Pa, P=1500 W, t_{on}=4 ms and t_{off}=40 ms

However, Fig. 5 also illustrates that when q is excessively increased OTR has a little bit rising, which might be caused by the brittleness of coatings or the bigger particles in the coatings. The evidence can be seen in the AFM images shown in Fig. 4. At high O_2 concentration bigger particles aggregate on the substrate to form a loose film. Therefore, we predict that to achieve a low OTR values from microwave surface–wave assisted PECVD SiO_x coatings, not only the carbon or hydrocarbon should be removed from the compounds in an appropriate way, but the formative particle size should also be controlled.

4 Conclusion

The oxygen permeability of SiO_x coating on plastic PET webs prepared by microwave surface-wave assisted plasma enhanced chemical vapor deposition was investigated in this paper. A broad range of processing parameters which affect the morphology and composition of coatings has been explored in detail. A decreasing carbon content of coatings was accompanied by decreasing gas permeation rates, i.e. the gas permeation was more sensitive to the coating composition. The quartz-like coatings exhibits better barrier properties than the organosilicon ones. O_2 concentration in the mixture gases not only influences the chemical composition, but also plays an important role in surface morphology. We also found that the higher the oxygen concentration, the larger the grains. As a result, more gas and moisture would permeate through the path formed by the big grains.

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