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Research on the Characterization and the Properties of SiOx Coating on Plastic Film

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Abstract. The nano-thickness SiOx deposited on polyethylene terephthalate (PET) film and biaxially oriented polypropylene (BOPP) were fabricated by plasma enhanced chemical vapor deposition (PECVD) in a radio frequency (13.56 MHz) glow discharge. The nano-coatings were characterized by using Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and ultrasonic atomic force microscopy (UAFM). With AFM and UAFM, the topography and ultrasonic amplitude images were obtained. In particular, the UAFM images reveal the subsurface defects in the coating. The tensile property, contact angle and OTR of the PET present and absent of the SiOx coating were investigated experimentally respectively. The results can show that the SiOx coating can improved the barrier and the tensile strength.

Introduction

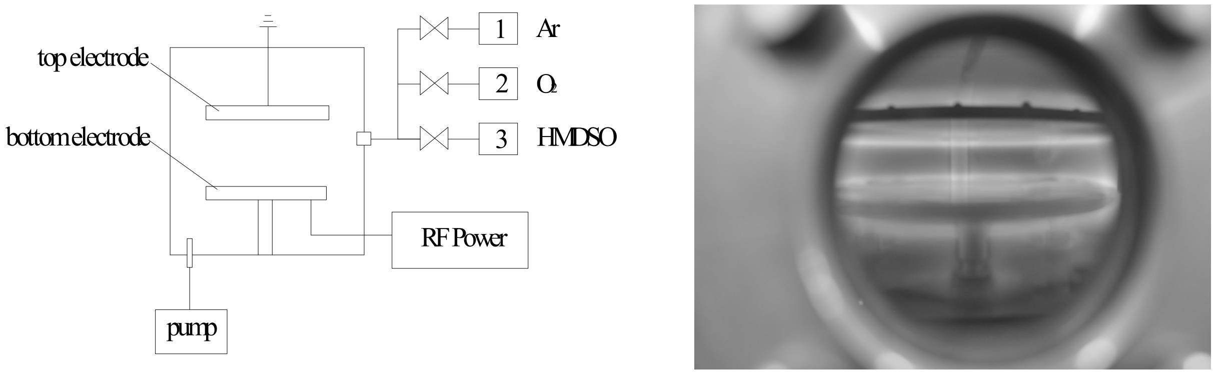
SiOx-coated films have got attention in industries of pharmacy, food and beverage packaging due to excellent gas-barrier properties keeping with a visible-light transparency. Plasma enhanced chemical vapor deposition (PECVD) has been often utilized to deposit SiOx films deposited on plastic substrates [1], which has resulted in improvement of gas-barrier properties. Sometimes there are defects in the subsurface of deposited films. The detection of defects is difficult, and hence, the gas barrier property has not been well improved [2]. In order to improve gas barrier characteristics, the detection method should be confirmed. An ultrasonic atomic force microscopy (UAFM) are thought to be an advantageous tool for the detection of defects in comparison with a conventional atomic force microscopy (AFM) [3] and scanning electron microscopy (SEM). A cross-sectional high-resolution transmission electron microscopy (TEM) can also serve to detect defects, however, sample making prior to the observation is not easy, which causes damages of the sample during the sample making[4].

In this work, we prepared the SiOx coating on the PET and BOPP film by PECVD and characterized the coating by using Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and ultrasonic atomic force microscopy (UAFM) and contact angle. And the properties including the oxygen transmission rate (OTR), contact angle and tensile strength were measured.

Experiment

SiOx deposition. The processes of SiOx coating were as followings: substrates polyethylene terephthalate (PET) and biaxially-oriented polypropylene (BOPP) films were cleaned ultrasonically in the ethanol, acetone and de-ionized water for 5 min in consequent before mounted on a sample holder. Figure 1 shows a schematic diagram (a) of experimental facilities and the discharge photography (b)of mixture gas. SiOx coatings were deposited in a radio frequency (RF, 13.56 MHz)-PECVD. During the process, the flow rates of oxygen and monomer hexamethyldisiloxane

(HMDSO) were set at 2:1 and 1:1, respectively. The RF power was kept at 200W, except the deposition time was varied from 5, 10, 15, 20 to 25 minutes.



(a) (b)

Fig.1 The schematic diagram of the plasma setup（a）and photography (b) of mixture gas discharge at 200W

Characterization of the SiOx coating. The chemical structure of SiOx-coatings were characterized by Fourier transform infrared spectroscopy (FTIR) (Shimadzu, FTIR-8400, Japan). The atomic force microscopy (AFM) and ultrasonic atomic force microscopy (AFM) images were measured by original AFM(CSPM 5000, Ben Yuan, China) and modified UAFM. In the UAFM system, a sample was vibrated by ultrasonic waveform at the ultrasonic frequencies. The tip-sample was contacted by setting the contact mode in AFM measurement. The displacement of cantilever vibration induced by ultrasonic waveform was monitored by photo-diode detector. Then the images obtained from original contact-mode AFM and ultrasonic amplitudes were simultaneously recorded at the same region of sample [5,6]. The images, depending on the elastic modulus and stiffness of scanned samples, were used to evaluate defect status in samples based on this resonance frequency shifting [7,8]. Using the UAFM method, the subsurface defect were shown in the ultrasonic amplitude images [6,9].

Measurement of properties of SiOx film. The property of SiOx coated films were carried out in oxygen permeation analyzer (Illinois Instruments, model 8001, USA) for OTR measurement, where the humidity is kept at 0 or 65% at a room temperature of 23 °C. The contact angle was measured by contact angle analyzer. The tensile strength was measured by the tensile strength tester.

Results and discuss

FTIR spectra

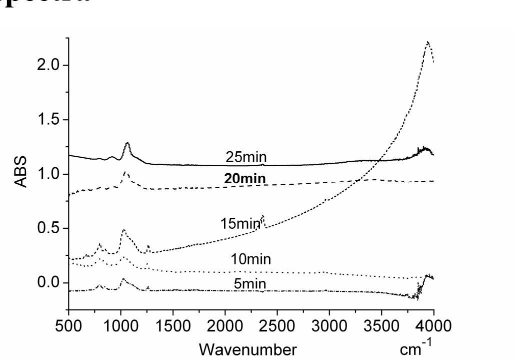


Fig.2 FTIR spectra of the SiOx coatings in different discharge times

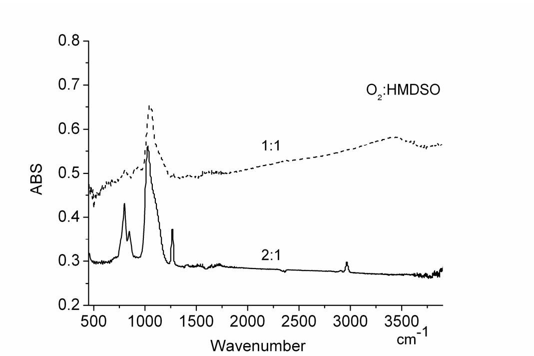


Fig.3 FTIR spectra of the SiOx coatings in different the ratio of O_2/HMDSO

The SiOx formation is confirmed from the FTIR spectra. It is seen that the film components did not change through the exposure time. The absorption peaks at 1062 cm^{-1} assumed to the stretching vibration of Si-O-Si bond [4] are obviously appeared in the spectra. In particular the absorption peaks in the range of 1030 to 1070 cm^{-1} for stretching vibrations of Si–O–Si are significantly increased along with the exposure time. For different flow rates, the peak and responding to the wavenumber have a difference a little.

UAFM and AFM images. It is known that AFM images depend on the low/high depth in morphology in contact mode. With the ultrasonic waveform applied to the samples the ultrasonic amplitude images based on the magnified cantilever amplitude should provide the valuable images, where the brightness is relevant to the amplitude of the cantilever. The higher amplitude, the whiter of the brightness in the images.

Based on the Hertz contact theory and the vibration model [7] of the AFM micro-cantilever, the image contrast obtained from the ultrasonic amplitude image depend on the average resonance frequency and ultrasonic frequency.

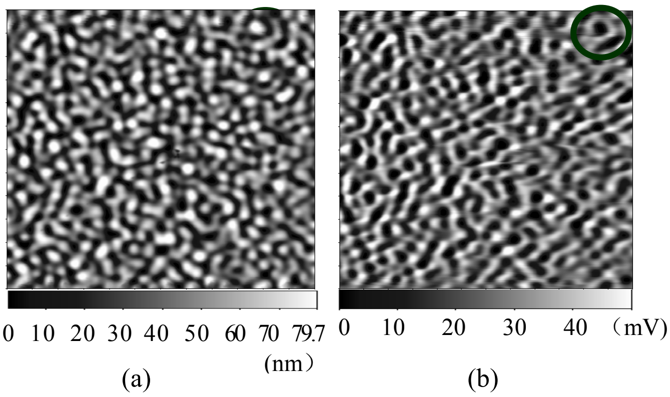


Fig.4 Topography (a) and ultrasonic amplitude (b) images of SiOx film excited at the 100 kHz frequency

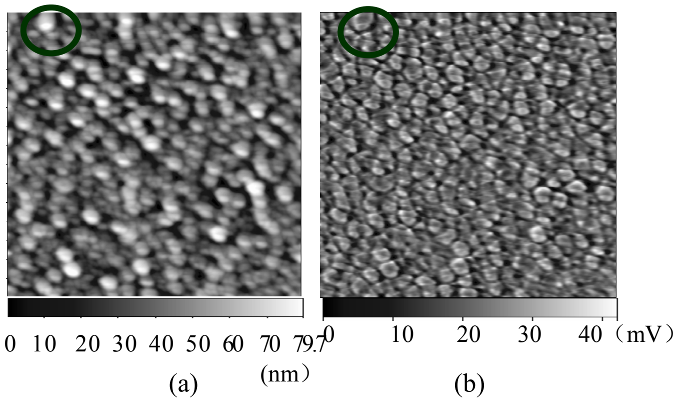


Fig.5 Topography (a) and ultrasonic amplitude (b) images of SiOx film excited at the 400 kHz frequency.

Fig.4 and Fig.5 show the topography and the ultrasonic amplitude images for different 12μm×12μm area when the sample was excited at the 100 kHz and 400kHz frequencies respectively. The sample was prepared in the same condition in Fig.4 and Fig.5. It was interesting that the contrast of the brightness was consistent between the ultrasonic amplitude image and topography image, shown in Fig.5, but it was inverse, such as in Fig.4.

The reason is that the topography image can only reveal the morphology of the as-prepared coating, and the information under the subsurface can not be scanned based on this method. With an ultrasonic waveform applied on the substrate, however, the different elastic modulus and the local contact stiffness between the tip of probe and sample shall lead to a variation of resonance frequency and amplitude of cantilever, which can reveal the surface and subsurface structures qualitatively in ultrasonic amplitude image.

Properties of the plastic with SiOx coating

Barrier property. Table 1 shows OTR values of PET (70μm), BOPP (18μm), and SiOx coated ones（deposition time 20min, the ratio of O_2/HMDSO = 1:1）in humidities of 0% and 65%, respectively. One can see that the OTR values of the SiOx coated plastic film were significantly reduced comparing to the original films.

Tab.1 OTR of SiOx coated and original plastic films

Films	Thickness (μm)	OTR (cc/m^2/day) (23±0.5°C) Humidity（0%）	Humidity（65%）
Original PET	70	21.4	17.3
SiOx coated PET	70+0.090	5.71	4.77
Original BOPP	18	2031	1853
SiOx coated BOPP	18+0.090	42.1	37.8

For 70 μm-thick PET samples, OTR values of SiOx coated ones reduce from 21.4 cc/m^2/day and 17.3 cc/m^2/day to 5.71 cc/m^2/day and 4.77 cc/m^2/day at humidities of 0 and 65%, respectively; For BOPP, these value were reduced from 2031 cc/m^2/day and 1853 cc/m^2/day to 42.1 cc/m^2/day and 37.8 cc/m^2/day, respectively.

Contact angle and tensile strength. The contact angle of the PET film with SiOx coating can be 100° comparing with 60°of the PET film absent of the SiOx coating. The contact angle increases with the deposition time increasing firstly, but then decreases a little. This is because the Si-O bond is non-polar, so the SiOx has the hydrophobic property, but with the growth of nanoparticles, the specific surface area and surface energy increase. Contact angle increasing improves the hydrophobic property, so the property of barrier water can be improved.

The largest tensile force increases from the original 93.18N to 118.90N and the tensile strength increases from the 116.48MPa to 148.63MPa. The results show that the SiOx coating can improve the tensile strength.

Conclusions

In this work, the SiOx coating was prepared on the PET and BOPP film and charcterized by FTIR, AFM and UAFM. The ultrasonic amplitude images can show the subsurface informations except for surface defect by darker color due to very small amplitude of the cantilever. The results show that the SiOx coating can improve the barrier property and the tensile strength. In the further work, the properties and applications of the SiOx will be researched.

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