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Preparation of High-barrier Polyethylene Terephthalate bottle by Microwave Plasma Enhanced Chemical Vapor Deposition

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Abstract. In this work, we reported the investigation of diamond-like carbon (DLC) coating on the inner surface of polyethylene terephthalate (PET) bottles by Microwave Plasma Enhanced Chemical Vapor Deposition to improve their barrier properties. We used 2.45 GHz microwave to generate plasma, acetylene (C2H2) and argon (Ar) were used as monomer gas and diluted gas. The effects of plasma process parameters on deposition uniformity and barrier properties of thin films were studied in detail. In addition, we designed a new antenna shape to improve the uniformity of film deposition. We analyzed the microstructure and morphology of the DLC coating by atom force microscope (AFM). Fourier transform infrared spectroscope (FTIR) and Raman spectroscope were employed to investigate chemical composition and bonding structure. The deposition rate was obtained by Step Profiler. For the barrier properties, we measured the oxygen transmission rate (OTR) of the PET bottle coated with DLC film. It is noted that the uniformity of film deposition is affected by the process parameters and antenna shape, after optimizing the process parameters and antenna shape, the barrier property of PET bottles is improved obviously.

1. Introduction

A good packaging material must be able to simultaneously meet many requirements, such as convenient production, novel design, low cost, long shelf-life, retrievability and so on. Plastic is a popular packaging material, due to high cost performance, light quality, good mechanical strength, and most of the plastic materials are recyclable, especially polyethylene terephthalate (PET) material is used widely. However, although these materials have been used to protect the contents from external contamination, for certain products such as food or drink, people still have to try to prevent the infiltration of oxygen and ensure long-term storage and preservation. Therefore, the barrier improvement of PET packaging materials has become a very important research direction.

Diamond-like carbon (DLC) film is an amorphous carbon, its properties are very similar to diamond films, such as good optical properties, high hardness, high resistivity, unique tribological characteristic and so on [1-3]. Besides, the DLC structure is adjustable, as the different sp^2 and sp^3 hybridized orbital content demonstrate a different properties [4]. Compared to the diamond film, DLC film is easy to prepared by Chemical Vapor Deposition(CVD) or Plasma Enhanced Chemical Vapor Deposition (PECVD), such as ion beam deposition, magnetron sputtering, RF plasma-activated chemical vapor deposition, plasma source ion implantation and so on [5]. As a very efficient deposition method, microwave plasma was widely studied due to a high plasma density but no external the magnetic field which simplifies the device [6]. In practical applications, it is necessary to deposit film fast and evenly, we experimentally studied uniformity of DLC films deposition. As known the properties of the DLC film in mechanical, optical , barrier property and electrical are relevant to microstructure and morphology of the films, so in this work we analyzed the carbon bond characterization by Fourier transform infrared spectroscope (FTIR) and the microstructure and morphology of the DLC coating by atom force microscope (AFM). In the experiment, we explored how the quartz antenna length influenced the deposition distribution, some plasma parameters were also experimented like microwave power, duty cycle, monomer radio and work pressure. Finally, the barrier property of PET coated DLC film as application of was measured in this work.

This study aims to improve the barrier performance of PET bottles by DLC film coating. At the same time, the improvement of barrier performance is affected by the uniformity of film deposition, so the research will also focus on the uniformity of film deposition.

2. Experiments

2.1 Experimental set-up

We use microwave plasma chemical vapor deposition unit to deposit DLC film on internal surface of PET bottle, as shown schematic diagram of experimental set-up in Figure 1. The deposition system consists of plasma generation system, vacuum system, gas path system, cooling system. The operating frequency of the microwave source of the device is 2.45 GHz. The microwave energy was launched from the magnetron then transmitted by the rectangular waveguide, and coupled to the resonant cavity by antenna (the antenna was made up of two quartz tube and a copper pipe). The microwave surface wave propagation was realized on the plasma interface and the surface of the quartz medium, and then the high density plasma was generated. The discharge gas and the reaction monomer entered the reaction chamber through the internal pipe of the quartz antenna.

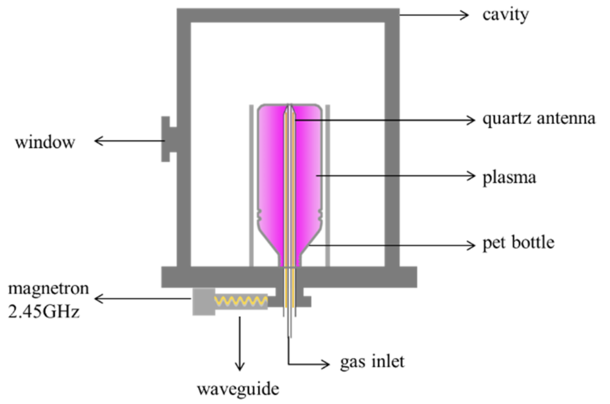


Figure 1. Schematic diagram of experimental set-up

2.2 Deposition

During deposition, we used acetylene C_2H_2 as carbon source, Argon (Ar) as diluted gas to deposit DLC film. DLC film was deposited on the inner wall of PET bottle (500 ml) to improve its barrier performance. In addition, other materials will also be used as substrates to assist in the analysis of the structure and performance of the film, including glass slides, monocrystalline silicon, polyethylene terephthalate (PET) web, and KBr tablets. Acetone, ethanol, deionized water were used as cleaning detergents respectively in ultrasonic condition, before samples were put into the chamber.

Prior to the deposition of DLC films, we pretreated substrates by Ar plasma, for the purpose of cleaning the substrate and activating the surface, which will benefit to the film nucleation and growth .The parameters of Ar discharge pretreatment were listed in table 1.

Table 1. The parameters of Ar plasma pretreatment

Gas	Ar
Microwave power	400W
Time	10s
Discharge mode	continuous

For coating deposition, we used pulse plasma. The pulse microwave power was 1500W, the duty cycle was 4:40 ms （t_{on}:t_{off}=4:40ms） , the gas pressure was 30 Pa, The flow ratio of argon and acetylene was 1:6, and exposure time was 3min. To improve coating uniformity, we adjusted the process parameters and used quartz antennas of different shapes, as described in detail later in this article.

Table2. The parameters of DLC film deposition

Base pressure	2 Pa
Discharge gas	Ar, C_2H_2
Microwave power	1500W
Discharge mode	Pulse
Duty cycle(t_{on} : t_{off})	4:40 ms
Gas pressure	30Pa
Gas flow ratio(C_2H_2:Ar)	6:1

3. Results and discussion

3.1 FTIR spectroscopy

Figure 2 is the FTIR spectroscopy of the deposited DLC film. The film deposition parameters were described in Table2 of this paper. The wave number around 1100cm^{-1} corresponds to the stretching vibration of the straight chain C-C bond and $(CH_3)_2CHR$. The hydrocarbon stretching vibration in the range of 2800-3100 cm^{-1} was appeared obviously, including sp^3 carbon-hydrogen bond (2800-3100 cm^{-1}) stretching vibration and sp^2 carbon-hydrogen bond (3000-3100cm^{-1}) stretching vibration.

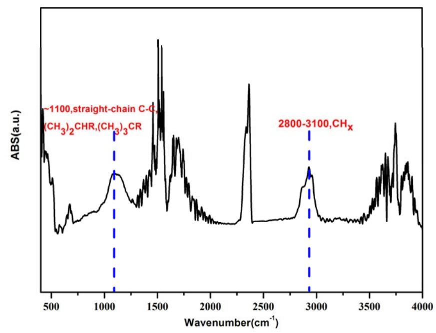


Figure 2. FTIR spectroscopy of the deposited DLC film

We analyzed the structure and composition of the DLC film in detail through Gaussian peak-differentiating and imitating the FTIR spectra in the wavenumber range of 2800-3100cm^{-1} as shown in Figure 3 The absorption peak is in the range of 2800~3100cm^{-1} mainly correspond to the component of CH_x （$0<x<4$） group in the film, the absorption peaks around 2870, 2925 and 2960 cm^{-1} are corresponded to sp^3-CH_2 symmetric, sp^3-CH_2 asymmetric and sp^3-CH_3 asymmetric stretching respectively, the absorption band ranging from 3000 to 3100 cm^{-1} is sp^2-bonded carbon. The carbon in films is mainly presented in sp^3 hybridization, and a small amount of sp^2 hybridization. The results show that the main components of the deposited films are hydrogenated amorphous carbon.

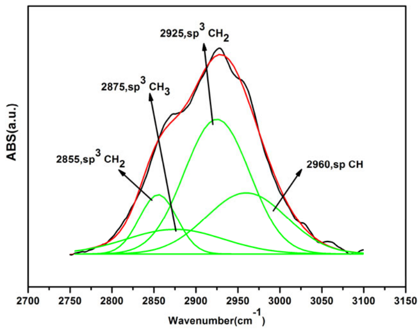


Figure 3. Gaussian peak-differentiating and imitating in the wavenumber range of 2800-3100cm^{-1}

3.2 Microstructure and morphology

Figure 4 shows the AFM morphology of DLC film and scan area range was 5×5 μm, the film deposition parameters were described in Table2 of this paper. The thickness of the deposited film measured by the step instrument was about 510nm, and the surface roughness (Ra) was 11.6nm after scanning, imaging, analyzing by atomic force microscope, which showed the surface of the film was significantly smooth. From AFM surface morphology image, we can examine the topography features and observe the surface smoothness, coating surface was dense and smooth with small particle size, and the image indicates that the film is compact and no obvious flaws and pores on the surface, which is very important for gas barrier properties.

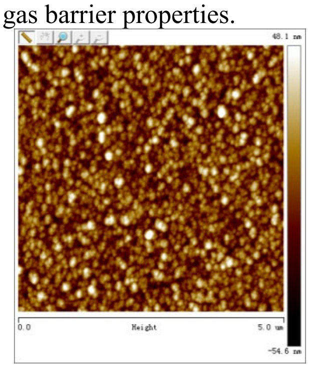


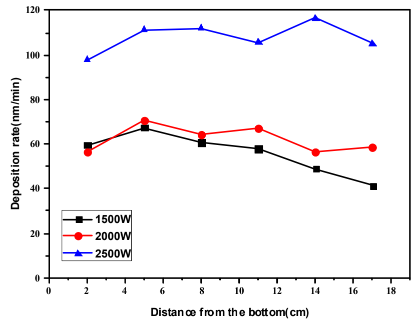
Figure 4. AFM morphology of DLC film

3.3 Uniformity

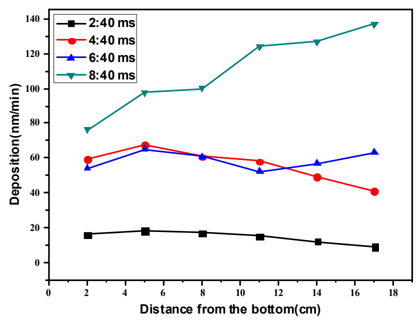
In practical applications, the uniformity of the film deposited in large area is important, especially in the preparation of high barrier bottles by coating method. However, when the film is deposited by microwave PECVD, the microwave energy dissipates along the axis of the antenna, resulting in the uneven distribution of the film deposition rate along the antenna direction. In this paper, we studied the factors affecting the uniformity of film deposition in detail.

3.3.1 Plasma parameters.

Figure 5 shows the distribution of deposition rate along the axial direction of the antenna on different process parameters. Figure 5(a) shows the deposition trend with different microwave power, as seen, when the power was 1500W, the deposition rate of upper half part was lower than that of lower part, but as power increased to 2500W, the trend exchanged and the uniformity of film growth became better, the average deposition rate achieved around 100nm/min. Figure 5(b) is on various duty cycle t_{on}:t_{off} from 2:40 ms to 8:40 ms, as shown in the figure, when duty cycle value was small equal to 2:40 ms, the deposition rate was very low, although film deposition looked uniformly. The deposition attained above 100nm/min when t_{on}:t_{off}=8:40 ms, and the deposition rate during upper area around antenna was higher. As for the deposition uniformity, 6:40 ms was the best. When changing proportion of monomers, deposition rate distribution along axial direction along antenna is shown in Figure 5(c), from the figure, the uniformity seemed to become worse as the monomer ratio (C_2H_2:Ar in flow rate) increased, the film deposition uniformity was best as C_2H_2:Ar=1:1, while film grew more quickly in lower part than the upper as C_2H_2:Ar=8:1. Figure 5 (d) was on various pressure from 20 Pa to 40 Pa, it was observed that the deposition rate enhanced with the work pressure increased, when work pressure was 20 Pa, obtained the most uniform deposition, the middle part shown fastest rate on 40 Pa.



a



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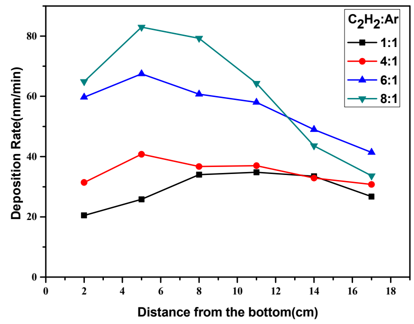

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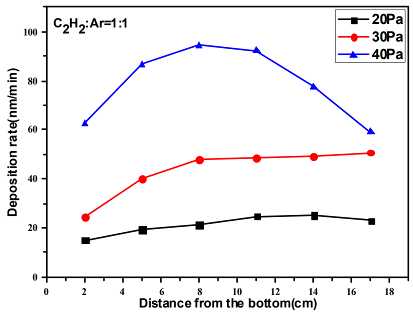

d

Figure 5. Deposition rate along the axial direction of the antenna (a) - on different microwave power; (b) - on duty cycle; (c) - with different monomer radio; (d) - with different work pressure

3.3.2 Antenna length.

In Figure 6 when quartz antenna length was shorter(about 20cm), the uniform was worse in the range of 0 cm to 17 cm from bottom, and the deposition rate was faster than that of longer antenna below 8 cm position, then reduced rapidly, in comparison, 25 cm antenna can achieve a uniform film deposition.

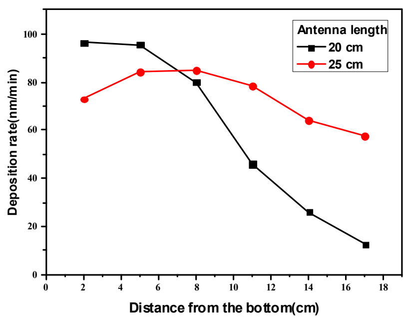

Figure 6. Deposition rate distribution along the axial direction of different antenna lengths

3.3.3 Antenna shape.

In this study, the quartz tube antenna, as the energy transmission medium, consists of an internal quartz tube (intake-tube), a copper tube in the middle (microwave energy transmission) and an external quartz tube (surface wave transmission medium). When the energy was transmitted along the quartz medium surface of conventional antenna (marked as Antenna-1, cylindrical structure with equal outer diameter), we deposited DLC film on the inner wall of the PET bottle, the film couldn't cover the bottom of the bottle.
Therefore, we try to optimize the structure of the antenna by adjusting the diameter of the upper part of the quartz antenna and changing the spatial distribution of the electromagnetic wave propagating along the dielectric surface, so as to improve coating coverage on the bottom of PET bottles. When the diameter of the upper end of the antenna (marked as Antenna-2) is enlarged, it is found that the antenna with this structure can improve the DLC deposition situation of pet bottle inner wall (The deposition rate distribution of new and former antennas is shown on Figure 7).

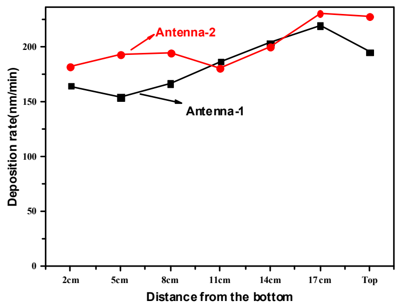

Figure 7. Deposition rate distribution of new and former antennas

3.4 The barrier property

We deposited DLC film on the inner wall of 500ml PET bottle by microwave PECVD technology to prepare high barrier bottle. It has been shown earlier in this article that the antenna structure has a significant effect on the distribution of film deposition. Therefore, we compared the effect of conventional antenna and modified antenna on improving the barrier property of PET bottles. Except for different antenna shapes, other parameters remain the same as shown in Table 3 (No.1 corresponds to conventional antenna, No.2 corresponds to improved antenna). The results show that the barrier properties of PET bottles can be improved obviously after coating DLC films by microwave PECVD technology. When using a conventional quartz antenna, the OTR of a 500ml PET bottle can be reduced from 0.058 cc/(pack-day) to 0.0038cc/(pack-day). More importantly, after adjusting the antenna shape, the OTR of PET bottle coated DLC film can as low as 0.0018 cc/(pack-day).

Table 3. Preparation process parameters and the corresponding OTR

Sample	Pulse microwave power(w)	Duty cycle ((t_{on}:t_{off}(ms))	Flow ratio (C_2H_2:Ar (sccm))	Pressure (Pa)	Time (min)	OTR (cc/(pack-day))
No.1	1500	4:40	6:1	30	15	0.0038
No.2						0.0018
Uncoated PET bottle						0.058

4. Conclusions

In this paper we produced High-barrier Polyethylene Terephthalate bottle deposited DLC films by Microwave Plasma Enhanced Chemical Vapor Deposition and investigated the composition and microstructure of the DLC film. In order to optimize the preparation method of High-barrier PET bottles, we also studied the uniformity of film deposition specifically. We mainly studied the influence of plasma parameters, antenna length and shape on DLC film deposition distribution. Results shows that, the antenna length and shape can influence the deposition uniformity obviously, and the antenna shape developed in this research can effectively improve the distribution of DLC film coating, so as to achieve the purpose of improving the barrier properties of pet bottles. In addition, the plasma parameters like microwave power, duty cycle, the proportion of monomers and inert gas and work pressure can also influence the growth rate and uniformity of DLC film.

In conclusion, this study found that the DLC film coating on the inner wall of pet bottles by Microwave Plasma Enhanced Chemical Vapor Deposition can greatly improve their barrier properties. Especially when optimized antenna shape is used for coating modification, the OTR of the PET bottle can be as low as 0.0018 cc/(pack-day), approximately 32 times lower and that will be very useful in package field.

Acknowledgments

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