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Quality improvement of packaging film by DLC coating

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Diamond-like carbon (DLC) thin films were deposited on packaging films such as polyethylene terephthalate (PET) and polyvinylidene chloride (PVDC), using a plasma immersion ion implantation-deposition (PIII-D) technique. Ar and C_2H_2 gas were utilized as the working gases and discharged by radio frequency (RF) at 13.56 MHz. Process starts from sputtering by argon plasma with pulse mode for surface cleaning. The system operates at gas flow rate 6 sccm of C_2H_2. , RF power at 200 W , bias voltage -3.0 kV and varies time for best quality improvement of packaging film. Gas permeability was measured by gas permeability tester. Thickness of DLC film was measured by Atomic Force Microscope (AFM).Colors of coated films were measured by colorimeter. The crystalline structure of DLC film has been evaluated by Raman spectroscopy. It was found that oxygen transfer rate of PET and PVDC films were reduced by 21.2% and 22.9% respectively. Thickness of DLC film increase when increase processing time in which correlate with colors. Raman spectra results the D-peak and G-peak confirm that DLC films were fabricated on both films.

Keywords: Diamond-like carbon, Gas barrier, PET, PVDC

1. INTRODUCTION

Many kinds of polymer are widely used for food packaging because they are convenient, light weight, cheap and can recycle or reuse. To keep food such as fruits or vegetables for a long time have to prevent oxygen gas to made food rotten. So packaging film ought to have good gas barrier properties.

Diamond-like carbon (DLC) films have been widely known, characterized by high hardness, low friction coefficients, high wear resistance, high electrical resistance and chemical inertness [1,2]. Recently, the high gas barrier properties of DLC films have been reported beside the characteristics mentioned above, and are expected to apply to food or beverage packing field [3,4]. Shirakura et al. [4] reported that the DLC coating on the inner surface of PET bottles increased the oxygen gas barrier by 20 to 30 times comparing with uncoated bottles.

Mitsubishi Heavy Industries, Ltd. (MHI) has developed a DLC plasma coating system which has the world's highest levels of productivity and gas barrier performance. This coating system is capable of forming a extremely thin but quite high gas barrier DLC (Diamond Like Carbon: carbon similar in physical properties to diamond) film on the inner surface of the bottle using plasma CVD (Chemical vapor deposition) [5].

In this paper, we coated DLC on surface of polyethylene terephthalate (PET) and polyvinylidene chloride (PVDC) film and determine thickness of film by an atomic force microscope (AFM), gas transfer rate by gas permeability tester and color by colorimeter.

2. EXPERIMENT

2.1 Sample preparations

PET and PVDC films were cut into square sheet 11x11 cm 60 μm thick. Films were cleaned by ethanol and attached on conducting holder prior the mask. (see Fig 1 (a) and (b))

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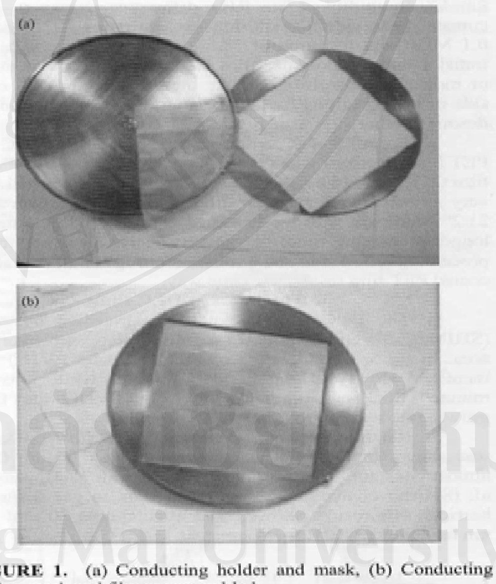

FIGURE 1. (a) Conducting holder and mask, (b) Conducting holder, mask and film are assembled.

2.2 DLC coatings

The experimental setup was shown in Fig 2. Sample was cleaned by sputtering with 150 W 13.56 MHz RF power, 4.0 sccm Argon flow rate and bias voltages at -2.4 kV for 5 min. The implantation process utilized C2H (acetylene) plasma, discharged with 200 W RF power, gas flow rate 6.0 sccm at an operating pressure 2.3 x 10-3 Torr. Bias voltage was applied at -3.0 kV with fixed pulse width 20 μs and 200 Hz pulse frequency. Processing time was

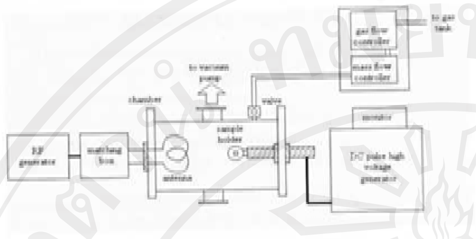

FIGURE 2. A schematic diagram of PIII-D system.

vary up to 15 min. Process was similar to Cuong et al. [6] which varied mix CH4 and H2 gas ratio at RF power of 300 W, made film growth rate to 8 nm/min.

3. RESULTS AND DISCUSSIONS

3.1 Oxygen transfer rate

Oxygen Transfer Rate (OTR) was performed by gas permeability tester (M & E development center). OTR was measured under condition which constant temperature 23 C°, humidity 17% RH, difference between high concentration side(P1) and low concentration (P2) side is 0.1 MPa and test area of 78.5 cm2. Main process of gas transfer through polymer film has 3 steps. First gas atoms or molecules absorb on surface then diffuse through other side of wall resulting by the concentration gradient and last desorb to other side. (see Fig 3)

From Fig 4 It can be seen that OTR of PVDC and PET films decrease when processing time increase. In PVDC film OTR reduced by 22.9% compare with the uncoated with very linear decrement. For PET films OTR reduced by 21.2% compare with the uncoated, and tend to saturated at longer processing time. Ikeyama et al. [7] also reported at processing time 1 min and 3 min that nitrogen transfer rate of coated PET film results the same way.

3.2 Thickness of DLC films

The DLC film thickness was verified by AFM (SHIMADZU SPM-9500 J2) scanning along the interface area. In fig 5, the thickness of DLC films on PVDC film increased slowly in the first 10 minutes while over 10 minutes thickness jump rapidly. For PVDC the DLC growth rate was approximately 15 nm/min.

Relation between OTR and DLC film thickness was shown in Fig 6, when thickness over 100 nm OTR almost constant. This results correlated with N. Boutroy et al. [8] who coated DLC on PET bottles as gas diffusion barriers. His results showed that at thickness 80 and 175 nm tendency of OTR were constant.

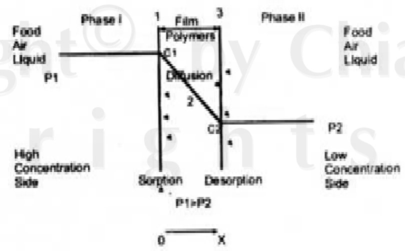

FIGURE 3. Process of gas transfer through polymer film.

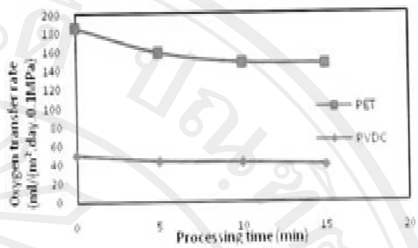

FIGURE 4. Oxygen transfer rate of PVDC and PET films with varying processing time.

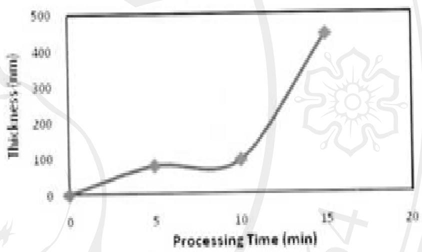

FIGURE 5. Thickness of DLC films coated on PVDC with varying processing time.

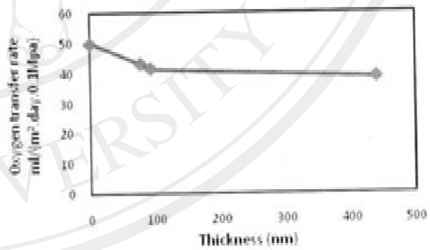

FIGURE 6. Oxygen transfer rate of PVDC with thickness of DLC films.

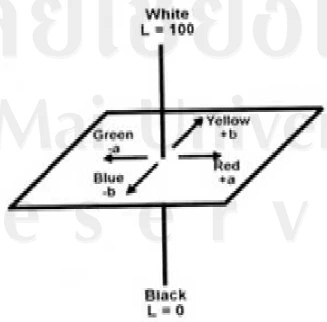

FIGURE 7. Significance of L, a, b color space.

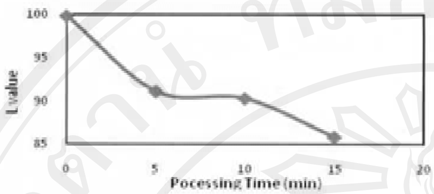

FIGURE 7. Graph of L values with processing time of PVDC film.

3.3 Colors of coated films

Colors of coated film was measured by colorimeter (HunterLAb Color Quest2). The instrument inform 3 values: lightness, L and opponent dimensions (a, b). The significance of these values is as shown in Fig 7. Film transparency can be determined by the L value. L value close to 100 means film is very clear, in opposite if L value close to 0 means the film is opaque.

Table 1 shows that when processing time increase L values will decrease. In case of PVDC result was support with thickness when plot L value vs processing time as shown in Fig 8, when processing time about 10-15 min L values drop rapidly compare with Fig 5 at the same processing time thickness jumped rapidly, because thickness of DLC films made both films more opaque.

TABLE 1. Colors changed of PVDC and PET films.

Processing Times (min)	L	a	b
PVDC			
uncoated(0)	99.93	-0.01	0.02
5	91.15	0.30	6.02
10	90.35	0.36	13.14
15	85.90	1.21	18.11
PET			
uncoated(0)	100.00	-0.01	0.00
5	93.56	0.19	6.05
10	92.46	0.42	12.17
15	85.36	0.63	18.02

3.4 Raman spectroscopy

Fig 9a and 10a show Raman spectra of uncoated films there are no peak of DLC, where Fig 9b)-9d) and 10b)-10d) the D and G peak [9] presented which also, the intensity of D peak tends to increase as processing time increase, especially in PET film, can confirm DLC formation on both films.

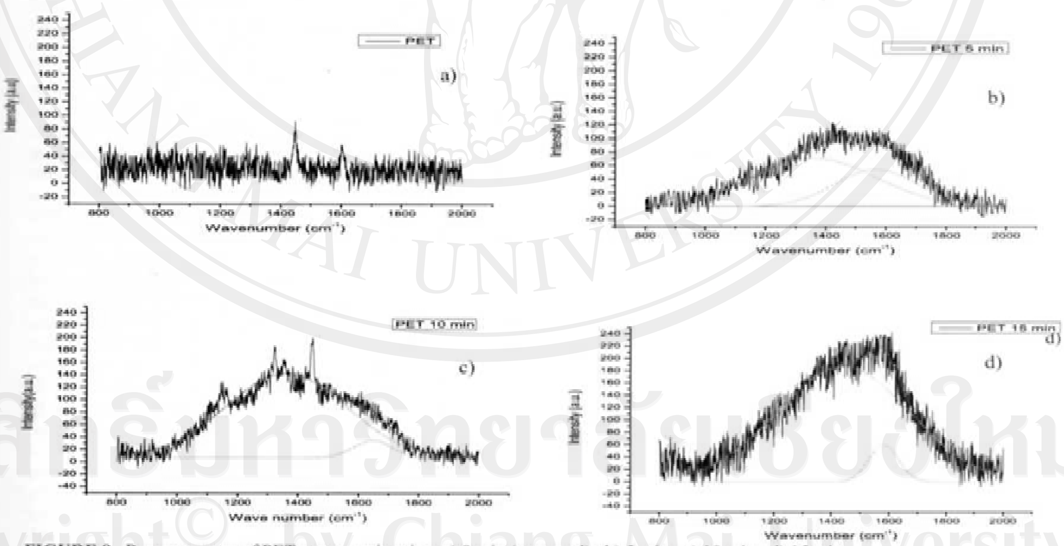

FIGURE 8. Raman spectra of PET at processing time a) 0 min (uncoated), b) 5 min, c) 10 min, d) 15 min

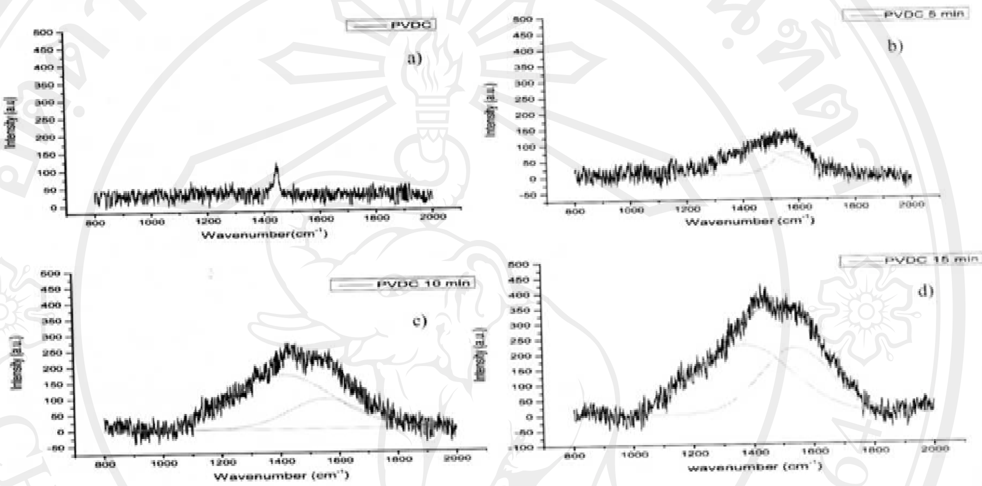

FIGURE 9. Raman spectra of PVDC at processing time a) 0 min (uncoated), b) 5 min, c) 10 min, d) 15 min

4. CONCLUSION

DLC films could be deposited on PVDC and PET films. Effect of increasing process time made OTR reduced by 22.9% for PVDC films and 21.2% for PET films respectively. The results obtained may less than DLC coated on inner surface of PET bottles with intense pulse PIII by Shirakura et al, [10]. The relation between thickness versus processing time and L values versus processing time are not linear but correlate to each other. Increasing of DLC thickness will make packaging films more opaque so it make L values decrease. Raman spectra confirm the DLC formation on both films.

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