

The effect of coatings formed by low temperature tetramethoxysilane plasma treatment on water-vapor permeability of poly(L-lactic acid) film

Yoshimitsu Uemura*[†], Yoh-suke Maetsuru, Tomoharu Fujita, Masahiro Yoshida, Yasuo Hatate and Kenji Yamada**

*R&D Division, Kagoshima TLO Co., Ltd., 1-21-40 Korimoto, Kagoshima 890-0065, Japan
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

**Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology,
Kokuraminami-ku, Kitakyushu 802-0985, Japan
(Received 5 January 2005 • accepted 24 August 2005)

Abstract—One of the most promising applications of poly(L-lactic acid) (PLLA) is food packaging. However, PLLA has a poorer gas barrier property than ordinary food packaging polymers. An improvement of the water-vapor barrier property is therefore required. In this study, low temperature plasma treatment on a stretched PLLA film in the presence of tetramethoxysilane (TMOS) was carried out in order to improve its water-vapor barrier property. The flux of water-vapor permeation through a stretched PLLA film treated with low temperature plasma in the presence of TMOS was decreased to 60% of an untreated stretched PLLA. The effects of plasma treatment parameters on the water-vapor permeability were investigated.

Key words: Poly(L-lactic acid), Water Vapor Permeability, Low Temperature Plasma, Tetramethoxysilane

INTRODUCTION

Poly(lactic acid) (PLA) has been used as a DDS material [Nah et al., 2000; Song et al., 2002] because of its bio-organism-benign character. Recently, poly(L-lactic acid) (PLLA) has been considered as a promising food packaging and contacting material because of its mechanical strength and superior optical transparency [Mills, 1999]. It is noteworthy that other features of this polymer are its carbon neutrality and biodegradability [Gruber, 2001], and food-contact safety [Conn et al., 1995]. The food packaging and contacting applications include disposable cutlery, straws, stirrers, lids, cups, plates, containers, wrapping films and sealed bags. For the last two applications (wrapping films and sealed bags), PLLA has a certain drawback—a poorer gas barrier property than other ordinary food packaging polymers [Yoon et al., 2000; Lehermeier et al., 2001]. Therefore, improvement of the water-vapor barrier property is required for wide-spreading use of PLLA. Since conventional food packaging and contacting polymers are from fossil fuel, combustion of their wastes causes net increase in carbon dioxide in the atmosphere. On the other hand, since PLLA is produced from corn-starch [Mills, 1999], combustion of PLLA wastes does not cause a net increase in carbon dioxide.

In this study, an attempt was made to improve the water-vapor barrier property of a stretched PLLA by low temperature plasma treatment in the presence of tetramethoxysilane (TMOS). By applying this treatment, according to a previous paper, it is expected that a layer mainly consisting of silica forms on the PLLA film [Teshima et al., 2002]. Permeability of gases through silica is much less than that through polymers. The flux of water-vapor permeation of one of the treated stretched PLLA films was decreased to 60% of the untreated stretched PLLA film. The effects of plasma treatment pa-

rameters on the water-vapor permeability were investigated.

EXPERIMENTAL

1. Material

A stretched PLLA film provided by Mitsui Chemicals Co. Ltd. was used in this study. The thickness of the film was 100 μm .

2. Low Temperature Plasma Treatment of PLLA Film

The stretched PLLA film was treated with low temperature plasma in the presence of TMOS in order to improve the water-vapor barrier property. Fig. 1 shows a schematic diagram of the apparatus for low temperature plasma treatment.

A piece of PLLA film was placed in a plasma irradiation tube made of Pyrex. The vacuum system of the apparatus was evacuated at 0.01 Torr for 30 min. Then, TMOS vapor was introduced

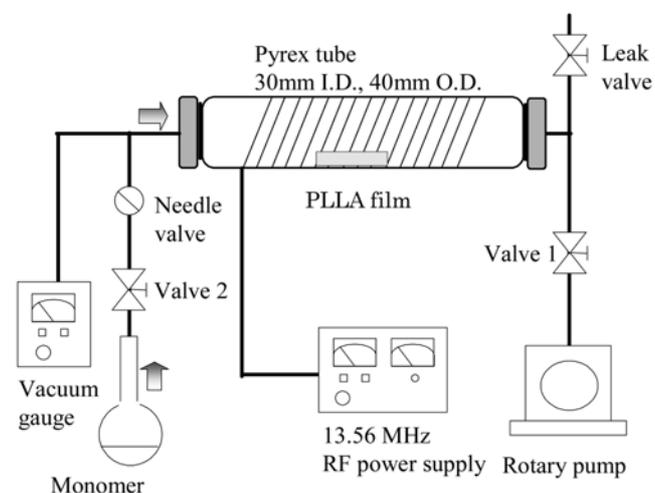


Fig. 1. Schematic illustration of plasma treatment apparatus.

[†]To whom correspondence should be addressed.

E-mail: uemura@ktlo.co.jp

from a flask attached to the vacuum system. The pressure of TMOS was controlled at 0.1 Torr by Needle valve 2. After 30 min replacement of the atmosphere by TMOS vapor in the vacuum system, plasma irradiation was started and carried out for a prescribed time period (5, 10, 15 or 30 min). The RF power applied ranged from 5 to 50 W.

Although both side treatments may result in a better barrier property, one side treatment is thought to be good enough to investigate the effects of plasma treatment conditions. Therefore, all PLLA films were treated at one side in this study.

3. Water Vapor Permeation Measurement

The permeation flux of water-vapor was measured by using 'the permeation cup' (Fig. 2, JIS Z0208) and a permeation measurement apparatus (Fig. 3). The right-most chamber (a desiccator) of the permeation measurement apparatus was designed to maintain the partial pressure of water vapor at a desired level (90%RH in this study) as shown in Fig. 3.

The permeation cup (made of aluminum) was specifically designed in order to measure the permeation flux of water vapor through a polymer film. Fig. 2 shows a setup of the cup and a specimen film. A polymer film (diameter 60 mm) was put on the cup. An aluminum ring was put on the film in order to fix the film on the cup. Sealing between the film and the cup was done with a melted mixture of paraffin wax and polyisobutylene as shown in Fig. 2 (left). After the polymer film was fixed to the cup, the cup was put into the chamber of the permeation measurement apparatus (Fig. 3). The atmosphere on one side of the film was kept dry by CaCl_2 . The other

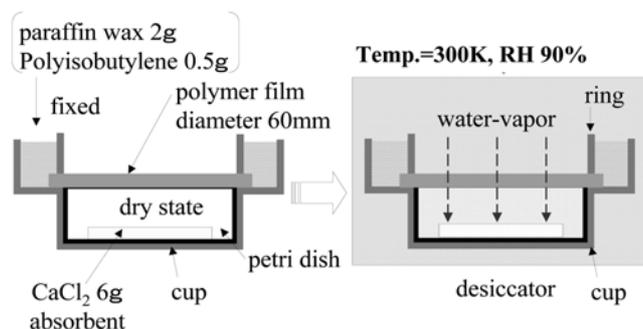


Fig. 2. The permeation cup and the principle of the permeation measurement.

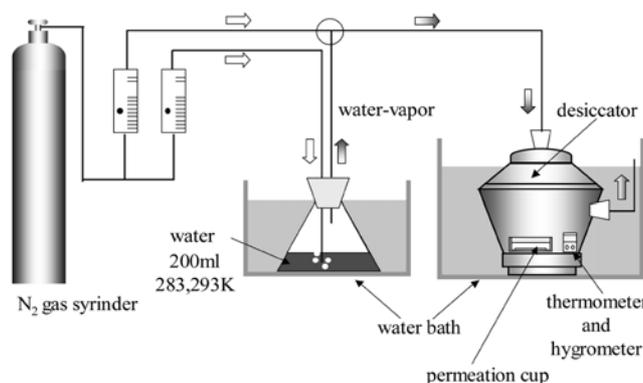


Fig. 3. A schematic illustration of the permeation measurement apparatus.

Table 1. The results of water vapor permeation for PLLA films

Section	Plasma conditions		Water vapor flux ($\text{g}/(\text{m}^2 \cdot \text{d})$)
	RF [W]	Time [min]	
1	5	15	23
	10	15	18
	15	15	24
	20	15	27
	40	15	26
2	50	15	(deformed)
	20	5	25
	20	10	26
3	20	30	24
	5	5	28
	10	5	25
	40	5	25
Untreated			31

side was kept at 90% of relative humidity. The flux of water-vapor permeation was calculated from the increase in the weight of the whole cup.

4. Film Surface Measurement

In order to inspect surface morphology and species, AFM (Digital Instrument, Nano Scope SPM III) and XPS (Shimadzu, ESCA-1000) measurements were carried out for the films (untreated and treated).

RESULTS AND DISCUSSION

Table 1 shows the results of water vapor permeation for the films treated by plasma irradiation. The result for an untreated film is also shown in the last line. All the treated films show an Si signal in XPS measurement. This means that a coating containing silicone was formed on the PLLA film by the plasma treatment. According to a previous paper [Teshima et al., 2002], a silica layer (containing small amounts of -OH and - CH_3) formed on a PET film by plasma-enhanced CVD in the presence of TMOS under all the conditions they applied. Their result implies that the composition of surface layer is not sensitive to the preparation condition. In our case, it is therefore likely that a silica-like layer formed on PLLA film.

As can be seen from section 1 of Table 1, the flux decreased up to 10 W of RF deposition power. A higher RF power than 15 W resulted in a larger flux than that of the lower RF power. The maximum RF power 50 W resulted in thermal deformation of the film. The appropriate RF power for gas barrier properties is dependent on other conditions (film type, monomer type and monomer partial pressure) according to previous studies [Teshima et al., 2002; Uemura et al., 2004].

The film treated by plasma at conditions of pressure=0.1 Torr, RF power=10 W and deposition time=15min gave the minimum permeation flux (i.e., the best barrier property). For the PLLA film treated by the best condition of plasma treatment, the flux of water-vapor permeation of the film was decreased to 60% of an untreated PLLA film.

In order to elucidate how the plasma treatment influenced the water-vapor permeability through the surface coating morphology,

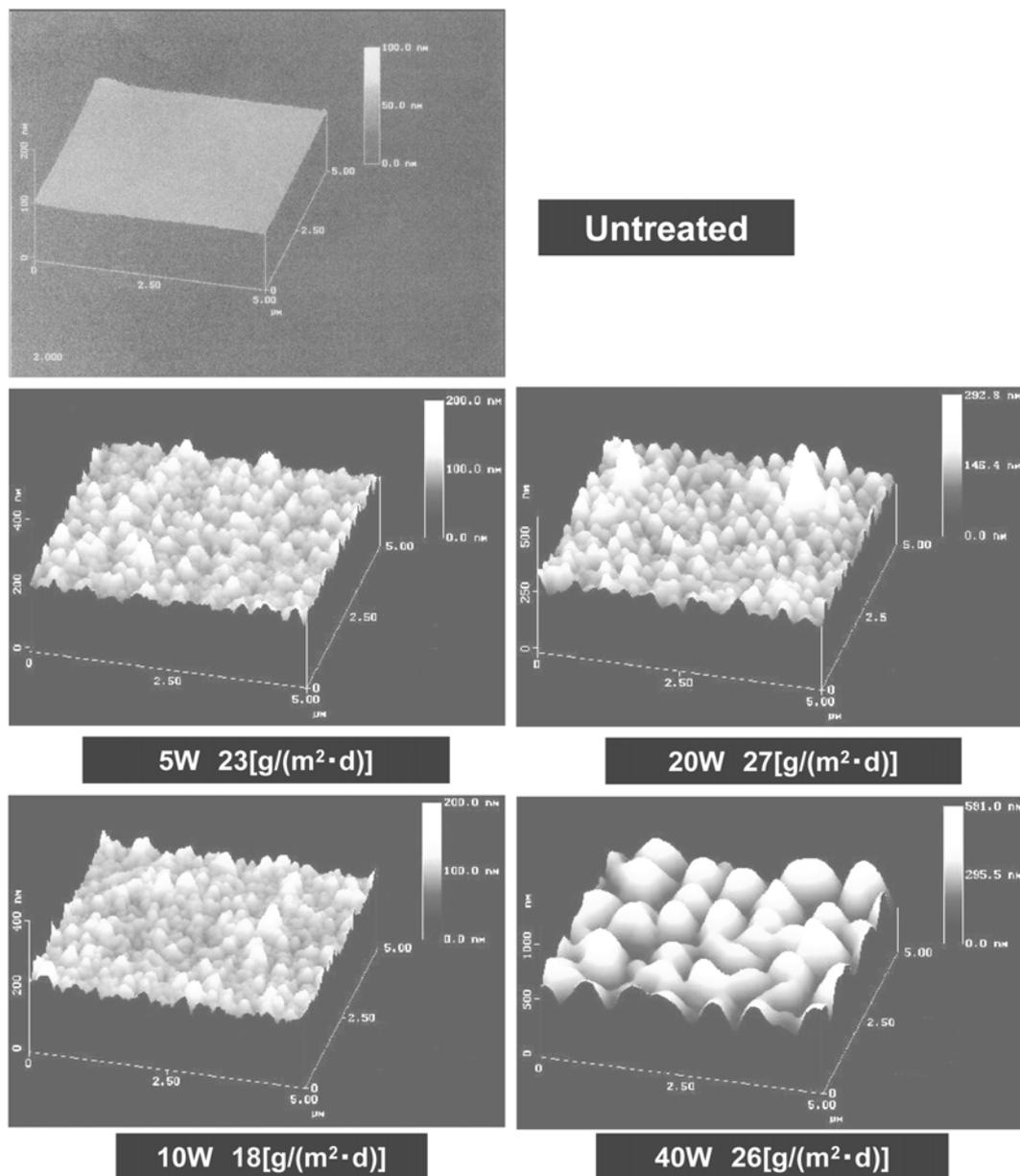


Fig. 4. Surface morphology of untreated and treated surfaces measured by AFM (treatment time=15 min).

AFM measurements were carried out for some of the treated films and an untreated film. Fig. 4 shows the results. The untreated film shows a rather smooth surface compared with the treated films. The three samples of 5, 10 and 20 W show a similar surface morphology. This similarity may be for only the surface geometrical aspect of the deposited layer, not internal characteristics of the deposited layer because of the following two facts. First, AFM can detect only surface profile, and second, these three samples show different permeability (Table 1). On the other hand, the surface of 40 W showed a different morphology, which implies a coarser coating texture. Further investigation was carried out by using the etching mode of XPS. Fig. 5 shows the results. In this figure, the XPS Si(2p) signal intensity is plotted against the number of Ar etchings. Before etching, the sample of 40 W showed the highest signal intensity among all the samples. This implies the coating of 40 W is thicker than

that of others. But the resistivity of 40 W coating against etching is quite weaker than others, because after the first etching the signal intensity of 40 W coating became a similar level to the others. Among the samples of 5, 10 and 20 W, there is no significant difference for AFM morphology and XPS etching resistivity. Although, from these data, we do not fully explain the tendency of water vapor permeability in the section 1 of Table 1, it is very likely that the coating characteristics, including the morphology, density and so forth, are a determining factor.

From the discussion above, including the results of permeability, AFM and XPS measurements, we may draw a possible picture for surface coating formation as illustrated in Fig. 6. The larger the RF power, the higher the concentration of intermediates formed in gas phase. Treatment at 5 W gives a defective layer because of insufficient concentration of intermediates. At 10 W, the layer becomes

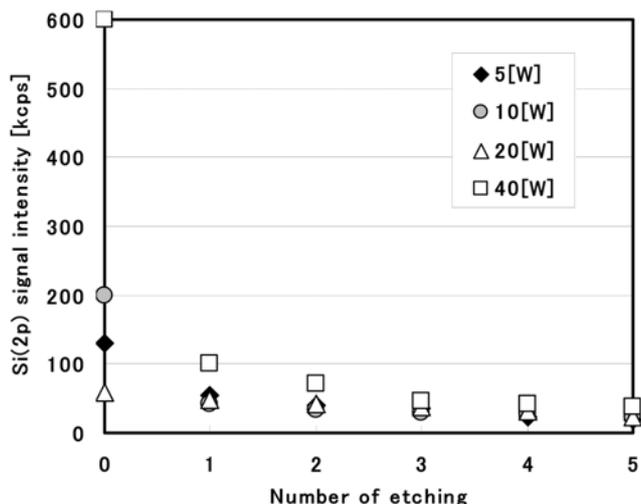


Fig. 5. Surface Si signal intensity as a function of the number of etching.

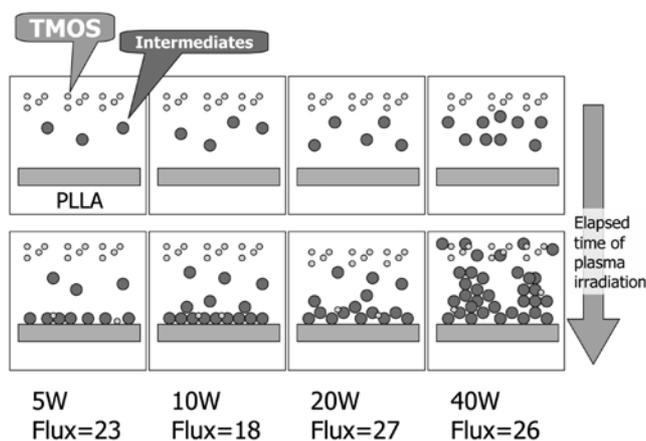


Fig. 6. A possible mechanism of surface coating formation.

the most dense among all the samples. At 20 W, the higher intermediates concentration hinders formation of a dense layer. An ablation effect [Inagaki, 1996], which has a larger effect at higher RF power, may give an additional negative effect on the layer barrier property. At higher power (40 W), a higher concentration of intermediates gives a very coarse (inside) and rough (surface) layer.

CONCLUSIONS

A stretched PLLA film was treated by low temperature plasma in the presence of tetramethoxysilane in order to improve its poor water barrier property. The effects of RF power and deposition time on the water-vapor permeability were investigated. From the water-vapor permeability and surface measurements using AFM and XPS of these films, the following observations were made.

1. By the plasma treatment, a coating containing silicon was formed

on the PLLA film.

2. For the PLLA film treated by the best condition of plasma treatment, the flux of water-vapor permeation of the film was decreased to 60% of an untreated PLLA film.

3. At 5 min deposition time, the RF power had little effect on the water-vapor permeability.

4. At 15 min deposition time, a medium RF power (10 W) was favorable for lowering the water-vapor permeability. Although a high RF power (40 W) resulted in a thicker coating, the resistivity to Ar etching was the weakest. A mechanism of the coating formation was proposed.

5. The deposition time showed little effect on the water-vapor permeability under the conditions in this study.

ACKNOWLEDGMENT

The authors would like to thank Mitsui Chemicals Co., Ltd. for providing the untreated stretched PLLA film.

REFERENCES

- Conn, R. E., Kolstad, J. J., Borzelleca, J. F., Dixler, D. S., Filer, Jr. L. J., Ladu, Jr. B. N. and Pariza, M. W., "Safety assessment of polylactide (PLA) for use as a food-contact polymer," *Food and Chemical Toxicology*, **33**, 273 (1995).
- Gruber, P. R., *Commodity polymers from renewable resources: polylactic acid, implications for R and D in the chemical sciences and technology carbon management*, National Academic Press, Chapter 11 (2001).
- Inagaki, N., *Plasma surface modification and plasma polymerization*, Technomic, Lancaster, USA, p.38 (1996).
- Lehermeier, H. J., Dorgan, J. R. and Way, J. D., "Gas permeation properties of poly(lactic acid)," *Journal of Membrane Science*, **190**, 243 (2001).
- Mills, R., *Cost performance of novel PLA resins in high clarity, oriented film applications*, Proceedings for the 15th Annual World Congress on Specialty Plastic Films, Session VIII4 (1999).
- Nah, J.-W., Jeong, Y.-I. and Koh, J.-J., "Drug release from nanoparticles of poly(DL lactide-co-glycolide)," *Korean J. Chem. Eng.*, **17**, 230 (2000).
- Song, K. H., Lee, C.-H., Lim, J. S. and Lee, Y.-W., "Preparation of L-PLA submicron particles by a continuous supercritical antisolvent precipitation process," *Korean J. Chem. Eng.*, **19**, 139 (2002).
- Teshima, K., Inoue, Y., Sugimura, H. and Takai, O., "Gas barrier properties of silicon oxide films prepared by plasma-enhanced CVD using tetramethoxysilane," *Vacuum*, **66**, 353 (2002).
- Uemura, Y., Fujita, T., Yoshida, M., Hatate, Y. and Yamada, K., *Effect of low temperature plasma treatment on water-vapor permeability of plasticized PLLA film*, Proceedings for APCCHE 2004, 2B-09 (2004).
- Yoon, J.-S., Jung, H.-W., Kim, M.-N. and Park, E.-S., "Diffusion coefficient and equilibrium solubility of water molecules in biodegradable polymers," *Journal of Polymer Science*, **77**, 1716 (2000).