Aminoalkoxysilane으로 제조한 산소 차단 필름의 투과특성 연구

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The permeation of oxygen barrier film prepared with aminoalkoxysilanes

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INTRODUCTION

In recent years, the flexible transparent barrier films, which act as a barrier to oxygen and water vapor, have been widely used in conventional packaging as substitute for glass and aluminum foil packaging, and proposed as encapsulation for novel products, like flexible organic light emitting devices (FOLED). Polymer films offer a number of key advantages over alternative bulk materials, such as light weight, complex shape and design freedom, transparency or tailored optical characteristics, and also cost-effectiveness. In contrast, the disadvantages of these films are the lack of thermal stability, and high permeability of gases like water vapor and oxygen. To use these materials in gas barrier applications, films with low gas permeability have been requested. On the other hand, inorganic materials have high mechanical strength and low gas permeability. It is thus possible to create new kinds of materials if polymer films and inorganic materials are combined. Aminoalkoxysilane, which is a kind of organically modified siloxanes (ORMOSIL), has the inorganic silica backbone providing mechanical strength and an amorphous structure, and the organic groups offering flexible properties that can make the crack-free film. For the preparation of oxygen barrier films with aminoalkoxysilanes, the sol-gel process was applied. The sol-gel process has some advantages including low temperature reaction and ability to control the final composition easily. It has been used for special industrial applications such as thin films, powders, fibers, and membranes. One of the attractive features of the sol-gel process is that it enables the low temperature process. This is compatible with application of OLED encapsulation layer that process must be performed at relatively low temperatures to prevent damage to the OLED active components.

Aminoalkoxysilane has been one of the most widely applied silane coupling agent, employed in many fields of modern chemistry and technology for chemical modification of various oxide surfaces.

Also, many features of coatings formed by aminoalkoxysilane have already been investigated. Tadanaga et al. pretreated Nylon6 film with 3-aminopropyltriethoxysilane (APTEOS) sol to improve the affinity of tetraethoxysilane (TEOS) coating layers with the substrate. Peixin Zhu et al. 3-aminopropyltrimethoxysilane (APTMOS) was used for poly (ethylene-terephthalate) (PET) surface modification.

In this study, aminoalkoxysilane was used only coating material for oxygen barrier films. The oxygen transmission rates (OTR) of aminoalkoxysilane barrier films have been investigated so as to know their own barrier properties. In order to archive higher barrier property, multilayer structure was formed. The effects of solvent, water ratio, and coating times on oxygen permeability have been studied. The practical use of aminoalkoxysilanes is rather limited because of the lack of stability in humid atmosphere. Therefore, we prepared oxygen barrier film with 3-glycidoxypropyl-trimethoxysilane (GPTMS) for modification into hydrophobic surface.

EXPERIMENTAL

The materials investigated were a poly (ethylene-terephthalate) (PET) film coated with 3-aminopropyltriethoxysilane (APTEOS) [Aldrich, 99%] and 3-aminopropyltrimethoxysilane (APTMOS) [Aldrich, 97%] by means of sol-gel process. Aminoalkoxysilane was mixed in alcohol and THF with molar ratio of 5, 10, and 15. After water was added to the mixture, this mixture was stirred at room temperature in a closed container. The molar ratio of water to aminoalkoxysilane was 3, stoichiometrically. The solution was cast on a PET film. The obtained barrier film was dried at the room temperature, 50℃, and 80℃ for 24 hours, and then kept in the desiccator before the characterizations. The composite membranes were characterized by various methods, such as Fourier transform infrared (FT-IR, JASCO-430) and ^{29}Si nuclear magnetic resonance (^{29}Si-NMR, Varian UI-200) spectroscopy. The morphology of cross-section and surface of the coating films were characterized with the scanning electron microscopy (SEM, JEOL, JSM-5310LV). A constant volume-variable pressure method was used to determine steady state permeability coefficients at 30℃ and 1atm of upstream pressure. The barrier film was mounted on the permeation cell and degassed by exposing both sides of the film to vacuum. The steady-state rate of pressure rise in a downstream receiving volume was used to determine the oxygen transmission rate. The permeation apparatus is shown schematically in Fig. 1. At steady state the following expression was used to calculate the permeability coefficient.

$$P = \frac{22{,}414V}{RT\frac{p_1}{l}}\frac{dp_2}{dt}$$

Where V is the downstream reservoir volume, p_1 is the upstream pressure, A is the cross sectional area, l is thickness of the barrier film, and dp_2/dt is the rate of change in downstream pressure

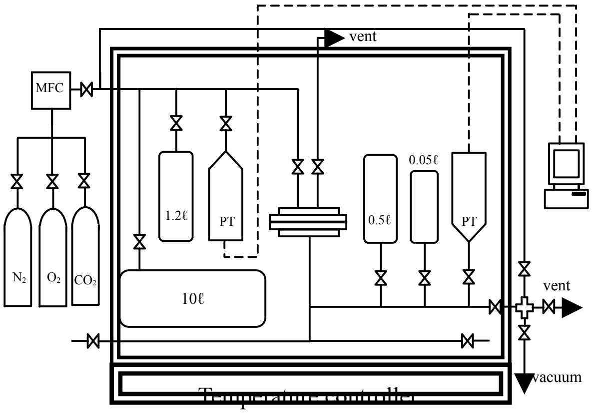

Fig. 1 The experimental apparatus for permeability measurement

RESULTS AND DISCUSSION

The oxygen barrier films that were prepared with only aminoalkoxysilanes enable the formation of transparent, flexible and crack-free thin films. Moreover, those films exhibited very good barrier properties. Fig. 2 represent OTR of PET substrate coated with APTEOS depend on the solvent ratio and drying temperature. Closed square symbols in Fig.2 describe OTR of PET substrate, and closed circle and triangle symbols denote that of solvent ratio 5 and 10, respectively. Both case of the solvent ratios are 5 or 10, OTR of the barrier films represent the lowest value at the drying temperature of 25℃. When the solvent ratio is 10, the barrier film represents better barrier property as well. These results correspond to FT-IR results showed in Fig. 4 and 5. Even if quantitative analysis too difficult by only FT-IR, it can make a prediction from the change of relative area. The case that solvent ratio is 10 and drying temperature is 25℃, it is shown that siloxane peak is larger than silanol peak. In order to prevent pin-holes and have better barrier properties of the barrier film, multilayer structures on the PET film are prepared by casting 1, 3, and 5 times. The results are represented in Fig. 3.

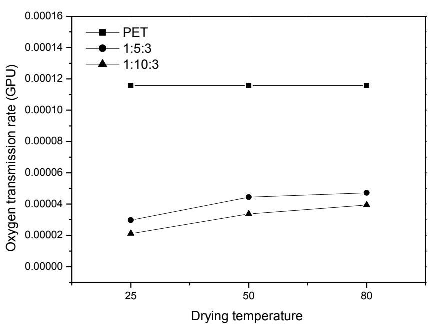

Fig. 2 Oxygen transmission rate of APTEOS coated on PET film as a function of drying temperature (℃)

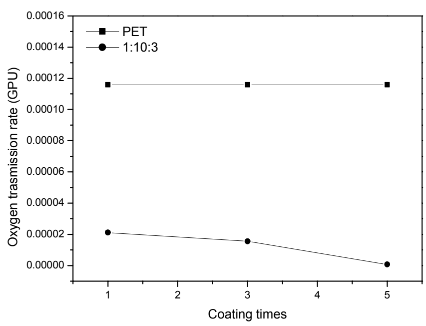

Fig. 3 Oxygen transmission rate of APTEOS coated on PET film as a function of coating times

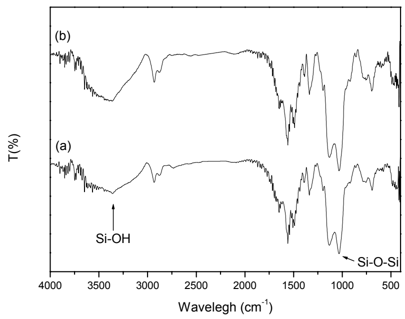

Fig. 4 FT-IR spectra of APTEOS film prepared by solvent ratio (a) 5, and (b) 10

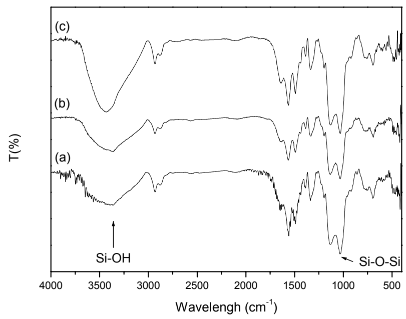

Fig. 5 FT-IR spectra of APTEOS film prepared by drying temperature (a) 25℃, (b) 50℃, (c) 80℃

Therefore, significant improvement in permeation-barrier performance can be achieved by using multilayered structures. The APTEOS coating on the PET prepared by casting 5 times shows the very good oxygen permeability of 7.06 x 10^{-7} GPU.

CONCLUSIONS

OTR were prepared by APTEOS. All the films were transparent, flexible and crack-free. when the solvent ratio is 10, OTR of the barrier films represent the lowest value at the drying temperature of 25℃. These results correspond to FT-IR results. It has significant improvement in permeation-barrier performance could be achieved by using multilayered structures. The APTEOS coating on the PET prepared by casting 5 times shows the very good oxygen permeability of 7.06 x 10^{-7} GPU.

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