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(Citation)
Journal of the Ceramic Society of Japan,128(4):229-232

(Issue Date)
2020-04-01

(Resource Type)
journal article

(Version)
Version of Record

Journal of the Ceramic Society of Japan 128 [4] 229-232 2020
DOI http://doi.org/10.2109/jcersj2.20004

JCS-Japan

NOTE

Preparation and gas barrier properties of organic–inorganic hybrid gas barrier membranes using 3-glycidoxypropyl silsesquioxane

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Organic–inorganic hybrid gas barrier layers using 3-glycidoxypropyl silsesquioxane with random structures on plastic film were prepared by cross-linking reaction between glycidoxy functional group of 3-glycidoxypropyl silsesquioxane and amino functional group of p-xylylenediamine (PXDA). The effects of PXDA content on the gas barrier property of the membranes were investigated. Oxygen permeability coefficient and water vapor transmission rate of the hybrid layer were the same order of poly(vinylidene chloride). Pencil hardness (750 g load) of the hybrid layers on the polyethylene terephthalate (PET) substrate were HB. The pencil hardness of the PET was B. Thus, the pencil hardness of the hybrid layers was slightly higher than that of PET. These characteristics were attributed to the sufficient dispersion of inorganic segments (siloxane network, –Si–O–Si–) and organic segments in the hybrid.

Key-words : Organic–inorganic hybrid, Silsesquioxane, Gas barrier membranes

[Received January 10, 2020; Accepted February 13, 2020]

High gas barrier membranes are a key component to a variety of applications, such as food and medical packaging, flexible electronics.[1)] Polyvinylidene chloride (PVDC) film and a plastic film coated with PVDC are utilized in packaging for high oxygen and water vapor barrier and transparency.[2)] Recently, flexible and transparent high gas barrier materials with heat resistance and good mechanical property have become increasingly important for electrical and electronic field application, such as flexible electronics and solar panels.[3)] From this point of view, PVDC must be replaced with other high gas barrier materials. Glass and ceramic can be candidates for high gas barrier materials instead of PVDC. Deposition of SiO_x and Al_2O_3 layers on polymer films using vapor deposition and chemical vapor deposition methods has been used for high gas barrier applications in food and pharmaceutical technologies.[4)] However, since glass and ceramics are brittle and it is difficult to form a thick film for high gas barrier application, thus development of a new gas barrier material having both strength and flexibility is desired.

Silsesquioxanes are organic–inorganic hybrid materials that possess both the mechanical, thermal and chemical stability of inorganic materials (glass and ceramics) and flexibility of organic materials (polymer). They are a specific type of organosilicate with the formula as $[RSiO_{1.5}]$ (R is organic substituent), having three –Si–O– bonds per Si atom and one R–Si– bond.[5),6)] The silsesquioxanes include random structures, ladder structures, cage structures, and partial cage structures.[7),8)] The silsesquioxanes with cage structures are polyhedral oligomeric silsesquioxanes (POSS).[5),6)] Polymer/silsesquioxane nanocomposites or hybrids using POSS have been studied due to significant improvements of the polymer property in mechanical, thermal, separation and gas barrier property.[9)–11)] Reported polymer/silsesquioxane materials were indicated good mechanical, thermal and gas barrier property. However, polymer/silsesquioxane nanocomposites or hybrids using silsesquioxanes with random structures were not much reported.[12),13)]

In the present paper, we wish to report the preparation of organic–inorganic hybrid gas barrier layers using 3-glycidoxypropyl silsesquioxane with random structures and p-xylylenediamine (PXDA) as cross-linking agent on plastic films by cross-linking reaction. The effect of PXDA content on oxygen and water vapor barrier properties was investigated. The pencil hardness, flexibility and transparency of the prepared membrane were also reported.

Organic–inorganic hybrid gas barrier membranes using 3-glycidoxypropyl silsesquioxane were prepared via cross-linking reaction. The coating solutions were composed of 3-glycidoxypropyl silsesquioxane with random structures (GP-100, Mn = 1780, Mw = 1950, Mz = 2170, Mw/Mn = 1.10, Mz/Mw = 1.11, Toray Fine Chemicals Co., Ltd.), PXDA and methanol (MeOH). **Table 1** shows the compositions of the coating solutions and sample name.

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Table 1. Sample name and composition of the coating solutions

Sample	Composition of the coating solution		
	GP-100 content (mass %)	MeOH content (mass %)	PXDA content (mass %)[a]
PXDA20			10
PXDA50			25
PXDA70	10	90	50
PXDA100			75
PXDA120			100

[a]PXDA content (mass %) is to GP-100.

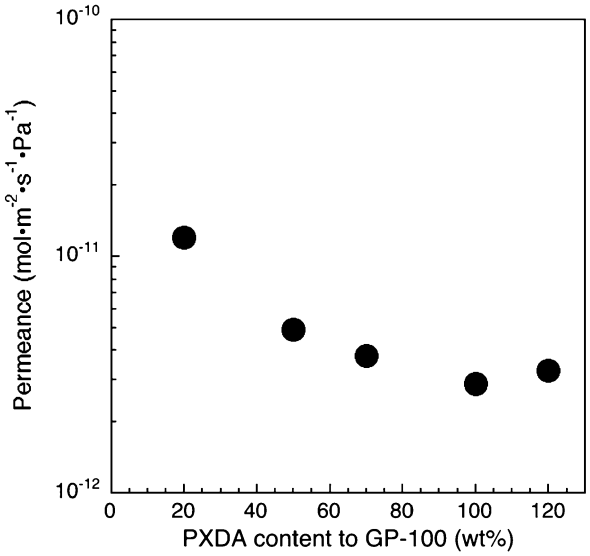

Fig. 1. Oxygen permeances of the membranes.

Commercial reagent grade chemicals were used. GP-100 was added to a half amount of MeOH at room temperature. After the mixture was stirred for 1 h, a mixture of a certain amount of PXDA (20–120 mass %) was added. Then the mixture was stirred for 3 h to obtain a homogeneous solution. The prepared coating solution was homogeneous and clear. Polypropylene (PP) films (thickness of 70 µm) were used as the substrates for oxygen permeation and polyethylene terephthalate (PET) films (thickness 25 µm) were used as the substrates for water vapor permeation. The substrate was spun at a speed of 1000 rpm for 30 s and 0.5–0.7 cc of the solution was dropped onto the substrate. Following the spin-coating procedure, the membrane was heated to 373 K for 2 h. The prepared membranes were transparent and the thickness of hybrid layers were measured by contact-type film thickness meter (Hakattaro G, Seiko EM Co. Ltd.). Oxygen permeance through the membranes at 313 K was measured by the variable pressure method.[14] Water vapor transmission rate of the membranes was measured by the dish method (JIS Z0208).

The oxygen permeances of the organic–inorganic hybrid gas barrier membranes are shown in **Fig. 1**. The oxygen permeances of the membranes decreased to PXDA100 (100 wt % PXDA to GP-100) and then increased as the amount of PXDA increased. The increased oxygen permeance of PXDA120 is due to the high concentration of PXDA, the large molecular size of PXDA, and the

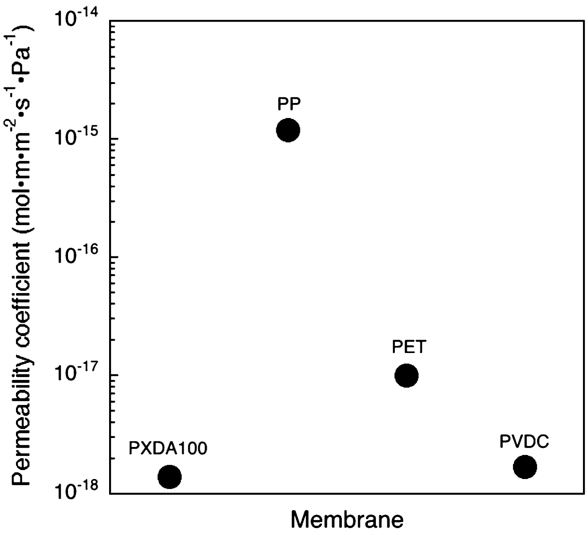

Fig. 2. Oxygen permeability coefficients of PXDA100, PP, PET and PVDC.

defects in the hybrid layer due to the rigid structure. The oxygen permeances of PXDA100 was 2.9×10^{-12} $mol{\cdot}m^{-2}{\cdot}s^{-1}{\cdot}Pa^{-1}$ and that of the PP film (substrate) was 2.0×10^{-11} $mol{\cdot}m^{-2}{\cdot}s^{-1}{\cdot}Pa^{-1}$. These values indicate that organic–inorganic hybrid coatings using GP-100 is effective in suppressing oxygen permeation.

In the case of multi-layer membranes, the following Eq. (1) is used for the permeability coefficient P of the entire system and the permeability coefficient P_n of each layer.

$$\frac{L}{P} = \frac{L_1}{P_1} + \frac{L_2}{P_2} + \cdots + \frac{L_n}{P_n} \quad (1)$$

Where L and L_n are the thickness of the entire system and each layer, respectively. Using this Eq. (1), the oxygen permeability coefficient of the organic–inorganic hybrid gas barrier layer on PP film was calculated.

Figure 2 shows the oxygen permeability coefficient of PXDA100, PP, PET and PVDC. The oxygen permeability coefficient of PXDA100 calculated from permeance and thickness was 1.4×10^{-18} $mol{\cdot}m{\cdot}m^{-2}{\cdot}s^{-1}{\cdot}Pa^{-1}$. This value was almost the same order as PVDC (1.7×10^{-18} $mol{\cdot}m{\cdot}m^{-2}{\cdot}s^{-1}{\cdot}Pa^{-1}$ at 298 K).[15]

The water vapor transmission rates (WVTR) of the organic–inorganic hybrid gas barrier layer was also measured and calculated by using Eq. (1), thickness is normalized as 25 µm. The hybrid layer thickness of PXDA20, PXDA50, PXDA70, PXDA100, PXDA120 were 0.7, 0.6, 0.6, 0.6, 0.7 µm, respectively. Each hybrid layer thickness was almost the same. WVTR of the organic–inorganic hybrid gas barrier membranes (thickness 25 µm) are shown in **Fig. 3**. The WVTR of the membranes (thickness 25 µm) also decreased to PXDA100 as the amount of PXDA increased, and then the WVTR of the membranes increased. The WVTR of the PXDA100 was $4.2\,g{\cdot}m^{-2}{\cdot}day^{-1}$, while that of the PET film was 24.0 $g{\cdot}m^{-2}{\cdot}day^{-1}$. This value for PXDA100 was in the same order as PVDC ($1\,g{\cdot}m^{-2}{\cdot}day^{-1}$).[16] This high water barrier

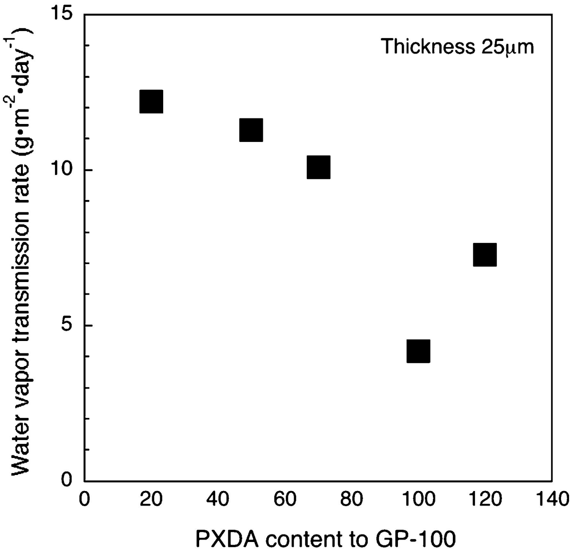

Fig. 3. WVTR of the membranes.

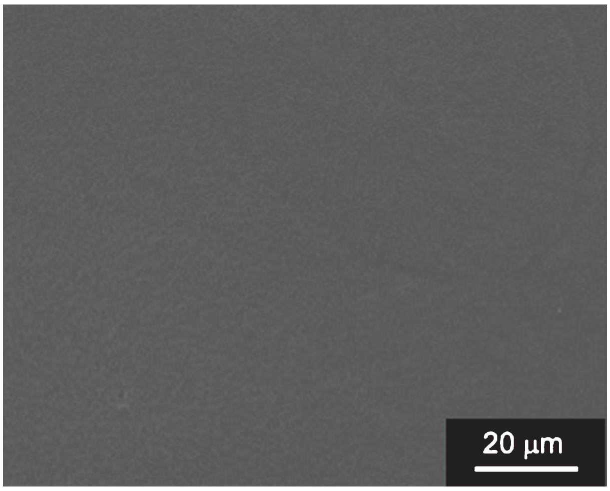

Fig. 4. SEM micrograph of the surface morphology for PXDA100.

property is to depress of the suppression of swelling due to the cross-linking reaction between amino and glycidoxy functional groups in the membrane.

Low permeance can be explained by the fact that a dense structure is formed and there are no defects, as shown in **Fig. 4**. Figure 4 shows scanning electron microscope (SEM) micrographs of the surface morphologies for PXDA100. The organic–inorganic hybrid membrane had no cracks and showed a smooth surface.

These results revealed that the organic–inorganic hybrid gas barrier membrane prepared using GP-100 has high oxygen and water vapor barrier properties. This characteristic is a new characteristic of organic–inorganic hybrid gas barrier membrane by dispersion of inorganic segment (siloxane network, –Si–O–Si–) and organic segment (epoxy resin). As the heating treatment progresses, new bonds are formed between the amino functional groups of PXDA and the glycidoxy functional groups of GP-100, creating additional cross-linking. The cross-linking through these reactions could prevent swelling of the membranes. Therefore, the hybrid coating layer could be applied to oxygen and water vapor barrier.

Table 2. Properties of the inorganic–organic hybrid gas barrier membrane

Sample	Pencil hardness	Flexibility test	Light transmittance (wave length = 550 nm)
PET	B	N.A.	86.1%
PXDA100	HB	No cracks	87.4%

N.A.: Not available.

Table 2 shows the properties of the prepared organic–inorganic hybrid gas barrier membrane (PXDA100) and PET film (substrate). Pencil hardness of the membrane was HB. This value is higher than that of PET film (B), and is due to the inorganic matrix being a main component of the membrane. For the flexibility test, a 2 mm diameter stainless steel rod was attached to the membrane, bent 10 times along the rod circle, and the membrane surface was observed with an optical microscope. No cracks observed on the membrane surface. This result indicated the prepared membrane was flexible. This flexibility and hardness are new properties of the organic–inorganic hybrid gas barrier membranes due to the dispersion of inorganic and organic segments at the molecular level and the effect of GP-100. Light transmittance (wave length = 550 nm) of the PET with organic–inorganic hybrid gas barrier membrane (PXDA100) was higher than that of PET itself. This is due to depress of light reflectance. The membrane possessed lower refractive index than PET because main component of the membrane was GP-100. Therefore, it functioned like an antireflection film. This transparency is important for applications such as display panels and packaging materials.

In conclusion, the organic–inorganic hybrid gas barrier layers using 3-glycidoxypropyl silsesquioxane on plastic films were prepared by cross-linking reaction. Oxygen permeances and water vapor transmission rates of the hybrid membranes were evaluated as the function of PXDA content. The oxygen permeability coefficient and the water vapor transmission rate (thickness 25 µm) were calculated from measured oxygen permeances and measured water vapor transmission rate of the hybrid membrane and thickness of the membrane. The calculated values revealed that the hybrid barrier membranes obtained by the cross-linking reaction show oxygen and water vapor barrier properties.

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