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Kuraoka, Koji
Miki, Kazumi

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NOTE

Gas barrier properties of inorganic–organic nanocomposite gas barrier membranes with high content of layered double hydroxide (LDH) using surface modified LDH

Koji KURAOKA^{1,2,†} and Kazumi MIKI¹

¹Graduate School of Maritime Sciences, Kobe University, 5–1–1 Fukaeminami, Higashinada, Kobe 658–0022, Japan

²Research Center for Membrane and Film technology, Kobe University, 1–1 Rokkodai-cho, Nada, Kobe 657–8501, Japan

Inorganic–organic nanocomposite gas barrier membranes with high content of layered double hydroxide (LDH) using surface modified LDH on plastic film were prepared by cross-linking reaction. The effect of LDH content on the gas barrier properties [oxygen permeation and water vapor transmission rate (WVTR)] of the membrane was investigated. The oxygen permeability coefficient of the nanocomposite layer was small, and about one-tenth of polyvinylidene chloride (PVDC) and WVTR (thickness 25 μm) of the nanocomposite layer was on the same order as PVDC. The pencil hardness (750 g load) of the nanocomposite membrane was higher than that of substrate, polyethylene terephthalate film. The value was HB. The balance between high gas barrier properties and hardness were thought to be due to the well-dispersed inorganic component (LDH) and organic component in the nanocomposite. From the results, it was found that the reported inorganic–organic nanocomposite membranes can be applied to gas barrier membranes.

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Membranes or films with a high barrier to oxygen and water vapor are important components for a variety of applications such as food and medical packaging and flexible electronics. Polyvinylidene chloride (PVDC) has been applied in packaging filed¹⁾ because PVDC films and PVDC coated plastic films show high oxygen and water vapor barrier and transparency. Recently, transparent and flexible high gas barrier materials have become increasingly important for electrical and electronic field application, such as flexible electronics and solar panels.²⁾ From this viewpoint, new high gas barrier materials should be developed. Glass and ceramic can be candidates for high gas barrier materials instead of PVDC. Deposition of SiO_x and Al_2O_3 films on plastic films using vapor deposition and chemical vapor deposition methods has been used for high gas barrier applications in the food and medical packaging fields.³⁾ Organic–inorganic hybrids,^{4),5)} polymer/clay composites,^{6)–8)} and polymer/graphene composites⁹⁾ were also candidates for high gas barrier applications.

Polymer/clay nanocomposites as advanced plastic materials have been studied by significantly improving polymer properties with low clay content in mechanical and thermal properties^{2),10)} and gas barrier properties.^{6),7),11)} The preparation of polymer/clay nanocomposites with higher clay

volumes may be a promising way to further improve properties. However, it is difficult to form a clay-rich nanocomposite with transparency and flexibility, which is rarely reported in the literature.^{12)–14)} Transparent and flexible clay films have been reported.^{13),14)} Even if the clay content was 80 mass %, it had high transparency and high flexibility. The prepared film showed thermal stability and gas barrier properties. However, the long processing time of this film preparation can limit its practical applicability.

In the present paper, we focused on layered double hydroxide (LDH), whose structure is generally expressed as $[\text{M}_\text{I}^{2+}_{1-x}\text{M}_\text{II}^{3+}_x(\text{OH})_2][(\text{A}^{n-})_{x/n}\cdot y\text{H}_2\text{O}]$ (M_I^{2+} and M_II^{3+} are divalent and trivalent metal ions respectively, A^{n-} is interlayered anion). Incorporating LDH nanoplatelets (inorganic nanosheets) into polymers significantly improves the mechanical, gas barrier, optical, and thermal properties of polymer systems.^{8),15)} The assembly of small amounts of organic compounds and LDH nanoplatelets in the preparation of gas barrier membranes has the advantage that it is expected to extend the diffusion path of gas molecules due to the high aspect ratio and impermeability of LDH nanoplatelets. We would like to report the preparation of inorganic–organic nanocomposite gas barrier membranes using surface modified LDH with high inorganic compound content on plastic film by cross-linking reaction. The effect of LDH content on oxygen and water vapor barrier properties was investigated.

[†] Corresponding author: K. Kuraoka; E-mail: kuraoka@maritime.kobe-u.ac.jp

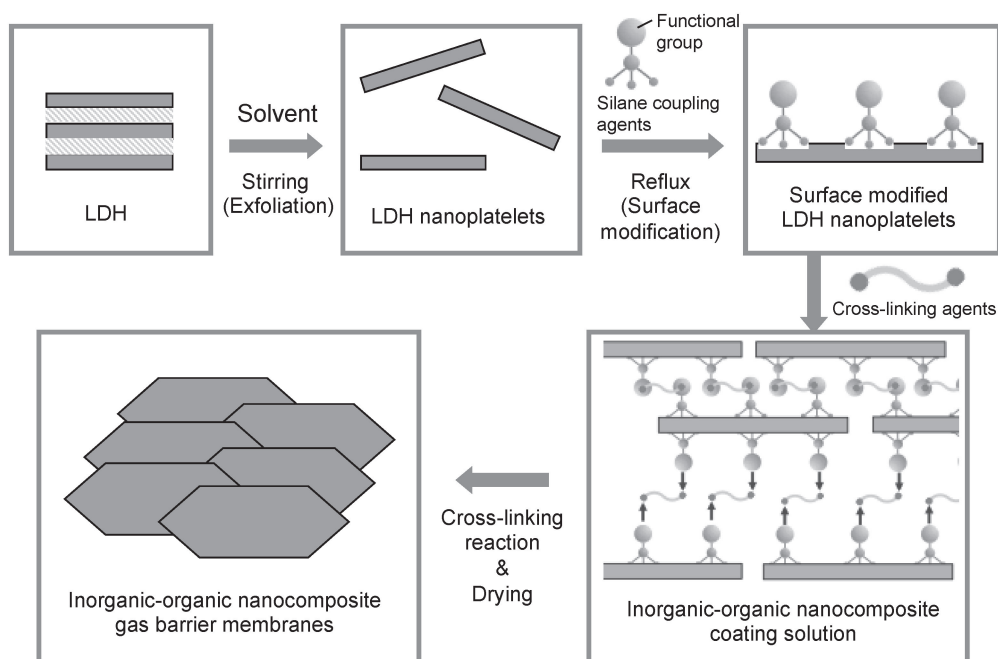


Fig. 1. Schematic diagram of experimental process.

Table 1. Sample name and composition of the coating solutions

Sample	Composition of the coating solution		
	LDH content in FA (mass %)	UPTMOS content (mol %) ^a	Denacol content (mol %) ^b
De10	2	100	10
De25			25
De50			50
De75			75
De100			100

^a100 mol % UPTMOS means that the molar ratio of hydroxyl group in LDH to ethoxygroup in UPTMOS is 1:1.

^bDenacol content (mol %) is to UPTMOS.

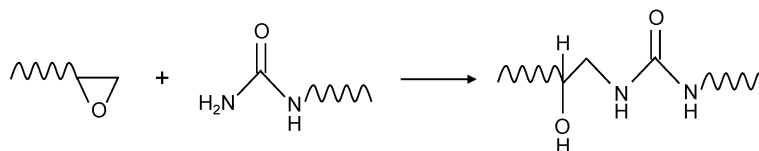
Figure 1 shows inorganic–organic nanocomposite gas barrier membranes using surface modified LDH were prepared via cross-linking reaction. The coating solutions were composed of LDH (T-HTB610, Tayca Corporation, particle size: about 500 nm), 1,4-Butanediol diglycidyl ether (Denacol, Denacol EX-214L, Nagase ChemteX Corporation), 3-ureidopropyltrimethoxysilane (UPTMOS) and formamide (FA). The compositions of the coating solutions and sample name were shown in Table 1.

A typical preparation of membrane (De25) is as follows. A mixture of LDH (0.4 g) and FA (19.6 g) was stirred for 48 h to exfoliate LDH. After the LDH was dispersed in FA for 48 h, a transparent colloidal dispersion was obtained, and the Tyndall light scattering were observed in the dispersion. Then UPTMOS (0.72 g) was added to the solution. The mixture was heated at 313 K for 24 h to obtain a homogeneous solution, and then Denacol (0.16 g) was added at room temperature. The prepared coating solution was homogeneous and clear. LDH content of the coating solution (De25) without FA (solvent) was 31.3 mass %. This means that high clay content membranes can be

produced. Polypropylene (PP) films (thickness: 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 3000 rpm for 30 s and 1.0 cc of the sol was dropped on to the substrate. Following the spin-coating procedure, the membrane was heated to 373 K for 12 h. Thermal cross-linking reaction between ureide or amine and epoxy groups is a well-known reaction and is used to prepare cross-linked polymer.¹⁶⁾ The reaction scheme is shown in Scheme 1. A one-step reaction between the ureido of UPTMOS and the epoxy group of Denacol produces –CO, –N, –NH and –OH, creating covalent and hydrogen bonding sites.

Oxygen permeation through the membranes at 313 K was measured by a variable pressure method.¹⁷⁾ The water vapor transmission rate (WVTR) of the membranes was measured by dish method (JIS Z0208).

Figure 2 shows the oxygen permeances of the inorganic–organic nanocomposite gas barrier membranes. As the amount of Denacol increased, the oxygen permeances of the membranes decreased to De25 (25 mol % Denacol to UPTMOS) and then increased. The increased oxygen permeance of De50, De75 and De100 is thought to be due to the high concentration of non-cross-linked Denacol and the large molecular size of Denacol. The decrease in oxygen permeance of De25 is due to the dense structure of the nanocomposite layer caused by sufficient cross-linking between LDH and Denacol. The cross-linking reaction between ureide groups of surface modified LDH nanoplatelets and epoxy groups of Denacol occurs ureide groups:epoxy groups = 1:1 (in molar ratio) as shown in Scheme 1. This means De50 (Denacol: 50 mol %) is ideal composition to react all functional groups. However, each



Scheme 1. Reaction scheme of cross-linking reaction between an epoxy and an ureide group.

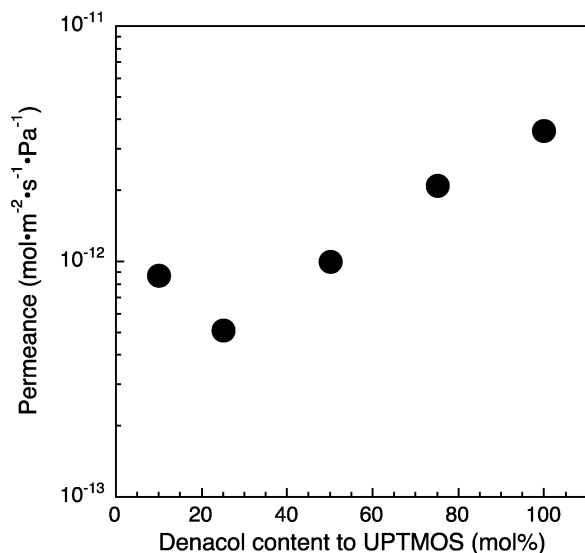


Fig. 2. Oxygen permeances of the membranes.

surface modified LDH nanoplatelets has several ureide groups, in order to form a cross-linking structure, it is sufficient that at least one functional group reacts, and not all functional groups need to react. The oxygen permeances of De25 was $5.2 \times 10^{-12} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, and that of the PP film (substrate) was $2.0 \times 10^{-11} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. These values indicate that inorganic–organic nanocomposite coatings using surface modified LDH are effective in suppressing oxygen permeation. Observation of the surface of De25 by a scanning electron microprobe (SEM) revealed a smooth surface without cracks as shown in Fig. 3. Thus, the low permeation can be explained by the formation of dense structures and reduced defects.

The oxygen permeability coefficient of De25, PP, PET and PVDC as shown in Fig. 4. The oxygen permeability coefficient of De25 calculated from thickness and permeance was $1.6 \times 10^{-19} \text{ mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. This value was about one-tenth of PVDC ($1.7 \times 10^{-18} \text{ mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at 298 K).¹⁸⁾

Figure 5 shows WVTR of the inorganic–organic nanocomposite gas barrier membranes (thickness 25 μm) with a thickness normalized to 25 μm . The nanocomposite layer thickness of De10, De25, De50, De75, De100 were 0.4, 0.3, 0.3, 0.4, 0.4 μm , respectively. Each nanocomposite layer thickness was almost the same. Similar to oxygen permeance, the WVTR of the membranes (thickness 25 μm) also decreased to De25 as the amount of Denacol increased and then increased. The WVTR of De25 was $5.0 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$, and that of the PET film (substrate) was $24.0 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. This value was the same order as PVDC

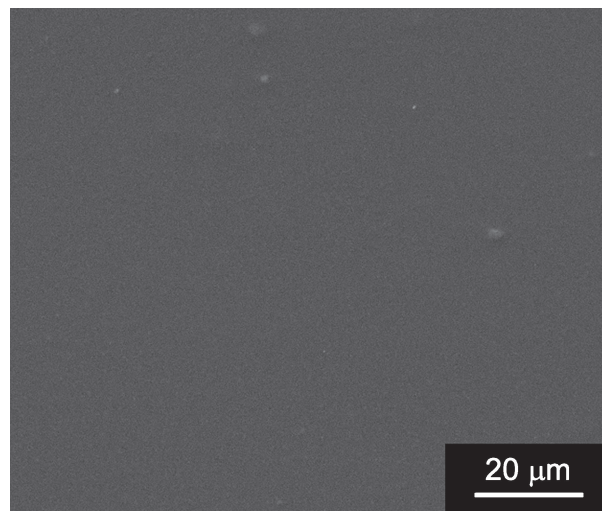


Fig. 3. SEM micrograph of the surface morphology for De25.

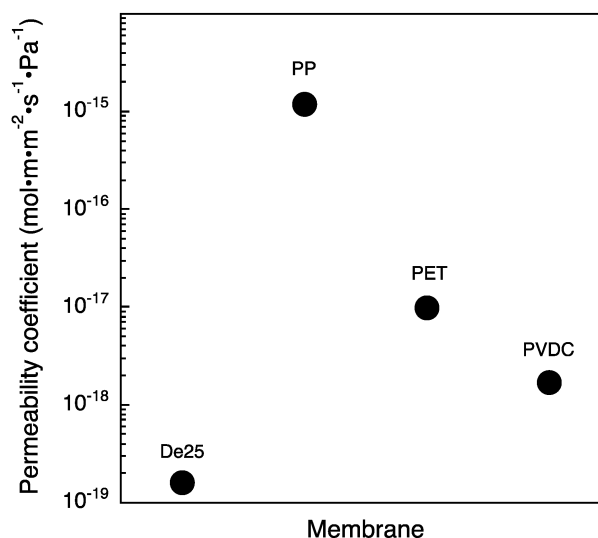


Fig. 4. Oxygen permeability coefficients of De25, PP, PET and PVDC.

($1 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$).¹⁹⁾ The reported WVTR of epoxy resins was $10\text{--}14 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ (thickness 0.1 mm).²⁰⁾ It means that the calculated WVTR (thickness 25 μm) is $40\text{--}56 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. This value is much higher than the De25 value. This high value is due to epoxy resin swelling caused by amino and hydroxyl groups in the molecular structure.

The inorganic–organic nanocomposite gas barrier membranes prepared using surface modified LDH have high oxygen and water vapor barrier properties from these results. This characteristic is a noble property of inorganic–organic nanocomposite gas barrier membrane by high

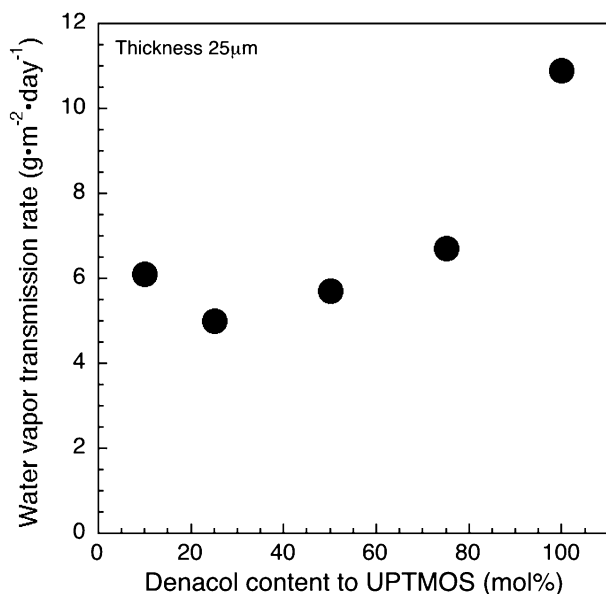


Fig. 5. WVTR of the membranes.

dispersion of inorganic component (LDH) and organic component (epoxy resin). As heat treatment progresses, new bonds are formed between ureide groups of surface modified LDH and epoxy groups of Denacol, creating additional cross-linking. These cross-linking due to reaction can prevent the membrane from swelling. Therefore, the nanocomposite membranes can exhibit high oxygen and water vapor barrier properties.

The other properties of the prepared inorganic–organic nanocomposite gas barrier membrane (De25) were evaluated. The Pencil hardness of the membrane was HB. Due to the high content of inorganic compounds (LDH nanoplatelets) in the membrane, this value was higher than that of the PET substrate (B). For the flexibility test, a 2 mm diameter stainless rod was attached to the membrane, bent 10 times along the rod circle, and then the membrane surface was observed with optical microscope. The membrane surface without cracks was observed. This result means that the prepared membrane is flexible and adhesion between the nanocomposite coating and the substrate was strong enough. This flexibility with hardness is a new property of the inorganic–organic nanocomposite gas barrier membrane due to the high dispersion of inorganic and organic components and the effect of LDH nanoplatelets. Light transmittance (wave length = 550 nm) was measured by ultra violet-visible spectrophotometer. Light transmittance of the inorganic–organic nanocomposite gas barrier membrane (De25) coated on the PET (86.4%) was slightly higher than that of PET itself (85.9%) because the LDH content in the membrane was high and the refractive index of the membrane was lower than PET. Therefore, it functioned like an antireflection film. This transparency is important for practical application in packaging filed and flexible electronics filed.

In conclusion, we investigated that gas barrier properties of inorganic–organic nanocomposite gas barrier membranes using surface modified LDH prepared by cross-linking reaction. The oxygen permeances and WVTR of the nanocomposite membranes were evaluated as a function of the Denacol content. The oxygen permeability coefficient and the WVTR (thickness 25 μm) indicated that the nanocomposite barrier membrane obtained by the cross-linking reaction showed higher oxygen and water vapor barrier properties.

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