

Scratch resistance and oxygen barrier properties of acrylate-based hybrid coatings on polycarbonate substrate

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Abstract—Organic/inorganic hybrid coating materials were synthesized using acrylate end-capped polyester, 1,6-hexanediolacrylate, tetraethoxysilane (TEOS), and 3-trimethoxysilylpropylmethacrylate (TMSPM). The hybrid materials were cast onto a polycarbonate (PC) substrate and cured by UV irradiation to give a hybrid film with covalent linkage between the inorganic and the organic networks. The coating layer was characterized by FT-IR and ²⁹Si-NMR, and pencil hardness and oxygen permeation rate of coated films were investigated. The pencil hardness of all samples examined in this study was higher than 1H, whereas that of uncoated PC substrate was 6B. The hardness enhancement after coating may due to incorporation of organic acrylate resin. The oxygen permeability coefficient of the film coated with hybrid material on 3-aminopropyltriethoxysilane (APTEOS) pretreated polycarbonate substrate was 1.67×10^{-3} GPU, the lowest value in this work, whereas that of uncoated PC substrate was 8.07×10^{-3} GPU. The lower oxygen permeation rates of these films are attributed to the good adhesion between organic/inorganic hybrid coating layer and PC substrate and a dense structure induced by an increase of network density.

Key words: Oxygen Permeation, Hardness, TMSPM, Polycarbonate

INTRODUCTION

Polymer films have been used widely for various industries because of their transparency, easy processability, flexibility, lightness, and so on. Recently the uses of transparent resins such as polycarbonate (PC) and polymethylmethacrylate (PMMA) have been investigated as a replacement for the glass substrate for flexible display applications [1]. Most of their properties are desirable in the flat panel display industry [2]. However these films have poor abrasion resistance, high permeability of water vapor and variable gases, and UV transmission. Therefore it is important to improve the abrasion resistance and gas barrier properties of plastic substrate. On the other hand, inorganic materials have high thermal and mechanical strength and low gas permeability. It is thus possible to prepare new kinds of materials with good abrasion resistance and high barrier properties by the combination of organic and inorganic elements [3]. Organic modified ceramics (ORMOCER) constitute the organic functional groups incorporated into the inorganic silicate, and have the possibility to prepare the new hybrid materials [4,5]. By systematically varying the inorganic and the organic network densities and the polarity of the hybrid polymer material matrices, it is possible to develop coating materials with advanced properties. A variety of organic/inorganic hybrid materials, with widespread uses and properties, have been prepared using the sol-gel method [6,7]. Sol-gel process is known to be one of the practical methods for preparing organic-

inorganic hybrid materials from alkoxysilanes. Schimdt et al. [8,9] have developed hard coatings using metal or semimetal oxide colloids such as alumina, zirconia, titania, or silica together with epoxy and methacrylate functionalized alkoxysilanes as major components. Sol-gel process is also suitable for coating the thin films on organic polymer substrates due to the mild reaction conditions of metal oxide network. It was reported that hybrid materials forming a thin coated layer on polymer films reduced gas or vapor permeabilities and showed good mechanical strength [10]. Nass et al. [11] investigated the physical properties of ORMOCER coating on polymer substrates by sol-gel process, and Wang and Wilkes [12] reported that the organic/inorganic hybrid materials from the ORMOCER are useful for various coatings on organic polymer substrates.

Among various alkoxysilanes, 3-trimethoxysilylpropylmethacrylate (TMSPM) has been favored as a silane coupling agent of sol-gel derived hybrids since the methacrylate group easily polymerizes under UV irradiation or thermal treatment with other components. Bonilla et al. [13] investigated organic/inorganic hybrid interpenetrating networks composed of polyurethane, PMMA and silica. In their work, TMSPM was used as a coupling agent for preparing optically transparent films. Rubio et al. [14] reported that TMSPM was used to compatibilize the organic and inorganic components for preparing PMMA/silica hybrid materials.

In this study, organic/inorganic hybrid coatings based on UV curable acrylate end-capped polyester were formed on PC substrate, and were characterized by analysis of scratch resistance and gas permeabilities. The effect of composition of the coating sol on these properties was discussed.

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EXPERIMENTAL

1. Film Preparation

Before applying the coating, the bisphenol A polycarbonate substrates (GE Plastic Co.) were treated with isopropylalcohol to remove the traces of grease, and then dried at room temperature. In this study three kinds of coating materials were investigated. First, organic acrylate coating materials were prepared. Acrylate end-capped polyester, Ebecryl 830 (EB830, SK Cytec Co.) and 1,6-hexanedioldiarylate (HDDA, Sigma Co.) were mixed with ethyl acetate. The weight ratio of the mixture of EB830 and HDDA to ethyl acetate was maintained at 4, and the ratio of EB830 to HDDA was varied. To the mixture was added 4 wt% of Darocur1173 as a photoinitiator, and 1 wt% of PA-57 as a surfactant. In this paper, organic coating materials synthesized as above are designated as CONSTITUENT I. Second, ORMERCER coating materials derived from tetraethoxysilane (TEOS, 98%, Sigma Co.) and 3-trimethoxysilylpropyl-methacrylate (TMSPM, 98%, Sigma Co.) were synthesized. One mole of TEOS was mixed 4 mol of ethanol and 4 mol of acidic water (pH 2), and the solution was stirred for 2 hrs. And then TMSPM was dropped into the prehydrolyzed TEOS. In this study, the weight ratios of TEOS : TMSPM were 1 : 1, 2 : 1, 3 : 1, and 4 : 1. The mixture was stirred in closed vessel at room temperature for 24 hrs. ORMERCER coating materials are designated as CONSTITUENT II in this paper. Third, organic/inorganic hybrid coating materials were prepared as follow. The desired amounts of CONSTITUENT I and TMSPM were mixed, and stirred for 3 hrs. To the mixture was added prehydrolyzed TEOS. The final mixture was stirred in closed vessel at room temperature for 24 hrs. The weight ratio of CONSTITUENT I and CONSTITUENT II in the final hybrid mixture were 1 : 3, 1 : 2, 1 : 1, 2 : 1 and 3 : 1. In this paper, hybrid coating materials synthesized as above are designated as CONSTITUENT III. The coating was carried out on pretreated PC substrate by spin coater. The coated films were cured by using UV irradiation for 3 min. Light intensity was measured to be 3,330 mJ/cm². The thickness of coating layer measured using a micrometer was 2-8 μ m.

2. Characterizations

The coating layer was characterized Fourier transform infrared (FT-IR, JASCO-430), ²⁹Si nuclear magnetic resonance spectroscopy (²⁹Si-NMR, Bruker Avance II), and pencil hardness test device (Yoshimtsu C 221D). FT-IR spectra was obtained in transmission mode between 400 and 4,000 cm⁻¹. The coating materials, deposited on silicon wafer and cured by UV irradiation, were pulverized mixed with KBr and pelletized for infrared spectroscopy. Molecular structure of coating layer was determined from 500 MHz ²⁹Si-NMR spectra recorded on a Bruker Avance II solid-state NMR spectrometer by using the cross-polarization combined with magic angle spinning (CP/MAS) technique. The magic angle spinning frequency was 5 kHz. The ²⁹Si experiments were performed with a contact time of 3 ms, delay time of 10 s and a number of scans of 3072. Pencil hardness was measured under the constant weight (1 kg) in order to compare surface hardness of coating films based on ASTM D3363. The pencil is held firmly against at a 45° angle to horizontal coating surface and pushed away from the operator. From soft (9B) to hard (9H), the hardest pencil grade that does not damage to the coating surface was termed as the pencil hardness. The morphology of coating surface was examined with scanning electron

microscopy (JEOL JSM-6701F).

3. Permeability Measurements

Permeability measurements were made for pure O₂ using the apparatus employed in our laboratory. The procedure has been described in detail at previous work [15,16]. The permeability coefficient (P) was calculated with following expression,

$$P = \frac{22,414 L V \Delta p}{RT A p_1 \Delta t}$$

Where V is the volume of measuring chamber, T is the temperature, p₁ is the upstream pressure of a penetrant gas, R is the universal gas constant, and A and L are the cross sectional area and the thickness of the film, and $\Delta p/\Delta t$ is the rate of change in downstream pressure. The permeability coefficient, P is usually expressed in GPU, which is corresponding to 10⁻⁶ cm³ (STP)/cm²·sec·cmHg.

RESULTS AND DISCUSSION

1. Structural and Morphological Analysis

Organic/inorganic hybrid materials were synthesized using acrylate end-capped polyester (EB830), HDDA as a reactive solvent, TMSPM as a coupling agent between organic and inorganic phase, and TEOS as a inorganic precursor. The hybrid materials were cast onto a pretreated PC substrate and cured by UV irradiation to give a hybrid film with covalent linkage between organic and inorganic networks.

FT-IR spectroscopy has been used to study hydrolysis and condensation reactions of silanes and the degree of formation of the organic network through polymerization of acrylate groups. Fig. 1 shows the FT-IR spectroscopy of CONSTITUENT II. The large broad band around 3,000-3,650 cm⁻¹ is assigned to the OH vibration of silanol originated from the hydrolysis. As the amount of TEOS is increased, the area of this absorption band at 3,000-3,650 cm⁻¹ is decreased. It can be concluded that the more siloxane bonds are formed when the more sufficient TEOS is added. The bands at 453 cm⁻¹ (δ , Si-O-Si), 753 cm⁻¹ (ν s, Si-O-Si) and 1,075 cm⁻¹ (ν as, Si-O-Si) indicate formed siloxane linkages as other literatures [17]. Fig. 2

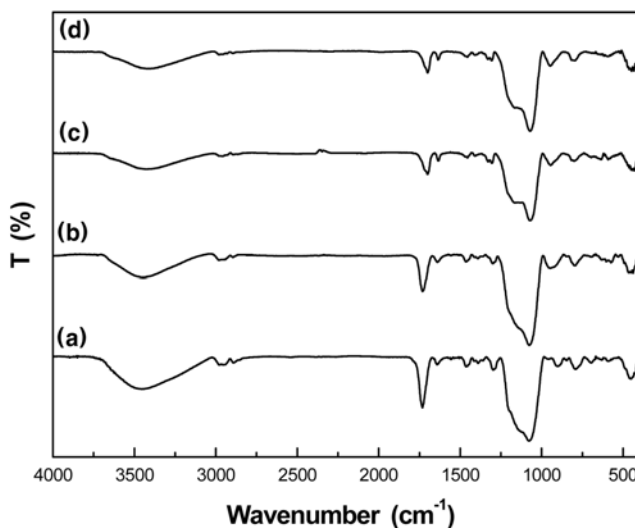


Fig. 1. FT-IR spectra of constituent II by varying the weight ratio of TEOS and TMSPM (a) 1 : 1 (b) 2 : 1 (c) 3 : 1 (d) 4 : 1.

shows FT-IR spectroscopy of CONSTITUENT III. The broad strong band at $3,000\text{--}2,850\text{ cm}^{-1}$ and intense band at $1,465\text{ cm}^{-1}$ correspond to the C-H stretching vibration and the $\text{-CH}_2\text{-}$ stretching vibration of

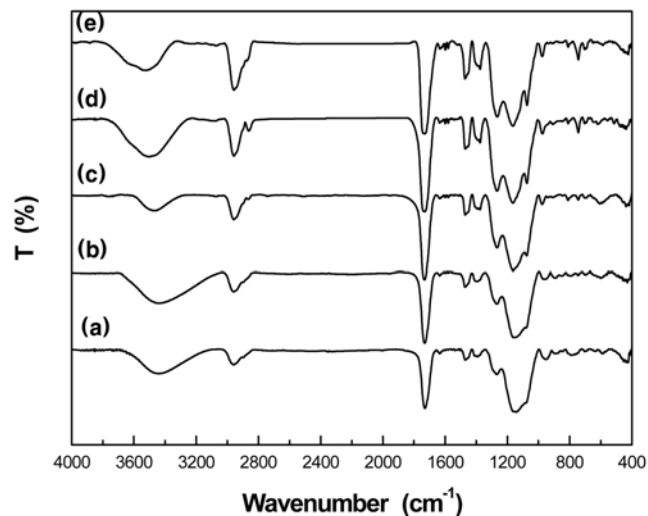


Fig. 2. FT-IR spectra of constituent III by varying the weight ratio of constituent I and constituent II (a) 1 : 3 (b) 1 : 2 (c) 1 : 1 (d) 2 : 1 (e) 3 : 1.

alkanes, respectively. As the ratio of CONSTITUENT I to CONSTITUENT II is increased, the absorption intensity of these peaks

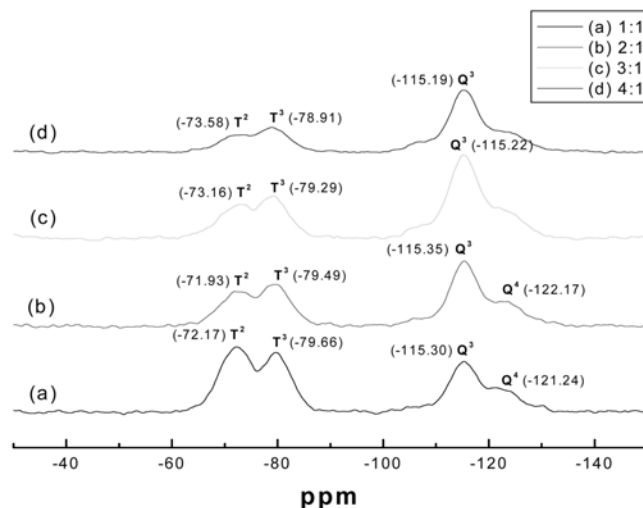


Fig. 3. Solid state ^{29}Si -NMR spectra of TMSPM-silica sol (constituent II) coated film (a) TEOS : TMSPM=1 : 1 (b) TEOS : TMSPM=2 : 1 (c) TEOS : TMSPM=3 : 1 (d) TEOS : TMSPM=4 : 1.

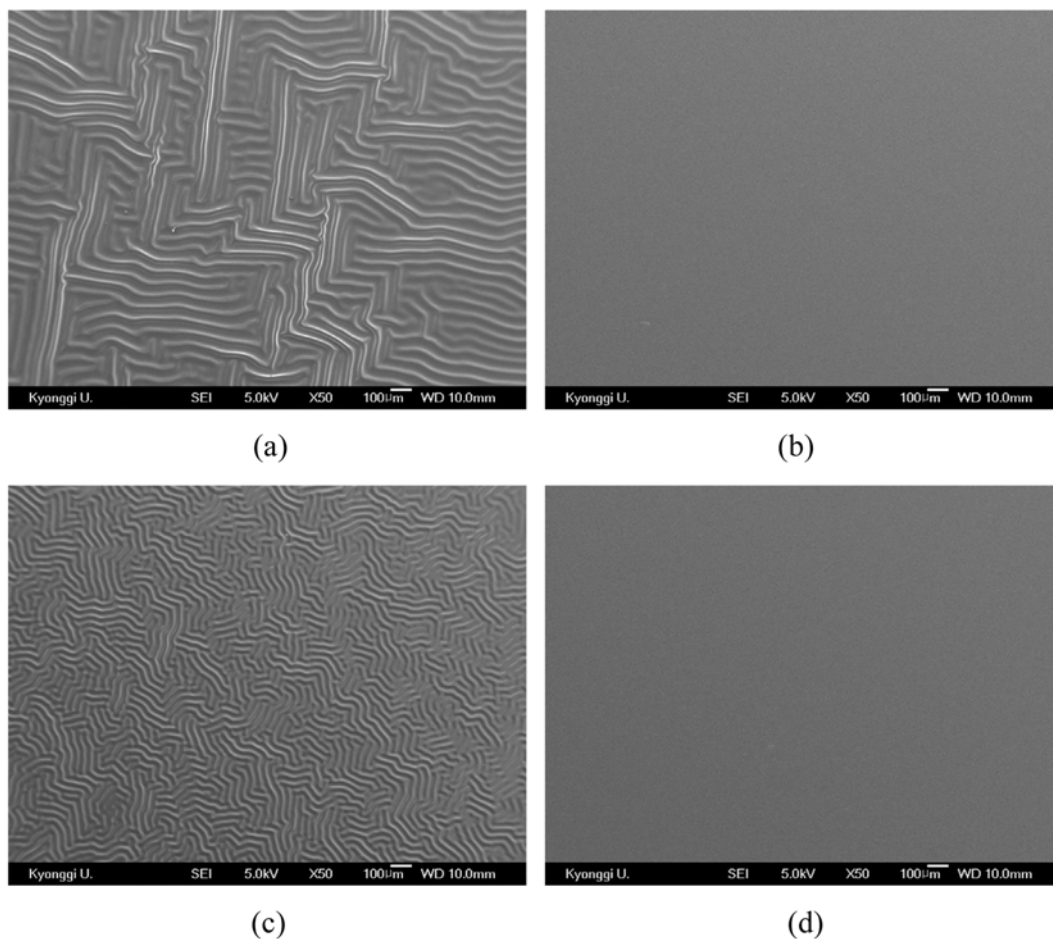


Fig. 4. SEM photographs of the surface of coated PC films (a) EB830 : HDDA=2 : 1 (b) EB830 : HDDA=4 : 1 (c) constituent I : constituent II=2 : 1 (d) constituent I : constituent II=1 : 1.

was increased. And there was very weak absorption band at $1,636\text{ cm}^{-1}$, characteristic for an unreacted acrylate double bond. Therefore it can be concluded that the formation of the organic network through polymerization of acrylate groups is almost completed.

^{29}Si -NMR spectroscopy provides additional structural information regarding the nature of silicon species present and the various local environments of the atoms involved in the polysiloxane backbone and the attachment of the pendant groups in the hybrid material. Fig. 3 represents solid state ^{29}Si -NMR spectra of coating films formed from CONSTITUENT II with various ratios. Seven peaks for silicon atoms with different degrees of condensation are possible. T and Q notation was used for the different silicate species in NMR spectroscopy. Silicon site are denoted as T^y and Q^y (where T indicates a trifunctional silicon site in TMSPM, Q indicates a tetrafunctional silicon site in TEOS and y is the number of siloxane bridges attached to the silicon site). And the assignments are based on previous studies of analogous systems [18,19].

As shown in Fig. 3, the absence of T^0 , T^1 , Q^0 , Q^1 and Q^2 peaks in all of spectra suggested that these materials were highly condensed. In this study, the represented values are slightly shifted relative to the value of previous studies [18,19]. This shift is not sufficient to demonstrate a change in the degree of condensation of the silicon atom, but may result from an increase in the steric hindrance around the silicon atom due to growth of the oligomers [19]. As the amount of TEOS is increased, T^2 and T^3 peaks decreased, whereas Q^3 and Q^4 peaks increased until the weight ratio of TEOS to TMSPM ratio is 2. The reason may be due to slow hydrolysis of TEOS [20].

The surface morphology of coated film has been investigated with various compositions of coating solution. Fig. 4 represents SEM photographs of the surface of coated PC films. In this study, the coated film prepared from CONSTITUENT I of EB830 : HDDA = 2 : 1 has opaque surface after UV curing. However the film coated with CONSTITUENT I (EB830 : HDDA = 4 : 1) has clear and transparent surface. For the films coated with CONSTITUENT III, the higher ratio of CONSTITUENT I induces more opaque and thicker coating surface. This may be due to high crosslink density of organic constituents. As the ratio of CONSTITUENT II to CONSTITUENT I is increased to 3, coating surface had some cracks. In general, the increasing of inorganic precursor and alkoxy silane content in organic/inorganic hybrid materials leads to adding more Si-O-Si segments, which induces the more rigid hybrid network.

2. Pencil Hardness and Oxygen Permeation

The hardness of the coatings was determined using a calibrated set of drawing pencils that range from 9B, the softest, to 9H, the hardest. The pencil hardness of all samples obtained in this study was higher than 1H, whereas that of uncoated PC substrate was 6B. This confirms the effectiveness of the scratch resistance of these coatings. The pencil hardness of coated films with CONSTITUENT I and CONSTITUENT III, respectively was 2H-3H, while that of CONSTITUENT II was 1H at whole composition. Other literature reported that incorporation of TEOS together with silane functionalized organics greatly improved the abrasion resistance due to the Si-O-Si backbone of the inorganic network [21]. In contrast to other works, the results of our work may explain that the hardness enhancement by organic acrylate resin is predominant than the formation of inorganic network, and hardness enhancement is restrictive due to inherent soft surface property of polycarbonate film itself. Although

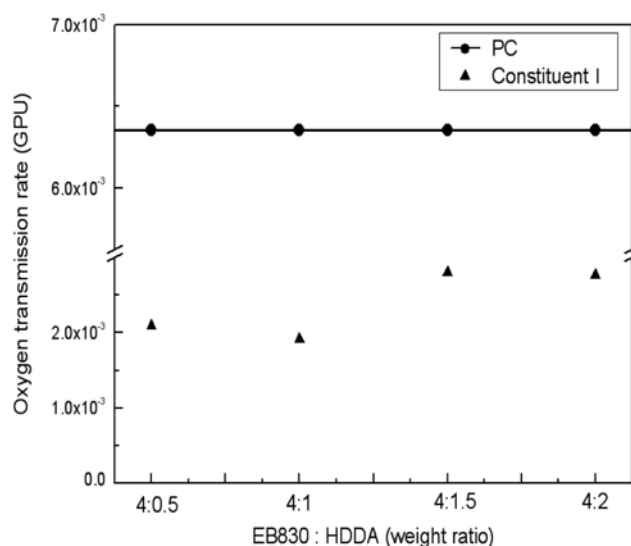


Fig. 5. Oxygen transmission rate of constituent I coated film with various weight ratios of EB830 and HDDA.

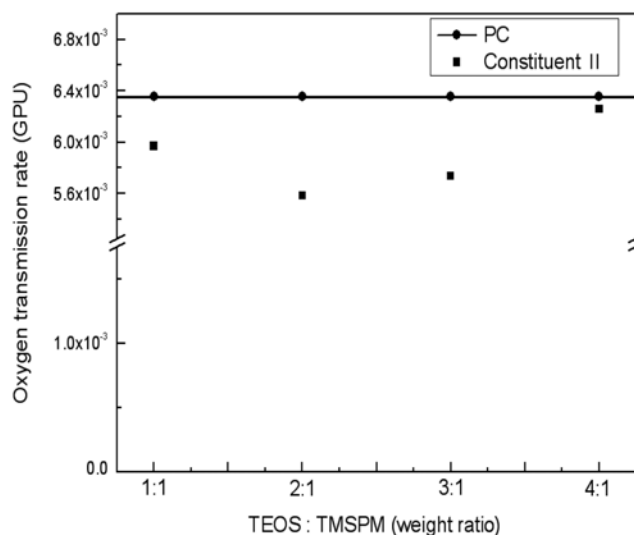


Fig. 6. Oxygen transmission rate of constituent II coated film with various weight ratios of TEOS and TMSPM.

pencil hardness test by ASTM D3363 has been popularly used through various industries, the result of such a simple test cannot give sufficient information about inherent hardness and scratch behavior. It was reported that there are many factors such as elastic modulus, fracture toughness, friction coefficient and so on that may affect inherent hardness of coating [22]. Therefore it can be suggested that more quantitative analysis would be considered as our further subsequent works.

The oxygen permeation rates of coated PC films with various amounts of constituents are illustrated in Fig. 5-8. The permeability coefficient of oxygen for uncoated PC substrate was 8.07×10^{-3} GPU. As shown in Fig. 5, the permeability coefficient for the film coated with CONSTITUENT I (EB830 : HDDA = 4 : 1) was 1.91×10^{-3} GPU. Also it can be seen that the permeability coefficient is slightly increased with the amount of HDDA. This result can be attributed to

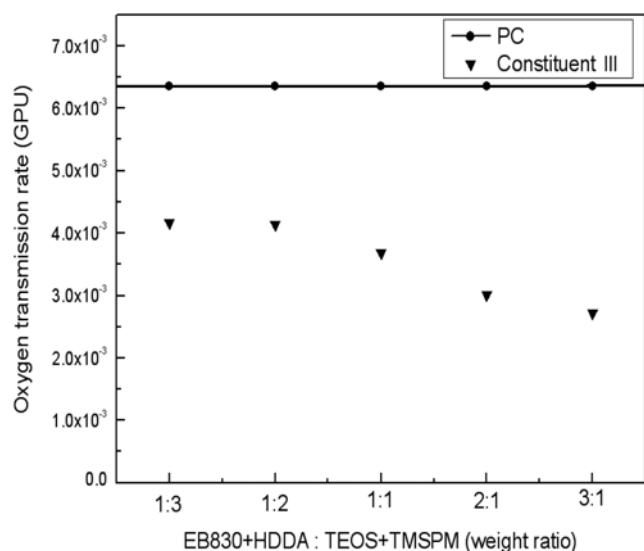


Fig. 7. Oxygen transmission rate of constituent III coated film with various weight ratio of constituent I and constituent II.

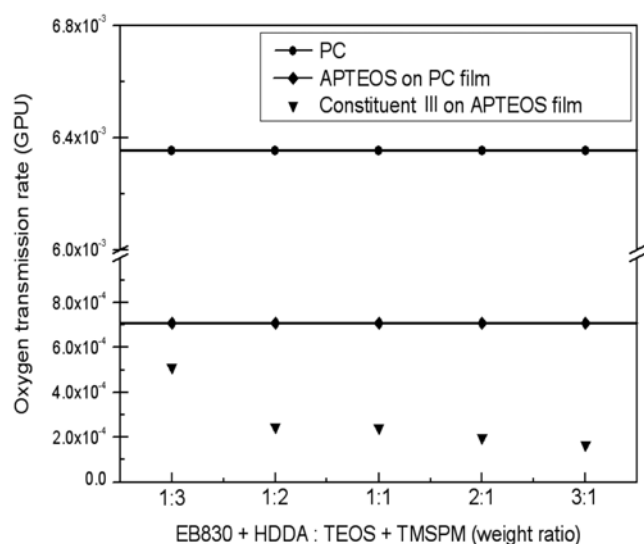


Fig. 8. Oxygen transmission rate of constituent III coated APTEOS film with various weight ratio of constituent I and constituent II.

linear alkyl chain structure of HDDA. HDDA is subject to form the only linear crosslink. It means the decrease of organic network density and the larger available free volume for oxygen permeation. Fig. 6 represents oxygen permeability coefficient of the film coated with CONSTITUENT II, compared with that of uncoated PC substrate. The oxygen permeability coefficient for TEOS : TMSPM = 2 : 1 shows the lowest value of 5.58×10^{-3} GPU. It is well known that ORMERCER coating is more effective in suppressing the gas permeation than organic coating. However in this study, even if inorganic crosslinks are successfully formed, as confirmed by structural analysis, the oxygen permeation rates of the films coated with CONSTITUENT II had higher values than CONSTITUENT I. One of the reasons can be a poor adhesion between coating layer and

PC substrate. At previous work, we reported the significance of the adhesion between coating layer and polymer substrate to enhance the gas barrier property [23]. Fig. 7 represents oxygen permeability coefficient of the film coated with CONSTITUENT III, organic/inorganic hybrid coating materials. For preparing organic/inorganic hybrid coating materials, the weight ratio of EB830 and HDDA in CONSTITUENT I was 2 : 1, and that of TEOS and TMSPM in CONSTITUENT II was 4 : 1, according to the permeation result of the film coated with CONSTITUENT I and CONSTITUENT II, respectively. It can be seen that as CONSTITUENT I content of these hybrid materials is increased, the oxygen permeability decreased from 4.17×10^{-3} GPU up to 2.72×10^{-3} GPU. These values are higher than permeability coefficients for CONSTITUENT I. This can be also explained the poor adhesion between coating layer and PC substrate, as stated above. In this work, in order to settle the adhesion problem, PC substrates were pretreated with 3-aminopropyltriethoxysilane (APTEOS). APTEOS has been one of the most widely applied coupling agents and adhesion promoters [24-26]. APTEOS (98%, Sigma Co.) was mixed with solvent to molar ratio of 15 and then distilled water was added to the mixture for hydrolysis. The molar ratio of water to APTEOS was 3. After being stirred for 24 hrs at room temperature in closed vessel, the solution was used for spin coating. APTEOS coated film was dried for 24 hrs at 50°C before applying the coating with CONSTITUENT III. Fig. 8 shows oxygen permeability coefficient of APTEOS coated PC film and CONSTITUENT III coated APTEOS film with various weight ratio of CONSTITUENT I and CONSTITUENT II. The oxygen permeability coefficient of APTEOS coated film was 7.07×10^{-4} GPU. After coating with various composition of CONSTITUENT III onto APTEOS coated PC film, the oxygen permeability was decreased to 1.67×10^{-4} GPU, which is the lowest value among the films examined in this work. The lower permeation rates of APTEOS pretreated films are attributed to the good adhesion between organic/inorganic hybrid coating layer and PC substrate and a dense structure induced by an increase of network density. It can be concluded that both the pretreatment with APTEOS and the coating with organic/inorganic hybrid materials are essential to enhance the oxygen barrier property of PC substrate.

CONCLUSION

Organic/inorganic hybrid coating materials were successfully prepared with covalent links by reacting EB830, HDDA, TEOS and TMSPM, which were confirmed by FT-IR and ^{29}Si -NMR analysis. By varying the ratio of the organic and inorganic constituents, it was possible to develop coating materials with improved oxygen barrier property and scratch resistance. The coating of acrylate functionalized hybrid materials was effective in enhancing the scratch resistance and oxygen barrier property. The pencil hardness of all of the samples examined in this study was higher than 1H, whereas that of uncoated PC substrate was 6B. This confirms the effectiveness of the scratch resistance of these coatings. In this work, the hardness enhancement by organic acrylate resin was predominant than the formation of inorganic network by ORMERCER materials. The oxygen permeability coefficient of the film coated with hybrid material on APTEOS pretreated polycarbonate substrate was 1.67×10^{-4} GPU, whereas that of uncoated PC substrate was 8.07×10^{-3} GPU.

The lower permeation rates of these films are attributed to the good adhesion between organic/inorganic hybrid coating layer and PC substrate, and a dense structure induced by an increase of network density. It can be concluded that both the pretreatment with APTEOS and the coating with organic/inorganic hybrid materials are essential to enhance the oxygen barrier property of PC substrate.

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