# 졸-겔 공정을 통한 TEOS/GLYMO/urushiol 하이브리드 필름의 제조

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# Preparation of hybrid thin film using TEOS/GLYMO/urushiol by sol-gel process

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## Introduction

The sol-gel process is now accepted as the useful method for preparing organic-inorganic hybrid materials from metal alkoxides[$M(OR)_x$ ;M = Si, Ti, Zr, Al, OR = alkoxy group $OC_nH_{2n+1}$]. Hydrolysis and condensation polymerization of these alkoxides results in the formation of a three-dimensional metal oxide network. This process has several advantages such as the low temperature process, the easy preparation of high purity materials, and the variety of the shapes of the products[1]. The sol-gel process is also known to be one of the practical methods for the coating of oxide thin films on various substrates such as glasses[2], metals, and organic polymers[3]. This process is suitable for the coating of thin films on organic polymer substrates since the metal oxide network is formed at relatively low temperatures. However, it is difficult to make crack-free thin films on organic polymers when only $Si(OR)_4$, $Ti(OR)_4$(R= methyl through butyl) is used as a starting material. Schimidt et al. succeeded in ORMOCER(organically modified ceramics) coating on polycarbonate or poly(ethylene terephtalate)[4], and Wang and Wikes succeeded in organic-inorganic hybrid coating on polycarbonates[5]. Such organic-inorganic composites are useful for the coating of thin films on organic polymer substrates.

Over the past decades, oriental lacquer has been generally used as the paint because it has properties of excellent gloss and long-term durability. In addition, it possesses excellent insecticidal, waterproof, heatproof and anticorrosive properties[6]. The oriental lacquer consists of urushiol, water, glycoprotein, and lacaase. It is reported that these characteristics of the oriental lacquer is shown by the properties of urushiol, the main component of the oriental lacquer[7]. As seen in fig.1, urushiol is a mixture of 3-substituted catechol derivatives with $n$=15 carbon chains with 0-3 olefins, being contaminated with other minor phenolic lipids such as those having $n$=17 carbon chains instead of a $n$=15 carbon chain[7].

In the present work, the silica-based organic-inorganic hybrid thin film was coated on a biaxially oriented polypropylene(BOPP) substrate using tetraethoxysilane(TEOS)/3-glycidoxypropyltrimethoxysilane(GLYMO)/urushiol as precursors. And the morphology and gas permeability of hybrid film were evaluated by uruhshiol content

## Experimental

TEOS and GLYMO were obtained from Aldrich and was used without further purification. Urushiol was extracted from the oriental lacquer. The oriental lacquer was dissolved in the acetone. Then it was separated to the soluble part and the insoluble part. Urushiol was obtained by evaporation of acetone in the soluble part.

TEOS, GLYMO and urushiol were mixed in ethanol. The molar ratio of ethanol and water to the alkoxide were kept at 1 and 2, respectively. And different amount of urushiol was added to each solution. The mixture was stirred with a magnetic stirrer for 5min and then acidic water (pH 0.5) was added to the solution. Hydrochloric acid in the acidic water was used as catalyst in the hydrolysis and condensation reaction. After being stirred for 24hr at room temperature in a closed container, the obtained solution was used for coating. The coating was carried out on the corona-treated biaxially oriented polypropylene(BOPP) substrate by the casting method. Then the coated films were dried at room temperature for 7days. The thickness and surface of the coated films were characterized by a scanning electron microscopy(SEM). To investigate characteristics of the hybrid materials, sols were characterized by Fourier transform infrared(FT-IR) and $^{29}$Si-NMR analysis. The gas permeability of the coated films was measured using the variable volume method employed in our laboratory.

## Results and discussion

The FR-IR spectra of the sols obtained from the individual precursors of the studied system, presented in Fig.2, show the well-established characteristic vibration bands. In the IR spectrum of the TEOS, the characteristic bands of the Si-O-Si vibration at about 800 and 1,100$Cm^{-1}$ are observed. The band at 1,175 and 960$Cm^{-1}$ corresponds to the $Si\text{-}O\text{-}C_2H_5$ vibration. In the IR spectrum of the T/G/U system, the asymmetric and symmetric stretching of methyl C-H bonds is found at 2,975 and 2,991 $Cm^{-1}$ in T/G/U system. The Si-O-aryl group absorbs at 950Cm-1 due to stretching of the Si-O bond.

The surface morphologies of the coated films were observed with a SEM at various urushiol compositions. The SEM microphotographs are shown in Fig.3-6. The average thickness of the coated layer is about 10㎛ for the ternary (TEOS/GLYMO/urushiol) system. Fig. 3. shows the surface of coated film with the only TEOS system. When only TEOS was used as the starting material, severe cracks were observed in the thin films coated on the substrates, as is often the case with other results[8]. In order to make a crack-free film, urushiol and GLYMO was added into the TEOS solution. Fig.4-5. shows the surface of crack-free film with the TEOS/urushiol(7/3) and TEOS/GLYMO/urushiol(7/3/1) system, respectively.

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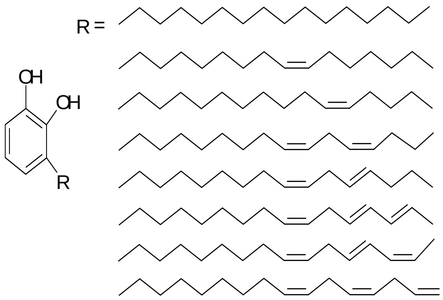


Fig. 1. Molecular structure of urushiol

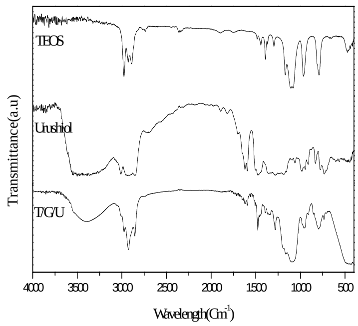


Fig. 2. IR spectra of the systhesized sample

Fig.3. SEM imagel of only TEOS system.

Fig.4. SEM image of T/U(7/3) system.

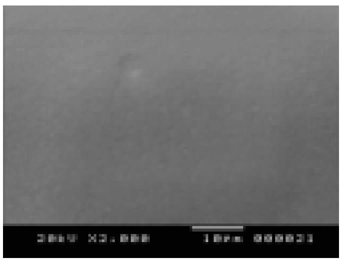

Fig.5. SEM image of T/G/U(7/3/1)system.

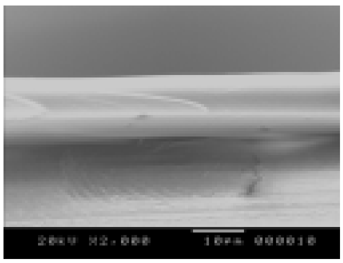

Fig.6. Cross-sectional area of T/G/U(7/3/1) system.