



Preparation and Optical Properties of Silica-Poly(ethylene oxide) Hybrid Materials

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Abstract. Structural evolution and optical properties of the silica-poly(ethylene oxide) hybrid films prepared from γ -glycidoxypropyltrimethoxysilane (GPTS) and 1-methylimidazol (MI) are studied. Polymerization of the epoxy groups is achieved by using 1-methylimidazol as a thermal curing agent. In liquid state ^1H & ^{13}C NMR spectroscopy, it is found that silica condensation mainly occurs without epoxy ring opening. The epoxide polymerization is confirmed by using FT-IR, solid state CP-MAS ^{13}C -NMR, and differential scanning calorimetry (DSC). The hybrid material is densified due to the epoxide polymerization as well as silica condensation with thermal curing. As a result, the thermal curing increases refractive index and extinction coefficient and shifts UV optical absorption edge to longer wavelength.

Keywords: sol-gel, silica-poly(ethylene oxide) hybrid material, epoxide polymerization, optical properties

1. Introduction

The sol-gel process, originally directed towards the synthesis of purely inorganic materials, is increasingly being extended to the preparation of inorganic-organic hybrid materials, called ORMOSIL or ORMOCER [1–3]. The method comprises a chemical synthesis of materials having an oxide backbone and an additional organic component as a network modifier or former. Starting from hydrolyzable molecular compounds, such as alkoxy compounds of silicon for instance $\text{R}'\text{Si}(\text{OR})_3$, hydrolysis and condensation, i.e. formation of inorganic polymeric network, is induced by addition of water. Whereas non-reactive organic groups R' such as alkyl or phenyl groups act as network modifiers, the use of reactive epoxy, methacryl or vinyl groups permits formation of the additional organic network by means of thermally or UV-induced polymerization reactions [4, 5].

The silica-polymer hybrid materials have been extensively studied for application of chemical and

mechanical protection coatings on glasses, metals and plastics [6] because they show outstanding abrasion resistance as well as chemical stability and are endowed with various functionality by tailoring functional compounds. The representative silica-polymer hybrid material is silica-poly(ethylene oxide) (PEO) hybrid materials. It was reported that the silica-PEO hybrid materials were synthesized by mixing water-soluble PEO and hydrolyzing TEOS [7, 8]. However, the silica-polymer hybrid materials which comprise silica and organic polymer networks made from organo-alkoxysilane can have high homogeneity on a molecular level based on the silica network and a high degree of organic crosslinking. Thus, the silica-PEO hybrid materials can be prepared by using γ -glycidoxypropyltrimethoxysilane (GPTS) as a precursor. The silica polymeric network is formed by hydrolysis and condensation of methoxy radical in the presence of water, and PEO polymeric network is made by polymerization of epoxy ring with addition of polymerization initiator. However, in the presence

of water and acid, the epoxy group could react with water to form glycol by opening epoxy rings to terminate the polymerization [4]. Thus, a two step process to hydrolyze and condense was used to polymerize epoxide without hydrolytic ring opening in GPTS [9]. However, their structural evolution with reaction and the epoxide polymerization is still unclear.

In the present study, the silica-PEO hybrid material is prepared by sol-gel reaction of GPTS, followed by thermal cured epoxide polymerization using polymerization initiator, 1-methylimidazol (MI). The structural evolution by thermal curing is examined and the epoxide polymerization is confirmed. Concurrently, the variation in the optical properties of the silica-PEO hybrid thin films is investigated.

2. Experimental

2.1. Synthesis of the Silica-PEO Hybrid Solution

The silica-PEO hybrid solutions were prepared by using γ -glycidoxypropyltrimethoxysilane ((MeO)₃SiC₃H₆OCH₂CH(CH₂O)), GPTS, Aldrich) as the starting precursor. The water for hydrolysis was added to the GPTS solution, and the solution was stirred for 16 h. In order to maintain epoxy group in the GPTS, the molar ratio of water to GPTS is 1.5 : 1 and the pH of the solution was adjusted at 5.5 by bubbling CO₂ through it (prehydrolyzed GPTS). 1-methylimidazol (C₄H₆N₂, MI, Fluka) was introduced to the prehydrolyzed solution and then stirred for 3 h (GPTS/MI solution) [9, 10]. 2-methoxyethanol was used as a diluting solvent to control the viscosity of the final solution. The prepared solution was then deposited on Si(100) wafers and fused silica substrates by the spin-coating method.

2.2. Structure Analysis

The structural evolution with the hydrolysis and condensation of the solution was examined by using ¹H & ¹³C nuclear magnetic resonance (NMR) spectroscopy (Bruker AM 300). Before the liquid state NMR measurement, each solution was dissolved in chloroform-d (CDCl₃, Aldrich). Differential scanning calorimetry (DSC, DuPont TA2200) was used to monitor the epoxide polymerization in the range of 25–250°C. Before DSC measurement, the sample was dried in a

vacuum oven to remove water. The epoxide polymerization of silica-PEO hybrid materials was confirmed by solid state cross polarization-magic angle spinning (CP-MAS) ¹³C-NMR spectroscopy (Bruker DSX400). Two different rates of magic angle spinning, 7 and 9 KHz were used to find spinning side bands. The changes of epoxy groups in the glycidoxypropyl radicals were investigated by Fourier-transformed infrared (FT-IR, Bruker EQUINOX55) spectroscopy. All the measurements were performed in the 1500–500 cm⁻¹ range with a resolution of 4 cm⁻¹.

2.3. Optical Characterization

The morphology of the film was observed with a scanning electron microscope (SEM, Philips 535M). The refractive index and the thickness of the films deposited on silicon wafers were measured by an ellipsometer (GAERTNER L116C) at a wavelength of 632.8 nm. Also, the variation of the refractive index and extinction coefficient as a function of wavelength was determined by using spectroellipsometer (J.A. Woollam WVASE32). The optical transmittance was examined using a UV/VIS/NIR spectrophotometer (Shimadzu UV-3101PC).

3. Result and Discussion

3.1. Preparation of Silica-PEO Hybrid Materials

GPTS was hydrolyzed with water by bubbling CO₂ through the stirring prehydrolyzed GPTS, and then the solution was reacted with MI for 3 h (GPTS/MI solution). The structural changes with addition of MI to the prehydrolyzed GPTS solution was investigated. Figure 1 shows ¹H NMR spectra of the prehydrolyzed GPTS and the GPTS/MI solutions. The two peaks appear at the chemical shifts, ~2.5 and 2.7 ppm due to the two protons in β position corresponding to the epoxy ring, @ in the structural model. When the epoxy group participates in a reaction such as hydrolytic ring opening or epoxide polymerization, the epoxy peak area should decrease. Therefore, the change of the epoxy content can be found by comparing the sum of epoxy peak area with the standard one (©, $\delta = \sim 1.6$ ppm). The ratio of epoxy peak area to the standard peak did not change after reacting with MI, which implies that epoxy content of GPTS was not changed, within the

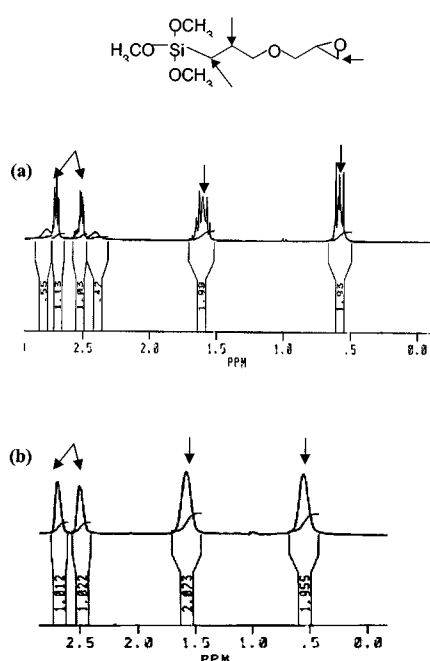


Figure 1. Liquid state ¹H NMR spectra of (a) prehydrolyzed GPTS and (b) GPTS/MI solutions. Structural model is shown for the assignments of the peak position.

error of the measurement. This is already confirmed using the epoxy titration in a previous study [9]. However, all the peaks are broadened and the silanol peaks ($\delta \approx 2.4$ and 2.8 ppm) disappear after reacting with MI when the polymeric structure is formed through the silica condensation.

While the reaction of metal alkoxides has been studied using the NMR of metal nuclei [11], both liquid and solid state ¹³C NMR spectra can also give useful information. It is known that the glycol peaks, which are formed by hydrolytic ring opening reaction, are located at 59 and 69 ppm [12]. As shown in Figure 2, there is no change of chemical shift and no glycol peaks after reacting with MI, although more methanol is produced via further hydrolysis and condensation of methoxy groups. All the peaks are broadened. In particular, the peak of carbon adjacent to silicon near 10 ppm (A) is broadened more than the other ones. This can be understood as follows. As the environment of the silicon is changed, the carbons adjacent to silicon have slightly different chemical shifts around 10 ppm. Thus, it is found that the addition of MI into the prehydrolyzed GPTS solution leads to silica condensation but not epoxy reaction.

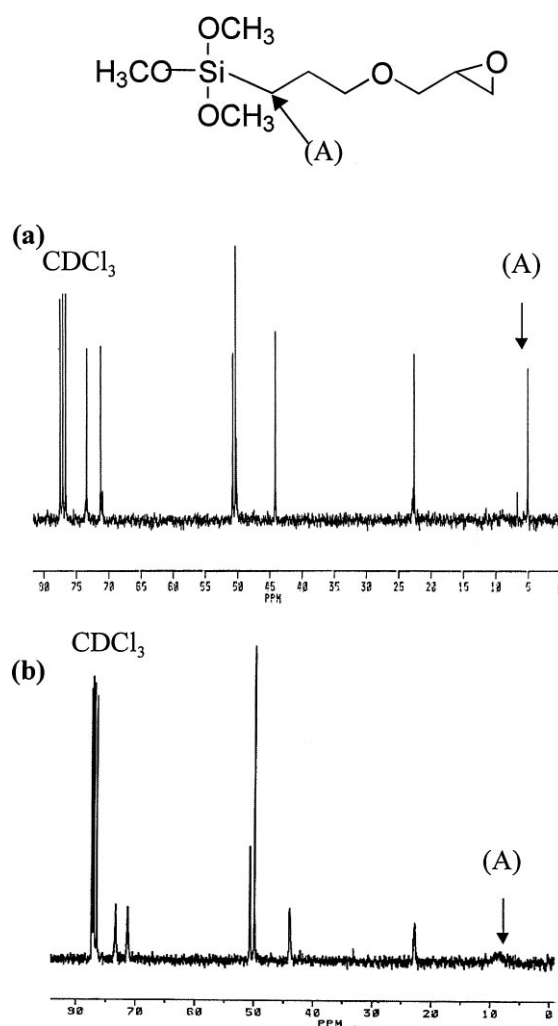


Figure 2. Liquid state ¹³C NMR spectra of (a) prehydrolyzed GPTS and (b) GPTS/MI solutions. Structural model is shown for the assignments of the peak position.

The prepared GPTS/MI solution was heat treated to favor the epoxy polymerization to obtain the silica-PEO hybrid materials. Figure 3 represents DSC results for the GPTS/MI gel after evacuating water at 5°C/min heating rate. It presents a broad exothermic peak starting at 85°C and finishing at 237°C which corresponds to the epoxy polymerization. The maximum polymerization occurs at 180°C and its enthalpy change is about 82.2 J/g.

In order to examine the structural change with thermal curing of the GPTS/MI gel, the solid state CP-MAS ¹³C-NMR was used. The GPTS/MI gel was dried at room temperature and crushed to make powders. Each sample was cured at 130°C for 10 min and at 180°C

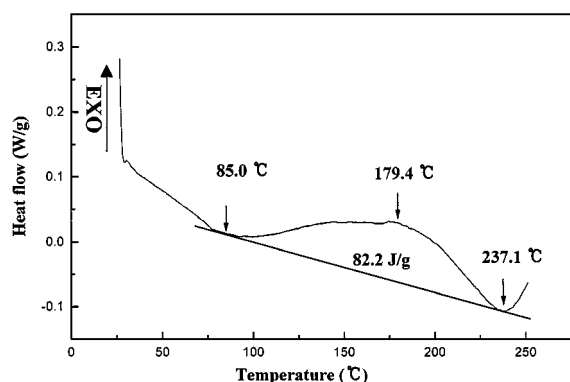


Figure 3. DSC curve of the epoxide polymerization in silica-PEO hybrid materials with heating rate of 5°C/min.

for 30 min. There was no spinning side band as a result of using two different rates of magic angle spinning, 7 and 9 kHz. As shown in Figure 4, the epoxy peak at ~51 ppm decreases and the new peak at 64.5 ppm appears on heat treating at higher temperature and longer time. Also, the glycol peak at 59 and 69 ppm is not detected. Thus, it is found that the epoxy ring is polymerized without the formation of glycol. The new

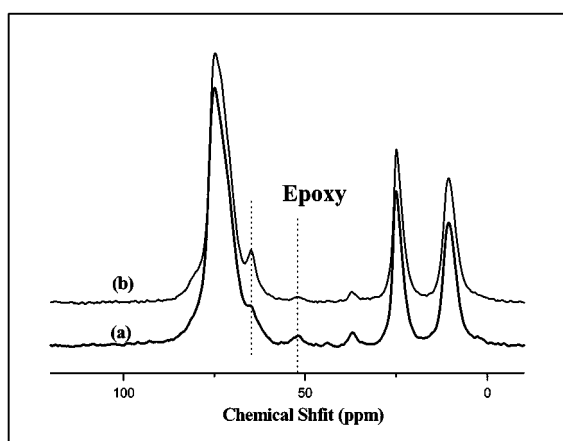
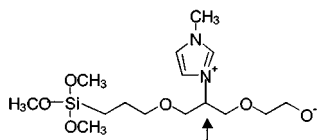


Figure 4. Solid state CP-MAS ^{13}C -NMR spectra of the silica-PEO hybrid material (a) cured at 130°C for 10 min and (b) cured at 180°C for 30 min. Structural model is shown for the assignments of the peak position.

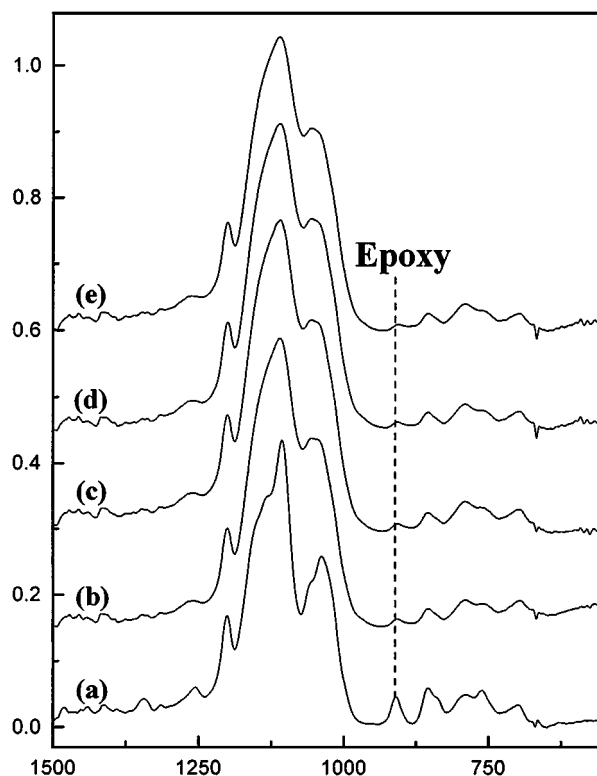


Figure 5. FT-IR spectra of GPTS/MI coating films with various curing time, (a) 0 min (b) 5 min (c) 10 min (d) 20 min (e) 30 min, at 180°C after drying at 80°C for 10 min. The dashed line indicates the epoxy asymmetric stretching mode.

chemical shift at 64.5 ppm might be due to the initiation of polymerization by MI [13].

The GPTS/MI solution was coated on Si(100) wafers by spin coating at 7000 rpm for 30 sec and dried at 80°C for 10 min. The FT-IR spectra of the coated films as a function of curing time at 180°C are shown in Figure 5. The peaks at 910, 1030 and 1080 cm^{-1} are attributed to $\nu_{\text{as}}(\text{C}-\text{O}-\text{C}$ ring), $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ and $\nu_{\text{as}}(\text{Si}-\text{O}-\text{C})$, respectively. Apparently, the epoxy asymmetric stretching mode at 910 cm^{-1} disappears as the curing time increases. The Si-O-Si asymmetric stretching mode around 1030 cm^{-1} is broadened due to enhanced silica condensation with longer curing. Thus, it is found that the epoxy group is polymerized to poly(ethylene oxide) and the silica condensation is accomplished with increasing curing time.

The structural evolution for the preparation of the silica-PEO hybrid material can be modeled as shown in Figure 6. In the first step, GPTS undergoes partial hydrolysis and methanol is produced in the solution (a). This methanol acts as a co-solvent of GPTS and water to

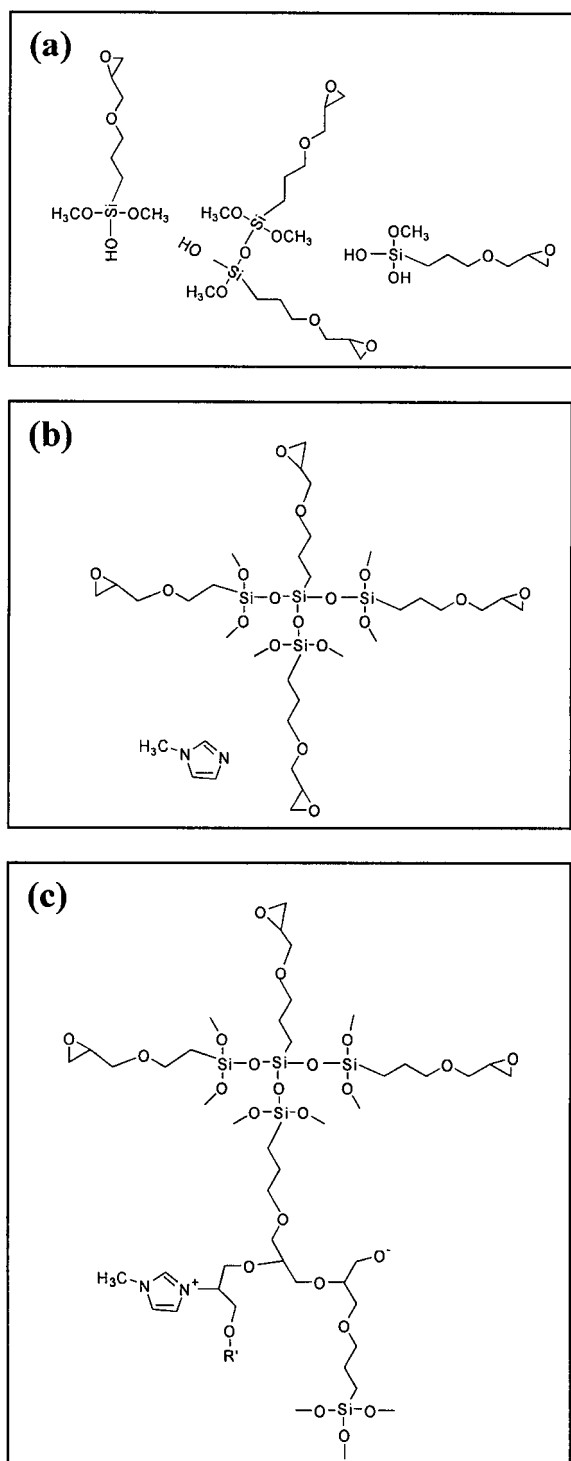


Figure 6. Schematic model of the structural evolution as the reaction proceed i.e. (a) 1 mol GPTS and 1.5 mol H₂O are mixed and stirred for 16 h with CO₂ bubbling, (b) prehydrolyzed GPTS with 0.1 mol MI are stirred for 3 h, and (c) the silica-PEO hybrid material is polymerized by thermal curing.

homogenize the hybrid solution. As MI is added in the prehydrolyzed GPTS solution, the more hydrolysis and condensation of GPTS occurs and the silica network is formed with maintenance of the epoxy group (b). Finally, as the hybrid material is thermally cured MI acts as an initiator and epoxy groups are polymerized to poly(ethylene oxide) units. Therefore, both silica and poly(ethylene oxide) networks are formed in the hybrid material.

3.2. Optical Characteristics of Silica-PEO Hybrid Films

The morphology and cross-section of the silica-PEO hybrid film on an Si(100) wafer are shown in Figure 7.

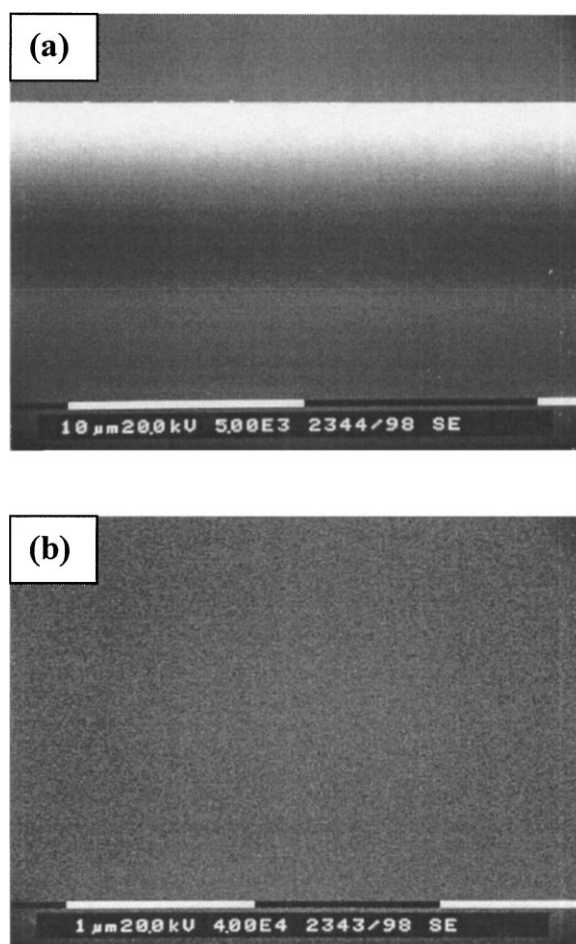


Figure 7. SEM images of (a) cross-section and (b) surface morphology of silica-PEO hybrid films by single spin coating at 7000 rpm for 30 sec on Si(100) wafer.

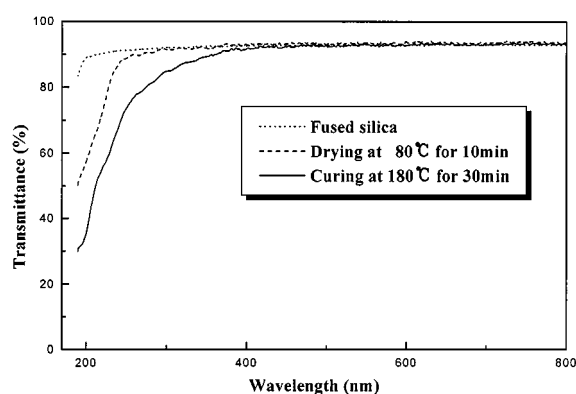


Figure 8. UV transmittance spectra of the films on fused silica substrate dried at 80°C for 10 min and cured at 180°C for 30 min.

The coating solution was not diluted. Thick and crack-free films are obtained by single spin coating at 7000 rpm for 30 sec. After the coating, the films are dried at 180°C for 30 min. The film has a smooth surface and its thickness is near 8 μm . Thus, homogeneous and thick optical quality films of silica-PEO hybrid films can be prepared.

From the above discussion, it is found that the structure of silica-PEO hybrid film is changed by thermal curing. To investigate the optical transmittance, the silica-PEO hybrid solution was coated on a fused silica substrate using spin coating at 7000 rpm for 30 sec. Fused silica substrate was selected because of its excellent transparency in the UV region. As shown in Figure 8, the hybrid film is very transparent in the visible and infrared regions. Its optical absorption edge shifts to longer wavelength when heat treated at higher temperatures and longer times. This is further evidence for the epoxide polymerization of the silica-PEO hybrid material.

An ellipsometer was used to determine both the thickness and refractive index of the hybrid film. According to a model of spin coating by Meyerhofer [14], the film thickness is proportional to the viscosity of the coating solution. 2-methoxyethanol was used to adjust the viscosity of the silica-PEO hybrid solution to enhance thin film formation. There are no side reactions between the hybrid solution and 2-methoxyethanol. Figure 9 shows the refractive index and the thickness of the hybrid film as a function of curing time at 180°C. The thermal curing increases the refractive index from 1.484 to a maximum of 1.495. Whereas the film thickness decreases gradually as the curing time increases, this means the film is densified due to the

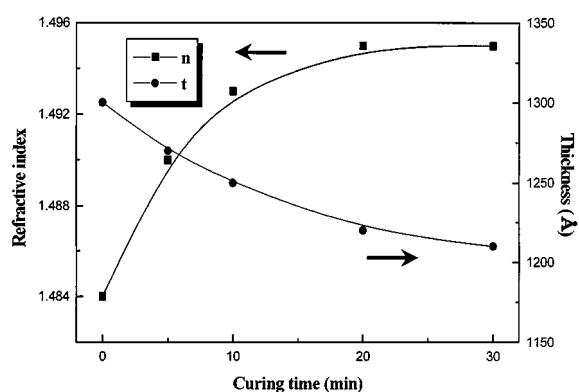


Figure 9. The change of refractive index and thickness of silica-PEO hybrid films as a function of curing time at 180°C.

epoxide polymerization as well as drying, causing the film shrinkage. Thus, the densification and the epoxide polymerization raise the refractive index with larger curing.

The variations of the refractive index and extinction coefficient of the dried and cured films measured using a spectroscopic ellipsometer are plotted in Figure 10. All of the films exhibit a refractive index and extinction coefficient decrease in the range between 400 and 800 nm. The cured films have the higher refractive index and extinction coefficient than the dried films. Also, the cured films show less dispersion, variation of the refractive index with wavelength, than the dried films. This is because of the epoxide polymerization as well as densification of the film. Also, it is observed that the extinction coefficient is tailed in the short wavelength for the cured film. This is analogous to UV transmission spectra as shown in Figure 8. This absorption edge tail by thermal curing is made by the epoxide polymerization and probably the incorporation of MI in the polymer network that can be an absorption center in the UV region.

4. Conclusion

Silica-PEO hybrid materials were prepared from γ -glycidoxypropyltrimethoxysilane (GPTS) and 1-methylimidazol (MI). MI acts as a base catalyst so that the silica network is formed through hydrolysis and condensation reaction of GPTS. Also, MI acts as a polymerization initiator for the epoxide polymerization. Thus the epoxy groups in the hybrid materials are polymerized with thermal curing without forming glycol.

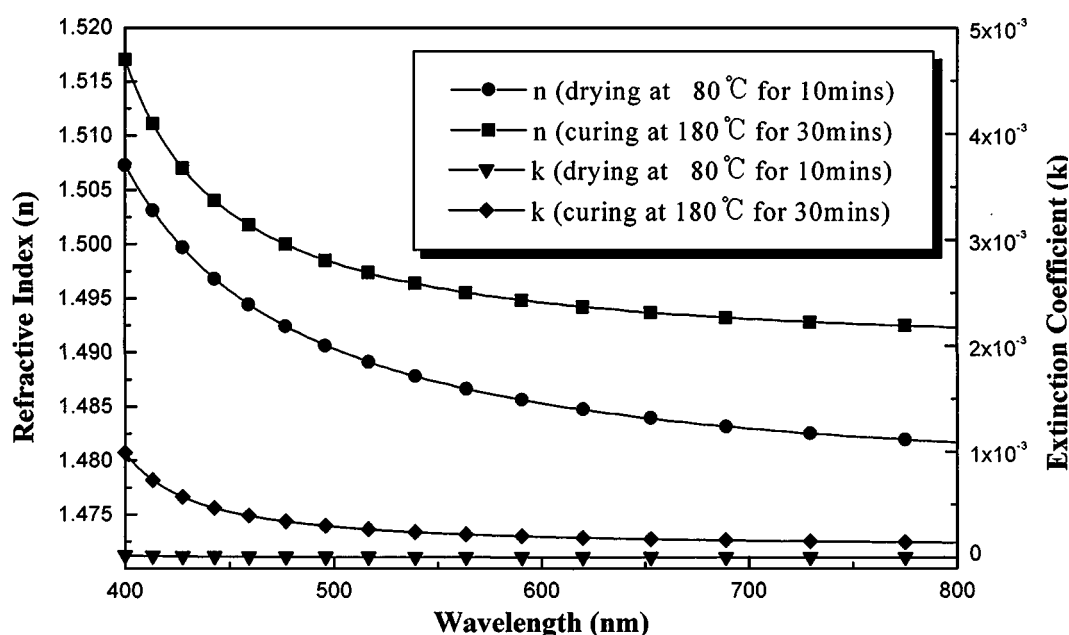


Figure 10. The spectroscopic refractive index and extinction coefficients of dried and cured silica-PEO hybrid films.

Thick and crack free silica-PEO hybrid films are obtained by spin coating. The hybrid films are very transparent in the visible and infrared regions. Also, their optical absorption edge shifts to longer wavelength when heat treated to higher temperatures for longer times. The thermal curing of dried sample at 180°C increases the refractive index at 632.8 nm from 1.484 to a maximum of 1.495. The refractive index and the extinction coefficient increase in the range of 400–800 nm through thermal curing due to epoxide polymerization and densification.

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