

방사능탐지용 CAYS 함침 이중구조 폴리설폰막의 형상 및 특성에 제막공정의 습도가 미치는 영향

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Vapor Exposure Effect of a Casting Solution on the Embedding and Radioactive Detection of CAYS in Double-layered Polysulfone Film

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요 약: 방사능 오염도 측정에 사용하기 위한 이중구조 고분자막이 폴리설폰과 세륨활성화된 이트륨실리케이트(CAYS)를 이용하여 제조되었다. 제조된 막은 순수 고밀도 고분자 지지층과 이에 제막된 고분자 용액의 상전환 공정에 의해 고형화된 CAYS 함침 활성층의 이중구조로 구성된다. 제막공정에서 대기방치 공정이 생략되었을 때 CAYS를 포함하는 활성층은 전형적인 비대칭 구조를 지니며, CAYS 입자들이 고분자 구조 사이에 박혀있는 형상을 지닌다. 제막공정에서 대기에 방치하는 시간이 증가할수록 막의 형상은 스폰지 구조를 띠며 CAYS는 고분자 구조로부터 분리되어 막 내부에 셀 같은 공간에 밀집되어 존재함을 보였다. 한편, 두 층 사이의 계면형상은 고분자 고형화 과정에서의 상전환 속도와 밀접한 관련되었으며, 대기방치 시간의 증가에 따라 계면의 구분이 뚜렷하게 나타나지 않았다. 방사능 탐지 특성에서 스폰지 구조를 지니는 막의 고분자 구조는 방사성핵종이 통과할 수 없는 밀집된 형상을 지니면서 탐지효율의 감소를 초래하는 것으로 나타났다.

Abstract: Double-layered polymer films to assay the radioactive contamination were formulated using polysulfone (PSF) and cerium activated yttrium silicate (CAYS), consisting of a dense support layer and a CAYS-holding top layer, prepared via the diffusion-induced phase inversion. As the vapor exposure process was omitted, the CAYS-holding layer showed a typical asymmetric structure, with CAYS being transfixed into the polymer network spread with large macropores. With the increase in vapor exposure time before immersion, morphology of the films transformed from asymmetric to sponge-like structures, with CAYS being localized in cellular structure. The border structure between the two layers reflects the phase inversion behavior of a cast solution during the coagulation. In the radioactive detection, the polymer phase in a film holding a sponge-like structure is so dense that the radionuclides, deposited on the film, could not filter through the phase, consequently resulting in the loss in the detection efficiency of the film.

Keywords: phase inversion, polysulfone, membrane, fluor, radioactive detection

1. Introduction

Low energy radionuclides are widely used in pharmaceutical and medicinal studies to trace transport routes of those agents in a specific body, because of

their characteristics of being easily detected without destruction[1,2]. However, radioactive contamination of those radionuclides on table tops and floors in a research lab can reach over the hazardous level through a consecutive accumulation, even though their original radioactivity is relatively low. To reduce the possible harmful effect to lab personnel, the working places

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have to be regularly monitored and cleaned before the contamination becomes over the safety level[3]. But, because of their low energy state, the detection of common β -radionuclides such as ^{14}C or ^3H is operated by an indirect detection through the wipe test rather than by a direct detection using an instrument such as the Geiger-Muller gauge, which is efficient to detect the high energy contaminants only. The wipe test involves the smearing of a potentially contaminated area using a wiping medium and subsequent quantification of picked-up radioactivity using a proper gauge such as a scintillation counter[4].

A wiping medium suitable to the wipe test has to be physically strong enough to endure its friction with a contaminated surface during the wiping process, and chemically stable enough to hold its structure in contact with typical solvents such as water or alcohol. A fluor such as CAYS, which is scintillated by reacting with the radioactive materials, can be embedded into the medium structure in order to directly detect the radioactivity without the help of a scintillation liquid. For a fluor-impregnated medium, the porous polymer membranes, commonly used as a separation process, can be an adequate candidate because of its physical and chemical stability. A mono-layer structure film, however, prepared by the conventional phase inversion method has shortcomings such as the cross-contamination across the film or its low tensile strength, all due to their too much porous substructure[5]. To improve the detection efficiency as well as the physical strength, polymer films of double-layered structure have been developed, being made of an active layer over a dense support layer[6,7]. This kind of a polymer matrix is designed to being applied to an automatic counting machine, in which the wiping medium needs to hold at least a layer of dense structure enough to endure the vacuum application for its attaching and detaching on the machine. Even though the double-layer structure is superior to the single-layer one in both strength and stability, the optimization in structure and function is far from being reached.

The formulation of an active layer in a double-layered

film can be made of embedding an inorganic fluor, CAYS, on the polymer base, polysulfone. The CAYS-holding layer is formed by the phase inversion of a PSF solution cast over the dense support layer. It is well known that in the diffusion-induced phase transition of a polymer solution, the phase inversion kinetics, being affected by solution rheology and thermodynamic stability, makes a significant impact on the film morphology and their corresponding function such as the permeation property and molecular cutoff[8-14]. With an extra ingredient of CAYS, this kind of structural and functional variation would affect the embedding and function of CAYS on the polymer matrix[15,16]. Therefore, the detailed study of the morphology of a polymer composite and its concurrent detecting capacity of radioactive agents is required to optimize the polymer composite as an adequate radioactive detecting device. This report tries to find out what the effects of vapor exposure on film morphology and CAYS impregnation are. The correlation between the variation of morphology and CAYS impregnation and the detection efficiency of the prepared film is also studied.

2. Experimental

2.1. Membrane Preparation

The bottom layer supporting an active layer was formed by evaporating a PSF/methylene chloride (MC) (25 g/ 80 g) solution cast with a 300 μm clearance gap on a glass plate using an applicator (Sheen, England). To formulate the active top layer, a ternary solution including CAYS (P-47, SPI Supplies) dispersed in a fully dissolved PSF/dimethylformamide (DMF) (4.5 g/ 25 g) solution was prepared. The solution was cast with a 200 μm clearance gap from the glass plate over the solidified dense film, obtained from the evaporation of the PSF/MC binary solution. The plate was then placed in a conditioning chamber of 75% humidity for vapor exposure, and then immersed into a water bath after the pre-set exposure time.

The CAYS with an average size of 3 to 5 μm was supplied from SPI Supplies. PSF (Mn 22,000), MC

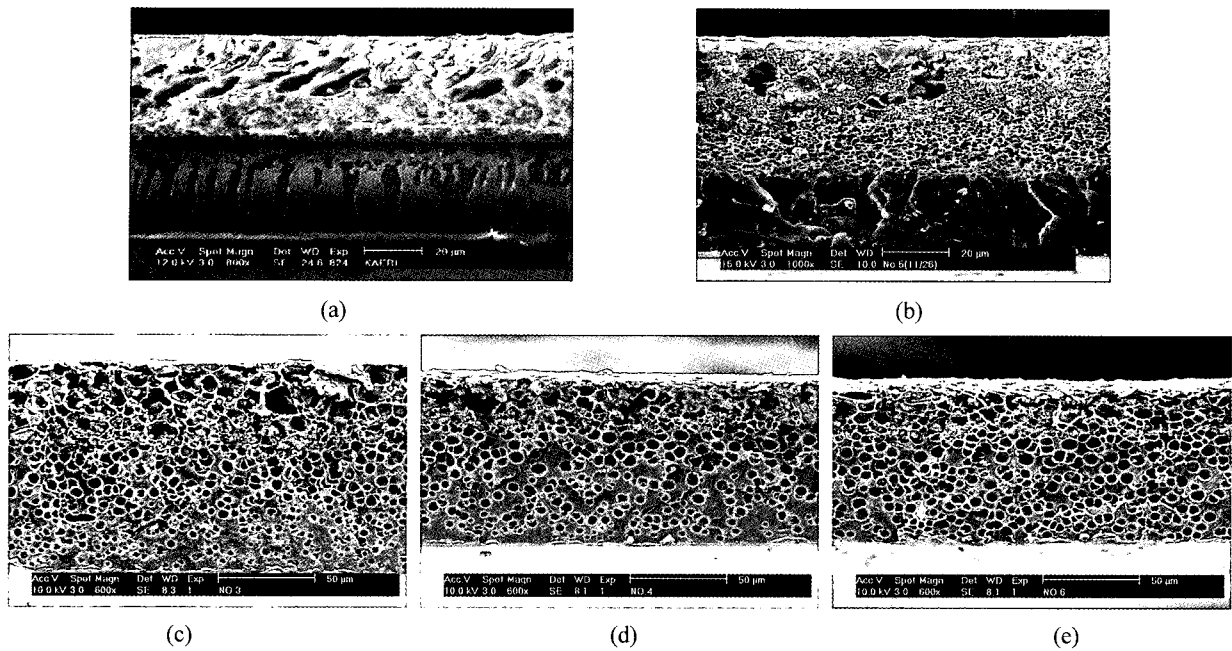


Fig. 1. Cross sections of double-layer films prepared by water vapor exposure and immersion precipitation: no exposure (a), 10 seconds (b), 3 minutes (c), 1 hour (d), and 24 hours (e) of the exposure time

and DMF were purchased from Aldrich.

After being kept in the bath for 24 h, the coagulated films were removed from the bath, dried and stored at an ambient condition before the test.

2.2. SEM

Morphology of the solidified membranes was observed by using a scanning electron microscopy (SEM, Philips XL30W). Samples were freeze-fractured under the cryogenic condition using liquid nitrogen and coated with a gold and palladium (60:40) alloy before being tested.

2.3. Radioactivity Detection Test

For the radioactive detection test of the prepared films, a radioisotope solution of aliquots of 30 μL was deposited on the film specimen. The radioactive solution is of a common radionuclide diluted in isopropanol, ^{14}C -oleoyl-coenzyme A, with its radioactive concentration of 2.3 Bq/ μL . After being spotted on a film surface and dried at room temperature, the radionuclides' activity was quantified by using both PMT (photo electron multiplier tube) and LB (low back-

ground α/β counter). Their radioactivity measurement was recorded as CPM (radioactive counts per minute).

3. Results and Discussion

A supporting layer, solidified by vacuum evaporation of the binary solution of PSF and methylene chloride, holds a feature of transparency and a dry thickness of $45 \pm 2.5 \mu\text{m}$. On the dense supporting layer, a second casting solution for the formation of an active layer was cast over. The cast polymer solution is transformed from liquid to solid on the way to being coagulated. Either a solvent elimination from or a non-solvent addition into the solution triggers an eventual coagulation or collapsing of polymer particles.

By immersing into a water bath just after casting, the cast solution transforms into a solidified film containing well-developed macropores in an asymmetric structure (Fig. 1(a)), typical of the polymer membrane structures coagulated via the rapid polymer phase separation. The interface between the top layer and the bottom layer reveals a clear-cut border, holding relatively small spherical voids formed by the nascent nucleated polymer-

lean phases. However, with the increase of vapor exposure time before immersion into a water bath, morphology of both the upper layer and the interface between two layers is significantly varied, depending on the ingredients' composition change and their concurrent phase separations.

Over the course of vapor exposure a cast solution lacking CAYS undergoes a transformation from transparent to translucent, and finally to opaque, because of light scattering in the solution. This kind of scattering is due to the nucleated polymer-lean phases with non-solvent water adsorbed from outside. It is known that a PSF and DMF binary solution can be phase-separated with as little as 1.5 wt% of water, revealing that the solution is very sensitive to water[17,18]. The film prepared with just 10 sec exposure, followed by water immersion, still keeps an asymmetric structure, yet it already shows a moderate variation on morphology in that macropores are significantly suppressed (Fig. 1(b)). The interface between two layers is not as much as clear-cut as that of the film prepared with no vapor exposure, showing the penetration of the top layer solvent to the support layer.

On the contrary, with the exposure time more than 3 minute, the graded asymmetric structure gives way to the sponge-like structure (Fig. 1 (c)), which indicates that the nucleation of polymer-lean phase is already in progress before immersion into a water bath. The otherwise clear distinction on the interface boundary becomes blurred, and well-developed spherical voids are formed across the film. This kind of structure indicates that with 3 minute exposure a significant amount of solvent already advances to the support layer. Also, at first glance, the morphology of the films prepared with more than one hour exposure seems similar to that of the film prepared with 3 minute exposure, having the spherical voids and blurred interface. With further exposure to 24 hours, however, the relatively irregular pores graduates into homogeneous round pores across the whole composite film, which indicates that the entire portion of the swelled support layer as well as the cast solution in the upper

layer coagulates at a relatively homogeneous state. And the interface formed between two layers on casting almost disappears with 24 hour exposure.

An interfacial structure between the two layers offers clues to the phase transition characteristics of a cast polymer solution. Once cast over the support layer, the second solution layer suffers a dual impact during vapor exposure: a water vapor imbibition from the top surface contacting the humidity air and a solvent penetration toward the support layer on the boundary between two layers. With the solvent penetrated from the upper layer to the bottom support layer, the border becomes swelled, extending beyond its original interface. The penetration of water molecules through this highly concentrated region is limited so that the concentrated solution would go into the liquid-liquid phase separation via the nucleated polymer-lean phase. Therefore, it is clear that the irregularity on border is primarily the result of the solvent penetration during the exposure, but it isn't until the followed nonsolvent water mixes with the solvent and form the nucleated polymer-lean phase that the penetrating solvent stop diffusing into support layer. Consequently, the increase in structure irregularity entailing the polymer-lean phases deep inside the structure indicates the more delayed phase transition, even though the impact of a concentration variation on structure may not be excluded.

As the vapor exposure is not applied before immersion coagulation, polymer molecules in the skin region of a cast solution rapidly collapse forming nodule structures because of fast exchange between solvent and non-solvent. And, the collapsing movement of polymer molecules is too rapid for CAYS to be separated from the polymer, inducing the impingement of CAYS in the matrix. Therefore, the film surface reveals a dense structure with CAYS mixed-up with the polymer. As shown in Fig. 2, any liberated CAYS is not found on the surface of the film prepared without the vapor exposure. In contrast, the CAYS expelled from the polymer matrix shows up on the surface of films prepared with more than 3 minute vapor exposure, revealing that the nucleated polymer-lean phases are

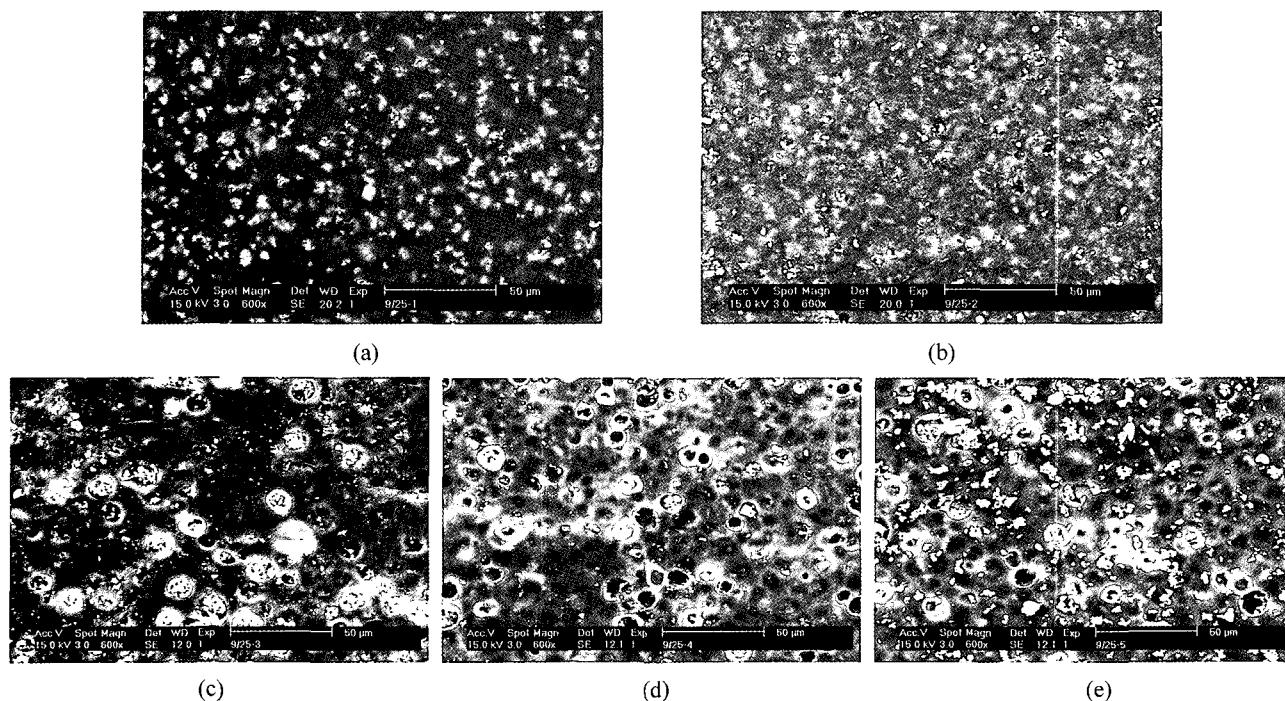


Fig. 2. Surface of double-layer films prepared by water vapor exposure and immersion precipitation: no exposure (a), 10 seconds (b), 3 minutes (c), 1 hour (d), and 24 hours (e) of the exposure time.

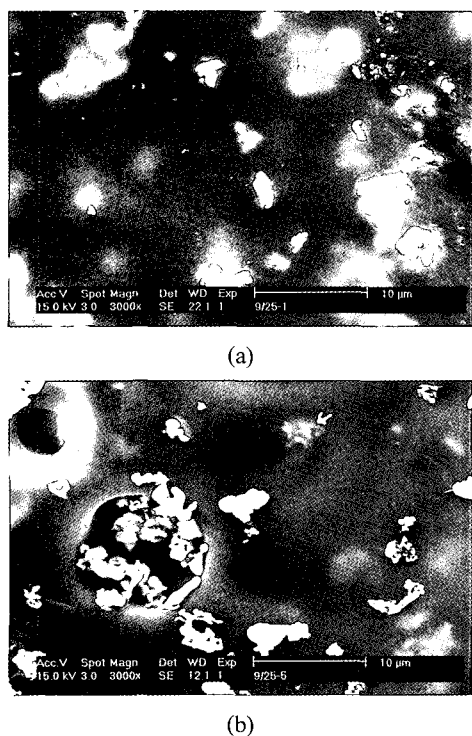


Fig. 3. Enlarged surface of the films prepared by water vapor exposure and immersion precipitation: no exposure (a), and 24 hours (b) of the exposure time.

formed during the vapor exposure period. In Fig. 3(b), CAYS particles and round void shapes on the film surface punctuate the film feature formed by the nucleated polymer-lean phases.

The radioactive detection test was performed using two different techniques. One is the PMT method that detects and quantifies the amount of photons released by scintillation reaction between radionuclides and CAYS, and the other is LB directly quantifying the radioactive energy from radionuclides. The LB counting is affected by pore structures in a film because tortuosity, or sinuous pathways, can induce the quenching during the energy transfer from the deposited radionuclides to the detector. The PMT counting is influenced by overall CAYS distribution effect on the reaction of radionuclides with CAYS, as well as the morphology effect including pore structures. In this measurement, photons generated at scintillation sites have to elbow their way out to the film surface before reaching the detector.

As shown in Fig. 4, the LB detection test finds the

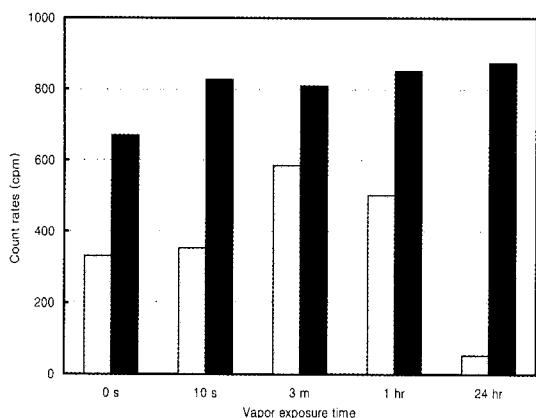


Fig. 4. Radionuclide detection efficiency with vapor exposure time; LB (■) and PMT (□).

lowest CPM value for the film prepared without the vapor exposure, and the detected radioactivity increases with the vapor exposure time, showing the highest for the film prepared by the 24 hour exposure. The deeper the radionuclides locate inside a film, the lower the detection value, because of quenching effect due to energy loss during passing through polymer networks. Therefore, the highest value of the film prepared with the 24 hour vapor exposure indicates the spotted radionuclides stay relatively at the top surface of the film, its spherical pores being closed each other. On the contrary, the film prepared without vapor exposure holds the radionuclides deep into the large macropore structure, inducing the quenching of the radioactive energy of the deposited radionuclides.

The radioactive counting value using the PMT increases with the vapor exposure time, peaking at the film prepared with the 3 minute exposure. With further increment of exposure time, however, the value drops rather than increases. In the PMT measurement, the CAYS's efficiency depends largely on how many CAYS particles contact or react with the radionuclides. A morphology inducing the loss of proximity between radionuclides and CAYS, such as a polymer enveloping on CAYS or the separation of CAYS from polymer structure, works as a shortcoming in the detection of radioactivity.

Therefore, the relatively low value of the film prepared with no vapor exposure indicates that the de-

posited radionuclides filter through the film surface to react with CAYS ingrained inside the film, but the energy of scintillated photons is significantly diluted during the escaping from the reacted sites because of its highly macroporous structure. The highest value of the 3 minute evaporation reveals that the deposited radionuclides still filter through the film structure and react with CAYS, their reaction being concentrated in the upper part of the active layer.

For the film prepared with the 24 hour exposure, in contrast, the scintillation efficiency of CAYS significantly drops, even though the film morphology is relatively similar to that of the films prepared with 3 minute or 1 hour evaporation. This kind of low reaction should be due to the pores' morphology, being shut down to surrounding pores, consequently hampering the deposited radionuclides trying to penetrate inside the structure. As well known in the PSF separation membranes [19] prepared using a similar casting solution without CAYS, the water permeate flux through a membrane significantly drops with the increase in the vapor exposure time of a casting solution, with the membrane structure similar to the 24 hour exposure film consisting of the spherical voids from the nucleated polymer-lean phase. As for the CAYS-impregnated film, the polymer-phase enveloping the well-developed polymer-lean phase prevents radionuclide molecules from passing through the film structure, significantly degrading the proximity between CAYS and the radionuclides.

4. Conclusion

In the formulation of a double-layer polymer film structure, coagulated including the vapor exposure process, the morphology of a film reflects the characteristics of the phase transition of the active top layer. And the impregnation of CAYS in the film is also significantly affected by the vapor exposure. On the film prepared without vapor exposure, the highly porous structure in the top layer as well as the sharp delineation on the two layer's boundary indicate that

after being cast over the support layer, the top layer is formed by rapid coagulation. On the contrary, both the spherical cellular voids and the CAYS expelled from the polymer structure on the film coagulated with the 24 vapor exposure proves that the solution is solidified via the nucleation of polymer-lean phase and their growth. The radioactive detection results also reflect the film morphology and CAYS impregnation inside the films. LB counting results on the film prepared without vapor exposure show that a significant amount of radionuclides diffuses into inside the film structure, passing through macropores, even though its reaction is not efficient enough to react with CAYS. On the contrary, PMT results reveal that CAYS are totally isolated inside the film structure, concurrently inducing detection loss due to the proximity loss between the radionuclides and CAYS.

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