

Effect of Nonsolvent Coagulant on the Morphology and Radionuclide Detection Efficiency of CAYS-Impregnated Polysulfone Films

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ABSTRACT: Single- or double-layered porous films consisting of polysulfone (PSF) and cerium-activated yttrium silicate (CAYS) were prepared through the phase inversion of polymeric solutions. For a single-layered structure, a casting solution including *n*-methylpyrrolidone (NMP) as a solvent was cast on a glass substrate and solidified by immersing into a nonsolvent bath. In a double-layered structure, the bottom layer is a dense PSF film, prepared by vacuum coagulation of a methylene chloride/PSF solution. The top layer was formulated by coagulating the NMP solution, cast over the dense film, in a nonsolvent bath. The morphology and the radionuclide detection efficiency of the prepared films were significantly affected by the nonsolvent coagulants used. The water-coagulated, double-layered film showed a relatively clear-cut interface between the two lay-

ers, indicating the rapid coagulation of the second layer. On the contrary, the film coagulated by isopropanol retained well-developed sponge structures highly intertwined in the interface, associated with the delayed precipitation of the second layer. When spotted on the prepared films, radionuclides stayed mainly on the top surface of the isopropanol-coagulated film, but went deep into the substructure of the film coagulated with water. In comparison with the mono-layered films, the double-layered ones improved the detection capacity of the spotted radionuclides, owing to the dense support layer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1903–1909, 2006

Key words: films; morphology; phase separation; voids; radionuclide; fluor

INTRODUCTION

The use of low energy radionuclides continues to rise in many research fields such as the tracing of a drug's metabolism because of their efficacy in being nondestructive and relatively easy to detect.¹ The application of these materials, however, brings about the radioactive contamination of a working area that has to be monitored and controlled for the safety of the personnel. To determine this kind of radioactive contamination in a specific place, the wipe test is commonly used because it is not disturbed in a circumferential environment.^{2,3} It is classified as the indirect method in that a supposedly contaminated area is smeared with a wiping medium, its radioactivity being counted with either the help of a scintillation cocktail or the reaction with the scintillators imbedded in the wiping medium.^{4–7}

To optimize the wipe test, we have developed an automatic scintillation-counting machine,⁸ which can

be used without a scintillation cocktail, with the added benefit of reducing human error by wiping. This instrument is an easy-to-use gauge that can be applied wherever the radioactive contamination is doubtful, and gives a fast analysis of a contamination degree on-site, saving valuable time and specialist personnel. The instrument consists of three major components: a disposable wiping medium, an electronic device for controlling the wiping process, and a radioactive detection appliance. Its reliability as a measuring instrument depends on both the efficient pick up of radioactive contaminants and the efficient detection of radioactivity. To be adopted to the machine, a wiping medium has to be physically strong enough to endure the abrasion of wiping and sensitive enough to monitor the radioactivity picked up by wiping.

A polymeric single-layered film, holding a radionuclide detection material in the polymer matrix, may be considered an appropriate candidate for a wiping medium. The polymer composite can be formed by impregnating an inorganic fluor in a solid polymer matrix,^{9,10} which can illuminate it by absorbing energy and emitting a portion of the energy at the ultraviolet, visible, or infrared region. The activity of the radioisotopes adsorbed both on the film surfaces and inside the pores can be detected by measuring the photons

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scintillated by the reaction between the radionuclides and the fluor.

But, single-layered scintillation films have a drawback in their application to the counting machine. When formed with a large amount of cerium-activated yttrium silicate (CAYS), a dense film is too brittle to be used as a wiping medium, even though its detection efficiency is promising. On the contrary, the highly porous structure shows better radionuclide holding and better physical stability but a significant reduction in the detection efficiency, largely because of the radionuclides leaking through the pores. And also, a high portion of CAYS embedded in a film is inefficient for radioactivity detection because they are widely dispersed across the film.

To prepare a composite film capable of being applied to an automatic radionuclide detection appliance, double-layered solid scintillation polymer films were prepared. The structure consists of both a dense support layer and a porous top layer. The top layer working as the active layer is formed by coagulating the CAYS-suspended solution. The coagulation process includes the conversion of a polymer solution into a three-dimensional structure by immersion in a non-solvent bath. CAYS particles are impregnated in the final membrane matrix, and their impregnation characteristics in the film are significantly affected by the transition phenomena of the polymer solution during the coagulation process. In this article we address the nonsolvent effect of the membrane morphology and the radioactive counting efficiency of the prepared films.

EXPERIMENTAL

Membrane preparation

The solution composition for single-layered films was 4.5 g polysulfone (PSF)/25 g *n*-methylpyrrolidone (NMP). In double-layered films, the support layer was formed by casting and evaporating a PSF/methylene chloride (MC) (25/80 g) solution. The top layer was prepared using the same composition as that of the solution used to formulate the single-layered structure. The ternary solution for the fluor impregnation was prepared by dispersing CAYS (P-47, SPI Supplies) in a fully dissolved PSF/NMP solution, with the CAYS consisting of 3–5- μm particles. PSF (M_n , 22,000), MC, and NMP were purchased from Aldrich.

Single-layered films were produced by casting the CAYS-dispersed solution in a 200- μm clearance gap on a clean glass plate at 25°C and, then, immersing the cast solution film into an isopropanol or water coagulation bath at 25°C. Double-layered films were produced through two separate castings. First, the PSF/MC solution was cast in a 300- μm clearance gap on a clean glass plate and dried in a vacuum oven at

30°C. After 48 h, the glass plate was removed from the oven, and the prepared CAYS-dispersed solution was cast over the PSF film in a 200- μm clearance gap from the glass plate. The freshly cast film, containing the solid first layer and the liquid second layer, was immersed in a water or isopropanol bath.

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

Cloud point measurement

The cloud points of the casting solutions were obtained by measuring the amount of the coagulant, water or isopropanol, added to the binary solution of PSF and NMP until the mixture revealed the cloudy feature. The detailed procedure is explained in a previous article.¹¹

Scanning electron microscopy

Morphology of the solidified membranes was observed using a scanning electron microscope (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.

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 a common radionuclide diluted in isopropanol, ¹⁴C-oleoyl-coenzyme A, with a radioactive concentration of 2.3 Bq/ μL . After being spotted on a film surface and dried at room temperature, the radionuclides' activity was quantified using both a PMT (photo electron multiplier tube) and an LB (low background α/β counter). Their radioactivity measurement was recorded as CPM (radioactive counts per minute).

RESULTS AND DISCUSSION

Before the preparation of CAYS-impregnated films, single-layered and double-layered films were prepared without CAYS, and their morphology was compared with each other. As shown in Figure 1(a), a macroporous and asymmetric structure of the water-coagulated film typifies a film formed through an instantaneous demixing with a nonsolvent coagulant with a specific affinity, higher to solvent but lower to polymer.^{12–14} The isopropanol-coagulated film, by contrast, shows a dense skin layer backed by a relatively homogeneous, spongelike structure (Fig. 1(b)), which may be induced by the delayed demixing, in-

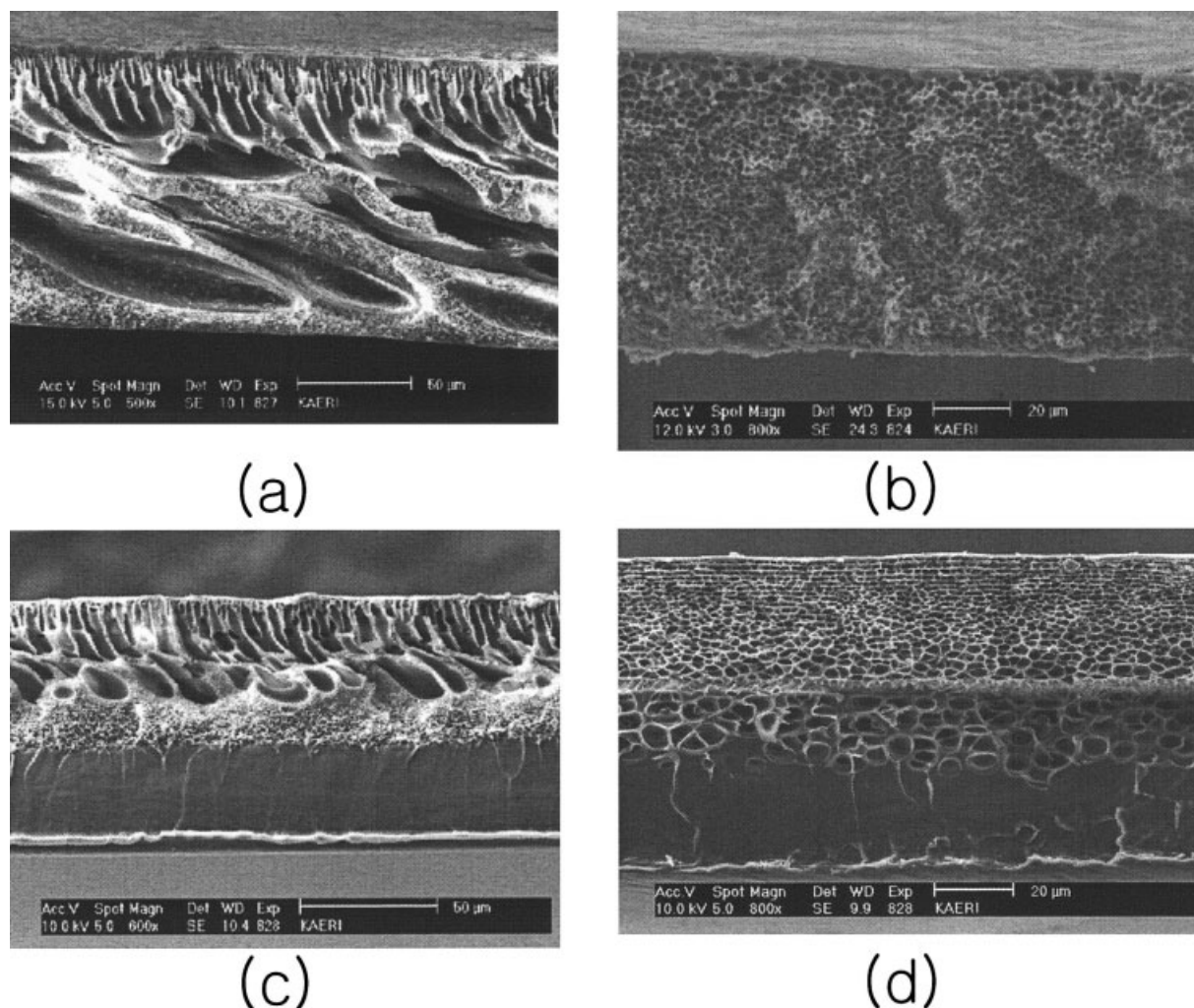


Figure 1 Cross sections of PSF films prepared without CAYS: single-layered structures by water (a) and isopropanol (b) coagulation, and double-layered structures by water (c) and isopropanol (d) coagulation.

cluding the nucleation of the polymer-lean phases near the thermodynamic equilibrium.

In double-layered films (Figs. 1(c) and 1(d)), the top layers keep a structural similarity with the single-layered membranes, except the macropores that were relatively suppressed in the water-coagulated film. On the interface between the two layers, however, distinct structures are formed depending on the nonsolvent coagulant used. A border in the intertwined interface is ambiguous in the isopropanol-coagulated film, showing the lack of a uniformed interface when compared with a relatively clear-cut structure in the water-coagulated film. Also, in the isopropanol-coagulated film, more developed and larger round pores are found in the leading edge of their penetration front, advancing to the support layer.

This kind of difference in the interface boundary seems to reflect the variation in the precipitation rates of the polymer in a cast solution. In the formation of a top layer structure, a cast solution over the dense

support film holds homogeneity until the solution reaches thermodynamic instability through a mutual diffusion with the solvent and the nonsolvent coagulant, and then it sets into a solid structure with a further exchange of the two ingredients. During this kind of process, the solvent inside the top layer penetrates into the support layer, ahead of the nonsolvent advancing from the top surface contacting with the nonsolvent coagulant. Its penetration stops at the point where it loses its chemical potential for a solvating power through mixing with the advancing nonsolvent. Therefore, the longer it takes to precipitate, the deeper the leading edge of the solvent or nonsolvent goes into the support layer.

To analyze this kind of phase inversion phenomena, thermodynamic and rheological characteristics in a system need to be investigated.^{15,16} One way to diagnose the thermodynamic stability of a solution is to measure the cloud point, to find the nonsolvent content that is required to convert a homogeneous solu-

TABLE I
Cloud Points Data of the Ternary System Consisting of
Polysulfone/*n*-Methylpyrrolidone (NMP)/Water or
Isopropanol at 25 °C

Polysulfone (g)	NMP (g)	Water (g)	Isopropanol (g)
4	26	2.10 (6.54) ^a	11.95 (28.49) ^a
5	26	2.02 (6.12)	11.85 (27.65)

^a Values in parentheses indicate weight percentages.

tion into a heterogeneous one. As indicated in Table I, water can demix the same binary solution with as much as one-sixth the amount of isopropanol, which indicates isopropanol's relative affinity to PSF. As the amount of nonsolvent in a cloud point increases, so does its role in delaying the phase separation during nonsolvent coagulation, or the slow down of the precipitation rate.

A high polymer concentration in the border region, along with the decrease in the nonsolvent's chemical

potential, can also contribute to the delay of the demixing of a cast solution. Build-up in a polymer concentration through solvent penetration in a dense polymer layer works as a hindrance against the fast penetration of the nonsolvent. Both hindered by the high polymer concentration and reduced in the precipitating power by mixing with solvent, the nonsolvent causes the leading edge of the polymer solution to be phase-separated near the thermodynamic equilibrium, causing the nucleation of the polymer-lean phase. Consequently, the structural irregularity in the interface would appear in the isopropanol coagulation because of its delayed precipitation.

As for those prepared with CAYS (Fig. 2), the morphology of the membranes shows structures similar to those of the membranes prepared without CAYS; asymmetric and macroporous for the film prepared by water coagulation and spongelike for the film prepared by isopropanol coagulation. CAYS particles seem to be plugged into the film matrix in the water-

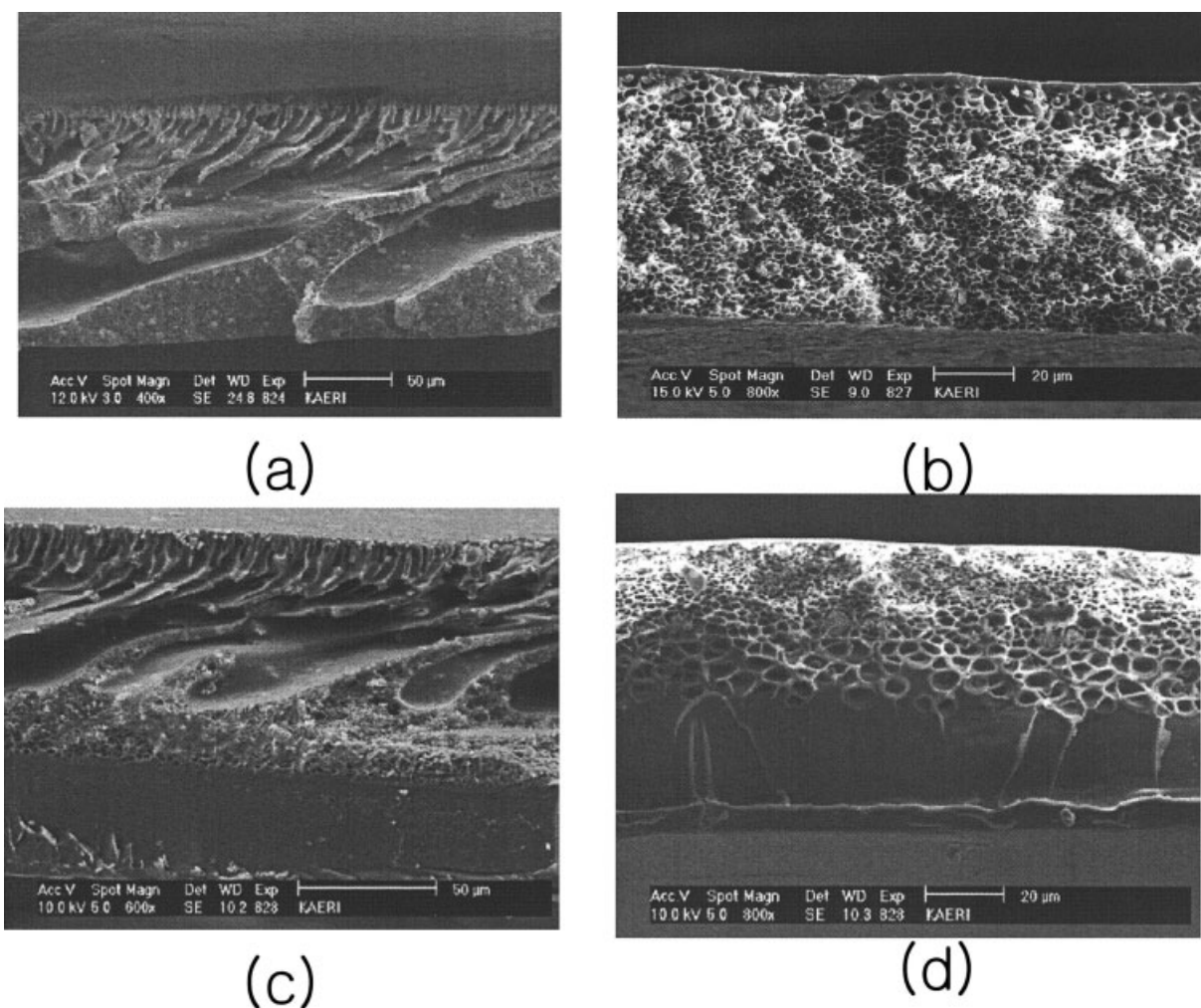


Figure 2 Cross sections of PSF films prepared with CAYS: single-layered structures by water (a) and isopropanol (b) coagulation, and double-layered structures by water (c) and isopropanol (d) coagulation.

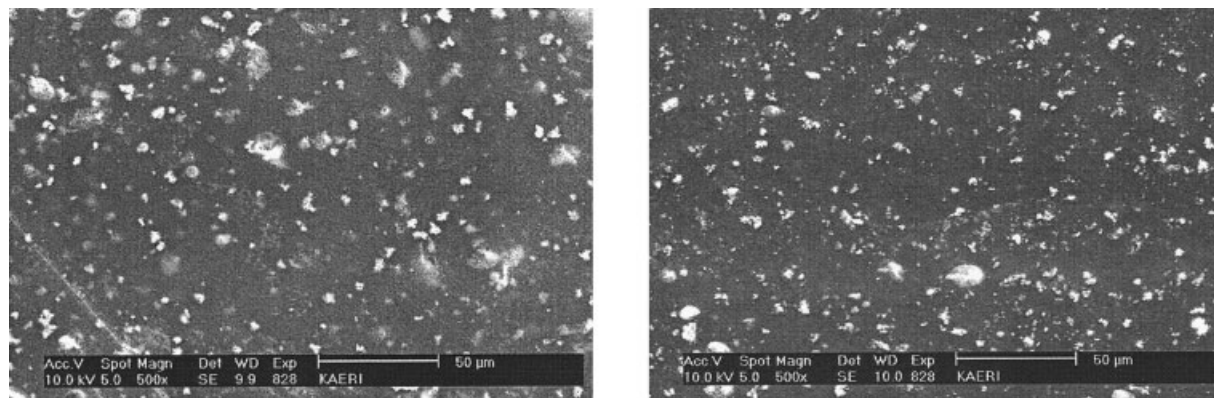


Figure 3 Surfaces of double-layered membranes prepared by water (a) and isopropanol (b) coagulation, with CAYS.

coagulated membranes (Figs. 2(a) and 2(c)), whereas they are localized in the polymer-lean phase in the isopropanol-coagulated films (Figs. 2(b) and 2(d)). In the single-layered film, CAYS that strayed from the film matrix were found on the bottom contacting the glass plate, but not on the top surface. This phenomenon indicates that in the bottom region of a cast solution, CAYS particles are expelled into the nucleated polymer-lean phase. In a double-layered structure, CAYS were not found near the interface between the two layers, indicating that CAYS could not follow the solvent penetration front into the bottom layer. This kind of CAYS distribution may be closely connected with the combined effect of the high polymer concentration near the interface and the inorganic fluor's immiscibility with the polymer.

Figure 3 shows that as in the water-coagulated film, the surface of the isopropanol-coagulated film holds evenly dispersed CAYS particles, safely embedded in the polymer matrix near the surface, even though the substructure of both the films are significantly different from each other. This phenomenon reveals that at the initial moment of the mutual diffusion, the kinetic movement in the surface region is too rapid for CAYS to be separated from the polymer molecules even when the precipitation rate is significantly different because of the coagulant used. The overall film morphology and impregnation of CAYS in polymer films can be described through schematic diagrams in Figure 4.

PMT and LB tests were applied to measure the radioactivity of the radionuclides picked up by the film. LB detects radioactivity directly without the aid of a scintillation medium, but cannot detect a low-energy radionuclide. On the other hand, PMT can detect low-energy radionuclides such as ^{14}C by measuring the photons released through the interaction between the radionuclides and the fluors. But the counting efficiency in the PMT measurement is lower than that of the LB counting because in the PMT measurement, the radionuclides should react with the fluor enveloped in the polymer.

To determine the detection capacity of the prepared films for radionuclides, identical aliquots (30 μL) of radioisotope ^{14}C are directly spotted on the film surface. In the detection of radionuclides adsorbed to a film, a porous structure of a film has a trade-off effect. It has an advantage in holding or picking up the contaminant, but induces a possible loss in the counting efficiency because of the increase in the tortuosity in the film, which causes the reduction of the radioactive energy or photons during their passing out of the structure. As shown in Table II, LB CPM values for the films prepared by the isopropanol coagulation are similar with each other even if they were single- or double-layered, strongly indicating that the spotted radionuclides stay mainly on the film surfaces. The formation of a dense surface structure in the membranes prepared by delayed phase transition is well known.^{13–15} On the contrary, in the water-coagulated films, the CPM is lower than those of the isopropanol-coagulated films. In particular, the CPM of the water-coagulated, single-layered film is of the lowest, which indicates that the radionuclides go deep into the porous structure, inducing the autoabsorption of the radionuclide energy. However, the CPM of the water-coagulated, double-layered film are close to those of the isopropanol-coagulated films, revealing that the autoabsorption of the radionuclides is significantly reduced by its dense support and suppressed macropores.

In the PMT assay, the CPM for the prepared films are significantly reduced because of the scintillation discount due to the polymer enveloping the CAYS embedded in the matrix. CPM values of the double-layered membranes are lower than those of the mono-layered membranes, which is not because of the detection efficiency but because of the overall decrease in the CAYS content. The thickness of a CAYS-holding layer in a double-layered film is about half that of a single-layered film and correspondingly there is less CAYS to react with the adsorbed radionuclides.

The CPM of the water-coagulated films are higher than those of the isopropanol-coagulated ones. For the

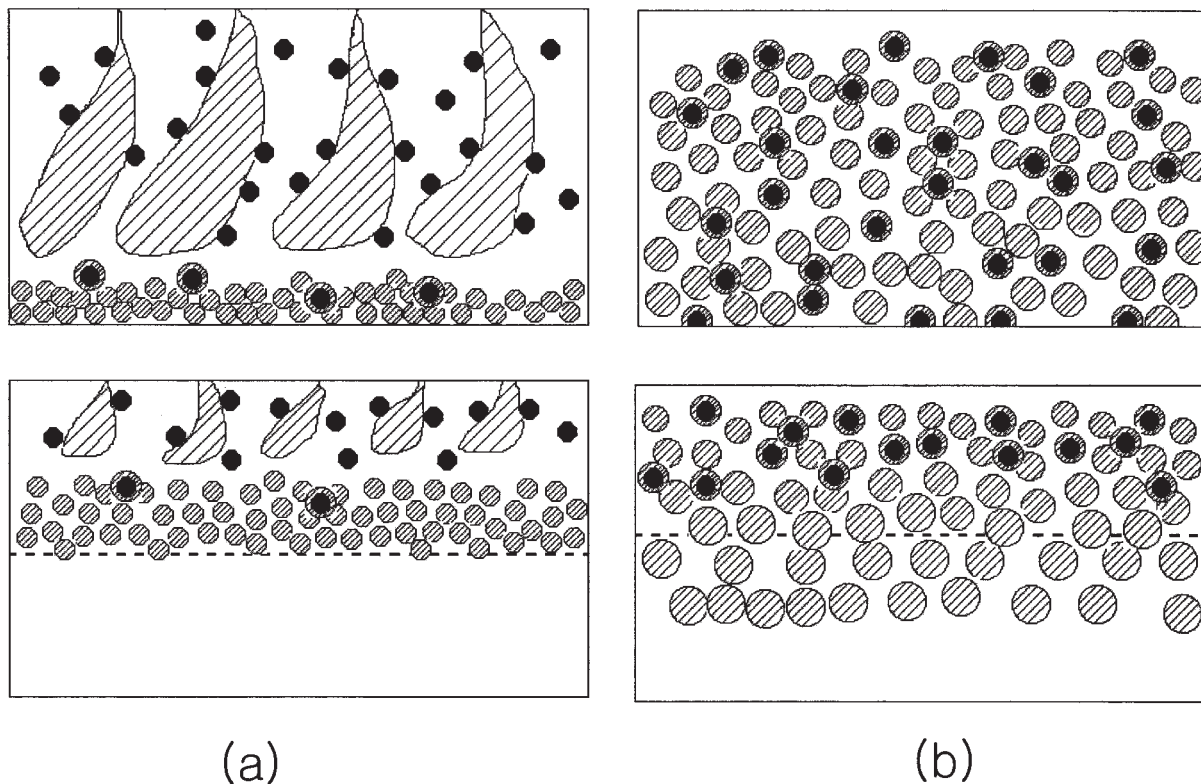


Figure 4 Schematic diagram of CAYS-impregnated membranes coagulated by water (a) and isopropanol (b); shaded parts for porous area and black dots for CAYS.

double-layered films, in particular, even though the CPM from the LB of the water-coagulated film are lower than those of the isopropanol-coagulated film, the CPM from the PMT show the reversed effect. These results reveal that a significant amount of radionuclides react with the CAYS inside the highly porous structure of the water-coagulated films. Considering that a portion of the scintillated lights is quenched during their passing out of the structure, the total scintillated amount highly overrides the reaction for the isopropanol-coagulated film, concentrated on the top surfaces.

TABLE II

Comparison of Radioactive Counts per Minute (CPM) of ^{14}C -Oleoyl-coenzyme A Detected Following Spot Test on the Prepared Membranes

Coagulant	LB counts (CPM)	PMT counts (CPM)
Single-layered		
Water (A)	298.4 (6.8) ^a	64.0 (2.6) ^a
Isopropanol (B)	363.7 (8.2)	63.1 (3.5)
A/B	0.82	1.01
Double-layered		
Water (A)	343.1 (3.2)	44.7 (1.8)
Isopropanol (B)	355.2 (5.3)	43.6 (1.1)
A/B	0.97	1.03

^a Values in parentheses indicate % SD.

The overall morphological and the radioactive detection data suggest that the double-layered films improve the morphological disadvantages such as the inefficient CAYS distribution and the physical weakness of the single-layered films, with a tight and dense supporting layer. This structural improvement induces an advantage for the secure holding of radionuclides, reducing their possible loss from the membrane matrix. With the isopropanol coagulation of a cast solution, the prepared film showed the dense top layer and the spongelike substructure. And, rather than going inside the substructure, the radionuclides spotted on the film stayed on the top surface. When prepared by water coagulation, the film forms an effective pore structure that improves the overall pick-up efficiency with an increase in overall reactive sites.

CONCLUSIONS

The composite films consisting of PSF and CAYS were formulated to be applied to a radioactive measuring instrument while ensuring detection reliability. Their morphology was significantly varied from the asymmetric and highly porous structure to the homogeneous and spongelike one, depending on the nonsolvent coagulant used. The variation in the precipitation rate of a cast solution induced a structural discrepancy in the interface

between the two layers in a double-layered structure, along with these morphological changes. Isopropanol-coagulated film showed a boundary highly intertwined and well developed with the nucleation of the polymer-lean phases, compared with the water-coagulated film consisting of a clear-cut boundary and less-developed polymer-lean phases. In the radionuclide detection using LB, the double-layered structure was superior to the single-layered one, largely because of the reduction in energy loss and the secure holding of the spotted radionuclides through the suppression of the macropores as well as a dense support layer. Also, the CPM of the water-coagulated film were lower than those of the isopropanol-coagulated film, which is due to the radioactive quenching induced by the passing out of the macropores. In the scintillation detection using PMT, however, the radioactive detection entailing an increase in the overall reaction area through the pores in the water-coagulated film bettered the detection of an isopropanol-coagulated film concentrated on the film surface.

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