

An Approach for Preparing an Absorbable Porous Film of Silk Fibroin–Rice Starch Modified with Trisodium Trimetaphosphate

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ABSTRACT: The absorbable porous material, especially gelatin porous film, is widely used for surgical use to stop bleeding, but its price is quite high. Thus, a new material at lower price with desirable properties is required. This article presents an approach to prepare a porous film of silk fibroin–rice starch (SF–RS) modified with trisodium trimetaphosphate (STMP). The preparation was performed using freeze-drying method aiming to increase the porosity and improve some other properties of the modified porous film. The solutions of SF and RS (5 : 95 weight ratio) and STMP were mixed and adjusted to pH 12 before being neutralized to pH 7 and freeze-dried for 48 h. Result from the SEM images showed that the average pore size of the SF–RS film increased from 17 to 126 μm after STMP was added up to 5.0% w/w. Similar to the SF–RS–STMP hydrogel, the linkages within the modified SF–RS porous film also occurred mainly between the O–H groups of RS and the triphosphate group of STMP. Moreover, cross-linking density of the porous film increased with the increasing content of STMP, evidenced from the increase of relative methylene blue adsorption. The addition of STMP also affected the physical properties of the modified porous film such as degree of swelling, oxygen permeability, but not the water solubility. Whereas, the residual ash of the modified porous films was lower than 2.0% and the degradation of the film ceased after soaking in 0.01M PBS solution for about 2 weeks. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41517.

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INTRODUCTION

Many researches and development have focused on biomedical materials in the forms of dense films, porous films, and sutures. Typical natural polymers have been reported as both absorbable dense and porous materials due to their unique properties including non-toxicity, biocompatibility, and bio-degradability.¹ The dense films, especially hydrogels, are generally used for external use as wound dressings, whereas the absorbable porous film is used by surgeons to stop bleeding in soft tissues, soft organs, and deep narrow spaces.² Gelatin porous film is usually preferred to stop bleeding during the surgical operation but it is quite expensive. Therefore, many researches have been performed to produce low-cost porous biomaterials by blending some specific polymers with other biopolymers such as chitosan, carboxymethyl cellulose.³ Baimark et al.⁴ reported the blending of SF with starch for microparticle preparation to be used in controlled-release drug delivery system. They found that thermal stability and water dissolution of the SF–starch blended microparticles were increased and decreased, respectively.

In addition, intermolecular interaction in the SF–starch blended microparticles was stated to be hydrogen bonding between the N–H groups of SF and the O–H groups of starch, thus making SF conformation change from random coil to β -sheet conformation after blending. However, these SF–starch blended microparticles were prepared using a water-in-oil emulsion solvent diffusion method, of which the organic solvent was used. Besides the direct blending of each component, many cross-linking agents have also been used for some specific purposes. The cross-linking agents may be used to modify solubilized biopolymers as insoluble materials for some biomedical applications. Gotoh et al.² used cyanuric chloride (CY) as a cross-linker to bind lactose with SF for using as a scaffold for hepatocyte attachment. The cross-linkage occurred through the reaction of the chlorine atoms of CY with the hydroxyl group in oligosaccharides and the phenolic hydroxyl group of tyrosine residue and the ϵ -amino group of lysine residue in SF, respectively. Shalviri et al.⁵ reported the use of STMP to cross-link starch with xanthan gum for producing a controlled-drug

delivery system. The evidence that showed the involvement of STMP in reacting with starch and xanthan gum was the decrease of the FTIR intensities of the O—H groups of starch and xanthan gum. Furthermore, the appearance of P=O stretching peak at 1244–1266 cm^{-1} also suggested that both starch and xanthan gum reacted with STMP. Souto-Maior et al.⁶ also observed the cross-linking of pectin and STMP. The FTIR intensity of the O—H groups of pectin also decreased due to interaction of the O—H groups of pectin with the phosphate groups of STMP. Moreover, the P=O and P—O—P stretching peaks were found at 1327 and 954 cm^{-1} , respectively. Compare with our previous work,⁷ as the hydrogels (dense films) were prepared from cross-linking the SF–RS blend with STMP using solution casting method. Results from the study showed that the linkages within the hydrogels occurred mainly between the O—H groups of RS and the triphosphate group of STMP. The hydrogel at 5 : 95 weight ratio of SF and RS with 1.0% w/w STMP tended to be more flexible and translucent than the SF–RS hydrogel. Some properties of the modified hydrogel including water solubility, degree of swelling, tensile strength, and residual ash are acceptable to be used as absorbable surgical hydrogel. However, to increase more water absorption of the hydrogel, a novel approach to produce highly porous films (sponge form) without the use of organic solvents is of interest. In this study, the porous films of SF–RS at the optimum weight ratio of 5 : 95, modified with various percentages of STMP were prepared by freeze-drying method in an alkaline medium. The modified porous films were then characterized in terms of its morphology, porosity, mechanical properties, cross-linking density, degree of swelling, water solubility, oxygen permeability, residual ash, and degradation in 0.01M PBS solution.

EXPERIMENTAL

Materials

Silk waste was purchased from Jun Thai Silk Group Co., Thailand. SF powder was prepared from silk waste as previously described by Moonsri et al.⁸ RS (Era-Tab, 99%) was obtained from Erawan Pharmaceutical Research and Laboratory Co., Thailand. STMP and PBS (pH 7.2) were purchased from Sigma-Aldrich chemical Co., USA. All other chemicals were analytical grade.

Porous Film Preparation

A mixed solution of SF and RS at a weight ratio of 5 : 95 was prepared by mixing a 5 mL of 3% w/v SF and a 95 mL of 3% w/v RS, in a 250 mL beaker. Then the solution was adjusted to pH 12 using NaOH and stirred with a constant speed for 30 min at room temperature. After that the mixture was neutralized to pH 7 using HCl before pouring into a polyethylene plate, then freezing at -10 to -20°C for 24 h and freeze-drying for 48 h. Next, the dry SF–RS film was removed from the mold, rinsed several times with deionized water and oven-dried until the weight of the film was constant. The same procedure was repeated for the preparation of the SF–RS porous film modified with 0.1–5.0% w/w STMP (SF–RS–STMP) except the step before the adjustment of pH 12, each of 10% w/v STMP at different volumes ranging from 0.03 to 1.50 mL was added to obtain the desired concentration of STMP. Both dry films of

SF–RS and SF–RS–STMP were then kept in a desiccator for further characterization.

Characterization of the Porous Film

Morphology. The morphology of the porous film was analyzed using a scanning electron microscope (SEM, JSM-5910 LV, JEOL, Japan). The dry sample was frozen in liquid nitrogen, and cracked to expose the cross-sectional part. This sample was mounted on a copper stub and sputter-coated with gold. The average pore size of the porous film then was analyzed using an Image J program (National Institutes of Health, MD).

Percent Porosity. The porosity of the porous film was determined by the liquid displacement method.⁹ A 0.80 g of the dry sample was immersed in a 5 mL (V_1) of hexane (contained in a 25.0 mL graduated cylinder) for 5 min to allow the hexane liquid to penetrate the sample pores. Then the total volume was recorded (V_2). After that, the swollen sample was removed from the graduated cylinder and the remaining hexane volume was recorded (V_3). The percent porosity (ε) of the porous film was calculated using eq. (1).

$$\varepsilon = \frac{(V_1 - V_3)}{(V_2 - V_3)} \times 100 \quad (1)$$

Mechanical Property. Compressive strength of the porous film sample (1.2 cm diameter \times 1.3 cm thickness) was examined according to the ASTM F451–95 (ASTM, 1992) using a universal mechanical testing machine (H10KS, Hounsfield, England). A test was performed on a dry disc with a crosshead speed of 1 mm/min and 10 kN load cell.

Cross-Linkage. To verify the existence of the STMP linkage with SF and RS, the functional groups of the blend in the 1.0% w/w STMP-modified SF–RS (SF–RS–1% STMP) porous film was compared with the porous film of SF–RS using a Fourier transform infrared (FTIR) spectroscopy. Initially, each of the samples was prepared using a potassium bromide pellet technique at room temperature. The FTIR spectra of all samples were recorded with a Spectrum 2000 FTIR spectrometer (Perkin Elmer, Watham, USA) in the range between 4000 and 400 cm^{-1} . The extent of STMP cross-linking in the porous film can be determined through the measurement of the cross-linking density via the relative amount of methylene blue adsorbed (RMB_{ads}).¹⁰ Each of the porous film sample (0.10 g) was separately immersed in 25.0 mL of 10^{-5}M methylene blue (MB) solution at pH 7.0, 30°C at different times ranging from 30 min to 4 h. Then the disappearance of the MB color was measured using an ultraviolet-visible spectrophotometer (UV/Vis T80, PG Instruments, England) at 665 nm. Later, the cross-linking density was calculated by determining their RMB_{ads} bound to the dry sample using the following equations,^{3,10} respectively.

$$\text{RMB}_{\text{ads}} = \frac{A_0 - A_2}{A_0 - A_1} \quad (2)$$

where A_0 is the initial absorbance of the MB solution, A_1 and A_2 are the absorbances of the MB solution after immersing the dry samples of the SF–RS and SF–RS–1% STMP into the MB solution, respectively. While the cross-linking density can be calculated by this equation.

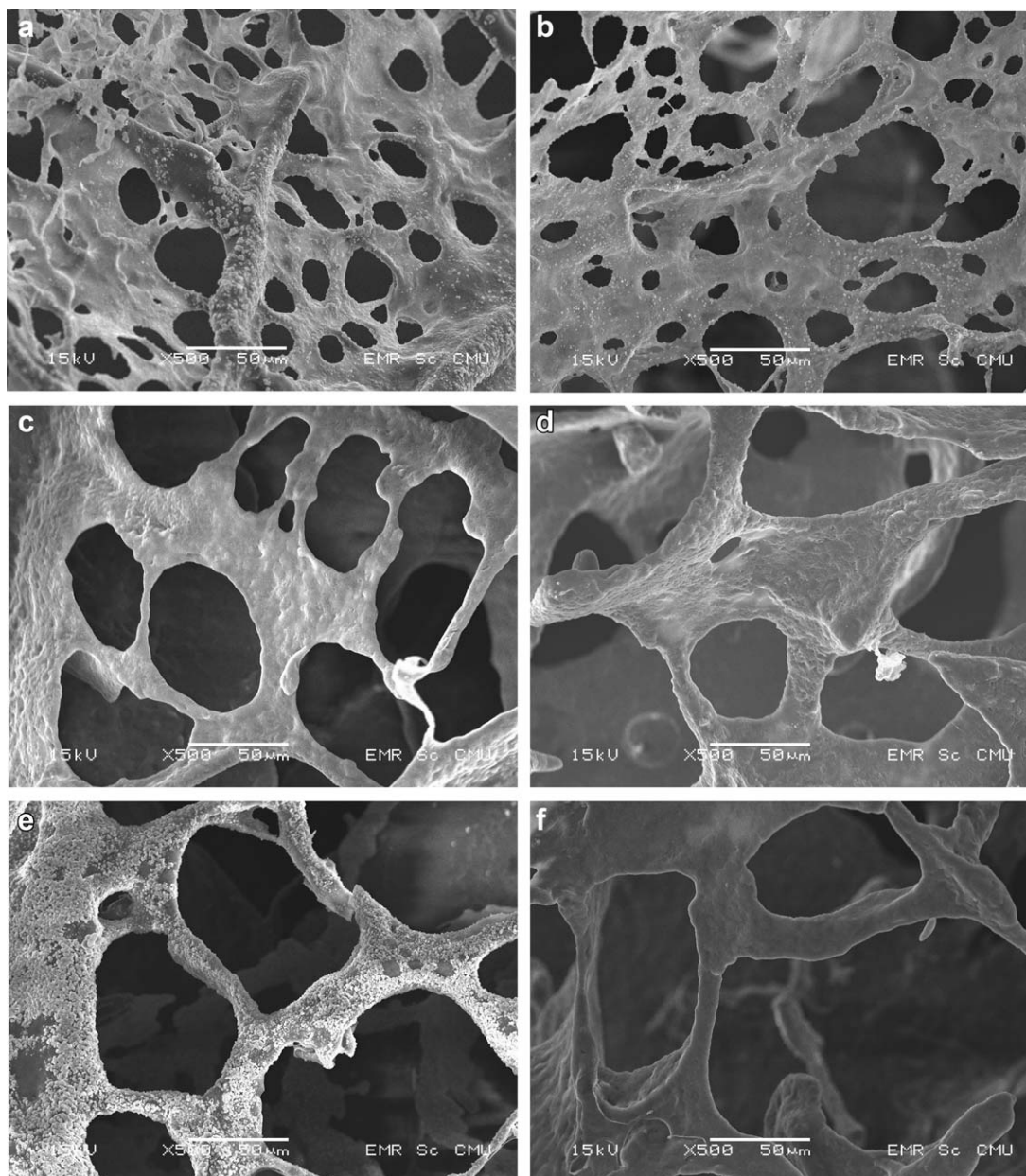


Figure 1. SEM images ($\times 500$) of the porous films of (a) SF-RS and (b–f) SF-RS with various percentages of STMP.

$$\text{Cross-linking density} = \frac{RMB_{ads,c} - RMB_{ads,nc}}{RMB_{ads,nc}} \quad (3)$$

where $RMB_{ads,c}$ and $RMB_{ads,nc}$ are the relative amounts of MB adsorbed by the cross-linked films with various percentages of STMP and by the non cross-linked film, respectively.

Degree of Swelling and Water Solubility. Each of the porous film samples was accurately weighed (W_1) and separately immersed in distilled water at room temperature for 24 h. After that the swollen porous film was removed and the excess water was wiped off from their surface, then the swollen sample was reweighed (W_2). The swollen sample was then oven dried at 40°C for 24 h and reweighed (W_3). Degree of swelling (DS) and

percent water solubility (S) of the sample were calculated using the following equations,^{11,12} respectively.

$$DS = \frac{W_2 - W_1}{W_1} \quad (4)$$

$$S(\%) = \frac{(W_1 - W_3)}{W_1} \times 100 \quad (5)$$

Oxygen Permeability (OP). Oxygen permeability of the porous film was measured using the oxygen permeability apparatus previously described by Kuchaiyaphum et al.¹³ The oxygen gas was passed through each porous film sample (10 cm diameter \times 0.3 cm thickness) mounted in the sample chamber. The pressure of the penetrated oxygen gas was measured in terms of Δh

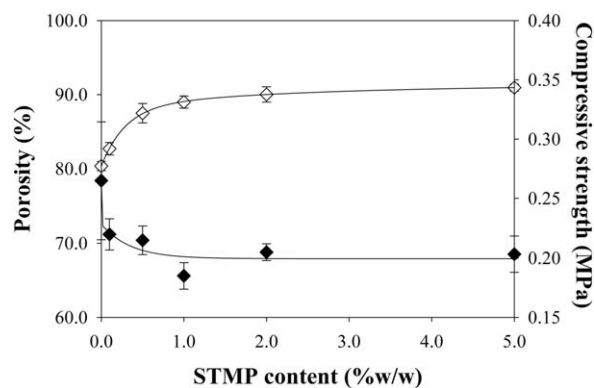


Figure 2. Percent porosity (\square) and compressive strength (\blacklozenge) of the modified porous SF-RS films at various STMP contents.

and the percent OP of each sample was then calculated using eq. (6).

$$OP(\%) = \frac{\Delta h_t}{\Delta h_o} \times 100 \quad (6)$$

where, Δh_t and Δh_o are the height differences of the liquid measured from the U-tube manometer, with and without a porous film mounted in sample chamber, respectively.

Residual Ash. Each of the porous film samples was accurately weighed (W_1) and incinerated in a crucible using an electric furnace (Euro-therm, model 3504, USA) at 850°C for 3 h. Percent residual ash of each sample was calculated using the following equation.¹⁴

$$\text{Residual ash}(\%) = \frac{W_4}{W_1} \times 100 \quad (7)$$

where W_4 is the weight of the ash.

Degradation. Degradation of the SF-RS-1% STMP porous film was investigated in 0.01M PBS at pH 7.4 and 37°C, according to ASTM F1635-11. Each of the sample (0.10 g) was accurately weighed (W_5). Then the samples were immersed separately in 0.01M PBS at different soaking times from 1 to 8 weeks. After that, the samples were washed with deionized water to remove the salts, then oven dried at 40°C for 24 h, and reweighed (W_6). Percent degradation of the porous film sample was then calculated using the following equation.¹⁵

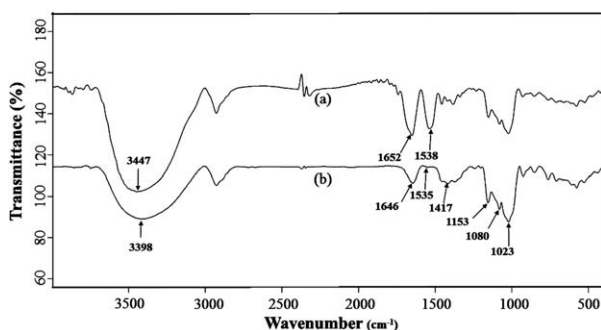


Figure 3. FTIR spectra of (a) SF-RS and (b) SF-RS-1% STMP porous films.

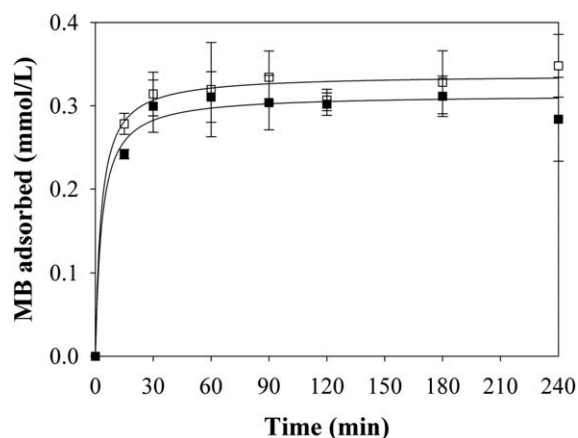


Figure 4. Methylene blue (MB) adsorption onto the porous films of SF-RS (\blacksquare) and SF-RS-1% STMP (\square) at various soaking times.

$$\text{Degradation}(\%) = \frac{(W_5 - W_6)}{W_5} \times 100 \quad (8)$$

RESULTS AND DISCUSSION

The porous films of the prepared SF-RS and SF-RS-STMP blend were yellowish white, flexible, moderate swelling, and slightly soluble in water. However, the modified porous films became more rigid when more STMP was added.

Morphology and Pore Size

From the cross-sectional SEM images of the porous films of SF-RS and SF-RS-STMP with different percentages of STMP as shown in Figure 1, they show the pores of both films that occur due to the sublimation of water during the freeze-drying step. The SF-RS film shows smoother surface with smaller pore sizes compared with the modified films. The SF-RS-5% STMP film has the largest pore size of about 126 μm , which reflects the highest porosity of the modified film.

Porosity and Compressive Strength

From Figure 2, percent porosity of the porous SF-RS film drastically increases with the increase of STMP content up to 1.0% w/w, then it increases only slightly afterward which is agreeable to its compressive strength behavior that remains almost constant when the STMP content is higher than 1.0% w/w. This is

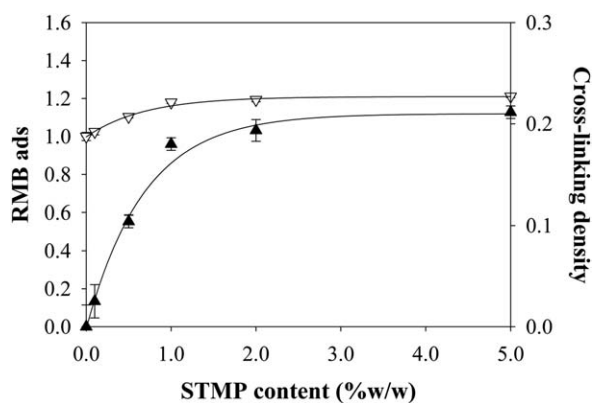


Figure 5. Relative methylene blue adsorbed (∇) and crosslinking density (\blacktriangle) of the modified SF-RS porous films at various STMP contents.

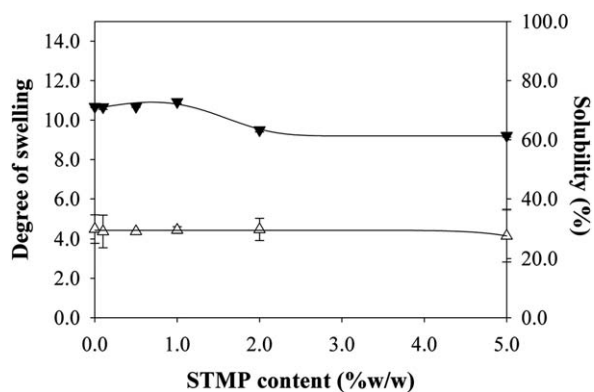


Figure 6. Degree of swelling (\blacktriangledown) and water solubility (Δ) of the modified SF-RS porous films with various STMP contents.

because the porous material can usually be compressed quite easily. The higher the porosity is, the lower the compressive strength of the material becomes. As the porosity of the films is almost the same, although the film with 5% w/w STMP has the largest pore size, thus the film with 1% w/w STMP was selected for further study.

Cross-Linkage

Results shown in Figure 3 indicate the existence of the STMP linkage with the SF and RS in the modified porous film that occurs mainly between the O—H groups of RS and the triphosphate group of STMP after 1.0% w/w STMP was added. The overlapping of O—H and N—H (stretching) peaks of the SF-RS at 3447 cm^{-1} is shifted to 3398 cm^{-1} with a decrease in its intensity due to the interaction of O—H groups of RS with triphosphate groups of STMP. Since the peaks due to C=O (stretching) and N—H (bending) in the SF-RS film at 1652 and 1538 cm^{-1} , were assigned as amide I and II of the SF, respectively, while the peak at 1023 cm^{-1} belongs to C—O (stretching) of the RS. Compare with SF-RS-1% STMP, the amide I and II peaks shift slightly to lower wavenumbers at 1646 and 1535 cm^{-1} , respectively, and decrease in their intensities. This is due to the interaction of the triphosphate groups of STMP with the COOH groups and the NH_2 groups of SF, respectively, based on the differences in their acid-base nature of the functional groups.¹⁶ Likewise, comparing the spectra of both films

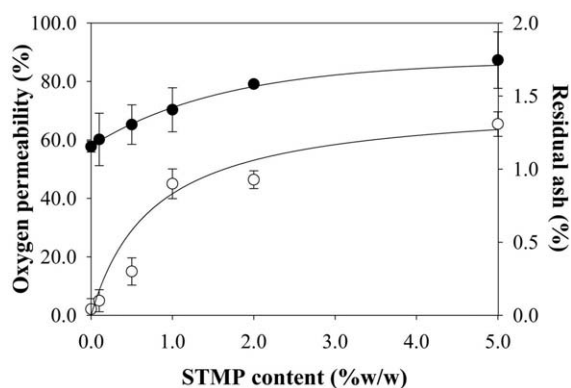


Figure 7. Percent oxygen permeability (\bullet) and residual ash (\circ) of the modified SF-RS porous films with various STMP contents.

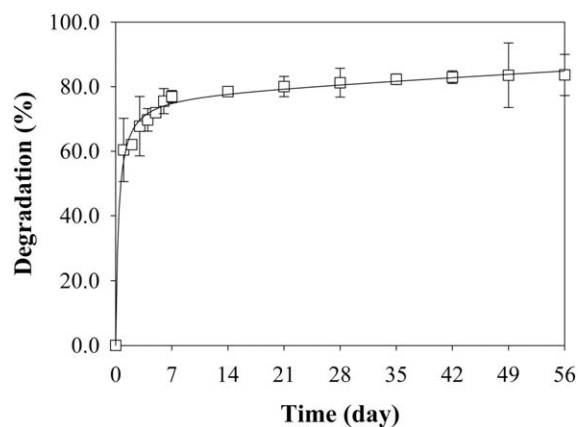


Figure 8. Degradation of the modified SF-RS-1% STMP porous film at various soaking time in 0.01M PBS, pH 7.4 and 37°C .

in the region of $1000\text{--}1200\text{ cm}^{-1}$, the increase in the intensities of the peaks *i.e.* at 1153 , 1080 , and 1023 cm^{-1} as C—O (anti-symmetric stretching), C—H (bending), and C—O (stretching), respectively, after modifying with STMP is attributed to the superimposition of the P—O—C peaks and the additional peak of C—O—P at 1417 cm^{-1} .

Figure 4 depicts the adsorption of MB onto the porous films of SF-RS, and the SF-RS-1% STMP at various soaking times. The saturation of the MB adsorption onto the porous films occurs after soaking the dry samples in the MB solution for 60 min. Generally, MB is a cationic dye which has a high affinity to negatively charged surfaces. The MB adsorption onto both SF-RS and SF-RS-1% STMP porous films occurs through the charge interaction of the O—H groups of the RS and also the triphosphate group of the STMP with the MB. The MB adsorption onto the SF-RS-1% STMP porous film is evidently more than that of the SF-RS porous film. This is because the SF-RS porous film has only the O—H groups of RS that can interact with the MB while the interacting groups of the SF-RS-1% STMP porous film consist of both the O—H groups of RS and the triphosphate group of STMP. Therefore, the additional adsorption of MB onto the SF-RS-1% STMP porous films reflects the amount of triphosphate group of STMP in the SF-RS-1% STMP films. Moreover, the values of the RMB_{ads} and crosslinking density of the porous films (Figure 5) increase with the increase of STMP contents. The crosslinking density of the modified film increases largely after adding STMP during the first stage owing to more network have been formed. But after the content of STMP exceeds 1.0% w/w, the RMB_{ads} and the crosslinking density tend to increase slightly. The reason that causes the adsorption of MB to occur at a faster pace at lower concentrations of STMP is due to the ease of accessibility of MB on interacting with the triphosphate group of STMP, but at higher content of STMP, more cross-linking that occurs would cause the retardation of the movement of MB into the pores of the films.

Degree of Swelling and Water Solubility

Since the degree of swelling of the porous films is related to its porosity, thus water can be more easily absorbed in the porous films due to the openness of the film structure. In Figure 6, the

Table I. The Physical Properties of the Modified SF–RS Porous Films at Various STMP Contents

STMP (% w/w)	Average pore size (μm)	Porosity (%)	Compressive strength (MPa)	Cross-linking density (%)	Degree of swelling	Solubility (%)	Oxygen permeability (%)	Residual ash (%)
0.0	17	80.4 \pm 0.6	0.26 \pm 0.05	0.00 \pm 0.02	10.7 \pm 0.0	30.0 \pm 4.8	57.7 \pm 1.8	0.0 \pm 0.1
0.1	19	82.7 \pm 0.8	0.22 \pm 0.01	0.02 \pm 0.02	10.7 \pm 0.1	29.2 \pm 5.5	60.2 \pm 9.0	0.2 \pm 0.2
0.5	64	87.5 \pm 1.3	0.22 \pm 0.01	0.10 \pm 0.01	10.7 \pm 0.0	29.3 \pm 0.3	65.2 \pm 6.7	0.5 \pm 0.3
1.0	70	89.0 \pm 0.8	0.18 \pm 0.01	0.18 \pm 0.01	10.9 \pm 0.1	29.7 \pm 1.1	70.3 \pm 7.5	1.0 \pm 0.1
2.0	81	90.0 \pm 1.0	0.20 \pm 0.01	0.19 \pm 0.01	9.5 \pm 0.1	29.9 \pm 3.8	79.1 \pm 1.0	0.9 \pm 0.1
5.0	126	91.0 \pm 0.5	0.20 \pm 0.02	0.21 \pm 0.01	9.2 \pm 0.1	27.7 \pm 8.8	88.3 \pm 9.6	1.3 \pm 0.4

degree of swelling of the modified porous films with 0–1% w/w STMP increases only slightly,¹⁷ in contrast to a large increase in its cross-linking density. This may be due to the openness of the film structures within that range of STMP contents is high enough to allow water molecules to be absorbed with minimal obstruction. However, the degree of swelling of the porous film slightly decreases when the STMP contents increase more than 1% w/w because the stiffness of the network becomes prominent, thus in turn causes a decrease in the degree of swelling of the films, but its solubility does not apparently change as the percentage of STMP is varied.

Oxygen Permeability and Residual Ash

Results displayed in Figure 7 reflect the ease of oxygen gas penetrating through the modified SF–RS porous films with more STMP contents. It is due to the expansion of the pore size of the films as more networking appeared with the increase of STMP contents. Considering the percentage of the residual ash of the porous films remained, the ash also increases with the increase of the STMP contents because more phosphorus residue is left over. However, all of these values are less than 2%, which can be acceptable for biomedical application.¹⁴

Degradation

As degradation of biomaterials in 0.01M PBS at 37°C is required to be studied for utilizing them in various biomedical applications. Results in Figure 8 indicate the hydrolytic degradation behavior of the modified SF–RS–1% STMP porous film at different soaking times. The porous films degraded much quicker during the first week then became almost unchanged after two week onwards. This behavior can be acceptable for using in biomedical applications as well.

Finally, all the physical properties of the STMP modified SF–RS porous films that depend on the STMP contents as discussed earlier are summarized in Table I.

CONCLUSIONS

The modified SF–RS porous films (5 : 95 weight ratio) with 0.1–5.0% w/w STMP were successfully prepared by freeze-drying. Results from SEM images showed the appearance of interconnecting pores within the modified SF–RS porous films, especially at 5% STMP added, the modified SF–RS film has the largest pore size and highest porosity. The FTIR spectra showed that the linkages within the modified porous film occurred

through the interaction of the O–H groups of RS with the triphosphate group of STMP. The addition of STMP affected the crosslinking density, the degree of swelling, oxygen permeability of the modified porous films, while its water solubility did not change. Finally, the test of the amount of residual ash remained after incineration and the study on film degradation in 0.01M PBS solution have proven that the prepared modified porous film is appropriate for biomedical applications.

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