PHYSICAL CHARACTERISTICS OF CHITOSAN BASED FILM MODIFIED WITH SILICA AND POLYETHYLENE GLYCOL

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ABSTRACT

Recently, development of film materials is focused on finding the films with high chemical and physical stabilities. Organic based material such as chitosan produces films with low physical stability, and hence addition of inorganic materials is necessary. In this research, the effect of silica and polyethylene glycol (PEG) addition on the properties of chitosan based films has been investigated. Precursors used to produce films included chitosan with the deacetylation degree of 83% and sodium silicate solution as the silica source. A simple synthesis in a one-pot process was carried out by mixing 1%(w) of chitosan solution in 2%(v/v) acetate acid and sodium silicate solution (27% SiO_2) in various composition ratios and casting the solution on a glass dish. The tensile strength and percentage of elongation decrease with increasing the silica content. The tensile strength tends to decline with addition of PEG, but the elongation percentage of the film increases. Hydrophilicity of the film decreases with the addition of silica and increases with the addition of PEG. The addition of silica and PEG does not change significantly the morphology of the film and functional groups indicating the domination of physical interaction among active sites in the film components.

Keywords: *composite; silica; film; chitosan*

ABSTRAK

Baru-baru ini, pengembangan material film difokuskan pada film yang mempunyai stabilitas kimia dan fisik yang tinggi. Material organik seperti kitosan menghasilkan film dengan stabilitas mekanik yang rendah, sehingga diperlukan penambahan material anorganik. Dalam penelitian ini, pengaruh penambahan silika dan polietilen glikol (PEG) pada sifat film kitosan dipelajari. Prekursor yang digunakan untuk mensintesis film adalah kitosan dengan derajat deasetilasi 83% dan larutan natrium silikat sebagai sumber silika. Sintesis sederhana dilakukan dalam satu wadah dengan mencampurkan 1% (b) larutan kitosan dalam 2% (v/v) asam asetat dan larutan natrium silikat (27% SiO_2) pada berbagai rasio komposisi serta pencetakan larutan pada cetakan kaca. Nilai kuat tarik dan persen perpanjangan akan menurun dengan penambahan silika. Nilai kuat tarik cenderung menurun dengan penambahan PEG tetapi harga persen perpanjangan meningkat. Hidrofilisitas film menurun dengan penambahan silika dan meningkat dengan penambahan PEG. Penambahan silika dan PEG tidak signifikan mengubah struktur amorf dan gugus fungsional film yang mengindikasikan dominasi interaksi fisik di antara situs aktif yang ada pada komponen film.

Kata Kunci: *komposit; silika; film; kitosan*

INTRODUCTION

Chitosan is biopolymer derivate of chitin and a polysaccharide found abundantly in crustacean exoskeletons of crab, shrimp, and lobster as a well as in cuttlebone of cuttlefish. The structure of chitosan is a linear chain of linked 2- acetoamido-2 deoxy-β-D-glycopyranose units. Chitosan is also multifunctional polymer containing large numbers of reactive amine groups together with hydroxyl groups which make it a hydrophilic material and capable of reacting with other groups. These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the chitosan film. It is especially attractive due to its film forming characteristic and finds multiple uses in application of coating, drug delivery, nutrients, controlled release of food ingredients,

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separation techniques, optical material, and so forth [1-2].

However, the poor physical/mechanical properties and high degree swelling of chitosan film in an aqueous system limit its practical application. One way to overcome these limitations effectively and conveniently is by creating chemical cross-linking. On the other hand, formation of organic-inorganic composite film provides another approach to improve the physicochemical properties of chitosan and other biomaterials. Introduction of silica into the chitosan film increases its oxygen permeability, biocompatibility, and biodegradability [1-8].

The interest of inorganic-organic film has to be found in the possible tailoring of the solid-state properties in relation to the nature and relative content of the constitutive organic and inorganic component [2]. Chitosan-silica composite for pH-sensitive film [2] and biodegradable/biocompatible materials prepared from tetraethoxysilane (TEOS) [2], tetraethoxysilane/vinyl triethoxysilane (TEOS/VTES) [1], 3-aminopropyltriethoxy silane [7], α-(glycidyloxypropyl)trimethoxysilane (GPTMS) [1], polydimethylsiloxane [8] have been reported.

Besides above materials, sodium silicate solution from rice hull ash silica has been reported as precursor silica for preparation of silica based films [9]. Silicate films showed moderate strength and flexibility, their barrier properties for non-polar organic solvents could be utilized for separating polar components from non-polar in the vapor phase or adsorption of polar compounds from a non-aqueous medium. The addition of sodium silicate from rice hull ash silica in the production of chitosan-silica film has been reported [10]. Based on the results of this study it can be concluded that the addition of silica affects the pore size of the chitosan-silica film. Particles of silica are ideal porogens for producing porous chitosan-silica film with controlled porosity and good mechanical properties [11].

The silica network is formed from the self condensation reaction of the hydrolyzed Si-OH groups. In spite the formation of hydrogen bonding between the silanol groups and the chitosan film that is expected to promote the compatibility between the organic and the inorganic phases, the lack of covalent bonding in the silica and polymer domains certainly to limit their compatibility [2]. The thermo stability and mechanical performances of the composite films are higher than that of chitosan film and increased with increasing the amount of silica added. However, the mechanical performance deteriorates with the excessive silica [1-3, 5-8]. Addition of food-grade plasticizers (polyethylene glycol, PEG) to film-forming alleviates this problem. When plasticizer is added, the molecular rigidity of a polymer is relieved by reducing the intermolecular forces along the polymer chain. The plasticizer improves flexibility and reduces brittleness of the film [11].

In this paper synthesis and characterization of chitosan-silica film in a one-pot process using sodium silicate solution as the silica source is reported. Additionally, the effect of the polyethylene glycol addition on the properties of the chitosan-silica composite film was evaluated. The physical properties of chitosan based film modified with silica and polyethylene glycol was observed.

EXPERIMENTAL SECTION

Materials

Chitosan with the deacetylation degree of 83% was supplied from CV Ocean Fresh Bandung. Polyethylene-glycol (MW 400), sodium silicate solution (8% Na_2O, 27% SiO_2), sodium hydroxide and acetic acid (2% v/v) all in analytical grade were purchased from Merck.

Instrumentation

The instruments used for characterization included Fourier Transform Infrared (FTIR) spectrometer (Shimadzu Prestige-21) for identifying the presence of functional groups, Scanning Electron Microscope (SEM, JSM-6360 LA) for characterizing the morphology. A Shimadzu X-ray diffractometer (XRD) with Cu-Kα radiation was used for evaluating the crystalline level of the films, Pearson Panke equipment Ltd for measuring the mechanical parameters, and Thermogravimetric Analysis (TGA) (Perkin-Elmer TGA-7) for evaluating thermal stability.

Procedure

Preparation of chitosan-silica film

Chitosan solution 1 w% was prepared by dissolving 1 g of chitosan in 100 mL 2%(v/v) acetic acid solution. Appropriate amount of sodium silicate with different mass ratio (0.1-1.5 g) were mixed with 100 mL chitosan solution, and the mixture was thoroughly stirred until there was no air bubble in the solution. The compositions of the films were varied as presented in Table 1. Film was obtained by casting the mixture on a glass plate and was allowed to evaporate the solvent under an ambient temperature for 3 days. The film was neutralized with a 5%(w/v) NaOH solution after drying. Afterward, the film was washed with water to remove the remaining NaOH. Finally, the film was stored in a desiccators before use. The optimum ratio mass of chitosan to silica is obtained from the film giving the highest tensile strength. The same work was carried out

Table 1. Amounts of chitosan and silica for preparing film with different mass ratio

No.	Chitosan 1% (w) in 2% (v/v) acetate acid (g)	Sodium silicate solution (27% SiO_2) (g)
1	1	0.1
2	1	0.2
3	1	0.3
4	1	0.4
5	1	0.5
6	1	0.6
7	1	0.7
8	1	0.8
9	1	0.9
10	1	1.0
11	1	1.5

Table 2. Tensile strength and percent elongation of chitosan-silica composite film

No.	Film composition (chitosan:silica, in g)	Tensile strength (MPa)	% Elongation
1	1 : 0	24.1 ± 1.1	19.7 ± 0.1
2	1 : 0.1	23.8 ± 1.2	19.0 ± 0.3
3	1 : 0.2	23.5 ± 1.0	18.3 ± 0.4
4	1 : 0.3	23.2 ± 0.8	17.8 ± 0.2
5	1 : 0.4	23.0 ± 1.2	15.7 ± 0.4
6	1 : 0.5	23.2 ± 1.0	15.0 ± 0.3
7	1 : 0.6	23.6 ± 0.9	14.3 ± 0.1
8	**1 : 0.7**	**24.2 ± 0.8**	**14.1 ± 0.1**
9	1 : 0.8	24.0 ± 0.9	14.0 ± 0.1
10	1 : 0.9	23.9 ± 0.9	13.7 ± 0.3
11	1 : 1.0	23.7 ± 1.2	13.5 ± 0.1
12	1 : 1.5	19.1 ± 1.3	13.0 ± 0.2

by adding varying the mass of PEG (0.05-0.50 g) on chitosan-silica to evaluate effect of PEG content on the film properties.

Characterizations

The mechanical properties of the film in dry state were performed at 25 °C using a universal material testing instrument with a crosshead speed of 10 mm/min. The results were presented in mean values of three independent measurements. The surface morphology was investigated with Scanning Electron Microscope after gold coating. The fractured cross-sections of the films were achieved by breaking the samples deeply cooled in liquid nitrogen. Fourier Transform- Infrared (FT-IR) spectra were obtained under dry air at a room temperature on KBr pellets in the range of 4000-500 cm^{-1}. An X-Ray diffractometer was used to record the diffractograms of the films at 25 °C. The X-Ray source was Ni-filtered Cu Kα radiation (40 kV and 30 mA). The dry films were mounted on a sample holder and the pattern was recorded in the reflection mode at an angle 2θ over a range of 3.0200° to 70° at a speed of 5°/min. Thermo-gravimetric (TG) data was performed for a 10 mg sample from room temperature to 800 °C at heating rate of 10 °C/min in a dynamic (30 mL/min) synthetic air atmosphere. For determination of swelling index (SI), a procedure reported by Chen et al. [6] was used. The pH dependent on swelling properties of the film, pre- weighed dry samples was immersed in buffer solutions at pH of 2.0-11.0. After 24 h, the swollen films were removed, excess water was bottled from the surface, and then were weighted. The following equation was used to determine SI.

$SI (\%) = [(w_w - w_d) / w_d] \times 100\%$,

where w_w and w_d are the sample weights after swelling for 24 h and dry state, respectively. In each specimen, three samples were tested.

RESULT AND DISCUSSION

The Effect of Silica and PEG on the Mechanical Property of the Films

Effect of the silica addition on the tensile strength and the elongation percentage at break are presented in Table 2. The tensile strength of film tends to decrease with the increase of the chitosan-silica ratio up to 1.0:0.7; at higher content of silica, the tensile strength drastically decreases. The optimum ratio showing the highest tensile strength is 1.0:0.7. The addition of silica more than 0.7 g ratio of chitosan, both properties above deteriorate supporting a conclusion that silica may harden and toughen chitosan. The percentage of elongation decreases with increasing the

Table 3. Tensile strength and percent elongation of chitosan-silica-PEG composite film

No.	Film Composition (chitosan:silica:PEG, in g)	Tensile strength (MPa)	% Elongation
1	1 : 0.7 : 0.05	22.8 ± 0.9	14.5 ± 0.2
2	1 : 0.7 : 0.10	22.1 ± 0.8	14.6 ± 0.3
3	1 : 0.7 : 0.15	22.1 ± 0.9	14.9 ± 0.2
4	**1 : 0.7 : 0.20**	**22.8 ± 0.7**	**15.4 ± 0.2**
5	1 : 0.7 : 0.25	22.5 ± 1.2	15.4 ± 0.1
6	1 : 0.7 : 0.50	22.3 ± 1.0	15.6 ± 0.2

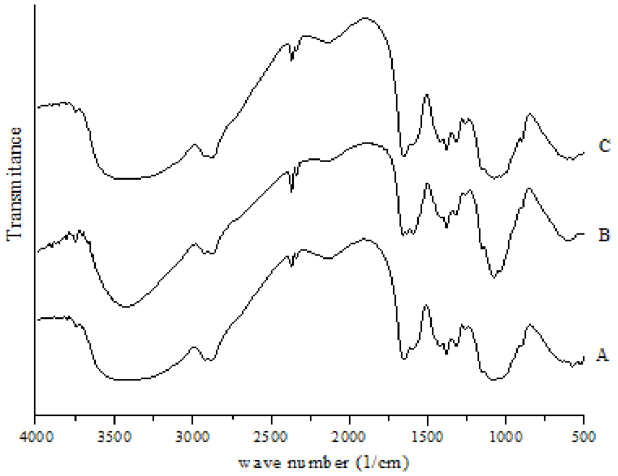

Fig 1. FTIR spectra of chitosan film (A), chitosan-silica = 1:0.70 (B), chitosan-silica:PEG = 1:0.70:0.20 (C)

silica content. The high silica content would bring chitosan-silica films to high inorganic characters such as the brittleness and makes low elongation at break. The test results revealed that formation chitosan-silica films did not bring positive effect on improving the mechanical properties of the film.

Effect of the PEG addition on the tensile strength and elongation percentage of the chitosan-silica films is expressed in Table 3, showing that blending with PEG changes the properties of the film. The tensile strength tends to decline with addition of PEG 0.05 g and more than that mass shows constant in the tensile strength. It may be attributed to the strong inner-stress existing in the film [13]. The elongation percentage of the film increases with addition of PEG, suggesting the reduced stiffness and improved ductility for the films. A mixture of these two polymers with different composition greatly influences the mechanical properties. The addition of PEG leads to formation of hydrogen bonds between PEG and chitosan and crosslinks the blend. The poly blend may be compatible due to the attractive intermolecular interactions [13-14].

FTIR Analysis

Analysis of FTIR spectra (Fig. 1) was carried out to predict the interaction between the chitosan and the silica frame work. As seen in FTIR spectra of chitosan film, a peak at 2877.79 cm^{-1} indicates alkyl C-H stretching vibration while a broad peak at 3425.58 cm^{-1} can be attributed to either O-H or N-H (primary amine) bonds or both. The peak at 1149.57 cm^{-1} corresponds to the symmetric stretching of the C-O-C bond, while the peak at 1095.57 cm^{-1} is due to the skeletal vibrations involving the C-O stretching and is generally regarded as the fingerprint peak for the structure of chitosan.

In FTIR spectra of chitosan-silica film (Fig.1B) the broad band gradually shifts to left (3487.3 cm^{-1}) and the intensity increases, owing to the addition of the N-H bonds at (3509-3300 cm^{-1}) and O-H bond from sodium silicate. Furthermore, band in film spectra at around 1000-1100 cm^{-1} was assigned to –C-O-C stretching. The increase in the intensity of that band for chitosan-silica, suggesting the formation of –Si-O-C bonds, since Si-O stretching also appeared at the same wave numbers of C-O stretching. The characteristic peak at 1550 cm^{-1} was assigned as $–NH_2$ group, which apparently increased after being incorporated with sodium silicate. This observation indicated that the hydrogen-bonding interactions between amino groups and hydroxyl groups of chitosan are weakened [15].

In FTIR spectra of chitosan-silica-PEG film (Fig 1(C)), the O-H stretching vibrations (3184 cm^{-1}) and amide band (1636 cm^{-1}) from chitosan are shifted to the low wave numbers. The intermolecular interaction between chitosan and PEG should be ascribed to the hydrogen bond. Furthermore, C-O stretching vibration from C-O-H of chitosan (1151 cm^{-1}) was shifted to low wave number. All these imply the existence of an attractive intermolecular interaction between chitosan and PEG, as suggested in the literature [14]. Hence, the intermolecular interaction between chitosan and PEG should be ascribed to the hydrogen bond.

Morphological Study

The morphology of the chitosan-silica films is evaluated based on the scanning electron microscopy (SEM) images presented in Fig. 2. It may be observed that the surface of film chitosan is smooth and the texture is plain without pores. Chitosan film gives a

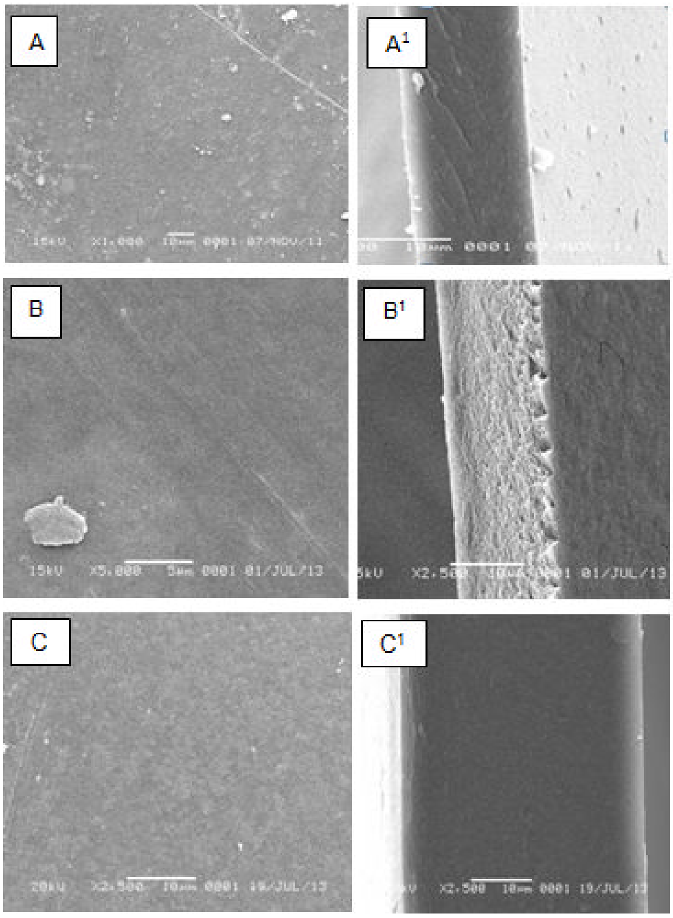

Fig 2. SEM images of film surface of chitosan (A), chitosan-silica (B) and and (chitosan-silica-PEG (C). Superscript shows image of cross surface

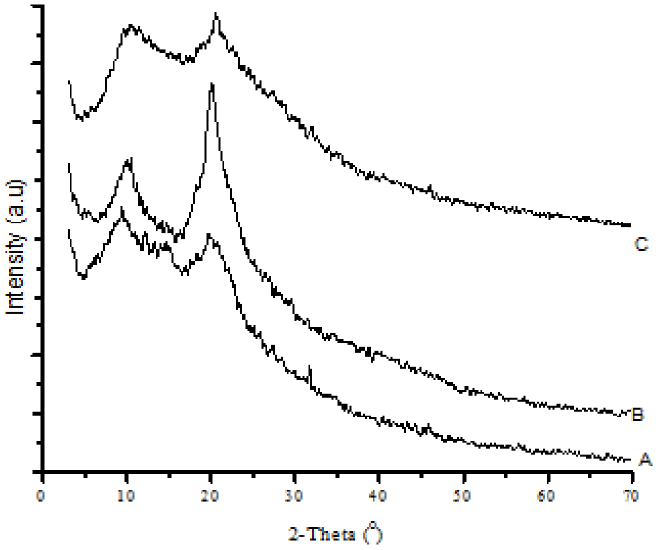

Fig 3. XRD patterns of the composite chitosan (A), chitosan-silica = 1:0.70 (B), and chitosan-silica-PEG = 1:0.70:0.20 (C) films

dense structure and very small porosity. Blending sodium silicate with chitosan (film B) improves the porosity of film and the morphology of blending PEG (film C); however, shows no change significantly the porosity. Addition of PEG causes the pores in the chitosan-silica film is reduced due to the physically trapped PEG on the solid surface. This result supports the conclusion based on the FTIR spectra showed that the possibility of interaction between component molecules are very small and did not significantly affect material properties. This result is contradicted with that reported by Zeng and Fang [13] suggesting the pore size increases with the addition of crosslinking agents. It is probably sodium silicate solution as the silica source does not act as a crosslinking agent.

Structure of the films is examined based on XRD patterns presented in Fig. 3. The peaks around 2θ = 9.26°, 20.37°, and 22.06° should be assigned to chitosan: the peak around 2θ = 22.06° corresponds to the amorphous structure. The diffraction of chitosan blending with silica tends to crystallize in the form hydrated crystalline structure (2θ = 10.62°) and amorphous structure (2θ = 21.84°). Once blending with amount of PEG, the main crystalline structures changes into hydrated one (2θ = 11.1°). Three produced films (chitosan, chitosan-silica and chitosan-silica-PEG) give similar peaks with 2θ around 9.26, 20.37, and 22.06° which should be assigned to an amorphous solid structure. The addition of silica and PEG in chitosan film does not change significantly the morphology; that it is relevant to the result reported by He et al. [14].

Thermal Analysis

The thermal properties of the films were measured by TG presented in Fig. 4. For chitosan film (not shown), the weight loss takes place in two stages. The first stage starts at 60 °C with weight loss of 10%. The second stage begins at 240 °C and reaches a maximum at 380 °C with weight loss of 41.4% [18]. For chitosan-silica film (Fig. 4A) and chitosan-silica-PEG (Fig. 4B), the first stage of decomposition occurs between ambient and 200 °C being accounted to around 14% weight loss, corresponding to dehydration of the films. The second stage of decomposition which starts from around 200 to 550 °C is attributed to a weight loss due to the decomposition of polymeric network [15,18-20]. For the chitosan-silica film, the second stage starts from 240 to 550 °C with the weight loss of 60.0%. Blending chitosan-silica with PEG, the second stage starts from 240 to 550 °C with the weight loss of 62.2%. As the amount of PEG is increased, the intra-molecular interactions between the terminal hydroxyl groups of PEG predominate, the attractive

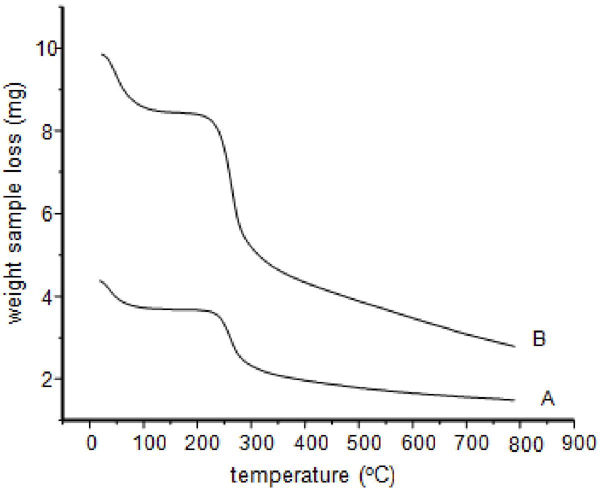

Fig 4. TGA thermograms of chitosan-silica (A) and chitosan-silica-PEG (B) films

bonds are inhibited, the blend becomes incompatible and as a consequence the thermal stability of the chitosan-silica film is lower than that of chitosan-silica-PEG one. This result is contradicted with result reported by Reiad et al. [16]. It was observed that thermal stability of chitosan blending PEG is higher than that of chitosan, but thermal stability decreases at too high mass ratio of chitosan to PEG.

Swelling Tests

Fig. 5 presents the swelling capability represented by swelling index (%) of the films. The sensitivity of the film toward pH is from the nature of chitosan. The pH-responsive behavior is due to the large quantities of amino groups on the backbone and acting as a weak polybase. Acidic media gives a pronounced effect on swelling behavior compared to the neutral and basic one, swelling index decreases with increasing pH value. The protonation of the $-NH_2$ group in the film thus ensures chain relaxation, leading to efficient solvent diffusion. In neutral and basic media, the swelling is mainly driven by solvent diffusion, but the chain relaxation effect due protonation absence of amino groups [13]. The enhanced hydrophilicity caused by the addition of PEG can be attributed to the immobilization of PEG chains on the material surfaces.

CONCLUSION

Chitosan-silica film is successfully synthesized in a one-pot process using sodium silicate solution as the silica source and the presence of small silica improves the tensile strength. The results showed that the chitosan-silica film with weight ratio of chitosan to sodium silicate 1.0:0.7 gives the highest tensile strength.

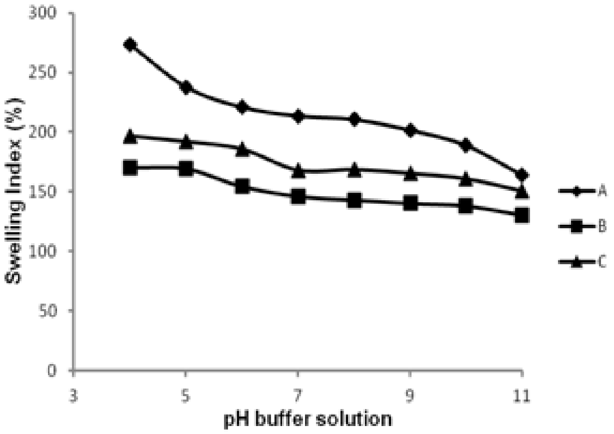

Fig 5. Plot of swelling index (%) for chitosan film (A), chitosan-silica film = 1:0.70 (B), and chitosan-silica:PEG film = 1:0.70:0.20 (C) in a buffer solution with various pHs

The presence of the PEG improves the percentage of elongation. A chitosan-silica-PEG film with the weight ratio of chitosan:silica:PEG 1:0.7:0.20 gives the highest value of the elongation percentage. Hydrophilicity of the film increases with the addition of PEG and decreases with the addition of silica. In general, the modifying with silica and PEG influenced the physical properties and water adsorption. Based on our results, chitosan-silica-PEG film has the potential to be used as biomaterials and separation materials in industries

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