

Novel Polyion Complex Films from Chitosan and Quarternized Poly(4-vinyl-*N*-carboxymethylpyridine) Containing Zwitterion Structure Units

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ABSTRACT: Novel polyion complexes films of chitosan and quarternized poly(4-vinyl-*N*-carboxymethylpyridine) containing zwitterion structure units were prepared by casting method. The aim of this work was to produce a hydrophilic film with the potential use as a hydrophilic membranes of the types used in membranes distillation and osmotic distillation for separating azeotropic, close-boiling, and aqueous organic mixtures. Their structure and properties were studied by infrared, wide-angle X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, tensile tester, and swelling measurements. The results indicated that polyion complexes occurred between chitosan and quarternized poly(4-vinyl-*N*-carboxymethylpyridine) containing zwitterion structure units. The thermostability of these blends decreased with the increase of

quarternized poly(4-vinyl-*N*-carboxymethylpyridine) content. Initially, appreciable improvement in tensile strength and breaking elongation were achieved with increase of quarternized poly(4-vinyl-*N*-carboxymethylpyridine) content to 30%, the maximum value of 46.65 MPa tensile strength and 25.67% breaking elongation were achieved, respectively. The maximum degree of swelling was achieved when the weight ratio of chitosan versus poly(4-vinyl-*N*-carboxymethylpyridine) was 50 : 50. Meanwhile, the relationship between their structure and properties was also discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3070–3076, 2007

Key words: polyion complexes; chitosan; quarternized poly(4-vinyl-*N*-carboxymethylpyridine)

INTRODUCTION

In recent years, the pervaporation has become interesting areas of technique for separating azeotropic, close-boiling, and aqueous organic solvents. The method has shown many advantages, such as good permselectivity, high heat efficiency, easy operation, and so on. Consequently, membrane-based pervaporation technology has all requisite for replacing extractive distillation for the separation of organic solvent, besides combining with simple distillation for the enrichment of organic solvent to high pure level. The new membrane materials had continuously been investigated. Chitosan,¹ sodium alginate, poly(acrylic acid) (PAA)/polysulfone (PSF) composite, poly(vinylidene fluoride)/poly(styrene sulfonate) composite, polypyrrolidone/poly(methacrylic acid) composite, sulfonated cellulose/poly(dimethylammonium chlo-

ride) ion complex, PAA/polymer with quaternary ammonium groups on the main chain ion complex, κ -caraginan/poly[1,3-bis(4-alkylpyridium)propane bromide] ion complex membranes,² ionomeric membranes of perfluorosulfonic acid (PFSA) polymer,³ polydimethylsiloxane-coated polyetherimide membranes,⁴ poly(vinyl alcohol)-poly(*N*-vinyl pyrrolidone) blends,⁵ sodium alginate, poly(vinyl alcohol) blend membranes,⁶ and so on, which have been used for the dehydration from the organic solvents and have shown high water-permselectivity. In addition, the graft- and block-copolymerization membranes have also shown high water-permselectivity such as poly(vinyl alcohol) (PVA)-*g*-(nylon4), polycarbonate-*g*-vinylpyridine, PSF-*g*-acrylamido (AAm), PVA-*g*-(*N*-Iso-propylacrylamido), poly(butyl terephthalate)-block-poly(ethylene oxide),² porous substrates of high density polyethylene-*g*-vinyl monomers,⁷ sodium alginate-*g*-polyacrylamide,^{8,9} polyacrylonitrile-*g*-poly(vinyl alcohol),¹⁰ and so on. Among the membrane materials, the hydrophilic polysaccharide polymers such as chitosan have gained special interest because they have shown the highest flux and separation factors of any hydrophilic materials tested for the pervaporation dehydration. The separation of organic mixture by using the polyelectrolytes complex which was

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especially emphasized as one of the membrane materials because of its high chemical stability, as well as its hydrophilicity, and due to its ionic characteristic. Polyelectrolyte complexes result from the interaction of macromolecules carrying complementary ionizable groups. It is expected that the polyelectrolyte complex membranes is likely to control the rate and selectivity of fluxes for solute by changing in the chemical and physical properties of the membrane induced by changing local conditions.¹¹

Chitosan is a polysaccharide polymer derived from chitin, and its repeating unit configuration is 1,4-linked 2-amino-2-deoxy- β -D-glucan. Chitosan is readily soluble in acidic solutions and the cation-charged chitosan can interact with an anionic polyelectrolyte to form polyion complexes. Quarternized poly(4-vinyl-*N*-carboxy methylpyridine) containing zwitterion structure units is synthesized via the chemical reaction of poly(4-vinylpyridine) and chloroacetic acid and it contains lots of carboxylate groups. Consequently, chitosan and quarternized poly(4-vinyl-*N*-carboxymethylpyridine) are prone to become polyion complex, which is expected to become permselectivity membrane.

To improve the industrial acceptance of the pervaporation process, research efforts are aimed at developing new membranes with better performance. However, understanding of the mechanical properties and structure of their blend membrane is also very important in practical application. In this article, the aim of this work is to produce a hydrophilic film with the potential use as a hydrophilic membrane of the types used in membranes distillation and osmotic distillation for separating azeotropic, close-boiling, and aqueous organic mixtures. Structure characterization of blends, particularly, the polyion complex between the two polymers, are investigated by infrared (IR), wide-angle X-ray diffraction (WXR), thermogravimetric analysis (TG), scanning electron microscope (SEM), electron tensile test, and swelling measurements. The relationship between the structure and their physicochemical properties are discussed.

EXPERIMENTAL

Preparation of blend films

Poly(4-vinyl) pyridine (PVP) was prepared by radical polymerization in mass at 60°C for 18 h under N₂ atmosphere according to the method of reference,¹² and AIBN (0.5 wt %) was used as initiator. The resulting product was dissolved in absolute ethanol and precipitated in ether, filtered and dried under vacuum to obtain the white product. Its molecular weight ($M_n = 3.1 \times 10^4$) was determined by Ubbelohde viscometer. The quarternization of the polymer was carried out by heating the solution of polymer

and chloroacetic acid in DMF at 75–78°C for 1 h. The resulting quarternized product was precipitated from chloroform.

Chitosan was prepared from chitin (purchased from Nanxing Chitosan, Suixi, Guangdong, China) by the method of Mima et al.¹³ Its degree of deacetylation was measured to be 90.2% by the method of Nakajima.¹⁴

Chitosan was dissolved in a 2 wt % acetic acid water solution to prepare a concentration of 2 wt % solution (I). Quarternized poly(4-vinyl-*N*-carboxymethylpyridine) (QPVP) was dissolved in deionized water to a concentration of 4 wt % (II). A mixture of (I) and (II) was stirred energetically and degassed, then was spread over a glass plate. The films were obtained after drying at room temperature for 72 h. By changing the weight ratio of I to II to 100 : 0, 90 : 10, 70 : 30, 50 : 50, and 30 : 70, a series of blend films coded as CH-0, CH-1, CH-2, CH-3, and CH-4, were prepared, respectively.

Characterization of films

IR spectra of the films in the mode of attenuated total reflection were recorded with a Nicolet (USA) 170SX Fourier transform infrared (FTIR) spectrometer. Film samples of about 30 μ m thickness were coated with gold in 13.3 Pa vacuum degrees, and then their surface morphologies were observed on a Hitachi S-570 scanning electron micrograph. The WXR patterns of the films of 30 μ m thickness were recorded with a Shimadzu XRD-6000 (Japan) diffractometer by using a Cu K α target at 40 KV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 45 to 5°. The TG of the film samples with 1 mm length and 1 mm width were performed by Shimadzu DT-40 instrument (Japan) under a nitrogen atmosphere with a flow capacity of 30 mL/min from 20 to 500°C at a heating rate of 10°C/min.

The weight of completely dried samples (W_0) was measured directly, and then the dried samples were dipped into the distilled water for 10 min, and they attained weight (W_t). The degree of swelling (Q_w) was calculated with the following equation:

$$\text{Degree of swelling } (Q_w) = (W_t - W_0)/W_0 \times 100\%$$

The tensile strength (σ_b) and breaking elongation (ϵ_b) of the films were measured on a versatile tensile tester (CMT-6503, Shengzhen SANS Test Machine, China) with a tensile rate of 5 mm/min according to the Chinese standard method (GB4456-84). The size of the samples was 70 mm in length, 10 mm in width, and the distance between two crossheads was 50 mm. The experimental temperature and relative humidity were 20 and 47%, respectively.

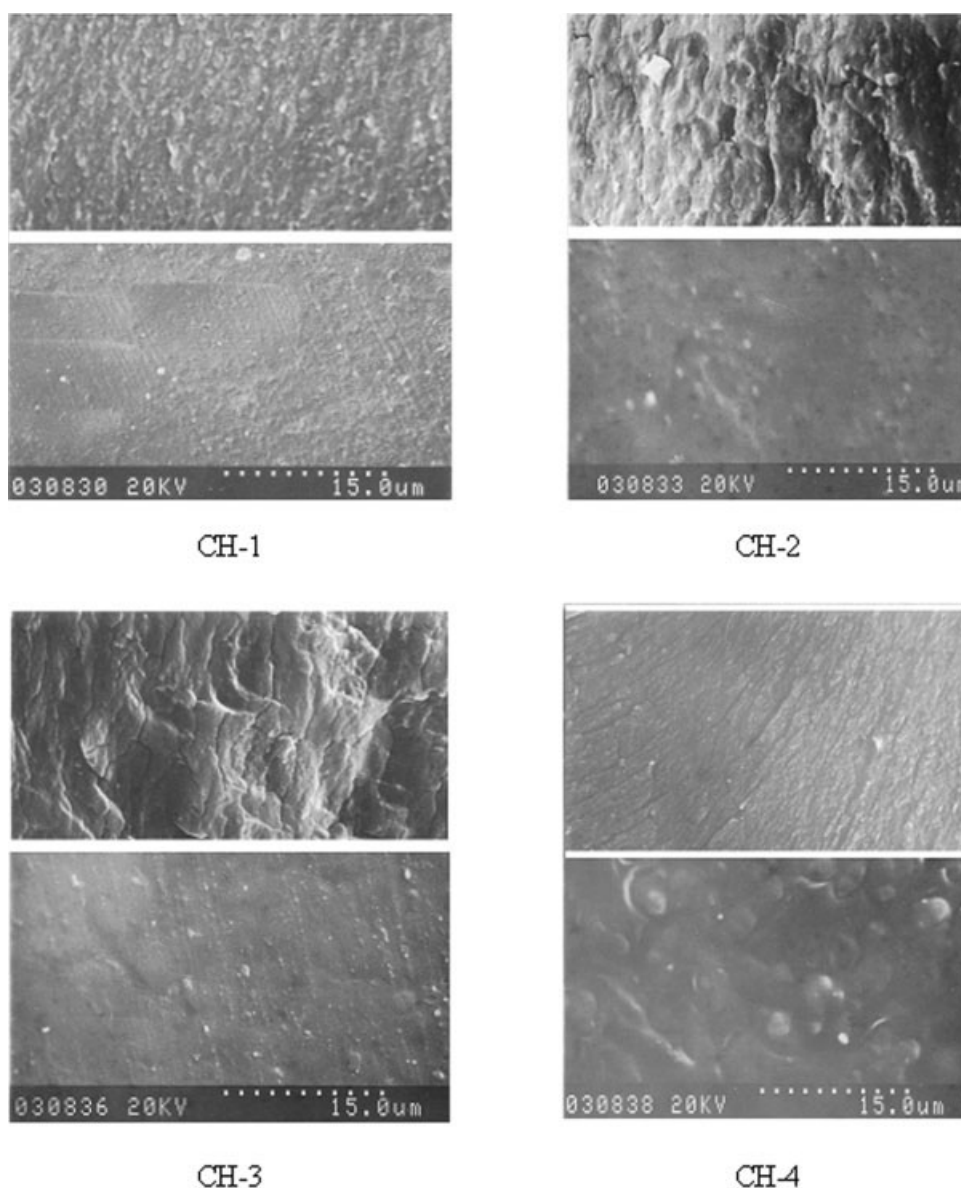


Figure 1 SEM photographs of blend films.

RESULTS AND DISCUSSION

Morphological characterization of the films

The scanning electron photographs of the blend films are shown in Figure 1. The bottom part of each photo is the surface of the blend films, and the top part is the cross section of the blend films. The pure CH-0 exhibits a smooth surface and homogenous cross section (not shown in Fig. 1). The surface of all blend films show a smooth surface structure, with some grain embed in the surface, and the numbers and scale of the grain become increasingly more and larger with increasing content of QPVP. The cross-section morphology of the blend films CH-1 is obviously different from that of CH-2 and CH-3, which exhibits looser structure and embedded a great number of the

grain in bulk, which could be the gel point created by the electrostatic interaction between chitosan and QPVP. But the cross section morphology of CH-2 and CH-3 turn out to be compact and lamella. For this reason, although there are several kinds of groups in the chitosan including amino groups, hydroxyl groups, acetamido groups, etc., the electrostatic attraction between carboxyl groups and protonated amino groups are the strongest interaction among all the possible secondary bonds between chitosan and QPVP. So the electrostatic attraction plays a predominant role during the formation of complex, it can be deduced that when the ion complex formation occurred with the electrostatic interaction between the carboxyl groups ($-\text{CH}_2\text{COO}^-$) of QPVP and the protonated amine groups ($-\text{NH}_3^+$) of chitosan, the chain mobility of the

blend films could be reduced by ion complex to a large extent. Thereby, the resulting films tend to have a more compact structure as the QPVP content increased.^{11,15} But this does not mean that other interactions such as hydrogen will not exist definitely. On the contrary, they may be beneficial to the stabilization of the complex. Meanwhile, the crosssection morphology of CH-4 shows homogeneity and it is looser than that of CH-3 and CH-4. The reason may be that the electrostatic interaction between chitosan and QPVP is reduced because the content of chitosan polycation is reduced.

The IR Spectra of the films

The information on the molecular interaction between the components could be obtained by spectroscopic vibration analysis. The IR spectra of the films within the range of 2000–650 cm^{-1} in the mode of attenuated total reflection are shown in Figure 2. From IR spectra of CH-0, the peaks at 1537 and 1255 cm^{-1} for pure chitosan are assigned to the characteristic bending absorption band of amino group and the stretching of acetylaminde III.¹⁶ The absorption bands at 1150 cm^{-1} (antisymmetric stretching of the C—O—C bridge), 1069 and 1023 cm^{-1} (skeletal vibrations involving the C—O stretching) are characteristics of its saccharide structure.¹⁷ The weak band at around 1640 cm^{-1} are assigned to the characteristic absorption band of ammonium group, it implies that the $-\text{NH}_2$ of chitosan in acidic solution is protonated, and chitosan is a polycation. The molecular structure of QPVP revealed that 1640, 1571, and 1516 cm^{-1} are refer to the vibration of NR_4^+ , $\text{C}=\text{N}$, and $\text{C}=\text{C}$ (pyridine ring),¹⁸ 1740 and 1470 cm^{-1} are refer to the asymmetrical and symmetrical characteristic vibration absorption band of carboxylate groups, as shown in curve QPVP in the Figure 2. The difference between the blend films and pure chitosan or quaternized poly(4-vinyl-*N*-carboxymethylpyridine) can be seen from Figure 2. No band at 1740 cm^{-1} assigned to carboxylate groups is found in the blend films. With the weight of QPVP increasing, the intensity of the band at 1640 cm^{-1} gradually increases and broadens, and the band is split into two peaks. The new bands of CH-1, CH-2, CH-3, and CH-4 occur at 1629, 1625, 1621, and 1619 cm^{-1} , respectively, which are caused by the electrostatic interaction between the $-\text{CH}_2\text{COO}^-$ groups and the protonated $-\text{NH}_2$ of chitosan. The new band is assigned to the asymmetrical vibration of the $-\text{COO}^-$ of QPVP.¹⁹ The phenomena are similar to those of the polyion complex from the chitosan and alginate.^{17,20} It proves that the reaction occurs as suggested in the following equation:

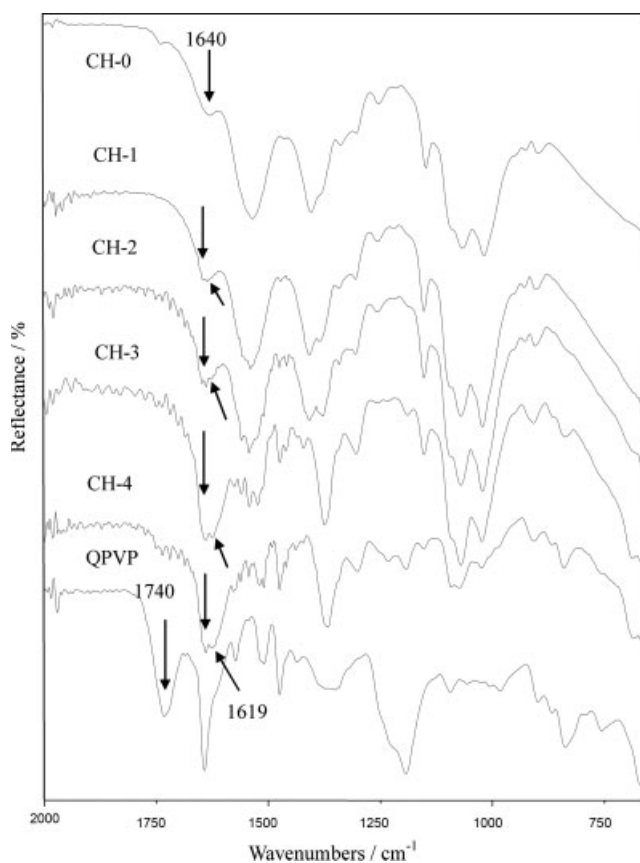
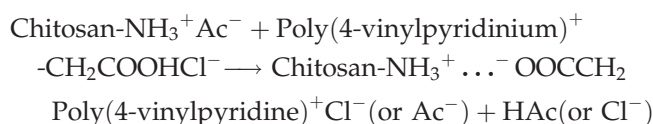


Figure 2 IR spectra of pure polymers and blend films.



The reaction causes gelation between chitosan and QPVP because of the electrostatic interaction. The result is in agreement with the morphology of blend film.

The WXR D analysis of the films

Figure 3 shows the WXR D patterns of pure polymers and the blend films. By comparing blend films with pure film, it can be concluded that X-ray diffraction patterns of the blend films appear as superimposed images which are not the simple combination of the pure components. We can recognize three crystal peaks at around 8.3, 11.32, and 18.22° (2θ) in the XRD pattern of CH-0, it agrees with the reports in reference.²¹ The pure quaternized poly(4-vinyl-*N*-carboxymethylpyridine) shows a rather amorphous substrate. With the increase of QPVP content, the intensity of blend films corresponding to 8.3, 11.32, and 18.22° (2θ) become gradually lowered, those peaks shifts

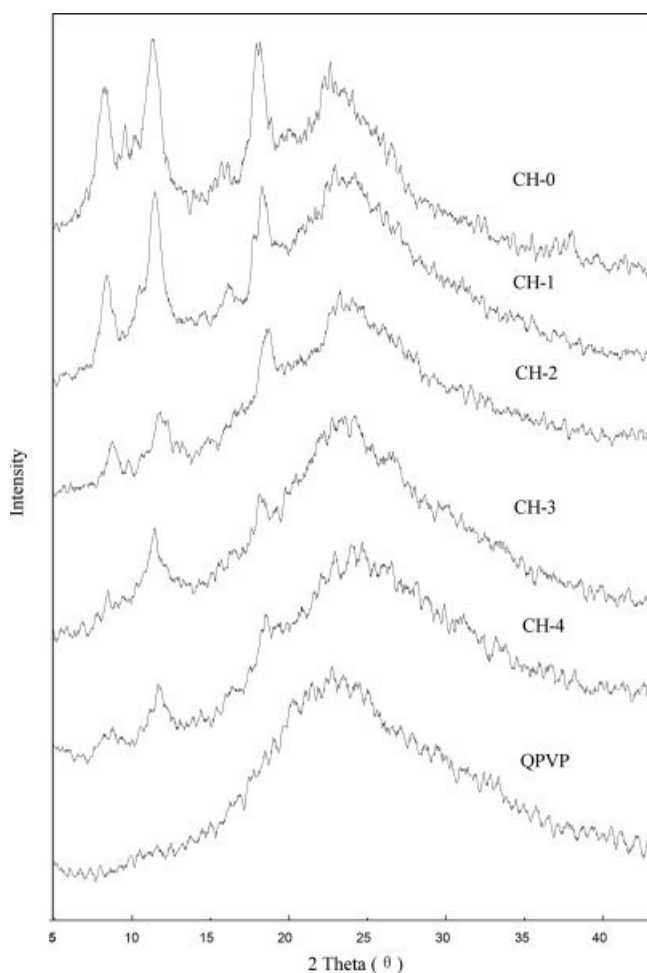


Figure 3 WXR D diffraction patterns of pure polymers and blend films.

increasingly to lower bragg angle, and amorphous rang area corresponding to $2\theta = 22.68^\circ$ also decreases gradually. It is obvious that the electrostatic interaction between chitosan and quaternized poly(4-vinylpyridine) prevents or disturbs chitosan from crystallization, and breaks the hydrogen bonding between amino groups and hydroxyl groups.²⁰ No new diffraction peaks in the blend films are found, it implies that the polyion complexes exists in amorphous state.

The thermal properties of the films

The TG curves of pure and blend films are shown in Figure 4. The pure CH-0 showed two steps of weight loss within the temperature range of 30–500°C. The initial loss at about 100°C is due to a loss of moisture. The second weight loss is found within the range of 250–350°C, which is attributed to starting degradation of molecular structure.²² Pure QPVP exhibits three steps of weight loss. The stage within 140–230°C is related to the thermal process involving the break-

down of the carboxy methyl side groups. The thermal degradation within 230–360°C is assigned to the degradation of PVP.²³ As seen from Figure 4, the TG curve of blend film CH-1 is similar to that of pure chitosan, it shows two steps of weight loss. The TG curves of blend films CH-2, CH-3, and CH-4 exhibit three stages of weight loss. By comparing with that of pure chitosan, we find that the thermal stability of all blends gradually decrease with the increase of QPVP content, which are similar to that of polyion complex from chitosan and alginate.²⁰ The thermal degradation temperatures of blend films clearly decrease, indicating that QPVP had destabilizing effect on chitosan. The existence of QPVP in the blends might aggravate the degradation of chitosan at high temperature. It indicates that the electrostatic interaction of polyion complexes could induce the fall of thermal stability. By comparing with CH-3 and CH-4, the thermal stability of CH-4 is higher than that of CH-3, which indicates that the electrostatic interaction in blend film CH-4 is lower than that of CH-3 because the content of chitosan in CH-4 is lower than that of CH-3. The fact also proved that the electrostatic interaction of polyion complexes could induce the fall of thermal stability.

The degree of swelling of the films

Generally speaking, the chemical structure can affect the water absorbability of blending films. Taking the chemical structure into account, the blend films can promote the water absorbability because QPVP contains a lot of ammonium groups. The degree of swelling as a function of the QPVP weight is shown in Figure 5. An increase of QPVP weight up to 50% raises the degree of swelling in the distilled water, which

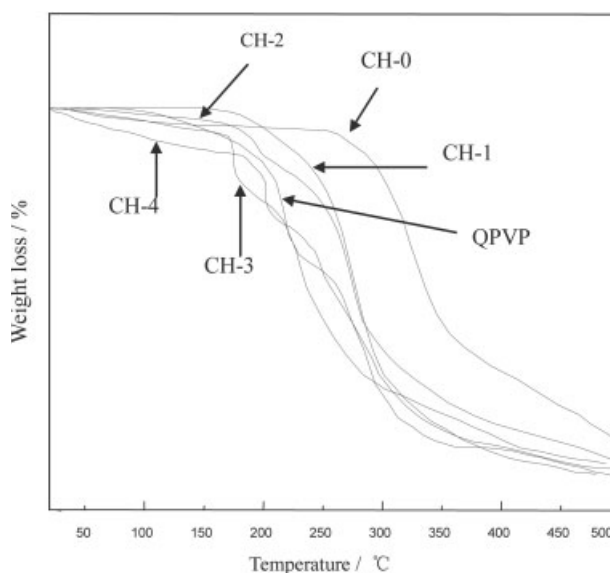


Figure 4 TG curves of pure polymers and blend films.

could be attributed to the formation of the polyion complexes between chitosan and QPVP and an introduction of quaternary ammonium groups which have a higher affinity for the water molecule. On the contrary, when the QPVP weight attains 70%, the degree of swelling slightly decreases, which could be attributed to the decrease of chitosan/QPVP ionic linkages per each chain. On the other hand, the blend films are exposed to water until equilibrium is achieved. The blend films are partially soluble in water, which is similar to the facts of polyion complex from chitosan and alginate.²⁰ It proves that crosslinked network structures are created in the polyion complexes. The facts suggest that the blend films introducing QPVP could be used as a hydrophilic membrane with the potential use as a hydrophilic membrane of the types used in membranes distillation and osmotic distillation, and they increase the separation factor.

The mechanical properties of blend films

Characterization discussed earlier has displayed an ionic linkage network structures between both molecules in the blends. Tensile tests can provide an answer to this question about the effect of the ionic linkage network for the mechanical properties. The tensile strength and breaking elongation dependence on the content of QPVP for the films are shown in Figure 6. The tensile strengths of the blend films change with the increase of QPVP content, and the maximum value of 46.65 MPa tensile strength is achieved when the retention of QPVP is 30 wt %. The change of breaking elongation is similar to that of the tensile strength, and the maximum value of 25.67% breaking elongation is achieved. The conclusion can be drawn that the blend of chitosan and QPVP has enhanced the mechanical properties of the blend films, and the

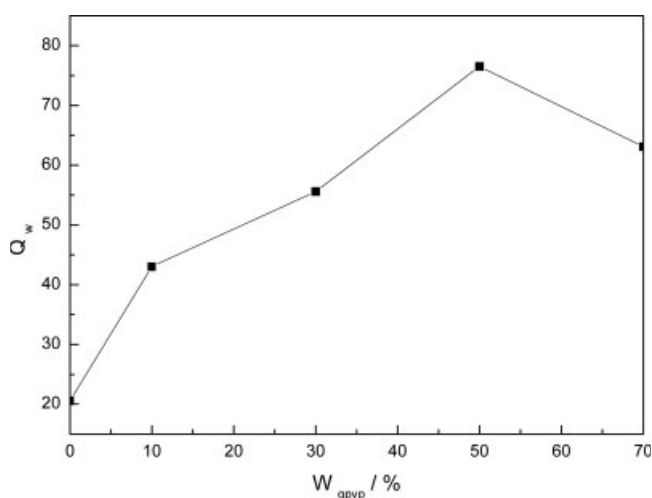


Figure 5 The degree of swelling of all samples.

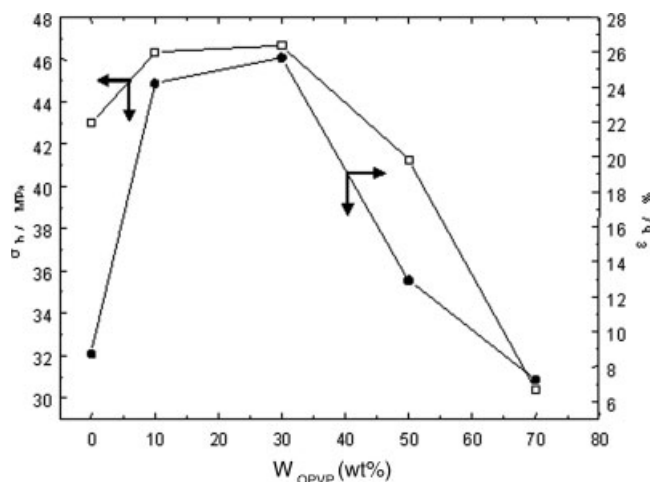


Figure 6 The tensile strength and breaking elongation dependence on QPVP content.

enhancement of tensile strength may be attributed to a greater number of chitosan/QVP ionic linkages per each chain. When the content of QPVP is more than 30%, the declining tendency of mechanical properties is found because the inherent mechanical property of QPVP is poor, and the rigid structure of blend films is enhanced. Moreover, the breaking elongation obviously changes because there is synergistic effect between ionic linkages and a lot of quaternary ammonium groups that are similar to ionomer that has good ductibility.²⁴ The blend films containing higher QPVP content have a more compact network structure and lesser chain mobility. So the weight QPVP do not exceeds 30%, the blend films show the best breaking elongation. It is worth noting that the polyion complex occurs partially in chitosan bulk, and with the increase of QPVP containing zwitterion structure units, which can improve the mechanical properties of polyion complex. The maximum occurred at the content of about 30% QPVP, which corresponds to optimum compatibility between chitosan and QPVP.

CONCLUSIONS

Novel polyion complexes films of chitosan and quarternized poly(4-vinylpyridine) containing zwitterion structure units were prepared by casting method. Their structure and properties were studied by IR, WXR, SEM, TG, tensile tester, and swelling measurements. The results indicate that polyion complexes occur between chitosan and quarternized poly(4-vinylpyridine) containing zwitterion structure units because of the electrostatic interaction between the carboxyl groups ($-\text{CH}_2\text{COO}^-$) of QPVP and the protonated amine groups ($-\text{NH}_3^+$) of chitosan. The thermostability of these blends decrease with the increase

of quarternized poly(4-vinylpyridine) content, which suggests that QPVP had destabilizing effect on chitosan. The existence of QPVP in the blends might aggravate the degradation of chitosan at high temperature. It indicates that the electrostatic interaction of polyion complexes could induce the fall of thermal stability. Initially, appreciable improvement in tensile strength and breaking elongation are achieved with a QPVP content of 30%, the maximum value of 46.65 MPa tensile strength and 25.67% breaking elongation are achieved, respectively. The enhancement of tensile strength and breaking elongation may be attributed to a greater number of chitosan/QVP ionic linkages per each chain. An increase of QPVP weight upon to 50% increases the degree of swelling in the distilled water, which could be attributed to the formation of the polyion complexes between chitosan and QPVP, and an introduction of quaternary ammonium groups which have a higher affinity for the water molecule. Especially, It is worth noting that the polyion complex occurs partially in chitosan bulk, with the increase of QPVP containing zwitterion structure units which can improve the mechanical properties of polyion complex and swelling degree, which could be used as a hydrophilic membrane with the potential use as a hydrophilic membrane of the types used in membranes distillation and osmotic distillation, and increase the separation factor.

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