

Characterization of Films from Chitosan and Quaternized Poly(4-vinyl-*N*-butyl) Pyridine Solutions

Changhua Liu, Chaobo Xiao

Department of Chemistry, Wuhan University, Wuhan 430072, China

Received 10 June 2003; accepted 22 October 2003

ABSTRACT: All Blend films were prepared from a mixture of 2 wt % chitosan in acetate solution and 4 wt % quaternized poly(4-vinyl-*N*-butyl) pyridine (QPVP) in aqueous solution and dried at room temperature for 72 h to obtain the films. Their structure and properties were studied by infrared (IR), wide-angle X-ray diffraction (WXR), scanning electron microscopy (SEM), thermogravimetric analysis (TG), and differential scanning calorimetry (DSC). Crystallinities of the blend films decreased with the increase of QPVP when weight of QPVP content was less than 15.0 wt %. The thermostability, tensile strength, and breaking elongation

of the films in dry state were better than those of chitosan film. Tensile strength of the blend film dried at 40°C under vacuum for 24 h achieved 56.38 MPa when the weight ratio of chitosan to QPVP was 9 : 1. The structural analysis indicated that there was a strong interaction between chitosan and QPVP resulting from strong adhesion between both polymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 559–566, 2004

Key words: chitosan; quaternized poly(4-vinyl-*N*-butyl) pyridine; blend film; miscibility

INTRODUCTION

Chitosan, a naturally abundant polysaccharide, is well known to consist of 2-deacetamido-2-deoxy- β -D-glucose through $\alpha\beta$ (1 \rightarrow 4) linkage. Chitosan has one amino group and two hydroxyl groups in the repeating hexosamide residue. Chemical modification of the groups and the regeneration reaction give rise to various novel biofunctional macromolecular products having the original organization or a new type of organization. Many reviews have been written that outline chitin and its derivatives' usefulness in such areas as pharmaceutical and biomedical applications, paper production, textile finishes, photographic products, cements, heavy-metal chelating agents, membranes, hollow fibers, and waste removal.^{1–4}

Investigation of blends and composites of synthetic polymers with naturally occurring macromolecules, or their derivatives, is a broad area of material science that is very rich in potential. In particular, modification of chitosan, by means of blending with other polymers, is a convenient and effective method of improving physical properties for practical utilization. Many articles have reported on the modification of chitosan: for instance, blends with poly(vinyl alcohol) have modified hydrophilic properties⁵; films of chitosan/nylon-4 blends show good mechanical properties and retain the excellent che-

lating ability of chitosan⁶; the compatibility and morphology of chitosan–poly(ethylene oxide) blends are closely related to the blend⁷; blends of chitosan with strongly crystalline polyamides (nylon-4 and nylon-6) and weakly crystalline polyamides (caprolactam/lauro lactam and zytel) have also been investigated.⁸ However, blends with the same charge of polyelectrolyte have not been extensively reported. Quaternized poly(4-vinyl-*N*-butyl) pyridine is a special functional polymer used in such as liquid crystalline polysalts, electrolyte polymers, and biofunctional polymers. Vilene Co. Ltd. (Japan)⁹ has reported that poly(4-vinyl) pyridine, quaternized by C₄–C₁₈ bromoalkane and phCH₂Br, has the ability to strongly attack bacteria and promote an affinity for microorganisms. Poly(4-vinyl) pyridine, quaternized by phCH₂Br, can prevent and inhibit germ infection brought out by microorganisms in soil. Ossamn et al.¹⁰ have reported that quaternized (4-vinyl-*N*-octyl) pyridine can adsorb 99.9% bacteria in water over a period of 1 h. So research on blends from chitosan and QPVP is significant for practical utilization. This article is aimed at researching an approach to modify chitosan by blending it with quaternized poly(4-vinyl-*N*-butyl) pyridine. The morphological structure, miscibility, and thermal and mechanical properties were studied by infrared (IR), wide-angle X-ray diffraction (WXR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), scanning electron microscope (SEM), and electron tensile test. The relationship between the structure and their physicochemical properties is discussed.

Correspondence to: C. Xiao (cbxiao@whu.edu.cn).

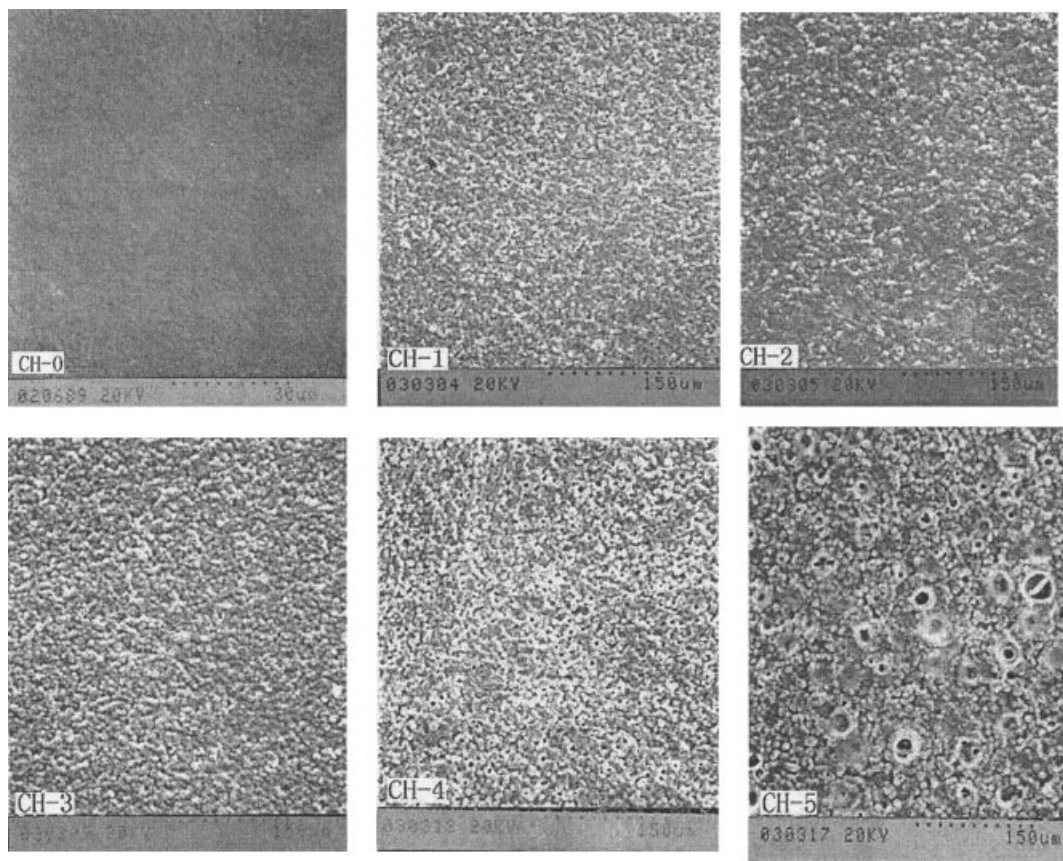


Figure 1 SEM photographs of the films.

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 ref. [11], with AIBN (0.5 wt %) as initiator. The resulting product was dissolved in absolute ethanol and precipitated in ether, filtered, and dried under vacuum to give a white product. Its molecular weight ($M_n = 3.1 \times 10^4$) was determined by a Ubbelohde viscometer. The quaternization of the polymer was carried out by heating the solution of polymer and *n*-bromobutane in nitromethane at 75–78°C under N₂ for 72 h. The resulting quaternized product was precipitated from ether.

Chitosan was prepared from chitin (purchased from Nanxing Chitosan Ltd. Co., Suixi, Guangdong, China) by the method of Mina et al.¹² Its degree of deacetylation was measured to be 90.2% by the method of Nakajima.¹³

Chitosan was dissolved in a 2 wt % acetate acid-water solution to prepare a concentration of 2 wt % solution (I). QPVP was dissolved in deionized water to a concentration of 4 wt % (II). A mixture of I and II was stirred energetically and degassed and 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, 95 : 5, 90 : 10, 85 : 15, 80 : 20, and 60 : 40, a series of blend films, coded as CH-0, CH-1, CH-2, CH-3, CH-4, and CH-5, respectively, were prepared.

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 μm thickness were coated with gold in a 0.1τ vacuum degree; then their surface morphologies were observed on a Hitachi S-570 scanning electron micrograph. The X-ray diffraction (XRD) patterns of the films of 30 μm thickness were recorded with a Shimadzu XRD-6000 (Japan) diffractometer by using a CuK_α target at 40 KV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 45 to 5°. The crystallinities of the films were calculated by¹⁴

$$X_c = F_c / (F_c + F_a) \times 100\%$$

where F_c and F_a are the areas of crystal and amorphous regions, respectively. The TG and DSC of the film samples with 1 mm length and 1 mm width were

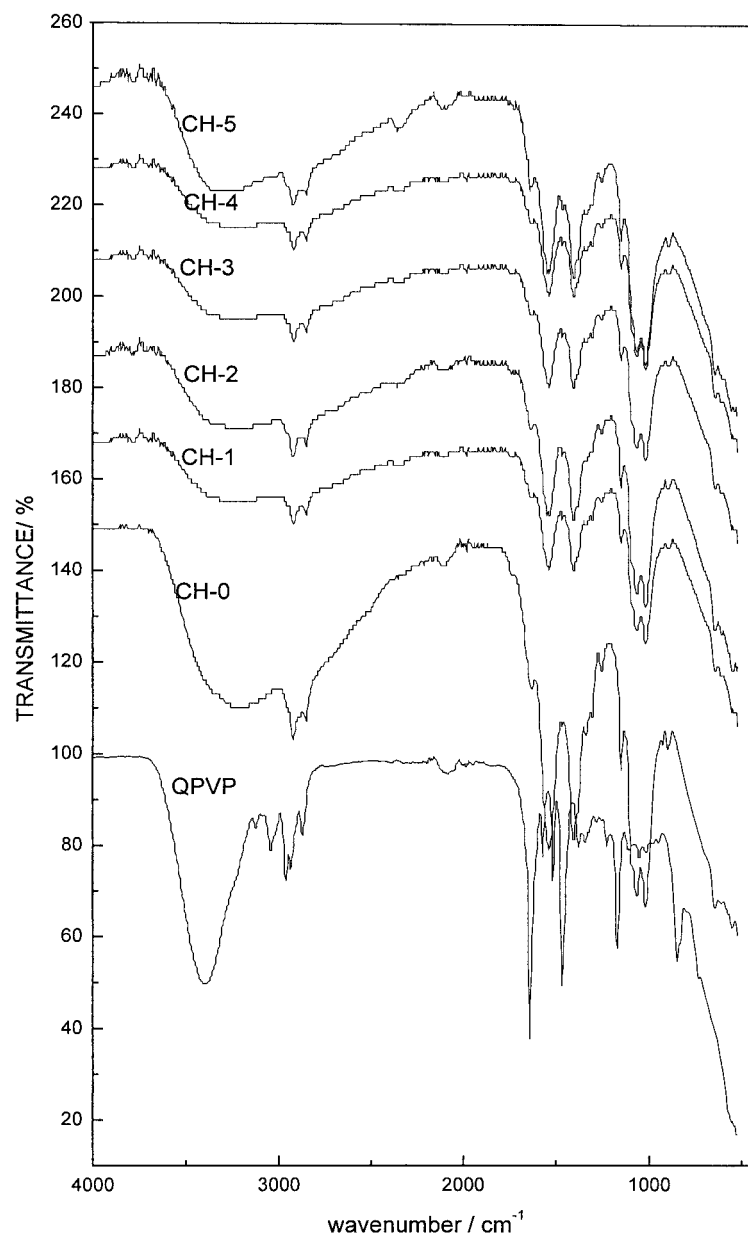


Figure 2 IR spectra of the films.

performed by a Systsys 16TG/DAT/DSC instrument (France) 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 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 Co., Ltd., China) with a tensile rate of 100 mm/min according to the Chinese standard method (GB4456-84). The size of the samples was 70 mm length, 10 mm width, and 50 mm distance between two clamps. The experimental temperature and relative humidity were 20°C and 47%, respectively.

RESULTS AND DISCUSSION

Structure and miscibility

The SEM micrographs of the films are shown in Figure 1. As seen from Figure 1, CH-0, the surface of pure chitosan film is smooth and uniform. Pores are not detected. The other films exhibit different structural features. Globular elements, about 2–5 μm in diameter, are distinguished. Moreover, the arrangement of these elements gives rise to round or irregularly shaped mesopores of about 0.5 μm in diameter. When the content of QPVP is less than 15 wt % (CH-1, CH-2, CH-3), the arrangement of these elements is compact.

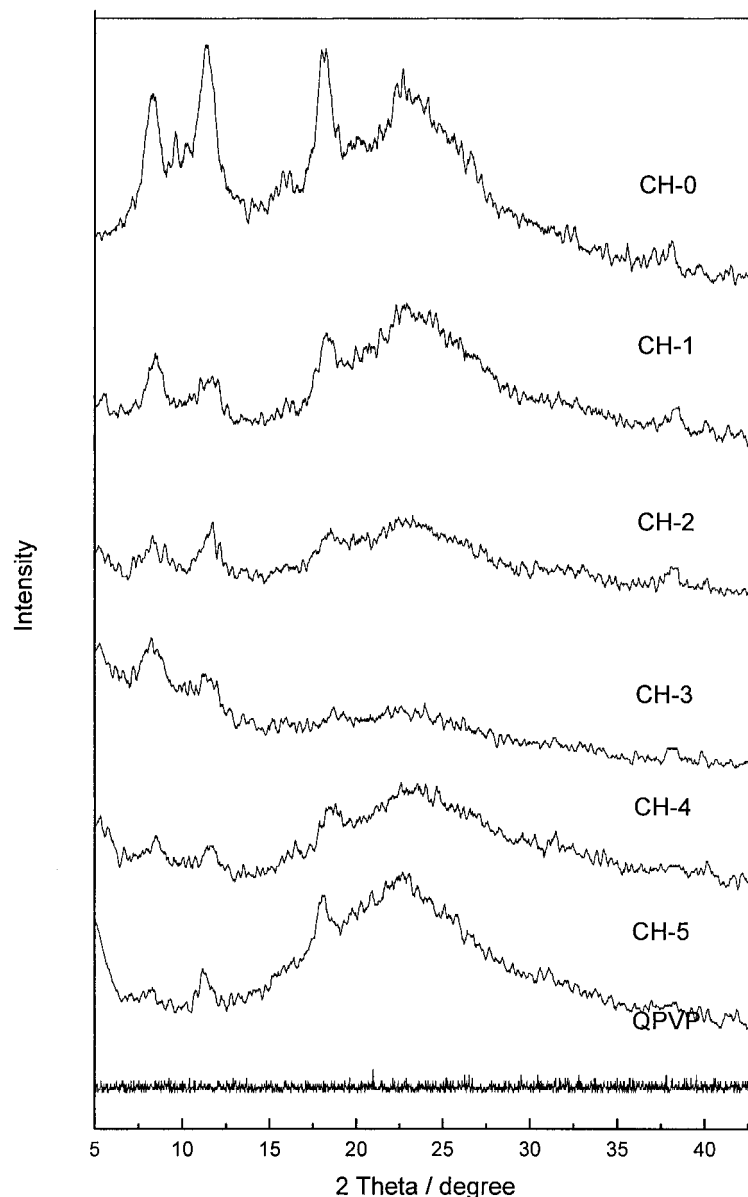


Figure 3 WXR D diffraction patterns of the films.

If the content of QPVP is more than 20 wt %, the mesopores are more numerous than for CH-1, CH-2, CH-3, and the size of the mesopores is bigger, which causes the change of tensile strength and breaking elongation discussed in the next section. The micrographs, shown in Figure 1, indicate that blends of chitosan and QPVP form mainly a two or more phase (maybe an intermolecular complex) system. The SEM micrographs of the blends are similar to those of reported polyamide 6/chitosan⁸, cellulose/polyamide 66 blends.⁹ The morphological properties of the blended films described here point toward structural ordering created by a molecular affinity between their components. In this manner, an intermolecular complex or an orderly arrangement of two or more phases

is formed.¹⁵ The molecular interaction in such a structure should also be reflected in other macro- and microscopic properties of the films. Thereafter, noticeable differences between the properties of the blending films and those of pure chitosan are expected, which indeed are observed when IR spectra, XRD patterns, mechanical properties, and thermal stabilities of the films are compared.

Further information on the molecular interaction between the component microdomains and interfaces between themselves could be obtained by spectroscopic vibrational analysis. The IR spectra of the films and QPVP powder, in the mode of attenuated total reflection, are shown in Figure 2. A characteristic absorption peak at 1640 cm^{-1} for QPVP is observed,

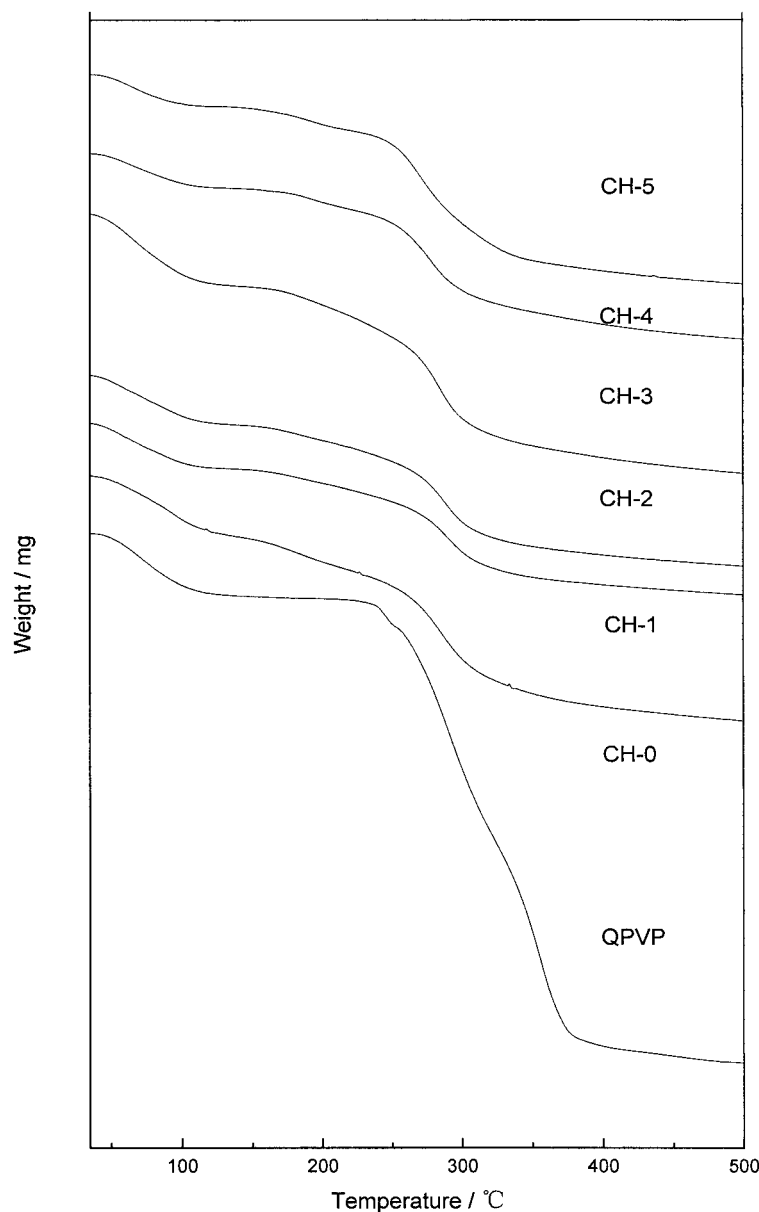


Figure 4 TG thermograms of the films.

indicating successful quaternization of the polymer.¹⁶ The absorption band at 3193 cm^{-1} for pure chitosan is assigned to the stretching of N—H groups bonded to —OH; the peaks at 1537 and 1255 cm^{-1} are assigned to the characteristic bending absorption band of amino group and the stretching of acetlyamine III.¹⁷ For the blend films, the absorption band at 3193 cm^{-1} , a striking characteristic, shifts increasingly to around to 3282 cm^{-1} , and the intensity of absorption decreases gradually with the increase of QPVP content, indicating the impairment of intramolecular or intermolecular hydrogen bonds in chitosan. Moreover, the intensity of absorption peak at about 1640 cm^{-1} increases gradually, and the absorption peak at 1536 cm^{-1} splits to become a double peak with the increase of QPVP

content. This fact indicates that an interaction between chitosan and QPVP has occurred. In other words, the residual —NH₂ and —OH groups of chitosan were involved in the intermolecular chitosan/QPVP connectivity that led to the components partial compatibility.

Figure 3 shows the XRD patterns of the blend films. In contrast, X-ray diffraction patterns of the blend films appear as superimposed images of each of the pure components. The crystallinities of CH-0, CH-1, CH-2, CH-3, CH-4, and CH-5 are 34.10, 24.55, 16.60, 16.40, 18.0, and 22.44, respectively. We can recognize three crystal peaks at around 8.3 , 11.32 , and 18.22° (2θ) in the XRD pattern of CH-0, which agrees with the reports in ref. [18]. The pure quaternized poly(4-vinyl-

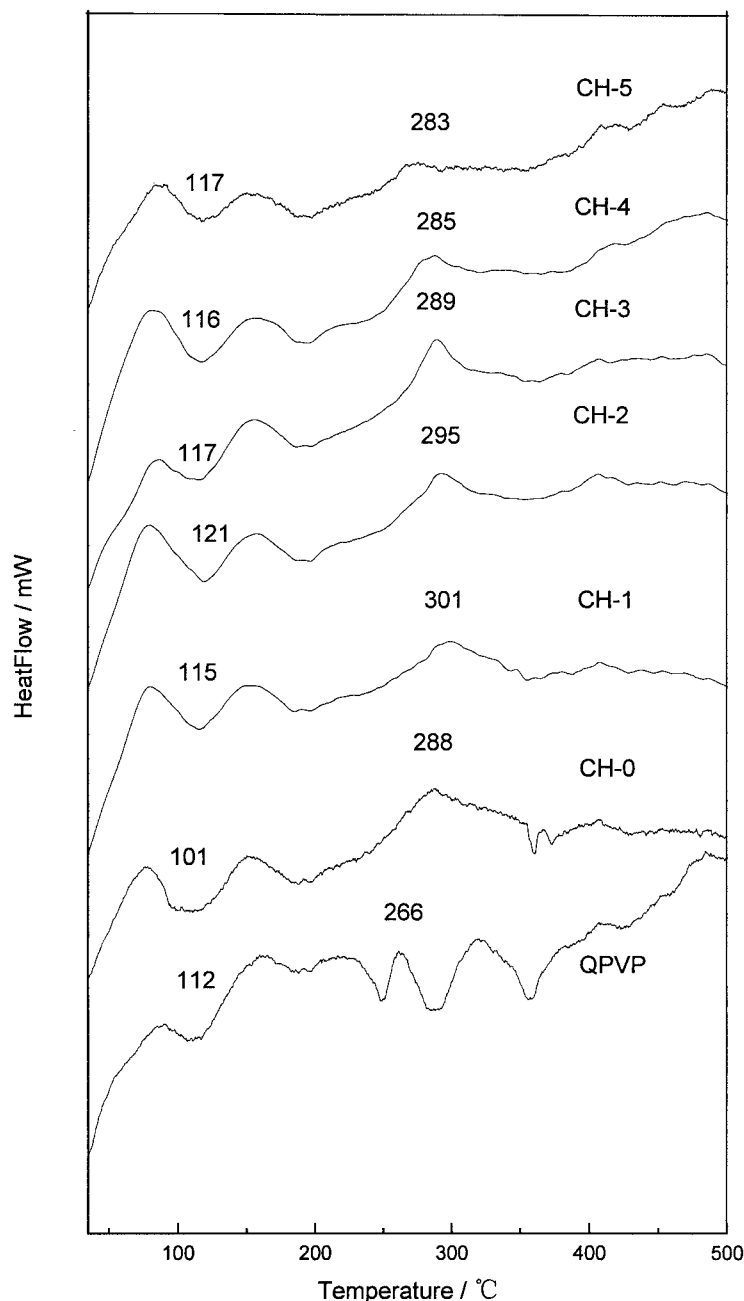


Figure 5 DSC thermograms of the films.

N-butyl) pyridine shows a rather amorphous substrate. With the increase of QPVP content, the intensities of CH-0, CH-1, CH-2, CH-3 corresponding to $2\theta = 8.3$, 11.32 , and 18.22° become gradually lowered, and amorphous area corresponding to $2\theta = 22.68^\circ$ also decreases gradually, but the diffraction peaks of CH-4, CH-5 at $2\theta = 8.3$, 11.32 , and 18.22° become gradually strengthened again, and amorphous area at $2\theta = 22.68^\circ$ also increases gradually. It is obvious that the interaction between chitosan and quaternized poly(4-vinyl-*N*-butyl) pyridine prevents or disturbs chitosan from crystallization in comparing the diffraction pat-

tern of CH-0 with that of blend films. When the content of QPVP is more than 20 wt %, it is possible that larger microdomains or more immiscibility, displayed in Figure 1, of each of the components caused the diffraction patterns of CH-4, CH-5.

Thermal stability

Figure 4 shows the TGA thermograms of QPVP powder and the films. The greatest weight loss points of QPVP and CH-0 at 266 and 288°C , respectively, are attributed to partial breaking of the molecular struc-

ture. The blends of CH-1, CH-2, however, show better thermostability than QPVP, and the film of CH-0 at the point of maximum weight loss rate corresponding to higher temperatures. The thermostability is ordered as CH-1 (301°C) > CH-2 (295°C) > CH-3 (289°C) \approx CH-0 (288°C) \approx CH-4 (285°C) > QPVP (266°C). It implies that the thermostability of CH-1, CH-2 is enhanced due to the introduction of the QPVP.

The DSC thermograms of the QPVP and the films are shown in Figure 5. The samples all show endothermic peaks in the range of 100–121°C, corresponding to the dehydration of the samples. All the samples show exothermic peaks at around 295°C, which resulted from the greatest thermal degradation of the samples. The thermostability of CH-1, CH-2 films are higher than that of QPVP and CH-0, indicating strong interaction between the two kinds of molecules. By contrast, the existence of interaction between chitosan and QPVP is further supported by this thermal analysis and the interaction could be regarded as an intermolecular complex. Meanwhile, as discussed above, microscopic studies, IR analysis, and XRD analysis indicate an intermolecular complex or an orderly arrangement of two or more phases created by interaction of the two molecules. Those facts indicate that the system displays a partial miscibility between the homopolymers in the blends.

Mechanical properties

Characterization discussed above has indicated partial miscibility between both molecules in the blends. Tensile tests can provide confirmation. The tensile strength and breaking elongation dependence of 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, with the maximum value 56.38 MPa appearing when the retention of QPVP is 10 wt %. The change of breaking elongation is similar to that of the strength and reaches a maximum when the retention of QPVP is 10 wt%. The conclusion can be drawn that the blend of chitosan and QPVP has considerably enhanced the mechanical properties of the blend films in the dry state, and the enhancement of tensile strength may be due to strong adhesion at the interface between both molecules, which gives rise to an intermolecular complex or an orderly arrangement of two or more phases. When the content of QPVP is less than 15 wt %, strong adhesion created partial miscibility or compensated immiscibility. So the tensile strength and breaking elongation are higher than those of the pure chitosan. When the content of QPVP is more than 20 wt %, the increased immiscibility or larger microdomains impair the tensile strength and breaking elongation. The macroproperties of the films agree with the microscopy structure discussed above.

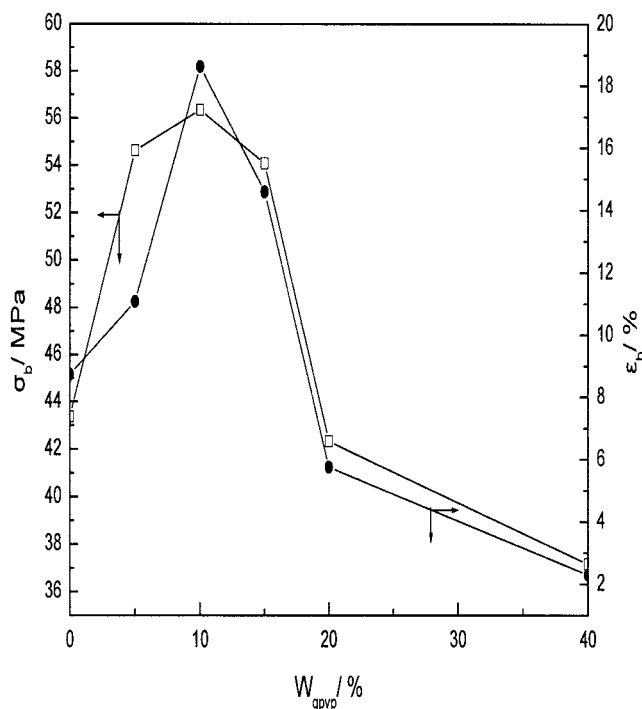


Figure 6 Effects of QPVP (W_{QPVP}) content on the tensile strength (σ_b) and breaking elongation (ϵ_b) of the films.

CONCLUSION

A series of blend films was prepared by blending 2 wt % chitosan acetate water solution and 4 wt % quaternized QPVP in aqueous solution and drying at room temperature for 72 h to obtain films. The mechanical properties in the dry state and thermal stability are superior to those of chitosan film and achieve their maximum when the weight ratio of chitosan to QPVP is 9 : 1. The crystallinity of the blend films first decrease and then increase with the increase of QPVP content. All results lead to the conclusion that a strong adhesion at the interface exists between chitosan and quaternized QPVP in the blends prepared from solution. An intermolecular complex, or an orderly arrangement of two or more phase, caused by the interaction of intermolecules was confirmed by the results of SEM and IR and WXR. The enhancement of mechanical properties and thermal stability may be due to strong adhesion existing between these polymers.

References

- Rathke, T. D.; Hudson, S. M. *J Macromol Sci, Rev Macromol Chem Phys* 1994, C34 (3), 375.
- Muzzarelli, R. A. A. *Chitin*. in *Naturally Chelating Polymers*; Pergamon Press: New York, 1973.
- Muzzarelli, R. A. A. *Chitin*; Pergamon Press: New York, 1977.
- Zikakis, J. P., Ed. *Chitosan and Related Enzymes*; Academic Press: Orlando, FL, 1984.
- Blair, H. S.; Guthrie, J.; Law, T.; Turkington, P. *J Appl Polym Sci* 1987, 33, 641.

6. Kim, D. Y.; Ratto, J. A.; Blumstein, R. B. *Polym Prepr* 1991, 31 (1), 112.
7. Zhao, W.; Yu, L.; Zhong, X.; Zhang, Y.; Sun, J. *J Macromol Sci Phys* 1995, B34 (3), 231.
8. Ratto, J. A.; Chen, C. C.; Blumstein, R. B. *J Appl Polym Sci* 1996, 59, 1451.
9. Kawabate, Nariaki; Fukamoto, Osamu; Minami, Akinori. *Jpn. Pat.* 05-58807, 1993.
10. Itabashi Ossamn, et al. *Chem Ind (London)* 1992, 12, 450–451.
11. Yang, M. J.; She, Y.; Li, Y. *J Mater Sci Lett* 2002, 21, 1477–1479.
12. Mina, S.; Miya, M.; Iwamoto, R.; et al. *J Appl Polym Sci* 1983, 28, 1909.
13. Nakajima, T.; Sugai, K.; Ito, Y. *Kobunshi Ronunshu* 1980, 37, 705.
14. Rabek, J. F. *Experimental Methods in Polymer Chemistry: Applications of Wide-Angle X-ray Diffraction (WXR) to the Study of the Structure of Polymers*; Wiley-Interscience: Chichester, UK, 1980; p. 505.
15. Fuentes, S.; Retuert, P. J.; Ubilla, A.; Fernandez, J.; et al. *Biomacromoleculars* 2000, 239–243.
16. Yang, M. J.; She, Y.; Li, Y. *J Mater Sci Lett* 2002, 21, 1477–1479.
17. Yao, K. D.; Peng, T.; Gosen, M. F.; Min, J. M.; et al. *J Appl Polym Sci* 1993, 48, 343.
18. Urbanczyk, W.; Lipp-Symonowicz, B. *J Appl Polym Sci* 1994, 51, 2191–2194.