

Anti-Bacterial and Swelling Properties of Acrylic Acid Grafted and Collagen/Chitosan Immobilized Polypropylene Non-Woven Fabrics

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ABSTRACT: The various weight ratios of collagen/chitosan were used to immobilize the various grafted amounts of acrylic acid (AA) grafted polypropylene nonwoven fabric. For a given value of grafting percentage of AA and the immobilizing time period, the values of the immobilizing percentage of collagen/chitosan are increased with the increasing of chitosan contained in the mixtures of collagen/chitosan. The antibacterial properties are also increased with the increasing of chitosan in the mixtures of collagen/chitosan and the immobilizing percentage of collagen/chitosan. The crosslinking reaction between the AA-grafted PP

nonwoven fabrics and collagen/chitosan with glutaraldehyde are clearly sustained by examination from the spectra of the surface reflection infrared spectroscopy (IR). The values of water uptake and water diffusion coefficients are decreased with the increasing of chitosan in the mixtures of collagen/chitosan and the immobilizing percentages of collagen/chitosan at the same pH value of buffering water. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 391–400, 2005

Key words: composites; crosslinking; diffusion; swelling

INTRODUCTION

Collagen, usually existed in skin, vessel, bone, tendon, and basement membrane, had been used as a biocompatible material.^{1–4} It is fabricated by three α -chains, which are formed by a [Glycine(Gly)-amino acid(X)-amino acid(Y)]_n series of polypeptide. Quteish and coworkers¹ used the type I collagen obtained from abstracting placenta of humans to graft on the material to evaluate the biocompatibility of those composite materials and found that collagen had good biocompatibility. Li² pointed out that the collagens obtained from different kinds of animals all had good biocompatibility. It is known that chitosan, partially de-acetylated from chitin, has excellent antibacterial properties and cell adhesive properties.^{5–8} Rao and coworkers⁷ showed the higher thromboplastic property of the chitosan molecule. Additionally, chitosan solutions were used as antibacterial agents⁸ and found to have higher antibacterial activity to *Escherichia coli* and an optimum antibacterial effect at pH 6.3. In some cases, the use of each collagen and chitosan to combine with another component, such as glycosaminoglycan or polyether,^{9–12} could improve some physical proper-

ties for convenience in use. In addition, using the combined collagen and chitosan to enhance antibacterial, water swelling, and other properties was also reported.^{13–15}

Generally, the application of skin wound healing needs to immobilize collagen and/or chitosan on the surface of the layer materials, which are usually in the form of film, fabric, sheet, or nonwoven, to enhance the mechanical properties. Those layer materials need excellent gas and water permeation properties and high adhesion to the biomaterials, such as collagen and chitosan. The modification of the surface of the layer materials is therefore necessary. Some methods,^{16–21} such as irradiation, plasma, and the redox system, combined with some chemical reagents are known in this field to treat the surface of the layer materials to modify the property of their surfaces and increase the immobility of biomaterials on those surfaces. Recent studies^{4,22–24} reveal that using crosslinking could improve the immobility of biomaterials on the modified surfaces of the layer materials. Van Wachem and colleagues²² showed that sheep collagens crosslinked with epoxy could have higher biocompatibility.

For a wound dressing, AA grafted PP nonwoven fabrics are generally used as the base layer to enhance the mechanical property of the biomedical materials. In this case, the base layer needs excellent gas and water permeation properties and high adhesion to the

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biomaterials, such as collagen and chitosan. Higher toxicity to cells for AA will decrease the proliferation of cells on the wound area, but the higher water absorbing property and reactivity will benefit the crosslinking between the PP nonwoven fabric and the biomaterials and will perform well when the wound is in the moist condition. It is well known that chitosan has good antibacterial properties and collagen has good biocompatibility; therefore, the combination of these two materials adhering with the wound tissue is expected to provide good antibacterial properties to benefit the healing of the wound. Wound dressing by the three layer structure of PP nonwoven fabric, AA grafting layer, and chitosan/collagen is expected to show good potential to be applied in the field.

In this study, we will use different weight ratios of the mixture of collagen/chitosan to immobilize on the surface of polypropylene nonwoven fabric, which was grafted with different amounts of acrylic acid, to study the water absorbing and antibacterial properties of these composite materials. Here, we examined the immobilized values of collagen/chitosan on polypropylene nonwoven fabrics grafted with various amounts of acrylic acid (AA), and the water uptake under various pH conditions, water diffusion coefficient, and bacterial inhibition ratio and zone under different conditions of those composite materials. At the same time, the differences of the FTIR spectra (surface reflectance) among polypropylene, AA-grafted polypropylene, and AA-grafted and collagen/chitosan-immobilized polypropylene nonwoven fabrics were also analyzed.

EXPERIMENTAL

Materials

In this study, we used polypropylene (PP) nonwoven fabric, 50 g/m², which was supplied by the Industrial Technology Research Institute (Taiwan).

The crosslinking and grafting agents were glutaraldehyde and acrylic acid (AA), respectively, and were obtained from ACROS Co., USA. Collagen and chitosan were obtained from SIGMA Co., St. Louis, MO. Other chemicals used were all reagent grade.

Methods

PP nonwoven fabric samples were pretreated with pure acetone at room temperature for 30 min to wash out the oil and impurities, and then grafted with acrylic acid (0.56, 0.69, and 0.83M, respectively) in the presence of benzoyl peroxide (0.62×10^{-2} M) initiator at 80°C for 90 min under nitrogen environment. The grafting solutions also contained toluene (25 g/L) and sodium chloride (0.17M). The grafted fabric samples were fully washed with cold tap water and then with

pure water under ultrasound for 10 min to remove the ungrafted monomers and homopolymers. Those fabric samples were then dried at 105°C and weighed to obtain the grafting percentage as follows:

$$\begin{aligned} \text{Grafting percentage (\%)} \\ &= [(\text{weight after grafting} \\ &\quad - \text{weight before grafting}) / \\ &\quad \text{weight before grafting}] \times 100 \quad (1) \end{aligned}$$

The AA-grafted fabric samples of the various grafting percentages (7, 11, and 15 wt %) were immersed in beakers of glass that contained specific concentrations of collagen, chitosan, and crosslinking agent (glutaraldehyde, 25 g) at 4°C for 6, 12, and 18 h, respectively, to immobilize the collagen/chitosan onto those fabric samples. In those immobilization solutions, the total weight of collagen and chitosan (both were dissolved with acetic acid) was 25 g and at the weight ratios of 100/0, 67/33, 50/50, and 33/67 for collagen/chitosan. Those immobilized fabric samples were fully washed with cold tap water, neutralized with 1 wt % sodium hydroxide at room temperature for 30 min, then washed with pure water under ultrasound for 10 min to remove the unimmobilized glutaraldehyde, chitosan, and collagen. Those collagen/chitosan-immobilized fabric samples were then dried at 20°C in a vacuum dryer and weighed to obtain the immobilizing percentage as follows:

$$\begin{aligned} \text{Immobilizing percentage (\%)} \\ &= [(\text{weight after immobilizing} \\ &\quad - \text{weight before immobilizing}) / \\ &\quad \text{weight before immobilizing}] \times 100 \quad (2) \end{aligned}$$

The antibacterial property (bacteria inhibition percentages and zones) of the AA-grafted and collagen/chitosan-immobilized PP nonwoven fabric samples were examined according to AATCC Test Method 100-1998, and staphylococcus aureus was used. Water uptake values under the different values of pH and the ratio of collagen to chitosan were measured according to the method described by Kabra and colleagues.²⁵

For the water absorbing kinetics, the simplified equation of Fick was employed to calculate the water diffusion coefficient as follows²⁵:

$$M_t/M_\infty = (4/\pi^{1/2})(Dt/L^2)^{1/2} \quad (3)$$

where D is the water diffusion coefficient, t is the swelling time, and L is the value of the thickness of the AA grafted and collagen/chitosan immobilized PP nonwoven fabric samples. From the slope of the linear

TABLE I
Values of Immobilizing Percentage of Collagen/Chitosan, Water Uptake, Water Diffusion Coefficient, Bacteria Inhibition Percentage, and Bacteria Inhibition Zone of the Various Acrylic Acid Grafted and Collagen/Chitosan Immobilized Polypropylene Nonwoven Fabrics under Different Conditions

Immobilizing agent	AA grafting percentage (%)	Weight ratio	Immobilizing time period (hr)	pH value of water	Water absorbing time (hr)	Immobilizing percentage (%)	Water uptake (%)	Properties		
								Water diffusion coefficient ($\times 10^8$ cm ² /s)	Bacteria inhibition percentage (%)	Bacteria inhibition zone (mm)
Collagen/Chitosan	7%	100/0	18	—	—	3.6	—	—	0	0
		67/33	18	—	—	12.2	—	—	50.5	2.1
		50/50	18	—	—	20.0	—	—	71.5	3.4
		33/67	18	—	—	47.6	—	—	100.0	8.8
	11%	100/0	18	—	—	8.7	—	—	0	0
		67/33	18	—	—	13.6	—	—	55.6	2.4
		50/50	18	—	—	26.0	—	—	88.7	4.3
		33/67	18	—	—	55.4	—	—	100.0	9.7
		100/0	6	—	—	5.4	—	—	0	0
		67/33	6	—	—	8.6	—	—	40.5	1.5
		50/50	6	—	—	13.5	—	—	56.3	2.4
		33/67	6	—	—	43.0	—	—	100.0	7.1
	15%	100/0	12	—	—	7.1	—	—	0	0
		67/33	12	—	—	13.6	—	—	56.5	2.3
		50/50	12	—	—	21.0	—	—	75.2	3.5
		33/67	12	—	—	60.0	—	—	100	9.4
		100/0	18	6.8	24	10.4	182.5	5.17	0	0
		67/33	18	6.8	24	17.2	146.8	3.04	65.3	2.6
		50/50	18	6.8	24	28.2	115.0	2.33	95.8	4.8
		33/67	18	6.8	24	70.1	83.8	0.89	100.0	12.0
		100/0	18	8.1	24	—	167.5	—	—	—
		67/33	18	8.1	24	—	132.5	—	—	—
		50/50	18	8.1	24	—	108.0	—	—	—
		33/67	18	8.1	24	—	80.0	—	—	—
100/0	18	9.3	24	—	140.1	—	—	—		
67/33	18	9.3	24	—	116.3	—	—	—		
50/50	18	9.3	24	—	91.3	—	—	—		
33/67	18	9.3	24	—	67.3	—	—	—		

plots between the values of M_t/M_∞ and the values of $(t/L^2)^{1/2}$ of those fabric samples, we can obtain the values of the water diffusion coefficient. In this study, the AA-grafted and collagen/chitosan-immobilized PP nonwoven fabric samples were dried at 37°C for 24 h under vacuum condition of 40 Torr to remove the water completely. The values of the thickness of those grafted and immobilized PP nonwoven fabric samples were examined with scanning electron microscopy (SEM).

Infrared spectroscopic measurements of the (a) polypropylene nonwoven fabric, (b) AA-grafted polypropylene nonwoven fabric, and (c) AA-grafted and collagen/chitosan-immobilized PP nonwoven fabric samples were recorded directly on Fourier transform infrared spectroscopy (FTIR, FTIR Spectrum One Perkin-Elmer) that had the equipment of attenuated total reflectance.

RESULTS AND DISCUSSION

The values of the immobilizing percentage of collagen/chitosan, water uptake, water diffusion coefficient,

bacteria inhibition percentage, and bacteria inhibition zone of the acrylic acid (AA) grafted and collagen/chitosan immobilized polypropylene nonwoven fabric samples are listed in Table I. The dotted lines in Figure 1 show the plots between the values of the immobilizing percentage of collagen/chitosan for the PP nonwoven fabric samples grafted with various amounts of acrylic acid and the weight ratio of the collagen/chitosan. The Table and Figure reveal that the values of collagen/chitosan immobilized are increased with the increasing of the values of acrylic acid grafted on PP nonwoven fabrics for a same weight ratio of collagen/chitosan, which may be caused by the higher density of the carboxylic acid groups contained on the AA-grafted PP nonwoven fabrics of the higher grafting percentage. Glutaraldehyde is a known crosslinking agent for the collagen to let it be immobilized onto the surface of the materials.^{26,27} The carboxylic acid group is a well-known group that can react with the reactive functional groups contained in any molecules or polymers; therefore, we can infer that the higher density of the car-

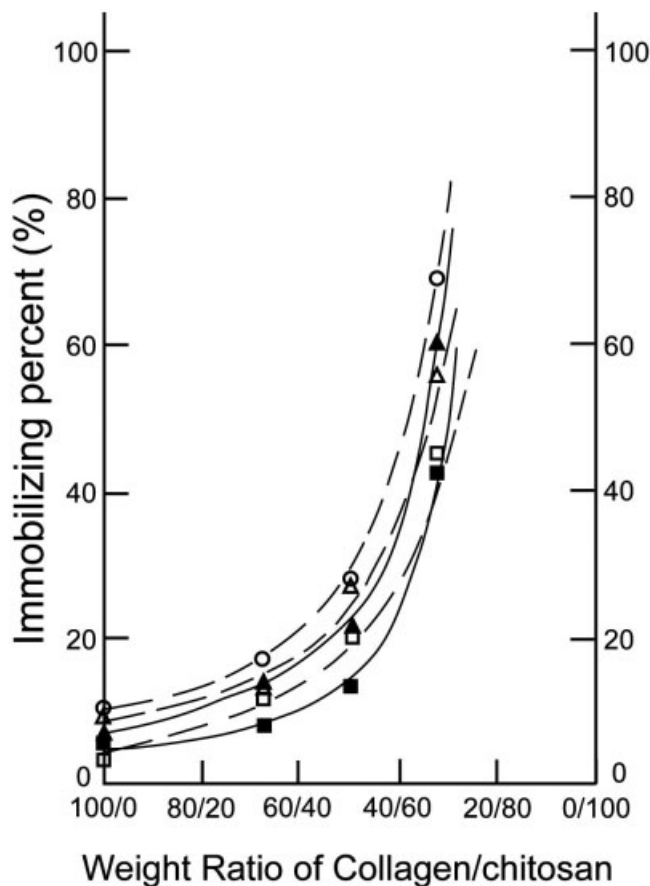


Figure 1 (a) The relationships between the values of immobilizing percentage of collagen/chitosan for the PP nonwoven fabric samples grafted with various amounts of acrylic acid and the weight ratio of collagen/chitosan and immobilized under various time periods. (O): 15% of AA grafting percentage and 18 hours of immobilizing time periods. (Δ): 11% of AA grafting percentage and 18 hours of immobilizing time periods. (□): 7% of AA grafting percentage and 18 hours of immobilizing time periods. (▲): 15% of AA grafting percentage and 12 hours of immobilizing time periods. (■): 15% of AA grafting percentage and 6 hours of immobilizing time periods.

boxylic acid group on the PP nonwoven fabrics that had a higher grafting percentage should have the higher crosslinking reaction between the carboxylic acid group and the functional groups of collagen/chitosan to have the higher values of immobilizing percentage.

The relationships between the values of the immobilizing percentage of collagen/chitosan for the various immobilizing time periods and the weight ratios of collagen/chitosan are plotted in the solid lines in Figure 1, which shows that the longer the immobilizing time period, the higher the immobilizing percentages for a given value of weight ratio of collagen/chitosan. This result may be attributed to the crosslinking reaction temperature that was at 4°C in this study; therefore, the crosslinking reaction was

certainly incomplete at a shorter immobilizing time period. The longer immobilizing time period, of course, has higher immobilizing percentages at a same value of weight ratio of collagen/chitosan.

Additionally, from Figure 1 and the data listed in Table I, we can find that the values of the immobilizing percentage are increased with the increasing of chitosan contained in the mixtures of collagen and chitosan and the immobilizing time period for all the cases of the values of AA-grafting percentage. This phenomenon is especially significant as the weight ratio of collagen/chitosan is lower than 50 to 50. The difference between collagen and chitosan is that the former has carboxylic acid, amino, and hydroxyl groups, but the latter has only amino and hydroxyl groups. This result may be caused by the higher reactivity of glutaraldehyde with the amine group than with the carboxylic acid and hydroxyl groups. Zhang and coworkers¹⁴ reported that glutaraldehyde could react with the amino group of chitosan to form the composite of collagen/chitosan. On the other hand, from the fact that the collagen immobilized on the AA-grafted polyester film could easily be washed out by water,²⁸ we can suggest that the collagen has lower reactivity.

Table I also lists the values of bacteria inhibition percentage and bacteria inhibition zone under the various conditions of grafting percentage, immobilizing time period, and weight ratio of collagen/chitosan. From those data, we find that the antibacterial properties (bacteria inhibition percentage and bacteria inhibition zone, respectively) are all increased with the increasing of the grafting percentage of AA and the immobilizing time period at a same weight ratio of collagen/chitosan. Those results may be caused by the higher collagen/chitosan contents on the grafted and immobilized PP nonwoven fabrics under a higher grafting percentage of AA and a longer immobilizing time period. The dotted lines in Figure 2(a) and the solid lines in Figure 2(b) show the relationships between the values of the bacteria inhibition percentage and the values of (a) the weight ratio of collagen/chitosan and (b) the immobilizing percentage, respectively, for the PP nonwoven fabric samples grafted with various amounts of acrylic. The dotted lines in Figure 2(a) reveal that the values of the bacteria inhibition percentage are increased with the increasing of chitosan contained in the mixtures of collagen/chitosan for all cases of grafting percentage of AA and increased with the increasing of grafting percentages of AA at a same weight ratio of collagen/chitosan. The solid lines in Figure 2(b) show that the antibacterial properties are also significantly increased with the increasing of the values of immobilizing percentage for all the cases of grafting percentage of AA, but similar for each sample of grafting percentage of AA under a given weight ratio of collagen/chitosan. In

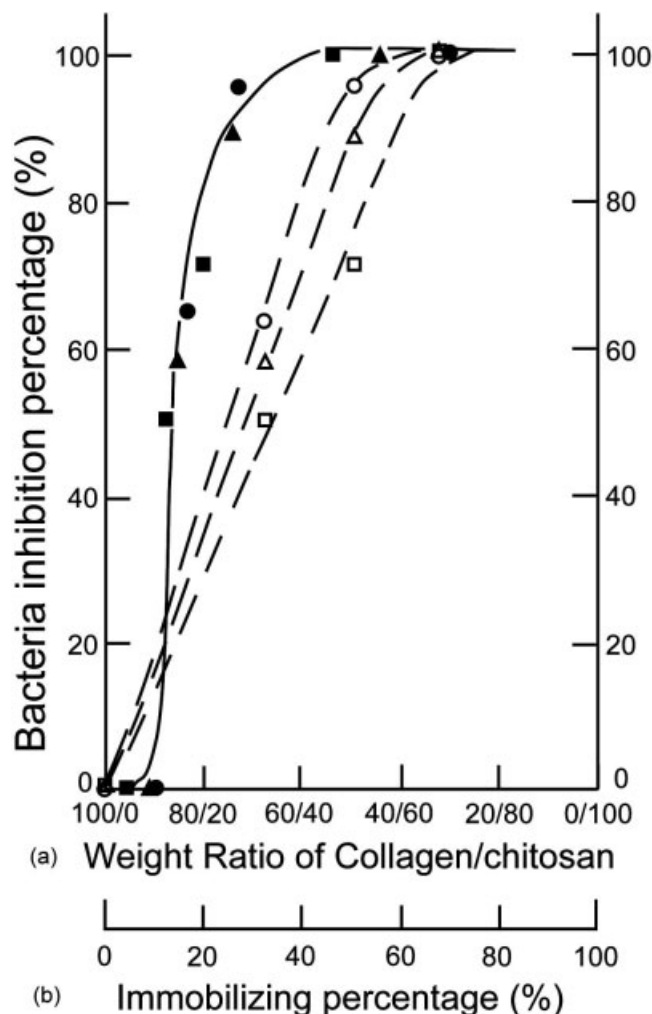


Figure 2 The relationships between the values of bacteria inhibition percentage and the values of (a) weight ratio of collagen/chitosan and (b) immobilizing percentage, respectively, for the PP nonwoven fabric samples grafted with various amounts of acrylic acid. (○, ●): 15% of AA grafting percentage and 18 hours of immobilizing time periods; (△, ▲): 11% of AA grafting percentage and 18 hours of immobilizing time periods; (□, ■): 7% of AA grafting percentage and 18 hours of immobilizing time periods.

addition, Figure 2(b) also shows that the bacteria inhibition percentages are suddenly increased with the immobilizing percentage at about 10% and then reach the maximum value at about 15%. These results clearly reveal that the amount of chitosan immobilized on the grafted and immobilized PP nonwoven fabrics are the main factor improving the antibacterial properties. It is well known that chitosan has good antibacterial properties⁵⁻⁸ and, hence, we can certainly believe that the higher the chitosan immobilized under a higher grafting percentage of AA, the higher the immobilizing time period, and the higher the chitosan containing weight ratio of collagen/chitosan, then the higher the antibacterial property of grafted and immobilized PP nonwoven fabrics.

The dotted lines in Figure 3(a) and the solid lines in Figure 3(b) show the relationships between the values of the bacteria inhibition zone and the values of (a) the weight ratio of collagen/chitosan and (b) the immobilizing percentage, respectively, for the PP nonwoven fabric samples grafted with various amounts of acrylic acid. Those Figures reveal that the antibacterial properties examined by the bacteria inhibition zone have the similar tendency as those examined by the bacteria inhibition percentage shown in Figures 2(a) and 2(b). There, the values of the bacteria inhibition zone are also suddenly increased with the immobilizing percentage at about 10%, but there is no maximum value found.

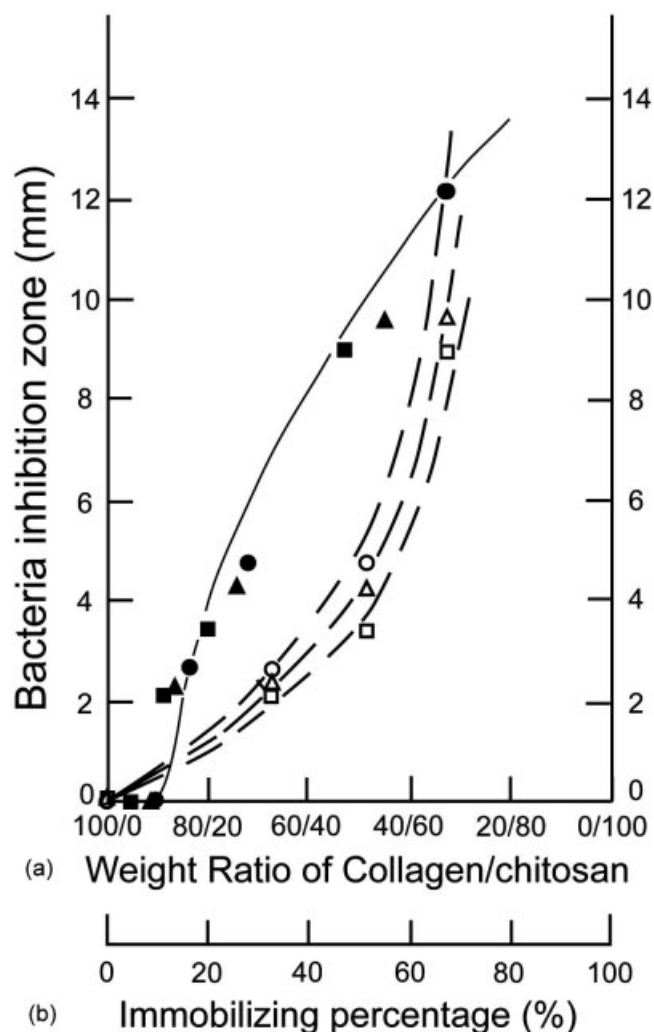


Figure 3 The relationships between the values of bacteria inhibition zone and the values of (a) weight ratio of collagen/chitosan and (b) immobilizing percentage, respectively, for the PP nonwoven fabric samples grafted with various amounts of acrylic acid. (○, ●): 15% of AA grafting percentage and 18 hours of immobilizing time periods; (△, ▲): 11% of AA grafting percentage and 18 hours of immobilizing time periods; (□, ■): 7% of AA grafting percentage and 18 hours of immobilizing time periods.

To study the antibacterial ability of chitosan, the patterns of the cluster of bacteria of (a) the PP nonwoven fabric, (b) the 15% AA-grafted and 70.1% collagen-immobilized PP nonwoven fabric, and (c) the 15% AA-grafted and 10.4% collagen/chitosan-immobilized PP nonwoven fabric are shown in Figures 4(a), 4(b), and 4(c), respectively. Additionally, Figures 5(a), 5(b), and 5(c) are, respectively, the patterns of the bacteria inhibition zone of (a) the PP nonwoven fabric, (b) the 15% AA-grafted and 70.1% collagen-immobilized PP nonwoven fabric, and (c) the 15% AA-grafted and 10.4% collagen/chitosan-immobilized PP nonwoven fabric. Both Figures 4 and 5 show the same tendency, that there is no antibacterial property for PP nonwoven fabric and AA-grafted and collagen-immobilized nonwoven fabric, but excellent antibacterial property for AA-grafted and collagen/chitosan-immobilized nonwoven fabric. These results again certainly reflect that the antibacterial properties for AA-grafted and collagen/chitosan-immobilized nonwoven fabrics are mainly attributed to the existence of chitosan.

The spectra of the surface reflection infrared spectroscopy (IR), shown in Figures 6(a), 6(b), and 6(c), are the (a) PP nonwoven fabric, (b) 15% AA-grafted PP nonwoven fabric, and (c) 15% AA-grafted and 10.4% collagen/chitosan-immobilized PP nonwoven fabric, respectively. The spectrum of PP nonwoven fabric shown in Figure 6(a) reveals two strong absorbing bands at about 1451 cm^{-1} and 1372 cm^{-1} , respectively, for the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of polypropylene. The spectrum of AA-grafted PP nonwoven fabric [Fig. 6(b)] reveals the same absorbing band of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of polypropylene and the absorbing band of $-\text{C}-\text{O}-\text{H}$ at about 1099 cm^{-1} and the carbonyl group ($-\text{CO}-$) at about 1755 cm^{-1} , simultaneously; that is, certainly, the carboxylic acid group of acrylic acid grafted on the surface of polypropylene. Additionally, the spectrum of AA-grafted and collagen/chitosan-immobilized PP nonwoven fabric [Fig. 6(c)] reveals that the same absorbing bands of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of polypropylene still exist and three new absorbing bands at 1646 cm^{-1} , 1551 cm^{-1} , and 1073 cm^{-1} are generated, but the carbonyl group of acrylic acid at 1755 cm^{-1} is weakened and shifted to around 1718 cm^{-1} . From the description by Silverstein and colleagues,²⁹ we can be sure that the shift at 1755 cm^{-1} to around 1718 cm^{-1} for the carbonyl group of acrylic acid must be caused by the crosslinking by glutaraldehyde, the new absorbing bands at 1646 cm^{-1} and 1551 cm^{-1} are the $-\text{CO}-$ and $-\text{NH}-$ groups of the amide of collagen and chitosan, respectively, and the new absorbing group at 1073 cm^{-1} is the ether group of the pyranose ring of chitosan. At the same time, we can find the $-\text{C}-\text{O}-\text{H}$ at 1099 cm^{-1} has almost disappeared. The above results clearly sustain the crosslinking reaction between the glutaraldehyde and collagen/chitosan-

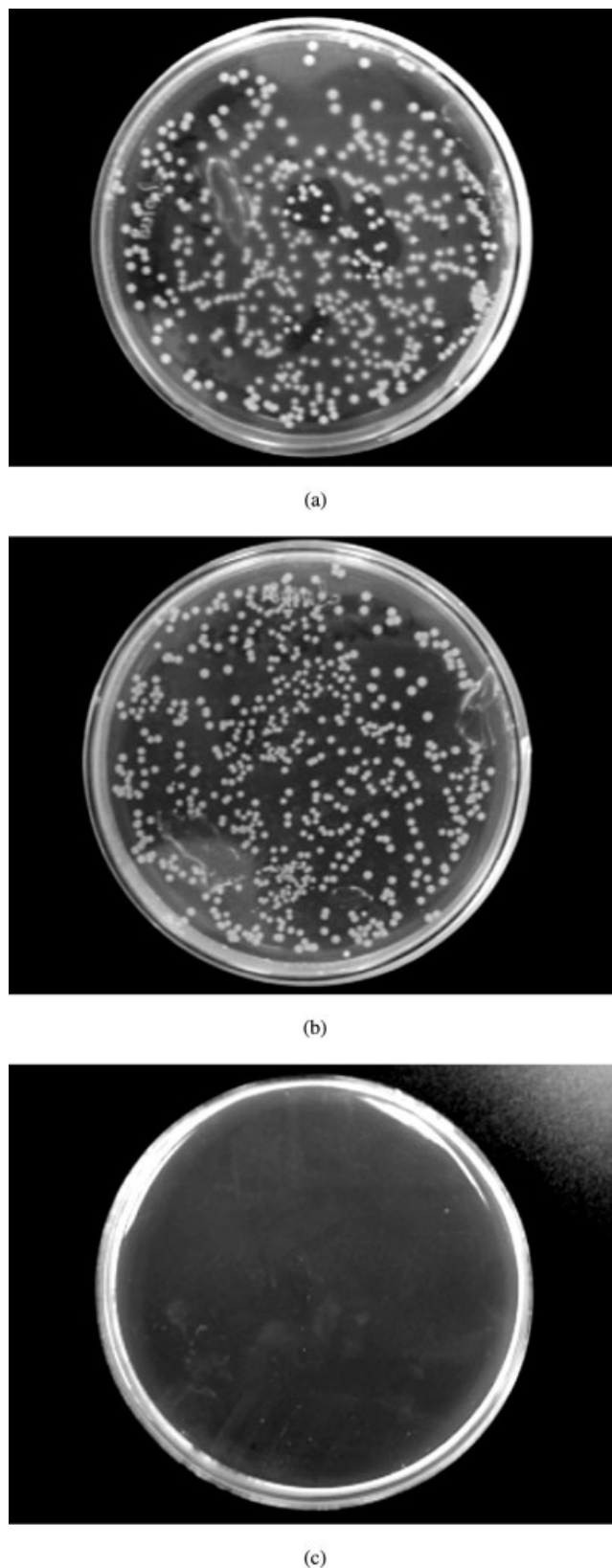
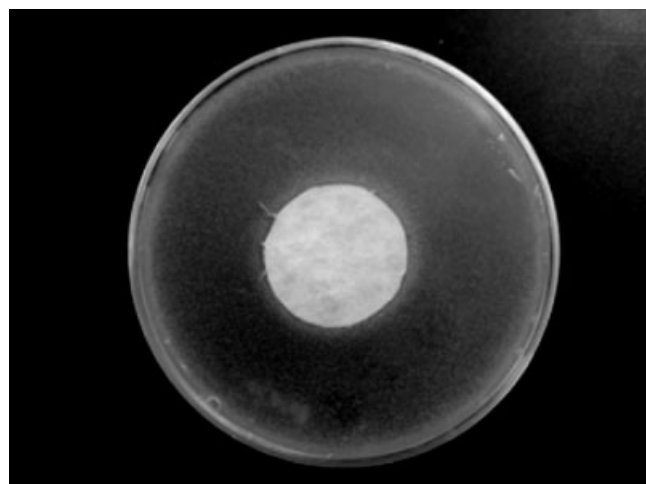
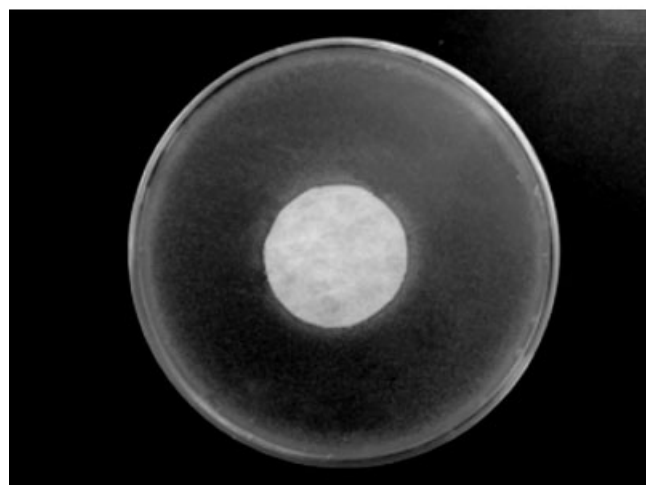


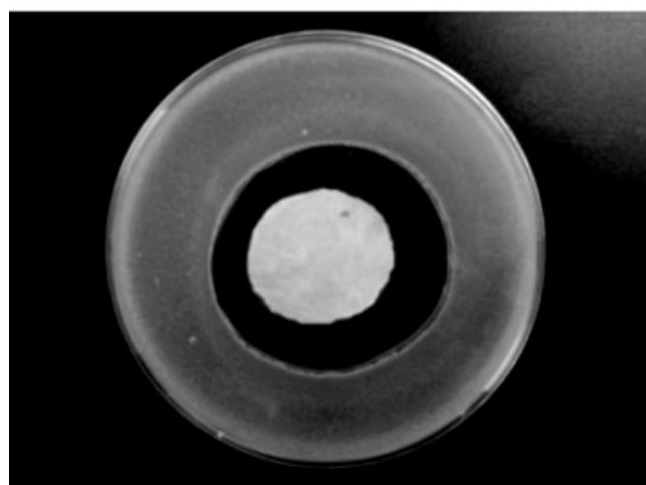
Figure 4 The patterns of the cluster of bacteria of (a) the PP nonwoven fabric, (b) the 15% AA grafted and 10.4% collagen immobilized PP nonwoven fabric, and (c) the 15% AA grafted and 70.1% collagen/chitosan immobilized PP nonwoven fabric.



(a)



(b)



(c)

Figure 5 The patterns of the bacteria inhibition zone of (a) the PP nonwoven fabric, (b) the 15% AA grafted and 10.4% collagen immobilized PP nonwoven fabric, and (c) the 15% AA grafted and 70.1% collagen/chitosan immobilized PP nonwoven fabric.

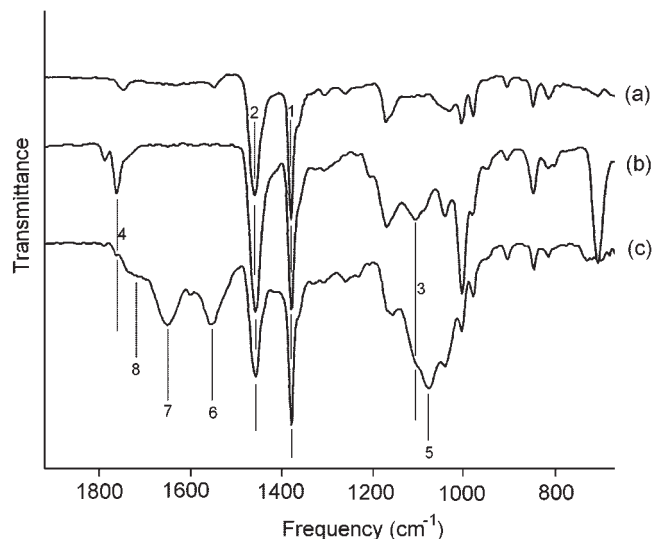


Figure 6 The spectra of the surface reflection infrared spectroscopy of (a) the PP nonwoven fabric, (b) the 15% AA grafted PP nonwoven fabric, and (c) the 15% AA grafted and 10.4% collagen/chitosan immobilized PP nonwoven fabric. 1.1451 cm^{-1} , 2.1372 cm^{-1} , 3.1099 cm^{-1} , 4.1755 cm^{-1} , 5.1073 cm^{-1} , 6.1551 cm^{-1} , 7.1646 cm^{-1} , 8.1718 cm^{-1} .

tosan and the immobilization of collagen/chitosan on the AA-grafted PP nonwoven fabric.

The relationships between the values of water uptake for the various pH values of the buffering water versus the weight ratios of collagen/chitosan, which are listed in Table I, are plotted in Figure 7(a) with dotted lines. The Figure and Table show that the values of water uptake are decreased with the increasing of chitosan contained in the mixtures of collagen/chitosan for all cases of the pH values of buffering water and increased with the decreasing of the pH value of buffering water at a same value of the weight ratio of collagen/chitosan. The fact that the lower pH value has the higher value of water uptake may be caused by the change of the hydrophilic groups contained in the immobilized collagen/chitosan. In addition, the lower values of water uptake for the higher chitosan contained in the mixtures of collagen/chitosan may be caused by the difference of the amount of collagen/chitosan immobilized on PP nonwoven fabrics. To confirm the effect of the amount of collagen/chitosan immobilized on PP nonwoven fabrics on the water absorbing property, the relationships between the values of water uptake and the immobilizing percentages of collagen/chitosan for the various pH values of the buffering water are plotted in Figure 7(b) with solid lines, which reveal that the values of water uptake are significantly decreased with the increasing of the immobilizing percentage at a same pH value of buffering water. This result is understandably to be caused by the decrease of hydrophilic groups of chitosan for the case of a higher immobilizing percent-

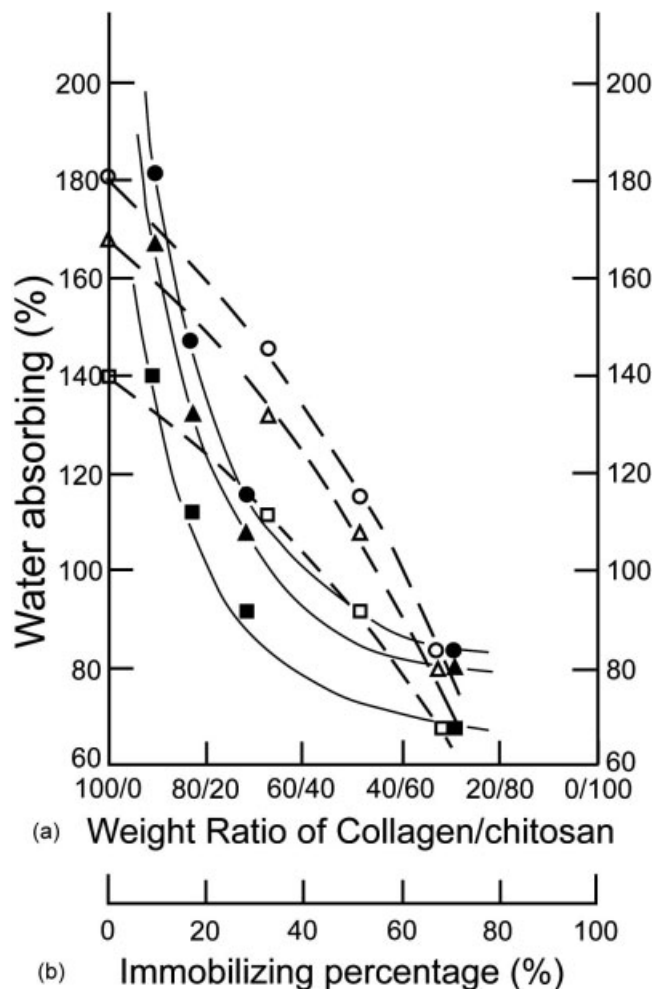


Figure 7 (a) The relationships between the values of water uptake for the various pH values of the buffering water versus the weight ratios of collagen/chitosan. (b) The relationships between the values of water uptake and the immobilizing percentages of collagen/chitosan for the various pH values of the buffering water. (○, ●): buffering water at pH 6.8; (△, ▲): buffering water at pH 8.1; (□, ■): buffering water at pH 9.3.

age of collagen/chitosan having higher crosslinking by glutaraldehyde. It is known that chitosan is easily crosslinked by glutaraldehyde.¹⁴ Figure 1 shows that the immobilizing percentages of the grafted and immobilized PP nonwoven fabrics are increased with the increasing of chitosan in the mixture of collagen/chitosan. The water absorbing property of grafted and immobilized PP nonwoven fabric, mainly caused by the hydrophilic functional groups contained in collagen/chitosan, therefore, is obviously decreased [Fig. 7(a)] with the increasing of chitosan contained in collagen/chitosan.

Figures 7(a) and 7(b) also reveal that the water absorbing property of the grafted and immobilized PP nonwoven fabrics are also decreased with the increasing of pH value of buffering water for a given value of

immobilizing percentage and weight ratio of collagen/chitosan. To avoid the formation of cationic chitosan, which formed from the reaction between the hydrogen ion and the amino group of chitosan and was able to be dissolved in water, the absorbing test of strong acid buffering water was not performed in this study. The lower pH value of buffering water has a higher water uptake value for the AA-grafted and collagen/chitosan-immobilized PP nonwoven fabrics at a given value of collagen/chitosan immobilized and the same weight ratio of collagen/chitosan may be caused by the partial ammonium groups formed under the lower pH conditions, which were formed from the interaction between the hydrogen ion and amino group of chitosan and collagen, to increase the water uptake. Some studies^{25,26} point out that the higher pH value of buffering water would have a lower water absorbing property for the crosslinked poly(vinyl alcohol)/chitosan.

For the water absorbing kinetics, the buffering water that had pH value at 6.8 was used to be absorbed by the AA-grafted and collagen/chitosan-immobilized PP nonwoven fabric samples, which were at various weight ratios of collagen/chitosan, under different absorbing time periods. Those results are shown in Figure 8 and reveal that the values of water absorbing are increased with the increasing of the absorbing time period at the initial time and then reach an equiponderant value. From this Figure, we can further find that the time periods needed to reach the equiponderant values are increased and the values of water absorbing equilibrium are decreased with the increasing of chitosan contained in the weight ratio of collagen/chitosan. As discussed above, it is caused by the fact that the higher crosslinking at higher chitosan contained in the mixtures of collagen/chitosan would

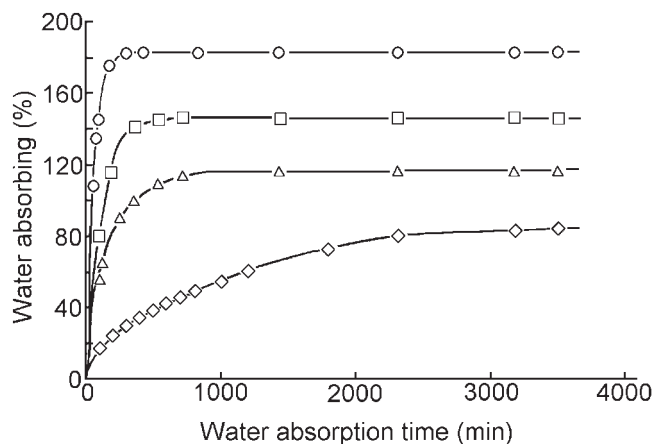


Figure 8 The rates of water adsorption for the different collagen/chitosan immobilized PP nonwoven fabrics, which were grafted with 15% acrylic acid. The weight ratios for collagen/chitosan are (○) 100/0, (□) 67/33, (△) 50/50, and (◇) 33/67. The pH value of buffering water is 6.8.

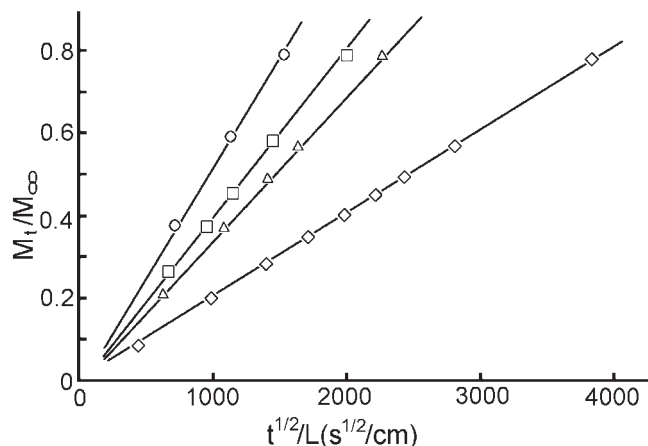


Figure 9 The relationships between the values of M_t/M_∞ and the values of $(t/L^2)^{1/2}$ for the different collagen/chitosan immobilized PP nonwoven fabrics, which were grafted with 15% acrylic acid. The weight ratios for collagen/chitosan are (○) 100/0, (□) 67/33, (△) 50/50, and (◇) 33/67. The pH value of buffering water is 6.8.

have the lower value of water absorbing equilibrium and a longer time period to reach the equiponderant value; however, the lower chitosan contained in the mixtures of collagen/chitosan would have higher water absorbing ability for lower crosslinking to increase the amount of water uptake and, hence, accelerate the reaching of equilibrium.

The relationships between the values of M_t/M_∞ and the values of $(t/L^2)^{1/2}$ shown in Figure 9 according to eq. (3) show the linear relationships over the initial absorbing time duration at the conditions of the value of $M_t/M_\infty < 0.8$. From those results, we believe that the use of the diffusion kinetic equation described by Kabra and coworkers²⁵ to study the water diffusion coefficient (D) of the various grafted and immobilized PP nonwoven fabrics is suitable. Table I also shows data of the water diffusion coefficient for the various weight ratios of collagen/chitosan. From the data list in Table I, we can find that the values of the water diffusion coefficient are decreased significantly with the increasing of chitosan contained in the weight ratio of collagen/chitosan. Obviously, the lower hydrophilic property of the higher crosslinking of collagen/chitosan would have higher repulsion to water than the higher hydrophilic property of the lower crosslinking of collagen/chitosan; therefore, the higher weight ratio of chitosan containing collagen/chitosan would have a lower value of water diffusion coefficient.

CONCLUSIONS

In this study, various weight ratios of collagen/chitosan were used to immobilize on the polypropylene nonwoven fabric, which had various values of graft-

ing percentage, to study the antibacterial and swelling properties. We find that the values of the immobilizing percentage of collagen/chitosan are increased with the increasing of the values of acrylic acid grafted on PP nonwoven fabrics and the immobilizing time period for a same weight ratio of collagen/chitosan and increased with the increasing of chitosan contained in the mixtures of collagen/chitosan at a same value of grafting percentage of AA and immobilizing time period. The antibacterial properties are increased with the increasing of the grafting percentage of AA and the immobilizing time period at a same weight ratio of collagen/chitosan and also increased with the increasing of chitosan contained in the mixtures of collagen/chitosan for all cases of grafting percentage of AA. The antibacterial properties are also significantly increased with the increasing of the values of the immobilizing percentage for all cases of grafting percentage of AA, but similar for each grafting percentage of AA under a given weight ratio of collagen/chitosan. There is no antibacterial property for PP nonwoven fabric or AA-grafted and collagen-immobilized nonwoven fabric. The values of water uptake are decreased with the increasing of chitosan contained in the mixtures of collagen/chitosan and immobilizing percentages at a same pH value of buffering water, and increased with the increasing of the grafting percentage and the decreasing of the pH value of buffering water at a same value of the weight ratio of collagen/chitosan. The values of the time periods needed to reach the equiponderant are increased and water diffusion coefficients are decreased significantly with the increasing of chitosan contained in the weight ratio of collagen/chitosan. The spectra of the surface reflection infrared spectroscopy (IR) clearly sustain the crosslinking reaction between the glutaraldehyde and collagen/chitosan and the immobilization of collagen/chitosan on the AA-grafted PP nonwoven fabric.

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