

Synthesis, Characterization, and Properties of Poly(vinyl acetate)- and Poly(vinyl alcohol)-Grafted Chitosan

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ABSTRACT: Graft copolymers of chitosan and vinyl acetate were synthesized by free radical technique using cerium (IV) as the initiator. Under controlled conditions, as much as 92% grafting with a grafting yield of 30–40% could be achieved. Chitosan-*g*-poly(vinyl alcohol) copolymers were derived by the alkaline hydrolysis of the chitosan-*g*-poly(vinyl acetate) precursor. Thermogravimetric, FTIR, and X-ray diffraction analyses of chitosan and the copolymers confirmed the grafting reaction between chitosan and vinyl acetate and also the subsequent hydrolysis. Both the copolymers possessed very good film-forming properties. Grafting resulted in a significant increase in mechanical strength of both the copolymers in the dry condition. Chitosan-*g*-poly(vinyl acetate) (CH-PVAc) proved more hydrophobic than did pure chitosan, whereas chitosan-*g*-poly(vinyl alcohol) (CH-PVOH) exhibited enhanced hydrophilicity as evident from their swelling characteristics and contact angle mea-

surements. The enhanced swelling of CH-PVOH was ascribed to the presence of the pendant poly(vinyl alcohol) group. At pH 1.98, the CH-PVAc copolymer films showed greater stability than do pure chitosan films, which is highly beneficial for specific biomedical applications. Both the copolymers showed lower glass transition temperature than do pure chitosan. Grafting did not affect the overall thermal stability, and the differential thermogram substantiated the grafting. The investigations indicate that the synthetic–natural hybrid copolymers having desirable mechanical properties and tailored hydrophilic/hydrophobic characteristics are realizable. These polymers could be exploited for varied biomedical applications. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1852–1859, 2007

Key words: chitosan; graft copolymer; vinyl acetate; hydrolyzed polymer; biomedical application

INTRODUCTION

Chitosan is the N-deacetylated derivative of chitin. Chitin is a white, hard inelastic, nitrogenous polysaccharide found in the outer skeleton of insects, crabs, shrimps, and lobsters, as well as in the internal structure of other invertebrates. Cellulose and chitin as biopolymers are the most abundant organic compounds in nature and estimated to be at levels approaching 10¹¹ tons annually.¹ As most polymers are synthetic materials, their biocompatibility and biodegradability are considerably limited than those of natural polymers such as cellulose, chitin, chitosan, and their derivatives. Although they are naturally abundant and renewable, a limitation exists in their reactivity and processability.^{2,3} The reaction of chitosan is con-

siderably more versatile than that of cellulose because of the presence of NH₂ groups. Chitosan is soluble only in aqueous acidic solutions such as acetic and hydrochloric acids via protonation of amine functions.⁴ The solubility depends upon the distribution of free amino groups and N-acetyl groups (Scheme 1).

Chitosan seems to fulfill a number of demands in the highly technological world. Khor has stated that the 21st century can be the century of chitin taking place as an extraordinary material, because chitin and its derivatives have exhibited high potential in a wide variety of fields including medical, pharmaceutical, cosmetics, bio-related science and technology, food industry, agriculture, and environmental protection.^{5–8} It is nontoxic and biodegradable, which has increased its applicability in the pharmaceutical and biomedical fields. Ravikumar has emphasized on the pharmaceutical applications of chitosan in his recent reviews.^{9–11} In a fascinating field like gene therapy, chitosan and its appropriate derivatives are recently found to be excellent candidates for controlled gene delivery.^{12,13}

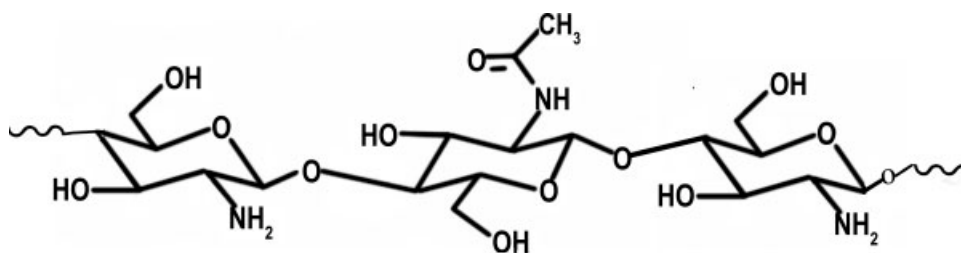
In view of many potential applications of chitin and chitosan, it is necessary to establish efficient appropriate modifications to explore fully the high potential of these biomacromolecules.¹⁴ Chemical modification

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Scheme 1 Structure of chitosan.

may become a breakthrough to promote utilization of chitosan, and among them, graft copolymerization is anticipated to be a promising approach allowing a wide variety of molecular designs.¹⁵ The properties of chitosan can be properly tuned by the nature and concentration of the graft.

The objective of this study is to develop graft copolymers of chitosan and vinyl acetate/alcohol monomers for the preparation of synthetic polymer hybrid materials with tailor-made properties. This paper describes the synthesis and characterization of chitosan-*g*-poly(vinyl acetate) copolymers, their hydrolyzed products, and a comparison of some of their properties.

MATERIALS AND METHODS

Chitosan with a deacetylation above 80% and viscosity (of 1% aqueous acetic acid solution at room temperature) above 75 cps was received from India Sea Foods, Cochin. Vinyl acetate, ceric ammonium nitrate, acetic acid, methanol, sodium hydroxide, and all other chemicals used were of analytical grade.

Grafting

Chitosan (2%, w/v) in aqueous acetic acid was reacted with varying amounts of vinyl acetate (VAc) in an inert atmosphere, using 0.1M ceric ammonium nitrate (CAN) as the initiator. Grafting was controlled by varying the amount of monomer and reaction time. In a typical experiment, 2 g (11.11 mmol) chitosan was dissolved in 100 mL of 2% aqueous acetic acid solution. This solution was taken in a three-necked round-bottomed flask, fitted with a condenser and stirrer. CAN (548 mg, 1 mmol) diluted in 10 mL of 1N nitric acid was added and the solution was heated to 60°C in an inert atmosphere. A specific amount of vinyl acetate monomer (e.g., 4 g, 47 mmol) was added dropwise and the reaction was carried out for 5 h under constant stirring. The products were precipitated using aqueous sodium hydroxide, filtered, soxhlet-extracted using methanol until a constant weight was obtained for the product and also until the methanol extract was devoid of free poly(vinyl acetate), as confirmed by FTIR. The different compositions were

coded as CH-4B, CH-6B, and CH-10B, 4, 6 and 10 being the weight in grams of monomer used for synthesis (Table I). To prepare chitosan-*g*-poly(vinyl alcohol), the chitosan-*g*-poly(vinyl acetate) copolymers were refluxed with 2% aqueous sodium hydroxide solution for 2 h. The copolymer was then washed extensively with distilled water and the corresponding compositions were labeled as CH-4A, CH-6A, and CH-10A respectively, where "A" denotes after hydrolysis and "B" denotes before hydrolysis. The % yield and % grafting were calculated using the following equations:

Percentage yield

$$= \frac{\text{Weight of the graft copolymer}}{(\text{Weight of chitosan} + \text{Weight of VAc})} \times 100$$

Percentage grafting

$$= \frac{(\text{Weight of the graft copolymer} - \text{Weight of chitosan})}{\text{Weight of chitosan}} \times 100$$

The monomer conversion was calculated with the following equation:

Percentage conversion

$$= \frac{(\text{Weight of the graft copolymer} - \text{Weight of chitosan})}{\text{Weight of monomer}} \times 100$$

FTIR spectral analysis

FTIR spectra of chitosan and both the CH-PVAc and CH-PVOH copolymers were studied by a Nicolet impact 410 FTIR Spectrophotometer. Potassium bromide pellet method was used to record the spectra of the powdered samples in the wave number range 400–4000 cm⁻¹.

X-ray diffraction analysis

X-ray diffraction (XRD) analyses of the chitosan and the copolymers in the powder form were performed

TABLE I
Graft Copolymerization of VAc onto Chitosan with Cerium (IV)

No	Weight of chitosan (mmol)	Weight of VAc (mmol)	Weight of CAN (mmol)	Time (h)	Monomer conversion (%)	Yield (%)	Grafting %	Polymer reference
1	11.11	47	1	5	12.5	42	25	CH-V4B
2	11.11	70	1	5	19.3	40	58	CH-V6B
3	11.11	116	1	5	18.4	32	92	CH-V10B

with a wide angle X-ray scattering, using Siemens D5005 X-ray Diffractometer.

Thermal studies

Glass transition temperature (T_g) of the copolymer films was evaluated by differential scanning calorimetry (DSC 2920 Differential Scanning Calorimeter, TA Instruments Inc.). Thermal stability of the copolymer films was studied on a SDT 2960 (Simultaneous DTA-TGA, TA Instruments Inc). For DSC analysis, 5–8 mg of the samples were crimped inside aluminum sample pans and heated under nitrogen atmosphere at a rate of 10°C/min from –50 to 70°C. The second heat cycle is used for the calculation of glass transition temperature. For TGA analysis, 10–12 mg of the film samples were taken in a platinum cup and heated under nitrogen atmosphere at a rate of 10°C/min from room temperature to 700°C.

Mechanical properties

Tensile properties of the CH-PVAc and CH-PVOH copolymer films were studied using Universal Testing Machine-Instron 1193. The films were conditioned in the testing atmosphere for 48 h. Rectangular strips of 10-mm width were elongated till break at a cross-head speed of 10 mm/min. Stress at break and the percentage elongation of the films both in dry and wet conditions were cal-

culated using the Instron series IX software. The computed values are the mean of six repeat measurements.

Swelling properties

Square film samples of 100-mm² size (of known mass) were immersed in phosphate buffer (pH 7.4) and aqueous acetic acid (pH 1.98) solutions for known intervals of time. The strips were removed and carefully blotted using filter paper to remove excess fluid and weighed. Swelling index is calculated as follows:

$$\text{Swelling index} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100$$

Contact angle measurements

Captive octane in water contact angle of the chitosan and grafted films were determined using a contact angle goniometer (GII, Kernco Instruments Co. Inc. Texas, USA) to study the hydrophilicity of the films. The films were conditioned in double distilled water for 3 days. The films were then placed on glass slides and fastened on both ends using teflon tapes and immersed in double distilled water. The octane/water contact angles were then measured by introducing octane droplets with a microsyringe.

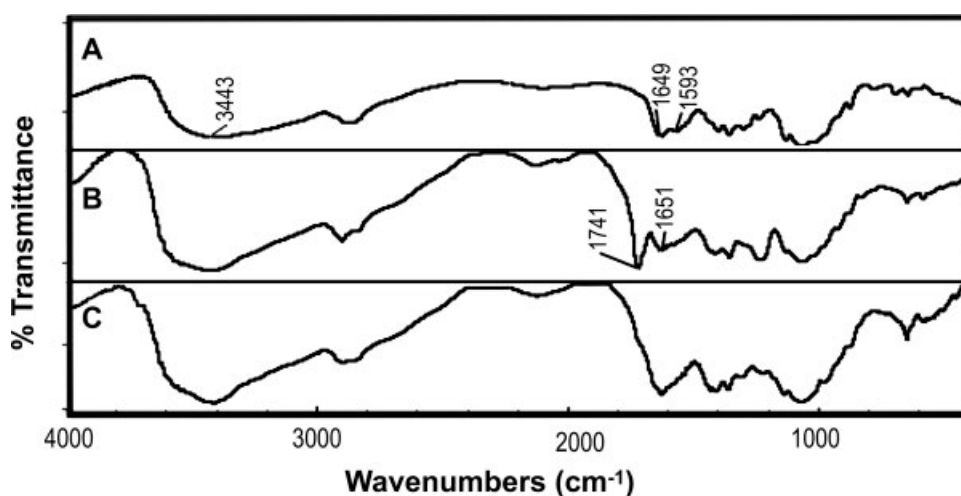


Figure 1 FTIR spectra of (A) chitosan, (B) chitosan-g-poly(vinyl acetate), and (C) chitosan-g-poly(vinyl alcohol).

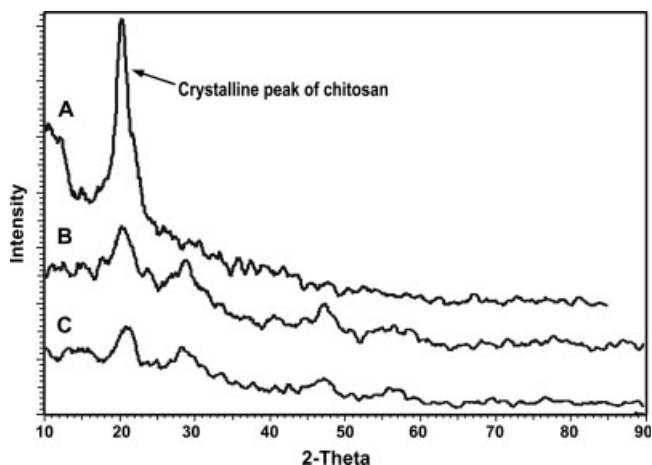


Figure 2 XRD pattern of (A) chitosan, (B) chitosan-g-poly(vinyl alcohol), and (C) chitosan-g-poly(vinyl acetate).

RESULTS AND DISCUSSION

Quiet a few papers have been published on the grafting of vinyl monomers on chitosan. Blair et al.¹⁶ have reported a method for the homogeneous grafting of chitosan and chitin with vinyl monomers such as methylacrylate, vinyl acetate etc., using AIBN as the initiator. Singh and Ray¹⁷ grafted 2-hydroxy ethyl methacrylate onto chitosan using ⁶⁰Co γ -radiation and studied the blood compatibility of the products. The graft copolymers of chitosan and poly(vinyl alcohol) were studied by Huang and Fang.¹⁸ Wang et al.¹⁹ explored the usefulness of chitosan poly(vinyl alcohol) films for the controlled release of bovine serum albumin. In a study Mathews et al.²⁰ showed that the biocompatibility and cell adhesion characteristics of poly(vinyl alcohol) hydrogel can be improved by blending chitosan with the hydrogel. In another study, Don et al.²¹ reported the preparation and characterization of chitosan-g-poly(vinyl alcohol)/poly(vinyl alcohol) blends and showed that the cellular compatibility of poly(vinyl alcohol) was improved due to the incorporation of chitosan. The studies of Chuang et al.²² also highlighted the potential of poly(vinyl alcohol)/chitosan-blended membranes for biomedical applications. Wei et al.²³ proposed the following mechanism

TABLE II
The Effect of Grafting on the Glass Transition Temperature of Chitosan

Sample codes	Glass transition temperature (°C)	
	Before hydrolysis	After hydrolysis
PVAc	28	70
CH-0	62	—
CH-4	No specific T_g	No specific T_g
CH-6	29	36
CH-10	30	41

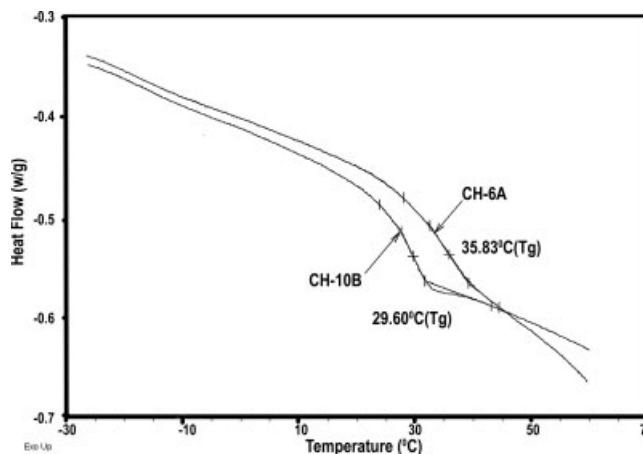


Figure 3 DSC scans of chitosan-g-poly(vinyl acetate) (CH-10B) and chitosan-g-poly(vinyl alcohol) (CH-6A).

of initiation of graft copolymerization of vinyl monomers onto chitosan. Chitosan forms an efficient redox initiation system with Ce ion, and a chelate complex is formed when Ce (IV) ion reacts with the adjacent hydroxyl-amino structure. At 40°C, the amino and hydroxyl groups are oxidized to —CH=NH and aldehyde groups respectively. At higher temperature (~ 90°C), the —CH=NH group is also hydrolyzed to form aldehyde group that forms the reaction complex to initiate polymerization. The graft copolymerization of HEMA and MMA onto chitosan is possible by similar reaction.^{24,25} Don et al.²⁶ reported the mechanical, thermal, and swelling properties of chitosan modified with poly(vinyl acetate). The copolymers were made by dispersion polymerization of chitosan and vinyl acetate. No attempt was made to isolate the graft copolymer from the homopolymer, poly(vinyl acetate). Therefore, the reported properties are those of the

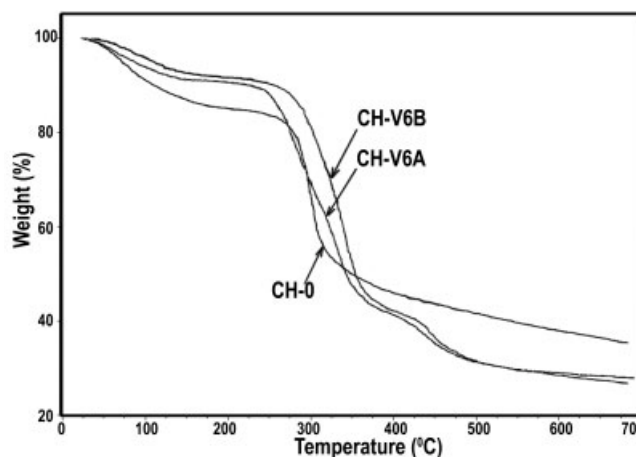


Figure 4 TGA thermograms of chitosan (CH-0), chitosan-g-poly(vinyl acetate) (CH-V6B), and chitosan-g-poly(vinyl alcohol) (CH-6A), in nitrogen atmosphere, heating rate = 10°C/min.

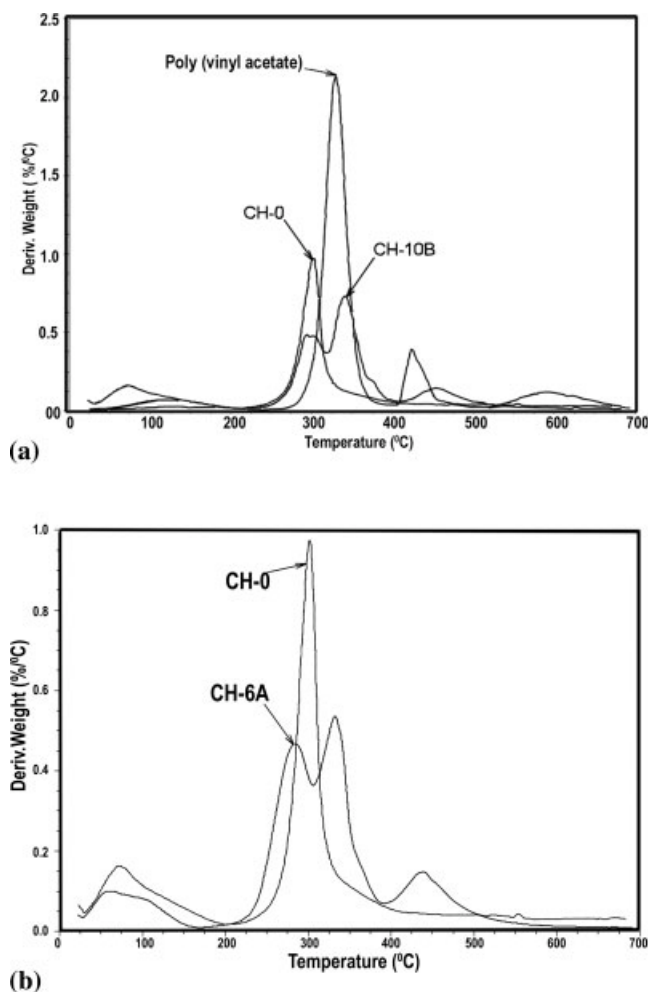


Figure 5 A: DTG thermograms of chitosan (CH-0), poly(vinyl acetate) homopolymer and chitosan-g-poly(vinyl acetate) (CH-10B), in nitrogen atmosphere, heating rate = 10 °C/min. B: DTG thermograms of chitosan (CH-0) and chitosan-g-poly(vinyl alcohol) (CH-6A), in nitrogen atmosphere, heating rate = 10 °C/min.

blends of chitosan-g-PVAc and homopolymer of PVAc, the latter being present in substantial quantities. The graft extent is also quite low.

The present work is focused on the synthesis and characterization of pure chitosan-g-poly(vinyl acetate), wherein the extent of PVAc grafting is also comparatively high. A maximum of 92% grafting with a grafting yield of about 32% was achieved on reacting the system for 5 h. The % grafting increased proportionally with the weight of the monomer in the feed. But the % yield was not found to follow the same trend. The extent of grafting was calculated after the removal of the homopolymer by Soxhlet extraction with methanol. The complete removal of the homopolymer was confirmed by FTIR analysis of the extract. The details of the amount of reactants, reaction conditions, grafting yield, etc. are given in Table I.

TABLE III
Mechanical Properties of the Chitosan-g-PVAc Films

Sample code	Tensile strength (MPa)		% Elongation	
	Dry	Wet	Dry	Wet
CH-0	35 ± 11	51 ± 7	15 ± 7	92 ± 7
CH-V4B	123 ± 16	25 ± 4	11 ± 3	153 ± 7
CH-V 6B	96 ± 17	55 ± 7	27 ± 10	151 ± 20
CH-V10B	117 ± 0.9	59 ± 10.2	13 ± 0.4	163 ± 8

FTIR spectral analysis

FTIR spectra were used to prove the grafting between poly(vinyl acetate) and chitosan and also to confirm the complete hydrolysis of the vinyl acetate segments of the graft copolymer to vinyl alcohol. The spectra of the chitosan-g-poly(vinyl acetate) showed the presence of the carbonyl absorption band at 1741 cm^{-1} , which confirmed the presence of PVAc grafts. In the case of the chitosan-g-poly(vinyl alcohol), the same peak was absent confirming the complete hydrolysis of the vinyl acetate segments to vinyl alcohol segments. Amide I and amide II bands of chitosan are located at 1649 and 1593 cm^{-1} respectively, and the symmetric stretching vibrations of the NH_2 groups of chitosan at 3443 cm^{-1} as seen in Figure 1. The characteristic peaks of chitosan were assigned to be 1650 cm^{-1} (amide I) and 3450 cm^{-1} (primary $-\text{NH}_2$) by Gupta and Kumar.²⁷

XRD patterns

Wide-angle XRD patterns of powdered chitosan and the copolymers are shown in Figure 2. Chitosan exhibited the major crystalline peak at $2\theta \sim 20^\circ$ in agreement with the literature values.²⁸ In graft copolymers, additional diffractions are seen at 2θ 28°, 48°, and 58°. Though each of these has not been assigned to specific diffractions, the different pattern of the copolymer vis-à-vis the parent molecule is indicative of a clear structural change in chitosan as a result of grafting with vinyl acetate. On hydrolysis of acetate to alcohol, all

TABLE IV
Mechanical Properties of the Chitosan-g-Poly(vinyl alcohol) Films

Sample code	Tensile strength (MPa)		% Elongation	
	Dry	Wet	Dry	Wet
CH-0	35 ± 11	51 ± 7	15 ± 7	92 ± 7
CH-V4A	136 ± 28	63 ± 5	15 ± 3	115 ± 10
CH-V 6A	95 ± 1	38 ± 8	25 ± 2	151 ± 38
CH-V10A	82 ± 23	47 ± 3	23 ± 7	169 ± 12

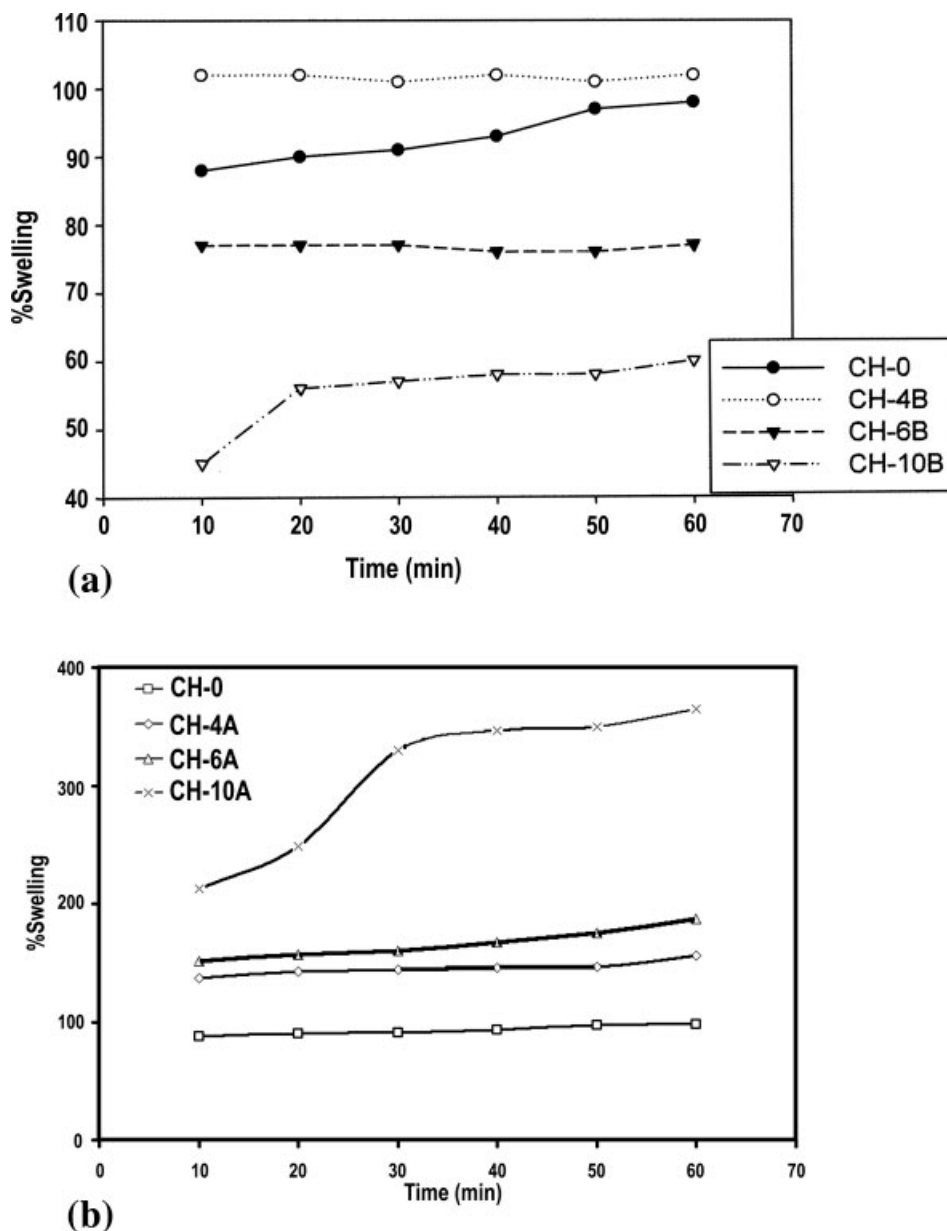


Figure 6 A: % swelling of chitosan-g-poly(vinyl acetate) at pH 7.4. B: % swelling of chitosan-g-poly(vinyl alcohol) at pH 7.4.

the peaks except that at $2\theta = 58^\circ$ are retained. Most likely, the polymer lattice configuration is not affected on hydrolysis.

Thermal studies

Chitosan shows a T_g at 62°C . When the poly(vinyl acetate) graft is less as in the case of CH-4B (25%), no detectable T_g is seen. However, as the poly(vinyl acetate) content gets enhanced, a single transition is seen for the copolymers CH-V6B and CH-V10B at 29 and 30°C , respectively (Table II). When the vinyl acetate segments are hydrolyzed, the glass transition temperature of the films also increased (36 and 41°C) because of hydrogen

bonding among the $-\text{OH}$ groups. The representative DSC scans of the chitosan-g-poly(vinyl acetate) and chitosan-g-poly(vinyl alcohol) films are given in Figure 3. Don et al.²⁶ reported that the residual ceric ion in the copolymer exhibited an endothermic peak at 240°C in the DSC scan of their copolymers. We did not observe such an oxidative degradation for our samples as residual ceric ions are absent in this case. Figure 4 shows the TGA thermograms for chitosan and the copolymers. The initial and the 50% decomposition temperature of both the copolymers are not significantly affected due to grafting. The two-stage mass loss pattern of the copolymers confirms grafting, which is more distinct in DTG thermograms as seen in Figure 5(a,b).

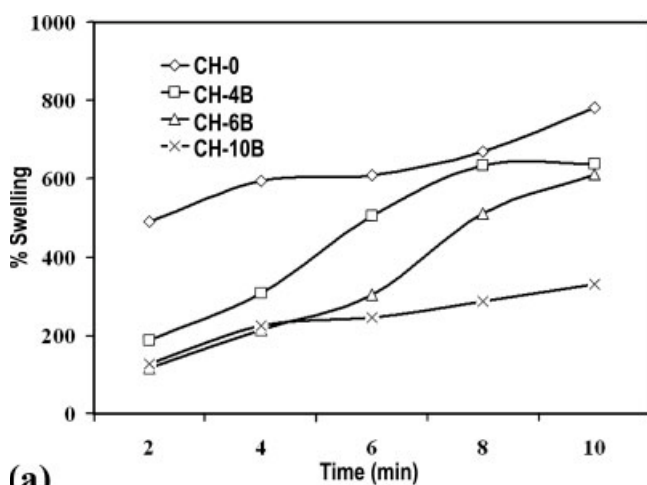
Mechanical properties

It is seen from Table III that the grafting results in an enormous increase in the tensile strength of chitosan film in the dry state with not much change in % elongation. The tensile strength of the films is marginally decreased on hydrolysis of the vinyl acetate to vinyl alcohol (Table IV). The % elongation increased considerably in the case of the graft copolymers under wet condition as the vinyl acetate segment retards the rigidity of the chitosan chain, making the copolymer more soft and extensible. The increased mechanical property of the chitosan-g-poly(vinyl acetate) copolymers and their acid resistance are highly beneficial for the fabrication of strong as well as degradable matrices. Don et al.²⁹ studied the preparation of chitosan-g-poly(vinyl acetate) copolymers and their adsorption of copper ions. To increase the mechanical strength and acid resistance, the copolymer membranes were crosslinked with glutaraldehyde. Wang et al.³⁰ repor-

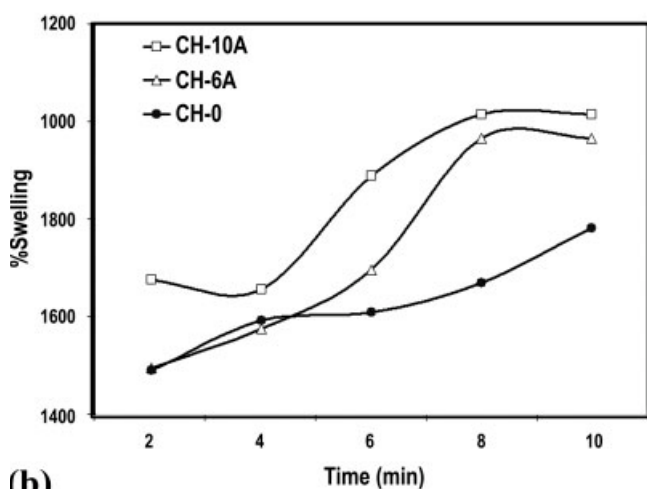
TABLE V
Effect of Grafting on Octane Contact Angle of Chitosan

Sample	Octane contact angle	
	Before hydrolysis	After hydrolysis
CH-0	149	149
CH-V4	145	160
CH-V6	91	117
CH-V10	92	121

ted the physical and chemical properties of a semi-interpenetrating polymeric network of chitosan and poly(vinyl alcohol) with glutaraldehyde as the crosslinker. The authors claimed that the addition of poly(vinyl alcohol) improved the mechanical properties of the hydrogel. Though the natural polymers can be fabricated into highly biodegradable matrices, the main disadvantage of them is their poor mechanical properties and handling inconveniences. Poly(vinyl acetate)-grafted chitosan films reported in this work possess both these qualities even in the uncrosslinked condition and are hence promising candidates for varied engineering and medical applications.



(a)



(b)

Figure 7 A: % swelling of chitosan-g-poly(vinyl acetate) at pH 1.98. B: % swelling of chitosan-g-poly(vinyl alcohol) at pH 1.98.

Swelling studies

The hydrophilicity of the copolymers is assessed by studying their water absorption capacity and their under-water octane contact angles. The % swelling of the samples are studied in phosphate buffer at pH 7.4 and in aqueous acetic acid at pH 1.98. It is already reported that chitosan is hydrophobic in nature and its swelling index at pH 7.4 is very low.²⁰ On grafting the hydrophobic monomer (i.e., vinyl acetate), chitosan is expected to increase hydrophobicity which is confirmed by our results. Figure 6(a) shows that all the chitosan-g-poly(vinyl acetate) copolymer films except CH-4B composition have less percentage swelling when compared to ungrafted chitosan films. In CH-4B, the percentage grafting is only 25%; it is concluded that moderate PVAc grafting is conducive to enhancing the swelling characteristics. On hydrolysis of the vinyl acetate to the corresponding vinyl alcohol, the copolymers become more hydrophilic. This is also evident from the Figure 6(b), where all the hydrolyzed films show higher percentage swelling at pH 7.4 than do chitosan.

At pH 1.98, chitosan and the copolymers of this study show interesting swelling behavior [Fig. 7(a)]. Briefly, chitosan has high percentage swelling and tends to dissolve within 10 min of exposure at this pH on account of protonation of the free $-\text{NH}_2$ groups. But dissolution time is enhanced to 30–40 min in the case of chitosan-g-poly(vinyl acetate) films for CH-4B composition, while CH-6B and CH-10B compositions

are stable for more than 24 h. The stability of CH-6B and CH-10B is due to the stabilization effect of vinyl acetate segment, which is grafted to an extent of 58 and 92% respectively. When the chitosan-g-poly(vinyl alcohol) films are kept at pH 1.98, the compositions CH-6A and CH-10A display higher percentage swelling than chitosan. This is due to the interaction of the pendent vinyl alcohol segments with water. The chitosan-g-poly(vinyl alcohol) films also showed increased acid resistance when compared to virgin chitosan films. The CH-6A and CH-10A compositions are stable for more than two hours at pH 1.98. Figure 7(b) shows the % swelling versus time of the hydrolyzed copolymer at pH 1.98.

The under-water octane contact angle values also support the fact that the conversion of the vinyl acetate segment to vinyl alcohol segments increases the hydrophilicity of the copolymer. Table V shows the octane contact angle values of the copolymers before and after hydrolysis.

Thus, the swelling studies ensure that the hydrophilic/hydrophobic tuning can be achieved by properly adjusting the extent of hydrolysis of the chitosan-g-poly(vinyl acetate) copolymers. The synthetic-natural hybrid copolymers having good mechanical properties and properly tuned hydrophilic/hydrophobic ratios are promising candidates which could be exploited for degradable, strong and pH sensitive membrane applications.

CONCLUSIONS

Chitosan-g-poly(vinyl acetate) copolymers were synthesized by CAN free radical technique. A maximum of 40% yield with 92% grafting could be achieved. The hydrolysis of the chitosan-g-poly(vinyl acetate) with aqueous sodium hydroxide solution led to chitosan-g-poly(vinyl alcohol). Both the copolymers showed enhanced mechanical properties with tunable hydrophilicity. The hydrolyzed copolymer was more hydrophilic than its precursor. The poor mechanical properties and the consequent difficulty in processing of chitosan could be obviated by way of graft copolymerization. The increased mechanical property of the chitosan-g-poly(vinyl acetate) is highly beneficial for the fabrication of strong, degradable matrices. Chitosan-g-poly(vinyl acetate) films are promising candidates for varied engineering and medical applications. The synthetic-natural hybrid copolymers with good mechani-

cal properties and properly tailored hydrophilic/hydrophobic characteristics could serve as promising candidates for potential applications demanding strong but degradable and pH sensitive membranes.

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