Synthesis and Properties of Chitosan-Modified Poly(vinyl acetate)

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ABSTRACT: A redox initiator, cerium ammonium nitrate, was used to initiate the graft copolymerization of vinyl acetate (VAc) onto the chitosan chain in a dispersion polymerization at 60°C. With an addition of 0.5–7.5 g of chitosan based on 50 g of VAc, the monomer conversion was found to be between 70 and 80% after 2 h of reaction. The grafting efficiency increased with the amount of chitosan added; yet, the grafting ratio increased slightly and then decreased. After the reaction, a stable dispersion system was observed and the surface of the latex particles was found to be rich in chitosan. All the experimental results indicated that the chitosan molecules not only took part in the graft copolymerization, but also served as a surfactant, providing the stability of the dispersion particles. If the dispersion aqueous solution was oven-dried, a particulate membrane was formed. The experimental results indicated that the incorporation of poly(vinyl acetate) to the chitosan chains increased the toughness and decreased the water absorption of the chitosan material. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3057–3063, 2002

Key words: chitosan/PVAC; synthesis; property

INTRODUCTION

Hybridization of natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials.[1] One of the natural polymers that has attracted great attention recently is chitosan. Chitosan is a high molecular weight polysaccharide composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of β-(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose. It is generally prepared by the partial deacetylation of chitin in a hot alkali solution. Chitin is the most abundant natural polymer next to cellulose and can be found in the skeletal materials of crustaceans and insects and cell walls of bacteria and fungi. Compared with other polymers, chitin and chitosan have several important advantages, including biocompatibility, biodegradability, and nontoxicity.[2,3] They can be used in the fields of wastewater treatment, food processing, cosmetics, pharmaceuticals, biomaterials, and agriculture. With its fibrous structure, chitin is hardly soluble in any solvent. Yet, chitosan can be dissolved in an acid solution and becomes a cationic polymer because of the protonation of amino groups on the C-2 position of the pyranose ring.

Although chitosan has found potential use in many areas, it is a brittle material and tends to absorb a quantity of moisture. Therefore, it would be desired to improve its toughness and water resistance. There are many routes to accomplish this objective, and in this article, a graft copolymerization of a vinyl monomer onto chitosan chains was employed. In this way, new materials with the desired properties can be achieved by the chemical combination of natural and synthetic polymers. Graft copolymerization has been studied for many years, especially in cellulose, including using electromagnetic radiation such as γ-ray and ultraviolet light and free-radical initiators such as azobisisobutyronitrile (AIBN),[4] iron(II)-hydrogen peroxide,[5] and transition-metal ions.[6–8] Commonly used transition-metal ions for initiating graft copolymerization are Ce(IV), Mn(III), Cr(VI), Co(III), Fe(III), and Cu(II). Among these, it has been shown that cerium salts are the most effective in grafting vinyl monomers onto a number of polysaccharides.[9–14] Therefore, cerium ammonium nitrate (CAN) was used in this article to initiate the graft copolymerization of vinyl acetate (VAc) onto chitosan. Poly(vinyl acetate) (PVAc) is known as a leathery and water-resistant polymer, which may improve the properties of chitosan material. After polymerization, the thermal properties, tensile mechanical properties, and water absorption of the final polymers were examined and are reported in this article.

EXPERIMENTAL

Materials

Chitosan (Tokyo Chemicals Inc., Tokyo, Japan) was purified before use. It was first dissolved into a 2% acetic acid solution and precipitated out by the addi-

Reaction conditions	System			
	SE101	SE105	SE110	SE115
CS (g)	0.5	2.5	5	7.5
VAc (g)	50	50	50	50
$Ce(NH_4)_2(NO_3)_6$ (mol)	1.08×10^{-2}	1.08×10^{-2}	1.08×10^{-2}	1.08×10^{-2}
CH_3COOH (g)	10	10	10	10
H_2O (g)	500	500	500	500
Temperature (°C)	60	60	60	60
Rotational speed (rpm)	250	250	250	500[a]

[a] The viscosity of the chitosan solution was too high for this system to have a high monomer conversion if the rotational speed maintained at 250 rpm.

tion of a concentrated NaOH solution. The precipitate was washed several times with a great amount of deionized water until the pH had reached 7. The degree of deacetylation of chitosan was found to be 86% by a colloid titration method.[15] In this method, a specific amount of a chitosan–acetic acid solution was titrated with 0.0025N potassium poly(vinyl sulfate) [PVSK; $(C_2H_3O_4SK)_n$, $n = 1500$ or above], where 0.1% toluidine blue was used as an indicator. The viscosity-average molecular weight was found to be 616,000 by a viscometric method, where the Mark–Houwink constants k and α were 1.38×10^{-2} and 0.85, respectively.[16] VAc from Acros Organics (Geel, Belgium) was distilled under reduced pressure. Only the distillate obtained at the middle stage of distillation was used for the polymerization. CAN [$Ce(NH_4)_2(NO_3)_6$] was reagent-grade from Showa Chemical Inc. (Tokyo). All the other chemicals were analytical grade or above and used as received without further purification.

Graft copolymerization

A specific amount of chitosan was first dissolved into 500 mL of a 2% (w/w) acetic acid solution, and then 1.08×10^{-2} mol of the CAN initiator was added. The solution was heated to 60°C in an isothermal water bath. It was then stirred at a speed of 250 rpm and purged with nitrogen. Subsequently, 50 g of the distilled VAc monomer was added to the solution and the polymerization was immediately started. After 2 h, a dispersion aqueous solution containing the chitosan/PVAc copolymer was obtained. To prepare the sample membrane, a drying process was employed. The dispersion solution was cast into a stainless mold and then dried at 50°C in a circulation oven for 48 h and another 12 h in a vacuum oven at 80°C.

The reaction conditions and the sample codes of the membranes are listed in Table I. In addition, the conversion was calculated with the following equation:

$$X(\%) = (W_1 - W_{CS})/(W_{VAc}) \times 100 \quad (1)$$

In the equation, W_{CS} and W_{VAc} are the initial weight of chitosan and the VAc monomer, respectively. W_1 is the final weight of the drying product containing both the PVAc homopolymer and the chitosan-*graft*-PVAc copolymer. To calculate the grafting efficiency (GE %) and grafting ratio (GR), an acetone solvent was used to extract the PVAc homopolymer from the drying product with a Soxhlet extractor. After 72 h of extraction, the remaining chitosan-*graft*-PVAc copolymer was dried and weighed (W_2). The GE (%) and GR were calculated with the following equations:

$$GE(\%) = (\text{weight of grafted PVAc chains}$$
$$\div \text{ weight of total monomer conversion}) \times 100$$
$$= (W_2 - W_{CS})/(W_1 - W_{CS}) \times 100 \quad (2)$$

$$GR = \text{weight of grafted PVAc chains}$$
$$\div \text{ weight of chitosan}) = (W_2 - W_{CS})/W_{CS} \quad (3)$$

Thermal properties

A differential scanning calorimeter (TA 2010 from TA Instruments) was used to observe the thermograms of the final membranes. Nitrogen gas was purged into the cell. Samples were placed in aluminum pans and scanned from −40 to 250°C at a heating rate of 10°C/min. A midpoint method was employed to estimate the glass transition temperature (T_g). A thermal gravimetric analyzer (TGA-7 from Perkin–Elmer) was employed to measure the weight loss of the samples under heating. Samples were first held at 100°C for 10 min and then heated from 100 to 600°C with a heating rate of 20°C/min.

Mechanical properties

The tensile properties—ultimate tensile strength, initial modulus, and elongation at break—were measured using a Universal tensile testing instrument

(RTM-1 from Yashima Works Co.). The tensile speed was 20 mm/min. All the specimens were prepared from the sample membranes and had the dimension of $5 \times 1 \times 0.5$ cm. Approximately five specimens were tested for each condition and the results were averaged.

Swelling studies

Samples were immersed in deionized water to observe the swelling behavior. The pH value of the water was controlled at 6. After the excess water was removed with filter paper, the weight of the swollen samples was measured at various time intervals. The procedure was repeated until there was no further weight increase. The degree of swelling was calculated by the weight of swollen sample at a specific time divided by the sample weight in the dry state.

RESULTS AND DISCUSSION

Reaction mechanism

In this study, CAN was used to initiate the graft copolymerization of VAc onto chitosan chains. Ceric ion is a strong redox initiator, which can oxidize the pyranose ring of polysaccharide and produce a free radical on it.[9–14] The reaction mechanism is shown in Scheme 1.
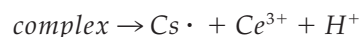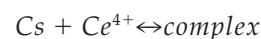
In the literature, two kinds of initiation reactions were proposed[9–14] (Scheme 1). One is the direct abstraction of the hydrogen atom from the carbon having a hydroxyl group. The following oxidation of this hydrogen atom by the ceric ion (Ce^{4+}) yields a proton, cerous ion (Ce^{3+}), and a free radical on the carbon. The other route is that the ceric ion reacts reversibly with the nucleophilic groups such as NH_2 and OH at C-2 carbon and C-3 carbon, respectively, to form a complex. Subsequently, the C—C bond between the functional groups cleaves to yield an aldehyde and a free radical. Chen[17] showed evidence of the formation of an aldehyde where ceric ion was used to initiate the graft copolymerization of styrene onto starch. Once the initiation reaction has started, the graft copolymerization of a monomer onto chitosan chains then takes place immediately with the traditional chain polymerization. Finally, a termination reaction occurs, where two chain radicals collide with each other, leading to dead polymers. Furthermore, it has to be emphasized that the chain-transfer reactions are very important in the present system because they affect the polymerization rate and polymer structure. Odian and Kho[9] and Kurita et al.[18] proved that both the polymerization rate and the grafting ratio depend on the amount of ceric ion because of the chain-transfer reaction to the ceric ion. As a result, the grafting ratio increases to a maximum and then decreases with the amount of

1. Initiation
   (1) Direct oxidation

   $$Cs + Ce^{4+} \rightarrow Cs\cdot + Ce^{3+} + H^+$$

   $$Cs\cdot + M \rightarrow CsM\cdot$$

   (2) Formation of complex

   $$Cs + Ce^{4+} \leftrightarrow complex$$

   $$complex \rightarrow Cs\cdot + Ce^{3+} + H^+$$
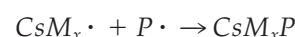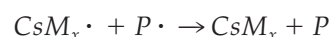
   $$Cs\cdot + M \rightarrow CsM\cdot$$

   where Cs is a chitosan chain; Ce^{4+} and Ce^{3+}, ceric and cerous ions, respectively; $Cs\cdot$, a chitosan chain radical; and M, the vinyl acetate monomer.
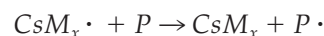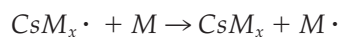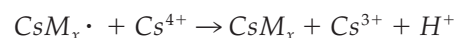2. Propagation

   $$CsM\cdot + M \rightarrow CsM_2\cdot$$

   $$CsM_x\cdot + M \rightarrow CsM_{x+1}\cdot$$

   where $CsM_x\cdot$ is a propagating PVAc chain grafted onto the chitosan.
3. Termination

   $$CsM_x\cdot + P\cdot \rightarrow CsM_x + P$$

   $$CsM_x\cdot + P\cdot \rightarrow CsM_xP$$

   where $P\cdot$ indicates all the propagating polymer chains, $P\cdot = \Sigma CsM_x\cdot + \Sigma M_x\cdot$, and $M_x\cdot$ is the PVAc chain radical; CsM_x, CsM_xP, and P are all dead polymers.
4. Chain transfer

   $$CsM_x\cdot + Cs^{4+} \rightarrow CsM_x + Cs^{3+} + H^+$$

   $$CsM_x\cdot + M \rightarrow CsM_x + M\cdot$$

   $$CsM_x\cdot + P \rightarrow CsM_x + P\cdot$$

Scheme 1 Reaction mechanism of graft copolymerization with the CAN initiator.

ceric ion added. It is also well known that chain transfer to a monomer and a polymer can occur to an appreciable extent in the polymerization of PVAc. This leads to an extensive branching of PVAc.[19] Although Scheme 1 only describes the graft copolymerization, homopolymerization of PVAc occurs at the same time. Therefore, they compete with each other for the monomer.

TABLE II
Total Monomer Conversion (X %), Grafting Efficiency (GE %), and Grafting Ratio (GR) of Various Reaction Systems After 2 h at 60°C

Measurement	System			
	SE101	SE105	SE110	SE115
X (%)	80.0	78.1	75.9	70.3
GE (%)	4.22	17.4	29.7	35.7
GR	3.39	3.42	2.74	2.36

Table II lists the conversion (X %), grafting efficiency (GE %), and grafting ratio (GR) of various systems after 2 h of reaction at 60°C. The conversion was in the range of 70–80% and slightly decreased with increase in the amount of chitosan. To calculate the GE % and GR, an acetone solvent was used to extract the PVAc homopolymer from the final polymer particles. Elemental analysis confirmed that there was no chitosan copolymer dissolved in the acetone because no trace of the nitrogen element was detected in the extract. The GE %, indicating the competition of graft copolymerization with homopolymerization for VAc monomer, increased with the amount of chitosan added. This is reasonable, because the more chitosan added the more pyranose rings were available for the initiation by the ceric ion. Consequently, there were more active sites on the chitosan chains for the graft copolymerization. Yet, the grafting ratio decreased when a greater amount of chitosan was added, as shown in the systems of SE110 and SE115, which means that increasing the chitosan amount did not get
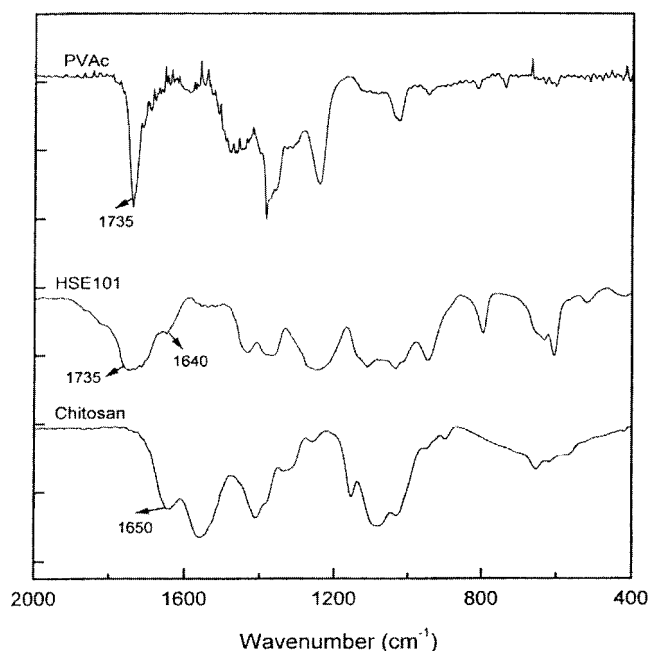

Figure 1 FTIR spectra of pure PVAc, chitosan, and copolymer sample SE101.

the same proportional increase in the amount of grafted PVAc chains, owing to the greater increase in solution viscosity as the chitosan was added.

Structures of dispersion particles

Figure 1 shows the FTIR spectra of pure PVAc, chitosan, and a copolymer sample SE101. The most important absorption peak in PVAc is at 1735 cm^{-1} caused by the C=O stretching vibration. The well-characterized absorption peak to describe chitin or chitosan material is the amide I absorption peak at 1650 cm^{-1} from the acetamide group (—NHCOCH$_3$). This peak was used to determine the degree of deacetylation.[3] Compared with the spectra of PVAc and chitosan, the observed absorption peaks at 1735 and 1640 cm^{-1} in the spectrum of the sample SE101 indicated its copolymer structure of chitosan/PVAc.

After the reaction, a stable dispersion solution was observed and the surface charge of the dispersed particles was found to be positive by measuring the zeta (ζ) potential. The positive charge was from the cationic chitosan chains. Because the water-insoluble PVAc chains were grafted onto the soluble, cationic chitosan chains in the reaction, we expected the hydrophobic PVAc chains to be aggregated inside the core and the hydrophilic chitosan chains to have migrated toward the outer shell of the particles. The positively charged chitosan molecules on the surface thus provide the electrostatic and steric stabilization of particles.[20–22] In an experiment, the ceric ion was used to try to initiate the polymerization of the VAc monomer alone without the addition of chitosan. The final conversion is as low as only 30% and the polymer precipitated out during the reaction. In addition, our previous article[20] also revealed that the surface charge of the latex particles synthesized from the methyl methacrylate with the potassium persulfate initiator in the presence of chitosan was positive and increased with the amount of chitosan added. Therefore, it was concluded that the chitosan molecules not only took part in the reaction, but also served as a surfactant, providing the stability of latex particles. If the dispersion solution was dried at 80°C, a particulate membrane was formed. This happened because the rigid chitosan on the particles' surface kept them from fusing together during the drying process.

TABLE III
T_g's of the Various Samples from Different Reaction Systems After 2 h at 60°C

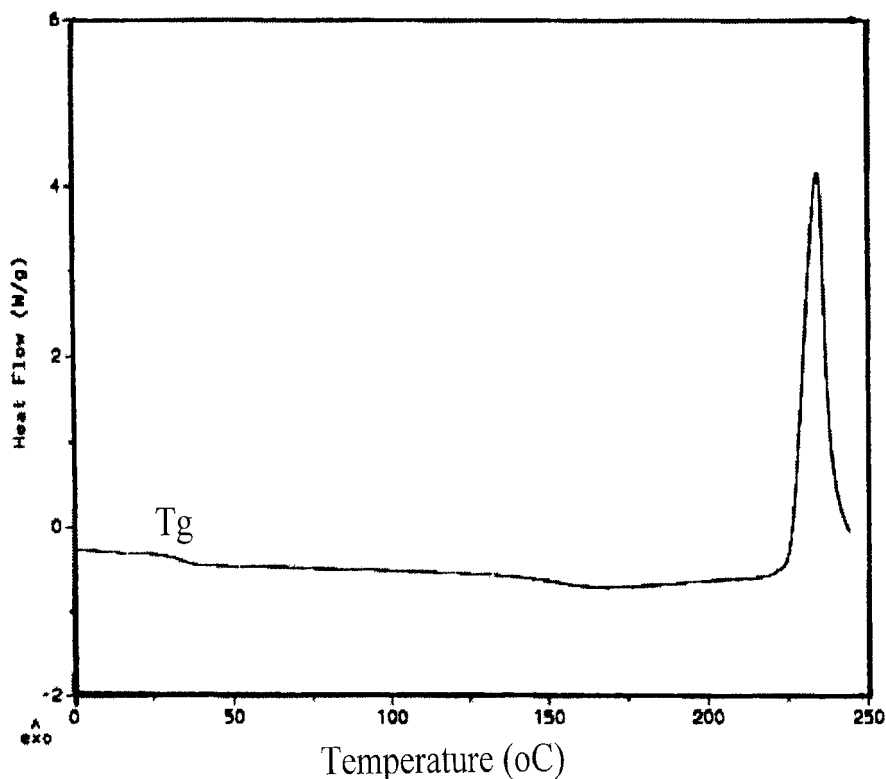| Measurement	System				
	PVAc	SE101	SE105	SE110	SE115
T_g (°C)	25	25	27	29	34

Figure 2 DSC thermogram of the SE115 sample. The heating rate was 10°C/min.

Thermal properties

The T_g of pure PVAc was about 25°C from the DSC thermogram. For the chitosan raw material, the first run in DSC revealed an endothermic peak centered around 140°C, which was due to the absorbed moisture, and hydrogen bonding in the chitosan chains. This peak disappeared in the second run, indicating that this phenomenon was not reversible. The T_g of chitosan could not be observed in the DSC thermogram because of its highly rigid chains. Table III lists the T_g values of the various samples from different reaction systems. A slight increase of T_g corresponding to the PVAc component was observed as the amount of chitosan added was increased. This happened because the chain segmental motion of PVAc was retarded more or less by the rigid chitosan chain. A typical DSC thermogram of the SE115 sample is shown in Figure 2. In addition to the T_g of PVAc at 34°C, another exothermic peak at 240°C was observed. Yet, neither pure PVAc nor chitosan has this peak in the DSC thermogram. Since the ceric ion is a strong oxidizing reagent, it is presumed that, at high temperatures, the residual ceric ion oxidizes the PVAc, chitosan chains, or both. This was proved by the thermal scan of pure PVAc and the chitosan sample physically mixed with CAN individually. An exothermic peak was indeed observed around 200–250°C for both of them. Furthermore, if the ceric ion was removed from the SE115 sample by a dialysis method where the cutoff molecular weight was 8000, the exothermic peak was no longer observed in the thermogram.

Figure 3 shows the TGA curves of pure PVAc, chitosan, and the copolymer sample SE101. PVAc started
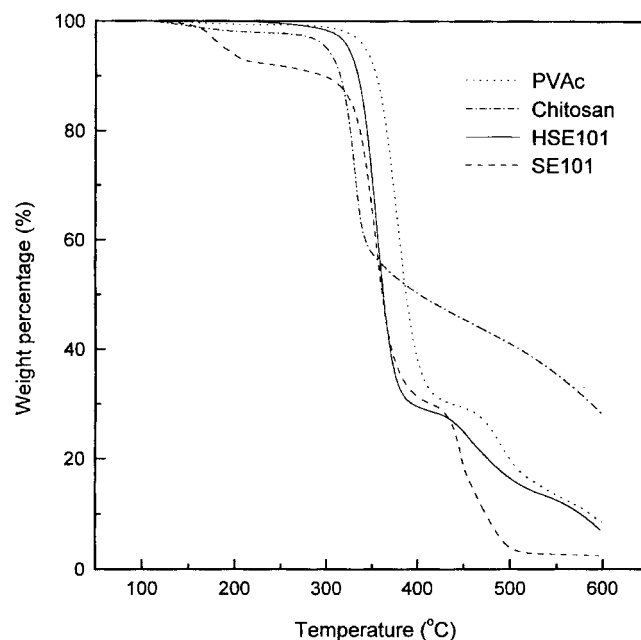

Figure 3 TGA curves of PVAc, chitosan, SE101, and HSE101 at a heating rate of 20°C/min under N_2. HSE101 is sample SE101 after removal of the residual ceric ion.
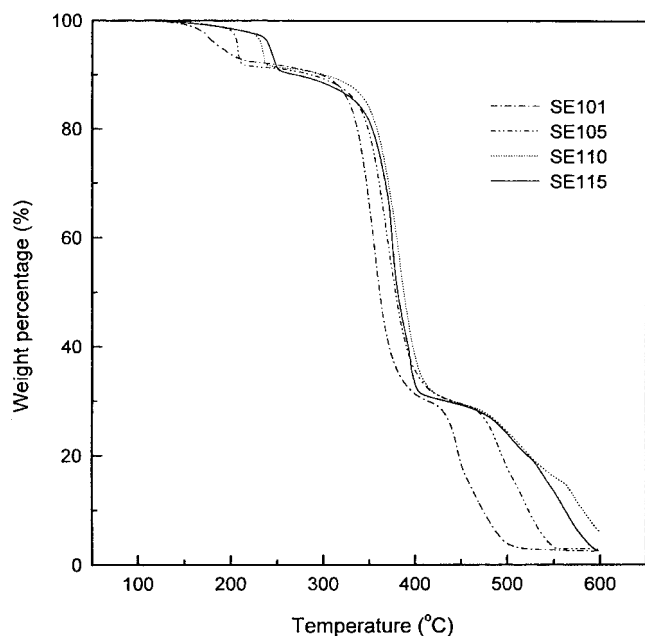
Figure 4 TGA curves of various samples with different amounts of chitosan added at a heating rate of 20°C/min under N_2.

shown in Figure 3. The first-stage degradation was no longer observed and, thus, the hypothesis was confirmed. The observed temperature difference of the oxidation reaction between DSC and TGA was due to the different instrumental methods and heating rates. The remaining degradation behavior of SE101 was similar to that of pure PVAc because the main component of SE101 was PVAc. Yet, the char yield at 600°C was much less than that of pure PVAc because the degradation of SE101 had been facilitated by the ceric ion. Once the ceric ion was removed, the char yield was back to the same amount as that in PVAc. Figure 4 shows the TGA curves of various samples with different amounts of chitosan added. A three-stage degradation behavior was observed for all the samples, and the maximum-rate degradation temperatures of the three stages all increased with the amount of chitosan added up to 5 g in SE110.

to degrade at 350°C and had a two-stage degradation behavior. Flake-shaped chitosan raw material had an onset degradation temperature at 300°C and a high char yield at 600°C. For the sample SE101, three degradation stages were observed where the maximum-rate degradation temperature was 200, 350, and 450°C, respectively. The first-stage degradation about 200°C was not seen both in pure chitosan and PVAc. It was first suspected that some residual acetic acid was not removed completely from the sample, although it had been oven- and vacuum-dried for a long period. Yet, it could hardly explain the weight loss as high as 10% in this degradation stage. The previous DSC results (Fig. 2) revealed an oxidative exothermic peak around 240°C. Therefore, it was assumed that the first-stage degradation was caused by the oxidative degradation of the sample by the ceric ion. Therefore, the ceric ion was selectively removed from the sample by a dialysis method. The sample HSE 101, after removal of the ceric ion from the sample SE101, was then heated to 600°C in the TGA and the degradation curve is also

Tensile mechanical properties and water-absorption capability

Chitosan is a rigid and brittle material, which has difficulties in processing. The graft copolymerization of leathery PVAc onto chitosan chains may improve its ductility. Table IV lists the tensile mechanical properties of various samples. The modulus and ultimate tensile strength increased with the amount of chitosan added, whereas the elongation at break decreased. In other words, the incorporation of PVAc increased the toughness of chitosan. The water-absorption capability of chitosan depends on many factors, including the ionic strength, pH value, and degree of deacetylation. In the literature,[2] it was reported that the pK_a value of chitosan is 6.3, and the water-absorption capability decreases with an increase in the pH value in the range of 2–6. Figure 5 shows the degree of swelling of various samples in deionized water at pH 6. The pure chitosan has a very high degree of swelling up to 14 because of its high affinity to water. Chitosan has many hydrophilic groups: both amino and hydroxyl groups. Pure PVAc almost has no absorption of water. Therefore, the incorporation of PVAc into chitosan decreased the degree of swelling, as shown in Figure 5.

TABLE IV
Initial Modulus (E), Ultimate Tensile Strength (UTS), and Elongation at Break (%) of Various Samples from Different Reaction Systems

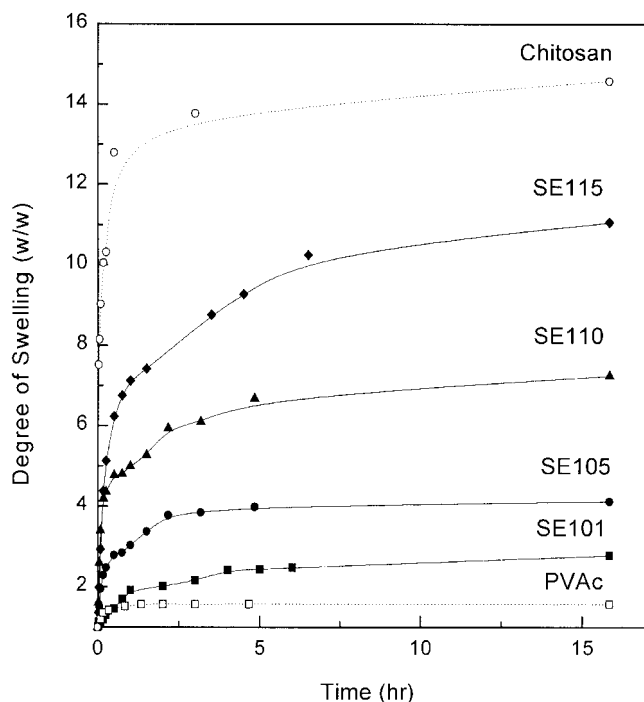| Measurement	Sample			
	SE101	SE105	SE110	SE115
E (MPa)	2.2 ± 0.4^a	17.0 ± 0.9	55.4 ± 2.4	74.7 ± 2.1
UTS (MPa)	0.91 ± 0.06	3.17 ± 0.13	7.00 ± 0.12	13.57 ± 0.80
Elongation (%)	660 ± 19	400 ± 32	170 ± 13	101 ± 12

[a] Standard deviation.

Figure 5 Degree of swelling of PVAc, chitosan, and various copolymer samples.

CONCLUSIONS

CAN was used to initiate the graft copolymerization of VAc onto the chitosan. After 2 h of reaction at 60°C, the monomer conversion was found to be between 70 and 80%. The grafting efficiency increased with the amount of chitosan added, yet the grafting ratio increased only slightly and then decreased. The experimental results indicated that the chitosan molecules not only took part in the graft copolymerization but also served as a surfactant, providing the stability of dispersion particles. If the dispersion solution was oven-dried, a particulate membrane was formed. Both the DSC and TGA results indicated that the samples underwent oxidative degradation by the residual CAN at high temperatures above 200°C. The experimental results also showed that the incorporation of PVAc to the chitosan chains increased the toughness and decreased the water absorption of chitosan.

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