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Preparation And Properties Of PAA-Chitosan/Sio_2 Hybrid Materials

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ABSTRACT

This study used different weight ratios of acrylic acid (AA) and chitosan to prepare copolymer, which were then used to produce a variety of hybrid materials by the sol-gel method. Using FTIR and NMR analyses, it was confirmed that the inorganic phase in the hybrid materials is connected to the organic phase by hydrogen bonding. It was also observed that more lumpy aggregates appeared on the surface of hybrid materials when more AA or tetraethyl orthosilicate (TEOS) was added. Hybrid materials were found to be better than composite in swelling, and the property improved when the ratio of chitosan increased. Swelling increased as TEOS concentration increased, but declined when an excess amount of AA was added. Hybrid materials, prepared from an appropriate ratio of AA and chitosan, possessed excellent anti-bacterial property, which had no correlation with TEOS concentration, but decreased when the AA ratio increased.

KEYWORDS

Chitosan;
Copolymer;
Sol–gel;
Swelling;
Anti-bacterial.

INTRODUCTION

Polymers with high water-absorbency are defined as water insoluble polymers. Their absorbent ability is such that they can swell to become 10- to several 100-fold larger than their original weight[1], and they also possess water retention capacity. Well-known water absorbent materials include cotton, paper, sponge etc. They absorb water into their structural spaces by capillarity, so their water absorbent ability and retention capacity are low. High water-absorbent resin is widely used in many areas where water absorbence and retention are important. Currently, the most common use of resin is in the fields of medical care and personal hygiene, such as liners, pads, diapers, clinical absorbent cotton etc., which accounts for more than 95% of the annual production of high water-absorbent resin[2]. It is noticeable that, in particular, liners and diapers are getting thinner and lighter, and more convenient to use. However, since this material is directly in contact with the human body, it is required to have a higher absorbency rate but not cause skin irritation, so that no inflammation or side-effects may occur.

Chitosan is the second largest type of biological polysaccharide, next to cellulose. It is produced through deacetylation of chitin. It is chemically stable and nontoxic with excellent membrane formation and regeneration properties, and can be dissolved in a low acidity solution. It is also an ideal biodegradable material[4-5]. In addition, the amine groups in chitosan allow it to be ionized to quaternary ammonium under acidic conditions, and become anti-bacterial[6–8].

An important method of improving the performance of high water-absorbent polymers is to have the larger surface area of particles and have porous, cross-linked structures and hydrophilic functional groups[9]. The sol-gel method is a simple way of producing inorganic membranes or inorganic reformed hybrid materials that cross-link the dispersed gel particles or uses metallic salt precursors, through hydrolysis and polymerization, to form porous and cross-linked structures inside the organic phase[10–13]. Moreover, the formed inorganic particles of ~100 nm in size can increase the specific surface area and also improve the mechanical properties of the hybrid materials. Therefore, it is widely applied in various areas, such as optoelectronics, biology and chemistry[14–16].

The study used acrylic acid monomers copolymerized with chitosan at different weight ratios, followed by the addition of different concentrations of tetraethyl orthosilicate (TEOS) to produce various hybrid materials by the sol-gel method. Their related properties are then analysed and discussed.

EXPERIMENTAL

Materials

Acrylic acid (AA; reagent grade; Alfa Aesar), chitosan (90% deacetylation, reagent grade; Toyobo Technologies, Japan;), formic acid, methyl alcohol, glycerin, ammonium persulfate (reagent grade; Wako Pure Chemical Industry, Japan), and tetraethyl orthosilicate (TEOS, reagent grade; Acros).

Methods

1. Preparation of chitosan-PAA/SiO_2 hybrid materials

A 5-g sample of chitosan was dissolved in 100 ml formic acid and stirred for 1 h. The chitosan/formic acid solution was then mixed with AA (at 1:25, 1:50 and 1:100 ratios) and 200 g distilled water, and stirred for 2 h. Then, 0.25 g ammonium persulfate, 0.2 g glycerol and 7.55 g TEOS were stirred in at room temperature for 2 h, and heated to 70°C. The chamber was subsequently filled with nitrogen gas and allowed to react for a further 3 h. The thicker membranes of 1mm were obtained by depositing the hybrid solution in a polystyrene Petri-dish and by letting the solvent to evaporate at room temperature. For comparison, a blank control (without added TEOS) was also prepared. The 0.5-g thin membrane, thus formed, was placed into a beaker, which was filled with sufficient methanol to cover the sample. It was left for 24 h and resoaked in fresh methanol for a further 24 h to complete refinement. Finally the sample was stored in plastic sachets ready for testing.

2. Analysis and testing

FT-IR/ATR spectra of the samples were recorded with a Bio-Rad Digilab FTS-200 spectrometer using an MCT detector. A diamond crystal was used as internal reflectance element. Single beam spectra were the result of 64 scans. The spectral resolution was 4 cm^{-1}. The chemical shifts of ^{13}C of the samples were measured with a solid-state nuclear magnetic resonance (NMR) spectrometer. The samples were analyzed using a Bruker Avance 400 ^{13}C-NMR spectrometer at 50 MHz, and the spectra were observed under cross-polarization, magic angle sample spinning and power decoupling conditions with a 90° pulse and 4 s cycle time. The surface morphologies of the films were observed with a JEOL Model JSM 6400 scanning electron microscopic. A gold coating was deposited on the samples to avoid charging the surface.

The swelling ratio was measured by immersing a preweighed dry sample in a appropriate swelling medium for 24 hours. Excess swelling medium was blotted out with filter paper before weighting. The weight-swelling ratio was calculated by using the following equation[17]:

Swelling ratio (g/g) = (W_s/W_d)

The W_s and W_d denote the weight of the swollen and dry sample, respectively. The swelling mediums are as follows: (a) distilled water (b) 50:50 (v/v) water/methanol (c) 10^{-2}M NaCl solution.

Anti-bacterial property of the same sample was tested according to method JIS1902-1998 of the Japanese Association for the Functional Evaluation of Textiles (JAFET), and the following equations were used to calculate bacterial growth, bacteriostatic and bactericidal value:

Bacterial growth (F) = log (M_b/M_a) (1)

F value >1.5 indicates significance in the experiment.

Bacteriostatic value (S) = log (M_b/M_c) (2)

S value >2.2 suggests the sample has a bacteriostatic effect.

Bactericidal value (L) = log (M_a/M_c) (3)

L value >0 suggests the sample has a bactericidal effect.

M_a= bacterial number in the sample of copolymer immediately after rinsing. M_b= bacterial number in the sample of copolymer after culturing for 18–24 h. M_c= bacterial number in the sample of composite hybrid material after culturing for 18-24h.

RESULT AND DISCUSSION

FTIR

From figure 1a, it indicates the functional groups >C=O and C-OH are at 1711 and 1163 cm^{-1}, respectively. As shown in figure1b-d, there are absorbance peaks of the functional groups >C=O from 1713 cm^{-1} shift to 1705 cm^{-1} and 1698 cm^{-1}, respectively, indicating the presence of PAA and SiO_2 (1c and 1d). Meantime, this indicates that in hybrid materials, there would be hydrogen bonds between the >C=O group in PAA or chitosan and the SiO_2 in the inorganic phase, this is similar to with past research paper[18-19]. In figure1 e, there are absorbance peaks of the functional groups CONH, >C=O and -CN appearing at 1631 and 1547 cm^{-1}, respectively; this is because chitosan is 90% deacetylated but the sample still contains some chitin. In addition, at 1066 and 1030 cm^{-1}, there are absorbance peaks of the C-OH functional group, and at 1150 cm^{-1}, there is an absorbance peak of the C-O-C functional group. In figure 1b–d, the C-O-C functional groups are also shown at 1104, 1097 and 1099 cm^{-1}, suggesting the presence of chitosan.

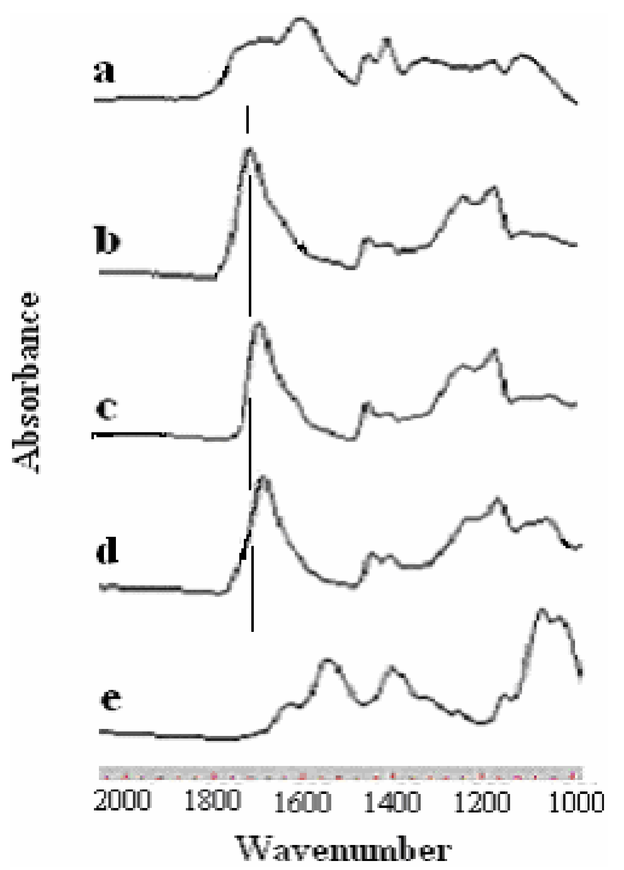

Figure 1: FT-IR spectra of hybrid materials: (a): PAA; AA/Chitosan ratio: (b): 100/1 (TEOS= 0%); (c): 100/1 (9%); (d): 25/1 (9%); (e): Chitosan

As shown in figure 2a-c, the absorbance peaks at 1054, 1045 and 1055 cm^{-1} may possibly belong to C-O-C and Si-O-Si, but as TEOS was not added in figure 2a, we can be certain that the peak at 1054 cm^{-1} is that of C-O-C. From the spectra in figure 2, we can see clearly that, around 1054 cm^{-1}, the peak becomes sharper following the increase in TEOS

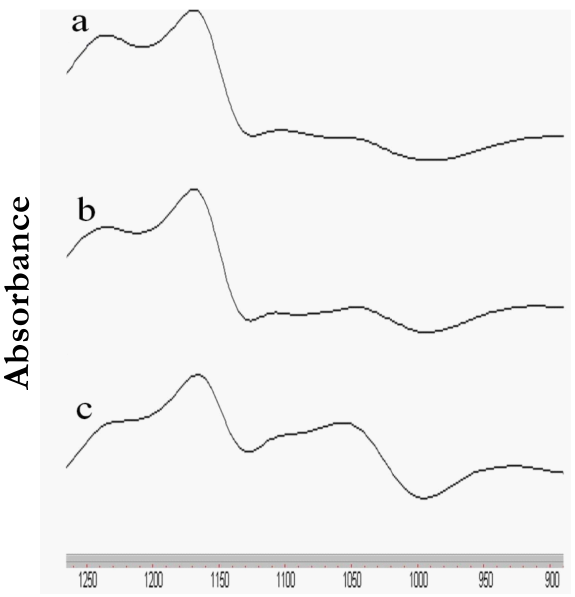

Figure 2: FT-IR spectra of copolymer and hybrid materials AA/Chitosan ratio: (a):100/1 (TEOS=0%) (b): 100/1 (9%), (c): 25/1 (9%)

concentration.

NMR

^{13}C-NMR analysis can be used to determine the direction of ^{13}C chemical shift in a high polymer structures, such as three-dimensional regularity, the arrangement of composite monomers and structural defects etc[20]. figure 3 shows the ^{13}C-NMR spectra of hybrid materials, which were prepared from chitosan, different ratios of AA/chitosan, as well as different weights of TEOS. figure 3a shows that, in the spectrum of chitosan, there is a C=O functional group at 174.1 ppm. This is due to the 85% acetylation of chitosan, leaving a small residual amount of chitin. figure 3b and c are spectra of hybrid materials made from different ratios of AA/Chitosan. At 179.7 and 181.1 ppm, C=O functional groups are also observed due to the addition of PAA, the value also increase. When TEOS was added, the C=O absorbance of the PAA-chitosan/SiO_2 hybrid materials shifted towards a higher wave peak. In addition, the absorbance peak of C_6-OH can also be found at 102.1 ppm in original chitosan, but after the addition of AA or TEOS, the absorbance peak shifts towards a higher wave peak, in particular, when TEOS is added. This is due to the production of $Si(OH)_4$ during TEOS hydrolysis, some parts of which are not polymerized as the reaction proceeds. This results in the -OH base binding to PAA or the -OH of chitosan through hydrogen bonding. Therefore, the absorbance peak of NMR has a significant shift towards a higher wave peak.

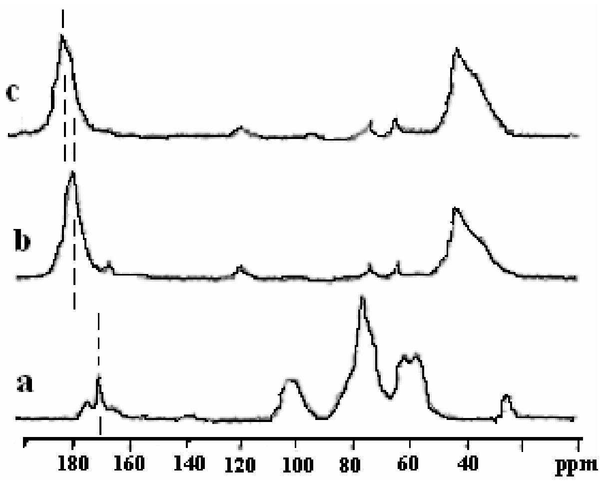

Figure 3: ^{13}C-NMR spectra copolymer and hybrid materials (a): Chitosan, (b,c): AA/Chitosan (25/1)/SiO_2 (TEOS=0, 9%)

Based on the results of FTIR and C-NMR, we can conclude that, there are hydrogen bond between PAA/Chitosan composite and SiO_2 formed after TEOS hydrolysis and polymerization[21-25].

SEM

Figure 4 is a scanning electron micrograph of hybrid materials, showing that the surface of chitosan is smooth. The roughness on the surface of the polymer, which was copolymerized with AA, are less numerous and the particles gradually become more lumpy. This is because the presence of PAA causes an expansion with water molecules. From figure 4, we can also ascertain that the surface of hybrid materials, made from a small amount of TEOS, have less SiO_2 particles with some cavities. However, addition of more TEOS can lead to more lumpy particles, as SiO_2 particles aggregate together.

Swelling

TABLE 1 shows the swelling of hybrid material in different solvents. From TABLE 1, it is known, regardless of solvent, that the swelling of hybrid

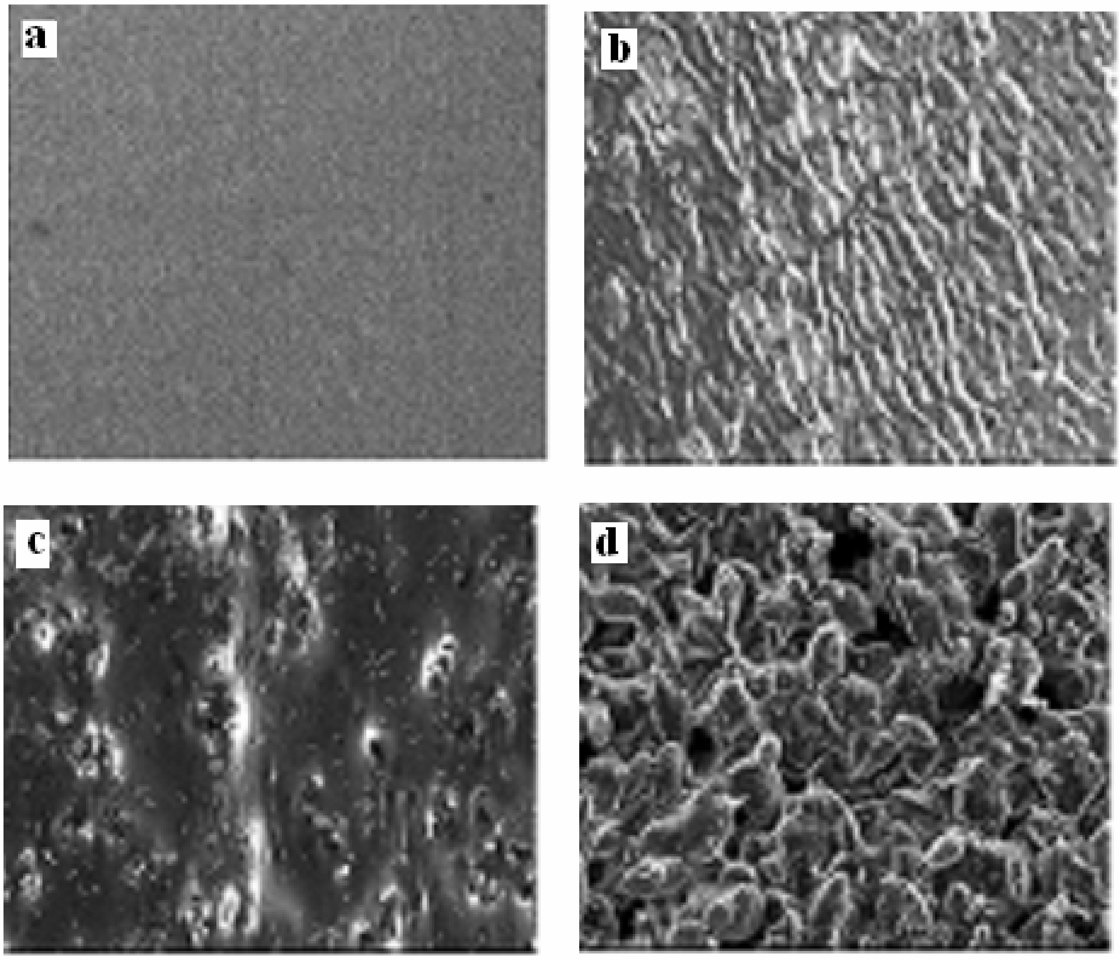

Figure 4: SEM of copolymers and hybrid materials. AA/Chitosan ratio: (25/1) (b,c,d), (a): Chitosan TEOS conc.: (b): (0%), (c): (3%), (d): (9%)

TABLE 1: Swelling property of hybrid materials

AA/Chitosan weight ratio	TEOS Conc. (%)	Swelling ratio		
		Solvents		
		H_2O	NaCl	H_2O/ Methanol
25 : 1	0	59.0	50.1	34.6
	3	75.8	56.4	45.0
	6	89.3	70.4	52.4
	9	91.6	78.8	53.6
50 : 1	0	137.0	115.0	71.6
	3	153.1	141.0	104.6
	6	198.0	181.0	165.6
	9	273.7	248.2	235.4
100 : 1	0	64.6	38.3	41.2
	3	117.5	95.4	81.0
	6	136.2	101.0	97.3
	9	162.9	118.3	105.2

materials increases as TEOS concentration rises, because, in the reaction process, TEOS forms a reticular structure in the organic phase. According to the Flory theory, when there is reticular structure inside molecules, more internal cavities are formed and, with the distribution of many hydrophilic functional groups, water molecules are firmly adsorbed inside the reticular structure. The reticular structure is beneficial to the strength of a material itself. When a large amount of solvent molecules diffuse into the material, it will not collapse and dissolve due to excessive expansion. Thus, the swelling of hybrid materials increases with an increase in TEOS concentration. With respect to the weight ratio of chitosan and AA, from TABLE 1, we can ascertain that the swelling of materials also increases following a rise in PAA content. When the weight ratio of AA to chitosan is 100:1, the swelling decreases of the composite, suggesting that the addition of excessive AA monomer. This is because the PAA and silica produce the chance increment of the hydrogen bond, thereby make the hybrid materials the occurrence shrinkage with the result that. It can also be determined from the different solvents that water gives the best swelling, whereas water-methanol gives the poorest swelling result. Because the permeate power of the methanol was the most strong, the easy breakage internal bonding of the hybrid materials.

Anti-bacterial properties

Anti-bacterial properties of various polymers and hybrid materials are shown in TABLE 2. It is known that, apart from the PAA polymer and the copolymer or hybrid materials made from AA/Chitosan in a weight ratio of 100:1, the rest of the copolymer or hybrid materials all possess bacteriostatic and bactericidal effects. However, the PAA/Chitosan copolymer or hybrid materials are significantly poorer than chitosan in terms of bacteriostatic or bactericidal activity, because some quaternary ammonium ions in chitosan molecules can bind ionically to the carboxyl groups of PAA, thereby, reducing these effects. These effects are not associated with TEOS concentration, but are significantly affected by the weight ration of chitosan. From TABLE 2, it can be seen that, when the weight ration of chitosan is relatively small, copolymer or hybrid materials have no bacteriostatic and bactericidal effect. This is possibly because too small amounts of chitosan are dissociated in the copolymer or hybrid materials, with little free quaternary ammonium ions.

TABLE 2: Antibacterial properties of copolymers and hybrid materials

AA/Chitosan weight ratio	TEOS conc. (%)	Antimicrobial value	Antiseptic value
PAA	0	0	<0
Chitosan	0	3.87	2.47
25 : 1	0	3.11	1.50
	3	3.20	1.54
	9	3.03	1.46
50 : 1	0	2.51	1.02
	3	2.42	0.98
	9	2.47	0.97
100 : 1	0	0.71	<0
	3	0.66	<0
	9	0.46	<0

CONCLUSIONS

This study examined the preparation of copolymer from AA/Chitosan at different weight ratios and the production of a variety of hybrid materials using the sol-gel method. The physical properties of the various copolymer and hybrid materials are also discussed. From the experimental results, the following conclusions can be drawn: (1) based on FTIR and NMR analyses, SiO_2 in hybrid materials can strongly bind to the organic phase via hydrogen bonding, (2) addition of more AA or TEOS leads to the production of hybrid materials with lumpy aggregates on the surface, (3) the swelling of hybrid materials are both better than those of copolymer, and it increases as TEOS concentration increases.

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