

# Study of Blend Films from Chitosan and Hydroxypropyl Guar Gum

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**ABSTRACT:** In this study blend films of chitosan (CH) and hydroxypropyl guar gum (HGG) were prepared using a conventional solvent-casting technique and were dried at room temperature. Their miscibility and other properties were studied by Fourier transform infrared spectroscopy, wide-angle X-ray diffraction, scanning electron microscopy, differential thermal analysis, ultraviolet analysis, and tensile strength tests. The physical and thermal properties of the films depended on the blending ratio. The maximum tensile strength and breaking elongation values achieved were 58.94 MPa and 17.25%, respectively, with a 60% content of HGG. Thermal stability also was improved, and the blend

film containing 60% HGG had greater thermal stability than did the other blend and pure CH films. In addition, the best optical transparency was observed from 500 to 800 nm in the blend film containing 60% HGG. The results indicate that intermolecular interactions that resulted from hydrogen bonding between CH and HGG occurred in the blend films. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1991–1995, 2003

**Key words:** chitosan; hydroxypropyl guar gum; blend films; hydrogen bond; miscibility; physical properties; thermal properties

## INTRODUCTION

Today's widespread use of synthetic polymers films has resulted in serious environmental pollution. Awareness of this ecological problem has led to the development of new biodegradable materials that can be valid alternatives in specific situations when recycling or incineration is difficult or not economical.<sup>1</sup> Consequently, as suitable materials for environmental conservation, natural polymers and biodegradable polymers have received attention, particularly through blending, which is an effective way to create new materials. Blending can usually be implemented more rapidly and economically than can other methods.<sup>2</sup>

Guar gum (GG) is a branched polygalactomannan isolated from the seed of two leguminous herbs, *Cyamopsis tetragonolobus* and *Cyamopsis psoralioides*.<sup>3</sup> It consists of a long linear  $\beta$ -(1-4)-mannose backbone (1000–1500 units) to which  $\alpha$ -(1-6)-galactopyranoside subunits are attached as single-unit side chains.<sup>4</sup> Among the vast class of chemically modified products, a major role is played by hydroxypropyl guar gum (HGG), a derivative of guar gum. HGG is currently used as a water blocking agent in the formulation of cartridge explosives, as a processing aid in the mining and mineral industry for the recovery and

separation of some metals from their ores, and as a slime depressant in froth flotation processes, in the preparation of workover and completion fluids for oil recovery operations, and in the formulation of pastes for rotary screen textile printing and water-based paints.<sup>5</sup> Furthermore, HGG has better water solubility and forms film more easily than does guar gum.

Chitosan (CH) is the deacetylated product of chitin and has distinct functional groups that can be easily modified to have good body compatibility and high biological activity.<sup>6</sup> As a kind of environmentally friendly material, CH has been widely used as a metal ion adsorption agent for polluted water, food additives, and biomedical materials.<sup>7</sup> However, its insolubility in water and brittleness when in a dry state have limited its applicability to biological and medical areas. There has been research into blending it into such blends as chitosan–konjac glucomannan,<sup>8</sup> chitosan–cellulose,<sup>9</sup> chitosan–silk fibroin,<sup>10</sup> and carboxymethylated chitosan–alginate.<sup>11</sup> Because of strong hydrogen bonds between the two components, the physical properties of the blends have been improved significantly. This article covers research on an approach to modifying chitosan by blending it with hydroxypropyl guar gum in order to improve its mechanical and thermal properties of chitosan in the dry state.

In this work blend films of chitosan and hydroxypropyl guar gum were prepared in different ratios using the casting solution method. The physical properties, thermal properties, and miscibility of the blend films were studied by tensile measurements, differential thermal analysis (DTA), Fourier transform

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infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), and ultraviolet spectroscopy (UV). The properties of the blend films were studied in detail in relation to the blending ratios. The results reported in this article may contribute to finding further applications of this blended material in biomedical and pharmaceutical fields.

## EXPERIMENTAL

### Materials

Chitosan was prepared from chitin (purchased from Nanxing Chitin Company, Ltd., Suixi, Guangdong, China) using the method of Mima et al.<sup>12</sup> Its degree of deacetylation was measured to be about 90.2% using the method of Nakajima,<sup>13</sup> and the viscosity average molecular weight was  $5.0 \times 10^5$ , according to the method of Wang et al.<sup>14</sup> Hydroxypropyl guar gum was provided by Professor Tian Bingshou's laboratory at Wuhan University. And the viscosity average molecular weight of HGG ( $M_{\eta}$ ) was  $3.69 \times 10^5$ , measured using the method of Geoffrey et al.<sup>15</sup>

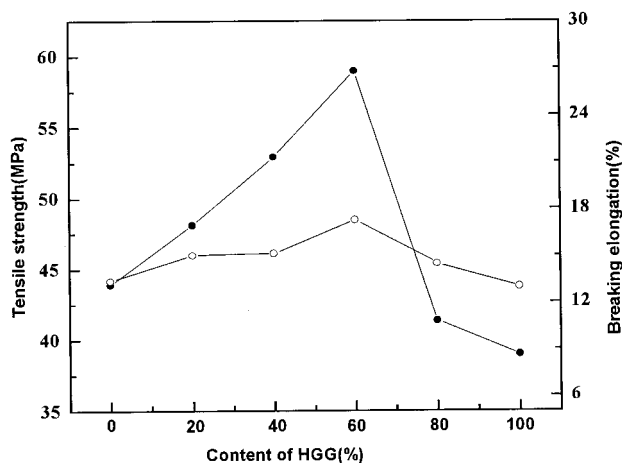
### Preparation of the films

The desired quantities of chitosan were dissolved in 2 wt % acetic acid water solution to obtain a concentration of 3 wt % solution. Hydroxypropyl guar gum was dissolved in deionized water to obtain a 3 wt % solution. Different quantities of hydroxypropyl guar gum solution were added to a desired amount of chitosan solution respectively to obtain a series of mixing solutions with different weight ratios (0:100, 20:80, 40:60, 60:40, 80:20, and 100:0 of HGG/CH). The pure and mixed solutions of HGG and CH were cast on a Teflon gasket and the water allowed to evaporate at room temperature (30°C). All films were dislodged carefully and then subjected to further drying under vacuum for 2 days. Dried films with a thickness of  $30 \pm 5 \mu\text{m}$  were obtained. The films of the different ratios listed above were coded as CH, CG-1, CG-2, CG-3, CG-4, and HGG, respectively.

### Measurements

Infrared spectra of the pure and blend films were measured with a Nicolet 170SX FTIR (USA) spectrometer used with KBr pellets. Wide-angle X-ray diffraction of the films was performed with a Rigaku Dmax-II X-ray diffractometer using a Cu  $K\alpha$  target at 40 kV and 50 MA. The diffraction angle ranged from  $5^\circ$  to  $35^\circ$ . The crystallinities of the films were calculated by

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



**Figure 1** Mechanical properties of the films as a function of HGG content (●: tensile strength; ○: breaking elongation).

where  $F_c$  and  $F_a$  are the areas of the crystalline and noncrystalline regions, respectively. The tensile strength and breaking elongation of the films were measured on an electron tensile tester AG-A (Shimadzu Co., Japan) with a tensile rate of 5 mm/min, at a gauge length of 50 mm and width of 10 mm. The temperature and relative humidity were 28°C and 60%, respectively. Differential thermal analysis (DTA) of powered samples of the films was performed in a nitrogen atmosphere by a Shimadzu DT-30 thermal analyzer, and the temperature was raised from 0°C to 500°C at a heating rate of 15°C/min. The morphology of film surfaces was examined by a Hitachi-570 scanning electron microscopy (Japan). The films were frozen under liquid nitrogen to fracture and were coated with gold under  $0.1 \tau$  vacuum conditions before the SEM experiment. The percentage of light transmittance ( $T\%$ ) of the films in the wavelength range of 200–800 nm was measured by a Shimadzu (Japan) UV-160A spectroscope.

### Characterization of films

#### Mechanical properties

Figure 1 shows the tensile strength and breaking elongation dependence on the HGG content. The tensile strength increased with increasing HGG content and achieved a maximum value of 58.94 MPa at 60% HGG content. Tensile strength was gradually reduced when HGG content increased further. The change in breaking elongation had a tendency similar to that of tensile strength, with 17.25% the maximum value achieved. It can be concluded that the blend of CH with HGG considerably enhanced the mechanical properties for the blend films in the dry state when the HGG content of the blend films was less than 60%. Enhancement of tensile strength and breaking elongation may have

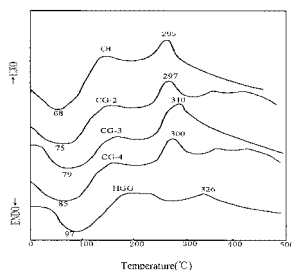


Figure 2 DTA curves of the pure and blend films.

resulted from the hydrogen bonding between CH and HGG.

### Thermal stability of the films

As Figure 2 shows, the thermal behavior of the pure and blend films was investigated by DTA. The films all showed endothermic peaks in the range of 60°C–100°C, corresponding to the loss of water absorbed in the films. The DTA curve of CH shows an exothermic peak at about 295°C, which can be attributed to the greatest thermal degradation of CH. An exothermic peak at 326°C in the pure HGG is a result of the greatest thermal decomposition of the main chain. With the addition of HGG, the greatest thermal degradation of the blend films shifted to a higher temperature: CG-3 (310°C) > CG-4 (300°C) > CG-2 (297°C). The significant changes in the DTA curves of the blend films suggest that CG-3 has a higher thermal stability than pure CH and other blend films. The main reason for this is a strong interaction resulting from hydrogen bonds between the  $\text{—NH}_2$ ,  $\text{—NHCOCH}_3$ , and  $\text{—OH}$  groups in CH and the  $\text{—OH}$  groups in HGG.

### Miscibility

With FTIR spectra, if two polymers are compatible, there should be considerable differences between the IR spectrum of the blend and the coaddition of the spectra of two components. The differences would be derived from chemical interactions, resulting in band shifts, intensity changes, and broadening. Figure 3 shows the Fourier transform infrared (FTIR) spectra of the films in the wavelength range of 4000–400  $\text{cm}^{-1}$  with different ratios of composition. For the pure CH, strong absorption bands centered at 3439  $\text{cm}^{-1}$  were concerned with the stretching vibration of N—H and O—H.<sup>16</sup> And the peaks at 2918, 1657, and 1607  $\text{cm}^{-1}$  could be assigned to C—H stretching, C=O stretching, and N—H bending, respectively. It can be seen that the broad absorption band<sup>17</sup> in HGG at 3429  $\text{cm}^{-1}$  is a result of the stretching frequency of the O—H groups. The bands around 1162 and 2926  $\text{cm}^{-1}$  were assigned to C—O stretching and C—H stretching, respectively. Two strong bands around 1100 and 1024

$\text{cm}^{-1}$  are a result of C—O—C stretching. After introducing the HGG, the bands of CH, centered at 3439  $\text{cm}^{-1}$  in the pure CH, were broadened. Furthermore, the stretching of C=O and N—H bonds at 1657 and 1607  $\text{cm}^{-1}$ , respectively, coupled with the stretching bands around 1642  $\text{cm}^{-1}$  in the pure HGG, a result of the intramolecular hydrogen bonds in HGG and a shift to a lower wave number around 1630  $\text{cm}^{-1}$ , suggests that the original intramolecular hydrogen bonds in pure HGG were destroyed and that new hydrogen bonds between CH and HGG occurred in the blend films.

Surface exposure to air of the pure and blend films was examined by SEM, and the morphology is shown in Figure 4. The surface morphology of pure CH film looks comparatively rough. On the contrary, HGG shows a smooth surface morphology. Compared with other blend films, the CG-3 blend film shows a smooth and homogeneous surface morphology, suggesting that high miscibility occurred at the composite ratio of 60:40 HGG:CH (by weight). And with increasing HGG content, the morphology of the blend film surfaces changed from rough to smooth, which may be related to improvement in the mechanical properties of the blend films. The mechanical properties of CG-3 were the best of all the blend films and may have been a result of its having better thermal stability, a result in accordance with the analysis results of the DTA curves.

Figure 5 shows X-ray diffraction of the pure and blend films. The pure CH film showed three charac-

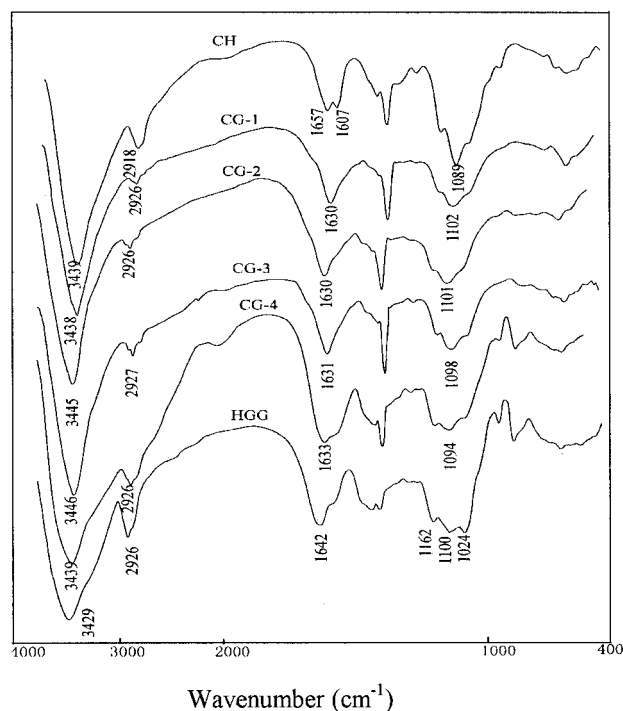
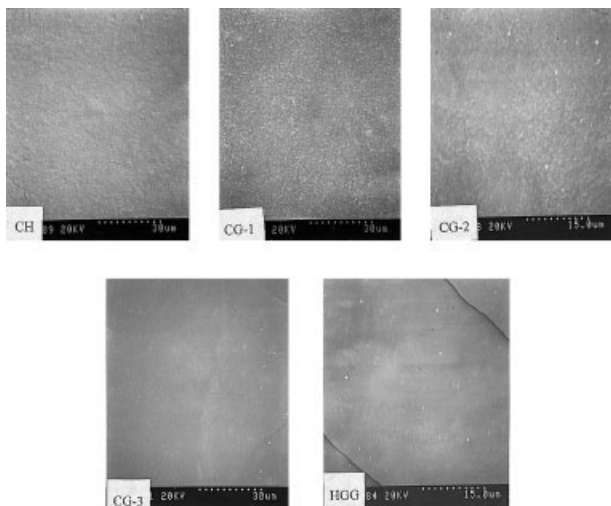
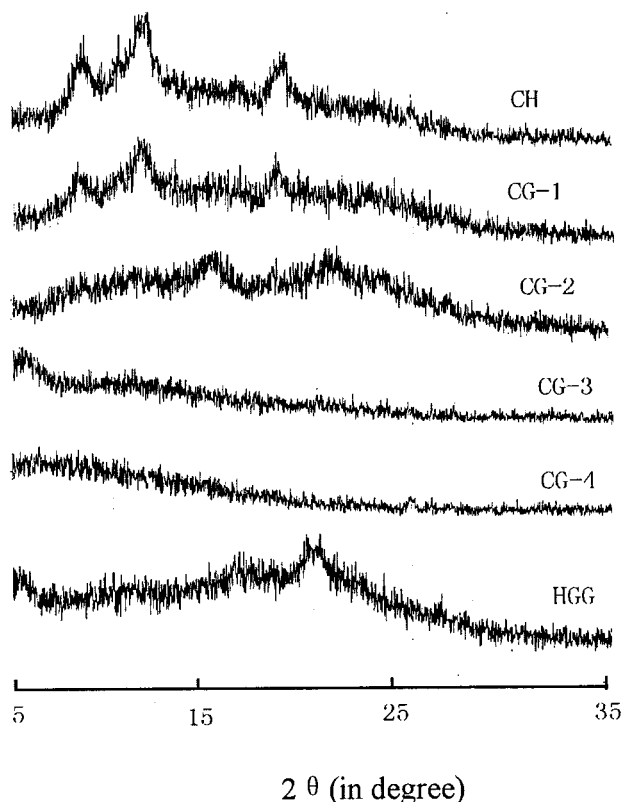


Figure 3 FTIR spectra of the pure and blend films.

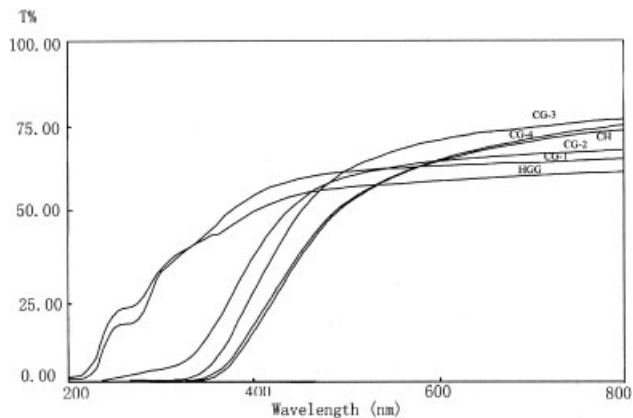


**Figure 4** SEM photographs of the pure and blend films.

teristic crystalline peaks, at  $2\theta = 8.5^\circ$ ,  $11.5^\circ$ , and  $18.5^\circ$ . A weak and broad characteristic peak at  $2\theta = 20^\circ$  appeared in pure HGG. However, with increasing HGG content, the characteristic peaks of pure CH film gradually disappeared, and the blend films of CG-3 and CG-4 showed characteristic amorphous patterns. The results indicate that the addition of HGG destroyed the original crystalline domains of CH. Meanwhile, intermolecular hydrogen-bonding interaction



**Figure 5** X-ray diffraction patterns of the pure and blend films.



**Figure 6** Percentage of light transmittance ( $T$ ) dependence of the wave number for the films.

occurred between CH and HGG, and the intra- and intermolecular hydrogen-bonding effects of the pure components must be present in the blend films.

The optical transmittance ( $T$ ) dependence of the wavelength ( $\lambda$ ) for the films are shown in Figure 6. The transmittance of films is generally an auxiliary criterion for judging the miscibility of blend macromolecular materials.<sup>18</sup> If miscibility of macromolecular materials is poor, there is low transparency, which results from refracted or reflected light at the interface. It can be seen from Figure 2 that the CG-3 film had the best optical transmittance from 500 to 800 nm, suggesting the best miscibility between CH and HGG. This is consistent with the above results. In addition, the transmittance in CG-1, CG-2, and CG-4 gradually increased with an increase in HGG in the range between 500 and 800 nm.

## CONCLUSIONS

A series of blend films from chitosan and hydroxypropyl guar gum were prepared by using the conventional solvent-casting method and were dried at room temperature. The compatibility between CH and HGG was elucidated by FTIR, WAXD, and SEM. FTIR spectra showed hydrogen-bonding interactions between the  $-\text{NH}_2$ ,  $-\text{NHCOCH}_3$ , and  $-\text{OH}$  groups in CH and the  $-\text{OH}$  groups in HGG. The results of WAXD showed characteristic amorphous patterns when the HGG content was more than 60%. Moreover, as the SEM results showed, the morphology of the blend films changed from CH-like to HGG-like over the entire composition range, which is consistent with the WAXD results. It is noteworthy that the tensile strength and breaking elongation of the films increased from 39 to 58.94 MPa and from 13% to 17.25%, respectively, as HGG content increased from 0% to 60% and that of the blend films, CG-3 achieved the greatest thermal stability, the best mechanical properties, and the best optical transmittance from 500 to 800

nm. All the testing results suggest that the best miscibility was attained by the blend film containing 60% HGG. Thus, the blending of CH with 60% HGG provided a novel application for CH as a film biomaterial having good physical properties.

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