Synthesis and Characterization of Collagen Hydrolysate/Poly (vinyl alcohol)/Silica Biodegradable Ternary Composite film[#]

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Abstract: An environmental friendly ternary composite film composed of collagen hydrolysate (CH) from chrome-tanned shavings, poly (vinyl alcohol) (PVA) and silica was prepared. The swelling behaviors, mechanical properties, thermal stabilities and dissolution behaviors of the composites were investigated. It was found that with increasing the collagen hydrolysate content, the swelling degree of composites increases. With the introduction of silica through sol-gel method, the swelling results obtained strongly indicate that the resultant CH/PVA/silica composite film have a remarkable increase in swelling resistance. Dissolution behaviors and nitrogen content determination showed that the dissolution of CH in buffer may be hindered by silica, whereas thermal stability was increased after the addition of silica. Additional crosslinking points in the composites may be formed by the introduction of silica.

Key words: collagen hydrolysate; poly (vinyl alcohol); silica; swelling properties; mechanical properties

1 Introduction

As a result of environmental problems caused by the massive production and use of leather for shoes, packaging, clothes and decorations, the last decades has witnessed a notable growth in developing composite materials based on leather deposits. As an important protein resource, collagen hydrolysate can be obtained by the hydrolysis of solid tannery wastes such as chrome-tanned shavings. In order to improve the physical properties of CH, the addition of synthesized polymer has been frequently used in several studies on biodegradable materials by casting or extrusion [1]. Poly (vinyl alcohol), a water-soluble polymer, has been used to synthesize composite materials with CH component, and the tensile strength and elongation at break of tapes were not negatively influenced by addition of CH into PVA/CH blends [2].

The present paper discusses the preparation and properties of PVA/CH/silica ternary hybrid materials. The addition of silica is to improve the physical properties, such as thermal and swelling properties of resultant composite film.

2 Experimental

2.1 Materials

Polyvinyl alcohol (PVA) with hydrolysis degree of 99%, average degree of polymerization 1750±50, and residual acetate groups content of 1.0% was manufactured by Tianjin Kermel Chemical Reagent Co., Ltd.. Collagen hydrolysate (powder form) was provided by Xinxiang Hongxing chemical company by hydrolysis of chrome-tanned shavings.

2.2 Preparation of PVA/CH/Silica composite films

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The ternary composite films were produced from a blend of PVA (5%) and CH solutions using casting technique. The mixed solution was homogenized for 30 min at 60 °C with a thermostatic bath. Then, nano-silica was added to the mixed solutions which alcoholysised by TEOS with HCl, and stirred for 50 min with an electromagnetic stirrer. Glutaraldehyde (cross-linking reagent) and glycerol was added and the mixed solution was held at 50 °C for 30 min. The solution was cast on 15×15 cm^2 glass plates and subjected to drying at room temperature for 3 days. The thicknesses of membranes were maintained by controlling the dry matter / area of plate ratio.

2.3 Characterization

Before any characterization was carried out, all the films were air-conditioned in desiccators with 58.9% concentration sulphuric acid (20% relative humidity) at room temperature for a week. All tests were performed in an air-conditioned room (T = 22 °C and relative humidity between 45% and 65%).

2.3.1 Equilibrium swelling experiments

The progress of the swelling process was monitored gravimetrically as described by other researchers [3]. A pre-weighed piece of sample was immersed in an aqueous reservoir and allowed to swell for a definite time period. The swollen piece was taken out at predetermined time intervals, pressed between the two filter papers to remove excess water and the weight (W_t) was recorded in a analytical balance until the weight changed slightly. The following equation was used to express the equilibrium degree of swelling (Q_e):

$$Q_e = \frac{W_e - W_0}{W_0} \times 100\,\%$$

Where W_e is the weighed swollen sample at equilibrium time, W_0 is pre-weighed sample. The degree of swelling was expressed in terms of the swelling ratio (SR) as given below:

$$SR = \frac{W_t - W_0}{W_0} \times 100\%$$

2.3.2 Determination of nitrogen content

Nitrogen content of composite film was measured by Kjedehl titrimetric method. Sample digestion was carried out according to the reference procedure [4]. Briefly, the powder of 0.1 g of sample was digested with 10 ml of concentrated H_2SO_4, in a block digester at 420 °C for at least 3 hours or until the clear solution was obtained. 50 ml water was added with and digestion tube was assembled to the distillation unit, where a 50 ml of 35% (w/v) NaOH was added and steam distillation was performed with the distilled inserted in a 25ml of 4% (w/v) boric acid solution. Continue the distillation until 100ml of the distillated was obtained. A few drops of an indicator solution were added to the distillate before titrating with a standardized 0.1M HCl solution for ammonium content.

2.3.3 Thermal properties

Thermal properties (thermo-gravimetric and derivative thermo-gravimetric analysis, TG and DTG) of the composite film were determined using a DSC TA 2010 differential scanning calorimeter controlled by a TA 5000 module according to Sobral et al. [5]

2.3.4 FTIR analysis

FTIR spectra of all samples were scanned using a Nicolet (USA) Nexus 470 FTIR spectrometer. The wave number range from 400 cm^{-1} to 4500 cm^{-1}, scanned for 32 times from spectrum integration. The scanning resolution was 4 cm^{-1}.

3 Results and discussion

3.1 Swelling behaviors of CH/PVA/silica film

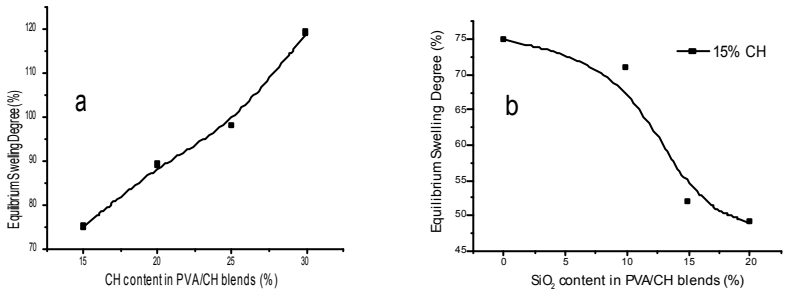

Fig. 1 Swelling degree in equilibrium of the PVA/CH films (a) and PVA/CH/silica films (b) in buffer solution

Fig. 1 shows the results of equilibrium swelling degree for PVA/CH and PVA/CH/silica films. For PVA/CH materials (Fig. 1a), with increasing the CH content, the equilibrium degree of swelling in aqueous solution increased. Generally, in cross-linked structure, the hydrophilic bonds and cross-linking points may prevent the water molecules to be absorbed by polymer chains. With increasing the CH content, the cross-linking density (the number of cross-linking points) in cross-linked structure may be increased, and more hydrophilic bonds will be sealed up. The equilibrium swelling degree of the films was reduced as a result.

It also can be seen that, the equilibrium swelling degree of all PVA/CH/silica blends (Fig. 1b) are lower than that of PVA/CH blends, and the equilibrium swelling degree of PVA/CH/silica materials decreases with increasing of silica content. These phenomena suggested that the presence of silica affects the equilibrium swelling degree of materials, and the difference compared to PVA/CH materials meant the difference of the molecular structure between PVA/CH and PVA/CH/silica materials and much fewer hydrophilic bonds in PVA/CH/silica structure than that in PVA/CH materials.

3.2 Dissolution properties of CH/PVA/silica film

Fig 2a shows the swelling ratio results of PVA/CH materials for different CH concentration soaked in buffer solution at different hours. The phenomenon suggested that some part of films dissolute in buffer solution after the equilibrium swelling degree. To understand which part of molecules dissolute in buffer solution for PVA/CH materials, the nitrogen content in films were measured, and the data were shown in Fig. 2b. It can be seen that, the nitrogen content of all the samples decreased dramatically, which indicates that CH are of low molecular weight and tends to be dissolved in buffer solution.

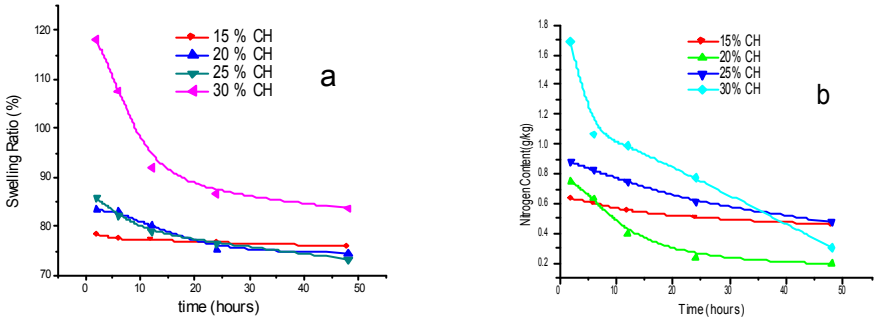

Fig. 2 The swelling ratio results (a) and the content (b) of PVA/CH materials for different CH concentration swollen in buffer solution at different hours

Fig. 3 shows the swelling ratio results of PVA/CH/silica materials in buffer solution compared with PVA/CH materials at different hours. It should be noted that the introduction of silica slightly decreases the

swelling ratio of PVA/CH/silica blends compared to PVA/CH materials. Furthermore, the nitrogen content in PVA/CH/silica film keeps in a level direction basically. These results suggested that the existence of silica not only restrain the dissolution of PVA molecules, but also effectively hinders the diffusion of CH component from composite film to buffer solution.

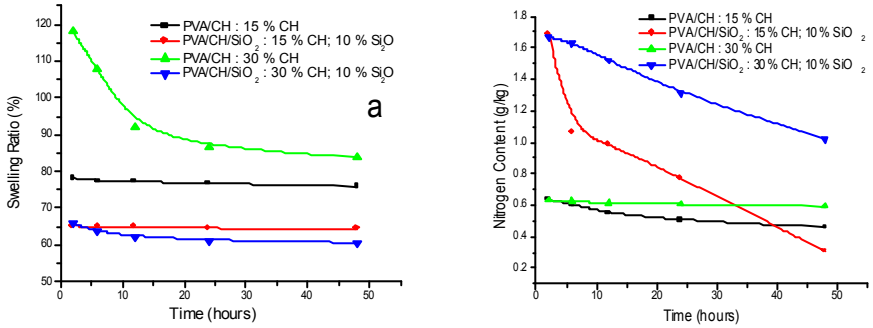

Fig. 3 Swelling ratio (a) and the content of nitrogen (b) of PVA/CH/silica materials in buffer solution compared to PVA/CH materials at different hours

3.3 Thermal analysis of CH/PVA/silica film

Fig. 4 shows TG and DTG curves of pure PVA and PVA/CH and PVA/CH/silica composite films. There are two distinct and well-separated turns (200-300 °C and 400-500 °C) in TG curves (Fig. 4a) and two corresponding weight-loss peaks in DTG curves for all samples (Fig. 4b). Therefore, the thermal degradation can be regarded as two-step degradation. For PVA/CH and PVA/CH/silica films, the TG and DTG curves of the composite shift to a higher temperature due to the presence of CH, and accordingly, the PVA/CH and PVA/CH/silica materials are more thermally stable than pure PVA. From the curves of DTG (Fig 4b), it can be seen that maximum weight loss rate of PVA/CH/silica materials is higher than that of others, which suggested that thermal stability of PVA/CH/silica materials is better than PVA/CH and pure PVA materials.

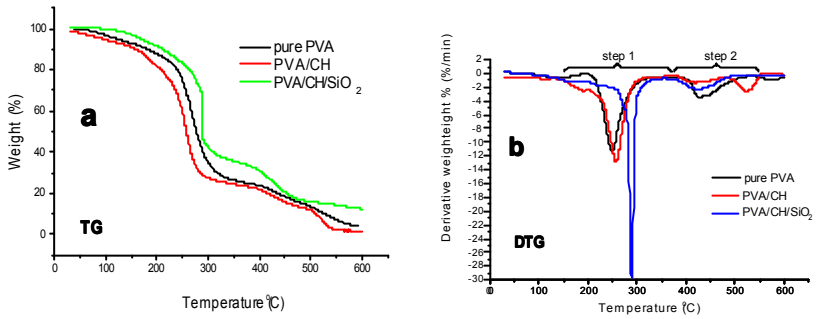

Fig.4 TG (a) and DTG (b) curves of PVA/CH/silica materials compared to pure PVA and PVA/CH

3.4 FTIR analysis of CH/PVA/silica film

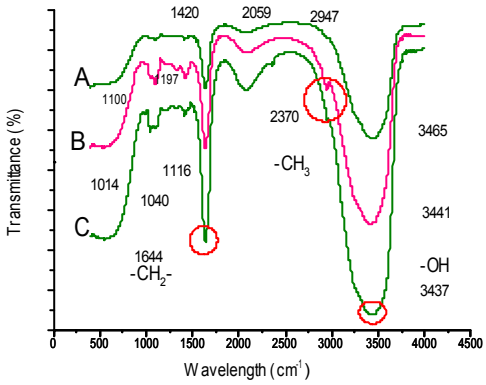

Fig. 5 FTIR spectra of pure PVA: (A), PVA/CH: (B), PVA/CH/silica: (C)

Fig 5 shows the FTIR spectra of PVA/CH and PVA/CH/silica compared to pure PVA. All samples show absorption peaks at 3400-3500 cm^{-1}, corresponding to the hydroxyl groups. For PVA/CH/silica composite material, the peaks occurring between 1000 and 1200 cm^{-1} are generally accepted to the anti-symmetric stretching vibrations of Si-O-Si bridging sequences, which is the structural backbone of the hybrid materials [6]. The $-CH_3$ group incorporated into the silica group is indicated by the presence of the two absorption peaks around 1197 cm^{-1} and 2947 cm^{-1}, which can be assigned to the vibration of Si-C bond and the $-CH_3$ unit, respectively [7].

4 Conclusions

The results of swelling and thermal analysis demonstrate that the addition of silica yields a PVA/CH/silica composite with good thermal stability, and the introduction of silica component leads to a remarkable decrease in equilibrium swelling degree. Furthermore, nitrogen content determination shows that the dissolution of CH in buffer solution can be effectively hindered by silica component.

References

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