Gelatin/Montmorillonite Hybrid Nanocomposite. I. Preparation and Properties

Jun Ping Zheng,[1] Ping Li,[1] Ya Lu Ma,[2] Kang De Yao[1]

[1]College of Materials Science and Engineering, [2] College of Science, Tianjin University, Tianjin 300072, People's Republic of China

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ABSTRACT: Gelatin/montmorillonite (MMT) hybrid nanocomposite was directly prepared with unmodified MMT and gelatin aqueous solution. Thermal and mechanical properties of the composite were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and tensile tests. The results indicated that an intercalated or partially exfoliated nanocomposite could be achieved, and the properties of the composite were significantly improved. A T_g peak of high temperature disappeared in the DSC curve of the composite, and the thermogravity and thermally decomposed rate decreased obviously. The tensile strength and Young's modulus were also improved notably, which varied with MMT content, as well as the pH of gelatin matrix. Meanwhile, SEM photographs showed a plasticizing trend of gelatin fracture surface due to intercalation with MMT. Furthermore, the wet mechanical behavior was initially studied. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1189–1194, 2002

Key words: gelatin; montmorillonite; nanocomposite; thermal properties; mechanical properties

INTRODUCTION

In recent years, the campaign for the protection of the environment and the preservation of limited natural resources urged us to develop high-performance natural degradable materials to replace the conventional synthetic ones. Gelatin is one kind of promising material with many merits, including low cost, biodegradability, nontoxicity, and biocompatibility. Although gelatin can be used as a valuable biopolymer in tissue engineering[1] (e.g., wound-dressing and bone scaffolding), its poor mechanical properties (especially in the wet state) limit its application as a structural biomaterial. Therefore, how to reinforce gelatin materials becomes a challenge for worldwide researchers. Many attempts such as vapor crosslink,[2] orientation technique,[3–5] and gelatin-based composites filled with hydroxyapatite,[6] tricalcium phosphate,[7] and carbon fiber[8] have been made and great progress has been achieved. However, the strength is still not high enough, especially in the wet state. Thermal properties of gelatin have been also improved mainly through an orientation technique.[4] However, there is still a long way to go before the application of high-performance gelatin or gelatin-based composites is perfected.

Fortunately, the development of polymer-layered silicate nanocomposites provided us with some new opportunities. Polymer/montmorillonite (MMT) nanocomposites have been reported a lot recently.[9–14] With only a low content of MMT, the strength, Young's modulus, heat resistance, and solvent resistance of the composites can be greatly improved.[9,12] However, all the matrices reported are neutral synthetic polymers, whereas an intercalation nanocomposite dealing with a natural amphoteric polyelectrolyte has not been reported so far.

In this work, we report a novel biomaterial—gelatin/MMT hybrid nanocomposite for the first time. The presentation is split into several parts: first, we present the preparation and properties of the composite. The second part will describe the swelling behavior of the composite and their influencing factors, and the last part will investigate whether the gelatin-based composites could be used as structural biomaterials such as osteosynthetic devices. We think this work could create a new path for the improvement of gelatin properties.

EXPERIMENTAL

Materials

Gelatin (Type B, extracted from bovine skin) was purchased from Sigma Chemical Co.(St. Louis, MO). Sodium MMT (Na^+ MMT, the particle size is 40 μm) was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences (Beijing, China). Glycerol (GLY, analytical grade) (Tianjin Chemical Reagent Plant, Tianjin, China) and dextran dialdehydes (self-

Correspondence to: J. P. Zheng (junpingzheng@eyou.com).

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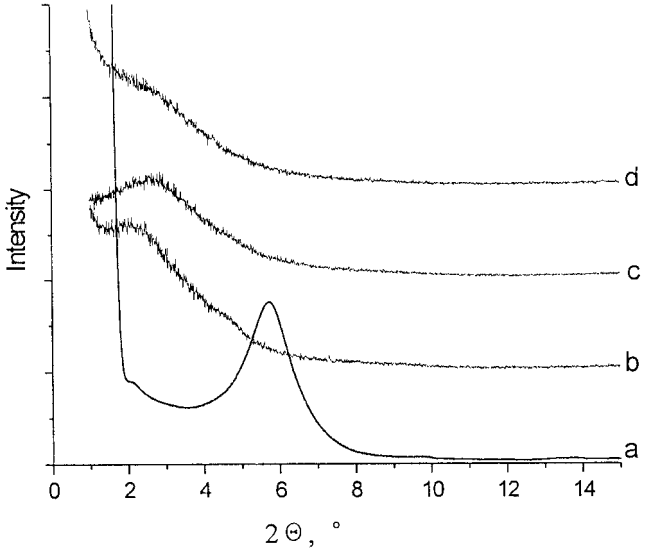

Figure 1 XRD patterns of pristine MMT and composites (a) MMT; (b) AGM; (c) NGM; (d) BGM.

made) were used as the plasticizer and crosslinking agent, respectively. Other reagents were all of analytical grade.

Preparation of gelatin/MMT nanocomposite

One gram of gelatin powder was soaked in 50 mL deionized water and heated at 70°C to obtain a homogeneous solution (adjusted pH with HCl or NaOH solution, respectively). Then, a gelatin solution was added dropwise into 2 wt % ultrasonically pretreated MMT suspension under vigorous stirring at 70°C. The achieved homogeneous mixture was divided into two parts: one was dried in a vacuum oven; the powder was further ground for X-ray diffraction (XRD), DSC, and TGA characterization. (The sample composed of 30% by mass of MMT was used.) The other mixture was filled with gelatin powder under agitation at 70°C to raise gelatin concentration. The sample, composed of 17% by mass of MMT, was used for mechanical properties tests. Then, 0.25 g glycerol was added and stirred for 20 min, and 10 mL 10% dextran dialdehyde solution was slowly added under the same conditions and stirred for another 10 min. The product was poured into the specially self-made mold and dried at ambient temperature for several days. The obtained samples were used for tensile tests.

Measurements

X-ray diffraction

To measure the change in the gallery distance of MMT before and after intercalation, XRD patterns were recorded at 2°/min on a Japan Rigaku DMAX-RC diffractometer by using CuKα radiation ($\lambda = 0.154$ nm) at a generator voltage of 50 kV and a generator current of 180 mA.

Differential scanning calorimetry

Glass transition temperature (T_g) was determined on a Netzsch DSC 204 differential scanning calorimeter. The measurements were carried out in the temperature range of 20–250°C at a heating rate of 10°C/min under nitrogen atmosphere.

Thermogravimetric analysis

The thermogravimetric measurements were performed on a Netzsch TG 209 instrument under nitrogen atmosphere at a heating rate of 10°C/min.

Scanning electron microscopy (SEM)

Examination of the fracture surfaces was performed on a Philips XL-30 scanning electron microscope. The fracture ends of the tensile specimens were sputter-coated with a thin layer of gold prior to examination.

Tensile tests

The tensile tests of the dumbbell specimens, 6.5 mm width at the straight edge, were carried out at room temperature by using a Testometric Universal Tester M500–10AX at a crosshead speed of 10 mm/min and a gauge length of 65 mm. At least five specimens were tested for each set of samples and the mean values are reported.

RESULTS AND DISCUSSION

Preparation of gelatin/MMT hybrid nanocomposite

It is known that the isoelectric point (IEP) of amphoteric polyelectrolyte gelatin is 5.05. Gelatin/MMT

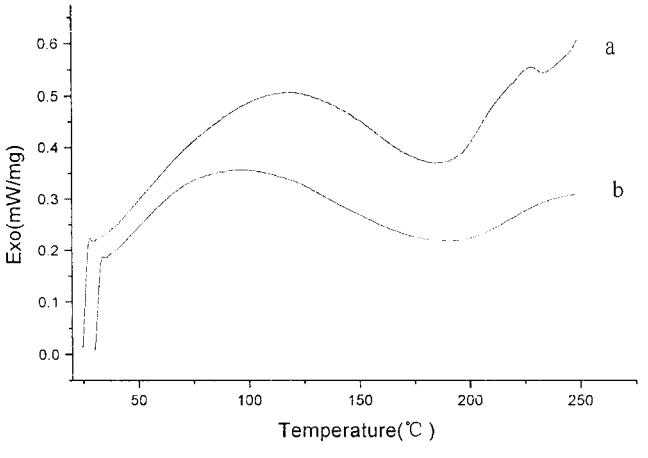

Figure 2 DSC curves of (a) gelatin and (b) composite.

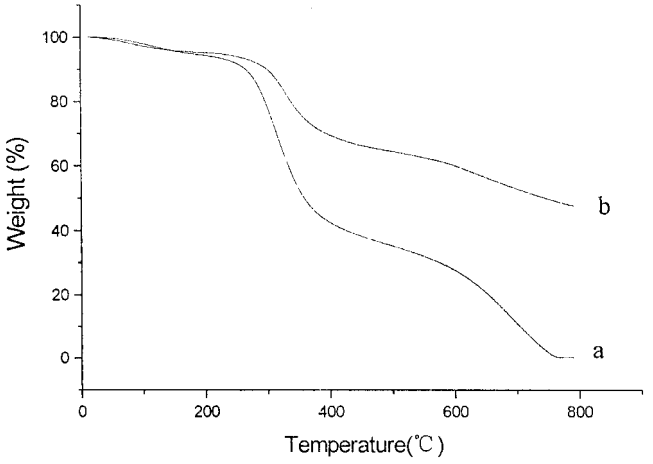

Figure 3 TGA curves of (a) gelatin and (b) composite.

composites prepared with a gelatin aqueous solution of different pHs (just below, equal to, and above IEP) are named AGM, NGM, and BGM, respectively. The XRD patterns of pristine MMT and composites are shown in Figure 1. Original MMT exhibits a sharp peak at $2\theta = 6°$, and through the Bragg's equation:$\lambda = 2d \sin \theta$; d_{001} is 1.47 nm. XRD patterns of composites change dramatically in comparison with pristine MMT. All diffraction peaks shift toward lower angle values, become broad, and even disappear, indicating that intercalation or exfoliation structures have been formed. For intercalation composites, the interlayer spacing increases from 1.47 to 4.42 nm due to the insertion of gelatin molecules into the sheets of MMT. The absence of the diffraction peak reveals the exfoliation structure.

Thermal analysis

Figure 2 shows the DSC curves of gelatin and gelatin/MMT nanocomposites. Pristine gelatin has two T_g peaks at 117 and 227°C, respectively. The low-temperature transition is assigned to the devitrification of blocks rich in α-amino acids, although the high one is attributed to the devitrification of blocks rich in imino acids such as proline and hydroxyproline.[15] In comparison, the first T_g peak of composite is weakened and shifts to 95°C, while the second one disappears. This result may be explained as follows: gelatin chains that intercalate into the interlayers of MMT are restricted by sheets of MMT, and the movement of segments is restrained.[16,17] In addition, there exists static electric interaction or hydrogen bond between charged groups of gelatin chains and the sheets of MMT; MMT also acts as physical crosslinking sites and reduces the activity of gelatin matrix. Therefore, the T_g peaks become weak and even disappear.

The TGA curves of Figure 3 reveal that the onset thermal-decomposed temperature of composite is 40°C higher than that of gelatin, and the thermal decomposed rate is obviously reduced. This result reveals that intercalation with MMT could significantly inhibit the weight loss of gelatin. Moreover, from the DTG curves of Figure 4, it can be seen that the maximum thermal decomposed rate and T_{max} of gelatin are 5.8%/min and 314°C, while the corresponding ones of composite are 3.2%/min and 330.5°C, respectively. Therefore, the thermal decomposed rate of composite drops to a large extent.

The improvement in thermal stability of the composite is mainly attributed to thermal resistance of MMT and the nanodispersion of MMT sheets in the gelatin matrix. FTIR analysis[18] shows that MMT is thermally resistant and not easy to decompose, which is verified that the samples remain unchanged when heated to 500°C. Furthermore, gelatin and MMT could exert a stronger interaction in composite, and MMT acts as physical crosslinking sites to retard the thermal decomposition of gelatin to a certain extent. In addi-

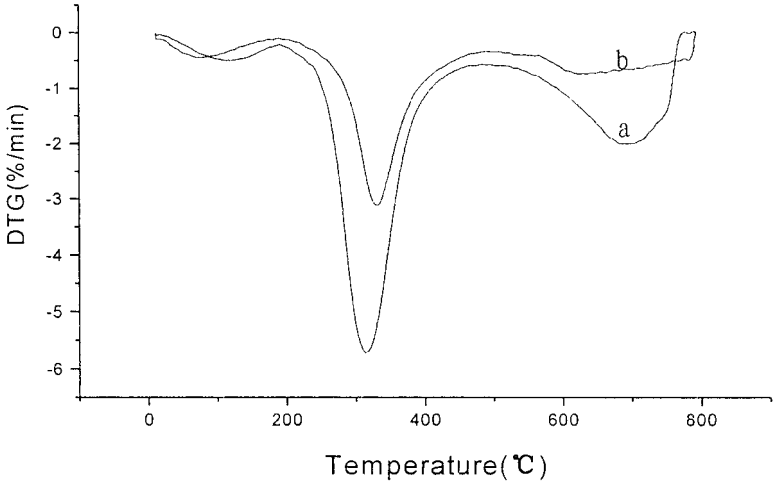

Figure 4 DTG curves of (a) gelatin and (b) composite.

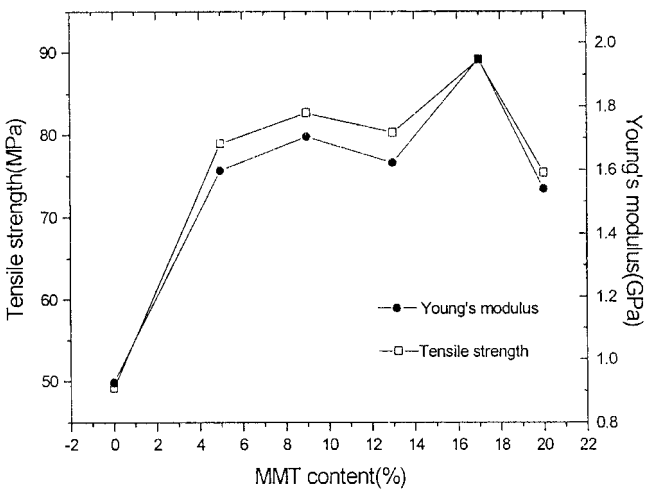

Figure 5 Effect of MMT content on tensile strength and Young's modulus of gelatin and composites.

tion, nanodispersive MMT sheets have an excellent barrier property in preventing the release of degraded gelatin fragments. As a result, the thermal degradation of gelatin could be delayed and the thermal stability of composite was improved. In a word, intercalation with MMT could notably improve thermal stability of gelatin.

Mechanical properties

The effect of MMT content on the mechanical properties of the composite is illustrated in Figure 5. It can be seen that intercalation with MMT can greatly improve the mechanical properties of gelatin. The composite with only 5 wt % MMT content exhibits a tensile strength of 78.9 MPa and a Young's modulus of 1.6 GPa, which are 1.6 and 1.8 times as those of original gelatin, respectively. When MMT content reaches 17 wt %, the tensile strength and Young's modulus are raised to 89.1 MPa and 2.0 GPa, respectively. This substantial enhancement of the mechanical properties is ascribed to the uniform dispersion of MMT layers in nanosize in gelatin matrix and the strong interaction between gelatin and MMT, which results in the increased tensile strength and Young's modulus. As the MMT content is over 17 wt %, the tensile strength and Young's modulus begin to decrease, which may arise from the aggregation of MMT particles with higher surface energy when the MMT content is high enough.

As an amphoteric polyelectrolyte, ionized states of gelatin vary with different pHs of media, which exerts an effect on the mechanical properties of the composites. Figure 6 shows the stress–strain curves of composites with various pHs of gelatin matrix. As shown in the figure, AGM exhibits the lowest stress and strain, while BGM gets the highest ones. At the IEP, the amount of $—NH_3^+$ and $—COO^-$ of gelatin is equal. The charge changes as below when pH is higher or lower than IEP,

$$NH_3^+—Gel—COOH \xleftarrow[pH<IEP]{H^+}$$

$$NH_3^+—Gel—COO^- \xrightarrow[pH>IEP]{OH^-} NH_2—Gel—COO^- + H_2O$$

It is known that crosslinking reaction occurs between —CHO of dextran dialdehydes and $—NH_2$ of the gelatin matrix.[19] With the drop in pH, the amount of $—NH_2$ gradually decreases because of protonation, leading to the decrease in active sites of crosslinking reaction and, consequently, lowering the crosslinking degree. As a result, mechanical properties decline.

The morphology of fracture surfaces of gelatin and composite are shown in Figure 7. The fracture surface of gelatin exhibits a smooth laminated structure made

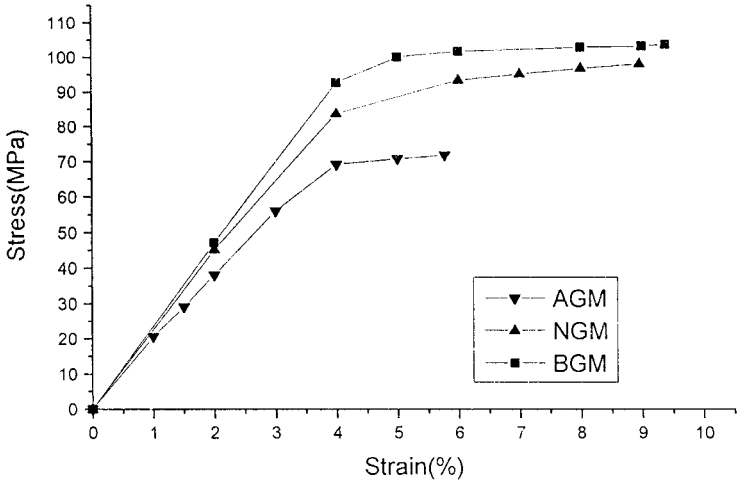

Figure 6 Stress–strain curves of composites with various pHs of gelatin matrix.

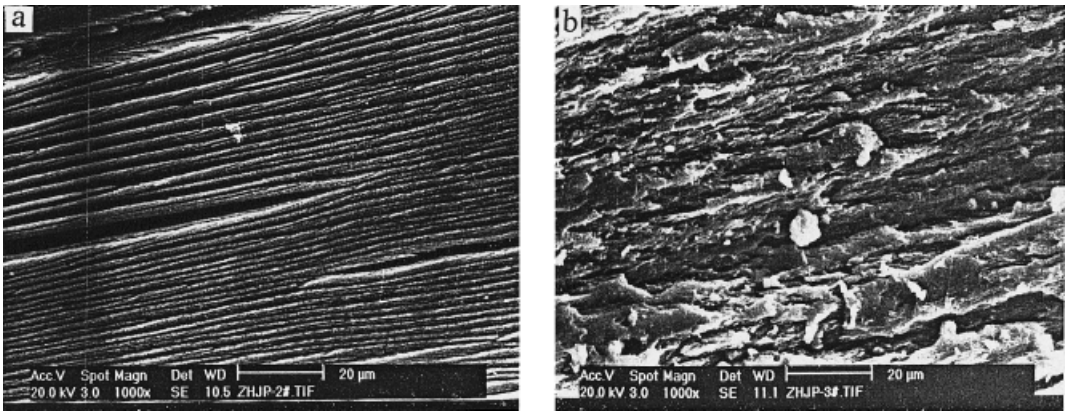

Figure 7 SEM photographs of fracture surfaces of (a) gelatin and (b) composite.

up of a thin parallel layer, reflecting its brittleness. Comparatively, the fracture surface of composite seems coarse, indicating an improved toughness.

Wet mechanical behavior

The application of gelatin to medical structure materials (e.g., bone-fixed materials) is usually limited because of its poor wet strength. There are few reports[20] regarding the modification of its wet mechanical behavior, which is studied initially here. Wet mechanical behavior curves of pure gelatin and composite are shown in Figure 8. Pure gelatin is rather weak after swelling 20 min, while the stress of composites can be maintained. The maximum stress is above 50 MPa for AGM and BGM. As stated above, the improvement of wet mechanical properties is ascribed to nanodispersion of MMT in the gelatin matrix and the barrier effect of MMT sheets to solvent molecules. MMT can not only improve the mechanical properties of gelatin in dry state, but also retard the permeability of solvent molecules during the swelling process. Therefore, the swelling has been inhibited and the declination of stress is delayed. From Figure 8, it also can be found that the wet mechanical behavior of gelatin with different pHs is different. The strength is decreased in the order of NGM, AGM, and BGM. This phenomenon is consistent with their swelling results. Swelling curves of 0–50 min are shown in Figure 9. It is evident that the swelling rate of NGM is faster than the others. This result may be related to the different interactions between MMT and gelatin of various states, which will be discussed in detail further.

CONCLUSION

In this study, gelatin/MMT hybrid nanocomposite was successfully prepared, and thermal as well as mechanical properties were investigated. XRD results reveal that an intercalated or partially exfoliated structure was achieved. DSC and TGA results indicate that intercalation with MMT could significantly improve

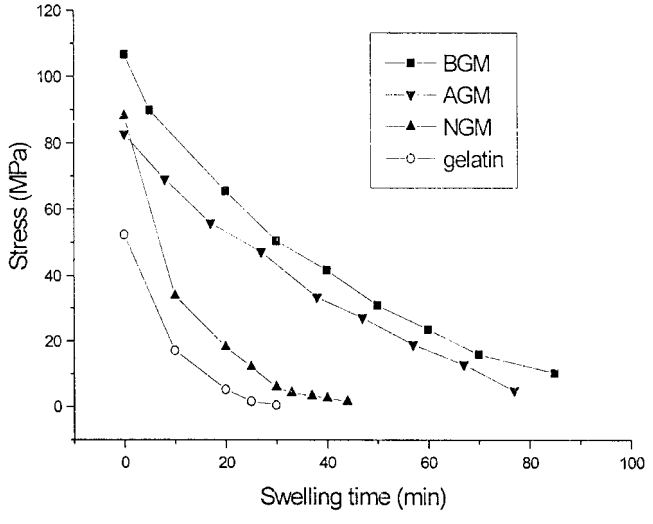

Figure 8 Wet mechanical behavior curves of gelatin and composites.

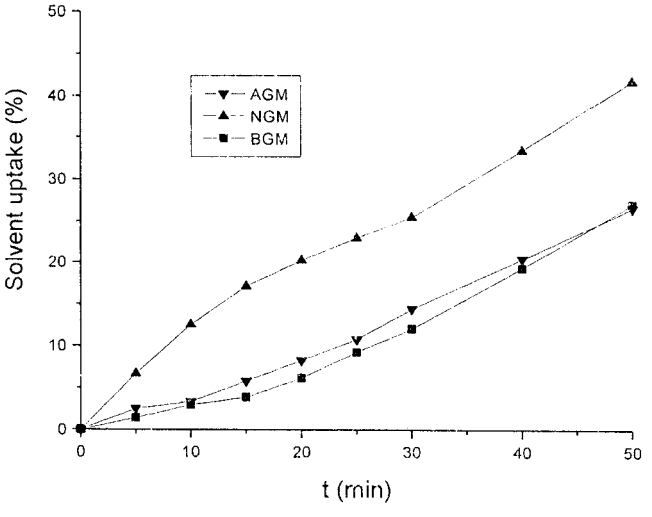

Figure 9 Swelling curves of composites with various pHs of gelatin matrix.

the thermal properties of gelatin. The T_g peak of high temperature disappears in the DSC curve of composite, and the thermogravity and thermal decomposed rate decrease obviously. In addition, the mechanical properties of composite have been improved notably. The tensile strength and Young's modulus reach maximum when MMT content is 17 wt %. SEM photographs demonstrate the plasticizing effect of gelatin fracture surface due to intercalation with MMT. Meanwhile, the mechanical properties of the composite depend on the pH of the gelatin matrix. Wet mechanical behavior was studied initially. Intercalation with MMT can exert substantial effects on wet strength of gelatin. Swelling of the composite is inhibited efficiently and the decrease of stress is delayed. Wet mechanical behavior is also related to the pH of the gelatin matrix. These results are mainly due to nanodispersion of MMT and its excellent barrier effect.

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