

## Effects of Montmorillonite on the Structure and Properties of Gelatin-Polyethylene Glycol Composite Fibers

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**ABSTRACT:** To improve the thermal and mechanical properties of gelatin-polyethylene glycol (PEG) composite fibers, montmorillonite (MMT) is incorporated into gelatin-PEG composite fibers during gel-spinning process. The effects of MMT on the structure and properties of gelatin-PEG composite fibers are investigated. The viscosimetry analysis and transmission electron microscopy measurements show that MMT has a good dispersion in spinning solution at low loading, while serious aggregation is observed with excess amount of MMT adding. The data of X-ray diffraction (XRD) show that MMT can be intercalated and exfoliated in gelatin-PEG-MMT nanocomposite fibers. Fourier transform infrared (FTIR) studies show the hydrogen bonding interactions between gelatin and MMT. The mechanical properties, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements indicate that the mechanical and thermal properties of nanocomposite fibers are improved as expected at low loading of MMT. However, excess amount of MMT decreases the mechanical and thermal properties of nanocomposite fibers due to poor dispersion and clay cluster induced gelatin chains aggregation. Moreover, it is found that the mechanical properties of gelatin-PEG-MMT nanocomposite fibers may be more sensitive to conformational change of gelatin molecules caused by the addition of MMT. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 773–778, 2013

**KEYWORDS:** clay; fibers; proteins; properties and characterization; composites

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### INTRODUCTION

Gelatin-based composite fibers have attracted more and more attention due to the merits of gelatin, including low cost, biodegradability, nontoxicity, and biocompatibility.<sup>1,2</sup> Generally, in the fibers preparation, gelatin is crosslinked or blended with other materials to improve the physical, thermal, and spinnable properties. Studies show that *N*-[3-(dimethylamino)propyl]-*N'*-ethylcarbodiimide (EDC), hydroxysuccinimide (NHS), glutaraldehyde, glyoxal, transglutaminase, and oxidized alginate are effective crosslinkers.<sup>1,3–7</sup> Biopolymers, such as hyaluronic acid,<sup>8</sup> alginate,<sup>6,9</sup> *Centella asiatica*,<sup>10</sup> silk fibroin,<sup>11</sup> and apatite<sup>12</sup> are successfully blended with gelatin to produce composite fibers. Poly( $\epsilon$ -caprolactone),<sup>13,14</sup> polyaniline,<sup>15</sup> polyvinyl alcohol,<sup>16</sup> and polyacrylonitrile<sup>4,17</sup> are also introduced into gelatin-based composite fibers. In our previous studies, polyethylene glycol (PEG) was added into gelatin spinning solutions as a modifier. It was found that PEG can significantly improve the spinnability of gelatin. However, it played a poor role in improving the thermal and mechanical properties of gelatin fibers.

Clay recently attracts a great deal of attention from materials scientists as a result of its inexpensiveness, chemical and

thermal stability and good mechanical properties. The effect of clay on improving the mechanical and thermal properties of polymer matrix has caused a lot of interest. Montmorillonite (MMT), one of the most common smectite clays, naturally abundant and toxin-free, is a promising reinforcer material in food, medicine, cosmetic, and healthcare recipients.<sup>18</sup> A variety of polymers have been evaluated with the addition of MMT, such as vinyl polymers, condensation (step) polymers, polyolefins, biodegradable polymers, and some specialty polymers.<sup>19</sup> The properties improvements are well obtained including high modulus,<sup>20–22</sup> increased strength and heat resistance,<sup>23</sup> and increased biodegradability of biodegradable polymers.<sup>24</sup> Specially, gelatin-MMT nanocomposites are widely studied by many researchers.<sup>25–29</sup> In Rao's study,<sup>28</sup> transparent gelatin-clay nanocomposites films were made through solution processing, of which mechanical performance and melting point increased distinctly. Zheng and coworkers had done a series of research on gelatin-MMT nanocomposites. The thermal stability and mechanical properties of the nanocomposites were significantly improved.<sup>25–27</sup> However, as far as we know, the effects of MMT on the structure and properties of gelatin-based composite fibers are not clear.



**Figure 1.** Gelatin-PEG-MMT nanocomposite fibers prepared by gel-spinning. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

In this article, gelatin-based composite fibers are prepared by gel-spinning with PEG6000 as the modifier. To improve the thermal and mechanical properties of gelatin-PEG composite fibers, MMT is incorporated into spinning solutions during gel-spinning process. The structure and properties of gelatin-PEG-MMT nanocomposite fibers are characterized. Our aim is to understand the dispersion of MMT in gelatin-PEG matrix and the effects of MMT on improving the performances of gelatin-PEG composite fibers.

## EXPERIMENTAL

### Materials

Gelatin type B was purchased from Aladdin Reagent Database, Bloom 250. (Shanghai, China). MMT was kindly supplied by Zhejiang Fenghong Clay Chemicals Co (Anji, China). The cationic exchange capacity of MMT was 100 mmol/100 g. PEG6000 was purchased from Kelong Chemical Reagent Company (Chengdu, China), which was of analytical grade.

### Preparation of Gelatin-PEG-MMT Nanocomposite Fibers

Certain amount of gelatin and PEG6000 ( $W_{\text{gelatin}} : W_{\text{PEG}} = 5 : 1$ , total weight = 25 g) was mixed in 75 mL distilled water. After fully swelling, the mixture was continuously stirred at 50°C for 1 h. Then, desired amount of MMT solution (0.5 wt %) was added in the mixture. And extra amount of distilled water was added to make sure the spinning solutions had a uniform concentration. After another 1 h with stirring at 50°C, the blend spinning solution was degassed and extruded into saturated sodium sulfate bath through a single nozzle 0.3 mm in internal diameter under compressed air. The fiber was rolled up with a speed of  $\sim 10 \text{ m min}^{-1}$ . Then, the obtained raw fibers were drawn with a drawing ratio of 3 by another roller and dried in air. Finally, the fibers were washed in distilled water and dried in air again. The photographs of the obtained gelatin-PEG-MMT nanocomposite fibers were shown in Figure 1. The nanocomposite fibers were named GM5000, GM2000, GM1000, and GM500 when the ratio of gelatin to MMT is 5000, 2000, 1000,

and 500 (w/w). And the gelatin-PEG fiber without MMT was named G0.

### Viscosity Measurements

The spinning solution was placed in a 600 mL beaker and equilibrated at  $50 \pm 0.1^\circ\text{C}$  for 1 h before the measurement. The viscosities of spinning solutions with different clay content were measured by a DV-II+Pro viscometer (Brookfield Engineering Laboratories, Inc., Massachusetts, USA) at  $50 \pm 0.1^\circ\text{C}$  and at a certain shear rate ( $\dot{\gamma}$ :  $35.2 \text{ s}^{-1}$ ). The viscosity value was obtained when it was unchanged during the measurements.

### Transmission Electron Microscopy Measurements

Transmission electron microscopy (TEM) was used to investigate the dispersion and nanostructure of MMT in composite spinning solutions. TEM observations were performed of ultra-thin films prepared by gelatin-clay spinning solutions with a JEM-100CX-II (JEOL Co., Tokyo, Japan) TEM at an acceleration voltage of 120 kV.

### FTIR Measurements

FTIR spectra of the composite fibers were obtained from discs containing  $\sim 2.0 \text{ mg}$  sample in  $\sim 20 \text{ mg}$  potassium bromide (KBr). The measurements were performed on a Spectrum One FTIR (PerkinElmer, Massachusetts, USA) spectrophotometer at the resolution of  $4 \text{ cm}^{-1}$  in the wave number region  $400\text{--}4000 \text{ cm}^{-1}$ .

### X-Ray Diffraction Measurements

The wide-angle XRD profiles were obtained using an 18 kW rotating anode X-ray diffractometer (MXPAHF, Mac Science Co., Yokohama, Japan) with a fixed  $\text{CuK}\alpha$  radiation of 0.154 nm. The diffraction angle was scanned from  $5^\circ$  to  $65^\circ$  at a rate of  $2^\circ \text{ min}^{-1}$ .

### Mechanical Properties Measurements

The tensile strength and breaking elongation of the gelatin-PEG-MMT composite fibers were measured on a fiber electron tensile tester (YG061, Laizhou Electronic Machine Co., Laizhou, China). The gauge length was 100 mm, and crosshead speed was  $100 \text{ mm min}^{-1}$ .

### TGA Measurements

TGA measurements were performed on a TG 209F1 instrument (NETZSCH Group, Selb, Germany) under nitrogen atmosphere to avoid thermo-oxidative reactions. The measurements were performed from  $30^\circ\text{C}$  up to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ .

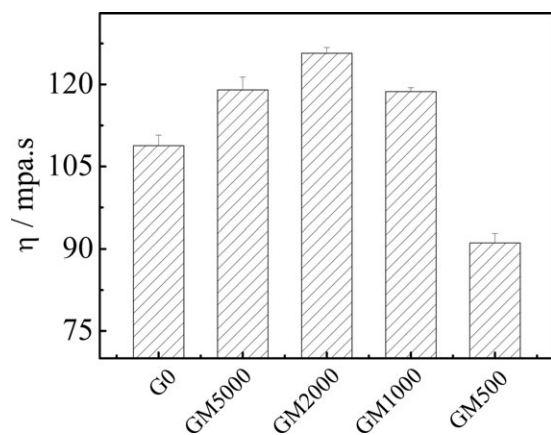
### DSC Measurements

The melting temperature ( $T_m$ ) of gelatin-PEG-MMT nanocomposite fibers was determined on a Netzsch DSC 200PC calorimeter. The measurements were performed at a heating rate of  $5^\circ\text{C min}^{-1}$  between  $25^\circ\text{C}$  and  $150^\circ\text{C}$  under nitrogen atmosphere.  $T_m$  was taken as that centered at the transitions.

## RESULTS AND DISCUSSION

### Viscosities of Spinning Solutions

The effects of MMT on the viscosities of spinning solutions are studied in Figure 2. It shows that the viscosity of gelatin-PEG spinning solution is 108.8 mPa s with no clay addition. The composite spinning solution with 1/5000 MMT content exhibits viscosity of 119.0 mPa s, which is higher than that of gelatin-PEG spinning solution. When MMT content reaches 1/2000,

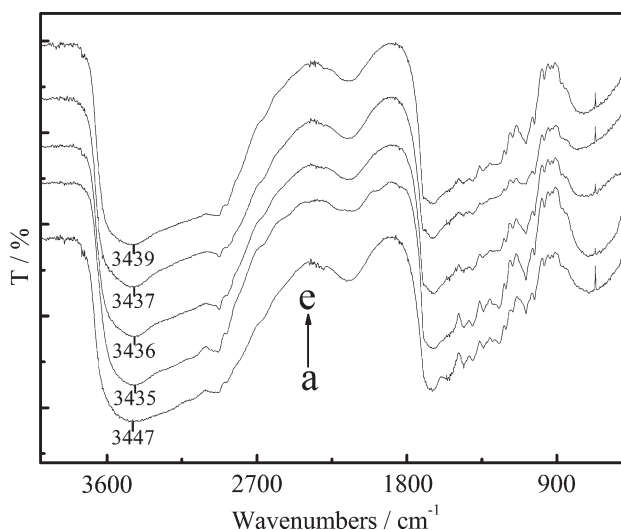


**Figure 2.** Viscosities of spinning solutions with different MMT content at a certain shear rate ( $\dot{\gamma}$ :  $35.2 \text{ s}^{-1}$ ).

the viscosity of spinning solution is raised to 125.7 mPa s. The result indicates the physical crosslinking action of MMT between gelatin molecules. As the MMT content over 1/2000, the viscosities of composite spinning solutions begin to decrease. Note that GM500 exhibits viscosity of 91.1 mPa s, which is even lower than that of G0 spinning solution. The decrease of viscosities may arise from the poor dispersion of MMT and the aggregation of gelatin chains induced by the overfull clay addition.<sup>30</sup> There are strong electrostatic interactions between MMT and protein and hydrogen bond interactions between carbonyl groups in protein and hydroxyl groups within clay galleries.<sup>25,28,31–35</sup> Overfull MMT loading will induce poor dispersion and aggregation of gelatin chains, which is accompanied by the decrease of intermolecular interactions, resulting in the decrease of viscosities. To further investigate the dispersion and morphology of MMT in gelatin-PEG composite spinning solutions, TEM measurement is applied.

#### TEM Measurement of Spinning Solutions

The TEM micrographs of GM5000 and GM500 spinning solutions are shown in Figure 3. It can be seen from Figure 3(A) that MMT layers in GM5000 spinning solution are well

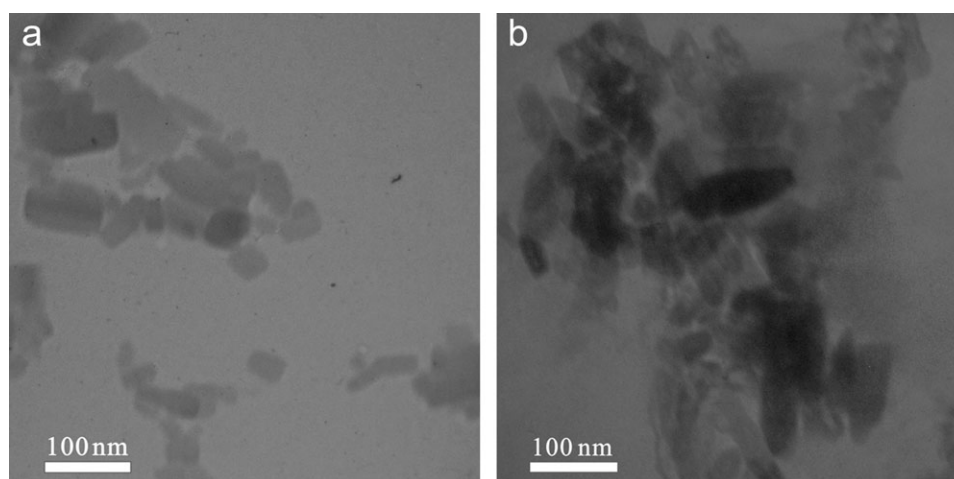


**Figure 4.** FTIR spectra of gelatin-PEG-MMT nanocomposite fibers. a: G0, b: GM5000, c: GM2000, d: GM1000, e: GM500.

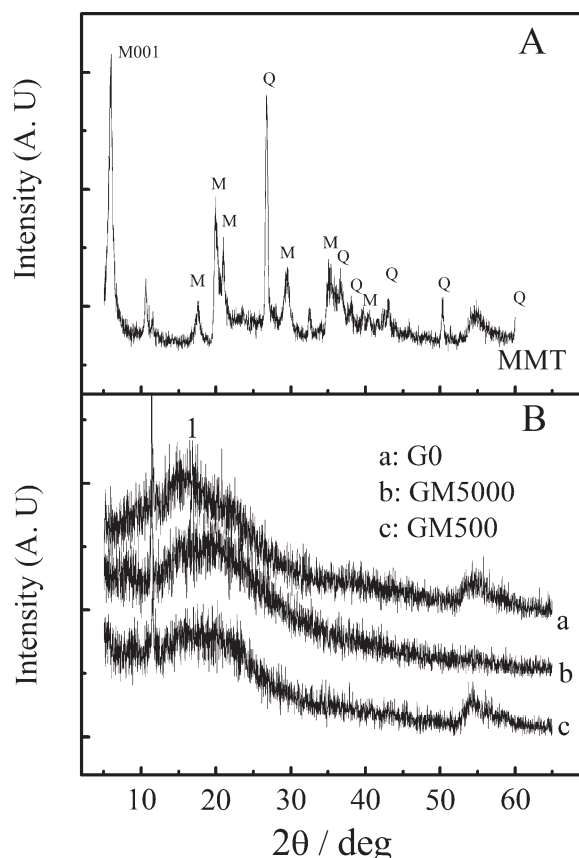
exfoliated. A large amount of exfoliated single clay platelets are observed. However, Figure 3(B) shows that MMT platelets are stacked together in GM500 spinning solution, while a few exfoliated single clay platelets are observed. The TEM results show much better MMT dispersion in GM5000 than GM500. The TEM observations agree well with the above viscosity results. On the basis of viscosity results and TEM micrographs, overfull clay addition will induce poor dispersion of clay in gelatin-PEG composite spinning solutions.

#### FTIR Analysis

Figure 4 shows the FTIR spectra of gelatin-PEG-MMT nanocomposite fibers with different clay content. The bands  $\sim 3440$ ,  $\sim 2930$ ,  $1636\text{--}1661$ , and  $1549\text{--}1558 \text{ cm}^{-1}$  are denoted as A, B, I, and II amide bands, respectively.<sup>36,37</sup> Generally, the amide A and B bands are mainly associated with the stretching vibrations of N—H groups. The amide I bands is originated from C=O stretching vibrations coupled to N—H bending vibration. The amide II bands arise from the N—H bending vibrations coupled



**Figure 3.** TEM micrographs of GM5000 (A) and GM500 (B) spinning solutions.



**Figure 5.** Wide-angle XRD patterns of MMT (A) and gelatin-PEG-MMT nanocomposite fibers (B).

to C–N stretching vibrations.<sup>36,37</sup> Figure 4 shows that the positions of B, I, and II amide bands in gelatin-PEG-MMT nanocomposite fibers are nearly unchanged while the amide A shifts to low-frequency shoulder in comparison with G0. MMT is commonly used in nanocomposites owing to the structure known as the 2 : 1 phyllosilicates. Its crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedrons by the tip. These layers organize themselves to form stacks with a regular van der Waals gap in between them called the interlayer or the gallery. Isomorphic substitution within the layers (for example, Al<sup>3+</sup> replaced by Mg<sup>2+</sup> or by Fe<sup>2+</sup>, or Mg<sup>2+</sup> replaced by Li<sup>+</sup>) generates negative charges that result in the ion-exchange capacity of MMT.<sup>38</sup> Hence, there are strong electrostatic interactions between MMT and protein and hydrogen bond interactions between carbonyl groups in protein and hydroxyl groups within clay galleries.<sup>25,28,31–35</sup> And shift of amide A band to lower wave numbers is generally associated with increased hydrogen bond interactions.<sup>39</sup> Changed position of the amide A band in Figure 4 indicates the hydrogen bond interactions between gelatin and MMT.

#### XRD Analysis

Figure 5 shows the wide-angle XRD patterns of MMT and gelatin-PEG-MMT nanocomposite fibers. In Figure 5(A), the peaks marked by (M) are the reflections indicative of 2 : 1 swelling

clays that confirm the characteristics of the MMT type. The other peaks marked by (Q) are impurities corresponding to quartz.<sup>40</sup> In general, three different types of polymer/clay nanocomposites are achievable: intercalated nanocomposites, flocculated nanocomposites, and exfoliated nanocomposites. In exfoliated nanocomposites, the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading. Usually, the clay content of exfoliated nanocomposites is much low.<sup>19</sup> In the present nanocomposite fibers, the MMT content is much lower than that of gelatin. As a consequence, the MMT layers should be separated in gelatin solutions. Figure 5(B) shows that the (001) diffraction peaks [M001 in Figure 5(A)] of GM5000 and GM500 are disappeared. The results confirm that the intercalation and exfoliation of MMT in gelatin solution has occurred. In addition, Figure 5(B) shows that the noncrystalline peaks [peak 1 in Figure 5(B)] of GM5000 and GM500 shift to higher diffraction angle and are significantly reduced, corresponding to the decrease of packing order. The result is often observed in other nanocomposites systems.<sup>28</sup>

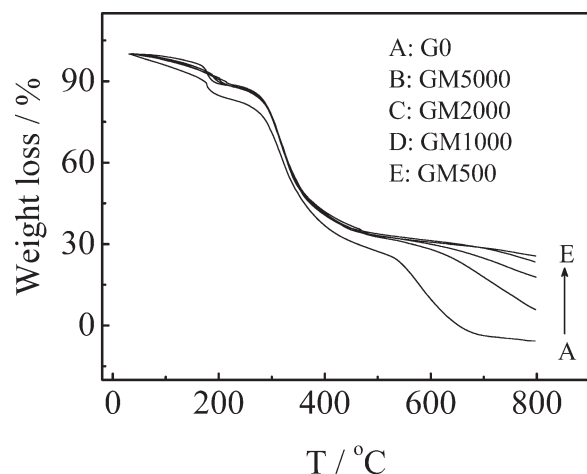
#### Fiber Tensile Properties

Table I shows the mechanical properties of gelatin-PEG-MMT nanocomposite fibers. It can be seen that the addition of MMT greatly improves the mechanical properties of gelatin fibers. GM5000 with only 1/5000 clay content exhibits a tensile strength of 142.7 MPa and a breaking elongation of 16.8%. When MMT content reaches 1/2000, the tensile strength and breaking elongation are raised to 168.2 MPa and 18.0%, which are 1.5 and 1.3 times as those of G0. As there are strong electrostatic interactions between MMT and protein and hydrogen bond interactions between carbonyl groups in protein and hydroxyl groups within clay galleries.<sup>25,28,31–35</sup> The physical crosslinking action of MMT between gelatin molecules should be one of the contributors to induce high tensile strength. As the clay content is over 1/2000, the tensile strength and breaking elongation begin to decrease, even weaker than those of gelatin-PEG fiber when the ratio of gelatin to MMT is 500. The results arise from the poor dispersion of MMT and the aggregation of gelatin chains induced by the excess MMT addition.<sup>25,41,42</sup> But then, Zheng et al.<sup>25</sup> have reported that gelatin-MMT nanocomposites films had the highest tensile strength and Yong's modulus when MMT content reached 17 wt %. The results indicate that the mechanical properties of gelatin-PEG-MMT nanocomposite fibers should be more sensitive to conformational change of gelatin molecules caused by the addition of MMT.

**Table I.** Mechanical Properties of Gelatin-PEG-MMT Nanocomposite Fibers with Different Content of MMT

| Samples | Tensile strength (MPa) | Breaking elongation (%) |
|---------|------------------------|-------------------------|
| G0      | 112.1 ± 9.6            | 13.6 ± 1.4              |
| GM5000  | 142.7 ± 11.7           | 16.8 ± 1.1              |
| GM2000  | 168.2 ± 11.6           | 18.0 ± 1.6              |
| GM1000  | 165.6 ± 12.0           | 17.9 ± 1.9              |
| GM500   | 45.9 ± 7.3             | 10.7 ± 0.9              |

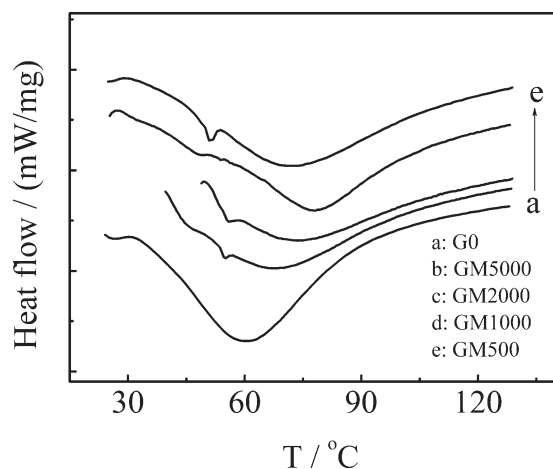




**Figure 6.** TGA curves of gelatin-PEG-MMT nanocomposite fibers with different MMT content.

### Fiber Thermal Stability

Figure 6 shows the TGA curves of gelatin-PEG-MMT nanocomposite fibers with different clay content. Thermal decomposition of composite fibers is a gradual process with three main stages in the TGA curves. The first one, in the range of 130–220°C, is assigned to the loss of low-molecular mass compounds, mainly adsorbed and bounded water. The second and main stage, in the range of 250–480°C, is mainly related to the degradation of the gelatin chains. The higher temperature step which exceeds 530°C can be attributed to the loss of clay structural water and the decomposition of more thermally stable structure.<sup>38</sup> Figure 6 shows that the addition of MMT produces a delay in mass loss in the temperature range of gelatin chains degradation (250–480°C). It is known that gelatin has a good electrostatic interaction and can further form hydrogen bond interactions with clay. MMT acts as physical crosslinker between gelatin molecules result in the thermal improvement of gelatin-PEG-MMT nanocomposite fibers. In addition, the incorporation of MMT into the gelatin matrix is found to enhance thermal stability by acting as a superior insulator and mass transport



**Figure 7.** DSC spectra of gelatin-PEG-MMT nanocomposite fibers with different content of MMT.

**Table II.** Melting Temperature ( $T_m$ ) of Gelatin-PEG-MMT Nanocomposite Fibers with Different Content of MMT

| Samples | $T_m$ (°C) |
|---------|------------|
| G0      | 60.1       |
| GM5000  | 68.1       |
| GM2000  | 73.4       |
| GM1000  | 77.8       |
| GM500   | 71.9       |

barrier during decomposition.<sup>19,28</sup> To further analyze the effect of MMT content on the thermal stability of composite fibers, DSC measurements were used to obtain more information.

Figure 7 shows the DSC spectra of gelatin-PEG-MMT nanocomposite fibers. Table II shows the melting temperature ( $T_m$ ) of gelatin-PEG-MMT nanocomposite fibers. It can be seen that the gelatin-PEG-MMT nanocomposite fibers have the higher  $T_m$  than that of gelatin-PEG composite fiber. GM5000 exhibits  $T_m$  of 68.1°C. When clay content reaches 1/1000, the  $T_m$  of GM1000 is raised to 77.8°C, which is 1.3 times as that of gelatin-PEG fiber. However, the  $T_m$  of GM500 is 71.9°C, which begins to decrease. This may arise from the poor dispersion of MMT and serious aggregation of gelatin chains. Agglomerated clay particles do not significantly affect the thermal stability of the polymer matrix.<sup>43</sup>

### CONCLUSIONS

In this study, MMT is introduced into gelatin-PEG spinning solutions to prepare gelatin-based nanocomposite fibers by gel-spinning. The effects of MMT on the structure and properties of gelatin-PEG-MMT nanocomposite fibers are investigated. The results indicate that the mechanical and thermal properties of nanocomposite fibers are improved as expected. However, under the excess addition of MMT, the mechanical and thermal properties of composite fibers are decreased instead, due to poor dispersion and serious aggregation of gelatin chains induced by excess clay loading. In addition, the data of XRD show that MMT is intercalated and exfoliated in the nanocomposites fibers. FTIR studies show the hydrogen bond interactions between gelatin and MMT.

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