

Interaction of Functional Groups of Gelatin and Montmorillonite in Nanocomposite

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ABSTRACT: As an amphoteric polyelectrolyte, gelatin could intercalate into the galleries of montmorillonite (MMT). In this paper, sodium laurate/MMT composites and sodium laurate/dehydroxylated MMT composites were introduced as low molecular simulation to investigate the interaction functional groups of gelatin and MMT. The composites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), thermogravimetric analysis (TGA) and ^{13}C nuclear magnetic resonance (^{13}C NMR). Furthermore, the effect of interaction between gelatin and MMT on the mechanical properties of the composites

was investigated. The results indicated that $-\text{COO}^-$, not $-\text{COOH}$, in gelatin chains could interact strongly with the MMT sheets. The reactive sites on MMT were hydroxyl groups, which could interact with $-\text{COO}^-$ in gelatin chains by forming hydrogen bonds. The gelatin/MMT composites prepared in alkaline media have better mechanical properties due to stronger interaction. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1556–1561, 2006

Key words: composites; clay; simulations; polyelectrolytes

INTRODUCTION

It is well known that montmorillonite (MMT), one of the layered aluminosilicate clay minerals, consisting of two silica tetrahedral sheets and an aluminum octahedral sheet, has superior capability to be intercalated as small or large molecules into the interlayer space of the (001) plane. The interlayer galleries are occupied by cations, such as Na^+ , Ca^{2+} , and Mg^{2+} , which can be exchanged by some organic cations. The exchange capability of cations of MMT has been a subject of special interest to scientists and engineers, and the cations' exchange mechanism has been widely identified and utilized in many fields. The Toyota Central Research and Development Labs has reported in 1993 the synthesis of nylon 6–clay hybrid with the organically modified MMT in which the interlayer Na^+ cations were exchanged by the ammonium cations of various ω -amino acids.¹ Since then, a large number of synthetic polymers had been introduced to form polymer-layered silicate nanocomposites.^{2–5} The organic modification of MMT before the intercalation process was very much necessary to improve the compatibility between MMT and the organic monomers or macromolecules.

The gelatin/MMT hybrid nanocomposites had been directly prepared with unmodified MMT and gelatin

aqueous solution in our previous work, and an intercalated or partially exfoliated structure was achieved. The thermal and mechanical properties of the composites were significantly improved because of intercalation with MMT, and the swelling behavior was also investigated.^{6,7} Gelatin is an amphoteric polyelectrolyte with an isoelectric point (pI) 5.05. In our previous experiments, gelatin/MMT hybrid nanocomposites have been successfully prepared in the media with different pH values. When $\text{pH} < \text{pI}$, the gelatin chains with more $-\text{NH}_3^+$ can bind with MMT sheets through static electric interaction and intercalate into MMT interlayers. When $\text{pH} > \text{pI}$, the gelatin chains with more $-\text{COO}^-$ can also intercalate into MMT interlayers. There should be a certain kind of interaction between MMT and $-\text{COO}^-$ (or $-\text{COOH}$) in gelatin molecular chains. However, the interaction between $-\text{COO}^-$ in organic molecules and MMT sheets has not been reported so far.

To investigate the intercalation interaction between gelatin and MMT in alkaline media, sodium laurate/MMT composites were prepared as models. In addition, the dehydroxylated MMT was introduced to ascertain the reactive sites on MMT, which could interact with $-\text{COO}^-$ (or $-\text{COOH}$). The effect of the interaction between gelatin and MMT on the mechanical properties of the composites was also studied.

EXPERIMENTAL

Materials

Gelatin (Type B, extracted from bovine skin) was purchased from Sigma Chemical (St. Louis, MO). Sodium

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laurate (analytical-grade; Yuanfan Chemical Reagent Plant, Shanghai, China) was used as received. Sodium montmorillonite (MMT, particle size = 40 μm) was supplied by Huate Chemical (Zhejiang, China). Glycerol (analytical-grade; Tianjin Chemical Reagent Plant, Tianjin, China) was used as the plasticizer. Other reagents were all of analytical-grade.

Preparation of sodium laurate/MMT composite

Fifty milliliters (0.1 mol/L) sodium laurate solution was added dropwise to 50 mL (2 wt %) MMT suspension under vigorous stirring at 60°C for 1 h. The pH values of sodium laurate solution and MMT suspension were adjusted before it was mixed with HCl or NaOH solution, respectively. The achieved mixture was centrifugated at 3500 rpm for 10 min, and the sediment was dried in vacuo. The powder was further ground for characterization.

Preparation of gelatin/MMT nanocomposite

Five grams of gelatin powder was soaked in 50 mL deionized water and heated at 60°C to obtain a homogeneous solution (adjusted pH with HCl or NaOH solution, respectively). Then, the solution was added dropwise to 2 wt % MMT suspension under vigorous stirring at 60°C for 1 h. Then, 0.15 g glycerol was added and stirred for 5 min. The product was poured into the specially self-made mold and dried in an oven at 50°C to fabricate gelatin/MMT composite films. The obtained samples were used for tensile tests.

Dehydroxylation of MMT

The dehydroxylated MMT was obtained by heating the original MMT powders at 800°C in an oven for 1 h.

Preparation of sodium laurate/dehydroxylated MMT composite and gelatin/dehydroxylated MMT composite

The procedures for preparation of sodium laurate/dehydroxylated MMT composite and gelatin/dehydroxylated MMT composite were similar to those for the preparation of sodium laurate/MMT composite and gelatin/MMT nanocomposite, except using dehydroxylated MMT instead of original MMT.

Measurements

XRD analysis

X-ray diffraction (XRD) patterns were recorded at 4 degree/min on a Japan Rigaku D/max 2500 diffractometer using Cu K α radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a generator current of 100 mA.

Thermo gravimetric analysis

Thermogravimetric analysis (TGA) was conducted on a Shimadzu TA-50 instrument under nitrogen atmosphere at a heating rate of 10°C/min.

IR spectra

The IR spectra of the samples were taken with a Bio-Rad FTS3000 Fourier transform infrared spectrophotometer with KBr pellets.

Tensile tests

The tensile tests of the specimens were carried out at room temperature by using a Testometric Universal Tester M350–20kN at a crosshead speed of 5 mm/min. At least five specimens were tested for each samples and mean values are reported.

Scanning electron microscopy

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.

Solid state ^{13}C NMR

The solid state ^{13}C NMR CP/MAS measurements were performed on an OXFORD Infinity plus 300WB spectrometer operating at a spinning frequency of 3 kHz. The 90° pulse time used in high proton-decoupled single pulse ^{13}C spectra was 4.5 μs and pulse delay was 5.0 s. The spectrum width was 40 kHz.

RESULTS AND DISCUSSION

The interaction between carboxylic anion ($-\text{COO}^-$) and MMT

To ascertain whether the $-\text{COO}^-$ or $-\text{COOH}$ in gelatin chains could interact with MMT in gelatin/MMT nanocomposite, sodium laurate/MMT composites were introduced as model to study the interactive functional groups of gelatin and MMT.

The XRD patterns of sodium laurate, MMT, and sodium laurate/MMT composites prepared with different pH values are shown in Figure 1. Original MMT exhibits a sharp peak at $2\theta = 7.05^\circ$, which is the diffraction peak of 001 plane. The sharp peaks at $2\theta = 2.85^\circ, 3.17^\circ, 5.58^\circ, 8.32^\circ$ can be observed in the XRD pattern of sodium laurate between 2° and 10° , which are crystalline diffraction peaks. There are no crystalline diffraction peaks of sodium laurate in c, d and e composites and the one between 2° and 10° is the d_{001} diffraction peak of MMT. On the other hand, the crystalline diffraction peaks of sodium laurate in f, g and

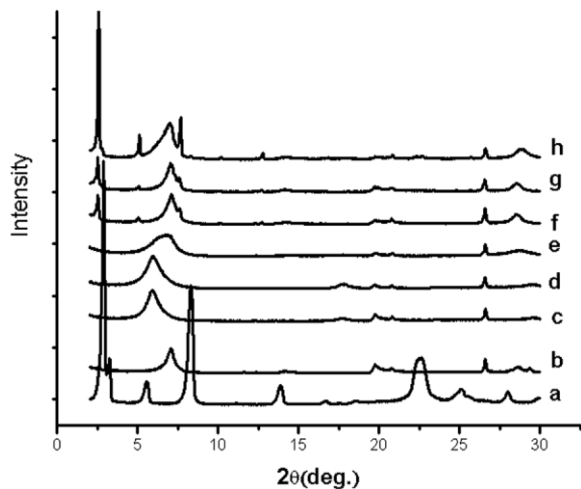


Figure 1 XRD patterns of sodium laurate, MMT, and sodium laurate/MMT composites prepared in different pH values; sodium laurate (a), MMT (b), and sodium laurate/MMT composites at pH of 1.87 (c), 5.47 (d), 7.00 (e), 8.95 (f), 9.89 (g), and 12.67 (h).

h composites become more obvious as the pH value rises. This phenomenon that sodium laurate appears in the composites prepared in alkaline environment and that there is more sodium laurate in the composites prepared in higher pH value indicates that the carboxylic anion ($-\text{COO}^-$), not the carboxyl ($-\text{COOH}$), could interact strongly with MMT.

The TGA curves of original MMT and the composites prepared in acidic or alkaline environments are shown in Figure 2. It is obvious that the curve of the composite prepared in acidic media is similar to that of original MMT, which has two distinct steps of weight loss. The first one at the temperature around 48–120°C is due to the free water evaporation. The difference between curve a and b at the first step is the

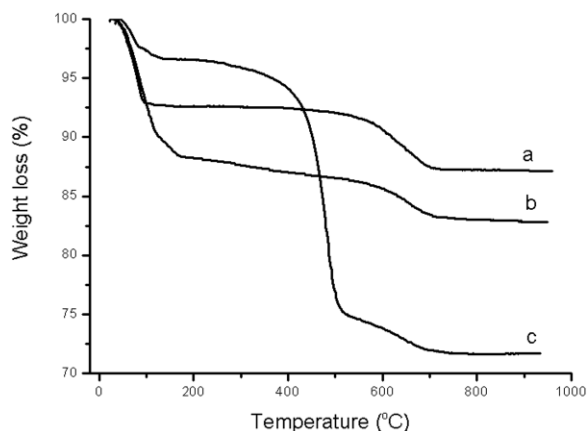


Figure 2 TGA curves of MMT and sodium laurate/MMT composites prepared in different pH values; MMT (a), sodium laurate/MMT composites at pH of 1.87 (b), and 12.67 (c).

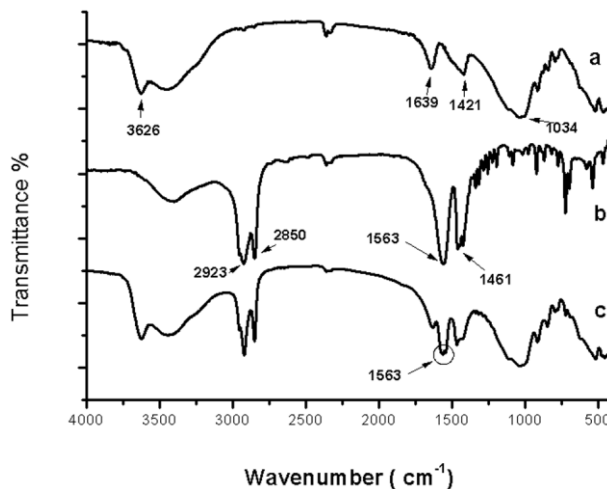


Figure 3 FTIR spectra of (a) MMT, (b) sodium laurate and (c) sodium laurate/MMT composite.

reflection of the different amount of adsorbed water and interlayer water, which is probably due to the different interlayer cations, Na^+ and H^+ , respectively, and causes the shift of the 001 diffraction peaks of MMT towards lower angle values (c and d patterns in Fig. 1). The second weight loss at the temperature around 550–720°C is due to the release of hydroxyl groups from different positions of the MMT structure.⁸ Besides the above two steps of weight loss, there is an obvious step of weight loss at the temperature around 400–500°C in the composites prepared at alkaline environment, revealing the weight loss of sodium laurate. In comparison, there is hardly any sodium laurate in the composite prepared in acidic media. These results indicate that the carboxylic anion could interact strongly with original MMT.

The Fourier transform infrared spectra (FTIR) spectra of MMT, sodium laurate, and composite (prepared in pH = 12.67 environment) are shown in Figure 3. The spectrum of MMT is characterized by its Al—OH stretching vibration at 3626 cm^{-1} , Si—O stretching vibration at 1034 cm^{-1} and deformation vibration of the hydroxyl groups at 1639 and 1421 cm^{-1} . The spectrum of sodium laurate has absorbances at 2923 and 2850 cm^{-1} (methyl and methylene stretching vibration) and 1563 and 1461 cm^{-1} ($-\text{COO}^-$ stretching vibration). In the spectrum of the composite, the characteristic peaks of MMT and sodium laurate could be found easily, but the $-\text{COO}^-$ of sodium laurate stretching vibration at 1563 cm^{-1} has split into three peaks. The result reflects the change of the chemical environments of $-\text{COO}^-$ on sodium laurate in the composite, which is induced by the interaction between sodium laurate and MMT.

To investigate the change of chemical environment of $-\text{COO}^-$ on sodium laurate in the composite, solid state ^{13}C NMR was introduced. ^{13}C NMR spectra of

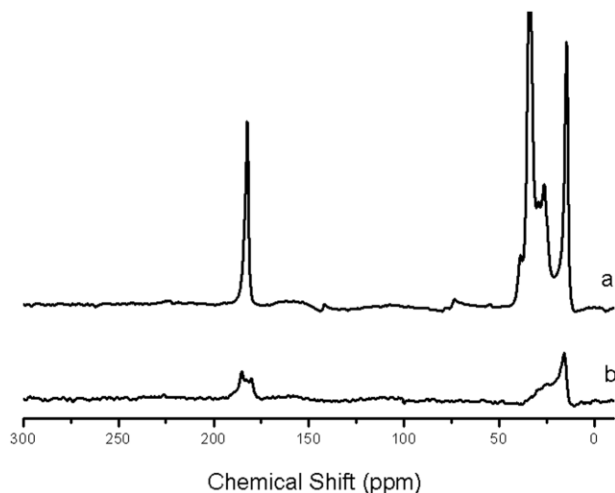


Figure 4 Solid state ^{13}C NMR spectra of (a) sodium laurate and (b) sodium laurate/MMT composite.

sodium laurate and sodium laurate/MMT composite (prepared in $\text{pH} = 12.67$ environment) are shown in Figure 4. In the ^{13}C NMR spectrum of sodium laurate there are mainly four resonance humps: 182.4 ppm (the carbon atom in $-\text{C}=\text{O}$), 34.1 ppm (the carbon atoms in $-\text{CH}_2-$), 26.5 ppm (the carbon atom in $-\text{CH}_2-$ connected with $-\text{CH}_3$), and 14.7 ppm (the carbon atom in $-\text{CH}_3$). The strength of the resonance humps in the composite is dramatically weaker than those in sodium laurate, which is due to the screen effect of the carbon atoms in sodium laurate by MMT. Besides screen effect, the resonance hump of the carbon atom in $-\text{C}=\text{O}$ in the composite has split into three humps (chemical shift 185.2, 182.6, and 180.2 ppm). This phenomenon indicates that the chemical environments of the carbon atoms have greatly changed because of the interaction between the carboxylic anion ($-\text{COO}^-$) and MMT.

The determination of reactive sites on MMT sheets

The chemical structural formula of sodium MMT could be expressed as: $\text{Na}_{0.7}(\text{Al}_{3.3}\text{Mg}_{0.7})\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$. According to a previous report,⁸ the hydroxyl groups on aluminum could be released from the MMT sheets when the temperature is above 700°C that caused the second step of weight loss on curve a in Figure 2. The dehydroxylated MMT was introduced to study whether MMT sheets without hydroxyl groups could interact with carboxylic anion ($-\text{COO}^-$).

The FTIR spectra of MMT and dehydroxylated MMT are shown in Figure 5. It can be observed that the peaks related to hydroxyl groups which are Al—OH stretching vibration at 3626 cm^{-1} and deformation vibration at 1639 and 1421 cm^{-1} have almost disappeared. So, there is hardly any hydroxyl group left on MMT sheets after dehydroxylation experiment.

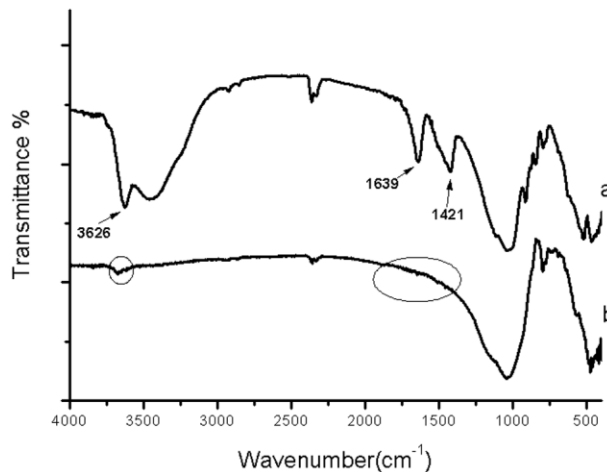


Figure 5 FTIR spectra of (a) MMT and (b) dehydroxylated MMT.

Figure 6 shows the XRD patterns of MMT and dehydroxylated MMT. The diffraction peak of 001 plane has greatly changed from $2\theta = 7.05^\circ$ of original MMT to $2\theta = 9.06^\circ$ of dehydroxylated MMT because of the decrease of interlayer distance. However, other diffraction peaks have no distinct change.

The XRD patterns of composites of sodium laurate/MMT and sodium laurate/dehydroxylated MMT (prepared in $\text{pH} = 12.67$ environment) are shown in Figure 7. The three crystalline diffraction peaks of sodium laurate in the composite containing original MMT between 2° and 10° are apparently stronger than those of sodium laurate/dehydroxylated MMT, indicating that there is few sodium laurate in composite containing dehydroxylated MMT. Therefore, the sodium laurate could not interact with dehydroxylated MMT. The result reveals that hydroxyl groups should be the reactive sites on MMT sheets. And the

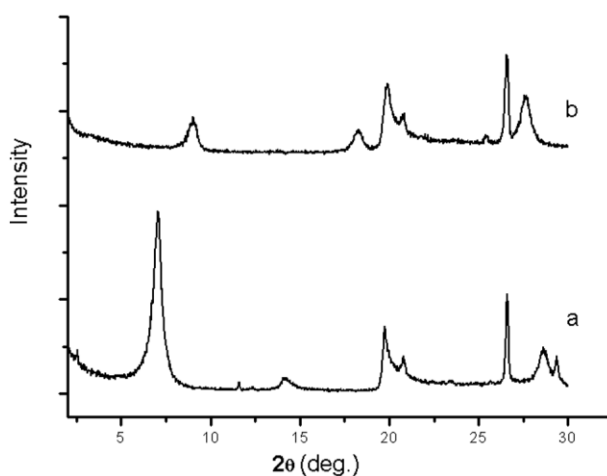


Figure 6 XRD patterns of (a) MMT and (b) dehydroxylated MMT.

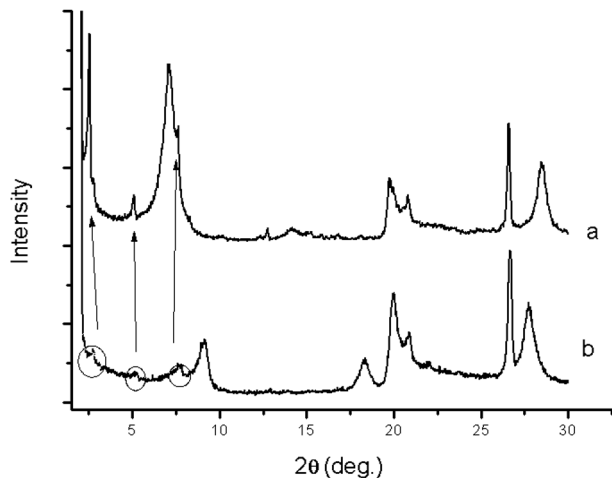


Figure 7 XRD patterns of (a) sodium laurate/MMT composite and (b) sodium laurate/dehydroxylated MMT composite.

interaction between —OH and —COO^- may be the hydrogen bond interaction that will be further studied and assured.

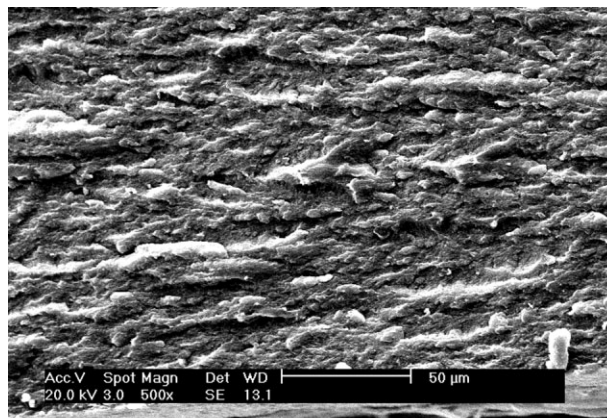
The effect of interaction between gelatin and MMT on the mechanical properties of the composites

As an amphoteric polyelectrolyte, gelatin could intercalate into MMT at various pH values.⁶ The interaction between gelatin and MMT sheets in composites prepared in acidic media is mainly static electric interaction, while the interaction in alkalic media may be hydrogen bond interaction. And the different interaction may have an effect on the mechanical properties of the composites. The tensile strength, Young's modulus, and elongation at break of the gelatin/MMT composites prepared in various pH values are shown in Table I.

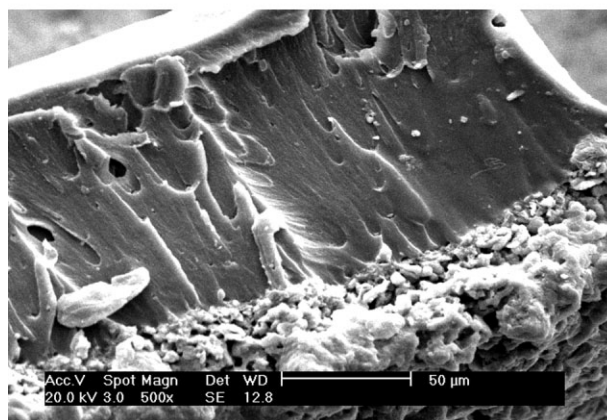
Gelatin/MMT composites prepared in $\text{pH} = 8.88$ has the maximum tensile strength and greater tensile strength could be achieved at higher pH values (be-

TABLE I
Tensile Strength, Young's Modulus, and Elongation at Break of Gelatin/MMT Composites Prepared at Various pH Values

pH values	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
3.80	53.0	1.02	4.1
5.05	66.8	1.03	6.0
5.33	71.4	1.23	5.3
7.35	78.6	1.14	6.4
8.88	80.4	1.21	6.1
11.0	46.7	0.94	4.2



(a)



(b)

Figure 8 SEM photographs of the fracture surfaces of (a) gelatin/MMT composite and (b) gelatin/dehydroxylated MMT composite.

tween 3.80 and 8.88). This result verified that the carboxylic anion could interact strongly with MMT, because gelatin chains have more —COO^- than —NH_3^+ in alkalic media that can interact with MMT. Because of the natural protein character, denaturation of gelatin may take place in $\text{pH} = 11.0$ medium and consequently the composite has the worst mechanical properties.

The SEM photographs of the fracture surfaces of gelatin/MMT composite and gelatin/dehydroxylated MMT composite are shown in Figure 8. The fracture surface of gelatin/MMT composite seems coarse because of the formation of intercalation composite. The fracture surface of the gelatin/dehydroxylated MMT composite is dramatically different from that of gelatin/original MMT composite. Most MMT particles aggregate at the bottom. The stratification of the composite is attributed to the dehydroxylation of MMT, which makes no reactive sites on MMT that the —COO^- in gelatin chains can interact with. It could be concluded that the hydroxyl groups are the reactive

sites on MMT sheets interacting with gelatin molecular chains.

CONCLUSIONS

It is ascertained by the means of low molecular simulation that the —COO^- functional groups could interact strongly with hydroxyl groups on MMT sheets. The pH values of the composites prepared in different media determine the interaction types of gelatin and MMT, which are static electric interaction (between —NH_3^+ and MMT layers, $\text{pH} < \text{pI}$) and hydrogen bond (between —COO^- and hydroxyl groups on MMT, $\text{pH} > \text{pI}$).

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