

Dispersion of Silicate Layers in Zein/Montmorillonite Composite Films Using Two Sonication Methods

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ABSTRACT

This study aimed to prepare zein/Montmorillonite (MMT) composite films by two methods: (1) An ultrasonic bath, and (2) A high power ultrasonic probe. Then, the structural, thermal, mechanical, and barrier properties of the obtained composites were evaluated. According to the X-Ray Diffraction (XRD) patterns, the composite films prepared by the first and second methods had microcomposite and exfoliated structures, respectively. Based on the results of the statistical analysis, the clay dispersion method and Montmorillonite (MMT) content significantly affected the mechanical, barrier, and thermal properties of the composite films. The results showed that mechanical and water vapor barrier properties of the nanocomposites were improved in the presence of small amounts (up to 3%) of MMT, while increased montmorillonite percentage in the microcomposite films weakened the mechanical, barrier, and thermal properties of these films. Therefore, the use of high power sonication is a suitable method for producing protein-based nanocomposites with an exfoliated structure.

Keyword: Barrier properties, Microcomposite, Nanocomposite, Ultrasonic bath, Ultrasonic. Probe.

INTRODUCTION

Polymer nanocomposites, especially the nanocomposites containing layered silicate, are good alternative for conventional composites. In the group of nanofillers, Montmorillonite (MMT) is the most usable one owing to its low cost, small size, high aspect ratio, severability, and uniform distribution in the polymer network [12]. Based on the physical state of the polymer, three methods are used to make layered silicate nanocomposites: intercalation of polymer and pre-polymer from solution, in situ intercalative polymerization, and melt intercalation technique [21]. The first method is a suitable method for preparing polymer/clay nanocomposite films. In this method, polymer is dissolved in its solvent

and the layered silicate is separately dispersed in the same solvent. The polymer solution and swollen clay are mixed with each other and then the solvent is evaporated. It is important to know that the physical mixture of a polymer and layered silicate may not form nanocomposites. Therefore, there are several methods for distributing the clay sheets in the polymer network, which include mechanical mixing, magnetic stirring, and sonication [2]. Three composite structures are obtained, depending on the used mixing technique and dispersion manner of clay layers in polymer network including phase-separated microcomposite, intercalated nanocomposites, or exfoliated nanocomposites [9]. Many researchers have reported that poor dispersion of

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nanoparticles could degrade the mechanical properties of polymers. Slight improvement in material properties is provided by phase-separated microcomposite structures, while the greatest interfacial interaction and phase homogeneity are obtained by exfoliated nanocomposites. Therefore, an important parameter for evaluating physical properties of polymer-clay nanocomposites is degree of exfoliation. Many dispersion techniques for achieving full exfoliation have been extensively explored by numerous researchers [2].

The aim of this study was to use two sonication methods to disperse MMT sheets in zein matrix and then evaluate the structural, thermal, mechanical, and barrier properties of these composites.

MATERIALS AND METHODS

Materials

Zein powder (90% crude protein on dry weight basis) was purchased from Suvchem (India). The MMT clay used in this study was Nanomer_I.34 TCN, surface-modified MMT, containing 25–30 wt% methyl dihydroxy ethyl hydrogenated tallow ammonium, which was supplied from Sigma-Aldrich (Milwaukee, WI, USA). PolyEthylene Glycol 4000 (PEG), glycerol, and calcium chloride were purchased from Merck Company (Darmstadt, Germany). Ethanol (96%) was purchased from Sepahan Teb Company (Isfahan, Iran).

Preparing Zein/ MMT Composite Films

The composite films were prepared by solvent casting method. In this process, 8 g of zein, 0.12 g of PEG, and 0.12 g of glycerol were dissolved in 40 mL of warm (45–50°C) 75% aqueous ethanol solution. A certain amount of MMT (0, 1, 3, 5, and 10 wt%) was dispersed separately in 12 mL of 75% ethanol solution once using an ultrasonic bath (Power: 80W and Frequency:

50 Hz) for 10 minutes and another time using a high power ultrasonic probe (Power: 420W and Frequency: 24 KHz) for 15 minutes. Then, the zein blend and clay suspension were mixed and heated up to 60°C. The mixture was sonicated again for a series of samples by the high power ultrasonic probe (5 minutes) and for another series by ultrasonic bath (2 minutes) in order to make sure of the proper dispersion of nanoparticles in zein. Thickness of the dried film was measured by a micrometer (electronic digital micrometer, DC of 516 and sensitivity of 0.001 mm) after conditioning [9].

X-Ray Diffraction (XRD) Analysis

To investigate the clay morphology in the composite films, the XRD patterns were recorded using an X-ray diffractometer (D8ADVANCE Bruker, Germany) at room temperature and Cu $K\alpha$ radiation with the wavelength of 0.15409 nm was generated at 30 kV and 30 mA. The samples were scanned in the range of $2\theta = 2$ to 10° with the step size of 0.04° . The angular and layer spacing values were related through Bragg's law, $\lambda = 2d \sin\theta$, where d is the spacing between diffraction lattice planes and θ is the measured diffraction angle [7, 8, 9, 15].

Evaluating Mechanical Properties

A tensile testing machine (STM20- Santam- Iran) was used to measure Tensile Strength (TS) and Elongation at break (E %) of the composite films following ASTM- D882-02 [8, 9].

Water Vapor Permeability

Water Vapor Permeability (WVP) is the rate of water vapor transmission through a flat plate of known material with a certain area and thickness induced by a known difference of vapor pressure across the

material. The films were conditioned at 50% Relative Humidity (RH) and 25°C for 48 hours before testing, then, the permeability of the composite films was determined according to ASTM E96-05. A glass container with the diameter of 2 cm and height of 4.5 cm was filled with 3 g of calcium sulfate to remove any humidity. Cap of the container had a hole with the diameter of 8 mm, covered by a piece of composite film with the thickness of 0.170±0.1 mm. Moreover, the container was weighed and placed in desiccators containing 1 L of distilled water at 23°C. The container was weighed every 24 hours for a week. WVP of the films was calculated using the following equation:

$$WVP = WVTR \times \frac{T}{\Delta P} \quad (1)$$

Where, *WVTR* is the steady state Water Vapor Transmission Rate ($\text{g m}^{-2} \text{h}^{-1}$), *T* is the film Thickness (mm), and ΔP is the vapor partial Pressure difference across the two sides of the film (kPa) [8, 9, 17, 19].

Thermal Properties

ThermoGravimetric Analysis (TGA, Q500, TA instrument, Rheometric Scientific, USA) at Argon atmosphere was used to evaluate the thermal stability of the prepared films. The samples were heated from 20 to 500°C at the heating rate of 10 °C min^{-1} [8, 9].

Statistical Analysis

To statistically verify the results, all the experiments were done in triplicate. Analysis of the results obtained via investigating the effect of montmorillonite on the mechanical, barrier, and thermal properties of the composites prepared from two dispersion methods was performed based on a factorial experiment in a randomized complete block design. All the parts of the analysis were performed in SAS statistical software (9.1).

RESULTS AND DISCUSSION

Structural Characteristics

Modern and advanced techniques are used for characterizing layered silicate nanocomposites. The most common method for determining the degree of dispersion of clay layers penetrated into the polymer matrix is X-ray diffraction method. In this method, using Bragg's law, $\lambda = 2d \sin \theta$, the distance between the layers of clay dispersed in the polymer matrix is measured. The change in the distance between the layers of clay that is measured by X-ray diffraction can be specified in the structure of nanocomposite and four states can be expected: if the distance between the layers of clay dispersed in a polymer matrix is unchanged, the clay nanocomposites have not been formed and clay acts like microfillers. If the distance between the layers of clay dispersed in the polymer matrix is reduced, degradation has occurred. Based on the Bragg's equation, the peak of the clay is displaced toward higher angles. If the distance between the layers of clay dispersed in the matrix polymer is increased, the intercalated structure has been found. In this case, according to the Bragg's equation, the peak of the clay is displaced towards lower angles. If the distance between the layers of clay dispersed in a polymer matrix is increased very high and reaches a very broad peak, the nanocomposite structure is an exfoliated and the peak of clay has been absent, according to the XRD patterns [11, 18].

The XRD patterns of MMT and composites of zein containing 0, 1, 3, 5 and 10% of MMT prepared by using an ultrasonic bath and, another time, by a high power ultrasonic probe are shown in Figures 1 and 2, respectively. As can be seen, in the case of the Nanomer_I.34TCN MMT, a diffraction peak at $2\theta = 4.8^\circ$ was identified. So, based on the Bragg's equation ($n\lambda = 2d \sin \theta$), the interlayer spacing was calculated as 18.27 Å. As seen in Figure 1, for the

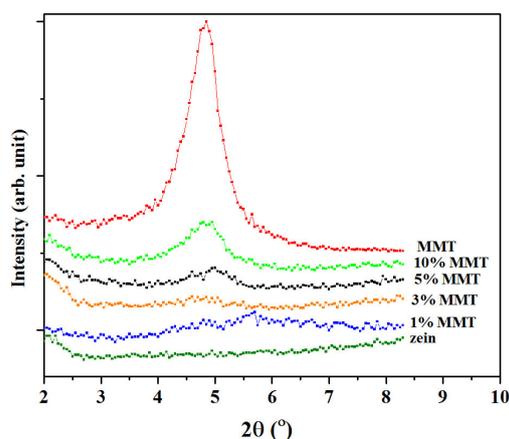


Figure 1. XRD patterns of MMT, zein film and microcomposites of zein-MMT prepared using an ultrasonic bath.

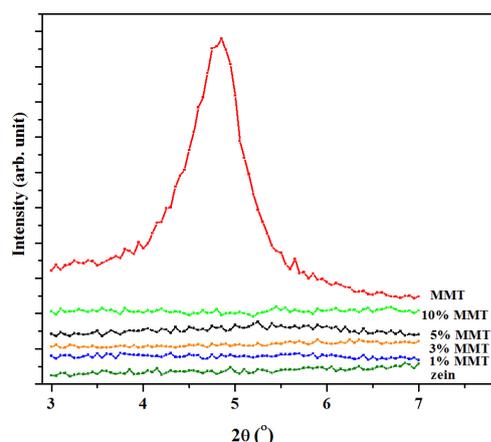


Figure 2. XRD patterns of MMT, zein film and nanocomposites of zein-MMT prepared using a high power ultrasonic probe.

composite obtained using ultrasonic bath, the peak of the montmorillonite was not shifted; so, the structure of the composites obtained by this technique was microcomposite. However, according to the XRD patterns of the composites prepared by a high power ultrasonic probe (Figure 2), the peak of montmorillonite was absent in the XRD diagram composite films and the structure of the composites prepared by this method was exfoliated. Furthermore, the results are in agreement with those reported by other researchers. In the XRD patterns found in the literature, the MMT peak either shifted to lower angles or disappeared, indicating the formation of intercalated or exfoliated structures, respectively [7, 8, 9, 13, 15].

The principal difference between the application of bath and probe ultrasonicators is the power levels used. The bath ultrasonicator produces low power ultrasonic waves and is not able to separate the agglomerated MMT sheets. In contrast, the probe ultrasound produces relatively strong ultrasonic energies as compared to the bath. Thus, in the films prepared using the high power ultrasonic probe, the MMT sheets are separated and dispersed in the zein network.

Mechanical Properties

Tensile Strength (TS) and Elongation at break ($E\%$) of the films are shown in Table 1. Statistical analysis of the mechanical properties data showed that the clay dispersion techniques, as an effective factor, significantly affected the tensile strength of the films; however, they had no significant effect on $E\%$. The MMT content, as another factor, also had a significant effect at 5% level on both properties. The pure zein film had the tensile strength of about 16 MPa. Tensile strength of the films prepared using a high power ultrasonic probe was improved by the addition of MMT and the film containing 10% MMT had the highest tensile strength. Tensile strength increment of these composites can be induced as the uniform distribution of MMT in the polymer network. Increasing distance of MMT layers and inter polymer chain into the layers of MMT, improves the mechanical properties of the nanocomposites. Also, improvement of the mechanical properties of these films can be attributed to the presence of clay with a high aspect ratio and, consequently, increasing the surface area between the polymer and filler and the establishment of

Table 1. Properties of zein/composite films prepared by two sonication methods.^a

	MMT%	Water vapore permeability (g mm h ⁻¹ m ⁻² Kpa ⁻¹)	Tensile strength (MPa)	Elongation at break (%)	50% weight loss temperature (°C)
Nanocomposites (Prepared by a high power ultrasonic)	0	1.73 ^{Aa} ± 0.15	16.2 ^{Ab} ± 3.5	9.65 ^{Aa} ± 0.76	352.63
	1	1.31 ^{Bb} ± 0.19	20.1 ^{Aa} ± 0.87	7.09 ^{Aab} ± 1.02	360.67
	3	1.35 ^{Bb} ± 0.22	20.58 ^{Aa} ± 2.59	6.41 ^{Aab} ± 1.25	363.45
	5	1.23 ^{Bb} ± 0.12	19.51 ^{Aab} ± 0.75	4.65 ^{Ab} ± 1.05	368.12
	10	1.93 ^{Ba} ± 0.15	22.62 ^{Aa} ± 0.62	7.27 ^{Aab} ± 1.03	373.23
	Microcomposites (Prepared by)	0	1.73 ^{Ab} ± 0.15	16.2 ^{Aa} ± 3.5	9.65 ^{Aa} ± 0.76
1		1.83 ^{Ab} ± 0.12	7.36 ^{Bb} ± 0.63	6.05 ^{Aab} ± 0.93	353.5
3		2.03 ^{Ab} ± 0.35	9.65 ^{Bb} ± 1.3	5.11 ^{Ab} ± 0.93	358.29
5		2.05 ^{Ab} ± 0.1	10.09 ^{Bb} ± 0.27	5.61 ^{Ab} ± 0.03	359.32
10		2.89 ^{Aa} ± 0.32	10.8 ^{Bb} ± 2.11	8.38 ^{Aab} ± 0.65	368.01

^a Capital letters used to compare the effect of sonication treatment on a certain percent of MMT and Lowercase letters to compare the effect of MMT percentage on a certain sonication treatment

strong hydrogen bonds between the two phases [10]. The tensile strength of the film prepared using the ultrasonic bath was reduced by adding MMT, which was due to the high absorption of nanoclay and destroying the uniform structure of the zein film. However, elongation of the nanocomposite and microcomposite films was decreased by increasing MMT content, which was related to the reduction of the affinity between the polymer chains and weakening the bonds between the chains. Similar results have been reported in other works, which confirmed that adding MMT to protein-based nanocomposite films improves the tensile strength and modulus of films [8, 9].

Water Vapor Permeability

Water Vapor Penetration (WVP) is a simple method for measuring the water permeability i.e. water that passes through a substance. Statistical analysis of the results showed that the dispersion techniques of MMT and MMT content, as effective factors, significantly affected the WVP of the films. The results presented in Table 1 demonstrate the amount of WVP of composites prepared using the two methods of clay dispersion. As can be seen, by

increasing MMT content from 1% to 5% in the nanocomposite films, the moisture uptake decreased around 28 %. It should be noted that this reduction was similarly observed in other works (Chitosan-MMT: 25.4%; Starch-MMT: 34.2%, Soy protein-MMT: 22.1%) [8, 16]. The observed reduction in WVP in the nanocomposite films seems to be due to the uniform dispersion of the MMT with a high aspect and, so, an increase in diffusion path length of water molecules through the polymer matrix. But, it significantly increased in the case of the sample with 10% MMT. This increase can be attributed to the hydrophilic nature of the WVP and also the arrangement of the clay layers in the polymer network. The least amount of water vapor permeability occurs when the clay sheets are arranged perpendicular to the path of diffusion and the amount of WVP increases with deviation of the layers' angle from the perpendicular orientation [4].

In the microcomposite films, by increasing MMT content, WVP was increasing. Agglomeration of MMT particles and their non-uniform distribution in the polymer network led to the increase of the moisture content by adding MMT in microcomposite films. Also, the water vapor transmission occurred via the hydrophilic



part of the films and depended on their ratio of hydrophilic and hydrophobic parts. MMT is hydrophilic and, thus, increases the water solubility and *WVP* of the films with a microcomposite structure [1, 3, 14].

Generally, there are three steps for the permeability rates of gases through any polymeric materials that consist of: (a) Absorption of the penetrating agents into the polymer; (b) Their diffusion through the polymer, and (c) Their desorption from the polymer surface. Several parameters affect permeability, which include the solubility and diffusivity of penetration into the polymer, chain packing and side group complexity, polarity, crystallinity, orientation, filler, and plasticization [1].

Thermal Properties

Thermal stability of the composite films was analyzed via measuring the weight loss of the volatiles using TGA. Figures 3 and 4 are the TGA diagrams of micro and nanocomposite films, respectively. As can be observed, there are two stages of thermal degradation. The first stage (indicated by an arrow in both Figures) is related to the weight loss of low molecular weight

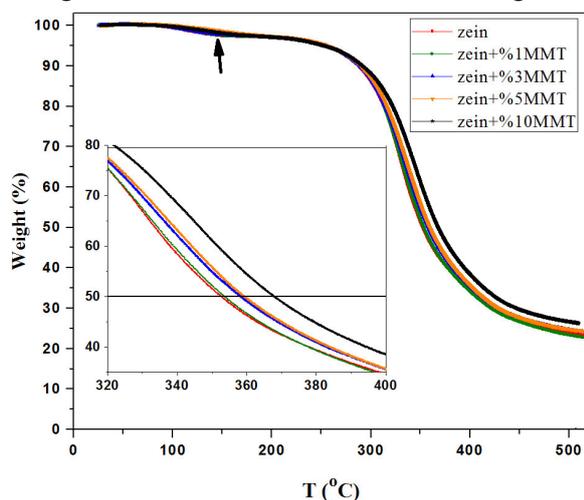


Figure 3. TGA curves of zein-MMT microcomposite films prepared using an ultrasonic bath. The arrow shows the weight loss of low molecular weight compounds. Inset shows an enlarged part of the curves from 320 to 400°C.

compounds such as plasticizer and solvent (70-180°C). Degradation of protein happens at the second stage in the temperature range of 270-430°C (inset Figures 3 and 4).

According to the statistical analysis, both methods of clay dispersion and MMT content significantly affected the thermal stability of the composite films. Temperature of 50% weight loss was higher in the nanocomposite films than microcomposite films for all percentages of MMT. As shown in Figure 3, the temperature at the point of 50% weight loss was on the increase from 353 to 368°C by increasing MMT percentage from 0 to 10% in the films with microcomposite structures. Non-uniform dispersion of MMT in the polymer network of the microcomposite films caused a slight increment in the thermal stability of these films.

According to Figure 4, by increasing MMT percentage from 0 to 10%, the temperature at the point of 50% weight loss was on the increase from 353 to 373°C, which can be attributed to the proper distribution of MMT layers acting as good thermal barriers in the protein network. Improvement of thermal stability in polymer nanocomposite was also caused by the

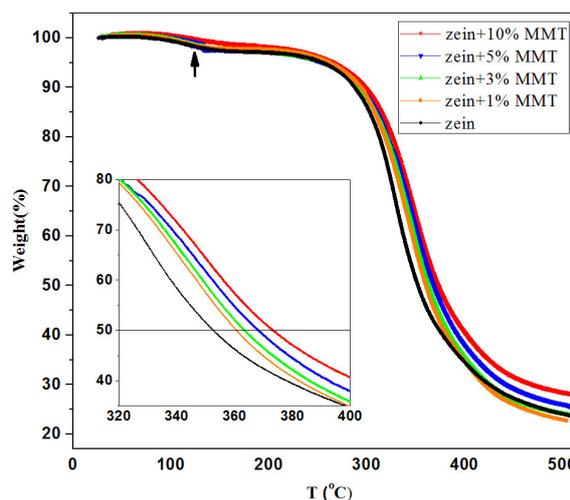


Figure 4. TGA curves of zein-MMT nanocomposite films prepared using a high power ultrasonic probe. The arrow shows the weight loss of low molecular weight compounds. Inset shows an enlarged part of the curves from 320 to 400°C.

increase in combustion gas diffusion pathway created from the dispersed MMT layers which acted as insulators. The delay in the mass loss in the nanocomposite was also in line with the related literature on gelatin/MMT nanocomposite films, wheat gluten/MMT nanocomposites, and polylactic acid MMT nanocomposites [3, 6, 9, 20].

CONCLUSIONS

This study showed that preparation of the composites using a high power ultrasonic probe is a more effective method to enhance the dispersion of nanoclays than the method in which composites are prepared using an ultrasonic bath. XRD patterns of the composite films prepared using a high power ultrasonic probe did not show any crystalline peaks because of the separation between MMT layers, thereby creating an exfoliated structure. However, as shown in the XRD patterns of the composite films prepared by an ultrasonic bath, the peak of the MMT was not shifted; so, the structure of the composites obtained by this technique was microcomposite. The results showed that MMT content and the method of clay dispersion method significantly affected the mechanical, water vapor barrier, and thermal properties of the composite films. Better dispersion of the montmorillonite layers in the polymer matrix resulted in better mechanical, barrier, and thermal properties in the zein films. These results indicated that the use of high power sonication could be a suitable method for producing protein-based nanocomposites with an exfoliated structure.

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پراکنندگی لایه های سیلیکات در فیلم های کامپوزیت زئین / مونت موریلونیت با استفاده از دو روش فراصوت

ز. داورپناه، ج. کرامت، ن. همدمی، م. شاهدی، و ط. بهزاد

چکیده

هدف از این پژوهش تهیه فیلم های کامپوزیت زئین / مونت موریلونیت با استفاده از حمام فراصوت و همزن فراصوت با توان بالا بود. سپس خصوصیات ساختاری، حرارتی، مکانیکی و ممانعتی کامپوزیت های حاصل ارزیابی شد. مطاق الگوهای پراش پرتو ایکس، فیلم های کامپوزیت تهیه شده به روش اول و دوم به ترتیب ساختار میکروکامپوزیت و نانوکامپوزیت ورقه ورقه داشت. براساس نتایج تجزیه و تحلیل آماری، روش پراکنش لایه های رس و میزان مونت موریلونیت تأثیر معناداری بر خصوصیات مکانیکی، ممانعتی و حرارتی فیلم های کامپوزیت داشت. نتایج نشان داد که خصوصیات مکانیکی و نفوذپذیری نسبت به بخار آب نانوکامپوزیت ها در حضور میزان ناچیز مونت موریلونیت (۳٪) بهبود یافت؛ در حالی که افزایش درصد مونت موریلونیت در فیلم های میکروکامپوزیت خصوصیات مکانیکی و ممانعتی را تضعیف کرد. بنابراین استفاده از امواج فراصوت با توان بالا یک روش مناسب برای تولید نانوکامپوزیت های پروتئینی با ساختار ورقه ورقه می باشد.