

Synthesis and properties of corn zein/montmorillonite nanocomposite films

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Abstract The objectives of this study were to apply fabrication techniques for the zein montmorillonite (MMT) nanocomposite films and characterize the obtained nanocomposite films. Zein MMT nanocomposite films were successfully produced from solvent casting and blown extrusion methods. The two methods could mix the zein MMT resulting in partially exfoliated nanocomposite structures according to X-ray diffraction and transmission electron microscopy. The thermal resistant of the zein nanocomposite films fabricated from both methods improved as the MMT content increased. However, the mechanical and barrier properties showed non-linear relationships with the MMT loadings. The impact of MMT on properties of zein films strongly depended on the preparation techniques. This can be the good starting point to further study in depth insight of the controllable MMT rearrangement in zein films which will remarkably improve zein film properties for packaging applications.

Introduction

Synthetic petroleum-based polymers have been used extensively especially in food packaging applications. However, they become a major source of solid waste due to their lack of degradability. The development of biodegradable polymers is a promising solution which has been growing interest during the past decades by the industry. Several biodegradable polymers have been studied including synthetic derived and natural renewable derived

polymers [1, 2]. Proteins are known as heterogeneous polymers. Their functionalities mainly depend upon their amino acids components [3, 4]. In general, the protein film formation involves partial denaturation of polypeptide chain by chemical and/or physical treatment which is followed by arrangement and orientation of the peptide chains and the formation of new bonds of partial denatured peptide chains. This results in the formation of protein matrix [2, 3]. Several plant and animal proteins have been studied for their film formation properties including wheat gluten, sorghum kafirin, peanut, corn zein, collagen, gelatin, fish myofibrillar protein keratin, egg white, casein and whey protein [1–4].

Zein, a major protein from corn, is obtained commercially from corn gluten meal (CGM) [5]. Zein has been proposed as a potential biodegradable packaging material among other cereal proteins. Zein films can be formed by different processes including solution casting and thermo-plastic processing. The solution casting involves dissolving zein in aqueous ethanol solution, casting or continuous spreading the solution to a non-sticky surface, and removing the solvent to obtain thin films [6]. Zein films can also be formed by precipitating zein solution in cold water and forming films by blown extrusion [7]. Zein stand alone films are found to be very brittle hence the plasticizers as oleic acid, palmitic acid, linoleic acid, glycerol, and polyethylene glycol are usually added to improve its elasticity [8, 9]. Use of plasticizers, chemical cross-linking, and laminating with other protein films are some of the methods which have been used to improve zein film properties [8, 10, 11].

However, production of zein films which is mechanically and physically close to synthetic films still remains as a challenging procedure. Therefore, it is necessary to find a new strategy to improve zein film properties to increase its use as food packaging material. Recently, polymer layered

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silicate nanocomposites (PLSN) technique has become attractive to many researchers which can improve mechanical, physical, thermal, and barrier properties of various types of polymer [12–15].

PLSN technique has been used to enhance mechanical and barrier properties of synthetic polymers [16–18]. The most commonly used nanoclays are montmorillonite (MMT), hectorite, and saponite. Natural nanoclay is hydrophilic, in order to use nanoclay with hydrophobic polymer, an organically modification is applied. It is believed that by including small amount (<5 wt%) of nanoclay could result in an increase in tensile strength and thermal stability and slower gas diffusion in the treated polymer [18]. The degree of improvement depends on the polymer-nanocomposite structure and the distribution of MMT platelets in polymer matrix [18]. For instant, the decrease in water vapor permeability of polymer nanoclay nanocomposite films is mainly attributed to the tortuous path. Water vapor diffusion due to the impermeable nanoclay layers distributed in the polymer matrix consequently increases the effective diffusion path length [19]. In terms of thermal properties, nanoclay was believed to act as insulators and mass transport barrier to the volatile compounds generated during the polymer decomposition process [20]. PLSN technique has been recently applied to some protein-based polymers including soy protein isolate [13, 21], wheat gluten [15], whey protein [13], and gelatin [22, 23].

There are a great number of ways to form PSLN including in situ polymerization, solution, and melt processing [16–18]. The melt processing has become very attractive as it could completely exfoliate nanoclays [24]. This process involves heating the polymer and nanoclays above the glass transition temperature of the polymer with or without the aid of shearing force. The PSLN formation strongly depends on the thermodynamic interaction between the polymer segments and the nanoclay surface [25]. Therefore, it is still a challenge to create suitable methodology for fabricating polymer-nanoclay hybrid which could result in great properties improvement.

To the best of our knowledge, there is no study in the literature on the synthesis of zein nanoclay nanocomposite films. Therefore, the objectives of this study were to prepare zein nanoclay nanocomposite films and characterize the structure and properties of the obtained films. Modified MMT was the nanoclay that used in this study and the term MMT will be used in the rest of this paper. There were two methods that were developed for fabricating zein MMT nanocomposite films; the solvent casting and blown extrusion. The solvent casting was a basic film preparation technique. On the other hand, the blown extrusion involved precipitating zein protein from solution into zein resin (above glass transition temperature of zein mixture) and blowing into zein balloon, which resembled the melt

intercalation method. This technique has been designed to avoid zein decomposition from high temperature [7]. After that, the structure and properties of the zein MMT nanocomposite films were investigated.

Experimental

Materials

Zein powder (90% crude protein dry weight basis) was purchased from Sigma-Aldrich (Milwaukee, WI, USA). The MMT clay used in this study was Nanomer® I.34 TCN, which is surface-modified MMT containing 25–30 wt% methyl dihydroxy ethyl hydrogenated tallow ammonium. The Nanomer® I.34 TCN was supplied from Sigma-Aldrich (Milwaukee, WI, USA). Polyethylene Glycol 600 (PEG) was purchased from Alfa Aesar (Ward Hill, MA, USA) and Glycerol (GLY) was purchased from Fisher Scientific Inc. USA. Ethanol (95%) was purchased from Decon Laboratories Inc. (King of Prussia, PA). Magnesium nitrate, anhydrous phosphorous pentoxide, and oleic acid were obtained from Sigma-Aldrich (Milwaukee, WI, USA).

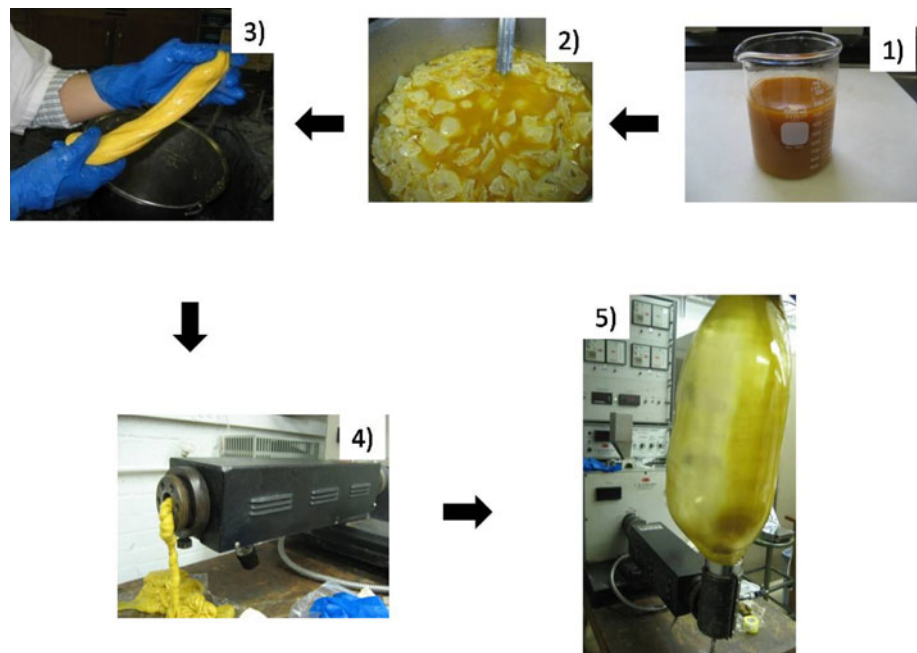
Zein/MMT nanocomposite films preparation techniques

Two different preparation techniques, solvent casting and blown extrusion, were used for fabricating zein MMT nanocomposite films. The plasticizers used in each preparation methods were different regarding the compatibility of the plasticizers to each method. Polyethylene glycol and glycerol were used in solvent casting method, whereas oleic acid was used in blown extrusion method.

In solvent casting method, zein MMT nanocomposite films were prepared with 0, 1, 3, 5, and 10 wt% modified MMT (noted SC-0 to SC-10). In this process, 8 g of zein, 0.12 g of PEG, and 0.12 g of GLY were dissolved in 40 mL of warm (45–50 °C) 75% aqueous ethanol solution. The certain amount of MMT was dissolved separately in 12 mL of 75% ethanol solution and sonicated for 5 min. The two mixtures were then mixed together and heated until 60 °C. The ratio of zein to ethanol solution was 1:6.5 (w/v). The zein MMT mixture was then sonicated for 2 min before casting. The ready solution was poured onto a Petri dish and left dried for 24 h at room temperature.

The blown extrusion films were prepared with 0, 1, 3, and 5 wt% modified MMT (noted as BE-0 to BE-5). The blown extrusion technique, as shown in Fig. 1 was adapted from Wang and Padua [7]. It is composed of two major steps: (i) resin formation (steps 1–3 in Fig. 1) and (ii) film formation (steps 4–5 in Fig. 1). The resin was formed by first dissolving 100 g of zein, 30 g of oleic acid, and certain

Fig. 1 The steps of the blown extrusion technique including 1 zein MMT solution, 2 precipitation, 3 resin formation, 4 cold extrusion, and 5 balloon formation



amount of MMT in 650 mL of ethanol solution. The mixture was stirred for 10 min after they reached 60–65 °C. Then, the solution was poured into an ice water bath for precipitation. The precipitate zein was collected and then formed into dough-like resin. The resin was hand kneaded until it was not sticky. To get rid of the excess water, the resin was passed 4 times through a single screw extruder (Model EPL-V501, C.W. Brabender, Hackensack, NJ). No heat was applied during the extrusion process. Zein resin was extruded to a balloon by the help of a blowing head. However, the sample with 5% MMT could not form into a balloon since the high amount of MMT has reduced the extensibility of the resin which could not facilitate balloon formation. The small piece was obtained from this sample which was enough just for a structure characterization. Uniform sampling from each type of films was done by measuring thickness with digital calipers. The thicknesses of the films were 0.04–0.08 mm for both cast film and blown films.

Characterization

X-ray diffraction (XRD) patterns were carried out by Rigaku D/Max diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a generator voltage of 45 kV and a generator current of 20 mA. The samples were scanned in the range of diffraction angle of $2\theta = 2^\circ\text{--}10^\circ$ at a rate of $0.48^\circ/\text{min}$.

Transmission electron microscope (TEM) was used to investigate the nanocomposite structure of the film samples. The film samples were fixed with a series of fixative

agents including Karnovsky's fixative, osmium tetroxide, potassium ferricyanide, and uranyl acetate, then dehydrated in an ethanol gradient, and embedded in epoxy resins. The ultra thin sections were cut with an ultramicrotome diamond and mounted on holey carbon grids. The samples were characterized by Phillip CM12 TEM (Mahwah, NJ) at 120 kV.

Measurements

Thermogravimetric analysis (TGA) was used to monitor the effect of MMT content on thermal properties of zein MMT nanocomposite films. The TGA was performed on Q50 TGA (TA instruments, Delaware, USA) in nitrogen atmosphere. The samples were heated from room temperature to 500 °C at a heating rate of 10 °C/min.

The tensile strength (TS) and percentage of elongation at break (%E) of films were determined using TA.HD Texture Analyzer (Stable Micro Systems, Surrey, UK) with a 30 g load cell. The films were cut into 2 cm by 7 cm strips and the samples were conditioned for 48 h at 52% relative humidity at 25 °C before analysis. The cross-head speed was 1 mm/min.

The water vapor permeability was measured using modified ASTM method. The film samples with 0.06 ± 0.018 mm thick were conditioned at 52% relative humidity (RH) and 25 °C for 48 h before testing. Each specimen was sealed by vacuum grease and 4 screws on Plexiglas cups containing 8 mL of distilled water each. The cups were 50 mm (inner diameter), 80 mm (outer diameter) and 10 mm (depth) with an exposed film area of

1964 mm². The cups were placed in desiccators containing a desiccant (phosphorus pentoxide), thus creating the RH gradient of 100%. The sample cups were weighed using four-digit balance every hour over 8-h period until the steady state of vapor flow was reached. The weight loss of sample cups was plotted over time. At least three samples of each film were tested and the test temperature was 25 ± 2 °C. The water vapor transmission rate (WVTR) was obtained from:

$$WVTR = \frac{\text{slope}}{\text{area}} (\text{g/days m}^2) \tag{1}$$

where slope is the slope of the linear regression of weight lost versus time (g/d) and area is an open mouth area of the cup (m²).

The water vapor permeability (WVP) was calculated from the following equation:

$$WVP = \frac{WVTR \times d}{(\Delta P)} (\text{g mm/days m}^2 \text{ kPa}) \tag{2}$$

where ΔP is the difference water vapor partial pressure across the test cups (kPa) and d is the film thickness (mm).

Fig. 2 Photographic pictures of zein MMT nanocomposite films prepared from solvent casting method (SC = solvent casting method, number = MMT content (wt%))

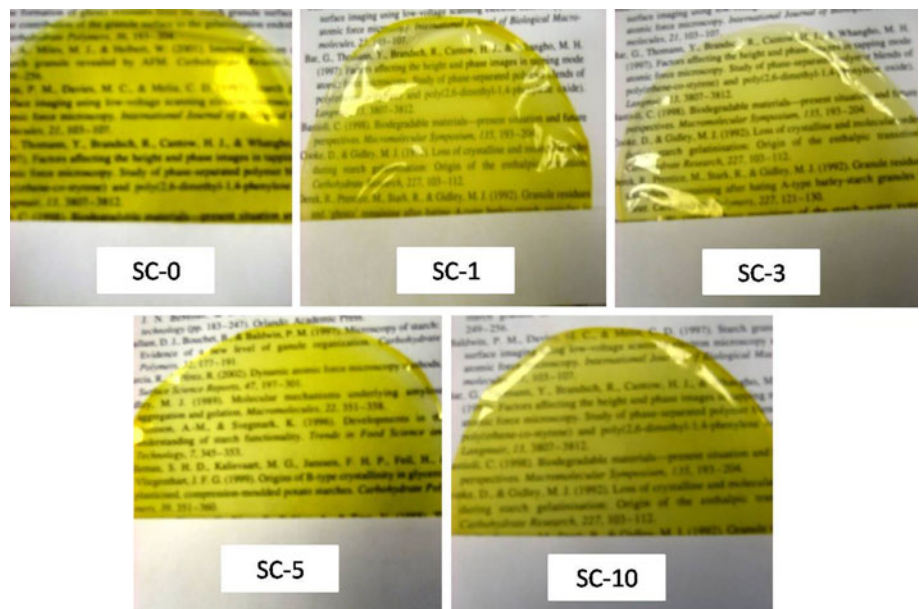
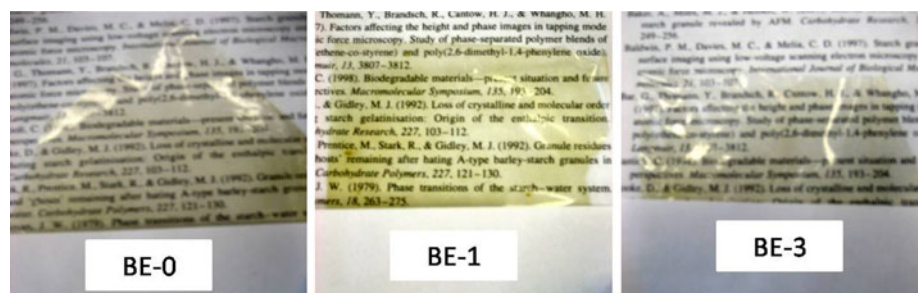


Fig. 3 Photographic pictures of zein MMT nanocomposite films prepared from blown extrusion method (BE = blown extrusion method, number = MMT content (wt%))



Results and discussion

Characterization of zein MMT nanocomposite films

The zein MMT nanocomposite films prepared by both solvent casting and blown extrusion methods are displayed in Figs. 2 and 3. The film samples obtained from both methods are glossy yellowish and translucent. It is clearly seen that MMT content do not affect the translucency of the films prepared from both techniques. Similar observation was found by Chang et al. [26] that the inclusion of MMT and synthetic mica (at 4–6 wt%) did not influence the translucency of the polylactic nanocomposite films as the disperse phase of MMT and synthetic mica had an average size smaller than the wavelengths of light.

The XRD patterns of solvent cast and blown extruded zein MMT nanocomposite films are shown in Figs. 4 and 5, respectively. The interlayer spacing was calculated from the diffraction peak using Bragg’s equation ($n\lambda = 2d \sin \theta$) It can be seen that the Nanomer® I.34TCN MMT had diffraction peak at 4.8° 2θ with the interlayer spacing of 18.27 Å (peak f of Fig. 4 and peak d of Fig. 5) which was in

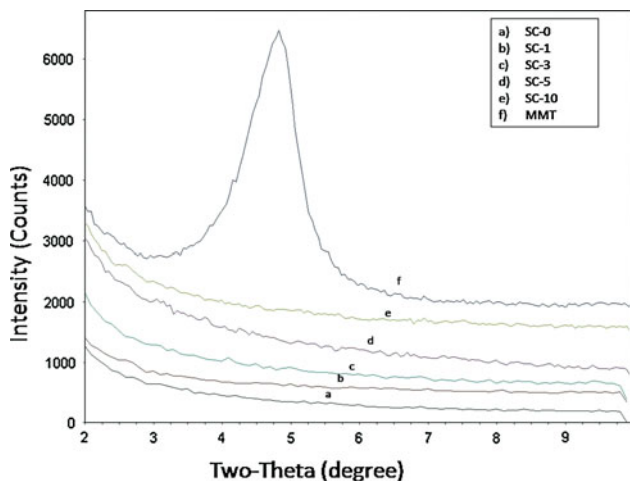
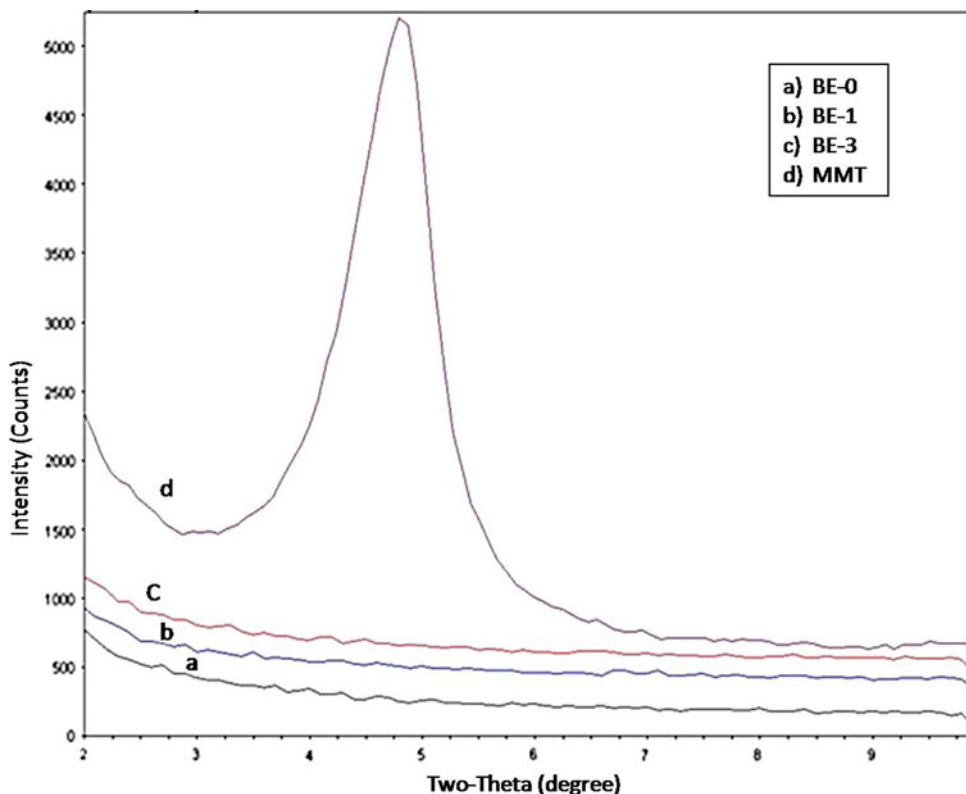


Fig. 4 XRD patterns of various MMT contents of zein nanocomposite films prepared by solvent casting method

agreement with the literature (19 Å) [27]. It is also found that the MMT peaks were absent in the XRD patterns of the hybrid films prepared from both techniques regardless of MMT content. The vanishing of MMT peaks can be a result of the lost of interlayer association which means that the MMT layers become apart or the MMT interlayer becomes larger than the XRD detection limit [28]. Moreover, there are some other factors which can also cause MMT peaks to vanish in XRD pattern including loss in periodicity of MMT

Fig. 5 XRD patterns of various MMT contents of zein nanocomposite films prepared by blown extrusion method



[29]. Therefore, the XRD result alone could only imply the possibility of some degree of exfoliated nanocomposite structure presented in zein MMT hybrid cast and extruded films.

Along with the XRD results, the dispersion of MMT platelets in zein nanocomposite films prepared from solvent casting and blown extrusion were also visually investigated using TEM (Fig. 6a, b). The TEM images of zein hybrid films prepared from both techniques show dark streaks of MMT platelets dispersed in zein matrix (light background). It is clearly seen that the single platelets were observed together with multilayered nanostructure within the zein matrix. This indicated some degree of MMT exfoliation and intercalation in zein matrix regardless of the preparation technique used.

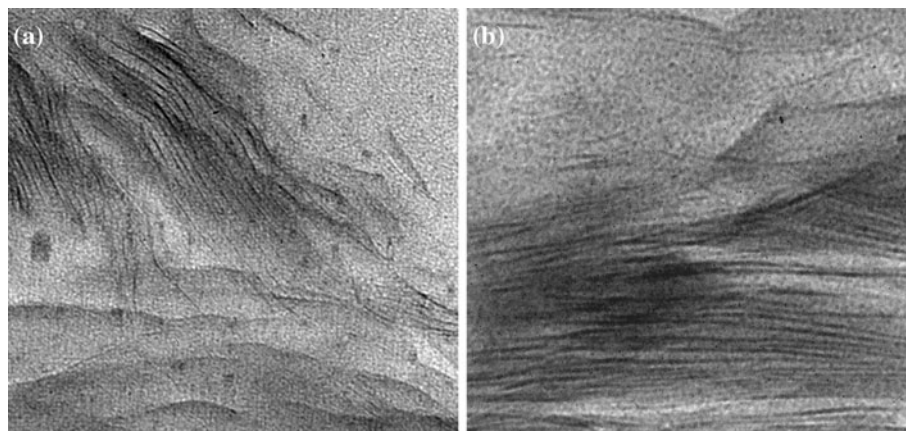
The combination of XRD and TEM results suggested that the zein MMT nanocomposite film prepared from solvent casting and blown extrusion techniques could lead to the formation of partially exfoliated nanocomposite structure.

Measurements of zein MMT nanocomposite film properties

Thermal stability

The TGA was used to investigate the thermal stability of zein MMT nanocomposite films by measuring loss of mass

Fig. 6 TEM images of **a** solvent cast zein MMT nanocomposite films with 5 wt% of MMT, and **b** blown extrusion zein MMT nanocomposite films with 5 wt% of MMT



which is caused by the volatile compound formation after thermal degradation as a function of temperature. The TGA curves as shown in Figs. 7 and 8, in general, exhibit two

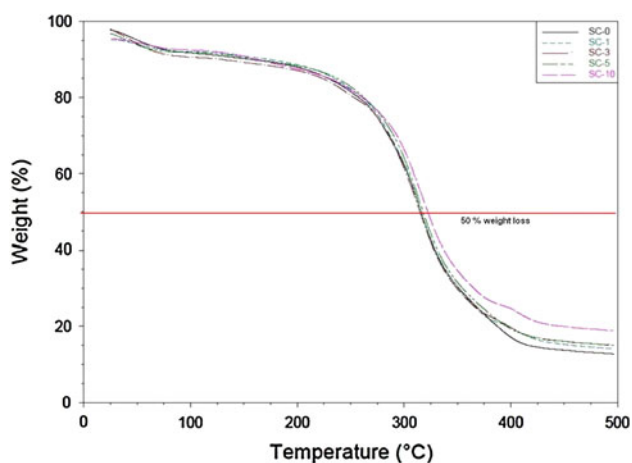


Fig. 7 Effect of MMT contents on TGA curve of zein MMT nanocomposite films prepared by solvent casting method

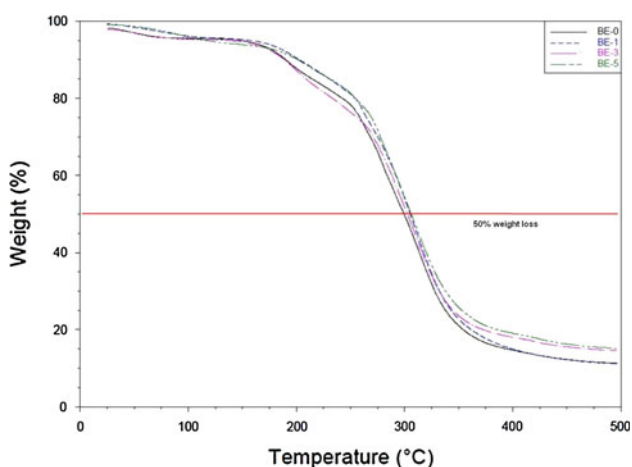


Fig. 8 Effect of MMT contents on TGA curve of zein MMT nanocomposite films prepared by blown extrusion method

stages of thermal degradation under inert condition. The first stage corresponded to the loss of low molecular mass compounds, i.e., plasticizers and solvent from 70 to 200 °C. The second stage (250–300 °C) was associated with the protein degradation.

It is believed that the temperature at which the polymer starts to degrade is the most important criteria to evaluate the thermal stability of polymer [23]. In this case, the temperature at which the weight loss of 20% occurred was focused. The temperature at 20% weight loss of zein MMT nanocomposite films prepared by solvent casting (Fig. 7) increased as the MMT content increased. The sample with 10 wt% MMT loading lost its 20% weight at about 10 °C higher than the unfilled sample. The remarkable impact of MMT on thermal stability of zein film was found in samples prepared by blown extrusion (Fig. 8). The temperature at 20% weight loss dramatically increased as the MMT loading increased. The inclusion of only 5 wt% MMT could delay about 10 °C. The delay in the mass loss in nanocomposite was also in accordance with the literatures including gelatin/MMT nanocomposite films [22], wheat gluten/MMT nanocomposites [15], and polylactic acid MMT nanocomposites [30]. The improvement of thermal stability in polymer nanocomposite is caused by the increase in combustion gas diffusion pathway created from the dispersed MMT layers which act as insulators [16].

It was shown that the zein MMT films prepared by blown extrusion were more sensitive to MMT loadings than the samples prepared by solvent casting. This could indicate that the MMT platelets were well-distributed within zein polymer by blown extrusion method. So the nanoclay platelets provided thermal barrier throughout the zein matrix and eventually delayed the thermal degradation of zein films.

This could suggest that the MMT content influenced the thermal stability of zein films. Moreover, the blown extrusion technique could provide highly dispersed and distributed MMT layers within zein polymer matrix which led to greatly thermal stability improvement.

Mechanical properties

Mechanical properties of zein MMT nanocomposite films prepared by solvent casting and blown extrusion methods were represented in Figs. 9 and 10, respectively. The general trend for both film production techniques was similar. As MMT increased, there was an increase in the elastic modulus. The zein MMT nanocomposite films prepared by solvent casting were quite brittle as compared to blow extrusion films. The brittleness of the cast films has been attributed to its glass transition temperature which is close to material temperature (room temperature in this

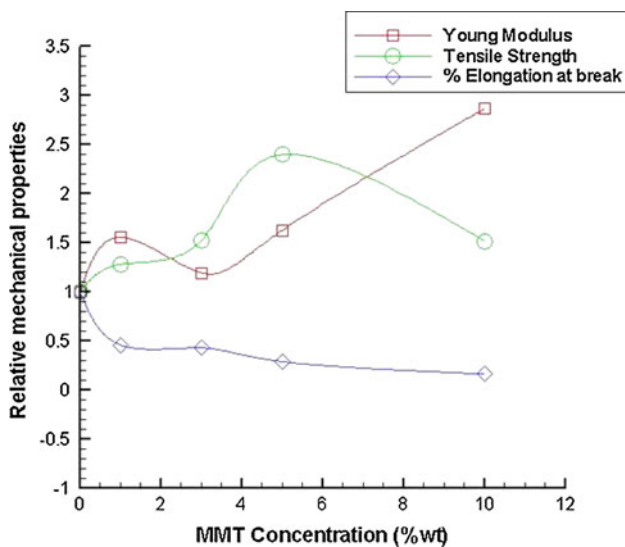


Fig. 9 Effect of MMT contents on the relative mechanical properties of zein MMT nanocomposite films prepared by solvent casting method

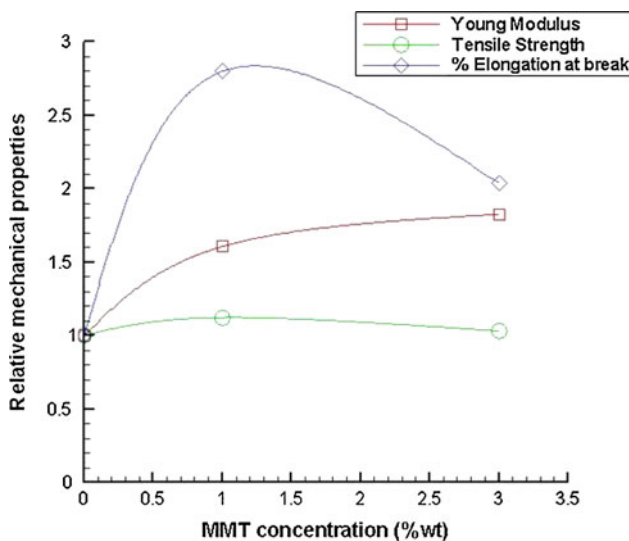


Fig. 10 Effect of MMT contents on the relative mechanical properties of zein MMT nanocomposite films prepared by blown extrusion method

case) [31]. The glass transition of the solvent casting zein MMT nanocomposite films as measured by modulated differential scanning calorimeter (data not shown) was around 36 °C. In order to obtain more ductile films, the higher level of plasticizers should be applied to the formula [32]. The effect of MMT content on mechanical properties of zein MMT nanocomposite films prepared by solvent casting was expressed in the relative values to the control film (SC-0) as shown in Fig. 9. The zein MMT nanocomposite films (SC1–SC10) had greater Young’s modulus and tensile strength than SC-0. It is obvious that it was not a linear relationship between the test values and MMT concentrations. The tensile strength which is the maximum tensile stress that the sample is capable of carrying, improved the most in SC-5 (2.5 times greater than SC-0) then leveled off in SC-10. The same observation was found in wheat gluten nanocomposite films prepared from solvent casting [15] and gelatin nanocomposite films [27]. This indicated the solvent casting technique has a critical MMT percentage where the dispersion of MMT is better. It could be concluded that at 5 wt% of MMT is the optimal level which could lead to a good interaction between MMT and zein matrix prepared by solvent casting and resulted in high tensile strength. In contrary, the percentage elongation at break values of zein MMT nanocomposite films dropped as the MMT level increased.

The zein MMT nanocomposite films prepared from blown extrusion, on the other hand, were not as brittle as the samples prepared by solvent casting. The relative mechanical properties blown extrusion nanocomposite films were slightly greater than of unfilled sample (Fig. 10). Unlike solvent casting nanocomposite films, the blown extrusion nanocomposite films had higher elongation at break than the control films, especially at 1 wt% MMT loading (~3 times). The extrusion process caused entanglement of zein molecules [33] which could result in zein network formation that corresponded to the better elongation than in samples prepared from solvent casting method.

Water vapor permeability

The WVP of zein MMT nanocomposite films prepared by solvent casting and blown extrusion is shown in Table 1. The WVP decreased as the MMT content increased up to SC-5 then the WVP rose up to be higher than control sample (SC-0) in SC-10. The WVP decreased the most about 60% in SC-3. In contrast, the blown extrusion samples showed that the WVP of filled sample was lower than the unfilled one. The BE-1 showed the lowest WVP. It is obvious that the improvement in barrier properties has a non-linear relationship with the MMT contents in samples prepared from both solvent casting and blown extrusion methods.

Table 1 Water vapor permeability (WVP) of zein nanocomposite films

Sample	WVP (g mm/days m ² kPa)
SC-0	11.58 ± 1.59
SC-1	7.17 ± 0.82
SC-3	4.56 ± 1.02
SC-5	10.20 ± 1.56
SC-10	14.80 ± 0.86
BE-0	8.15 ± 2.2
BE-1	4.77 ± 1.33
BE-3	6.27 ± 0.26

Properties are given with their standard deviation values

The improvement of water vapor barrier property of zein MMT nanocomposite films is due to the impermeable MMT layers distributed in the polymer matrix consequently increases the effective diffusion path length [19]. The level of improvement depends not only on the nanocomposite structure (intercalated, exfoliated or some intermediate) but also greatly depends upon the relative orientation of the sheets in the matrix. The MMT layers orientation which can result in highest tortuosity occurs when the MMT layers arrange perpendicular to the direction of diffusion. Any kind of deviation from those arrangements could result in inferior in barrier properties [34]. It could be that the solvent casting and blown extrusion techniques were able to exfoliate the MMT layers, but could not orient the layers alignment in the way that could have great impact on the barrier properties of the nanocomposite films.

Conclusions

The solvent casting and blown extrusion techniques have been applied to fabricate zein MMT nanocomposite films. The effects of MMT contents on their properties were also investigated. Solvent casting method was able to partially exfoliate MMT as monitoring by XRD and TEM. The thermal stability of cast zein MMT films improved as MMT content increased. However, the improvement of mechanical and barrier properties of the films were not in linearly relationship with MMT content. The critical MMT content which could result in tensile strength improvement was at 5 wt%, while it was at 3 wt% for water vapor permeability. The blown extrusion technique could fabricate thin zein MMT nanocomposite films, but the limitation of this technique was that it could apply at low amount of MMT (1–3 wt%). This technique could also result in partially exfoliated nanocomposite structure. The thermal resistant of the films increased dramatically with the MMT

content. Like solvent casting, the effects of MMT loadings on the mechanical and barrier properties of the films were non-linear relationships.

It is recommended that the selection of the preparation technique to prepare zein MMT nanocomposite films should base on the desire final properties of the nanocomposite films. The blown extrusion technique is good for preparing zein MMT nanocomposite films with thermal resistant improvement. On the other hand, the solvent casting technique can be used for preparing zein MMT nanocomposite films with improved tensile strength. These novel approaches should provide a better understanding of the mixing processes that can exfoliate some of the MMT platelets in zein protein which result in properties improvement.

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