The physical properties of zein nanoclay hybrid resin as a base for zein nanoclay nanocomposite films

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ABSTRACT

From our previous study, zein nanoclay nanocomposite films were successfully prepared by blown extrusion method. This method involved two main steps; i) formation of zein resin and ii) formation of zein film by blowing. The structure analysis of the nanocomposite films prepared by this method suggested partially exfoliated nanocomposite structure. However, the tensile and barrier properties of zein nanoclay hybrid films were not found to improve at the percentages used. The amount of nanoclay included in the zein resin had a percentage limit (< 5 wt %) during blown extrusion. The insufficient extensibility of the zein nanoclay resin caused rupture of the film during blowing after the critical level. Therefore, it is important to understand the interaction between zein and nanoclay in the resin form in order to design the proper preparation method. The objectives of this study were to understand the interaction of zein-nanoclay mixture in the resin form by characterizing the physical properties including extensional rheology of the hybrid resin using dough inflation system for the first time. It was found that the nanoclay was delaminated and dispersed within the zein matrix as shown in the TEM image. The extrusion played important role in mixing the nanoclay in zein resin but at certain amount of nanoclay content. The critical nanoclay content which improve the extensional properties of the zein hybrid resin without sacrificing the processability was below 5 wt% which was inconsistent with previous work. The measurement of extensional rheological properties of zein resin using dough inflation still requires testing parameters adjustment. These findings can be useful for adjusting the blown extrusion process to produce improved mechanical and film barrier properties. The incorporation of nanoclay within the biopolymer matrix provided a novel pathway to engineer mechanically durable and biodegradable packaging films.

Keywords: zein, nanoclay, nanocomposites, dough inflation system, extensional rheology

1 INTRODUCTION

The waste of petroleum-based packaging materials has become the worldwide major environmental concern. Therefore, the biodegradable materials derived from renewable resources have become under spot light as a potential approach to reduce the packaging material waste problems. Zein, a protein found in corn, is one of the potential bio-based materials which have been studied extensively. Similar to other biopolymers, corn zein films have poorer mechanical and barrier properties in comparison with other petroleum-based films [1]. To improve zein film properties, the polymer nanoclay nanocomposite technique was introduced to zein film preparation. The polymer nanoclay nanocomposite technique involves the intercalation/exfoliation of several layers of ~ 1 nm thick clay platelet in the polymer matrix which then improve the mechanical properties and barrier properties of the polymers by means of the high aspect ratio of dispersed nanoclay platelets in polymer matrix [2]. In previous study [3], zein nanoclay nanocomposite films were formed by extrusion blowing technique which comprises of the zein resin formation and zein bubble formation steps. It was shown that the blown extrusion could prepare zein nanoclay nanocomposite films with the partially exfoliated nanocomposite structure, however, the zein nanoclay hybrid resin failed to form bubble at the 5 wt% of nanoclay. The failure to form zein bubble after a certain nanoclay loading indicated the effect of nanoclay on the zein resin rheological properties which finally would have impact on the quality of the zein-nanoclay nanocomposite film. The role of nanoclay on rheological properties of polymer melt systems has been studied extensively in several polymers as reviewed by Shinha Ray [4]. It was believed that the rheological properties of nanocomposites strongly depend on the interaction of polymer and nanoclay based on the interfacial interactions at the nanoscale. For instance, in the uniaxial small elongational flow study, the Polylactide (PLA) nanocomposites exhibited great value of viscosity and tendency to have strong strain-induced hardening as a result of the nanoclay alignment 90 degree towards the extension direction. However, this was not hold true for every polymer [4]. Therefore, it is essential to investigate the role of nanoclay on rheological properties of zein resin in order to gain fundamental understanding of the processability of zein nanoclay nanocomposite films.

The dough inflation system has been useful for monitoring large biaxial extension of bread dough resembling the deformation in the real breadmaking conditions [5]. This new dough rheology testing apparatus was developed by Bogdan Dobraszczyk and Clive Roberts at the University of Reading in conjunction with a texture analyzer company, Stable Micro System [6]. The extensional flow measurement is always difficult to evaluate as a result of the high deformation level, nonuniformity within the structure and difficulties in converting the strain to the machine displacement. Therefore, the calculation of changes in sample dimension is essential [5]. The stability of the bubble studied by this system was directly related to the elongational strain hardening properties of the bread dough [6]. Strain hardening is the phenomena in which the materials can maintain their stability before failure during deformation [5]. The strain hardening is noticed as an increase in slope of the plot of stress (σ) versus Hencky strain (ε) where $\varepsilon = \ln (L/L_0)$; L= initial sample length and L_0= instantaneous sample length. For the materials in which obey a power law $\sigma=K\varepsilon^n$, the strain hardening index (n) can be obtained. It has been proved that the strain hardening obtained from dough inflation system correlated with the bubble failure strain [6]. The downsides of this system are that the large amount of sample is required; the measurement is destructive; and the well-defined and accepted method of measurement has not been established [5]. It has been known that the large extensional viscosity of the food materials plays an important role in several food processing events including extrusion, sheeting, molding, fiber formation, adhesion and bubble expansion [5]. Therefore, it is challenging to evaluate the biaxial extensional rheological behavior of the zein nanoclay hybrid resin in the similar manner of the film formation process. In this pioneer study, the observation on the extensional rheological properties of zein resin as affected by nanoclay loadings and extrusion were investigated by using dough inflation system.

2 MATERIALS AND METHODS

Zein powder (90% crude protein dry weight basis) was purchased from Sigma Aldrich (Milwaukee, WI, USA). The Nanomer ® I.34 TCN which was surface-modified nanoclay containing 25-30 wt. % methyl dihydroxy ethyl hydrogenated tallow ammonium and oleic acid were supplied from Sigma Aldrich (Milwaukee, WI, USA). Ethanol (95%) was purchased from Decon Laboratories Inc. (King of Prussia, PA).

2.1 Zein nanoclay hybrid resin preparation

The zein nanocomposite resins were prepared by first, dissolving 100 g of zein, 30 g of oleic acid and certain amount of nanoclay (0, 3, 4, 5, and 9 % w/w of zein.) in 650 ml of ethanol solution. The mixture was stirred for 10 minutes after they reached 60-65^{o}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 and labeled as fresh resin. Another set of resins prepared from the same manner was then passed four times through single screw extruder (Model EPL-V501, C.W. Brabender, Hackensack, NJ) and labeled as extruded resin.

2.2 Characterization

Transmission electron microscope (TEM) of the hybrid resin was carried out by Phillip CM12 TEM (Mahwah, NJ) at 120 KV.

The extensional rheological properties of zein nanoclay hybrid dough were obtained by the method described by Dobraszczyk [6]. The zein resin sheet preparation was done by rolling the zein resin to a required thickness and cutting into a certain round shape by cookie dough cutter provided by the dough inflation system. The sheet of zein resin was inflated at room temperature on the dough inflation system connected to a texture analyzer (TA.HD. Plus, Stable Micro Systems Ltd., Godalming, UK). The sheet of zein nanoclay hybrid resin was inflated by volume displacement of air. The pressure during inflation was monitored by pressure transducer and the volume of the bubble was calculated from the piston displacement. The experiment set up is shown in Figure 1. The dough inflation system can carry out several parameters including bi-axial extensibility (the length of the curve up to the point of rupture), L (mm); tenacity (the maximum pressure required during inflation of the bubble), P (mm); ; deformation energy (the energy necessary to inflate the ; strain hardening index, n; and stress (KPa) at bubble failure. The typical result of an inflating dough bubble is shown in Figure 2. The strain hardening of bread dough can be observed in stress-Hencky strain curve as its slope increases with increasing extension which indicates that the material is stiffened as the extension goes on. The more curvature of the curve indicates the greater the strain hardening of the materials [5]. Three samples of each treatment were measured.

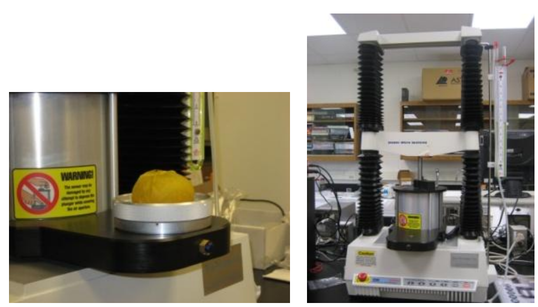

Figure 1: Extensibility testing of zein nanoclay resin using dough inflation system.

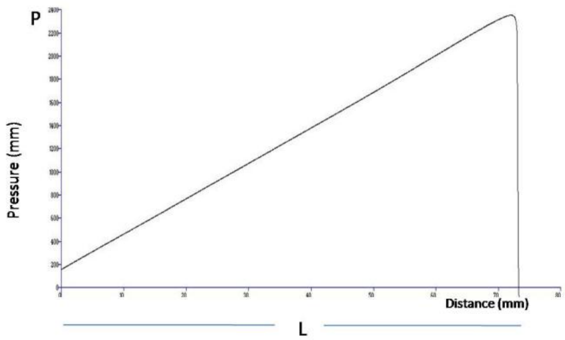

Figure 2: Typical dough inflation result of inflating dough bubble.

3 RESULTS AND DISCUSSION

The structure characterization of zein nanoclay hybrid resin was obtained from TEM as shown in Figure 3. It is clearly seen that at 9 % of nanoclay, the nanoclay platelets exfoliated in fresh zein resin. This has confirmed that the well-dispersion of nanoclay can occur at the resin formation step. We believe that the abrupt conformational change of zein protein during precipitation delaminate the stacking structure of nanoclay. A similar approach has been observed in polymer nanoclay nanocomposites prepared by in situ polymerization.

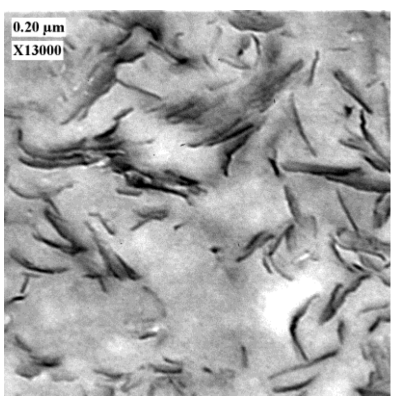

Figure 3: TEM images of zein nanoclay hybrid resin at nanoclay content of 9 wt. %.

Figure 4 and 5 show the tenacity and biaxial extensibility parameters which are obtained directly from the measurement. It is obvious that extrusion dramatically influences the biaxial extensional behavior of zein resins. The extrusion process creates entanglement of zein molecules which facilitates zein network formation that corresponds to the high elongational behavior [7]. It is seen that nanoclay improved the tenacity of the extruded zeinanoclay hybrid resins. Samples with 3 and 4% nanoclay loadings exhibited relatively higher tenacity values among other samples.This impact was not noticeable for fresh samples (Figure 4). At high percentage of nanoclay (9 %), the hybrid resins exhibited poorer tenacity. The similar trend was also found in the bi-axial extensibility values (Figure 5). The bi-axial extensibility improved by extrusion. The inclusion of nanoclay content increased the bi-axial extensibility of both fresh and extruded zein nanocomposite resins up to 4 % then the values declined by further increase in clay content. At nanoclay content greater than 5 %, zein nanoclay hybrid resin obviously lost its extensibility which was in agreement with Luecha et al. [3] where they found that the bubble could not be formed above 5% nanoclay content [3].

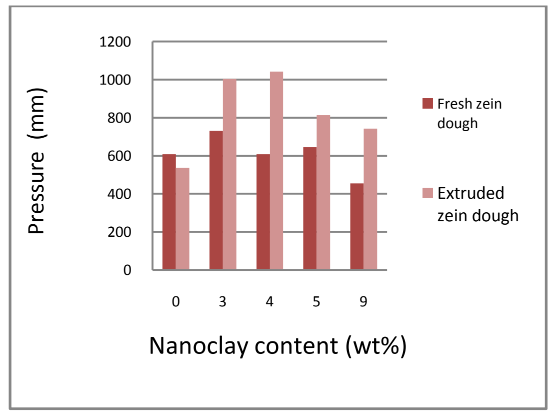

Figure 4: The tenacity of fresh and extruded zein dough at various nanoclay contents.

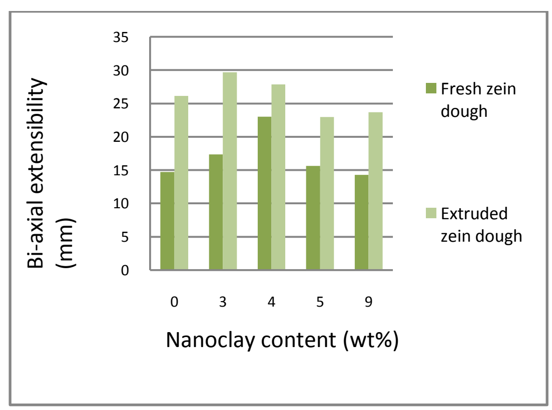

Figure 5: The biaxial extensibility of fresh and extruded zein dough at various nanoclay contents.

Figure 6 shows the stress at bubble failure. The extruded samples were capable of holding higher stress before rupture occurred. Moreover, extrusion definitely assisted the mixing of nanoclay in zein matrix and formed into strong resin as the stress at bubble failure increased extensively at the addition of nanoclay of 3 and 4 % then leveled off in the samples containing 5 and 9 %.

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The strain hardening index of zein nanoclay hybrid resins are shown in Figure 7. Surprisingly, the nanoclay content and extrusion did not have distinct impact on the strain hardening index as was first expected.

The zein nanoclay hybrid resins exhibit great variation in rheological properties among samples which caused the testing parameters adjustment more difficult. The inconsistencies were highestin the fresh resin withhigh amount of water. Some of the fresh samples were too sticky that could not be lifted from the base of the retainer even though the oil was applied to prevent stickiness. In contrary, some of the extruded resins were very elastic that the bubbles did not fall even though the rupture had occurred. This might influence the strain hardening index calculations.

The extensional rheological properties of thermoplasticized zein as a material for extrusion blown films have been studied by Oliviero et al. [8], by using rheometer equipped with elongational tool. The mixture of zein and plasticizer were mixed at high temperature to form thermoplasticized zein material which was then blown into bubble by extrusion blowing technique. At the small deformation levels, they found that the strain hardening parameter which was obtained from the slope of the transient elongational viscosity versus time curve at the region of rapid deformation could be an indicator for blown film process. The higher the strain hardening of the thermoplasticized zein the better the blown film formation characteristics [8].

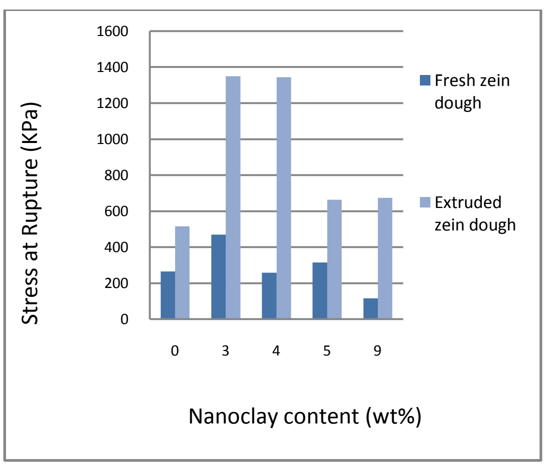

Figure 6: The stress at bubble failure of fresh and extruded zein dough at various nanoclay contents.

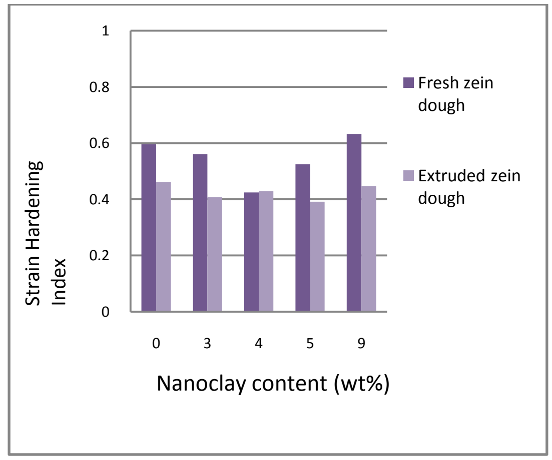

Figure 7: The strain hardening index of fresh and extruded zein dough at various nanoclay contents.

4 CONCLUSIONS

The dough inflation system was used for characterizing zein nanoclay hybrid resin for the first time. The extensional rheology of the zein resin was greatly influenced by extrusion. At nanoclay contents around 3 to 4% were the best loading range that could improve the zein resin properties as well as facilitate the blown film processing.

REFERENCES

[1] H. -M. Lai and G.W. Padua, Cereal Chem. 74: 771-775, 1997.

[2] M. Alexandre and P. Dubois. Material Science and Engr.28: 1-63, 2000.

[3] J. Luecha, N. Sozer, and J.L. Kokini, Journal of Material Science [accepted] 2010.

[4] S. Shinha Ray, Journal of Industrial Engineering Chemistry., 12, 811-842, 2006.

[5] B. Dobraszczyk, J. Smewing, M. Albertini, G. Maesmans, and J. D. Schofield. Cereal Chemistry, 80, 218-224, 2003.

[6] B. Dobraszczyk, Cereal Foods World, 42, 516-519, 1997

[7] M. Lau, “Effect of mechanical energy and moisture content on the rheological properties of zein-oleic acid dough during kneading, mixing and extrusion”. Thesis (M.S.) Rutgers University, 2007.

[8] M. Oliviero, E. D. Maio, and S. Iannace. Journal of Applied Polymer Sci. 115, 277-287, 2010.