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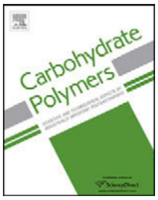

Effects of filler-matrix morphology on mechanical properties of corn starch–zein thermo-moulded films

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ABSTRACT

The effects of filler-matrix morphology on mechanical behaviour of thermo-moulded films based on native or amorphous corn starch as matrix, and zein (sizes of <100, <250, and >500 μm) as filler were investigated. The morphology and mechanical behaviour were characterized by Confocal Light Scanning Microscopy and three point bending test, respectively. For native starch blends, the zein network was relatively dense when initial zein size increased from 100 to 500 μm. However, small initial zein size favored continuous morphology for amorphous starch blends. It is noted that the stress at rupture values of native starch blends decreased when zein size increased, indicating relatively compact zein network damaged the stress of starch matrix. On the contrary, the variations of the stress at rupture values of amorphous starch blends were not significantly different, attributing to the heterogeneous morphology of incomplete zein network dispersed in the amorphous starch matrix.

1. Introduction

The starch and protein from vegetable origin are important for food applications as ready-to-eat breakfast cereal products, due to the renewability of raw material and widespread and variety of sources (Zhang & Zeng, 2008). Corn flour is composed of the endosperm, which is constituted of two main fractions of starch and protein (Shukla & Cheryan, 2001). Corn flour based ready-to-eat breakfast cereals belong to a family of products whose textural properties depend on the reorganization of their components when submitted to thermo-mechanical processing (Rokey, 1995).

In the past decades, the model blend system of corn starch and zein has been investigated to better understand the relationship between the mechanical properties and structure of corn flour based food materials. The structural modifications of the components of corn flour, mainly of corn starch and zein, under the thermal and mechanical processes have already been studied (Colonna, Tayeb, & Mercier, 1989; Lawton, 2002). The water vapour permeability, solubility, moisture barrier, water uptake properties, and mechanical properties of zein–starch composite films have been measured (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006; Gaspar, Benko, Dogossy, Reczey, & Czigany, 2005; Parris, Dickey, Kurantz, Moten, & Craig, 1997; Ryu, Rhim, Roh, & Kim, 2002). More recently, Habeych, Dekkers, van der Goot, and Boom (2008) represent that dispersion of zein in starch matrix can be achieved using shearing-based processing. Evidences of the weak adhesion between starch and zein have been put forward both experimentally and numerically (Guessasma, Hamdi, & Lourdin, 2009; Habeych et al., 2008). However, very little research has focused on the effect of filler-matrix morphology on the resultant mechanical properties of zein–starch blends. It is noted that the zein–starch blends can form co-continuous domains when zein content lies between 17 and 34% (Chanvrier, Colonna, Della Valle, & Lourdin, 2005; Chanvrier, Della Valle, & Lourdin, 2006). The mechanical properties of glassy blend materials were weakened by hydrophobic zein, as compared to the behaviour of pure starch.

A basic understanding of the relationship between filler-matrix morphology and mechanical properties is essential for a successful research and development of the thermo-moulded biofilms. The objective of the present study was to examine the effects of morphology on thermal and mechanical behaviour of thermo-moulded zein–starch blends. The continuous and separated domains were based on two types of starch, native and amorphous, and different granularity of zein powder, respectively. The typical model system was elaborated from 85% (w/w) corn starch, and 15% (w/w) zein with initial sizes of <100, <250, and >500 μm before thermo-moulding. The morphology and mechanical behaviour were characterized by Confocal Light Scanning Microscopy (CLSM) and three point bending test, respectively.

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2. Experimental

2.1. Materials

Corn starch was purchased from Roquette (F-62 Lestrem, France) with the initial moisture content of 13.5% (wb). Its native form was granular and semi-crystalline. Zein powder, a mixture of two alcohol-soluble polypeptides with molecular masses of 25,000 and 29,000 Da, was purchased from Fluka Biochemika (Germany). Losses due to drying and ash were less than 4 and 1%, respectively. Three sizes of zein powder (<100, <250, and >500 μm) were obtained by using the electric shaker and corresponding screen (speed: 20–30 rpm, time: 5–10 min).

2.2. Preparation of amorphous corn starch by cast method

Starch was used in its native and amorphous form. The amorphous corn starch was prepared by using the Parr 4835 autoclave (Parr instrument company, USA). Prior to heating, water was added to adjust a starch concentration of 10% (w/w). The suspension was treated at 130 °C and 2 bar for 20 min. After the above operation, the mould was cooled to near 60 °C. Then the starch solution was cast on the glass plates, and dried in an oven at 80 °C. Dried corn starch film was reduced to powder by a cryogrinder, and stored at a relative humidity of 59% (NaBr salt solution at 20 °C) for 30 days to achieve complete equilibrium.

2.3. Thermo-moulding

In order to generate different blend morphologies from the 85/15 starch/zein weight ratio, two types of thermo-moulding press were used: (1) a pressure controlled press and (2) a volume controlled press.

The press (1) was used to elaborate blends from amorphous starch and zein with different powder sizes. At a relative humidity of 59% (NaBr salt solution at 20 °C), both amorphous corn starch and blend powders contained 11% water content, whereas zein powder contained about 6% water content. Processing conditions were as follows: temperature 120 °C, duration 10 min, pressure 1 tone. Small parallelepiped samples (length: 35 mm, width: 10 mm, thickness: ca. 1 mm) were obtained from a quantity of ca. 0.5 g of raw materials. According to the different sizes of zein (<100, <250, and >500 μm) in the blends, the fabricated samples were coded as a-starch/zein100, a-starch/zein250, and a-starch/zein500, respectively. Pure films of zein and amorphous corn starch were coded as zein and a-starch, respectively.

The press (2) was used to elaborate blends from native corn starch and zein with different powder sizes. Water contents of starch and blend powders were adjusted to 28% (wb) in order to melt the crystalline fraction of native starch at 120 °C. Processing conditions were as follows: temperature 130 °C, duration 7 min, pressure 130 bars. This process was designed to favor the zein melt flowing between starch granules during thermo-moulding. Films requiring sample sectioning for mechanical tests were obtained (width: 1 cm; thickness: ca. 0.5 mm). According to the different sizes of zein (<100, <250, and >500 μm) in the blends, the fabricated samples were coded as n-starch/zein100, n-starch/zein250, and n-starch/zein500, respectively. Pure films of native corn starch were coded n-starch.

To achieve stable water content before the characterization, all thermo-moulded samples were stored under controlled relative humidity of 59% obtained from saturated NaBr salt at 20 °C.

2.4. Water content measurement

Moisture content of the raw materials and films were measured by gravimetric method after being stored at controlled relative humidity. An approximate amount of 2 g of samples were placed in an atmospheric oven at 130 °C for 4 h. The water content was deduced from the weight loss due to sample desiccation. Each experiment was done in triplicate.

2.5. Confocal Light Scanning Microscopy (CLSM)

CLSM (Zeiss LSM 410, Carl Zeiss, Germany) was used to observe the cross section of starch–zein blends. For each sample, three sections (ca. 20 μm) were prepared using a cryotome (Microm HM 500 OM) at −20 °C. The sections were placed on flat glass slides, and then protein coloration was performed by staining for 5 min in a 0.01% (w/v) fuchsin acid solution diluted in 1% (v/v) acetic acid. The colored sections were rinsed three times with distilled water and dried at room temperature. During the observation, water was added to the section, and then a slip was covered to prevent it from drying.

The observations were carried out in the epifluorescence mode of the microscope. Samples were excited by a green laser beam at 543 nm, and the emitted light was selected by a long-pass filter (>570 nm). The parameter of Pinhole was 25. The lens 40 and 10 chosen for the image sizes were 319.4 μm × 319.4 μm and 1272.5 μm × 1272.5 μm, respectively.

Image processing program was using Aphelion software (ADCIS, France), and component distribution (zein/starch area ratio) analysis was performed with Matlab 6.0 software (Math Works Company, France). The detailed procedure was described in reference (Li, Hua, Qiu, Yang, & Cui, 2008). Measurements were performed on more than 10 images for every blend. The mean values and corresponding deviation values of zein/starch area ratio were obtained.

2.6. Differential scanning calorimetry (DSC)

The glass transition temperatures of samples were measured by differential scanning calorimetry on a DSC Q100 (TA instrumental explorer, USA). Films were ground to powder and stored at constant relative humidity of 59% before being placed in pressure-tight cell (about 40 mg of matter per cell). After a first scan from 5 to 120 °C to delete any thermal events due to ageing phenomena occurring during the storage, samples were rapidly cooled to 5 °C (60 °C/min). The second scan was measured at 3 °C/min from 5 to 120 °C. Graphic determination of glass transition temperature (T_g) was carried out by Wunderlich method. T_g corresponded to a half-variation in calorific capacity during transition. The procedure was similar for all samples regardless of compositions. Three samples of each composition were measured and the average T_g values were calculated.

2.7. Dynamical mechanical thermal analysis (DMTA)

Thermo-mechanical measurements were carried out on a dynamical mechanical thermal analyzer (DMTA, MK IV, Rheometric Scientific, USA). Samples were coated with a silicone-based hydrophobic grease to limit dehydration during experiments at high temperatures, after being checked that it had no effect on thermo-mechanical properties. Thermo-moulded samples (a-starch/zein 35 mm × 10 mm × 1 mm, n-starch/zein 35 mm × 10 mm × 0.5 mm) were measured in a dual cantilever bending mode with a vibration frequency of 1 Hz, strain of 0.1% and a heating rate of 3 °C/min.

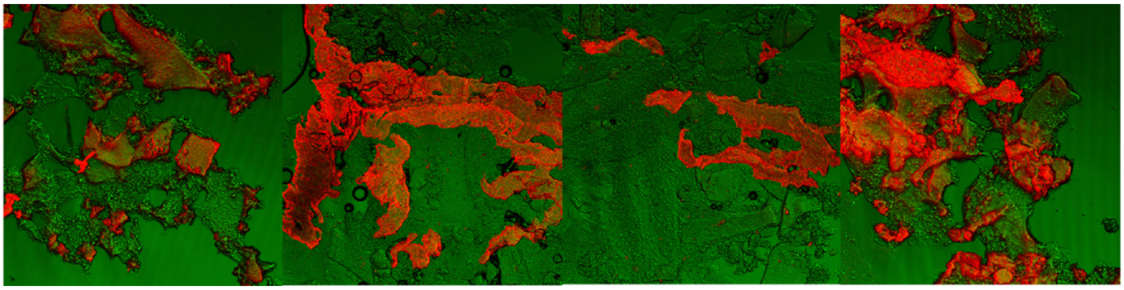

Fig. 1. LSM images of different parts of cross-sections for a-starch/zein500 film with zein size of >500 μm. The red and green parts present zein and corn starch components, respectively. The corresponding image scale is 1272.5 μm × 1272.5 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

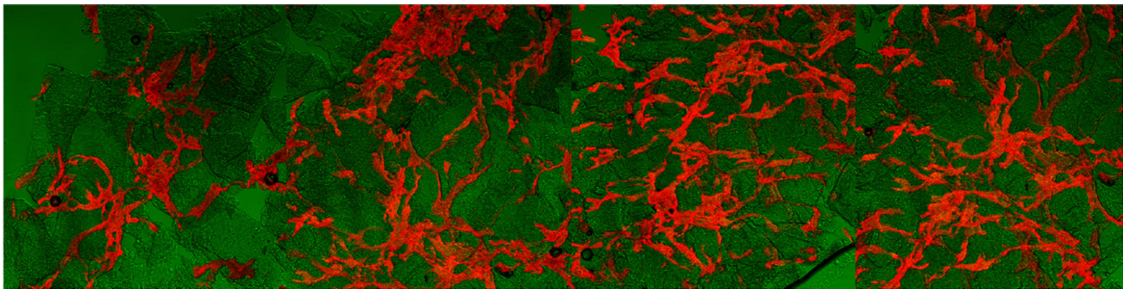

Fig. 2. LSM images of different parts of cross-sections for a-starch/zein100 film with zein size of <100 μm. The red and green parts present zein and corn starch components, respectively. The corresponding image scale is 1272.5 μm × 1272.5 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2.8. Bending test

Three-points bending test on an 1122 Instron universal testing machine were performed until samples broke: samples thickness e (measured with a vernier caliper), distance between supports L (length), crosshead speed adjusted to 20 mm min^{-1}, Stress σ, and strain ε, from the force F (N) vs. crosshead displacement (d) curves. The rupture stress corresponds to the maximum of the curve:

$$\sigma = F \cdot \frac{3L}{2e^2h}$$

with h (mm) being the sample width. Strain value at rupture was determined at the maximum stress:

$$\varepsilon = \frac{6de}{L^2}$$

with d (mm) being the displacement of crosshead. Flexural modulus E (GPa) was defined by the slope of the linear part of the curve stress vs. strain for low values of strain.

$$E = \frac{\sigma}{\varepsilon} = \frac{FL^3}{4e^3hd}$$

Measurements were performed on 10 samples for every product. The mean value was calculated and error bars corresponded to a 95% confidence interval.

3. Results and discussion

3.1. Morphology

The cross-sections of the thermo-moulded blend films were examined by CLSM through protein staining. In Figs. 1–3, the separated and matrix parts presented zein and corn starch components, respectively. The a-starch/zein500 samples showed aggregated zein with sizes from a few hundred microns to 1 mm, dispersed in the corn starch matrix (Fig. 1). The heterogeneous morphology sug-

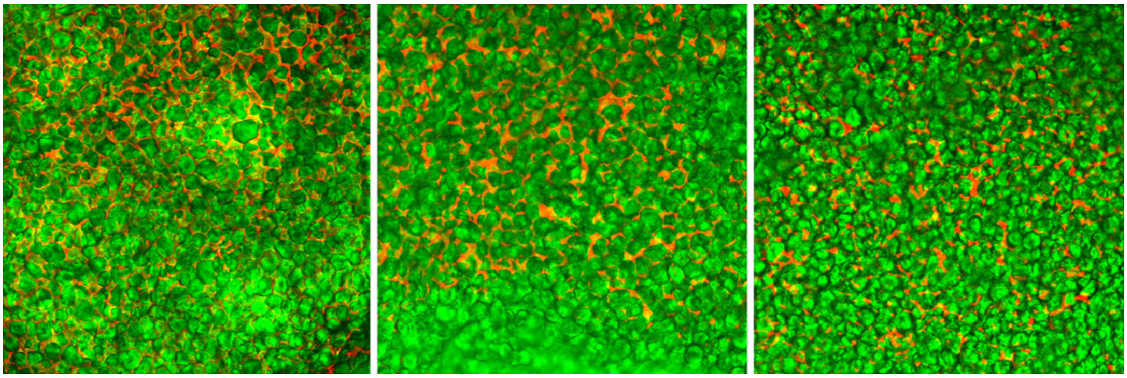

Fig. 3. CLSM images of cross-sections for n-starch/zein films with zein size of >500 μm (left), <250 μm (middle), <100 μm (right). The red and green parts present zein and corn starch components, respectively. The corresponding image scale is 319.4 μm × 319.4 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

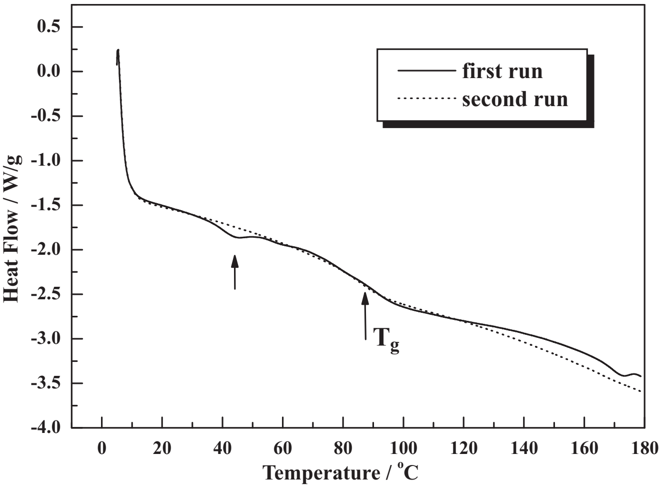

Fig. 4. The typical thermogram of a-starch/zein500 film obtained from DSC measurement.

gested that the aggregation of protein molecules induced a phase separation between hydrophobic zein and hydrophilic corn starch. When initial zein size decreased to 100 μm for a-starch/zein100 film, the beginning of protein network formation was observed from Fig. 2. The above results imply that small initial zein size favored continuous morphology for amorphous starch blends.

In Fig. 3, the morphology of the n-starch/zein blend films is quite different from that of the a-starch/zein blend films. Despite of the thermo-moulding process (28% water content, 120 °C) which allowed the complete fusion of crystal part of native starch granules, the process preserved the lenticular shape of native starch. Meanwhile, the process induced zein flowing between starch granules leading to relatively continuous domains. Based on the CLSM images analysis, the zein/starch area ratio values of n-starch/zein100, n-starch/zein250 and n-starch/zein500 films were 0.42 ± 0.15, 0.49 ± 0.18, and 0.57 ± 0.17, respectively. The highest zein/starch area ratio value of n-starch/zein500 film indicated that the densest zein networks were distributed in the corn starch matrix. Compared with n-starch/zein100 and n-starch/zein250 films, n-starch/zein500 film occupied relatively complete and dense protein networks, suggesting the effectiveness of intermolecular penetration.

To resume CLSM analysis, the zein size really plays a key role in the morphology for zein and starch blends. Different morphologies were observed for amorphous and native starch blends, which were relatively incomplete protein networks appeared for amorphous starch blends, and relatively continuous zein networks for native starch blends. Moreover, small initial zein size favored continuous morphology for amorphous starch blends. A reverse behaviour was observed for native starch blends. It seems that the zein network was relatively continuous and dense when zein size increased from 100 to 500 μm. Of course, relatively high quantity of water content for native starch blends should be emphasized in here.

3.2. *Glass transition temperatures and thermomechanical behaviour*

The typical DSC curve as a function of temperature for a-starch/zein500 film was shown in Fig. 4. From the figure, the film with the moisture content of 11% (wb) presented two peaks in the first run: one peak at 45 °C and another at around 90 °C. The peak at 45 °C disappeared during the second scan, which was due to the physical aging of the sample. The glass transition temperature (T_g) of 86 °C was measured from the midpoint of the heat capacity change in the second run.

Table 1
The water content (%) and glass transition temperatures (T_g, °C) of film samples measured by gravimetric method and DSC measurements, respectively.

Samples	Zein	a-Starch	a-Starch/ zein500	n-Starch/ zein100	n-Starch/ zein500
Water content (%)	5	10	11	12	12
T_g (°C)	70	87	86	73	71

From Table 1, water contents and glass transition temperatures of amorphous corn starch, zein and blend films were measured at the relative humidity of 59%. The glass transition temperatures of amorphous corn starch and zein powders were 79 and 65 °C, respectively (not shown). Amorphous corn starch and zein films possessed T_g at 87 and 70 °C, respectively, which were higher than those of the corresponding powder samples. The phenomena could be due to at least two factors. One is the water content values of films which were slightly lower than those of the corresponding powder samples. Another is the influence of thermo-moulding treatment. Numerous publications described the protein network formation and the decreased extractability when they were heated at temperature above 80 °C (Cuq et al., 2000; Woerdeman et al., 2004).

Usually, glass transition temperature of blend lies in the range of both components to show the miscibility to a certain extent. The glass transition temperature of a-starch/zein500 film at 86 °C was very close to the T_g value of pure amorphous corn starch, indicating the micro-phase separation between amorphous corn starch and zein. The results were in accordance with the CLSM observation. DSC measurement results of the blends from native corn starch and zein were also shown in Table 1. According to relatively higher water content, n-starch/zein500 and n-starch/zein100 films occupied the T_g values of 71 and 73 °C, respectively, which were lower than that of amorphous starch blend counterpart. Furthermore, the glass transition temperatures were close to T_g value of pure zein film. Considering zein as the minor part of blends, the observed results were not due to the zein network formation, which attested the fact that native corn starch was amorphous after thermo-moulding process.

The storage modulus (E') and mechanical loss factor (tan δ) of the films as a function of temperature were shown in Figs. 5 and 6. Fig. 5(A) depicted the variation of the storage modulus vs. temperature for a-starch and blend films. Considering the accuracy of the technique, E' values of amorphous corn starch at room temperature were not influenced significantly by adding the zein part. Usually, mechanical loss factor (tan δ) peak in the DMTA thermogram, the α relaxation, reflects the glass transition, and may be analyzed to provide information about the molecules motion (Ishida & Allen, 1996). Fig. 5(B) presented tan δ vs. temperature spectra of a-starch and blend films. Amorphous corn starch showed a main relaxation located at 110 °C with 10% water content. Even though corn starch and zein were not miscible, all blends showed prominent broad damping peaks, attributing to the main relaxation of corn starch and zein. The observed results suggested that micro-phase separation between amorphous corn starch and zein occurred, which confirmed the CLSM observation. It is noted that the damping peaks became broader when the zein sizes increased from 100 to 500 μm. Both peaks of components were even more distinguishable for a-starch/zein500 film. The increasing height and broadening width of tan δ peak was associated with relatively higher molecular mobility and thus was indicative of relatively lower degree of crosslinking network for a-starch/zein500 film. The above results further confirmed that zein sizes had its effect on the miscibility and multi-phase molecular mobility of the blends. It seems that small initial zein size favored continuous morphology for amorphous starch

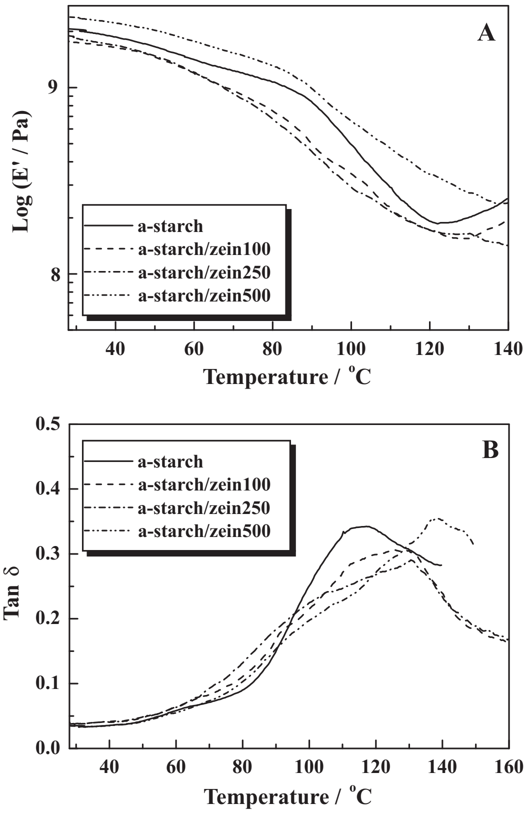

Fig. 5. E' (A) and tan δ (B) of amorphous corn starch and blend films stored in NaBr humidity.

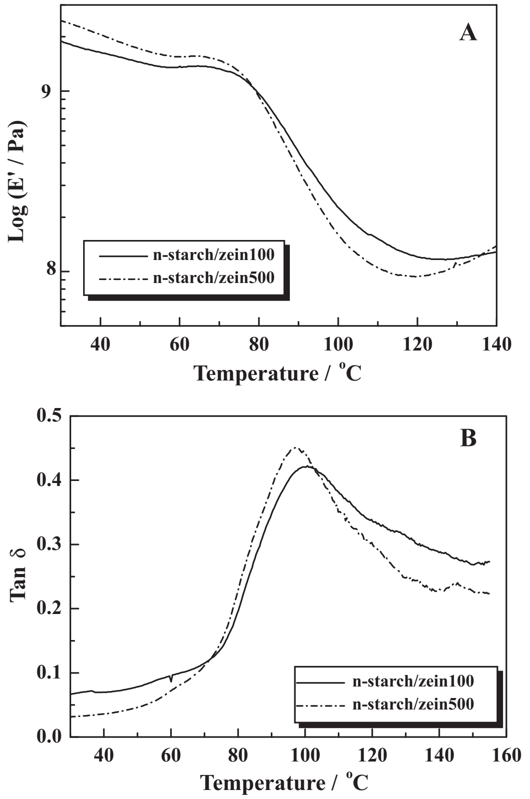

Fig. 6. E' (A) and tan δ (B) of native corn starch blend films stored in NaBr humidity.

blends, resulting in relatively lower molecular mobility to occupy relatively narrow damping peak.

Fig. 6(A) displayed the variation of the storage modulus (E') vs. temperature for n-starch/zein100 and n-starch/zein500 blends. The E' values were analyzed without any significant variation at glassy and rubbery states for the blends with different zein sizes. Consequently, the relatively narrow tan δ peaks for both n-starch/zein blends were shown in Fig. 6(B). The tan δ peak temperature of n-starch/zein100 film was located at 95 °C, almost the same value as that for n-starch/zein500 film. The high intensity of this peak associated with amorphous phase mobility also confirmed that semi-crystalline native starch was completely transformed to amorphous state by thermo-moulding treatment. Similar thermo-mechanical behaviour for both blends was attributed to similar zein networks included in starch matrix.

3.3. *Mechanical properties*

Tensile tests were difficult to perform on the samples in this study so the three-point bending test was used, although it resulted in various deformations of the samples: compression, traction and shear. The water content values indicated in Table 2 for a-starch/zein and n-starch/zein blends were 11 and 12% (wb), respectively. Therefore, the effect of such weak difference of water content on the mechanical properties can be neglected. The stress at rupture values (STRESS_r, MPa) of all film samples were also summarized in Table 2. The materials made from pure corn starch were more resistant to failure than the blends. The pure n-starch and a-starch films presented 36 and 27 MPa, respectively. Both n-starch and a-starch blends decreased their stress at rupture values comparable to the pure counterparts. However, the n-starch blends occupied relatively higher stress at rupture values than those of the corresponding a-starch blends. In addition, the stress at rupture values of n-starch blends decreased from 31 to 25 MPa when the initial zein sizes increased from 100 to 500 μm. Based on the co-continuous morphology of n-starch blends, relatively compact zein networks damaged the stress of native corn starch matrix when initial zein size increased (Chanvrier et al., 2005, 2006). On the contrary, the stress at rupture values of a-starch blends slightly increased from 20 ± 2 to 24 ± 3 MPa when the initial zein sizes increased from 100 to 500 μm. Considering the uncertainty of the experiment results, the variations of the research results were not significantly different. The stress at rupture values for a-starch blends decreased comparable with pure a-starch film. The phenomena should be explained that starch matrix was weakened by zein addition according to the heterogeneous morphology.

The values of strain at rupture (STRAIN_r, %) and flexural modulus (E, GPa) for thermo-moulded films were also shown in Table 2. The strain at rupture results clearly confirmed that all films were very fragile. The pure n-starch and a-starch films presented 2.4 and 0.80%, respectively. The n-starch blends possessed relatively higher strain at rupture values than those of corresponding a-starch blends. The a-starch blend films showed relatively lower strain at rupture values around 0.85%, which was close to the value obtained for the pure amorphous corn starch film. The fragility property of the a-starch blends was assumed to be related to the heterogeneous morphology. However, the n-starch blends were more fragile than the pure native corn starch film. The n-corn starch film broke at 2.4%, whereas the blend films presented the average strain at rupture value of 1.1%. Most of the time, the stress decrease was coupled with a strain increase according to the references (Adnan, Sun, & Mahfuz, 2007; Cho, Joshi, & Sun, 2006; Duffresne, Kellerhals, & Witholt, 1999; Jordan, Jacob, Tannenbaum, Sharaf, & Jasiuk, 2005; Osman & Atallah, 2005). Based on the homogeneous

Table 2
The water content (%) and mechanical properties of thermo-moulded films measured by gravimetric method and 3-point bending test, respectively.

	a-Starch	a-Starch/zein100	a-Starch/zein250	a-Starch/zein500	n-Starch	n-Starch/zein100	n-Starch/zein250[a]	n-Starch/zein500
Water content (%)	10	11	11	11	12	12	12	12
STRESS_r (MPa)	27 ± 7	20 ± 2	24 ± 3	24 ± 3	36 ± 4	31 ± 8	27 ± 4	25 ± 3
STRAIN_r (%)	0.80 ± 0.14	0.84 ± 0.07	0.86 ± 0.11	0.88 ± 0.12	2.4 ± 0.6	1.1 ± 0.3	0.95 ± 0.15	1.1 ± 0.2
E (GPa)	3.3 ± 0.4	2.5 ± 0.2	2.8 ± 0.5	2.8 ± 0.4	2.6 ± 0.8	3.0 ± 0.4	2.9 ± 0.3	2.3 ± 0.8

[a] The data were cited from the reference (Chanvrier et al., 2005).

morphology observation, the aggregation of zein could form the macromolecular network and bind the starch granules together to result in the decrease of the macromolecular mobility and an overall decrease of mechanical properties. The values of flexural modulus for the pure n-starch and a-starch films showed 2.6 and 3.3 (GPa), respectively. Despite of high experimental uncertainty, the flexural modulus values for the n-starch blends (n-starch/zein100 and n-starch/zein250) were higher than those of pure native corn starch and corresponding amorphous corn starch based blend films. The native corn starch matrix with zein added under the thermal compression conditions would form the zein network to bind starch granules together and contribute to the increased modulus of the materials.

4. Conclusions

The effects of morphology on mechanical behaviour of thermo-moulded starch/zein blends with a constant zein concentration of 15% (w/w) were investigated. The matrix and separated domains were based on two types of starch, native and amorphous, and different granularity of zein, respectively. The research results confirmed that different initial zein sizes (<100, <250, and >500 μm) had a strong influence on the morphology and thermo-mechanical properties for both blends. Small zein size favored continuous morphology for amorphous starch based blends. On the contrary, the zein network was relatively continuous and dense when zein size increased from 100 to 500 μm for native starch blends. In addition, both damping peaks became broader and more distinguishable when the zein sizes increased to 500 μm for a-starch blends, resulting from the micro-phase separation morphology. However, the similar thermo-mechanical results for n-starch blends were attributed to the similar co-continuous phase morphology. It is noted that the stress at rupture values of n-starch blends decreased when the zein sizes increased from 100 to 500 μm, indicating relatively compact zein network damaged the stress of corn starch matrix. On the contrary, the variations of the stress at rupture values of a-starch blends were not significantly different, attributing to the heterogeneous morphology of incomplete zein network dispersed in the amorphous corn starch matrix.

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