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Keywords	Drying temperature; particles distribution; physical properties
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Effect of drying temperature on structural and thermomechanical properties of konjac glucomannan-zein blend films

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Abstract

Konjac glucomannan (KGM)/zein blend films were successfully prepared by solution casting at different drying temperatures (40, 50, 60, 70 and 80 °C). The effects of drying temperature on the films' structural, thermomechanical, mechanical and water barrier properties were investigated. Microstructural observations indicated that zein particles were homogeneously dispersed in KGM continuous matrix, and the blend film dried at 60 °C showed the most compact and smooth surface. Dynamic mechanical thermal analysis curves showed that with increasing drying temperature from 40 to 60 °C, glass transition temperature (Tg) of films increased; however, with further increase in temperature, the Tg decreased, indicating the compatibility of film components was the highest when dried at 60 °C. The hydrophobicity of blend film dried at 60 °C was significantly stronger than that of other blend films, supported by the highest water contact angle, and the lowest swelling ratio and solubility. Moreover, the film dried at 60 °C showed the highest tensile strength, elongation at break, and the lowest water vapor permeability. Therefore 60 °C was preferred for KGM/zein blend film preparation. This study indicated that intermolecular interactions among film components were greatly influenced by the drying temperature, and should be carefully noticed for film preparation.

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1. Introduction

Edible packaging is a stand-alone sheet of material which can provide a barrier to mass transfer (moisture, oxygen, and solute movement) within the food itself or between the food and environment (Bourlieu, Guillard, Vallès-Pamiès, et al., 2009). The unique advantage of edible packaging is envisioned to simplify packaging system and to improve stability, safety and quality of food products, representing a better choice for food packaging in daily life (Janjarasskul et al., 2018). Edible packaging is developing rapidly by utilizing edible biopolymers as structural matrices. Generally, they are prepared from natural polysaccharides, proteins, lipids or combinations of these components (Jia, Fang, & Yao, 2009; Shi, & Dumont, 2014; Wu et al., 2018; Cheng et al., 2008; Homez-Jara et al., 2018). Among them, konjac glucomannan (KGM) as one natural water-soluble polysaccharide derived from the konjac tuber has special nutritional and health promoting functions as well as excellent film-forming capability, and it has bright application prospect for edible packaging preparation (Li et al., 2015; Wu et al., 2012; Chen et al., 2008; Lu, Wang, & Xiao, 2008). Zein is the major storage protein of corn and comprises ≈ 45-50% of the protein in corn (Shukla, & Cheryan, 2001). It is insoluble in pure water, and has good film-forming ability, relatively low price and abundant sources (Liang et al., 2015; Bisharat et al., 2018; Gu et al., 2013). According to our previous research (Wang et al., 2017; Ni et al., 2018), KGM and zein could form a stable homogeneous dispersion with appropriate mixing formula, and KGM/zein blend films could be formed by solution casting. KGM/zein blend films showed better mechanical, thermal, water vapor and oxygen barrier properties than pure KGM and zein films. The hydrophobicity of KGM/zein blend films was significantly stronger than that of pure KGM film (Wang et al., 2017). As an edible packaging material, KGM/zein blend films have promising prospects for development.

Drying is one of most challenging steps in the production of films, and improper drying conditions (e.g. high temperature or a long time) may lead to a variety of drying-induced defects such as blisters, warping, and cracks (Zhou et al., 2018). Presently, the influence of drying conditions on films has received considerable attention. During the drying period, with solvent evaporation and solute migration, various phenomena may occur such as molecular assembly and interaction, a transition from a rubbery to a vitreous phase, a phase separation (thermodynamic incompatibility), or crystallization (Liu et al., 2015; Denavi et al., 2009). This can be largely impacted by the drying temperature, as the solvent evaporation efficiency is mainly affected by temperature. For example, increasing drying temperature (from 30 to 50 °C) improved tensile stress at yield and elastic modulus of the konjac flour films, while decreasing its thickness, percent elongation at yield and water vapor permeability (Jomlapeeratikul, Poomsa-Ad, & Wiset, 2016). Liu et al. (2016) found drying temperature could be used to modulate the relative amount of triple helices and covalent bonds, and therefore control the physical properties of transglutaminase-modified gelatin films. Moreover, with increased drying temperature, the network structure of the films became more compact. Homez-Jara et al. (2018) found that the properties of chitosan edible film were largely influenced by drying temperature, e.g. low drying temperature (e.g. 2 and 25 °C) could improve moisture content, solubility, water vapor permeability, and optical properties; high drying temperature (40 °C) combined with higher chitosan concentration resulted in enhanced tensile strength, swelling power, and greenness value of the films, while diminishing their luminosity and decreasing the melting temperature.

As a continuation of our previous work on KGM/zein blend films (Wang et al., 2017), the objective of the current study was to assess the effect of drying temperature on structural and physicochemical properties of KGM/zein blend films. Films prepared under different drying conditions were characterized regarding microstructure, thermal, mechanical and water barrier properties. Aggregation and distribution of zein in films were observed using scanning electron microscopy (SEM), atomic force microscopy (AFM) and confocal laser scanning microscopy (CLSM). Thermal stability of films was analyzed through dynamic mechanical thermal analysis. The results obtained in this study could be used for function optimization of the films, and would contribute to a deeper understanding of the molecular interactions among KGM/zein blend films.

2. Materials and methods

2.1 Materials

Konjac glucomannan (KGM, Mw = 9.67 × 10^5 Da) was purchased from Li Cheng Biological Technology Co., Ltd. (Hubei, China). Zein (M_W = 2.5-4.5 × 10^4 Da) from corn was purchased from Beijing J & K Technology Co., Ltd. (Beijing, China). Glycerol (AR, purity ≧ 99%) and ethanol (AR, purity ≧ 99.5%) were purchased from Sinopharm (Chemical Reagent Co., Ltd., Shanghai, China). Rhodamine B (AR, purity ≧ 99%) was purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China).

2.2 Blend films preparation

Zein solution was prepared by dissolving 0.1 g zein with glycerol (15% based on total amount of KGM and zein, w/w) in 20 mL of ethanol/water solvent (80:20, v/v) under constant stirring at 500 rpm using a magnetic stirrer (ZNCL-S-5D KEER instrument Co., Ltd., China) for 15 min at 25 °C. KGM solution was prepared by dissolving 0.9 g KGM in 100 mL water with a continuous stirring electric mixer (OS20-Pro SCILOGEX Co., Ltd., American) at 600 rpm at 60 °C for 1.5 h. The blend film-forming solutions were prepared by slowly dropping zein solution into KGM solution at 60 °C for 30 min at stirring speed 1000 rpm. Then the blend solutions were carefully poured onto a glass plate (14 cm × 14 cm × 1.5 cm), and dried in an oven (DNG-9031A, Jing Hong Co., Ltd., Shanghai, China) to a moisture content approximately 9% (w.b.) in order to facilitate peeling films from the glass plate. The total content of KGM and zein was kept as 1.0 g per casting plate, and KGM/zein weight ratio was 9/1 (w/w).

The blend solutions were dried at different temperatures (40, 50, 60, 70 and 80 °C) in an oven, with corresponding drying time (24 h, 18 h, 14 h, 10 h and 7 h) to achieve approximate 9% moisture content (w.b.). According to drying temperature, the film samples were coded as 40 °C KZ, 50 °C KZ, 60 °C KZ, 70 °C KZ and 80 °C KZ, respectively. The impacts of air flow rate and moisture content of inlet air were not studied as the machine did not have corresponding functions to adjust/monitor them, and they were considered to be the same for all samples. Both with 15% glycerol addition based on total solid content, pure KGM film and pure zein film were prepared by separately drying 100 mL KGM solution (1%, w/v) and 20 mL zein solution (5%, w/v) on glass plates (14 cm × 14 cm × 1.5 cm) at 60 °C, as the reference samples. All film samples were conditioned at 25 ± 1 °C, 40 ± 2% relative humidity for 48 h before testing.

2.3 Atomic force microscopy

The topography of films was obtained using Veeco MultiMode atomic force microscopy (SPM9700, Shimadzu Co., Ltd., Japan) in tapping mode with silicon nitride probes. Resonance frequencies of 306-388 KHz were employed, and films were scanned at speed 1 Hz with resolution 256 × 256 pixels. AFM images with scan sizes of 5 μm × 5 μm were acquired. The roughness values of films were obtained.

2.4 Scanning electron microscopy

Samples were cut into 4 mm × 4 mm pieces for surface observation. The cross-section of samples was prepared by breaking samples (4 mm × 8 mm) after freezing in liquid nitrogen. The surface and cross-section of films were coated with gold at 7.5 Pa with thickness 20 nm, and then observed by Bio-Rad type SC 502 SEM (JEOL, Tokyo, Japan). The sputtered time was about 90 s and an accelerating voltage was 30KV. Images with the magnification of 1000 (cross-section) and 100 (surface) were recorded.

2.5 Confocal laser scanning microscopy

CLSM analysis (Leica TCS SP8) was used to visualize the distribution of zein in blend films. The zein was stained with rhodamine B (Rogers, Roos, & Goff, 2006). The dye solution was first prepared by mixing 4 mg of rhodamine B in 1 mL of water. Then 20 μL of the dye solution was added into 20 mL of zein solution, mixed at 150 rpm for 15 min at 25 °C to ensure that the solution was homogenous, and also to give time for the dye to bind to the protein. The dyed zein solution was dropped into the KGM solution and dried to obtain the dyed films. Before placed on the confocal plate for observation, the dyed films were rinsed with distilled water three times and cut into small pieces (0.5 cm × 0.5 cm). Film samples were excited by a red laser beam at 638 nm. Image-Pro Plus software (Media Cybernetics Inc., Maryland, America) was used to evaluate the particle size of zein in KGM/zein blend films based on 6 representative CLSM images. A total of 300 points were counted for each sample.

2.6 Dynamic mechanical thermal analysis (DMTA)

The thermomechanical properties of films were carried out using a dynamic mechanical thermal analyzer (Diamond DMTA, PerkinElmer Instruments Co., Ltd., America) by the following methodology. Films were cut into 1 cm × 4 cm size and clamped in the tensile geometry of the instrument. A temperature sweep test from -25 to 150 °C was performed at a heating rate of 3 °C/min, and fixed deformation amplitude of 10 μm (within the linear viscoelastic region). The test was performed in a single frequency mode (1 Hz). The storage modulus (G□) and loss factor (tan δ) of each film sample were obtained as a function of temperature.

2.7 Mechanical properties

Measurement of film samples was done according to ASTM D882-09 standard method (ASTM, 2009). The tensile strength (TS) and elongation at break (EAB) of films were tested by a Texture Analyzer (TA. XT Plus, Stable Micro Systems Co., Ltd., UK). Films were cut into strips of 10 mm × 50 mm size for the measurement and clamped between grips. An initial grip length was 50 mm and cross-head speed was set at 0.5 mm/s. The curves of force (N) as a function of deformation（mm） were recorded using Texture Expert software. Film thickness (μm) was measured by a micrometer (Shanghai Liu-ling Instrument Company, Shanghai, China). TS (MPa) and EAB (%) were calculated using the following equations (1) and (2):

$$TS = \frac{F}{T \times W} \qquad (1)$$

Where F is the maximum force, T is the thickness of the film, W is the width of the film.

$$\mathrm{EAB} = \frac{L - L_0}{L_0} \times 100\% \tag{2}$$

Where L_0 is the starting length of the film, L is the length after stretching of the film.

2.8 Water contact angle

The wettability of films was evaluated by water contact angle measured by a contact angle meter (DSA25, Krüss Co., Ltd., Germany) equipped with a CCD camera and an image analysis software. A droplet of distilled water (2.0 μL) was deposited on the air side surface of the film (2.0 cm × 2.0 cm) with a precision syringe, and the drop image was recorded by a camera. The contact angle was measured after stabilizing for 30 s.

2.9 Swelling and solubility in water

Film sample (2 cm × 2 cm) was immersed in 30 mL deionized water at 25 °C for 5 h, then the wet sample was taken out and wiped with filter paper to remove excess liquid and weighed. Swelling ratio was calculated by the following formula:

$$\mathrm{Swelling}\ (\%) = \frac{m_2 - m_1}{m_1} \times 100 \tag{3}$$

Where m_1 (mg) is the dry weight of the sample before immersion in water, m_2 (mg) is the sample weight after immersion in water for 5 h.

Film sample (3 cm × 3 cm) was immersed in 100 mL deionized water at 25 °C for 24 h, then the sample was taken out and dried at 105 °C for 1 h. The water solubility of the film can be calculated by the following formula:

$$\text{Water solubility (\%)} = \frac{W_2 - W_1}{W_2} \times 100 \quad (4)$$

Where W_2 (mg) is the dry weight of the sample before immersion in water, W_1 (mg) is the dry weight of the sample after immersion in water.

2.10 Water vapor permeability (WVP)

The water vapor permeability (WVP; 10^{-13}·g·cm/(cm^2·s·Pa)) of films was determined by water vapor permeability tester (PERME W3/031, Labthink international, China). The testing principle was according to Chinese National Standard GB/T 1037-1988. A sheet-cup (25 mm × 65 mm) was filled with deionized water (20 mL) before sealed with the film samples, and then put in the test chamber. The temperature and relative humidity of the test chamber were controlled at 25 °C and 90%, respectively.

2.11 Statistical analysis

All experiments were performed at least in triplicate for each sample. Origin 2017 (Originlab Corporation, Northampton MA) and Adobe Photoshop CS 6 (Adobe Systems, San Jose, CA) were used for statistical analysis and figure drawing. One-way analysis of variance (ANOVA) was performed at $p < 0.05$ by the Tukey's multiple range test using SPSS (version 19, Endicott, NY, USA).

3. Results and discussion

3.1 Microstructure of films and zein particles distribution

Significant surface topography differences were observed among different film samples (Fig. 1) by AFM, and the roughness parameters (Ra, average roughness; Rq, root-mean-square roughness) of films are shown in Table 1. Both pure KGM film (Ra=8.69 nm, Rq=12.99 nm) and zein film (Ra=4.46 nm, Rq=5.77 nm) had more smooth and homogenous surfaces compared with the blend films. For the blend films, with increased drying temperature, their Ra and Rq values showed a V-shape changing trend (Table 1). 40 °C KZ had the highest Ra（36.11 nm） and Rq (44.59 nm), and 60 °C KZ had the lowest Ra (20.22 nm) and Rq (26.78 nm). This indicated that the blend film dried at 60 °C had more uniform and compact surface than other blend samples.

Compared with that of pure films, the relatively rough film surfaces of blend films may be explained as follows. Before drying, zein particles were homogeneously distributed in KGM/zein film-forming solution as reported previously (Ni et al., 2018). During the drying process, the evaporation rate of ethanol was faster than that of water and increased the hydrophilic character of the solvent, leading to enhanced hydrophobic interactions between zein molecules and a higher degree of zein aggregation (Bisharat et al., 2018; Kim, & Xu, 2008). Thus the surfaces of blend films were relatively rough, and this phenomenon could be affected by drying temperature due to different solvent evaporation situation. When the drying temperature was increased from 40 to 60 °C, the roughness values of blend films had a downward changing trend. This might due to that film formation time became shorter as a result of the higher solvent evaporation rate, which reduced the time for zein migration and aggregation and resulted in smaller zein aggregates. Therefore the film surfaces became less rough. However, when the drying temperature was further increased from 60 to 80 °C, the blend film surfaces became rougher, indicating increased zein aggregates. Cabra et al. (2008) reported temperature-dependent behavior of the Z19 α-zein aggregates. They found there were increments in protein aggregation during heating and this was particularly evident in the 60-80 °C range, where the increment in high molecular weight aggregates and the decrement in the monomeric form were higher. Similarly, protein aggregation may be more favored with higher temperature in the range 60-80 °C, though with shorter evaporation time.

The microstructures of film surface and cross-section were observed by SEM (Fig. 2). For pure KGM film and zein film, the surface and cross-section were smooth and dense, whereas some pores appeared in pure zein film due to residual air. For blend films, the surface was rougher compared with that of pure films, with particles evenly distributed and embedded in the films. Among blend films, the surface of 60 °C KZ was relatively smooth, and the cross section of 40 °C KZ showed the loosest structure with the largest size of particles.

To further clarify the impact of drying temperature on zein aggregation in the blend films, a CLSM microstructure observation through protein staining (Fig. 3) was performed to visualize zein association states, and size distribution map of zein particles was also drawn (Fig. 4). Homogeneous distribution of zein particles in KGM continuous matrix was observed in all blend films (Fig. 3), and clearly 60 °C KZ showed the smallest zein particles. In the drying process, protein molecules unfolded due to heating, and in solvent exposure of hydrophobic residues and sulfhydryl groups led to the conformational changes and aggregation of protein particles (Broersen et al., 2006). A wave crest (5-20 μm) was found containing 62%, 64.7%, 80%, 77.3% and 73.3% of total zein particles in 40 °C KZ, 50 °C KZ, 60 °C KZ, 70 °C KZ and 80 °C KZ, respectively. The size of zein particles decreased with increased drying temperature from 40 to 60 °C, but increased with drying temperature from 60 to 80 °C. Thus drying temperature 60 °C g resulted in the most uniform and minimum zein particles in the films, and was preferred for film preparation. This was in agreement with previous analysis on AFM results. These results indicate that drying temperature is an important factor for KGM/zein blend film preparation due to its impact on zein aggregation.

3.2 Thermomechanical properties

The thermomechanical behavior of films was studied using a dynamic mechanical thermal analyzer (DMTA). The variation of storage modulus (G') and loss factor (tan δ) against temperature for pure KGM film, pure zein film, and the blend films were shown in Fig. 5. As the testing temperature increased, the G' values of all samples decreased, suggesting reduced stiffness and increased segmental motion of polymers. With increased drying temperature, the G□ values of the blend films decreased first and then increased, and that of 60 °C KZ was the lowest. This difference can possibly be attributed to the internal microstructure differences.

When the temperature rises to the glass transition point (Tg), the molecules enhance thermal motion due to sufficient thermal energy, and the free volume begins to expand, changing from freezing stage to moving stage. At this temperature, a sharp drop in the storage modulus is observed where the polymer changes from a glassy state to a rubber state. The loss factor (tan δ) is very sensitive to molecular mobility, thus Tg is usually determined as the temperature corresponding to the maximum of tan δ peak (α-relaxations) (Qiao, Tang, & Sun, 2011; Motedayen, Khodaiyan, & Salehi, 2013). Tg of pure KGM film and zein film were 79.8 and 108.1 °C, respectively. The lower Tg of KGM film in comparison to that of zein film may be due to more hydrophilic nature and flexibility of polymer chains. Blending zein with other hydrophilic polymers can often result in the composite films with lower Tg, e.g., polycaprolactone, whey protein concentrate (Corradini et al., 2004; Ghanbarzadeh, & Oromiehi, 2009). Similarly, 40 °C KZ, 50 °C KZ, 60 °C KZ, 70 °C KZ and 80 °C KZ showed Tg at 81.4, 89.7, 103.4, 96.5 and 90.8 °C, respectively (Fig. 5), and all were lower than the Tg of zein film. Change in Tg can also be an indicator of the compatibility of polymers. If two polymers are compatible, there is only one Tg in their mixtures; if they are incompatible, phase separation occurs and two Tg are observed in their mixtures, whose values are close to that of each component (Motedayen, Khodaiyan, & Salehi, 2013). All blend films had only one α-relaxations (a single Tg), indicating good miscibility/compatibility between the film components. With drying temperature from 40 to 60 °C, Tg increased from 81.4 to 103.4 °C. However, further higher drying temperature (60-80 °C) caused Tg decrease (from 103.4 to 90.8 °C). The shift of the main relaxation to a higher temperature usually indicates restricted molecular movement (Piyada, Waranyou, & Thawien, 2013). Tg of 60 °C KZ was the highest, and this may indicate that at this unique drying temperature, the film components had the highest compatibility and strongest intermolecular interactions. This can also be supported by previous results. As zein particles in 60 °C KZ were the smallest, they should have the largest surface area in the KGM continuous phase, benefiting molecular interactions due to the greater contact opportunities.

3.3 Tensile strength (TS) and elongation at break (EAB)

The dependence of the thickness, tensile strength (TS) and elongation at break (EAB) on drying temperature for the blend films were shown in Fig. 6. The thickness of blend films decreased with increased drying temperature, and the thickness of 80 °C KZ was even lower than that of pure KGM film (Fig. 6a). This was explained by that higher drying temperature may lead to denser film structure, like alginate films (Bagheri, Radi, & Amiri, 2019), konjac flour films (Jomlapeeratikul, Poomsa-Ad, & Wiset, 2016) and whey protein films (Alcantara et al., 1998). EAB values of all blend films were higher than those of pure KGM film and zein film (Fig. 6b), due to hydrogen bond interactions and Maillard reactions between KGM and zein molecules (Wang et al., 2017). This also supported the homogeneous distribution of zein particles in blend matrix. TS of all blend films was higher than that of pure zein film, and only TS of 60 °C KZ and 70 °C KZ were higher than that of pure KGM film. With increased drying temperature, a Λ-shape changing trend was found for TS and EAB of blend films, and 60 °C drying temperature resulted in the greatest TS and EAB values. This again supported the strongest interactions and the highest compatibility between KGM and zein at this drying temperature.

3.4 Surface hydrophobicity and water vapor permeability (WVP)

Water contact angle was determined to evaluate the surface hydrophobicity of films. Generally, films with larger contact angle values have higher surface hydrophobicity and lower surface wettability (Gu, Wang, & Zhou, 2013). Pure KGM film, pure zein film, and blend films exhibited significant differences in water contact angle (Fig. 7a). Pure KGM film and zein film showed the lowest and highest surface hydrophobicity. For the blend films, water contact angle values increased first and then decreased with increased drying temperature. The largest contact angle value was observed in 60 °C KZ and 70 °C KZ, indicating 60 °C KZ and 70 °C KZ had the highest surface hydrophobicity among blend films. This result was probably ascribed to the stronger intermolecular interactions between KGM and zein at this drying temperature (60, 70 °C), as well as the lower surface roughness of films.

Water vapor permeability (WVP) is an important property of packaging materials and is influenced by the hydrophobic or hydrophilic nature of the material and the presence of void spaces (Wang, & Padua, 2005). During water transmission through the films, the absorbed water could plasticize the film matrix, leading to a less dense structure where the chain ends had greater mobility, and thus increased the permeability of films (Gu, Wang, & Zhou, 2013). Pure KGM film had the highest WVP value due to its high hydrophilic nature, pure zein film had the lowest WVP because of its high hydrophobicity, and WVP values of the blend films were in the middle (Fig. 7b). Among blend films, the WVP values of 40 °C KZ, and 50 °C KZ were higher than that of 60 °C KZ, 70 °C KZ and 80 °C KZ. This was ascribed to that the distribution of large zein particles in 40 °C KZ and 50 °C KZ shortened the water diffusion path, as well as 40 °C KZ and 50 °C KZ had higher hydrophilicity. In many studies, the decrease in the WVP of a nanocomposite film was explained by an extended diffusive trajectory (Oymaci, & Altinkaya, 2016). Ozcalik and Tihminlioglu (2013) reported when layered silicates effectively distributed in the polymer film and created impermeable obstacles to permeating water vapor molecules, the effective path that a permeating water molecule must travel increased and the water vapor permeability decreased.

3.5 Swelling and solubility properties

The swelling and solubility of films in water were measured to assess the water resistance properties of films (Fig. 8), demonstrating the hydrophobicity from another aspect. Pure KGM film could not be tested as it was quickly dissolved. Pure zein film showed the lowest swelling and solubility, indicating the greatest hydrophobicity. Both swelling and solubility curves had a clear V-shape changing trend in the blend films. Increased drying temperature (40-60 °C) led to a rapid decrease in both swelling and solubility, followed by an increase at 60-80 °C. Therefore 60 °C KZ showed the highest hydrophobicity indicated by the highest water resistance properties, in agreement with the results of water contact angle of films. This may result from the changes in film microstructure and intermolecular forces.

4. Conclusion

The zein particles were evenly dispersed in KGM/zein blend films, and the particle size was significantly affected by drying temperature. Compared with other drying temperatures, 60 °C was found to confer the blend film with the superior properties, such as the highest tensile strength, elongation at break, water contact angle, the lowest water vapor permeability, swelling and solubility. Either higher or lower drying temperature led to weakened film properties. These phenomena were explained by that drying temperature 60 °C may contribute to the strongest intermolecular interactions between KGM and zein in the films, as the most uniform and smooth film surface, minimum size of zein aggregates in the film were observed with this drying temperature. Also at this drying temperature, the two components may reach the highest compatibility, as Tg was the highest at this temperature. The results indicated that drying temperature was of great importance for film preparation, as they significantly impacted the intermolecular interactions among film components, and it may be used to modulate the physical properties of the film for future applications.

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