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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 (T_g) of films increased; however, with further increase in temperature, the T_g 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.

Keywords	Drying temperature; particles distribution; physical properties
Manuscript category	Carbohydrates, Natural Polyacids and Lignins
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6 **properties of konjac glucomannan-zein blend films**
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63 **Abstract**
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65 23 Konjac glucomannan (KGM)/zein blend films were successfully prepared by solution
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71 25 drying temperature on the films' structural, thermomechanical, mechanical and water
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104 39 temperature, and should be carefully noticed for film preparation.
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110 **Keywords:** drying temperature; particles distribution; physical properties
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122 **44 1. Introduction**
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124 45 Edible packaging is a stand-alone sheet of material which can provide a barrier to
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127 46 mass transfer (moisture, oxygen, and solute movement) within the food itself or
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129 47 between the food and environment (Bourlieu, Guillard, Vallès-Pamiès, et al., 2009).
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131
132 48 The unique advantage of edible packaging is envisioned to simplify packaging system
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134 49 and to improve stability, safety and quality of food products, representing a better
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136 50 choice for food packaging in daily life (Janjarasskul et al., 2018). Edible packaging is
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139 51 developing rapidly by utilizing edible biopolymers as structural matrices. Generally,
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141 52 they are prepared from natural polysaccharides, proteins, lipids or combinations of
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144 53 these components (Jia, Fang, & Yao, 2009; Shi, & Dumont, 2014; Wu et al., 2018;
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146 54 Cheng et al., 2008; Homez-Jara et al., 2018). Among them, konjac glucomannan
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148 55 (KGM) as one natural water-soluble polysaccharide derived from the konjac tuber has
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150
151 56 special nutritional and health promoting functions as well as excellent film-forming
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153 57 capability, and it has bright application prospect for edible packaging preparation (Li
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156 58 et al., 2015; Wu et al., 2012; Chen et al., 2008; Lu, Wang, & Xiao, 2008). Zein is the
157
158 59 major storage protein of corn and comprises \approx 45-50% of the protein in corn (Shukla,
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160 60 & Cheryan, 2001). It is insoluble in pure water, and has good film-forming ability,
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162
163 61 relatively low price and abundant sources (Liang et al., 2015; Bisharat et al., 2018; Gu
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165 62 et al., 2013). According to our previous research (Wang et al., 2017; Ni et al., 2018),
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168 63 KGM and zein could form a stable homogeneous dispersion with appropriate mixing
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170 64 formula, and KGM/zein blend films could be formed by solution casting. KGM/zein
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172 65 blend films showed better mechanical, thermal, water vapor and oxygen barrier
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181 66 properties than pure KGM and zein films. The hydrophobicity of KGM/zein blend
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183 67 films was significantly stronger than that of pure KGM film (Wang et al., 2017). As
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186 68 an edible packaging material, KGM/zein blend films have promising prospects for
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188 69 development.

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191 70
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193 71 Drying is one of most challenging steps in the production of films, and improper
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195 72 drying conditions (e.g. high temperature or a long time) may lead to a variety of
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198 73 drying-induced defects such as blisters, warping, and cracks (Zhou et al., 2018).
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200 74 Presently, the influence of drying conditions on films has received considerable
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203 75 attention. During the drying period, with solvent evaporation and solute migration,
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205 76 various phenomena may occur such as molecular assembly and interaction, a
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207 77 transition from a rubbery to a vitreous phase, a phase separation (thermodynamic
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209
210 78 incompatibility), or crystallization (Liu et al., 2015; Denavi et al., 2009). This can be
211
212 79 largely impacted by the drying temperature, as the solvent evaporation efficiency is
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214
215 80 mainly affected by temperature. For example, increasing drying temperature (from 30
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217 81 to 50 °C) improved tensile stress at yield and elastic modulus of the konjac flour
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219 82 films, while decreasing its thickness, percent elongation at yield and water vapor
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222 83 permeability (Jomlapeeratikul, Poomsa-Ad, & Wiset, 2016). Liu et al. (2016) found
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224 84 drying temperature could be used to modulate the relative amount of triple helices and
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226 85 covalent bonds, and therefore control the physical properties of transglutaminase-
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229 86 modified gelatin films. Moreover, with increased drying temperature, the network
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231 87 structure of the films became more compact. Homez-Jara et al. (2018) found that **the**

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240 88 properties of chitosan edible film were largely influenced by drying temperature, e.g.
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242 89 low drying temperature (e.g. 2 and 25 °C) could improve moisture content, solubility,
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245 90 water vapor permeability, and optical properties; high drying temperature (40 °C)
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247 91 combined with higher chitosan concentration resulted in enhanced tensile strength,
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249 92 swelling power, and greenness value of the films, while diminishing their luminosity
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252 93 and decreasing the melting temperature.
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257 95 As a continuation of our previous work on KGM/zein blend films (Wang et al., 2017),
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259 96 the objective of the current study was to assess the effect of drying temperature on
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262 97 structural and physicochemical properties of KGM/zein blend films. Films prepared
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264 98 under different drying conditions were characterized regarding microstructure,
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266 99 thermal, mechanical and water barrier properties. Aggregation and distribution of zein
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269 100 in films were observed using scanning electron microscopy (SEM), atomic force
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271 101 microscopy (AFM) and confocal laser scanning microscopy (CLSM). Thermal
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273 102 stability of films was analyzed through dynamic mechanical thermal analysis. The
274
275 103 results obtained in this study could be used for function optimization of the films, and
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277 104 would contribute to a deeper understanding of the molecular interactions among
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279 105 KGM/zein blend films.
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285 286 107 **2. Materials and methods**

287 288 108 **2.1 Materials**

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299 109 Konjac glucomannan (KGM, $M_w = 9.67 \times 10^5$ Da) was purchased from Li Cheng
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301 110 Biological Technology Co., Ltd. (Hubei, China). Zein ($M_w = 2.5-4.5 \times 10^4$ Da) from
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304 111 corn was purchased from Beijing J & K Technology Co., Ltd. (Beijing, China).
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306 112 Glycerol (AR, purity $\geq 99\%$) and ethanol (AR, purity $\geq 99.5\%$) were purchased from
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308
309 113 Sinopharm (Chemical Reagent Co., Ltd., Shanghai, China). Rhodamine B (AR, purity
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311 $\geq 99\%$) was purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai,
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314 115 China).

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317 117 **2.2 Blend films preparation**

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321 118 Zein solution was prepared by dissolving 0.1 g zein with glycerol (15% based on total
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323 119 amount of KGM and zein, w/w) in 20 mL of ethanol/water solvent (80:20, v/v) under
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325 120 constant stirring at 500 rpm using a magnetic stirrer (ZNCL-S-5D KEER instrument
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328 121 Co., Ltd., China) for 15 min at 25 °C. KGM solution was prepared by dissolving 0.9 g
329
330 122 KGM in 100 mL water with a continuous stirring electric mixer (OS20-Pro
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332
333 123 SCIOLOGEX Co., Ltd., American) at 600 rpm at 60 °C for 1.5 h. The blend film-
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335 124 forming solutions were prepared by slowly dropping zein solution into KGM solution
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337 125 at 60 °C for 30 min at stirring speed 1000 rpm. Then the blend solutions were
338
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340 126 carefully poured onto a glass plate (14 cm \times 14 cm \times 1.5 cm), and dried in an oven
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342 127 (DNG-9031A, Jing Hong Co., Ltd., Shanghai, China) to a moisture content
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344
345 128 approximately 9% (w.b.) in order to facilitate peeling films from the glass plate. The
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347 129 total content of KGM and zein was kept as 1.0 g per casting plate, and KGM/zein
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349 130 **weight** ratio was 9/1 (w/w).

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360 132 The blend solutions were dried at different temperatures (40, 50, 60, 70 and 80 °C) in
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363 133 an oven, with corresponding drying time (24 h, 18 h, 14 h, 10 h and 7 h) to achieve
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365 134 approximate 9% moisture content (w.b.). According to drying temperature, the film
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368 135 samples were coded as 40 °C KZ, 50 °C KZ, 60 °C KZ, 70 °C KZ and 80 °C KZ,
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370 136 respectively. The impacts of air flow rate and moisture content of inlet air were not
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372
373 137 studied as the machine did not have corresponding functions to adjust/monitor them,
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375 138 and they were considered to be the same for all samples. Both with 15% glycerol
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378 139 addition based on total solid content, pure KGM film and pure zein film were
379
380 140 prepared by separately drying 100 mL KGM solution (1%, w/v) and 20 mL zein
381
382 141 solution (5%, w/v) on glass plates (14 cm × 14 cm × 1.5 cm) at 60 °C, as the reference
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384 142 samples. All film samples were conditioned at 25 ± 1 °C, 40 ± 2% relative humidity
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387 143 for 48 h before testing.
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392 145 **2.3 Atomic force microscopy**
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394 146 The topography of films was obtained using Veeco **MultiMode** atomic force
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396 147 microscopy (SPM9700, Shimadzu Co., Ltd., Japan) in tapping mode with silicon
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399 148 nitride probes. Resonance frequencies of 306-388 KHz were employed, and films
400
401 149 were scanned at speed 1 Hz with resolution 256 × 256 pixels. AFM images with scan
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404 150 sizes of 5 μm × 5 μm were acquired. The roughness values of films were obtained.
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408 152 **2.4 Scanning electron microscopy**
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417 153 Samples were cut into 4 mm × 4 mm pieces for surface observation. The cross-section
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419 154 of samples was prepared by breaking samples (4 mm × 8 mm) after freezing in liquid
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422 155 nitrogen. The surface and cross-section of films were coated with gold at 7.5 Pa with
423
424 156 thickness 20 nm, and then observed by Bio-Rad type SC 502 SEM (JEOL, Tokyo,
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426
427 157 Japan). The sputtered time was about 90 s and an accelerating voltage was 30KV.
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429 158 Images with the magnification of 1000 (cross-section) and 100 (surface) were
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431 159 recorded.
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435 161 **2.5 Confocal laser scanning microscopy**

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438 162 CLSM analysis (Leica TCS SP8) was used to visualize the distribution of zein in
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441 163 blend films. The zein was stained with rhodamine B (Rogers, Roos, & Goff, 2006).
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443 164 The dye solution was first prepared by mixing 4 mg of rhodamine B in 1 mL of water.
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446 165 Then 20 µL of the dye solution was added into 20 mL of zein solution, mixed at 150
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448 166 rpm for 15 min at 25 °C to ensure that the solution was homogenous, and also to give
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451 167 time for the dye to bind to the protein. The dyed zein solution was dropped into the
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453 168 KGM solution and dried to obtain the dyed films. Before placed on the confocal plate
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455 169 for observation, the dyed films were rinsed with distilled water three times and cut
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458 170 into small pieces (0.5 cm × 0.5 cm). Film samples were excited by a red laser beam at
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460 171 638 nm. Image-Pro Plus software (Media Cybernetics Inc., Maryland, America) was
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463 172 used to evaluate the particle size of zein in KGM/zein blend films based on 6
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465 173 representative CLSM images. A total of 300 points were counted for each sample.
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175 2.6 Dynamic mechanical thermal analysis (DMTA)

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

185 2.7 Mechanical properties

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

$$195 \quad TS = \frac{F}{T \times W} \quad (1)$$

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

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535 197 film.
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$$EAB = \frac{L - L_0}{L_0} \times 100\% \quad (2)$$

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539 198
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541 199 Where L_0 is the starting length of the film, L is the length after stretching of the film.
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545 546 201 **2.8 Water contact angle**

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548 202 The wettability of films was evaluated by water contact angle measured by a contact
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550 203 angle meter (DSA25, Krüss Co., Ltd., Germany) equipped with a CCD camera and an
551
552 204 image analysis software. A droplet of distilled water (2.0 μ L) was deposited on the air
553
554 205 side surface of the film (2.0 cm \times 2.0 cm) with a precision syringe, and the drop
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556 206 image was recorded by a camera. The contact angle was measured after stabilizing for
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558 207 30 s.
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564 565 209 **2.9 Swelling and solubility in water**

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567 210 Film sample (2 cm \times 2 cm) was immersed in 30 mL deionized water at 25 $^{\circ}$ C for 5 h,
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569 211 then the wet sample was taken out and wiped with filter paper to remove excess liquid
570
571 212 and weighed. Swelling ratio was calculated by the following formula:
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$$\text{Swelling (\%)} = \frac{m_2 - m_1}{m_1} \times 100 \quad (3)$$

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576
577 213
578
579 214 Where m_1 (mg) is the dry weight of the sample before immersion in water, m_2 (mg) is
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581 215 the sample weight after immersion in water for 5 h.
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587 217 Film sample (3 cm \times 3 cm) was immersed in 100 mL deionized water at 25 $^{\circ}$ C for 24
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594 218 h, then the sample was taken out and dried at 105 °C for 1 h. The water solubility of
595
596 219 the film can be calculated by the following formula:

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

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603
604 221 Where W_2 (mg) is the dry weight of the sample before immersion in water, W_1 (mg) is
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606 222 the dry weight of the sample after immersion in water.

608 609 610 611 224 **2.10 Water vapor permeability (WVP)**

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613 225 The water vapor permeability (WVP; $10^{-13} \cdot \text{g} \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$) of films was determined
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615
616 226 by water vapor permeability tester (PERME W3/031, Labthink international, China).
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618 227 The testing principle was according to Chinese National Standard GB/T 1037-1988. A
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620 228 sheet-cup (25 mm × 65 mm) was filled with deionized water (20 mL) before sealed
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623 229 with the film samples, and then put in the test chamber. The temperature and relative
624
625 230 humidity of the test chamber were controlled at 25 °C and 90%, respectively.

627 628 629 630 232 **2.11 Statistical analysis**

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632 233 All experiments were performed at least in triplicate for each sample. Origin 2017
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635 234 (Originlab Corporation, Northampton MA) and Adobe Photoshop CS 6 (Adobe
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637 235 Systems, San Jose, CA) were used for statistical analysis and figure drawing. One-
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640 236 way analysis of variance (ANOVA) was performed at $p < 0.05$ by the Tukey's
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642 237 multiple range test using SPSS (version 19, Endicott, NY, USA).

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653 **239 3. Results and discussion**

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655 **240 3.1 Microstructure of films and zein particles distribution**

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658 241 Significant surface topography differences were observed among different film
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660 242 samples (Fig. 1) by AFM, and the roughness parameters (Ra, average roughness; Rq,
661
662 243 root-mean-square roughness) of films are shown in Table 1. Both pure KGM film
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664 244 (Ra=8.69 nm, Rq=12.99 nm) and zein film (Ra=4.46 nm, Rq=5.77 nm) had more
665
666 245 smooth and homogenous surfaces compared with the blend films. For the blend films,
667
668 246 with increased drying temperature, their Ra and Rq values showed a V-shape
669
670 247 changing trend (Table 1). 40 °C KZ had the highest Ra (36.11 nm) and Rq (44.59
671
672 248 nm), and 60 °C KZ had the lowest Ra (20.22 nm) and Rq (26.78 nm). This indicated
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674 249 that the blend film dried at 60 °C had more uniform and compact surface than other
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676 250 blend samples.

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682 251
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684 252 Compared with that of pure films, the relatively rough film surfaces of blend films
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686 253 may be explained as follows. Before drying, zein particles were homogeneously
687
688 254 distributed in KGM/zein film-forming solution as reported previously (Ni et al.,
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690 255 2018). During the drying process, the evaporation rate of ethanol was faster than that
691
692 256 of water and increased the hydrophilic character of the solvent, leading to enhanced
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694 257 hydrophobic interactions between zein molecules and a higher degree of zein
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696 258 aggregation (Bisharat et al., 2018; Kim, & Xu, 2008). Thus the surfaces of blend films
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700 259 were relatively rough, and this phenomenon could be affected by drying temperature
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703 260 due to different solvent evaporation situation. When the drying temperature was
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712 261 increased from 40 to 60 °C, the roughness values of blend films had a downward
713
714 262 changing trend. This might due to that film formation time became shorter as a result
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716
717 263 of the higher solvent evaporation rate, which reduced the time for zein migration and
718
719 264 aggregation and resulted in smaller zein aggregates. Therefore the film surfaces
720
721
722 265 became less rough. However, when the drying temperature was further increased from
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724 266 60 to 80 °C, the blend film surfaces became rougher, indicating increased zein
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726 267 aggregates. Cabra et al. (2008) reported temperature-dependent behavior of the Z19 α -
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728
729 268 zein aggregates. They found there were increments in protein aggregation during
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731 269 heating and this was particularly evident in the 60-80 °C range, where the increment
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734 270 in high molecular weight aggregates and the decrement in the monomeric form were
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736 271 higher. Similarly, protein aggregation may be more favored with higher temperature
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738 272 in the range 60-80 °C, though with shorter evaporation time.

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743 274 The microstructures of film surface and cross-section were observed by SEM (Fig. 2).
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745
746 275 For pure KGM film and zein film, the surface and cross-section were smooth and
747
748 276 dense, whereas some pores appeared in pure zein film due to residual air. For blend
749
750 277 films, the surface was rougher compared with that of pure films, with particles evenly
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753 278 distributed and embedded in the films. Among blend films, the surface of 60 °C KZ
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755 279 was relatively smooth, and the cross section of 40 °C KZ showed the loosest structure
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758 280 with the largest size of particles.

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762 282 To further clarify the impact of drying temperature on zein aggregation in the blend
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771 283 films, a CLSM microstructure observation through protein staining (Fig. 3) was
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773 284 performed to visualize zein association states, and size distribution map of zein
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776 285 particles was also drawn (Fig. 4). Homogeneous distribution of zein particles in KGM
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778 286 continuous matrix was observed in all blend films (Fig. 3), and clearly 60 °C KZ
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781 287 showed the smallest zein particles. In the drying process, protein molecules unfolded
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783 288 due to heating, and in solvent exposure of hydrophobic residues and sulfhydryl groups
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786 289 led to the conformational changes and aggregation of protein particles (Broersen et
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788 290 al., 2006). A wave crest (5-20 μm) was found containing 62%, 64.7%, 80%, 77.3%
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791 291 and 73.3% of total zein particles in 40 °C KZ, 50 °C KZ, 60 °C KZ, 70 °C KZ and 80
792
793 292 °C KZ, respectively. The size of zein particles decreased with increased drying
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796 293 temperature from 40 to 60 °C, but increased with drying temperature from 60 to 80 °C.
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798 294 Thus drying temperature 60 °C g resulted in the most uniform and minimum zein
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800
801 295 particles in the films, and was preferred for film preparation. This was in agreement
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803 296 with previous analysis on AFM results. These results indicate that drying temperature
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806 297 is an important factor for KGM/zein blend film preparation due to its impact on zein
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809 298 aggregation.

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811 812 300 ***3.2 Thermomechanical properties***

813
814 301 The thermomechanical behavior of films was studied using a dynamic mechanical
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816
817 302 thermal analyzer (DMTA). The variation of storage modulus (G') and loss factor
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820 303 ($\tan \delta$) against temperature for pure KGM film, pure zein film, and the blend films
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822 304 were shown in Fig. 5. As the testing temperature increased, the G' values of all
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830 305 samples decreased, suggesting reduced stiffness and increased segmental motion of
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832 306 polymers. With increased drying temperature, the G' values of the blend films
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835 307 decreased first and then increased, and that of 60 °C KZ was the lowest. This
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837 308 difference can possibly be attributed to the internal microstructure differences.

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840 309
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842 310 When the temperature rises to the glass transition point (T_g), the molecules enhance
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844 311 thermal motion due to sufficient thermal energy, and the free volume begins to
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847 312 expand, changing from freezing stage to moving stage. At this temperature, a sharp
848
849 313 drop in the storage modulus is observed where the polymer changes from a glassy
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851 314 state to a rubber state. The loss factor ($\tan \delta$) is very sensitive to molecular mobility,
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853
854 315 thus T_g is usually determined as the temperature corresponding to the maximum of
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856 316 $\tan \delta$ peak (α -relaxations) (Qiao, Tang, & Sun, 2011; Motedayen, Khodaiyan, &
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858
859 317 Salehi, 2013). T_g of pure KGM film and zein film were 79.8 and 108.1 °C,
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861 318 respectively. The lower T_g of KGM film in comparison to that of zein film may be
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863
864 319 due to more hydrophilic nature and flexibility of polymer chains. Blending zein with
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866 320 other hydrophilic polymers can often result in the composite films with lower T_g , e.g.,
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868 321 **polycaprolactone**, whey protein concentrate (Corradini et al., 2004; Ghanbarzadeh, &
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870
871 322 Oromiehi, 2009). Similarly, 40 °C KZ, 50 °C KZ, 60 °C KZ, 70 °C KZ and 80 °C KZ
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873 323 showed T_g at 81.4, 89.7, 103.4, 96.5 and 90.8 °C, respectively (Fig. 5), and all were
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876 324 lower than the T_g of zein film. Change in T_g can also be an indicator of the
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878 325 compatibility of polymers. If two polymers are compatible, there is only one T_g in
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881 326 their mixtures; if they are incompatible, phase separation occurs and two T_g are
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889 327 observed in their mixtures, whose values are close to that of each component
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891 328 (Motedayen, Khodaiyan, & Salehi, 2013). All blend films had only one α -relaxations
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893
894 329 (a single Tg), indicating good miscibility/compatibility between the film components.
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896 330 With drying temperature from 40 to 60 °C, Tg increased from 81.4 to 103.4 °C.
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899 331 However, further higher drying temperature (60-80 °C) caused Tg decrease (from
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901 332 103.4 to 90.8 °C). The shift of the main relaxation to a higher temperature usually
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903 333 indicates restricted molecular movement (Piyada, Waranyou, & Thawien, 2013). Tg
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906 334 of 60 °C KZ was the highest, and this may indicate that at this unique drying
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908 335 temperature, the film components had the highest compatibility and strongest
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910 336 intermolecular interactions. This can also be supported by previous results. As zein
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912 337 particles in 60 °C KZ were the smallest, they should have the largest surface area in
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914 338 the KGM continuous phase, benefiting molecular interactions due to the greater
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916 339 contact opportunities.
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922 341 ***3.3 Tensile strength (TS) and elongation at break (EAB)***

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925 342 The dependence of the thickness, tensile strength (TS) and elongation at break (EAB)
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927 343 on drying temperature for the blend films were shown in Fig. 6. The thickness of
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930 344 blend films decreased with increased drying temperature, and the thickness of 80 °C
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932 345 KZ was even lower than that of pure KGM film (Fig. 6a). This was explained by that
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934 346 higher drying temperature may lead to denser film structure, like alginate films
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937 347 (Bagheri, Radi, & Amiri, 2019), konjac flour films (Jomlapeeratikul, Poomsa-Ad, &
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939 348 Wiset, 2016) and whey protein films (Alcantara et al., 1998). EAB values of all blend
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948 349 films were higher than those of pure KGM film and zein film (Fig. 6b), due to
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950 350 hydrogen bond interactions and Maillard reactions between KGM and zein molecules
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952
953 351 (Wang et al., 2017). This also supported the homogeneous distribution of zein
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955 352 particles in blend matrix. TS of all blend films was higher than that of pure zein film,
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958 353 and only TS of 60 °C KZ and 70 °C KZ were higher than that of pure KGM film.
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960 354 With increased drying temperature, a Λ -shape changing trend was found for TS and
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962 355 EAB of blend films, and 60 °C drying temperature resulted in the greatest TS and
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965 356 EAB values. This again supported the strongest interactions and the highest
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967 357 compatibility between KGM and zein at this drying temperature.
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971 972 359 ***3.4 Surface hydrophobicity and water vapor permeability (WVP)***

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974 360 Water contact angle was determined to evaluate the surface hydrophobicity of films.
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977 361 Generally, films with larger contact angle values have higher surface hydrophobicity
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979 362 and lower surface wettability (Gu, Wang, & Zhou, 2013). Pure KGM film, pure zein
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981 363 film, and blend films exhibited significant differences in water contact angle (Fig. 7a).
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984 364 Pure KGM film and zein film showed the lowest and highest surface hydrophobicity.
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986 365 For the blend films, water contact angle values increased first and then decreased with
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989 366 increased drying temperature. The largest contact angle value was observed in 60 °C
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991 367 KZ and 70 °C KZ, indicating 60 °C KZ and 70 °C KZ had the highest surface
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993 368 hydrophobicity among blend films. This result was probably ascribed to the stronger
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996 369 intermolecular interactions between KGM and zein at this drying temperature (60, 70
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998 370 °C), as well as the lower surface roughness of films.
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1009 372 Water vapor permeability (WVP) is an important property of packaging materials and
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1011 is influenced by the hydrophobic or hydrophilic nature of the material and the
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1013 presence of void spaces (Wang, & Padua, 2005). During water transmission through
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1015 the films, the absorbed water could plasticize the film matrix, leading to a less dense
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1017 structure where the chain ends had greater mobility, and thus increased the
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1019 permeability of films (Gu, Wang, & Zhou, 2013). Pure KGM film had the highest
1020 377
1021 WVP value due to its high hydrophilic nature, pure zein film had the lowest WVP
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1023 because of its high hydrophobicity, and WVP values of the blend films were in the
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1025 middle (Fig. 7b). Among blend films, the WVP values of 40 °C KZ, and 50 °C KZ
1026 380
1027 were higher than that of 60 °C KZ, 70 °C KZ and 80 °C KZ. This was ascribed to that
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1029 the distribution of large zein particles in 40 °C KZ and 50 °C KZ shortened the water
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1031 diffusion path, as well as 40 °C KZ and 50 °C KZ had higher hydrophilicity. In many
1032 383
1033 studies, the decrease in the WVP of a nanocomposite film was explained by an
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1035 extended diffusive trajectory (Oymaci, & Altinkaya, 2016). Ozcalik and Tihminlioglu
1036 385
1037 (2013) reported when layered silicates effectively distributed in the polymer film and
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1039 created impermeable obstacles to permeating water vapor molecules, the effective
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1041 path that a permeating water molecule must travel increased and the water vapor
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1043 permeability decreased.
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1054 391 ***3.5 Swelling and solubility properties***

1056 392 The swelling and solubility of films in water were measured to assess the water
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1058 resistance properties of films (Fig. 8), demonstrating the hydrophobicity from another
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1066 394 aspect. Pure KGM film could not be tested as it was quickly dissolved. Pure zein film
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1068 395 showed the lowest swelling and solubility, indicating the greatest hydrophobicity.
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1071 396 Both swelling and solubility curves had a clear V-shape changing trend in the blend
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1073 397 films. Increased drying temperature (40-60 °C) led to a rapid decrease in both
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1075 398 swelling and solubility, followed by an increase at 60-80 °C. Therefore 60 °C KZ
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1077 399 showed the highest hydrophobicity indicated by the highest water resistance
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1079 400 properties, in agreement with the results of water contact angle of films. This may
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1081 401 result from the changes in film microstructure and intermolecular forces.
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1088 403 **4. Conclusion**
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1090 404 The zein particles were evenly dispersed in KGM/zein blend films, and the particle
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1092 405 size was significantly affected by drying temperature. Compared with other drying
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1094 406 temperatures, 60 °C was found to confer the blend film with the superior properties,
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1096 407 such as the highest tensile strength, elongation at break, water contact angle, the
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1098 408 lowest water vapor permeability, swelling and solubility. Either higher or lower
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1100 409 drying temperature led to weakened film properties. These phenomena were
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1102 410 explained by that drying temperature 60 °C may contribute to the strongest
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1104 411 intermolecular interactions between KGM and zein in the films, as the most uniform
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1106 412 and smooth film surface, minimum size of zein aggregates in the film were observed
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1108 413 with this drying temperature. Also at this drying temperature, the two components
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1110 414 may reach the highest compatibility, as T_g was the highest at this temperature. The
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1112 415 results indicated that drying temperature was of great importance for film preparation,
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1125 416 as they significantly impacted the intermolecular interactions among film
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1127 417 components, and it may be used to modulate the physical properties of the film for
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1130 418 future applications.

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1149 427 **References**

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