

8-16-2019

# Sheet-extruded films from blends of hydroxypropylated and native corn starches, and their characterization

Hee-Young Kim  
*Iowa State University*

Buddhi P. Lamsal  
*Iowa State University, lamsal@iastate.edu*

Jay-lin Jane  
*Iowa State University*

David A. Grewell  
*Iowa State University, dgrewell@iastate.edu*

Follow this and additional works at: [https://lib.dr.iastate.edu/fshn\\_hs\\_pubs](https://lib.dr.iastate.edu/fshn_hs_pubs)

 Part of the [Agricultural Science Commons](#), [Food Chemistry Commons](#), [Food Processing Commons](#), [Human and Clinical Nutrition Commons](#), and the [Systems and Integrative Engineering Commons](#)

The complete bibliographic information for this item can be found at [https://lib.dr.iastate.edu/fshn\\_hs\\_pubs/29](https://lib.dr.iastate.edu/fshn_hs_pubs/29). For information on how to cite this item, please visit <http://lib.dr.iastate.edu/howtocite.html>.

---

This Article is brought to you for free and open access by the Food Science and Human Nutrition at Iowa State University Digital Repository. It has been accepted for inclusion in Food Science and Human Nutrition Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

---

# Sheet-extruded films from blends of hydroxypropylated and native corn starches, and their characterization

## Abstract

Sheet-extruded films from the blends of hydroxypropylated normal corn starch (HP) and native normal corn starch (NS) at weight ratios of 100:0, 90:10, 70:30, 50:50, 30:70, and 0:100 were prepared and characterized. Glycerol and water were added as plasticizers at 11 and 27% starch weight, respectively. The highest tensile strength (TS) and longest elongation to break (EB) for dry films were observed at 70:30 HP: NS ratio, which was 25.76 MPa, and 3.97%, respectively. However, TS and EB of this 70:30 blend extruded starch film exhibited low resistance upon wetting for 10s. The film TS and EB were reduced to 13.26 MPa and 3.35%, respectively. Addition of 0.5% (wt/wt starch) succinic acid (SA) as a cross-linker to 70:30 HP: NS starch blend before film extrusion positively affected both TS and EB of films upon wetting; rather higher TS (16.64 MPa) and EB (4.85%) values were observed, which indicated improvement in water resistance of the films. Sheet-extruded films from 70:30 HP: NS blends resulted in improved dry strength, and upon cross-linking with SA, improved wet strength as well. The films had smooth and compact structure, which was explained by esterification/transesterification reactions promoted by SA, and confirmed by Fourier-transform infrared spectroscopy analysis.

## Disciplines

Agricultural Science | Food Chemistry | Food Processing | Human and Clinical Nutrition | Systems and Integrative Engineering

## Comments

This accepted article is published as Kim, H.Y., Lamsal, B., Jane, J.L., Grewell, D., Sheet-extruded films from blends of hydroxypropylated and native corn starches, and their characterization. *Journal of Food Process Engineering* (accepted on June 30, 2019); 2019, e13216. Doi: [10.1111/jfpe.13216](https://doi.org/10.1111/jfpe.13216). Posted with permission.

1 **Title: Sheet-extruded films from blends of hydroxypropylated and native corn starches,**  
2 **and their characterization**

3

4 Running title: Extruded corn starch films

5

6 Hee-Young Kim<sup>a</sup>, Buddhi Lamsal<sup>a\*</sup>, Jay-lin Jane<sup>a</sup>, David Grewell<sup>b</sup>,

7 <sup>a</sup> Department of Food Science and Human Nutrition, Iowa State University, Ames, IA 50011,

8 USA

9 <sup>b</sup> Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA

10 50011, USA

11

12

13

14

15

16 \*Corresponding author. Tel: +1 515 294 8681; Fax: +1 515 294 8181.

17 *E-mail address:* [lamsal@iastate.edu](mailto:lamsal@iastate.edu) (B. Lamsal)

18

19 **ABSTRACT**

20 **BACKGROUND:**

21 Sheet-extruded films from the blends of hydroxypropylated (HP), and native normal corn  
22 starch (NS) at weight ratios of 100:0, 90:10, 70:30, 50:50, 30:70, 0:100 were prepared and  
23 characterized. Glycerol and water were added as plasticizers at 11% and 27% starch weight,  
24 respectively.

25 The highest tensile strength (TS) and longest elongation to break (EB) for dry films  
26 were observed at 70:30 HP: NS ratio, which was 25.76 MPa, and 3.97%, respectively.

27 However, TS and EB of this 70:30 blend extruded starch film exhibited low resistance upon  
28 wetting for 10s. The film TS and EB were reduced to 13.26 MPa and 3.35%, respectively.

29 Addition of 0.5% (w/w starch) succinic acid as a cross-linker to 70:30 HP: NS starch blend  
30 before film extrusion positively affected both TS and EB of films upon wetting; rather higher  
31 TS (16.64MPa) and EB (4.85%) values were observed, which indicated improvement in  
32 water resistance of the films. Sheet-extruded films from 70:30 HP: NS blends resulted in  
33 improved dry strength, and upon cross-linking with succinic acid, improved wet strength as  
34 well. The films had smooth and compact structure, which was explained by esterification/  
35 transesterification reactions promoted by succinic acid, and confirmed by FT-IR analysis.

36 **KEYWORDS**

37 Hydroxypropylated normal corn starch; Extrusion; Sheet-film, Tensile strength

38 **Practical Applications**

39 Manufacturing packaging films from biological sources, as well as coating materials,  
40 would be beneficial to the environment along with wider applications. Biobased packaging  
41 materials include both edible coatings and edible films along with primary and secondary  
42 packaging materials, and could also have non-food applications. They are derived from  
43 renewable sources and are potentially biodegradable through composting (which is a

44 technique for waste management). Hydroxypropylation of starch results in wider  
45 functionality, and sheet-extrusion can result in more flexible and transparent films. Blends of  
46 70:30 HP: NS resulted in stronger sheet-extruded films; testing of both dry and wet strengths  
47 of films indicated its suitability for both as edible coating (wet application), and other dry  
48 coatings/ films. These blend film can be an alternative to synthetic packaging films within  
49 their limitations.

## 50 **1. Introduction**

51 High shear and heat, like the one imparted by extruders disrupt the semi-crystalline  
52 structure of granular starch at higher moisture operation (French, 1984). This loss of  
53 structure, that consisted of concentric alternating amorphous and semi-crystalline growth  
54 rings, results in a homogeneous melt with thermoplastic properties, a prerequisite for starch  
55 be made into films for various food and non-food applications (Shanks and Kong, 2012;  
56 Zdrahala, 1997). Being abundantly available, renewable, and a low- cost raw material (US\$  
57 0.25-0.6/kg) (Chiellini et al., 2009; Lai & Padua, 1997; Mali et al., 2005), starch is  
58 considered as a promising biopolymer for many food and non-food packaging- related  
59 applications. However, limited mechanical performance and poor water resistance of starch-  
60 based films need to be improved for wider acceptance. Conventional processing techniques,  
61 e.g., solvent-casting, extrusion-blowing, and injection or compression molding, have been  
62 adapted to obtain thermoplastic starch (TPS) for film-related applications.

63 The relatively poorer film-functional properties of native starch can be improved, among  
64 other methods, by chemical modifications (Rouilly et al., 2004). Chemical treatments  
65 introduce new functional groups to starch molecules either through chemical derivatizations  
66 (etherification, esterification, cross-linking, and grafting at starch hydroxyl groups) or  
67 decomposition (acid or enzymatic hydrolysis and oxidation) to alter their properties (Lopez et  
68 al., 2010). Hydroxypropylation is one such chemical modification of starch in which it is

69 etherified with propylene oxide (Liu et al., 1999). Incorporation of bulky and hydrophilic  
70 hydroxypropyl groups into starch chains weakens or disrupts internal bonds in the starch  
71 granules that, in turn, alters physicochemical properties and functionalities (Gunaratne &  
72 Corke, 2007). Desirable properties of hydroxypropylated starch for use as films are  
73 flexibility, transparency, and processability (Chaudhary et al., 2008; Lafargue et al., 2007;  
74 Roth & Mehlretter, 1967). During extrusion, hydroxypropylated starch required lesser  
75 amount of torque and die pressure because of the lower melt viscosity (Chaudhary et al.,  
76 2008).

77 In spite of these improvements, 2 major issues with hydroxypropylated starch films can  
78 be identified, which are 1) decrease in tensile strength of films produced, and 2) increase in  
79 water sensitivity (hydrophilicity). Woggum et al. (2015) reported that the addition of  
80 propylene oxide up to 12%, w/w decreased tensile strength of the starch films from 6.18 to  
81 3.88 MPa, but increased water vapor permeability from 2.98 to 4.97 g mm m<sup>-2</sup> day<sup>-1</sup> KPa<sup>-1</sup>,  
82 respectively. These results were attributed to the bulky nature of hydroxypropyl groups,  
83 which sterically hinder the adjacent starch chains from effectively connecting and opening  
84 the starch structure. This allows free water molecules to hydrogen-bond with the starch  
85 chains (Gilfillan et al., 2013). Thus, hydroxypropylated starch has been usually blended with  
86 other natural polymers (i.e., gelatin) or synthetic polymers (i.e., maleated-polycaprolactone,  
87 poly-hydroxyamino ether), nanofillers (i.e., silica, montmorillonite) or fibers (i.e., sugar cane)  
88 to improve the tensile strength and water sensibility in cast and extruded films or foams  
89 (Dean et al., 2011; Frosta et al., 2011; Gilfillan et al., 2013; Nabar et al., 2005; Nabar et al.,  
90 2006; Zhang et al., 2013). However, the poor compatibility of hydroxypropylated starch and  
91 additives often lead to poorer physical and mechanical properties (Nabar et al., 2005).

92 Blending of hydroxypropylated starch with other starches could be a potential way to  
93 address the compatibility issues. When different types of starches are mixed together, the

94 mixtures behave differently than individuals in a single phase; many synergistic effects of  
95 blends have been reported (Karim et al., 2001; Yao et al., 2003). Nevertheless, to our best  
96 knowledge, research on the effect of simple binary mixtures of native starch and chemically  
97 modified (hydroxypropylated) starch for film applications has not been reported, except for  
98 acetylation (Lopez et al. 2013). Lopez et al. (2013) investigated 5 different blends of  
99 acetylated and native corn starches and glycerol at different ratios to obtain films with the  
100 optimal mechanical and barrier properties. The extruded films with blend of 10:70:20  
101 acetylated: native starch: glycerol weight ratio resulted in the maximum tensile strength  
102 among the ratios tested, although, the lowest water vapor permeability was observed for  
103 80:5:15 blend ratio.

104 Interacting starches or modified starches with organic acids, for example, citric acid,  
105 tartaric acid, and maleic acid, succinic acid etc. is another way to improve characteristics of  
106 resulting films (Ačkar et al., 2015). Di-carboxylic acids like succinic acid (SA) or malic acid  
107 are reported to reduce degree of crystallinity, and improve flexibility like the maximum strain  
108 at maximum load (Thessrimuang et al., 2019). Succinic acid has received attention as a green  
109 feedstock for the manufacturing of synthetic resins, biodegradable polymers, and chemical  
110 intermediates (Lynd et al., 1999), and plays a role as compatibilizers in starch and synthetic  
111 biopolymers such as PLA (polylactic acid) and PBAT (poly butylene adipate-co-  
112 terephthalate).

113 Thus, the objective of this study was to prepare and characterize films from blends of  
114 hydroxypropylated and native normal corn starches at different ratios using sheet-extrusion  
115 technique. The differences in physical, mechanical, and barrier properties of films at different  
116 blend ratios were compared. In some instances, succinic acid was also added into the blends  
117 to enhance water resistance of the films (Lynd et al., 1999).

## 118 **2. Materials and Methods**

119 **2.1. Materials**

120 Normal corn starch (NS) was provided by Grain Processing Corporation (Muscatine, IA,  
121 USA) under the trade name PURE-DENT B700. Hydroxypropylated normal corn starch (HP,  
122 Polartex 05732) was provided by Cargill (Minneapolis, MN, USA). Glycerol was purchased  
123 from Fisher Scientific (Fair Lawn, NJ, USA). All other chemical reagents used in this study  
124 were analytical grade.

125 **2.2. Compounding**

126 Based on the preliminary work, and an earlier work reported (Kim et al., 2017), six  
127 different starch blends (Blends #1-6) were mixed with glycerol and water at the weight ratio  
128 of 1:0.11:0.27 (Table 1) in a mechanical mixer (Kitchen Aid, Model # KS55, St. Joseph, MI)  
129 at 2½ mixing speed for 5 min, respectively. For Blends #7-9, small amount of glycerol was  
130 replaced by succinic acid and its effect on the film characteristics was investigated. All the  
131 blends were stored in sealed plastic bags at room temperature to equilibrate overnight before  
132 extrusion.

133 **2.3. Sheet-Extrusion process**

134 The sheet films with blends were prepared in two stages using a single screw extruder  
135 with the screw diameter 11 mm and length 500 mm (C.W. Brabender, Duisburg, Germany).  
136 In the first stage, the blend was extruded at a screw speed of 75 rpm through a 3 mm  
137 diameter die at the temperatures of 75/130/140°C from the feeding zone to the die zone,  
138 respectively. The extrudate ropes were pelletized by cutting into 5mm long pieces. The  
139 pellets were extruded again to obtain sheet-films 150 mm wide and 600 µm thick in the  
140 same single-screw extruder with a sheet-die of above dimensions. The temperature profile  
141 inside the barrel from feed to die was 75/160/90/90°C during sheet-extrusion, and the  
142 extruder was run at the screw speed of 75 rpm.

143 **2.4. Characterization of sheet-extruded films**



#### 144 **2.4.1. Mechanical properties: Tensile test**

145 The mechanical properties of the films were determined using a universal testing  
146 machine, Instron 4500 series (Norwood, MA, USA) in accordance with the ASTM D882-02  
147 guidelines (ASTM 2002). The rectangular specimens (20 × 68 mm) were equilibrated at  
148 25°C and 53% RH for 2 days, prior to testing. Initial grip distance and cross-head speed were  
149 50 mm and 50 mm/min, respectively. The tensile strength (TS, MPa) was calculated by  
150 dividing the maximum load at break by the cross-sectional area of the film specimen. The  
151 elongation at break (EB, %) was defined as the percentage change in the length of the  
152 specimen to the original length between grips at break (Muscat et al., 2012). Wet-strength of  
153 the film was determined by immersing the strip of film in water (35 mL) for 10 s and then  
154 gently wiping with a paper tissue to remove excess water (Wu et al., 2009). At least 5  
155 specimens were tested for each film produced for analysis.

156 The thickness of the film was determined using an electronic digital caliper (Marathon,  
157 Ontario, Canada) with an accuracy of 0.01 mm. The rectangular specimens (20 × 68 mm) of  
158 the films were equilibrated at 25 °C for 2 days in a sealed chamber containing the Mg (NO<sub>3</sub>)<sub>2</sub>  
159 saturated salt solution for constant RH of 53% (Bertuzzi et al., 2007). The thickness  
160 measurements of the equilibrated films were repeated on 3 random positions of each film  
161 specimen and average values were used.

#### 162 **2.4.2. X-ray diffraction pattern**

163 X-ray diffraction (XRD) patterns of the films were obtained using an X-ray  
164 diffractometer (X'pert APD, Philips, Netherlands) with Cu-K $\alpha$  radiation ( $\lambda=1.54056\text{\AA}$ ) at a  
165 target voltage and current of 40 kV and 30 mA, respectively. XRD data were collected at  
166 scanning angle  $2\theta$  from 5° to 40°. The relative crystallinity (RC, %) of the films was  
167 quantitatively calculated following the method of Nara and Komiya (1983):  $RC=A_c/(A_a+A_c)$ ,

168 where  $A_c$  was the crystalline area, and  $A_a$  was the amorphous area on the X-ray  
169 diffractograms.

#### 170 **2.4.3. Moisture content**

171 Moisture contents of the films were determined by measuring the weight loss upon  
172 drying in a convention oven at 110°C until a constant dry weight was reached (Ghasemlou et  
173 al., 2013). Three replicates samples for each blend and film was used to measure the moisture  
174 content.

#### 175 **2.4.4. Scanning electron microscopy**

176 The surface morphology of the films was observed by using a field emission scanning  
177 electron microscopy (FE-SEM, S-4700, Hitachi, Japan) at an accelerating voltage of 10 kV.  
178 Powdered samples were spread onto the copper grids coated with a carbon supported film and  
179 a thin Au-Pd conductive coating was then used to reduce the charge effect.

#### 180 **2.4.5. Fourier-transform infrared spectroscopy (FT-IR)**

181 The FT-IR scanning of the films were done to evaluate the interactions between film  
182 components (starch and plasticizer). Absorbance spectra of the films were acquired using a  
183 Tension 37 FTIR spectrophotometer (Bruker Co., Ettlingen, Germany) in attenuated total  
184 reflectance (ATR) mode. Films conditioned at 25 °C and 53% RH for 2 days were placed on  
185 the zinc selenide crystal. The spectra were obtained in 400-2100  $\text{cm}^{-1}$  range by accumulation  
186 of 16 scans at 4  $\text{cm}^{-1}$  resolution. Area measurements and baseline corrections were carried out  
187 using OPUS 7.2.139 software (Bruker Co., Ettlingen, Germany).

#### 188 **2.5. Statistical analyses**

189 Statistical analyses consisted of an analysis of variance (ANOVA) using SAS 9.4  
190 software (SAS Institute, Cary, NC, USA). Duncan's multiple range test ( $p < 0.05$ ) was used  
191 to identify statistical differences between mean values.

### 192 **3. Results and discussion**

193 **3-1. Tensile strength and elongation at break for HP/NS blend films**

194 A preliminary study was performed to arrive at appropriate level of plasticizer content  
195 (glycerol and water) and barrel temperature profile. When excess glycerol and water (e.g.,  
196 glycerol:  $\geq 33\%$ , water:  $\geq 76\%$ , based on the starch weight) were employed, extruded films  
197 had bubbles caused by steam generation in the material, as was also reported by Thunwall et  
198 al., (2008). This phenomenon was also observed when the die-end temperature of the  
199 extruder exceeded  $100^{\circ}\text{C}$ . To obtain homogeneous film without bubbles, the optimal  
200 condition for our system was as follows: 11% glycerol, and 27% water based on the starch  
201 weight and  $90^{\circ}\text{C}$  die temperature. This condition was maintained while evaluating optimum  
202 blend ratio of HP and NS for extrusion.

203 Fig. 1 shows the mechanical properties (TS and EB) of the films made from HP: NS  
204 blends at various weight ratios: 100:0, 90:10, 70:30, 50:50, 30:70, and 0:100. Dry films of  
205 HP: NS blend films at 90:10, 70:30, and 50:50 weight ratios exhibited higher TS than HP or  
206 NS alone. Especially, at 70:30 ratio, TS reached the peak at 25.76 MPa. This value was  
207 almost 2 times greater than those of films from unblended starches. However, thereafter TS  
208 value progressively decreased until the lowest value of 7.36 MPa was observed at 30:70 ratio.

209 The TS results for dry films (Fig. 1) suggests the synergistic interaction between HP and  
210 NS. Many researchers have reported that the films made from hydroxypropylated starch have  
211 lower TS than the films made from native starches (Kim et al., 2017; Muscat et al., 2012;  
212 Woggum et al., 2015). It was explained that the hydroxypropyl groups ( $-\text{CH}_2\text{CHOHCH}_3$ )  
213 may have played a role in disrupting inter- and intra- molecular hydrogen bonds between  
214 starch chains (Kim et al., 2017), resulting in weaker films. Supplementing the portion of HP  
215 with NS in this study led to films with increased TS. Nevertheless, it is noteworthy that the  
216 blending effect was considerably different depending on the NS amount blended. NS

217 contributed to improving the tensile strength of films up to 50% blend ratio, beyond that,  
218 however, tensile strength of the resulting films decreased (Fig. 1).

219 A similar trend was observed for the films tested under wet conditions, with wet-  
220 strength being lower than dry-strength, regardless of blends and film types (Fig. 1). The HP:  
221 NS blend films with weight ratios of 90:10, 70:30, and 50:50 exhibited distinctly different TS  
222 before and after water immersion. In the case of 70:30 blend, it reduced from 25.76 MPa to  
223 13.26 MPa. On the other hand, unblended (HP and NS films), and 30:70 blend films were  
224 almost not affected by water. The extent of change in TS was as follows: 10.51 to 9.39 MPa  
225 for HP, 10.97 to 10.64 MPa for NS, and 7.36 to 7.34 MPa for 30:70 blend films. It was  
226 possibly because HP and NS were physically bound during mixing and extrusion, so they  
227 may dissociate easily in water. It can be considered that blend films containing more than  
228 50% HP on total starch had lower wet tensile strength due to relatively more water molecules  
229 in them than in other blend films; incorporation of hydroxypropyl groups increase the  
230 hydrophilicity of the films (Kim et al., 2017).

231 The EB values for films, that indicate the film flexibility, is usually inversely related to  
232 the TS values (Alves et al., 2007; Myllärinen et al., 2002); however, in this study, film EB  
233 values under the drier conditions showed a positive correlation with TS. The films from  
234 70:30 weight ratio blend of HP: NS had the highest EB (3.97%) indicating more flexibility,  
235 as well as highest TS (25.76 MPa) among tested samples. After water immersion, EB for all  
236 films increased, except for 70:30 blend film. For this particular blend films, the difference in  
237 EB before and after water immersion was very small. Overall, simple blending of HP and NS  
238 at 70:30 ratio was effective to improve dry-strength of the film but its water resistance was  
239 not as strong.

### 240 ***3-2. X-ray diffraction patterns of HP: NS blend films***

241 Fig. 2 shows the X-ray diffraction profiles of HP: NS blend films with various weight  
242 ratios, with numbers in parenthesis indicating relative crystallinity %. The 100:0 and 90:10  
243 blend films exhibited an amorphous structure with peak at  $2\theta$  of  $20^\circ$ , while other films  
244 showed the strong peaks at  $13^\circ$  and  $20^\circ(2\theta)$  and weaker peak at  $17^\circ(2\theta)$ , indicating a typical  
245 V-type crystalline structure of starch (Kim et al., 2014). Considering that the peak barrel  
246 temperature of the extruder was  $160^\circ\text{C}$  during sheet-film extrusion, all starches were fully  
247 gelatinized and thus yielded an amorphous structure. Thus, the V-type crystalline structure  
248 may have been possibly induced through interaction with starch chains after extrusion  
249 process. At the minimum, NS at more than 10% was needed for the V-type formation. The  
250 relatively crystallinity (RC) of films with V-type structure was 3.65% (70:30 blend), 4.51%  
251 (50:50 blend), 6.29% (30:70 blend), and 6.09% for 100 NS film. XRD and RC values were  
252 not enough to explain why the biggest TS was observed at 70:30 HP: NS blend ratio, while  
253 the lowest TS was obtained at 30:70 blend ratio, as shown in Fig. 1.

### 254 **3-3. Effect of succinic acid on HP: NS blend films**

255 Results for the mechanical strength of films (Section 3.1) indicated that the 70:30 blend  
256 resulted in films with a prominent TS under the dry condition, but not a strong resistance to  
257 water, resulting in much lower TS values for wet films (Fig. 1). Therefore, to address this  
258 issue, succinic acid (SA) at proportions (0.38, 0.5, and 0.75%, based on the starch weight)  
259 were added to starch blends; the total weight was kept the same by reducing appropriate  
260 amount of glycerol for mixing in 70:30 HP: NS blends. During preliminary work, when the  
261 initial concentration of citric acid was 0.5%, wet-strength of 70:30 HP/NS film did not  
262 decrease much, compared to the loss in dry-strength. So, we needed to confirm that 0.5% SA  
263 was optimum concentration; so film wet-strength was compared for SA around 0.5% with at  
264 least 3 chosen levels.

265 As shown in (Fig. 3), an increase in the concentration of the SA from 0% to 0.75%  
266 (w/w) led to decrease in TS and EB values of the films under the dry condition. However, TS  
267 and EB values of the films under the wet condition showed increasing trend up to 0.5% (w/w)  
268 and decreasing trend thereafter. The maximal TS and EB values observed at 0.5% (w/w) SA  
269 was 16.64 MPa and 4.85%, respectively. The difference between dry and wet-strength was  
270 only 1.33 MPa at 0.5% (w/w) SA addition, which improved the water resistance of the films.  
271 Although the addition of 0.75% (w/w) SA showed a higher water resistance of the film after  
272 immersion, initial dry mechanical properties were considerably lower, which were thought to  
273 be likely due to cross-linking. SA was used as an additive in HP: NS blend films to promote  
274 cross-linking and is expected to contribute in improving the interactions between polymeric  
275 phases that resulted in films with better properties. Similar studies have been reported for  
276 other additives such as citric acid, tartaric acid, and maleic acid (Wang et al., 2010; Yun et  
277 al., 2006; Olivato et al., 2012 a, 2012b; Yoon et al., 2006). They play a role as  
278 compatibilizers in starch and synthetic biopolymers such as PLA (polylactic acid) and PBAT  
279 (poly butylene adipate-co-terephthalate).

280 Fig. 4 shows the moisture contents of starch blend pellets and films for different SA  
281 concentrations (0.38-0.75%, w/w starch). The pellets containing SA had more moisture than  
282 those without SA (control). A similar trend was also found in the films made from these  
283 pellets, even though the pellets were extruded further to obtain the films at relatively high  
284 barrel temperatures causing them to lose some moisture. However, with increase in SA  
285 concentration, moisture contents of the pellets and films gradually decreased, which possibly  
286 could be related to cross-linking reaction promoted by the presence of SA. The decrease in  
287 moisture content with increase in SA agreed with mechanical properties of the wet films  
288 (Figure 3).

289 ***3-4. Field Emission SEM (FE-SEM) of HP: NS blend films with succinic acid***

290 Fig. 5 exhibits the FE-SEM surface images of the extruded blend film sheets for  
291 different SA content (0 - 0.75% w/w). The surface of control film (Fig. 5a) was considerably  
292 different than SA-cross-linked films (Fig. 5b-d), with rough appearance and many void  
293 spaces, whereas, films with SA blends had smooth surfaces without noticeable voids,  
294 regardless of SA content. Due to the presence of SA, HP and NS were uniformly dispersed  
295 and cross-linked, resulting in improved interfacial compatibility, thus, the smoothness of the  
296 films. However, it's not easy to explain the discrepancy between SA film samples based on  
297 FE-SEM only.

### 298 ***3-5. FT-IR of HP: NS blend films with succinic acid***

299 Fig. 6 presents the FT-IR spectra of starch blend films with various SA contents (0.38-  
300 0.75%, w/w). Spectra of all film samples were almost similar, but slightly different in peak  
301 intensity only. A peak at approximately  $1715\text{ cm}^{-1}$ , produced by a carbonyl stretch (C = O)  
302 attributed to esters, was observed for all film samples (Olivato et al., 2012b). This peak is an  
303 evidence of the esterification and transesterification reactions (cross-linking) promoted by  
304 SA. An increase in the peak intensity was positively correlated with SA content, which can  
305 relate to the mechanical properties observed.

## 306 **4. Conclusions**

307 Relatively lower mechanical properties of starch film were improved by blending  
308 hydroxypropylated native normal corn starch; such properties were blend-ratio dependent.  
309 The maximal effect in mechanical properties was observed at HP: NS blend ratio of 70:30 by  
310 weight. However, starch films at this blend ratio had weaker resistance to water, with smaller  
311 TS value upon short exposure to water. Addition of succinic acid contributed to polymeric  
312 chain crosslinks resulting in films with relatively higher water resistance and flexibility.  
313 These blend film can be an alternative to synthetic packaging films within their limitations.

## 314 **5. Acknowledgement**

315 This research was supported by the IUCRC/NSF Center for Bioplastics and Bio-  
316 composites (CB<sup>2</sup>) at Iowa State University. We thank the Dr. Gordon Selling of USDA  
317 Agricultural Research Service at Peoria, IL, and VISKASE® Companies, Inc. for technical  
318 discussions during execution of the project.

## 319 **6. References**

- 320 Ačkar, Đ., Babić, J., Jozinović, A., Miličević, B., Jokić, S., Miličević, R., Rajič, M. and  
321 Šubarić, D., 2015. Starch modification by organic acids and their derivatives: A  
322 review. *Molecules*, 20(10), pp.19554-19570.
- 323 Alves, V. D., Mali, S., Beléia, A., & Grossmann, V. E. (2007). Effect of glycerol and  
324 amylose enrichment on cassava starch film properties. *Journal of Food Engineering*, 78,  
325 941-946.
- 326 ASTM (2002). *Standard test method for tensile properties of thin plastic sheeting, D882-02*  
327 *annual book of ASTM*. Philadelphia, PA: American Society for Testing and Materials.
- 328 Bertuzzi, M. A., Castro Vidaurre, E. F., Armanda, M., & Gottifredi, J. C. (2007). Water vapor  
329 permeability of edible starch based films. *Journal of Food Engineering*, 80, 972-978.
- 330 Chaudhary, A. L., Miler, M., Torley, P. J., Sopade, P. A., & Halley, P. J. (2008). Amylose  
331 content and chemical modification effects on the extrusion of thermoplastic starch from  
332 maize. *Carbohydrate Polymers*, 74, 907-913.
- 333 Chiellini, E., Cinelli, P., Ilieva, V. I., Imam, S. H., & Lawton, J. L. (2009). Environmentally  
334 compatible foamed articles based on potato starch, corn fiber, and poly (vinyl alcohol).  
335 *Journal of Cellular Plastics*, 45, 17-32.
- 336 Dean, K. M., Petinakis, E., Goodall, L., Miller, T., Yu, L., & Wright, N. (2011).  
337 Nanostabilization of thermally processed high amylose hydroxypropylated starch films.  
338 *Carbohydrate Polymers*, 86, 652-658.



339 French, D., 1984. Organization of starch granules. In: Whistler, R. L., BeMiller, J. N.,  
340 Paschall, E. F. (Eds.), *Starch Chemistry and Technology*. Academic Press, Orlando, FL,  
341 pp. 183-247.

342 Frosta, K., Barthes, J., Kaminski, D., Lascaris, E., Niere, J., & Shanks, R. (2011).  
343 Thermoplastic starch-silica-polyvinyl alcohol composites by reactive extrusion.  
344 *Carbohydrate Polymers*, 84, 343-350.

345 Ghasemlou, M., Aliheidari, N., Farmi, R., Shohae-Aliabadi, S., Keshavarz, B., Cran, M. J.,  
346 Khaksar, R. (2013). Physical, mechanical and barrier properties of corn starch films  
347 incorporated with plant essential oils. *Carbohydrate Polymers*, 98, 1117-1126.

348 Gilfillan, W. N., Sopade, P. A., & Doherty, W. O. S. (2013). Moisture uptake and tensile  
349 properties of starch-sugar cane fibre films. *International Sugar Journal*, 115, 23-27.

350 Gunaratne, A. & Corke, H. (2007). Functional properties of hydroxypropylated, Cross-linked,  
351 and hydroxypropylated cross-linked tuber and root starches. *Cereal Chemistry*, 84, 30-  
352 37.

353 Karim, A. A., Teo, C. H., Norziah, M. H., & Seow, C. C. (2001). Retrogradation behavior of  
354 binary starch mixtures of rice starch with other types of starches. In *Starch: Advance in  
355 Structure and Function*; Barsby, T. L., Donald, A. M., Frazier, P. J., Eds.; Royal Society  
356 of Chemistry: Cambridge, UK; pp. 59-66.

357 Kim, H.-Y., Jane, J.-J., & Lamsal, B. (2017). Hydroxypropylation improves film properties  
358 of high amylose corn starch. *Industrial Crops and Products*, 95, 175-183.

359 Kim, H.-Y., Lim. J. K., Kim. D., & Lim. S.-T. (2014). Formation of crystalline complexes  
360 between amylo maize dextrin and ceramide. *Carbohydrate Polymers*, 101, 407-414.

361 Lafargue, D., Pontoire, B., Buléon, A., Doublier, L. J., & Lourdin, D. (2007). Structure and  
362 mechanical properties of hydroxypropylated starch films. *Biomacromolecules*, 8, 3950-  
363 3958.

364 Lai, H. M., & Padua, G. W. (1997). Properties and microstructure of plasticized zein films.  
365 *Cereal Chemistry*, 74, 771-775.

366 Liu, H., Ramsden, L., and Corke, H. (1999). Physical properties and enzymatic digestibility  
367 of hydroxypropylated ae, wx, and normal maize starch. *Carbohydrate Polymers*, 40,  
368 175-182.

369 López, O. V., Zaritzky, N. E., & García, M. A. (2010). Physicochemical characterization of  
370 chemically modified corn starches related to rheological behavior, retrogradation and  
371 film forming capacity. *Journal of Food Engineering*, 100, 160-168.

372 López, O. V., Zaritzky, N. E., Grossmann, M. V. E., & García, M. A. (2013). Acetylated and  
373 native corn starch blend films produced by blown extrusion. *Journal of Food*  
374 *Engineering*, 116, 286-297.

375 Lynd, L. R., Wyman, C. E., & Gerngross, T. U. (1999). Biocommodity engineering.  
376 *Biotechnology Progress*, 15, 777-793.

377 Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. N., & Zaritzky, N. E. (2005).  
378 Mechanical and thermal properties of yam starch films, *Food Hydrocolloid*, 19, 157-  
379 164.

380 Muscat, D., Adhikari, B., Adhikari, R., & Chaudhary, D. S. (2012). Comparative study of  
381 film forming behavior of low and high amylose starches using glycerol and xylitol as  
382 plasticizers. *Journal of Food Engineering*, 109, 189-201.

383 Myllärinen, P., Partanen, R., Seppala, J., & Forssell, P. (2002). Effect of glycerol on behavior  
384 of amylose and amylopectin films. *Carbohydrate Polymers*, 50, 355-361.

385 Nabar, Y., Narayan, R., & Schindler, M. (2006). Twin-screw extrusion production and  
386 characterization of starch foam products for use in cushioning and insulation  
387 applications. *Polymer Engineering and Science*, 46, 438-451.

388 Nabar, Y., Raquez, J. M., Dubois, P., & Narayan, R. (2005). Production of starch foams by  
389 twin-screw extrusion: Effect of maleated poly (butylene adipate-*co*-terephthalate) as a  
390 compatibilizer. *Biomacromolecules*, 6, 807-817.

391 Nara, S., & Komiya, T. T. (1983). Studies on the relationship between water-saturated state  
392 and crystallinity by the diffraction method for moistened potato starch. *Starch*, 35, 407-  
393 410.

394 Olivato, J. B., Grossmann, M.V. E., Bilck, A. P., & Yamashita, F. (2012b). Effect of organic  
395 acids as additives on the performance of thermoplastic starch/polyester blown films.  
396 *Carbohydrate Polymers*, 90, 159-164.

397 Olivato, J. B., Grossmann, M.V. E., Yamashita, F., Eiras, D., & Pessan, L. A. (2012a). Citric  
398 acid and maleic anhydride as compatibilizers in starch/poly (butylene adipate-*co*-  
399 terephthalate) blends by one-step reactive extrusion. *Carbohydrate Polymers*, 87, 2614-  
400 2618.

401 Roth, W. B., & Mehlretter, C. L. (1967). Some properties of hydroxypropylated amylo maize  
402 starch films. *Food Technology*, 21, 72-74.

403 Rouilly, A., Rigal, L., & Gilbert, R. G. (2004). Synthesis and properties of composites of  
404 starch and chemically modified natural rubber. *Polymer*, 45, 7813-7820.

405 Shanks, R., & Kong, I. (2012). Thermoplastic starch. *Thermoplastic Elastomers, Chapter 6*,  
406 95-116.

407 Thessrimuang, N. and Prachayawarakorn, J., 2019. Characterization and Properties of High  
408 Amylose Mung Bean Starch Biodegradable Films Cross-linked with Malic Acid or  
409 Succinic Acid. *Journal of Polymers and the Environment*, 27(2), pp.234-244.

410 Thunwall, M., Kuthanová, V., Boldizar, A., & Rigdahl, M. (2008). Film blowing of  
411 thermoplastic starch. *Carbohydrate Polymers*, 71, 583-590.

412 Wang, N., Zhang, X., Han, N., & Fang, J. (2010). Effects of water on the properties of  
413 thermoplastic starch poly (lactic acid) blend containing citric acid. *Journal of*  
414 *thermoplastic Composite Materials*, 23, 19-34.

415 Wogugum, T., Sirivongpaisal, P., & Wittaya, T. (2015). Characteristics and properties of  
416 hydroxypropylated rice starch based biodegradable films. *Food Hydrocolloids*, 50, 54-  
417 64.

418 Wu, R.L., Wang, X.L., Li, F., Li, H.Z. & Wang, Y. Z. (2009). Green composite films  
419 prepared from cellulose, starch and lignin in room-temperature ionic liquid, *Bioresource*  
420 *Technology*, 100, 2569-2574

421 Yao, Y., Zhang, J. M., & Ding, X. (2003). Retrogradation of starch mixtures containing rice  
422 starch. *Journal of Food Sciences*, 68, 260-265.

423 Yoon, S.D., Chough, S.-H., & Park, H.-R. (2006). Effects of additives with different  
424 functional groups on the physical properties of starch/PVA blend film. *Journal of*  
425 *Applied Polymer Science*, 100, 3733-3740.

426 Yun, Y., Na, Y., & Yoon, S. (2006). Mechanical properties with the functional group of  
427 additives for starch/PVA blend film. *Journal of Polymers and the Environment*, 14, 71-  
428 78.

429 Zdrahala, R. J. (1997). Thermoplastic starch revisited structure/property relationship for  
430 “dialed-in” biodegradability. *Macromolecular Symposia*, 123, 113-121.

431 Zhang, N., Liu, H., Yu, L., Liu, X., Zhang, L., Chen, L., & Shanks, R. (2013). Developing  
432 gelatin-starch blends for use as capsule materials. *Carbohydrate Polymers*, 92, 455-461.

433

434 **Table Titles**

435 **Table 1.** Compositions (weight %) of blends used for film preparation.

436

	HP	NS	Glycerol	Water	Succinic acid
Blend 1	100	0	11	27	0
Blend 2	90	10	11	27	0
Blend 3	70	30	11	27	0
Blend 4	50	50	11	27	0
Blend 5	30	70	11	27	0
Blend 6	0	100	11	27	0
Blend 7	70	30	10.62	27	0.38
Blend 8	70	30	10.50	27	0.50
Blend 9	70	30	10.25	27	0.75

437 HP, hydroxypropylated normal corn starch; NS, normal corn starch

438

439 **Figure captions**

440 Fig. 1. Tensile strength (MPa) and elongation at break (%) of HP: NS blend films under dry  
441 and wet condition. HP: hydroxypropylated starch; NS: native normal corn starch

442 Fig. 2. X-ray diffraction patterns of HP: NS blend films. The numbers in brackets are relative  
443 crystallinity (RC) values. HP: hydroxypropylated starch; NS: native normal corn starch

444 Fig. 3. Dry and wet mechanical properties of 70:30 HP: NS blend films depending on  
445 succinic acid content. HP: hydroxypropylated starch; NS: native normal corn starch

446 Fig. 4. Moisture contents (%) of pellets and films made from HP: NS (70:30) and succinic  
447 acid. HP: hydroxypropylated starch; NS: native normal corn starch

448 Fig. 5. FE-SEM images of 70:30 HP: NS blend films containing 0% (a), 0.38% (b), 0.5% (c),  
449 and 0.75% (d) succinic acid (magnification, 500x). HP: hydroxypropylated starch; NS: native  
450 normal corn starch

451 Fig. 6. FT-IR spectrum of 70:30 HP: NS blend films containing succinic acid. HP:  
452 hydroxypropylated starch; NS: native normal corn starch

453

454

455

456 **Figure 1.**

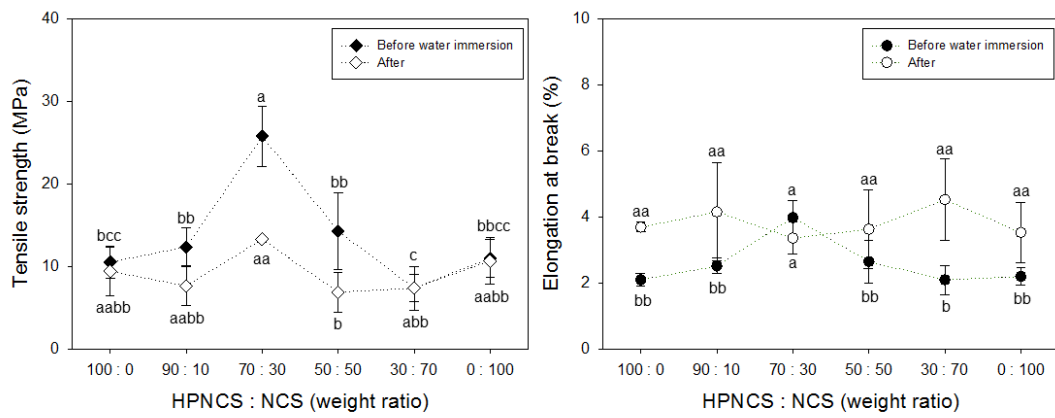


Fig. 1. Tensile strength (MPa) and elongation at break (%) of HPNCS/NCS blend films under dry and wet condition.

457

458

459

460

461

**Figure 2.**

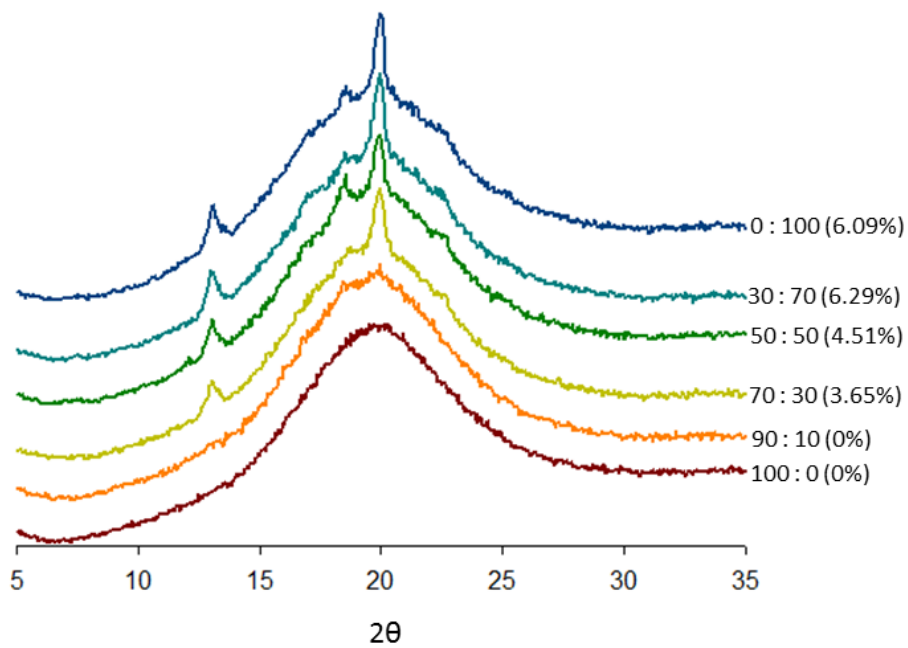


Fig. 2. X-ray diffraction patterns of HPNCS/NCS blend films. The numbers in brackets are relative crystallinity (RC) values.

462

463



464 **Figure 3.**

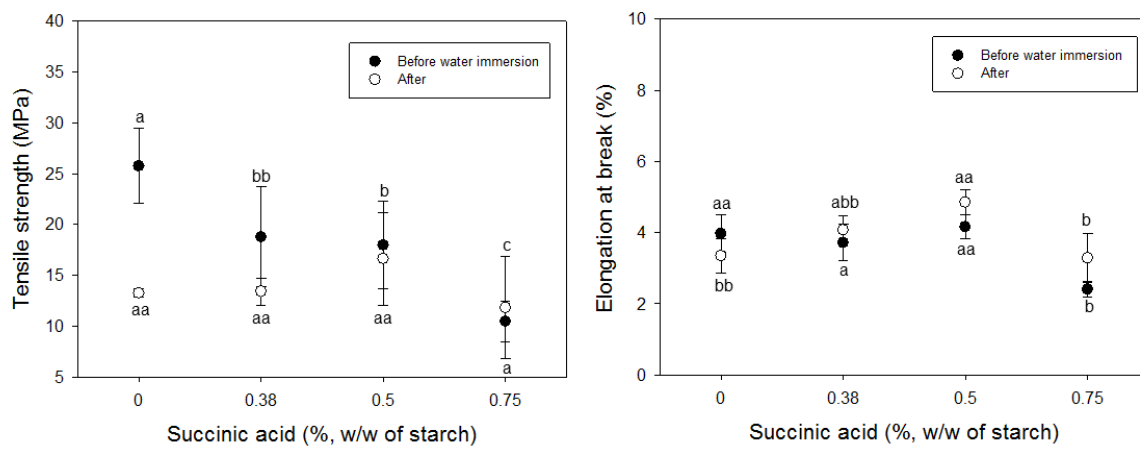


Fig. 3. Dry and wet mechanical properties of 70:30 HPNCS/NCS blend films depending on succinic acid content.

465

466

467 **Figure 4.**

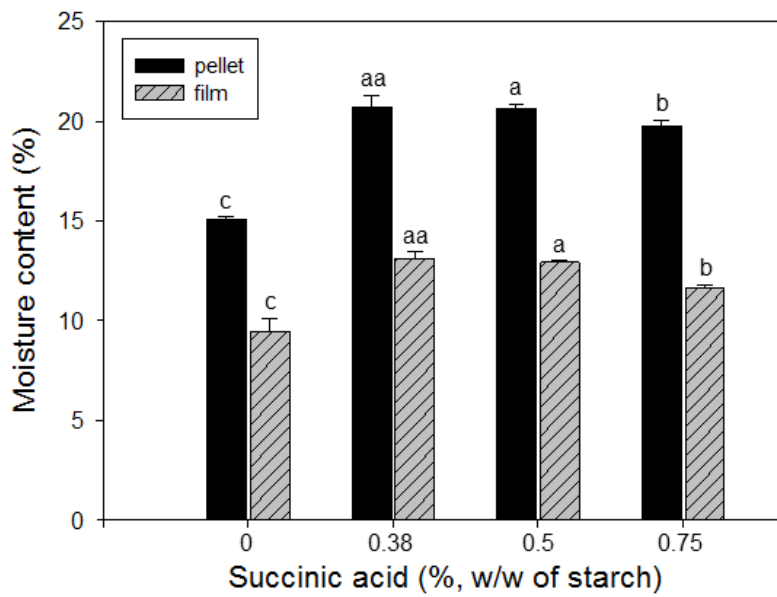


Fig. 4. Moisture contents (%) of pellets and films made from HPNCS/NCS (70:30) and succinic acid.

468

469

470

**Figure 5.**

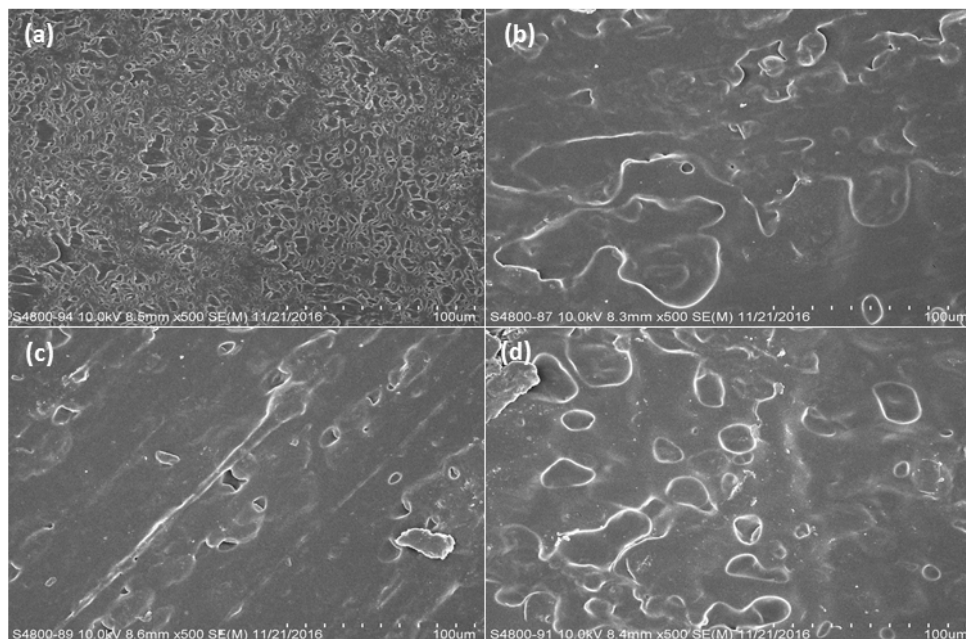


Fig. 5. FE-SEM images of 70:30 HPNCS/NCS blend films containing 0% (a), 0.38% (b), 0.5% (c), and 0.75% (d) succinic acid (magnification, 500x).

471

472

473

**Figure 6.**

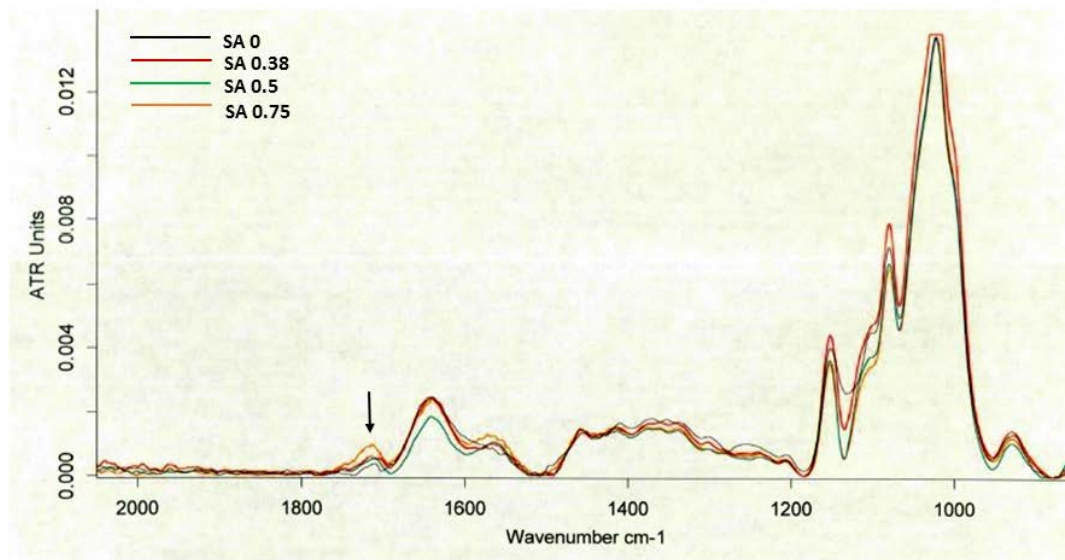


Fig. 6. FT-IR spectrum of 70:30 HPNCS/NCS blend films containing succinic acid.

474

475