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Research paper

Development and characterization of aqueous amylose-rich maize starch dispersion for film formation

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Abstract

Development and characterization of amylose-rich starch dispersion for film forming was performed. The influence of dispersion preparation temperature on amylose-rich maize starch (Hylon VII) film formation, and the physical properties of the films were investigated. The film-forming ability of the dispersions was evaluated with free films plasticized with glycerol and sorbitol, and the films were prepared at an elevated temperature (70°C) by a casting technique. The solid-state and particle properties of dispersions were investigated by means of X-ray diffraction (XRD), Fourier transform near infrared (FT-NIR) spectroscopy and laser diffraction particle size analysis. Free films were characterized with respect to their appearance, by FT-NIR spectroscopy, and by XRD. Mechanical stress–strain properties were also studied. Increasing the temperature of dispersion preparation results in higher crystallinity, thus affecting the film forming ability. Mechanically strong and elastic films can be formed from amylose-rich starch dispersion formed at 40°C. The more crystalline precipitate complex (obtained at 80°C) and the entirely amorphous gel (obtained at 10°C) formed non-continuous and cloudy films. The better film-forming properties of the dispersion formed at 40°C are probably due to the highly amorphous structure and smaller particle size. The study shows the possibility of using ambient tempered amylose–starch dispersion for film forming.

Keywords: High amylose maize starch; Temperature; Dispersion; Free film; Physical characterization

1. Introduction

Starch, the biodegradable polysaccharide consists of the essentially linear amylose and the branched amylopectin [1,2] consisting of α-D-glucose units. Starch has three main polymorph forms, A, B, and V. The A-type is characteristic of cereal starches and the B-type is found in tuber and amylose-rich starches. The V-type is obtained when amylose is co-crystallized with compounds such as alcohols [3], iodine and fatty acids [4]. The A- and B-types have a double helical conformation [5–7], whereas the V-type is single stranded. In the V-type, the co-crystallised compound occupies the channel in the center of the amylose helix.

Edible starch films can be used for food protection and preservation. The good oxygen barrier property of hydrophilic starch films is well documented [8–11]. Factors affecting the barrier properties have been extensively studied. An increased crystallinity and a decrease in water content of starch films lead to reduction in oxygen permeability [10,11].

Native starch could be a potential coating material for pharmaceutical dosage forms. However, a drawback is that starch is non-soluble in water and organic solvents such as ethanol at ambient temperature and coating with a starch solution is only possible with a gelatinized hot solution [12,13]. The development of a low viscous starch dispersion would enable a coating process without heating.

When a hot starch solution is allowed to stand and cool, either a gel or a precipitate is formed. The physical form is dependent on the concentration of the solution – a dilute solution forms a precipitate upon cooling, whereas a concentrated solution forms a gel [14]. The chain length of amylose also influences the aggregation process of aqueous amylose solutions, in that shorter chain lengths predominately lead to precipitates whereas longer chain lengths tend to form a gel [15]. The precipitation of starch

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by alcohol addition has been the focus of several studies. Precipitation was reported in the early 1940s in order to fractionate starch by an amylose-1-butanol complex formation [16]. Since then several modified complexing methods have been introduced [17-19].

Although film forming of hot solutions and gels is widely reported, little work have been done to develop a low viscous dispersion for film forming. The aim of the present study was to investigate the effect of dispersion preparation temperature on the structure and physical properties of the amylose maize starch films, and to study the relationship between the film-forming ability and the film structure.

2. Materials and methods

2.1. Preparation of dispersions

Amylose-rich maize starch (Hylon VII®, National Starch, Germany) with an amylose content of about 70% was used. Hylon VII® (2%) and purified water were stirred (100 rpm) and heated to 160°C in a pressure reactor (Fig. 1). The chamber slowly cooled to 95°C and the hot solution was subsequently cooled in an ice bath to a temperature of either 10, 40 or 80°C. As the temperature was reached, 25°C ethanol (1:1) was added with continuous blending. The formed dipersions are referred to as 'dispersion 10', 'dispersion 40' and 'dispersion 80'. Dispersion 10 was a gel because a gel was formed before the addition of ethanol. The dispersions were mixed with a magnetic stirrer for 1 h after the ethanol addition. The dispersions were analysed 24 h after preparation.

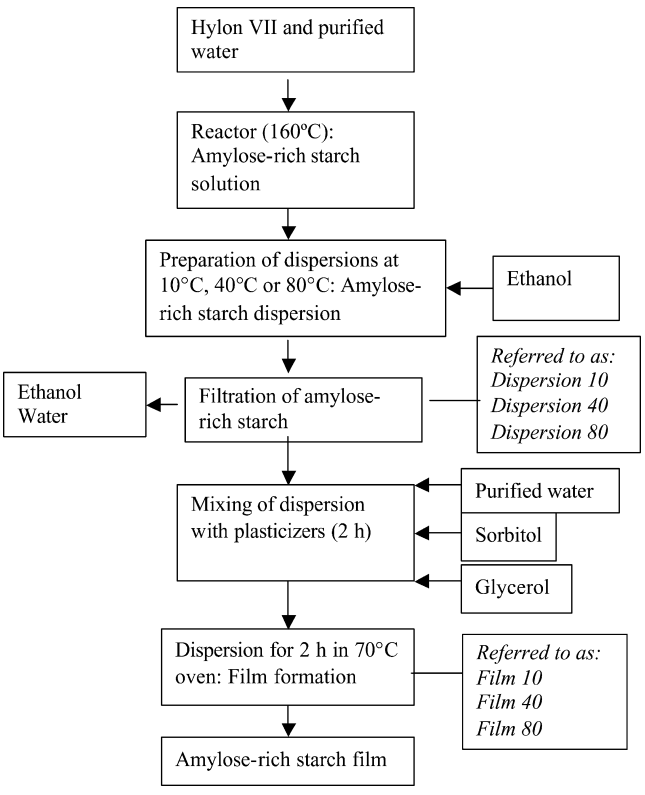

Fig. 1. Flow chart illustrating the manufacture of dispersions and films.

2.2. X-ray diffraction (XRD) measurements

X-ray diffraction studies were done using X-ray diffraction (XRD) theta–theta diffractometer (Bruker axs D8, Germany). The XRD experiments were performed in symmetrical reflection mode with CuK_α radiation (1.54 Å) using Göbel Mirror bent gradient multilayer optics. The scattered intensities were measured with a scintillation counter. The angular range was from 2 to 40°, in steps of 0.05°, and the measuring time was 10 s/step. The instrumental broadening was estimated as 0.03°, from a reflection of silicon. The crystalline component was determined from the diffraction pattern by subtracting the amorphous component. The relative crystallinity was then calculated by dividing the area of the peaks by the total area.

2.3. FT-NIR analysis and moisture content

The near-infrared spectra were measured with a Fourier transform (FT-NIR) spectrometer (Bomem MD-160 DX, Hartmann and Braun, Quebec, Canada) using Bomem-GRAMS software (v. 4.04, Galactic Industries Inc., Salem, NH, USA) and Teflon as a reference (99% reflective Spectralon, Labsphere Inc., North Sutton, NH, USA). The spectra were recorded over a range of 10 000–4000 cm^{-1} with a resolution of 8 cm^{-1}; an average of 40 scans were used ($n = 3$). Moisture content was determined using a Karl Fisher titrator (Mettler DL35, Mettler-Toledo, Swizerland) ($n = 3$).

2.4. Particle size distribution measurements

The particle size analysis was conducted with a laser diffraction particle sizer (Malvern 2600C, Malvern instruments, UK). The particle size was measured by the method of particles in liquid (PIL), i.e. ethanol ($n = 3$).

2.5. Preparation of free films

The day following preparation of the dispersion, the precipitates and gel were filtered, after which purified water and the plasticizers (glycerol and sorbitol) were added to achieve the required concentration (5%) (Fig. 1). The glycerol and sorbitol contents were both 50% of the polymer content (total 100%). The plasticizers were blended with the suspension for 2 h before casting the films. The suspension was poured onto Teflon plates and transferred into an oven at 70°C and 17% relative humidity (RH) (2 h). The films were stored in a controlled atmosphere, at 25°C and 60% RH, for 1 week before testing.

2.6. Mechanical testing of the films

Free films were studied with a material testing machine (Lloyd LRX, Lloyd instruments Ltd., Great Britain). The films were cut into strips and mounted on the material testing machine, with grips at 40 mm apart. The extension speed was 10 mm/min. Stress–strain curves were recorded, and the tensile strength (load at break/initial cross-sectional area) and elongation (%) at break were measured ($n = 3$).

3. Results and discussion

3.1. X-ray diffraction (XRD)

Fig. 2 illustrates the diffraction patterns of amylose-rich maize starch dispersions. The diffraction pattern of starch dispersion 10 includes a diffuse maximum, but does not include any reflection, which means that the sample is entirely amorphous. The diffraction pattern of dispersion 80 includes an amorphous part and clear reflections at 7.5, 12.9, 19.8 and 22.6° (2θ), which are characteristic of the single helical crystal structure of V_h-type [3]. The V_h-type diffraction pattern is typical for an inclusion complex of amylose and linear alcohol. Dispersion 40 is only very slightly crystalline (Table 1). The diffraction pattern of dispersion 40 includes an amorphous element and two weak reflections at about 12.9 and 19.8° (2θ). The reflections at 7.5 and 22.6° are missing for dispersion 40. These results are consistent with those obtained by Biliaderis and Galloway (1989), who studied the effect of temperature on the formation of amylose–lipid complexes [20]. Their results showed a complex formation and an increase of crystallinity at higher (90°C) precipitation temperatures.

Table 1
Crystallinities of amylose-rich starch dispersions and films

Temperature (°C)	Crystallinity (%)	
	Dispersion	Film
10	0	22
40	3	22
80	26	41

Fig. 3 illustrates the diffraction patterns of the starch films studied. The diffraction peaks for B-type is typically at 2θ Bragg angles 5.6, 15, 17, 22, and 24 [21]. The diffraction patterns of our films resemble that of B-type starch, which is typically formed of amylose-rich maize starch. The reflections at 15 and 17 have, however, been shifted to higher 2θ values. This indicates shorter distances of Bragg planes in our films. The V_h-type dispersion 80 has evolved during film forming, and possibly during equilibration, into B-type starch although the original V_h-type is still present in the diffraction pattern. Film 80 was non-continuous, whereas film 40 was continuous flexible and smooth. This result implies that the film forming is facilitated when the film is formed of an amorphous compound compared to a compound with a more crystalline character.

3.2. FT-NIR analysis and water content

The absorption bands of water in the NIR region were

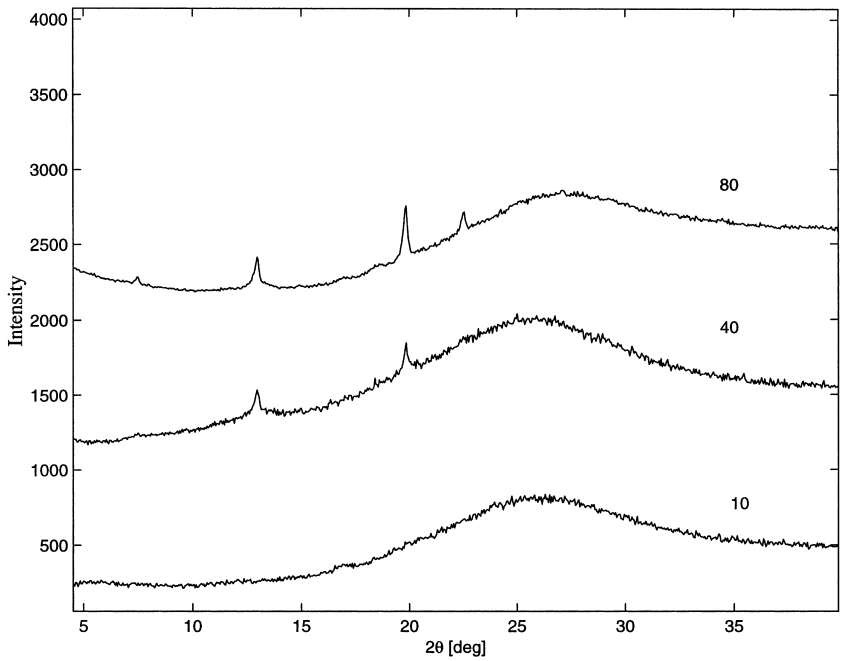

Fig. 2. XRD pattern of amylose-rich starch for dispersions prepared at different temperatures.

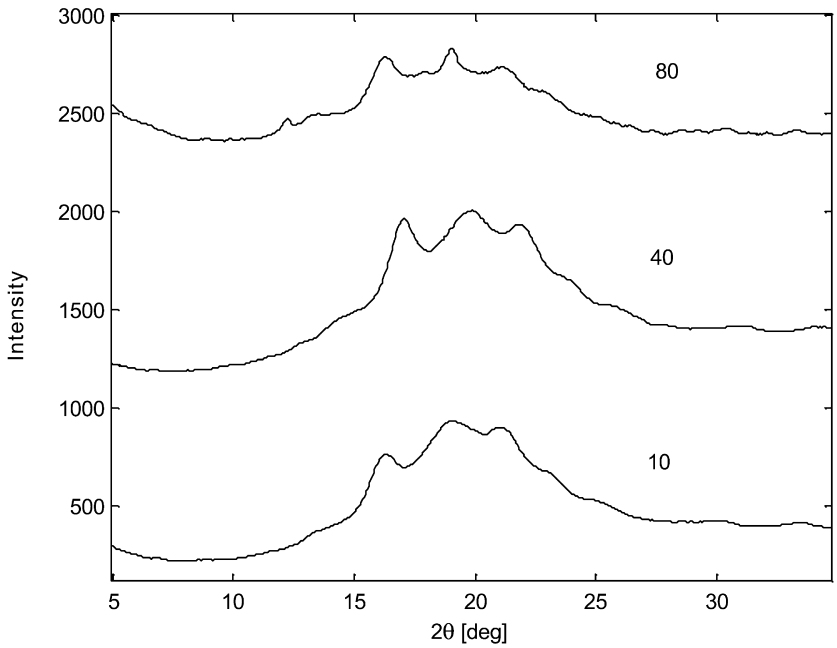

Fig. 3. XRD pattern of films prepared of dispersions prepared at different temperatures.

observed at around 1450 and 1940 nm. The band at around 1450 nm is the first overtone of OH stretching vibrations. The band at around 1940 nm is caused by a combination of OH stretching and bending vibrations [22], and it is often applied for analytical applications [23]. The main spectral features at the NIR region were the 1450 and 1940 nm bonds due to water, and these bands were present for both the precipitates (not shown) and films (Fig. 4b). Fig. 5 shows a close-up (1800–2100 nm) of the second derivative spectra of amylose-rich starch films. Film 10 and 80 have a peak location at approximately 1910 nm. The peak location for film 40 is at longer wavelengths, which indicate that water is more strongly associated, i.e. have more hydrogen bonds, with the starch structure [24]. Slight differences were also observed at the 2050–2200 nm region, which is the region of different combination bands of CH groups [23,24].

For the films 10, 40 and 80 the moisture contents, measured with the Karl Fisher-titrator, were 14.9% (0.4), 10.7% (0.2) and 15.3% (0.1), respectively (SD shown in brackets). Film 40 has either lower moisture content than the other two films or then part of the water in film 40 is so strongly associated with the structure that it cannot be measured by titration.

3.3. Particle size of precipitate

The particle size was smallest for dispersion 80. However, there was no clear difference between it and dispersion 40 (Table 2). Dispersion 10 clearly differed from 40 and 80, in having a much larger aggregate size. With regard to film forming, a small particle size is beneficial due to the larger surface area. Therefore, the poor film-forming property of the gel-like dispersion 10 could be partly due to the larger aggregate size, i.e. smaller surface area.

3.4. Appearance and mechanical properties of free films

The films prepared from dispersion 40 were transparent, clear, and flexible when handled. The films prepared from dispersion 10 and 80, however, were non-continuous, and therefore the mechanical properties of these cloudy films could not be tested. The tensile strength of the films prepared from precipitate 40 was 5 ± 0 MPa, which is lower than that reported in the literature for the free films prepared from amylose-rich maize starch [25]. This is due to the higher amount of plasticizers used in the present films. The tensile strength values for the amylose-rich starch films in the present study are similar to plasticized (20%) amylopectin films [26]. The elongation of the films in the present study was 26 ± 3%. The elongation is on the same level as for amylopectin films and is higher than those reported for amylose-rich starch films (5%) [26]. This can

Table 2
Particle size of the dispersions prepared at different temperatures; median, 10 and 90% fractiles ($n = 3$) (mean ± SD)

	Particle size (μm)		
	0.5	0.9	0.1
Dispersion 10	120 ± 4	312 ± 19	31 ± 1
Dispersion 40	24 ± 1	43 ± 2	10 ± 0
Dispersion 80	22 ± 0	41 ± 0	9 ± 0

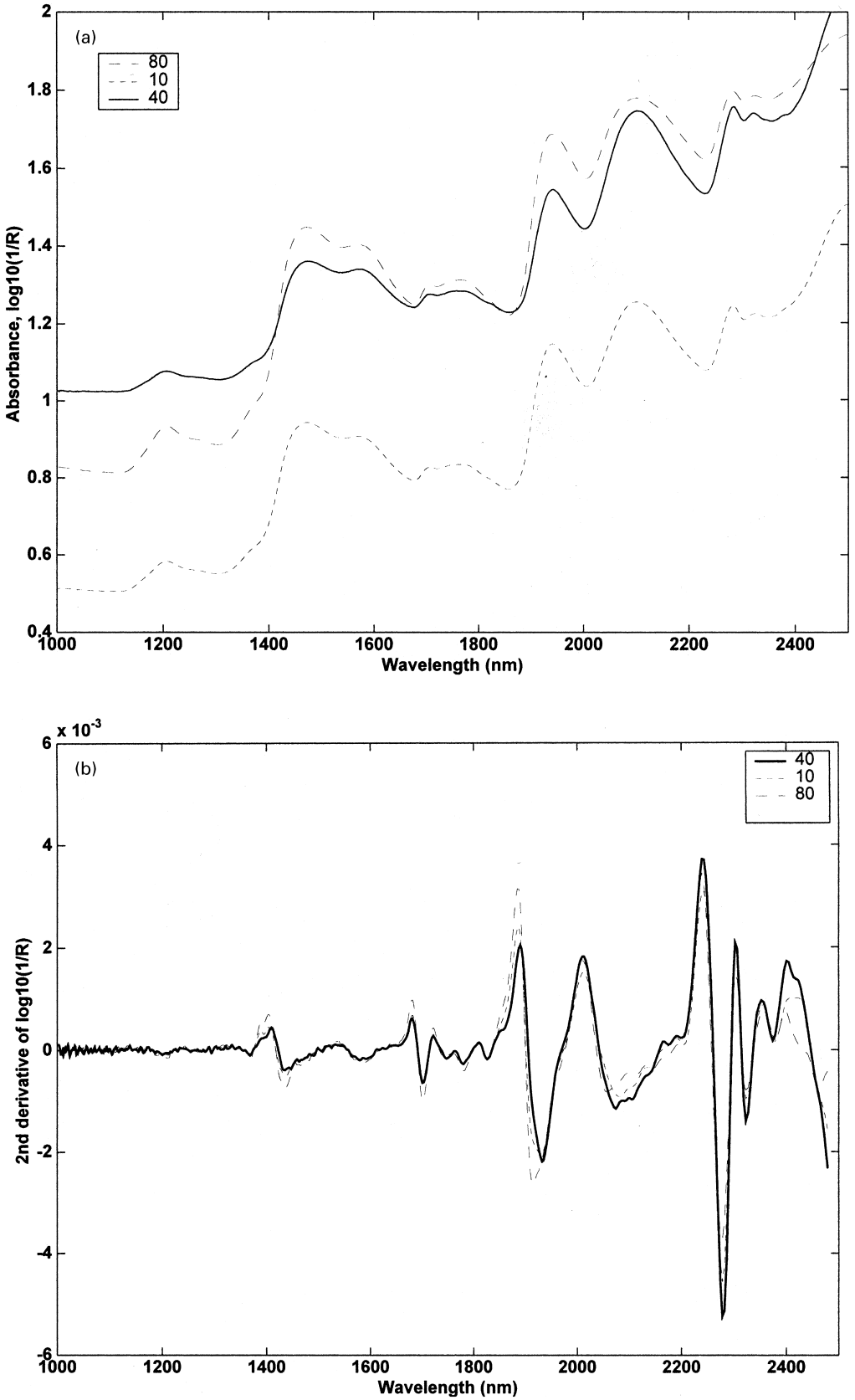

Fig. 4. The effect of dispersion preparation temperature on absorbance spectras of films: (a) absorbance log10(1/*R*), (b) second derivative of log10(1/*R*).

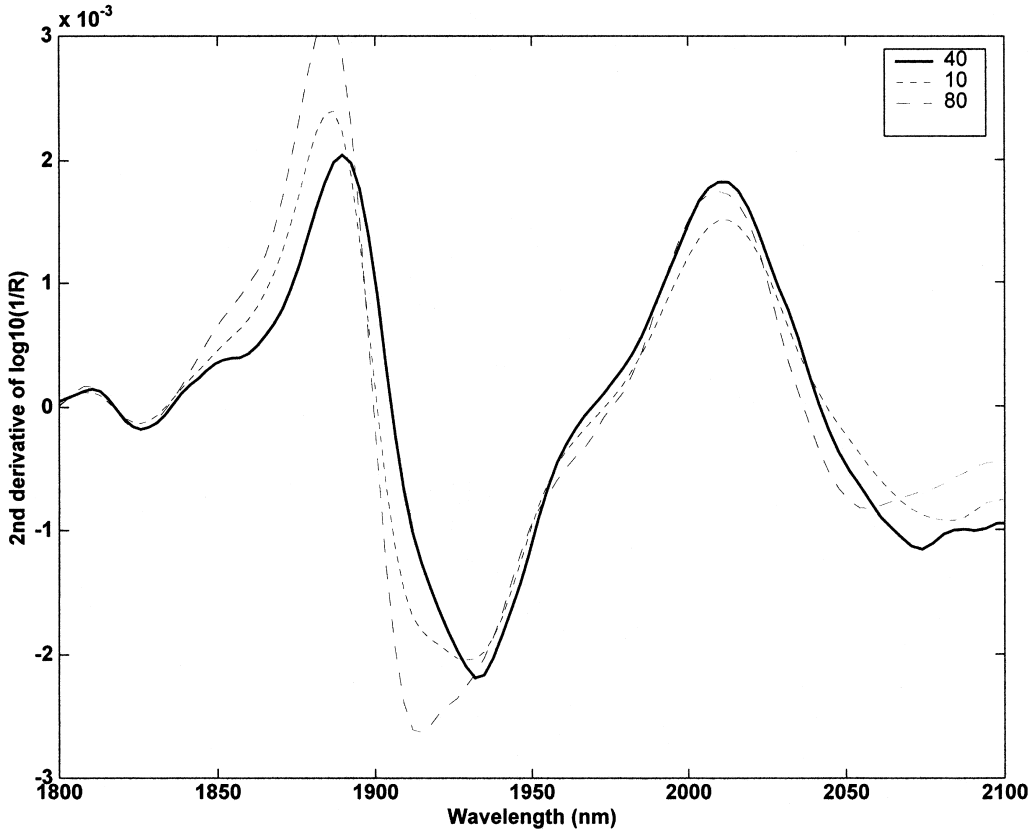

Fig. 5. The effect of dispersion preparation temperature on second derivative spectra (1800–2100 nm) of subsequently formed films.

also be explained by the high amount of plasticizer used in the films in the present study.

4. Conclusions

The temperature used in preparation of amylose-rich maize starch dispersion greatly affects the crystallinity and particle size of the dipersion. Increasing the temperature results in higher crystallinity, thus affecting the film formation ability. Mechanically strong and elastic films can be formed from amylose-rich starch dispersion formed at 40°C. The more crystalline starch–ethanol complex (obtained at 80°C) and the entirely amorphous dispersion (obtained at 10°C) formed non-continuous and cloudy films. The better film-forming properties of the dispersion formed at 40°C are probably due to the highly amorphous structure and a smaller particle size. The study shows the possibility of using ambient tempered amylose-rich starch dispersion for film forming.

Acknowledgements

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