



Understanding the role of plasticisers in spray-dried starch



Muhammad Bilal Khan Niazi^c, Mark Zijlstra^{a,b}, Antonius A. Broekhuis^{a,*}

^a Department of Chemical Engineering, Institute for Technology and Management, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

^b Champions Technologies Europe BV, Langestraat 169, 7491 AE Delden, The Netherlands

^c School of Chemical & Materials Engineering (SCME), National University of Sciences and Technology, NUST Campus, H-12, Islamabad, Pakistan

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ABSTRACT

Amorphous thermoplastic starch (TPS) films were produced by compression moulding of solution spray-dried TPS powder and by direct solution casting. Oxidised potato starch was used as a feedstock for production of plasticised formulations containing glycerol or urea, or their combinations with maltodextrin (DE = 19.1) as processing aid.

The crystallinity index of freshly moulded films made from solution spray-dried powder was significantly lower than that for casted films. FTIR analysis showed that starch interacted in hydrogen bond formation with glycerol and urea plasticisers, reducing the glass transition temperature to 136 °C and 106 °C, respectively. Formulations containing maltodextrin did not show a T_g . Glycerol-plasticised and co-plasticised films immediately started to retrograde in the presence of moisture, while urea based systems only showed slow recrystallization at the highest moisture exposure. In line with retrogradation behaviour, urea plasticised and co-plasticised films exhibited a more ductile behaviour, whereas glycerol based ones showed more brittle behaviour.

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1. Introduction

Starch is a natural polymer of D-glucose found in the majority of plants. It is low cost, abundant, and biodegradable, and, after plasticising, exhibits appealing material properties (Chaudhary, Torley, Halley, McCaffery, & Chaudhary, 2009; Koch, Gillgren, Stading, & Andersson, 2010; Zhou, Zhang, Ma, & Tong, 2008), as amorphous thermoplastic starch (TPS). TPS films are currently attracting significant attention as potential packaging material from both scientific and commercial entities. In 2002, 25% of all plastics throughout the world were used for packaging purposes (Adeodato Vieira, da Silva, dos Santos, & Beppu, 2011; Weber, Haugaard, Festersen, & Bertelsen, 2002).

However, challenges in creating thermoplastic starch films with suitable and consistent mechanical properties still exist as starch, being semi-crystalline by nature, suffers from retrogradation (Adeodato Vieira et al., 2011; Liu, Xie, Yu, Chen, & Li, 2009; Ma & Yu, 2004b). A higher crystallinity index leads to film brittleness and reduced flexibility, thus limiting practical use (Adeodato Vieira et al., 2011; Chaudhary et al., 2009; Hu, Chen, & Gao, 2009; Liu et al., 2009; Ma & Yu, 2004a, 2004b).

Casting and thermoplastic extrusion are the predominant techniques used for creating TPS films. Though these methods are

simple and cost efficient, the starch is processed using water as plasticiser which contributes to the retrogradation of the formulations (Mathew & Dufresne, 2002). Especially long drying times required in film casting counteract the formation of amorphous TPS films (Galdeano et al., 2009; Hu et al., 2009).

In addition to water, plasticisers are used to disrupt the hydrogen bonds between the starch polymeric chains, hereby influencing the mechanical properties of starch films. Plasticisers results in a greater mobility of the starch chains in TPS films, leading to better processability and more appealing film properties (Adeodato Vieira et al., 2011; Galdeano et al., 2009; Garcia, Martino, & Zaritzky, 2000; Laohakunjit & Nookhorm, 2004; Ma & Yu, 2004b).

From a product design point of view, it seems desirable to formulate and manufacture amorphous TPS films with better retrogradation and mechanical properties. Indeed, our previous studies showed that solution spray-drying (SSD) of starch/maltodextrin formulations could be a potential technology for the manufacture of amorphous thermoplastic starch based films. This technique produced amorphous TPS powder with low moisture contents and thus can play an important role to produce thin TPS films with better mechanical properties. This, as long as it can be processed into film structures (Bhandari, Datta, & Howes, 1997; Niazi & Broekhuis, 2012; Niazi, Zijlstra, & Broekhuis, 2013).

In order to create amorphous TPS films, this research will therefore focus on the processing of starch via compression moulding of spray-dried starch-plasticiser formulations. Glycerol and urea will be used as plasticiser, separately and in combination with

* Corresponding author. Tel.: +31 050 363 4918; fax: +31 050 363 4479.
E-mail address: a.a.broekhuis@rug.nl (A.A. Broekhuis).

Table 1
Code names and corresponding description.

Code	Description
Powder	
U.S	Untreated starch; Feedstock material
S.D	Spray dried starch
G.PS	Spray dried 30% Glycerol plasticised starch
U.PS	Spray dried 30% Urea plasticised starch
G.MD.PS	Spray dried 15% Glycerol and 15% maltodextrin (DE 19.1) plasticised starch
U.MD.PS	Spray dried 15% Urea and 15% maltodextrin (DE 19.1) plasticised starch
Films	
S.SC	Solution casted starch film
G.PS.SC	30% glycerol plasticised solution casted film
U.PS.SC	30% urea plasticised solution casted film
G.MD.PS.SC	15% glycerol and 15% maltodextrin (DE 19.1) plasticised solution casted film
U.MD.PS.SC	15% urea and 15% maltodextrin (DE 19.1) plasticised solution casted film

maltodextrins (DE = 19.1). For reference purposes, films will also be prepared by solution casting; this to study the role of moisture during the film-formation process. The high drying rate, attained in SSD, is expected to give rise to amorphous TPS powder containing little water and slow retrogradation of films, whereas moisture can play a role during the drying of solution casted films (Bhandari et al., 1997; Jayasundera, Adhikari, Adhikari, & Aldred, 2011).

Oxidised amylopectin is preferred as a feedstock for spray drying as it gives low viscosity solutions (Hu et al., 2009). Different end-product properties of powders and films were investigated. Crystallinity and thermal properties of spray dried powder were studied and analysed by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermal gravimetric analysis, respectively. Water uptake at different humidity levels, retrogradation, and mechanical properties of thermoplastic starch films were studied.

2. Materials and methods

2.1. Materials

Oxidised potato starch amylopectin (Perfecta-film X85; moisture content 15%) was a gift from AVEBE (the Netherlands). Analytical grade glycerol and urea were purchased from Sigma–Aldrich. Maltodextrin (DE = 19.1) was kindly supplied by Cargill (France). The coding of the samples used throughout this paper is given in Table 1.

2.2. Preparation of TPS-powder

Aqueous solutions of starch were prepared using 15% (w/w) of oxidised starch and 30% (w/w based on dry starch) plasticiser, which was heated at 95 °C for 25 min and stirred at a rate of 600 rpm. The obtained solution was fed to a Büchi mini-spray drier B-191 equipped with a 0.7 mm nozzle. SSD was carried out as described in previous work (Niazi & Broekhuis, 2012). All the spray-dried formulations were then converted into films by compression moulding while the solvent-casted films were made directly from water based solutions.

2.3. Preparation of TPS-films

TPS films (Ø10 mm × 0.5 mm) were obtained by compression moulding the TPS powder, using a Fontijne Holland Table Press TH400. The samples were compressed at 25 bars for 5 min. The applied moulding temperature for S.D, G.PS, and G.MD.PS was 140 °C, and respectively 120 °C and 130 °C for U.PS and U.MD.PS.

Solution casted films were made from the original water based solutions prepared in the same manner as described in Section 2.2. Subsequently 10 mL of the solution was poured into a Petri dish (7 cm diameter) and dried for 48 h at 45 °C. The solution-casted products are coded with the suffix SC.

2.4. X-ray diffraction (XRD)

The crystalline structures of the spray dried powders and the films were studied using X-ray diffraction. A Bruker D8 equipped with Cu radiation exhibiting a wavelength of 1.5418 Å was used to record diffractograms from 5° 2θ to 40° 2θ. A step size of 0.02° 2θ using a scan speed of 2 s/step was employed. The system was operated at 40 kV and 40 mA. The crystallinity index was determined using the method described by Shujun (2005). The software program Origin 8.1 was used for integrating the peaks. The total area was the area under the curve from 12° to 40° in the XRD spectrum (Shujun, 2005).

2.5. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis of freshly prepared formulations was done using an open pan Perkin Elmer TGA 7 from 25 °C to 900 °C with 5–10 mg of sample applying a heating rate of 25 °C/min. The TGA and the derivative of the TGA were determined as described in literature (Soliman, ElShinnawy, & Mobarak, 1997).

2.6. Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of the freshly prepared samples was determined by DSC measurements, using a DSC-60 Shimadzu Co. Prior to the analysis a reference was constructed using an empty aluminium pan. Samples were scanned at a rate of 10 °C/min from 10 to 200 °C. Open pan measurement was performed in order to remove any remaining water from the sample in the first run.

2.7. Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) analyses were performed on freshly prepared samples. The spectra were recorded using a Perkin Elmer FT-IR spectrometer spectrum 2000 equipped with an attenuated total reflection (ATR) unit. For each spectrum 32 consecutive scans at 4 cm⁻¹ resolution were averaged. All analyses were performed at ambient temperature.

2.8. Retrogradation of TPS films

Retrogradation was studied by storing the starch films (Ø10 mm × 0.5 mm) at three different relative humidity levels: 0% (dried silica), 50% (35.64% CaCl₂ solution) and 100% (distilled water). Rate of retrogradation measurements were carried out as described in the previous work. The crystallinity index was determined using the method described in Section 2.4.

2.9. Moisture uptake

To study moisture uptake, films were stored at 0%, 50% and 100% RH and gravimetrically analysed at regular time intervals. Measurements were taken every day during the first seven days. Hereafter, measurements were performed at day 14, 21, 28 and 56. Moisture uptake of the films was determined using Eq. (1) (Zhang, Zhang, Wang, & Wang, 2009).

$$\text{Moisture uptake} = \frac{\text{weight}_{\text{day},n} - \text{weight}_{\text{day},0}}{\text{weight}_{\text{day},0}} \times 100\% \quad (1)$$

The subscript 'day, n ' denotes the weight at the day of measurement, 'day,0' indicates the weight directly after film making. Moisture adsorption data were fitted according to the model reported in literature (Peleg, 1988).

$$M_t = M_0 + \left(\frac{t}{(k_1 + k_2 t)} \right) \quad (2)$$

where M_t is the moisture contents at time t , M_0 is the initial moisture content and k_1 is the Peleg rate constant (t/g water/g solids) and k_2 is the Peleg capacity constant (g solids/g water) (Mali, Sakanaka, Yamashita, & Grossmann, 2005b).

2.10. Mechanical properties

An Instron 4301 tensile tester was used to measure the mechanical properties of the TPS films in accordance with ASTM D1708. The crosshead speed used was 10 mm/min. In order to increase research validity each type of film was tested using at least 7 samples, enabling the removal of outliers. Before measurement the test specimens were conditioned at RH = 100% for 24 h. Mechanical properties were evaluated when the materials still were in a highly amorphous state (i.e. low crystallinity index).

2.11. Powder recovery

Yield from a spray-drying operation is defined as "the ratio of the actual amount of solid powder produced to the maximum amount of powder achievable" (Hanus & Langrish, 2007). The yield was calculated as the ratio of the amount of product obtained over the amount of starch and additive used as input material (Eq. (3)).

$$\text{Yield} = \frac{\text{weight}_{\text{product}}}{\text{weight}_{\text{starch}} + \text{weight}_{\text{plasticizer}}} \times 100\% \quad (3)$$

3. Results and discussion

In our previous work (under review), maltodextrins of different molecular weights were tested as additives in the production of amorphous SSD powders and their effect on compression moulded TPS films. Maltodextrins did not result in any recordable plasticisation and the films showed a high rate of retrogradation and poor mechanical properties. However, the yields in the spray-drying process improved in comparison to the processing of non-formulated starch.

In this study, we used the more common plasticisers for starch (Ma & Yu, 2004b; Ma, Yu, & Wan, 2006; Mathew & Dufresne, 2002), i.e. glycerol and urea, to produce TPS films and evaluated the properties of spray dried powder and the films made thereof. Glycerol and urea are both low molecular weight additives and contain hydrogen bond forming units. Therefore it is to be expected that both will work as plasticiser and show better film forming properties. As maltodextrine acts as a processing aid, also combinations of glycerol and urea with maltodextrin have been included in the study (Ma & Yu, 2004a). Solution casted and compression moulded films were evaluated side-by-side to investigate the difference in the rate of retrogradation and the ultimate crystallinity index of TPS films created by both techniques.

3.1. Crystallinity of freshly prepared TPS powder and films

The X-ray diffraction patterns of TPS powder and films with and without additives are shown in Fig. 1.

Virgin starch, U.S, has a semi-crystalline structure, indicated by the broad crystalline peaks at $2\theta = 17.2^\circ$, 19.6° , 22.3° and 23.6° (Fig. 1a) (Cullity & Stock, 2001; Liu et al., 2009). The peaks correspond to B- and V-type crystallinity (Teixeira, Da Roz, Carvalho, & Curvelo, 2007; vanSoest, Bezemer, deWit, & Vliegenthart, 1996). As B-type crystallinity relates to increased brittle behaviour for

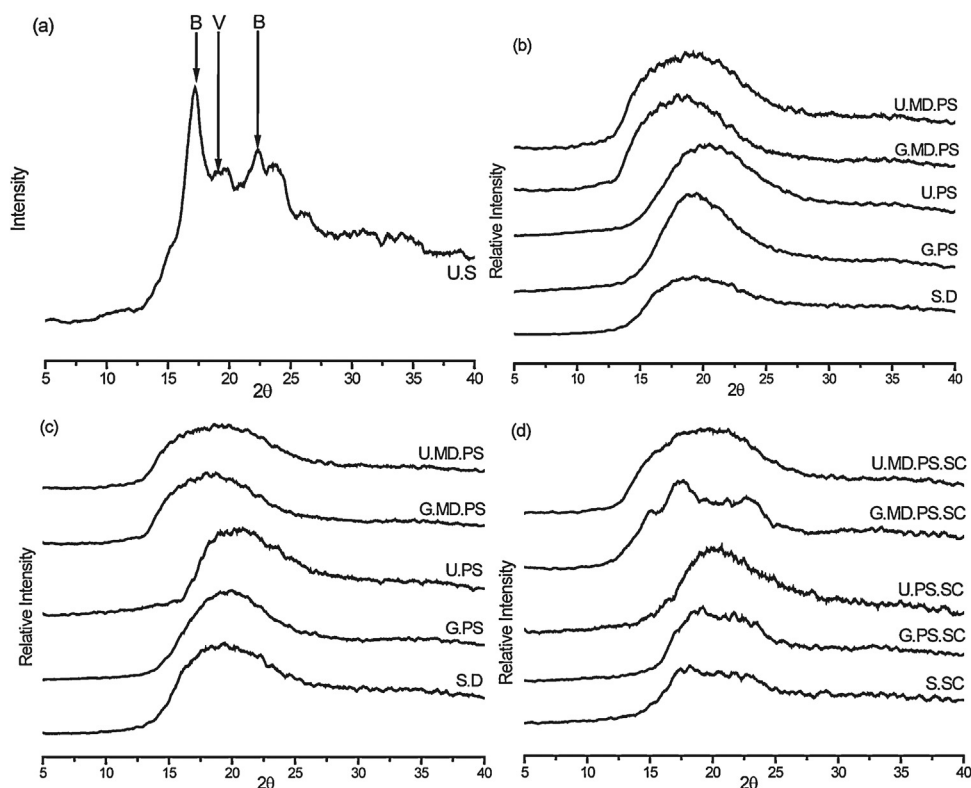


Fig. 1. (a) X-ray diffractogram of U.S. The arrows indicate characteristic peaks attributed to starch crystallinity. (b) X-ray diffractograms of the powders obtained after spray drying. (c) Films obtained via hot pressing of solution spray dried starch powders, (d) Solution casted films.

TPS films (vanSoest, Hulleman, deWit, & Vliegthart, 1996) the elimination of these crystal elements is required to create flexible films.

After SSD all freshly prepared powders were amorphous; no crystalline peaks were identified (Fig. 1b). As reported in literature (Ma & Yu, 2004a, 2004b), plasticisers (in this study water, urea or glycerol) break up the intra and inter-molecular hydrogen bonds between the starch chains while the high drying rate and rapid cooling during the spray drying operation inhibits crystallisation. Adding either glycerol or urea, or combinations with maltodextrine did not induce crystallisation during the processing step.

All freshly prepared films were amorphous and compression moulding did not lead to observable premature retrogradation (Fig. 1c). Non-plasticised starch S.D and co-plasticised films were mat and slightly hazy; glycerol and urea plasticised films were transparent.

The crystallinity index of the films (Fig. 1c) was compared to the films obtained via solution casting (Figs. 1d and 2). It was found that the films made by compression moulding of spray dried powder exhibited no crystal structures whereas the ones made by solution casting did. For the latter, Fig. 1d illustrates that urea containing films exhibited the lowest crystallinity index. This can be explained by the low molecular weight and the small molecular dimension of urea and, therefore, its more effective molecular mixing with effective formation of stable hydrogen bonds (Ma et al., 2006). The co-plasticised films showed similar results. The solution casted films containing glycerol as co-plasticiser showed a slightly higher crystallinity than the co-plasticised urea equivalent. This points again to the more effective interaction between starch and urea, and to the combined role of moisture and added plasticisers in relation to the low drying rate in the solvent casting operation.

The result that urea is the more effective plasticiser which ultimately leads to slower retrogradation of starches is in line with data observed for extruded starch formulations (Galdeano et al., 2009; Ma et al., 2006). Comparison of our data with the ones presented in the literature nevertheless suggests that the rate of retrogradation and the ultimate equilibrium crystallinity levels are lower for the films obtained from spray-dried powders. The differences in crystallinity achieved with this process can be attributed to the more efficient drying in the spray-drying operation. This leads to lower initial moisture contents in the starch-plasticiser network and to the reduction of starch-chain mobility caused by water plasticisation in, for example, the solution casted films.

3.2. Thermal properties

Thermal degradation and stability was investigated by both TGA and DTGA (Fig. 3). Apart from moisture loss at 100 °C, all samples were thermally stable up to a temperature of 160 °C or higher (Table 2). The curves were segmented into 3 or 4 identifiable regions depending on the composition of the formulations. All samples contain a region at 100–110 °C (labelled a) which corresponds to the loss of absorbed water. They also contain a region between 300 and 350 °C (b2) and one above 350 °C (c) which are characteristic for starch degradation followed by char production. The formulated systems show a fourth region between 150 and 300 °C (b1) that can be related to the decomposition of the additives or to specific unidentified degradative interactions between the additives and starch.

The S.D sample was different from the formulated ones and was taken as reference. It showed the typical starch TGA profile with some moisture loss in region (a) followed by complete decomposition (b2 and c).

The formulated samples exhibited the extra region in the degradation profile that can be ascribed to the additives. The additives cause a decrease in the onset of degradation (T_{dec}) from 294 °C for

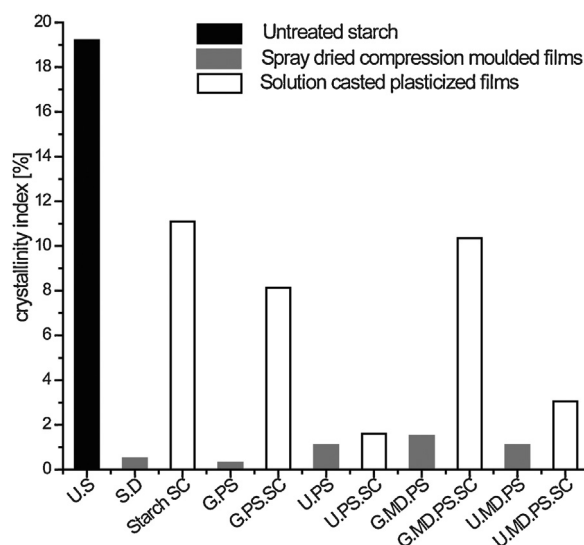


Fig. 2. Degree of crystallinity for films, XRD performed immediately after production.

S.D to 160 °C or higher for the plasticised samples. The onset temperatures and the minima in the DTGA-curves (Fig. 3) for section a, b₁ and b₂ are collected in Table 2. The addition of plasticiser caused a decrease for both the onset and peak values of T_{dec} . The weight loss in the b₁ region in the DTGA curve depends on the type of plasticiser used; G.P.S showed maximum weight loss of 20.3%, whereas U.P.S showed a weight loss of only 10.2%.

Another striking difference between urea and glycerol was observed for the co-plasticised powders. Addition of maltodextrine to the glycerol formulation resulted in a weight-loss reduction that could be explained by the 50% lower glycerol content in the formulation (20.3% weight-loss for G.P.S containing 30%, w/w, glycerol versus 13.5% for G.MD.P.S with only 15%, w/w). However, for the similar urea case, hardly any difference in weight loss in the b₁ region is observed (10.2% for U.P.S versus 11.2% for U.MD.P.S). These results clearly suggest a difference in the type or efficiency of mixing and interaction of the plasticisers with starch. A possible explanation has been postulated by Tajuddin, Xie, Nicholson, Liu, and Halley (2011) stating that very effective plasticisers penetrate between the amylopectin branches, whereas less effective and possibly higher molecular weight additives like glycerol interact primarily with the amylose-like linear structures and maltodextrine, for the mixed formulations, which together surround the branched amylopectin units. The picture postulated by Tajuddin et al. provides the image of “open umbrella” structures for amylopectin filled with urea and “coated closed umbrella” structures for glycerol formulated systems (Fig. 4). The dissimilar behaviour of glycerol and urea can also be seen as experimental support for the distinct effect of these plasticisers on the T_g and T_m of starch as described by Farhat, Blanshard, and Mitchell (2000).

3.3. Glass transition temperature

DSC measurements showed only glass transition temperatures for G.P.S and U.P.S. S.D showed no T_g which was attributed to the inter- and intra-molecular hydrogen bonds between the starch chains limiting chain mobility (Liu et al., 2009). As a result, S.D decomposed before it showed a glass transition.

In G.P.S and U.P.S the plasticiser molecules disrupted hydrogen bonds between starch molecules reducing the T_g . The lower T_g for U.P.S as compared to G.P.S was attributed to urea forming stronger hydrogen bonds with starch (Section 3.4). Galdeano et al. (2009)

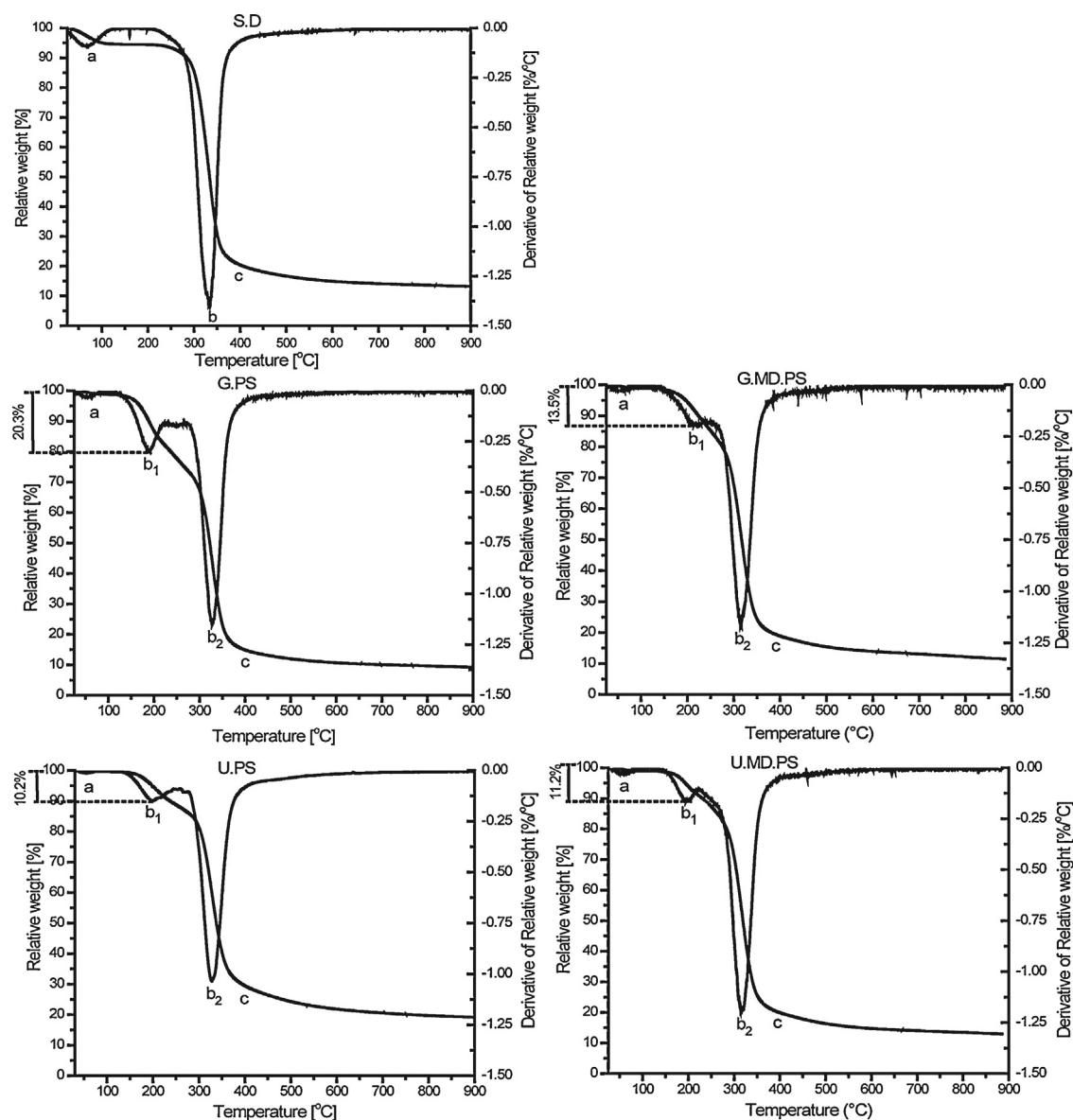


Fig. 3. TGA and DTGA-curves of the native starch and formulated spray dried samples.

also showed a lower T_g for urea as compared to glycerol for TPS films of oat starch made by solution casting.

The co-plasticised samples G.MD.PS and U.MD.PS also failed to show a glass transition point. The signal in the b1 region for these formulations nevertheless suggests the presence of a

separate phase in the starch matrix containing material that degrades below the actual starch degradation range. This phase could however not be identified in the DSC analyses. In addition, the observed yield improvement, i.e. reduction of powder tackiness, in the SSD process that was expected from the addition of

Table 2

Degree of crystallinity, moisture uptake, thermal and mechanical properties of TPS films.

Samples	Moisture contents	Thermal properties [°C]			Mechanical properties ^a			Degree of crystallinity of films			Relative weight change films		
		Powder [%]	Onset T_{dec}	Peak T_{dec} , or b1	T_g	Tensile strength [MPa]	Strain [%]	Modulus [MPa]	0 day [%]	RH 100%		RH 100%	
	7 day									56 days	1 day	7 day	56 days
G.PS	1.3	160	190	136	0.73 (0.14)	42 (11.78)	17.04 (9.71)	0.38	14.08	15.8	81.8	93.6	100.3
U.PS	0.4	165	199	106	0.20 (0.08)	99 (16.62)	0.83 (0.39)	1.05	3.8	9.84	78.4	201.6	250
G.MD.PS	0.8	175	216	n.o.	0.48 (0.14)	32.06 (13.7)	9.93 (1.86)	1.5	11.87	17.68	53.5	112.8	170.9
U.MD.PS	0.5	170	197	n.o.	0.19 (0.04)	97.03 (9.88)	5.74 (4.93)	1.1	10.87	16.22	44.9	112.4	132.58
S.D	5.2	294	n.o.	n.o.	^a	^a	^a	0.5	17.87	18.69	29.1	45	64.6

^a S.D could not be tested due to brittleness of the test sample; n.o. = not observe.

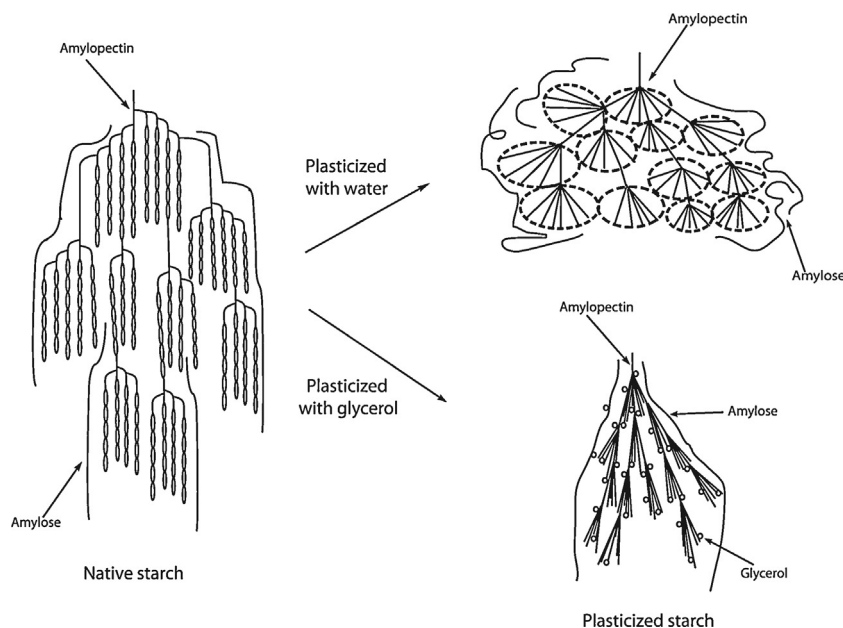


Fig. 4. Schematic representation of microstructural changes of starch under processing with different plasticisers.

Redrawn from Fig. 6. In reference Tajuddin et al. (2011).

maltodextrin indeed suggests the absence of low temperature softening. The presence of a peak in the b1 region and the absence of a glass transition point may be explained by the formation of a maltodextrine-amylose-plasticiser rich phase around the branched amylopectin structures (Tajuddin et al., 2011).

3.4. FT-IR analysis

FTIR analysis provides information about the interaction of starch and plasticisers. U.S and S.D were taken as reference samples for which also the difference between a crystalline and amorphous nature could be identified.

The spectra of U.S and S.D showed that the interactions with O–H, C–O–H and C–O–C changed by the spray-drying step. These changes were attributed to a reduction in both crystallinity and ultimate moisture content (James BeMiller, 2009; vanSoest, Tournois, deWit, & Vliegthart, 1995). The band at 996.4 cm^{-1} in U.S was no longer visible in the S.D spectrum whereas the peak at 1012 cm^{-1} became more pronounced, indicating decreased crystallinity (vanSoest et al., 1995). Finally, the peak at 3262 cm^{-1} in U.S, for O–H stretching, was higher for S.D and shifted to 3310 cm^{-1} . This showed that the spray dried sample has a decreased molecular order as compared to the feedstock material.

Formulated samples were in-line with literature and the absorption bands at $1012\text{--}1019\text{ cm}^{-1}$ were clearly visible for all nearly amorphous spray-dried samples. Starch chains in G.PS and G.MD.PS formed stronger hydrogen bonds as compared to S.D. This can be concluded from the shift in O–H stretch vibration from 3310 cm^{-1} (S.D) to 3292 cm^{-1} (G.PS) and 3293 cm^{-1} (G.MD.PS) (Table 3). Hence, FT-IR analysis confirmed that SSD of G.PS yielded TPS in which glycerol interacts with the starch chains. The spectra for U.PS and U.MD.PS exhibited a different structure when compared to the glycerol containing samples. The presence of amide structures caused the peak of hydrogen bonded O–H, at 3310 cm^{-1} , to change (Galdeano et al., 2009; Lehman, 2002). Absorption at 3333 cm^{-1} in U.PS, and the absorption at 3340 cm^{-1} in U.MD.PS were attributed to the N–H stretch of primary amides, obscuring the O–H stretch band. The short band in the range of $2908\text{--}2930\text{ cm}^{-1}$ was related to CH stretching in starch. This band was double peaked after using plasticisers in contrast to the single peak observed in native starch,

implying the formation of newer and stronger hydrogen bonds (Pushpadass, Marx, & Hanna, 2008). The rest of the spectrum is identical as published in literature (Galdeano et al., 2009; Lehman, 2002; Pawlak & Mucha, 2003).

Comparing the FT-IR spectra of G.PS and U.PS gives rise to distinct differences in wavenumbers. It can be seen that the wavenumbers corresponding to O–H and C–O stretching were lower for U.PS, indicating that urea formed more stable hydrogen bonds with starch (Table 3). The influence of N–H stretching vibrations at 3333 cm^{-1} and 3218 cm^{-1} in U.PS hindered the comparison of this band to G.PS and S.D. Similarly, in case of co-plasticised samples, U.MD.PS showed better hydrogen bond forming ability than G.MD.PS.

Similar observations were published by Ma et al. (2006) who prepared TPS in a single screw extruder and reported stronger hydrogen bonding for urea compared to glycerol.

In the current study, both glycerol and urea showed better hydrogen bonding strength as compared to TPS produced by single screw extrusion of formulations with the same plasticisers. The same holds for the comparison with films containing blends of urea and glycerol made by twin-screw extrusion (Pushpadass et al., 2008).

3.5. Retrogradation and moisture uptake of TPS films

Film retrogradation was studied at various humidity conditions by XRD for a period of 56 days (Fig. 5). The U.S line corresponds to the crystallinity index present in the feedstock material. The

Table 3
FT-IR absorption bands of the studied samples.

Samples (% moisture)	Wavelength [cm^{-1}]				
	3310–3270	2922–2921	1361	1078	1019–1017
U.S (15)	3262	2922	1339	1076	996.4
S.D (5.2)	3310	2922	1361	1078	1012
G.PS (1.3)	3292	2923	1366	1079	1018
U.PS (0.4)	3333	2922	1454	1078	1017
G.MD.PS (0.8)	3293	2838	1340	1080	1017
U.MD.PS (0.5)	3340	2923	1364	1078	1017

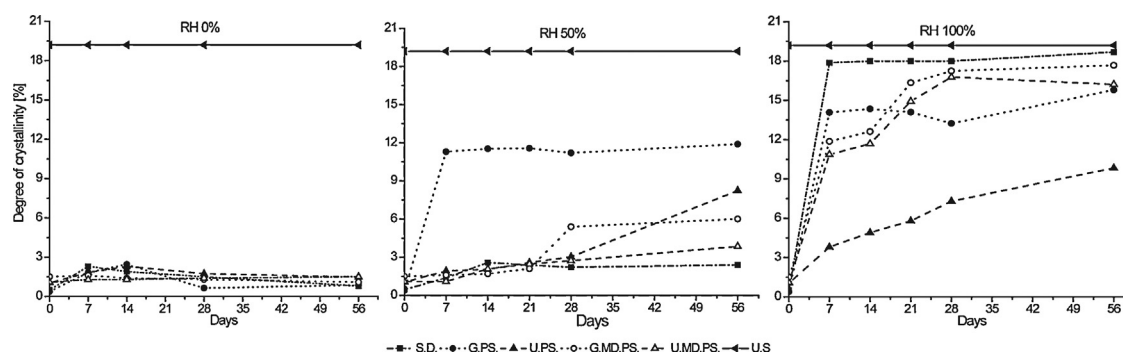


Fig. 5. Degree of crystallinity of TPS films at different humidity conditions. U.S indicates the degree of crystallinity in the feedstock material.

rearrangement of amorphous starch chains is influenced by water (Mathew & Dufresne, 2002). Therefore also relative weight changes during storage were measured and reported (Fig. 7). Both elements will be discussed in this section.

Storing the starch based films at RH0% caused no significant changes in the amorphous nature of the films up to 56 days (Fig. 5); the crystallinity index remained below 2.5%. Due to the absence of water and therefore the absence of moisture absorption at RH0%, the mobility of the starch chains remained limited which prevented retrogradation, and the films remained brittle.

At RH100% the studied samples showed a return of the initial B-type crystallinity present in the feedstock. However, S.D films showed an increase in A-type crystallinity since the peak at $15^\circ 2\theta$ noticeably increased (Fig. 6) (vanSoest, Bezemer, et al., 1996). Furthermore, the peak doublet at $22\text{--}24^\circ 2\theta$ was transformed to a singlet (vanSoest, Bezemer, et al., 1996; Varatharajan, Hoover, Liu, & Seetharaman, 2010). The increase in A-type crystallinity is comparable to findings after heat-moisture treatment (HMT) of starch. HMT is a methodology in which starch B-type crystals are transformed to A-type at a low humidity level and high temperatures. During SSD and during hot pressing high temperatures ($90\text{--}110^\circ\text{C}$) are applied under dry conditions ($<35\%$ water) (James BeMiller, 2009; Varatharajan et al., 2010). These conditions favour the formation of the more densely packed A-type crystals (James BeMiller, 2009). The change in XRD pattern is attributed to the dehydration of the water molecules present in the central channel of the B-type unit cell (Varatharajan et al., 2010). Dehydration of starch and high temperatures during SSD and compression moulding have led to increased formation of A-type crystallinity in this research.

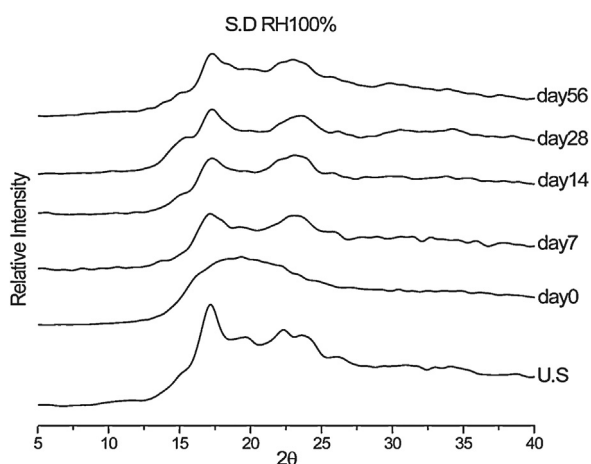


Fig. 6. X-ray diffractograms of S.D stored at RH 100% for 56 days.

As expected, films stored at RH50% showed an increase in weight upon storage, due to water uptake which turned all originally brittle films into flexible ones. Similar weight change profiles at RH50% were described by Roussanova, Murith, Alam, & Ubbink (2010) and Dangaran and Krochta (2006). Initially water is absorbed by the amorphous starch matrix, leading to an increase in weight (Dangaran & Krochta, 2006; Roussanova et al., 2010). Next moisture acts as a plasticiser which causes starch–starch hydrogen bond interactions to become starch–water interactions, thus creating a more open network. Finally, upon a further increase of the water content the samples become rubbery. In this regime structural rearrangements occur, causing re-crystallisation. This crystallisation may finally lead to the removal of moisture from the matrix resulting in a weight loss (Dangaran & Krochta, 2006). These phenomena were also observed in this study (Shi et al., 2007). G.P.S and G.M.D.P.S films showed the largest amount of water uptake at RH50%, but G.M.D.P.S showed better retrogradation properties, i.e. slower recrystallization. This high moisture absorption in G.P.S leads to an increased crystallinity index because of higher starch chain mobility. Co-plasticisation of maltodextrin with glycerol apparently limited the water uptake of the formulation and inhibited the rate of retrogradation by controlling chain movement at RH 50%. U.P.S showed somewhat lower moisture absorption than G.P.S but the retrogradation of this formulation was much slower. The presence of maltodextrin in the U.M.D.P.S formulation had a similar effect with slow retrogradation and somewhat higher moisture absorption.

At 100% relative humidity the differences between the formulations became more evident. The rate of moisture absorption and the ultimate equilibrium moisture levels are clearly the highest for the urea formulated starches, while the pure urea-case also provides the best retrogradation performance. The presence of maltodextrine caused both systems to retrograde in a similar manner although the ultimate moisture levels were the highest for the urea formulation. It finally is remarkable to note that both urea formulations show a decline in moisture contents after longer storage time, while the equilibrium moisture content for the G.M.D.P.S almost equalled that of the U.M.D.P.S formulation at 21 days storage, but continued to build towards a higher final moisture level.

Moisture uptake curves of TPS films are shown in Fig. 7. At the initial stage of the storage, the moisture adsorption was rapid and, with passage of time, the rate of water absorption decreased. Then, the moisture contents reached a plateau indicating that the TPS films became equilibrated. To improve the examination about water sorption performance at 100% RH, the moisture uptake data at different times were fitted using Eq. (2) (Peleg, 1988).

The Peleg parameters (Peleg, 1988), k_1 and k_2 are shown in Table 4. The constants k_1 and k_2 are related to mass transfer and maximum water adsorption capacity, respectively. Low values for k_1 and k_2 correspond to a high initial water adsorption rate and

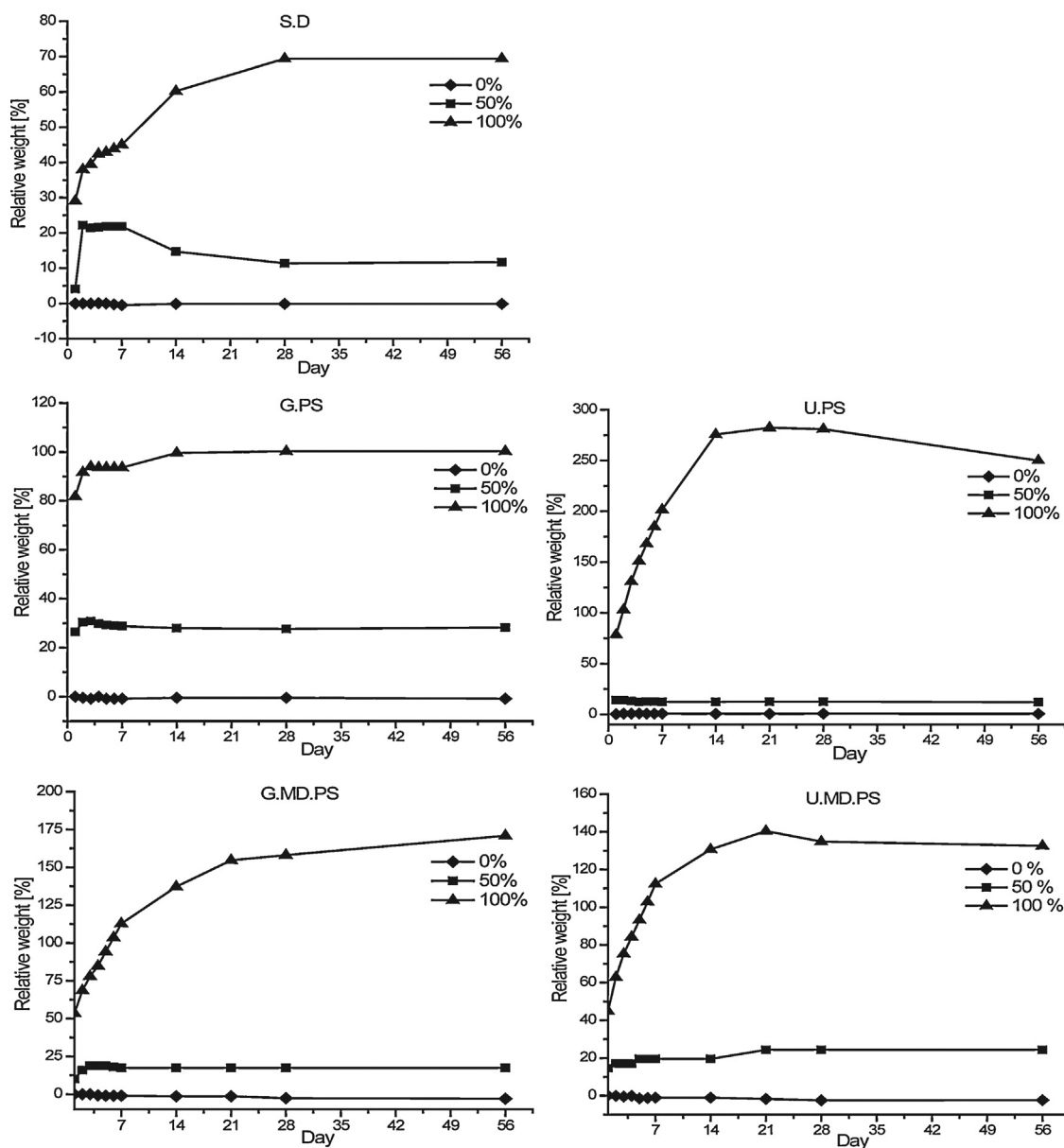


Fig. 7. Relative weight changes over time at different relative humidity per sample. Y-axis shows relative weight change in percentages. X-axis indicates the days.

a high adsorption capacity, respectively (Mali et al., 2005b). The coefficients of determination were found to be very high in all cases ($r^2 > 0.99$). G.PS showed the highest initial adsorption rate, followed by U.PS. Addition of maltodextrin to glycerol and urea plasticised TPS films, reduced the initial rates. The absence of hygroscopic additives in S.D resulted in the lowest value for the initial absorption rate, i.e. the highest k_1 value. The highest equilibrium moisture absorption (the lowest k_2 value) is observed for U.PS.

Table 4

Constant values (k_1 and k_2) and coefficient of determination (r^2) for sorption curve equations (Peleg model)^a of TPS films at 100% RH.

Sample	M_0	k_1	k_2	r^2
S.D	5.19	4.2×10^{-2}	1.5×10^{-2}	0.997
G.PS	1.34	2.7×10^{-3}	1×10^{-2}	0.999
U.PS	1.132	6.9×10^{-3}	3.7×10^{-3}	0.993
G.MD.PS	0.8	1.9×10^{-2}	5.6×10^{-3}	0.997
U.MD.PS	0.5	1.2×10^{-2}	7.2×10^{-3}	0.998

^a $M_t = M_0 + (t/k_1 + k_2 t)$, k_1 in h/(g water/g solids) and k_2 in g of solid/g water.

Both urea systems shown in Figs. 5 and 7 exhibit a reduction in moisture content as the result of increasing retrogradation. Both systems could be perfectly fitted to a modified Peleg model using the moisture absorption data including a correction term for moisture displacement due to recrystallization over time (fitted data given as graphical abstract).

In order to put the observed retrogradation data, the moisture uptake results and the thermal analysis together into a rational for the interaction of starch with plasticisers, the following general observations should be accounted for in a model:

- Low molecular weight plasticisers with high hydrogen bonding capability cause rapid moisture absorption with high equilibrium moisture contents and tend to delay retrogradation. From the plasticisers tested in this study, urea may be considered as a typical example for this behaviour.
- Formulations containing plasticisers that result in strong starch interaction, such as urea, may expel moisture with increasing retrogradation of the formulation

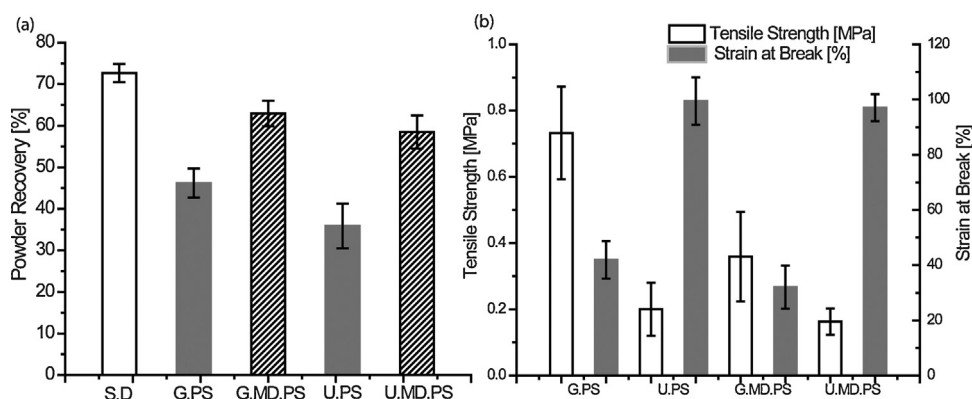


Fig. 8. (a) Tensile properties of the acquired TPS films and (b) Average powder recovery after spray drying ($n = 10$).

- Partwise replacement of plasticiser by maltodextrine reduces moisture uptake and accelerates retrogradation depending on the type of plasticiser used.

The results presented in this study and in our previous paper were combined with data on starch plasticisation collected from other researchers (Ma & Yu, 2004b; Ma et al., 2006; Mathew & Dufresne, 2002; Tajuddin et al., 2011) and the results seem to fit with the model proposed by Tajuddin et al. (2011). This model suggests that the miscibility of plasticisers with the different fractions of the starch amylose/amylopectin mixture strongly depends on the molecular weight and the hydrogen bonding capability of the additive. Highly bonding low molecular weight additives (such as urea, formamide and water) mix well and interact with all starch structures, including the amylopectin branches. The resulting break-up of intra-molecular bonding in the amylopectin branches opens the structure for more and rapid moisture uptake to high absorption levels which then increases the mobility of substructures that subsequently will lead to retrogradation of the amylopectin parts and the displacement of moisture and plasticiser from these parts of the formulation. Ultimately, moisture and plasticiser will become concentrated in the amylose-like residue surrounding the amylopectin fractions (including eventually added maltodextrine).

Less hydrogen bonding systems of higher molecular weight (like glycerol, sorbitol, xylitol, and mannitol) are expected to preferentially mix with the amylose rich surroundings of amylopectin. They nevertheless enable rapid moisture transport, which as small size plasticiser will break-up the amylopectin structure. Thus these larger plasticisers concentrate in the amylose fractions, the smaller ones in the amylopectin fractions which leads to a high retrogradation rate of the amylopectin fractions and moisture absorption will resemble that of un-plasticised starch. The addition of maltodextrine to formulations that contain linear amylose-like structures will lead to mixtures which absorb plasticisers that are less capable of diffusion into the amylopectin branches.

Thus, in case urea is used as the single plasticiser, all fractions of the spray-dried starch amylose/amylopectin mixture will contain urea and rapidly absorb moisture to reach a high equilibrium level. At some point retrogradation starts to displace both water and urea from the crystallising amylopectin part and the total moisture content will reduce over time. Glycerol also is expected to mix into all parts of the spray-dried starch system. This also allows for moisture to diffuse into all parts of the mixture of which the amylopectin fractions likewise start to retrograde as soon as sufficient chain mobility is reached. Due to its molecular dimensions and less hydrogen bonding capabilities, glycerol will be expelled more readily from the amylopectin phases and primarily concentrates in the amylose fractions. While glycerol is expelled more easily,

retrogradation is expected to be faster for glycerol than for urea modified systems.

In case maltodextrine is added as an additional component to these formulations, the rate of moisture uptake will depend on both the molecular weight of the dextrin and the nature of the plasticiser. The closer the dextrin resembles amylose (i.e. the higher the molecular weight), the more will the moisture uptake of the system resemble that of the unmodified starch system assisted by the activity of the actual plasticiser which continues to act as described above.

3.6. Mechanical properties

The mechanical behaviour of the TPS films is shown in Fig. 8(a) and Table 2. Proper test samples for U.S could not be made due to the brittle nature of starch. The higher elongation for the urea plasticised TPS films and the higher strength for the glycerol formulated samples showed that films formulated with urea were more plasticised than the ones formulated with glycerol. Furthermore the relative standard deviation for U.P.S was smaller. Similar results were obtained for the co-plasticised films, i.e. U.MD.P.S films were more flexible and gave a lower standard deviation as compared to G.MD.P.S. Both results can be related to the more effective plasticising behaviour of urea and suggests also a more homogeneous distribution for the urea formulations. The lower glass transition temperature of U.P.S indicates that the starch chains had more mobility. Increased flow/sintering during film making, resulted in the lower (relative) standard deviation for U.P.S and U.MD.P.S. Mali, Sakanaka, et al. (2005), Mali, Grossmann, Garcia, Martino, and Zaritzky (2005) and Hu et al. (2009) studied yam starch films and oxidised potato starch films, respectively, and found that the tensile strength decreased at higher concentration of plasticisers (Hu et al., 2009; Mali, Grossmann, et al., 2005). Both explained that the proximity between starch chains is reduced by the incorporation of plasticiser into the starch network, which decreased tensile forces and improved the movement of starch chains.

3.7. Powder recovery

The powder recovery of spray dried samples is shown in Fig. 8(b). S.D was taken as reference sample and showed a maximum yield of $73 \pm 4\%$. The formulated samples showed a significant decrease in yield due to powder sticking to the wall of the drying chamber. This could be reduced by the addition of maltodextrine to the formulation. When the inlet temperature is higher than the T_g , the particles exist in a rubbery and sticky state (Bhandari & Howes, 1999). Because the inlet temperature was higher than the T_g for the plasticised samples, losses increased

in the order $S.D < G.MD.PS < U.MD.PS < G.PS < U.PS$. Furthermore, the T_g decreases with increasing water contents. Both moisture contents and air temperature are the highest at the top of the drying chamber, enabling stickiness of the material. This explains the higher yield for sprayed samples without glass transition temperatures.

4. Conclusions

Spray-drying formulated starches, containing plasticisers and processing aids, from water solutions is considered to be an effective way of producing molecularly mixed amorphous starch systems. The effective mixing followed by drying and film production resulted in film performance different from films produced by classic extrusion technology or solvent casting. The difference in behaviour can be explained by more intimate mixing of the ingredients and a different role of moisture in the non-spray-dried systems.

The behaviour of compression moulded films in terms of moisture absorption (at different humidity levels) and rate of retrogradation was found to depend on the type of plasticiser and the presence of maltodextrine as a third formulation component. Urea was found to be a more effective plasticiser than glycerol, i.e. a lower T_g , a lower degree of retrogradation, a lower tensile strength and a higher elongation, which can be understood by the smaller molecular dimensions of urea and a more intimate interaction between urea and the amylopectin fractions in the system. Glycerol is nevertheless a good plasticiser although it is, according to the Xie model, expected to concentrate preferentially outside the amylopectin fractions or at the interface of the amylopectin fractions and the other starch-like fractions in the formulation. As such, glycerol promotes retrogradation at humid conditions, whereas urea inhibits retrogradation but causes high moisture absorption.

Replacing 50% of the plasticiser by maltodextrine resulted in a more non-formulated starch-like behaviour with higher retrogradation rates and the absence of a glass transition point, but a higher yield in the spray-drying process.

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