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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2013

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Niazi, M. B. K. (2013). *Production of plasticized thermoplastic starch by spray drying*. s.n.

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Chapter 6

Crosslinking of oxidized thermoplastic starch films

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(To be submitted)

Abstract

Following previous studies showing that malic acid is a potential plasticiser for starch, this study aims to explore ultraviolet (UV) cross-linking as a tool to steer the mechanical properties of thermoplastic starch (TPS) based films. Cross-linked amorphous thermoplastic starch (TPS) films were prepared through UV irradiation of compression molded films made from spray dried amorphous powder. Sodium benzoate (SB) was used as photosensitiser. The influence on the performance of TPS powders of malic and citric acid plasticizers and their combination with glycerol was evaluated. Amorphous TPS films were obtained, irrespective of the plasticizer or combination used. Under dry conditions (RH0%) all samples maintained their amorphous nature while at RH50% and RH100% retro-gradation was suppressed for all starch films. It is shown that the rate of moisture uptake, and as a consequence, the rate of retro-gradation, depends on the concentration of the glycerol in combination with citric and malic acid. High levels of carboxylic acid plasticizer in the formulations gave a more effective interaction of starch with plasticizers and better thermal stability. UV irradiation had no effect on the degree of crystallinity, improved the mechanical properties and decreased the solubility and degree of swelling. Furthermore, the use of photosensitiser further increased the mechanical strength and decreased the solubility and degree of swelling. Citric acid plasticized and co-plasticized films showed slightly better mechanical properties before and after UV irradiation treatment compared to malic acid, but citric acid formulations appeared to be very moisture sensitive prior to cross-linking.

Introduction

In recent years, there has been growing interest in the development of bio-based and biodegradable products to reduce the environmental impact of plastic waste. Thermoplastic starch (TPS) is a candidate and is biodegradable, renewable, and low cost. One of the first applications in the plastics market is the use of extruded foamed loose fills, to replace non-degradable petrochemical-based products [1, 2]. However, from a product design point of view, there are a number of challenges that seriously limit the development of new applications and need to be addressed before thermoplastic starch based films can actually replace current materials. In particular, the hydrophilic nature and poor mechanical properties of TPS seriously limit new product innovations [2]. Reduced shelf-life and loss of mechanical properties results from water absorption which depends on the relative humidity (RH) and initiates retrogradation of TPS products [3].

Numerous studies have been carried out in an attempt to overcome the hydrophilic nature and to improve the mechanical properties and shelf life of thermoplastic starch [1]. In a previous chapter 2, spray drying of starch/maltodextrin formulations was evaluated as a potential technology for the production of moisture-free amorphous TPS formulations. It was found that variation of the amylose to amylopectin ratio had little effect on the properties of samples dried from solution. Most properties, such as moisture contents, crystallinity, particle size distribution, viscosity and powder flow properties were similar for all solution dried TPS blends. Subsequently, amorphous TPS films were produced containing natural plasticizers, i.e. urea and glycerol, and it was found that low molecular weight plasticizers mix better and inhibited retrogradation. However, reduced retrogradation resulted in loss of mechanical properties: reduced tensile

strength and increased strain with moisture absorption (chapter 3&4). 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 reduced role of moisture in the spray-dried amorphous systems. Urea as a low molecular weight plasticizer, showed to be a more effective plasticizer than glycerol, i.e. delivered a lower T_g , a lower degree of retrogradation and a higher elongation (chapter 4). In chapter 5, malic acid was identified as a strong retrogradation agent as it inhibited recrystallization of starch over the full range of relative humidity levels i.e. 50% and 100% RH. Malic acid was also found to inhibit the retrogradation of mixed formulations containing the acid and urea, glycerol or maltodextrin. This study again showed that reduced retrogradation leads to high moisture absorption and high strain at break with loss of tensile strengths.

On the basis of these studies, the hypothesis was developed that improved TPS based films could be produced if the low retrogradation performance could be combined with low moisture absorption. Radiation processing and chemical derivatization has been proposed to produce water-resistant material. Therefore starches were formulated with carboxylic acids and cross-linking by UV irradiation was considered as a potential technique to improve the performance of the films. In literature, the mechanical properties and dissolution of such cross-linked starch blends showed significant improvement compared to non-cross-linked films [4-6]. Radiation processing is claimed to introduce covalent cross-linking of polymer molecules and is used to improve the properties of polymer products [7].

Citric acid (CA) and malic acid (MA) are inexpensive and non-toxic chemicals. It has been reported that citric acid [8] and malic acid (chapter 5) can form strong hydrogen bond interactions with starch and improve its thermal and water stability, and inhibit retrogradation. However, incorporating both citric [8] and malic acid (chapter 5) substantially reduced the tensile stress of the TPS films.

As a follow-up on previous chapter with plasticised amorphous starch, a study has been carried out to investigate surface cross-linking of thermoplastic starch films. Sodium benzoate is used as the photosensitiser, as it is known to be photolysed by UV irradiation. UV light excites and decomposes the photosensitiser to produce radicals upon irradiation and leads to macro-radical combination and cross-linking [3, 4].

In this work, we investigated the effect of UV irradiations on the structural and physical properties of amorphous TPS films, obtained via compression molding of solution spray dried powder plasticized by carboxylic acids (malic or citric acid), and carboxylic acids in combination with glycerol. Special emphasis was placed on retrogradation and mechanical properties of films. In addition to changes in crystallinity over time, molecular interaction and thermal properties of spray dried powder were studied and analyzed by FTIR analysis, differential scanning calorimetry (DSC) and thermal gravimetric analysis, respectively. Water uptake at different humidity levels, retrogradation, and mechanical properties of thermoplastic starch films will also be discussed.

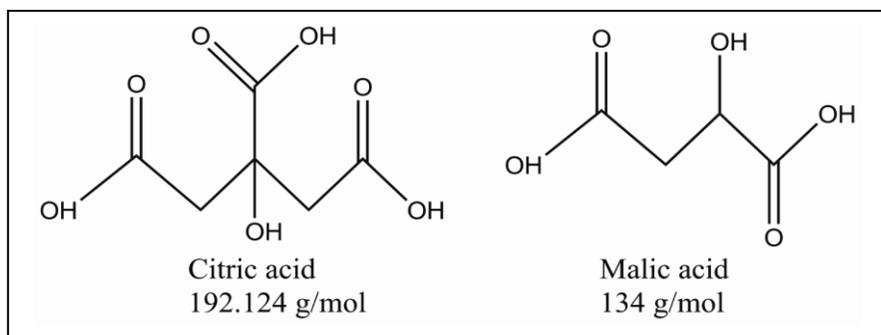


Figure 1 Plasticizers used for the preparation of TPS powder and films.

Experimental

Materials

Oxidized amylopectin from potato starch (Perfecta-film X-85, moisture content 15% w) was a gift from AVEBE (The Netherlands). Analytical grade glycerol, citric acid and DL-malic acid (99%) were purchased from Sigma-Aldrich. All these materials were used as received without further purification. Codes used for powders and films are depicted in Table 1. The digits in the codes indicate the weight percentage of plasticizer used relative to starch weight.

Preparation of TPS-powder

TPS powder was prepared as follows. An aqueous solution of starch was prepared by heating 15% (w/w) of dry oxidized starch with different plasticizer contents. Different combinations and ratios (w/w to dry starch) of plasticizer were added in aqueous starch solution and heated to 95°C for 25 minutes applying a stirring rate of 600 RPM to prepare homogeneous solutions. The obtained solutions were fed to a Buchi mini spray drier B-191 equipped with a 0.7 mm nozzle. The procedure used to produce amorphous powder was the same as described in previous chapters 3&4.

Preparation of TPS-films

TPS films (Ø10 mm x 0.5 mm) were produced by compression molding the TPS powder, using a Fontijne Holland Table Press TH400. Samples were compressed at 25 bar for 5 minutes. The molding temperature for all samples was 140°C.

Table 1

Material codes and corresponding description

Code	Description (w/w of starch)
U.S	Feedstock material
S.D	Spray dried starch
30G.PS	30% glycerol plasticized starch
30MA.PS	30% malic acid plasticized starch
25G.5MA.PS	25% glycerol, 5% malic acid plasticized starch
20G.10MA.PS	20% glycerol, 10% malic acid plasticized starch
30CA.PS	30% citric acid plasticized starch
25G.5CA.PS	25% glycerol, 5% citric acid plasticized starch
20G.10CA.PS	20% glycerol, 10% citric acid plasticized starch
PS.UV.RH50	Plasticized starch; ultra violet (UV) irradiated at 50% Relative Humidity
PS.UV.RH100	Plasticized starch; ultra violet (UV) irradiated at 100% Relative Humidity
PS.UV.SB.RH50	Plasticized starch soaked in sodium benzoate (SB) before ultra violet (UV) irradiated at 50% Relative Humidity
PS.UV.SB.RH100	Plasticized starch soaked in sodium benzoate (SB) before ultra violet (UV) irradiation treated at 100% Relative Humidity
SB	Soaked in sodium benzoate
UV	Ultra Violet irradiated

Surface photo cross-linking

TPS films (Ø10 mm x 0.5 mm) were produced as mentioned above and conditioned for 24hrs at two different humidity conditions i.e. RH50% and RH100%. Surface photo cross-linking was carried as described previously with some modifications [1]. After the initial 24hrs conditioning, some of the films were soaked in photosensitiser solution for 60 sec. The 1% aqueous photosensitiser solution was prepared by dissolving 1g sodium benzoate in distilled water. When the films were taken out, the excess solution on the surface was removed with paper tissue. The TPS films containing photosensitiser in the surface layer were again placed for 24hrs at their respective relative humidity conditions. After conditioning for 2 days (2*24 hrs), all films except sets of blanks were exposed to ultra violet irradiations at normal atmospheric condition with a Intelli-ray 600 watt shuttered UV flood light. The 100mW/cm² (320-390 nm) was evenly distributed in the chamber. TPS films were put at the distance of 15.5 cm from the top of the

chamber and kept under continues UV irradiations for 20 min at an intensity of 100%. After UV exposure, all the films were again conditioned for one more day at 50% RH. After 24hrs the tensile tests were performed for all samples.

X-Ray Diffraction (XRD)

The crystalline structures of the spray-dried powders and films were elucidated using XRD. 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. Powders were analyzed using a sample holder with a sample compartment of Ø25 mm x 2.0 mm. TPS films (Ø10 mm x 0.5 mm) were analyzed using an adjustable sample holder.

Thermal Gravimetric Analysis (TGA)

Open pan TGA was performed in a Perkin Elmer TGA 7.5-10 mg. The procedure applied to study the weight change in relation to temperature and decomposition temperature (T_{dec}) was as described in previous work (chapter 3&4).

Differential Scanning Calorimetry (DSC)

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

Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared analyses were performed to investigate any structural changes in the starch chain due to interaction between plasticizer and starch molecules. The procedure as described in previous work (chapter 4&5) was used.

Scanning Electron Microscopy (SEM)

A Jeol 6320F Scanning Electron Microscope was used for morphological characterization. The applied accelerating voltage for measurement was 3.0 kV. Before analysis, the samples were covered with a thin palladium/platinum conductive layer created with a Cressington 208 sputter coater.

Retrogradation and Moisture Uptake

Retrogradation of TPS films (Ø10 mm x 0.5 mm) was measured under different relative humidity conditions: 0%RH (dried silica), 50%RH (35.64% CaCl₂ solution) and 100%RH

(distilled water). The samples were prepared and analyzed by using the same method applied in previous chapters 3&4.

The degree of crystallinity was determined using the method described by Wang et al. [9]. The procedure used for integration and calculation of crystallinity was as explained in previous chapters 3&4. To study moisture uptake the films, stored at 0%, 50% and 100% relative humidity (RH), were gravimetrically analyzed. Measurements were performed 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 equation 1 [10].

$$\text{moisture uptake} = \frac{\text{weight}_{\text{day},n} - \text{weight}_{\text{day},0}}{\text{weight}_{\text{day},0}} \cdot 100\% \quad (\text{Eq. 1})$$

The subscript ‘day,n’ denotes the weight at the day of measurement, ‘day,0’ indicates film weight directly after film making. Moisture adsorption data were fitted according to the Peleg model (Equation 2; for 30G.PS, 25G.5CA.PS and 20G.10CA.PS formulations) and a polynomial modification of the Peleg model (Equation 3; for MA, CA and MA-co-plasticized samples) [11].

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

$$M_t = M_0 + \left(\frac{t}{(c_0 + c_1 t + c_2 t^2)} \right) \quad (\text{Eq. 3})$$

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) [12]. The Peleg parameters [11], k_1 and k_2 are shown in Table 2. 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 a high adsorption capacity, respectively [12]. The regression coefficients were found to be very high in most cases ($R^2 > 0.99$). The linear Peleg model (Equation 2) was not suited to fit the moisture absorption of the MA, CA and the MA co-plasticized formulations.

Table 2

Regression constants (k_1 , k_2 , c_0 , c_1 , and c_2) and regression coefficients (R^2) for sorption curve equations (2 & 3) of TPS films at 100%RH.

Sample	M_0	k_1	k_2	c_0	c_1	c_2	R^2
S.D	5.2	4.2×10^{-2}	1.5×10^{-2}	---	---	---	0.99
30G.PS	1.3	2.7×10^{-3}	1×10^{-2}	---	---	---	0.99
30MA.PS	1	---	---	2.6×10^{-2}	6.3×10^{-3}	-6.4×10^{-5}	---
25G.5MA.PS	1	---	---	9.3×10^{-3}	3.3×10^{-3}	-2.8×10^{-5}	---
20G.10MA.PS	1.9	---	---	1.1×10^{-2}	2.3×10^{-3}	-9.8×10^{-6}	---
30CA.PS	2	---	---	6.6×10^{-3}	1.3×10^{-2}	-3.8×10^{-4}	---
25G.5CA.PS	1.3	5.2×10^{-3}	2.9×10^{-3}	---	---	---	0.99
20G.10CA.PS	0.9	1.3×10^{-2}	2.9×10^{-3}	---	---	---	0.99

Mechanical Testing

The mechanical properties include the tensile strength (TS) and percentage elongation at break (%E). Five or more specimens were tested using an Instron 4301 tensile tester in accordance with ASTM D1708. The crosshead speed used was 10 mm/min. The samples were conditioned at two different relative humidity levels, i.e. RH50% and 100% RH at 25 °C for 24hr and the thickness and width of the samples were measured before testing. The same method was used for UV cross-linked TPS films.

Solubility and swelling behaviour

The Swelling behaviour (SB) and solubility (S) of films were measured by the method described by Yun et al. (2008) [13]. Dried TPS films were immersed in distilled water at room temperature (25 °C) for 24 hr. Moisture on the surface of the films was removed after the equilibrium was achieved (24 hr). The weight of the films was measured and swelling behaviour (SB) in TPS blend film was calculated as:

$$SB = \left(\frac{W_e - W_0}{W_0} \right) \quad (\text{Eq. 4})$$

Where W_e is the weight of the TPS film after 24 hrs, and W_0 is the first dry weight of TPS film.

The swollen TPS films were dried again for 24 hrs at 60 °C, and its solubility (S) was calculated by the following equation:

$$S = \left(\frac{W_0 - W_d}{W_d} \right) \quad (\text{Eq. 5})$$

Where W_0 is the first day weight of TPS films, and W_d is the dry weight of swollen TPS film.

Results and Discussion

In chapter 4&5, amorphous TPS films were produced via compression molding of solution spray dried plasticized starch powder. Urea, and malic acid inhibited retrogradation of starch but the mechanical properties were poor.

In this study, carboxylic acids are used as plasticizer with the aim to interact with starch through hydrogen bonding or, potentially, esterification [1, 4, 14], and cross-linking by UV irradiation is anticipated to increase the strength of TPS films. The selected plasticizers contain multiple hydroxyl and carboxylic structures which are expected to interact with starch by hydrogen bonding or even esterification through the intermediate formation of acid anhydrides that can react with the hydroxyl groups on starch. Such an esterification could improve the water resistance and limit moisture absorption. Narendra et al. (2010) [4] discussed the importance of citric acid as cross-linking agent to improve starch film properties, but also mentioned the significance of the amount of plasticizer in the formulation and the proper combination with co-agents for plasticization and cross-linking of TPS films. In this work, we used malic and citric acid in different combination with glycerol to observe and investigate the importance of the amount and combination of plasticizer in TPS films. In previous chapter 5, malic acid plasticized films showed signs of cross-linking but nevertheless showed loss of strength due to excessive moisture absorption. So, it is expected that UV irradiation will help to improve the mechanical strength of TPS films without affecting the degree of crystallinity of films.

Crystallinity of freshly prepared TPS powder and films

The X-ray diffraction patterns of TPS powder and films processed with different plasticizers are shown in Figure 2. All spray dried powders were amorphous (Figure 2a). Results were in line with previous work (chapter 3, 4&5). The B- and V-type crystalline peaks at $2\theta=15^\circ$, 17.5° , 19.6° , 21.3° and 23.6° in U.S were completely absent after solution spray drying (Figure 2a) [15, 16]. Short drying times attained in spray drying disabled association of starch chains into crystal lattices (chapter 2&3).

XRD analysis demonstrated that results of TPS films based on spray-dried material were in line with previous chapters 3&4, and completely amorphous (i.e. S.D and formulated analogues) with or without plasticizer (Figure 2b).

Freshly prepared plasticized and co-plasticized samples were transparent, irrespective of the amount of plasticizer used, except S.D samples, which were slightly mat. TPS films exhibited no B-type crystallinity (Figure 2b). As explained in previous chapters (chapter 3, 4&5), this phenomenon was attributed to the fact that the short drying times attained in solution spray drying disabled the reallocation of starch chains into crystal lattices and gave rise to amorphous powder and films. Hence, compression molding did not affect the amorphous character of the samples. Neither was the crystallinity affected by combining malic acid and citric acid with glycerol in different ratios. Furthermore compression molding did not lead to retrogradation or the return of starch crystallinity as described in previous chapter 2.

Narendra et al. (2010) showed cross-linking effects of citric acid in starch films by improved tensile strength, thermal stability and decreased dissolution of starch films in water and formic

acid. The plasticized non-cross-linked solution casted films showed crystallinity, with two prominent peaks of typical corn starch at about 17° and 22° [4].

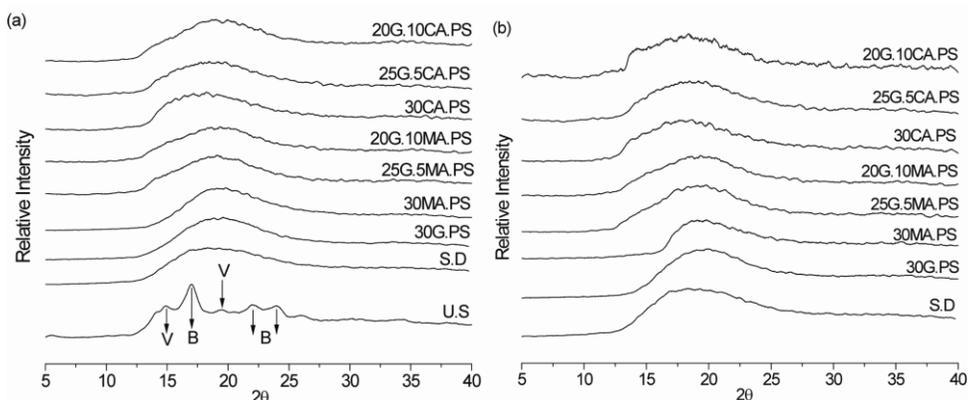


Figure 2 XRD spectra of (a) Freshly spray dried powder, (b) freshly prepared films by compression molding

Rui Shi et al. (2008) prepared solvent casted starch/polyvinyl alcohol (PVA) films at 140°C , plasticized with glycerol and citric acid with varying concentrations [14]. The wide-angle XRD patterns of the films were recorded and showed that most of the peaks in blends were present as for native materials. The presence of citric acid decreased the intensity of the peak at 19.3° as compared to native sample and inhibits the crystallinity, but could not create amorphous blends. Prepared films with all combination of glycerol and citric acid had prominent starch and PVA crystalline peaks.

X-ray diffraction analysis in previous chapters proved that the amorphous nature of TPS powder and films was obtained by true TPS solution spray-drying technology independent of plasticizer amount and combination.

Thermal Properties

Thermal properties of the TPS powders were investigated by TGA and DTGA (Figure 3 and Table 4). The analysis of TGA data is however not straightforward, therefore different (rough) sections were allocated based on DTGA minima, as done in previous chapters 4&5.

The spray-dried unmodified sample (S.D) differed from the formulated samples and was taken as reference sample. Only one single peak was observed for the decomposition of starch around 294°C . All formulated samples were thermally stable up to a temperature of 235°C . Overall the curves were characterized by weight loss sections at different temperature ranges depending on the plasticizer used, as reported in previous work (chapter 4&5). 30MA.PS showed a maximum T_{dec} of 232°C , whereas 30G.PS showed lowest T_{dec} of 190°C . 30CA.PS had T_{dec} of 227°C . This was ascribed to strong hydrogen bonding capability of carboxylic acids as compared to the glycerol plasticized sample, and possibly some esterification between the carboxylic acid group of the plasticizer and starch hydroxyl units (chapter 5). 30MA.PS showed better thermal stability as compared to 30CA.PS. X-ray diffraction analysis also proved the better stability of malic acid plasticized films as compared to citric acid with a lower rate of retrogradation. In co-

plasticized samples a fourth peak can be observed. This peak was attributed to the second plasticizer. Glycerol and carboxylic acids were used as co-plasticizers, so it could be associated to the cross-linked component [14]. The addition of plasticizer molecules caused a decrease in the decomposition temperature and an extra peak in the DTGA curve appeared (section b_1 & b_2 in Figure 3). The addition of malic acid and citric acid reduced the rate of weight loss and increased the residual weight. So the increased thermal stability of the TPS films may be explained by strong hydrogen bonding and potentially covalent bonding (esterification and cross-linking) by malic and citric acid. The varying amount of carboxylic acid plasticizer had an effect on the stability of formulations. The thermal stability increased with an increase in carboxylic acid component in the co-plasticizer combination. 20G.10MA.PS had higher thermal stability i.e. 190 °C, as compared to 25G.5MA.PS i.e. 182 °C. Similarly, 20G.10CA.PS has higher thermal stability as compared to 25G.5CA.PS. In all co-plasticized TPS blends, b_1 was observed at 178 °C, that represents the decomposition of glycerol in the blend and the second peak i.e. b_2 , that was representing the amount of carboxylic acid in the blend, varies according to type and amount of co-plasticizer.

It can be seen that the rate of weight loss and the residual weight percentage of 20G.10MA.PS and 20G.10CA.PS were higher than those of 25G.5MA.PS and 25G.5CA.PS, respectively, but lower than those of 30MA.PS and 30CA.PS. This may be, because the cross-linking was prevented in the presence of glycerol or occurred to a lesser extent. Compared with only carboxylic acid containing formulations, a part of malic or citric acid may have reacted with the glycerol, so the cross-linking degree decreased and the thermal stability of 20G.10MA.PS also decreased. With increase in glycerol contents, the thermal stability decreased. It seemed that the addition of carboxylic acid plasticizer enhanced the carbonization. FTIR, solubility and swelling analysis all explains the better stability and hydrogen bond interaction of carboxylic acid plasticized formulations as compared to glycerol formulated ones. According to Rui Shi et al. (2008), this phenomenon can be attributed to the cross-linking degree and the hydrogen bonds which increased as the carboxylic concentration increased [14].

Previous work (chapter 5) also showed a correlation of malic acid plasticized TPS blends with the thermal decomposition temperature. This explained the effective and better nature of carboxylic acid plasticizers as compared to hydroxyl ones. Rui Shi et al. (2008) prepared solvent casted starch/polyvinyl alcohol (PVA) films at 140 °C, plasticized with glycerol and citric acid with varying concentrations [14]. TGA analysis showed the better thermal stability of PVA/starch blends in the presence of citric acid plasticizer and illustrated a linear relationship for citric acid contents in co-plasticized formulations with glycerol to do cross-linking with starch molecule and increased the thermal stability.

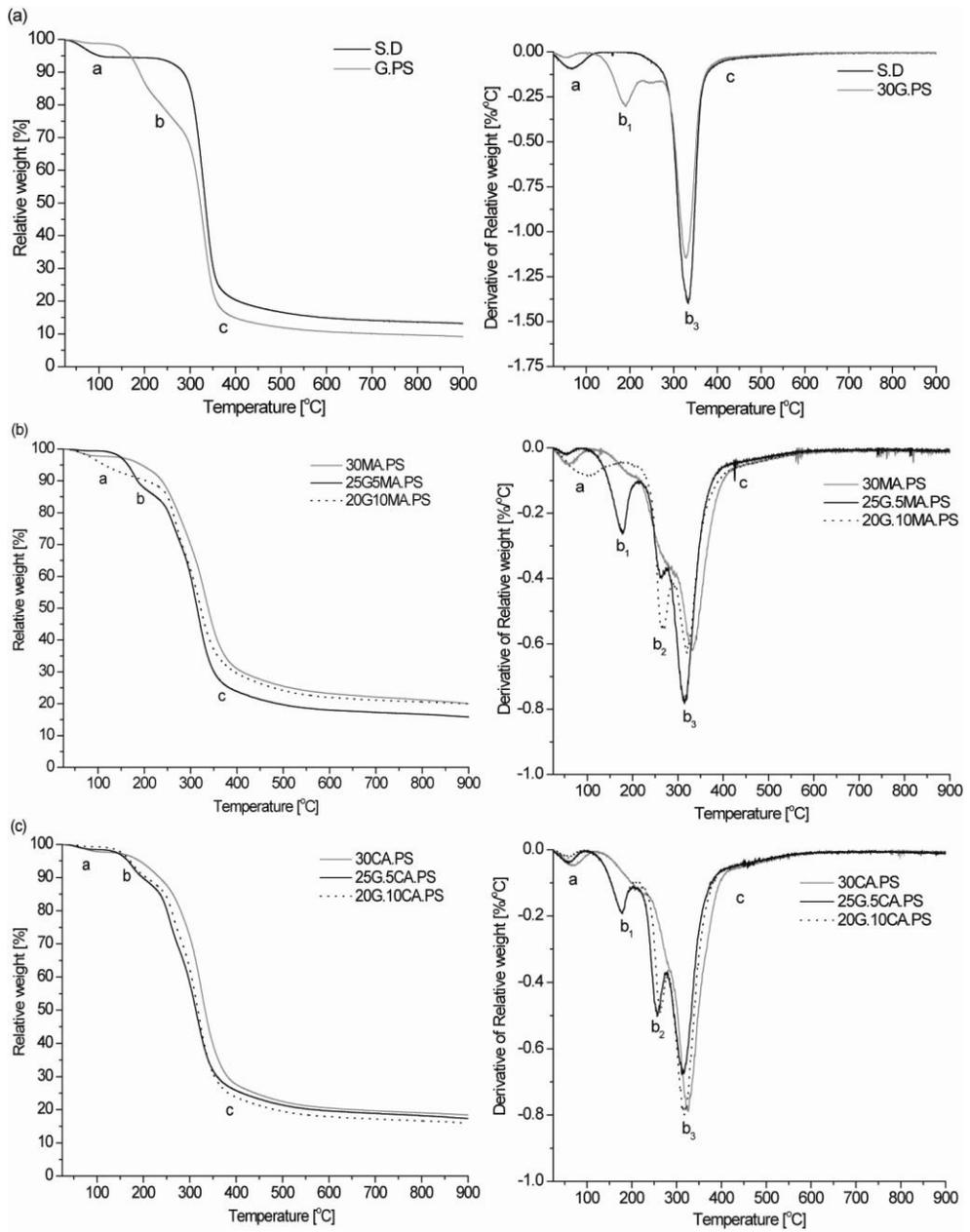


Figure 3 TGA and DTGA-curves of solution spray dried amorphous powder samples.

Glass transition temperature (T_g)

DSC analysis showed a T_g for all glycerol plasticized or co-plasticized formulations i.e. around 133 ± 3 °C, except 20G.10CA.PS. (Table 4). For S.D the strong inter- and intra-molecular hydrogen bonding between starch chains limited chain movement and this was the reason for the

absence of a T_g [17]. In 30G.PS and all co-plasticized formulations except 20G.10CA.PS, the plasticizer disrupted hydrogen bonds between starch molecules reducing the T_g .

FT-IR analyses

FT-IR analyses were performed to study the interaction between used plasticizers and starch. As explained in previous chapters 4&5, a red shift will occur upon hydrogen bond interactions for starch stretching vibrations of O-H, C-O and C=O. Characteristic absorption bands of the TPS samples are depicted in Table 3.

Feedstock (U.S) data will be used to describe the important absorption bands for all plasticized TPS samples. The U.S spectrum showed a broad band at 3262 cm^{-1} which was attributed to hydrogen bonded hydroxyl groups (O-H stretching) (Table 3). This band is associated with free, inter- and intra-molecular bounded hydroxyl groups [18, 19].

The peak at 2922 cm^{-1} corresponded to C-H stretching from CH_2 . The bands at 1339 cm^{-1} were assigned to C-H bending [20]. The absorption peaks at 1149 cm^{-1} and 1076 cm^{-1} were attributed to stretching vibrations of C-O in C-OH groups [21, 22]. Absorption at 996 cm^{-1} describes the C-O stretching in C-O-C groups [1, 19].

Spectra of U.S and S.D were compared and it can be seen that the interactions with O-H, C-O-H and C-O-C changed. As described in literature [23, 24], these changes were indicative of a reduction in crystallinity and water content. The peak at 1019 cm^{-1} became more visible, indicating decreased crystallinity [24]. Finally, the peak at 3288 cm^{-1} , for O-H stretching, was higher as compared to U.S. This showed that the spray dried sample has a decreased molecular order as compared to the feedstock material. A decreased molecular order resulted in fewer hydrogen bonding between the starch chains in S.D (chapter 3).

The spectra for formulated samples were in-line with literature and the absorption at 1019 cm^{-1} was clearly visible for all spray-dried samples, indicating low crystallinity (see chapter 4&5). All spectra showed shifts in the fingerprint section of starch, indicating interaction between starch and plasticizers. Comparing the spectra of citric acid and malic acid plasticized samples, a red shift was visible upon increasing carboxylic acid concentration in co-plasticized TPS films. The peak around 3310 cm^{-1} is assigned to the stretching vibration of hydroxyl groups. We noticed that the absorption value at 3310 cm^{-1} increased with carboxylic groups concentration. The absorption value increased in the order of 30CA.PS > 20G.10CA.PS > 25G.5CA.PS. A similar order was observed in case of malic acid. This could be explained by two facts: 1) the number of the hydroxyl and carboxyl groups increased as the CA and MA concentration increased, 2) when citric acid and malic acid used in combination with glycerol, a part of carboxylic acids were reacted with glycerol, so few hydrogen bonds were produced [14].

Table 3

FT-IR absorption bands of the studied samples.

Samples	Wavelength [cm^{-1}]					
	3310-3270	2922-2921	1722-1711	1361	1019-1017	994
U.S	3262	2922	--	1339	--	996
S.D	3288	2918	--	1356	1017	999
30G.PS	3203	2901	--	1370	1017	996
30MA.PS	3303	2902	1716	1394	1018	999
25G.5MA.PS	3270	2924	1717	1369	1015	994
20G.10MA.PS	3273	2926	1716	1368	1017	997
30CA.PS	3311	2902	1715	1394	1018	998
25G.5CA.PS	3273	2927	1717	1364	1015	994
20G.10CA.PS	3298	2928	1714	1334	1016	996

Carboxylic acid plasticized TPS blends showed additional absorption bands at 1711-1722 cm^{-1} (Table 2). Peaks in this range 1721-1750 cm^{-1} are ascribed to esterification of starch and carboxyl groups of plasticizer [14]. This peak was absent in G.PS, U.S and native starch. The height of the peak may be related to the degree of esterification (not shown here). The height of peak increased with increasing the carboxylic acid concentration, i.e. 30MA.PS had highest peak height, whereas 25G.5MA.PS had lowest. A similar sequence was observed for citric acid plasticized and co-plasticized blends (Table 3). This could be explained by the reaction of citric or malic acid with glycerol to obtain some glycerol esters [14].

It has been reported that a decrease in crystallinity has no effect on the absorption band at 1077 cm^{-1} but the one at 1022 cm^{-1} is sensitive to change in crystallinity and increases with decreasing crystallinity [25]. The same phenomenon was observed here. All the plasticized TPS blends were amorphous (as reported in XRD analysis) and had higher band value at 1017 cm^{-1} as compared to U.S. All the plasticized starches showed two peaks at 1017 cm^{-1} and 996 cm^{-1} . The COH bending vibration at 996 cm^{-1} is sensitive to water contents and involves water-starch interaction. The height ratio between these two peaks at 1017 and 996 cm^{-1} decreased with decreasing carboxylic acid concentrations in plasticizer. 30MA.PS and 30CA.PS had highest ratio between these two peaks, whereas 25G.5MA.PS and 25G.5CA.PS had the lowest.

Powder morphology

Surface morphology of TPS powder granules was examined by using SEM. Figure 4 shows the morphology of untreated starch and the solution spray dried powder samples. U.S was the reference sample and exhibits a similar morphology as published in previous chapters 4&5. U.S. material exhibited spherical and round shaped particles of irregular sizes. The surface of particles was homogeneous, smooth and regular.

Solution spray-dried TPS samples showed significantly different morphologies. Morphology was similar to previous chapters 3&4. Particles were spherical in nature however they contained dents, which are typical for spray dried powders [23, 24]. The degree of shrinkage was determined by the drying sequence [26, 27].

As explained in our previous chapters (3&4), the surface of the droplet is first covered by the formation of a ‘skin’ during spray drying, leaving the remaining liquid trapped inside. Further drying decreased the particle size as the liquid diffused through the dried surface. Hereby dents in the particle surface emerged. More importantly, S.D and all formulated solution spray dried samples showed a similar appearance (Figure 4). There was no noticeable difference in morphology between the samples. Hence, the difference in plasticizer combinations and nature did not lead to visible differences in morphology.

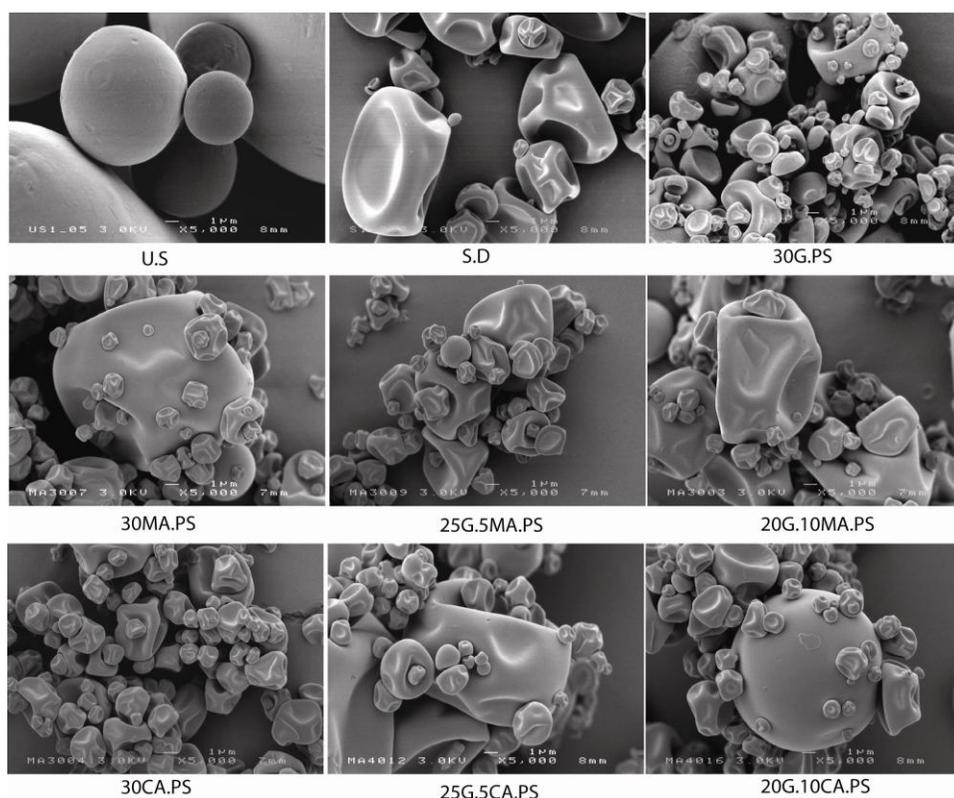


Figure 4 SEM micrographs of all spray dried TPS powder.

Retrogradation and moisture uptake

Film retrogradation was studied at various humidity conditions i.e. RH0%, 50% and 100% for 56 days by X-ray diffraction (Figure 4) (chapter 4&5). The U.S line corresponds to the degree of crystallinity present in the feedstock material.

The rearrangement of amorphous starch chains was influenced by moisture content [18, 28]. Therefore relative weight changes during storage were also reported. All films showed an increase in final crystallinity levels and relative weight in the order RH100% > RH50% > RH0% (Figure 5, 6, 7 and 8). All films maintained similar crystallinity levels at RH0% (Figure 5). The starch retrogradation was prevented due to absence of water. Plasticizer content showed no influence on re-crystallization over time.

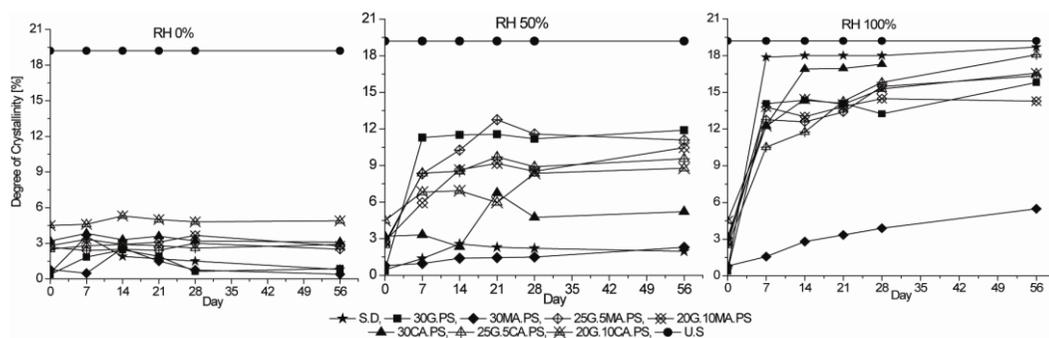


Figure 5 (a) Degree of crystallinity of films after 56 days of storage at different humidity levels, 30CA.PS was disintegrated after 28 days at 100%RH. Therefore reported results of 30CA.PS were for day 28.

At 50% relative humidity, the relative weight of film increased over time, and finally reached a plateau when in equilibrium with the environment. 30MA.PS and S.D had showed maximum resistance to retrogradation. 30CA.PS also inhibited retrogradation at RH50% but lower than 30MA.PS. These three samples showed no significant increase in crystallinity at RH50% over time. All the films except S.D. stored at 50% humidity became flexible due to moisture sorption and water acting as a plasticizer. The co-plasticized formulations of malic and citric acids with glycerol showed retrogradation with some increase in relative weight due to moisture uptake. This increase in crystallinity was attributed to the hygroscopic nature of glycerol. As described in previous chapter, first the amorphous starch matrix absorbs the water, leading to an increase in weight (chapter 4). The free volume in the polymeric matrix increased due to further increases in water contents. Certain starch-starch hydrogen bond interactions are being replaced by starch-water interactions, creating a more open network and due to further increase of the water content the samples become rubbery. In this regime structural rearrangements occur, causing re-crystallization. Crystallization causes a weight loss [29], which was also observed in this study (not shown here for brevity).

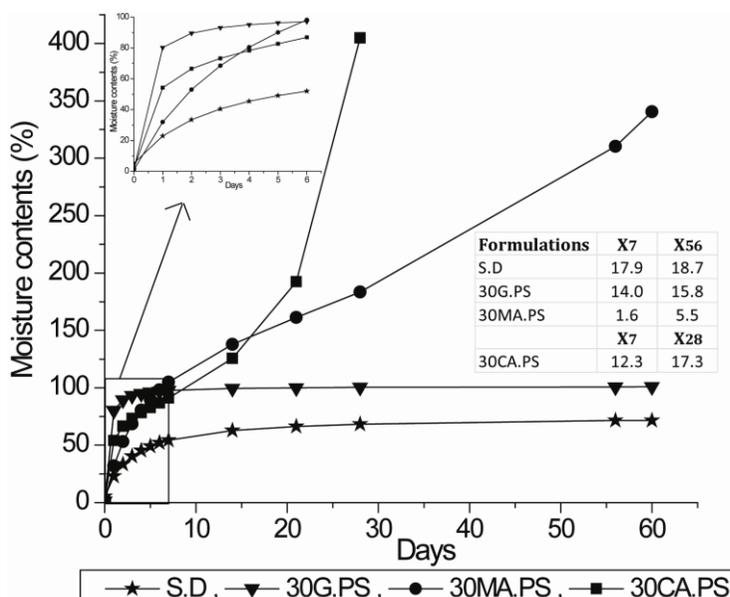


Figure 6 Sorption curves at 100%RH for 30% plasticized formulations (X7 and X56: the degree of crystallinity at day 7 and 56, respectively). 30CA.PS films disintegrated after 28 days).

All the co-plasticized samples and 30G.PS had a similar rate of retrogradation after 56 days, storing at RH50%. In our previous chapter, (1:1) glycerol and urea co-plasticized with malic acid showed resistance to retrogradation and had low degree of crystallinity after 56 days at RH50% (chapter 5). Hence, it showed that the rate of retrogradation depends on the concentration of hygroscopic plasticizer (glycerol) present as co-plasticizer. In this work, glycerol contents were higher as compared to malic and citric acids contents, so the rate of retrogradation was also significantly higher as compared to previous chapter.

The moisture absorption data recorded at 100%RH are very indicative for the special behaviour of malic acid compared to citric acid formulations as also shown in previous the chapter 5. Figure 6 presents an overview of the data for the 30%w single formulations including the crystallinity data at day 7 and day 56 (including S.D as a reference). The data of S.D and 30 G.PS were fitted to the Peleg absorption model. The 30MA.PS and 30CA.PS data however only followed the Peleg fit for the initial moisture absorption for two weeks; after that period a more complex fitting model had to be applied. The interesting behaviour of malic acid is explained in the previous work (chapter 5). 30CA.PS disintegrates after 28 days and had maximum moisture absorption, leading to the highest rate of retrogradation except S.D (Figure 5&6). 30MA.PS suppressed starch retrogradation (Figure 5). Results showed that 30MA.PS had better shelf life and resistance to retrogradation as compared to 30CA.PS. The relative weight [%] of both, 30MA.PS and 30CA.PS were the same till 21 days i.e. 170% approximately, but the degree of crystallinity was significantly different i.e. 4% and 17 % after 21 days, respectively.

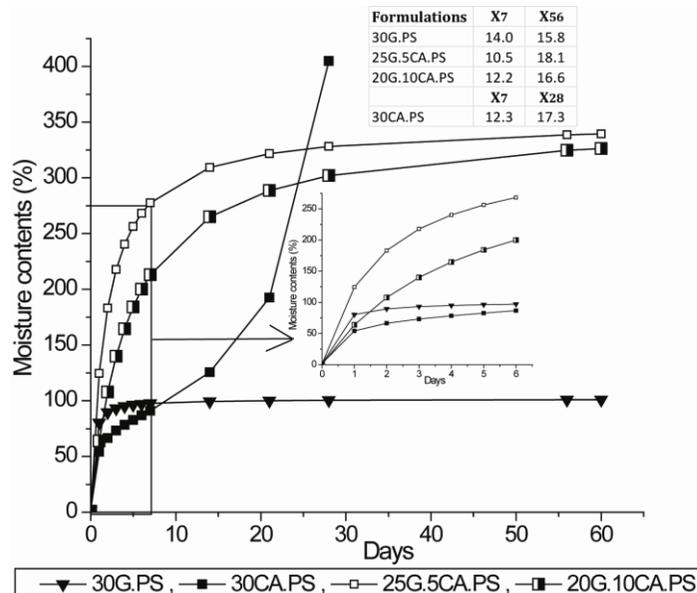


Figure 7 Sorption curves at 100%RH for citric acid plasticized and co-plasticized formulations (X7 and X56 are the degree of crystallinity at day 7 and 56, respectively. 30CA.PS formulation disintegrated after 28 days).

Figure 7 illustrates the results of citric acid plasticized and co-plasticized formulations at 100%RH. All the formulations had high moisture absorption except 30G.PS, and approaches the equilibrium state after 21 days except 30CA.PS. The data for 30G.PS and citric acid co-plasticized formulations were fitted to the Peleg absorption model except 30CA.PS. All the formulations showed significant retrogradation even after 1 week. 20G.10CA.PS showed less retrogradation and moisture absorption compared to 25G.5CA.PS. An increase in glycerol concentration enhanced the hygroscopic nature of the blend. The rate of absorption for 30CA.PS was slow (compared to CA co-plasticized films) for the first 21 days but then increased significantly and films disintegrated after 28 days.

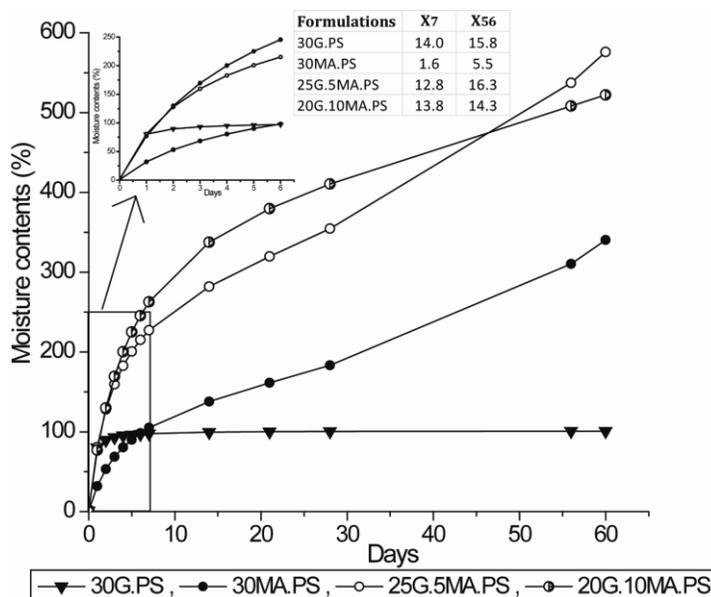


Figure 8 Sorption curves at 100%RH for malic acid plasticized and co-plasticized formulations (X7 and X56 are the degree of crystallinity at day 7 and 56, respectively).

Figure 8 describes the moisture absorption data recorded for malic acid plasticized and co-plasticized formulations. All malic acid films did not approach the equilibrium state and moisture adsorption data were fitted by applying the complex model (chapter 5). 30G.PS and malic acid co-plasticized formulations had high absorption rates for the first 7 days compared to 30MA.PS. Malic acid co-plasticized formulations could not inhibit retrogradation due to high concentration of glycerol. 25G.5MA.PS and 20G.10MA.PS showed similar rate of adsorption and retrogradation. Glycerol limits the ability of malic acid to inhibit retrogradation. Malic acid co-plasticized films with glycerol showed the largest relative weight increase followed by citric acid co-plasticized formulations. It can be attributed to their amorphous character and the hydrophilic nature of glycerol. Results were in line with previous chapter 5, in which the (1:1) malic acid glycerol formulation showed the highest relative weight increase after 56 days i.e. 600 % compared to 360% for 30MA.PS. 30MA.PS and citric acid co-plasticized TPS films showed comparable relative weight increments. Hence, citric acid in combination with glycerol resisted moisture uptake but could not inhibit retrogradation.

All films became flexible and maintained structural integrity for all 56 days except 30CA.PS. The results showed the exceptional behaviour of malic acid as individual plasticizer as it strongly inhibited retrogradation. Strong hydrogen bonding between starch and malic acid plus partial esterification/cross-linking may be the explanation for the remarkable retrogradation performance (chapter 5).

Table 4.

Degree of crystallinity, relative weight, thermal properties and mechanical properties of TPS films (30CA.PS become jell after 21days at 100%RH, so the presented results for degree of crystallinity and relative weight were for 21days)

Samples	Moisture contents Powder [%]	Thermal properties [°C]					Degree of crystallinity of films			Relative weight change films	
		T _{dec}	T _{dec}		T _g	0 day [%]	RH 100%		RH 100%		
			G (b1)	MA / CA (b2)			7 day	56 days	1 day	56 days	
S.D	5.2	294	--	--	nil	0.5	17.9	18.7	29.1	64.6	
30G.PS	1.3	190	160	--	136	0.38	14.1	15.8	81.8	93.6	
30MA.PS	2.1	232	--	281	nil	0.8	1.6	5.5	54.2	359.8	
25G.5MA.PS	1	182.3	178.5	262.8	133.6	2.67	12.8	16.4	110.2	530.6	
20G.10MA.PS	1.9	190.1	No peak	264.9	130.2	2.8	13.8	14.3	90	500	
30CA.PS	2.1	227.3	--	280.5	nil	3.2	12.3	17.3	50.1	179	
25G.5CA.PS	1.2	190	178.9	257.7	135	2.5	10.5	18.1	117.9	333.9	
20G.10CA.PS	0.8	197.7	177.8	264.2	nil	4.5	12.2	16.6	97.6	336.6	

Mechanical Properties

Mechanical behaviour of the formulated TPS films is shown in Figure 9. Due to the brittle and rigid nature of U.S. samples, mechanical properties for this sample could not be evaluated.

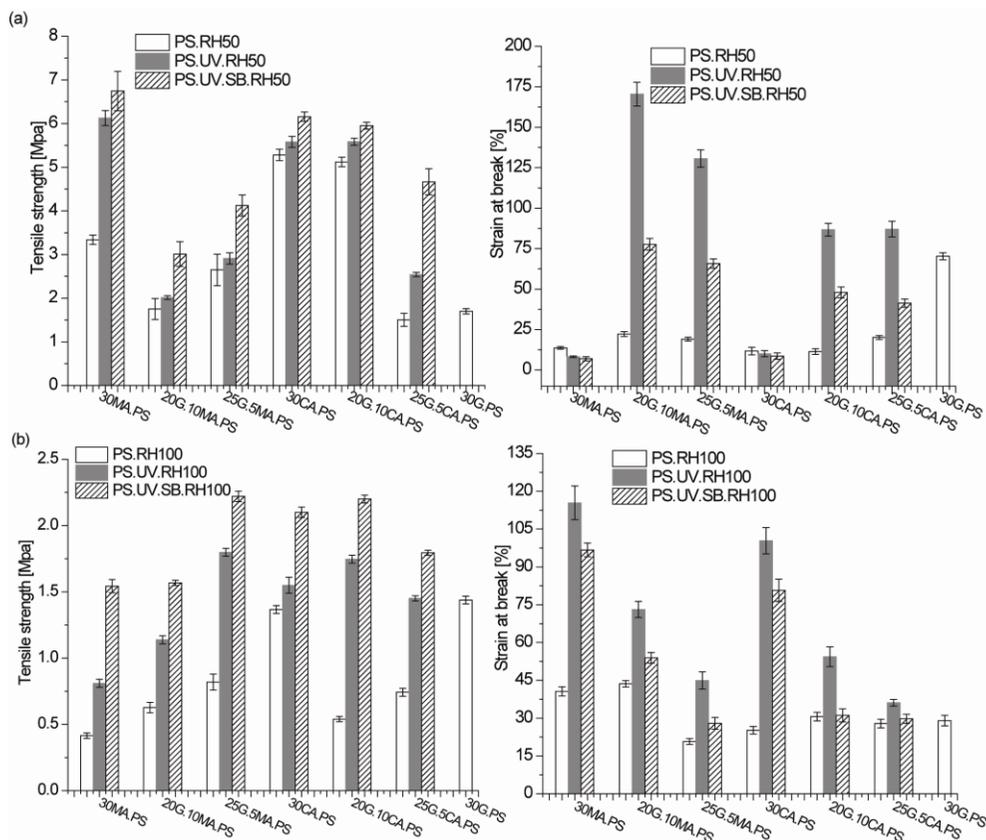


Figure 9 Mechanical properties of the TPS films, a) at 50% RH, b) at 100% RH.

Mechanical properties were determined at two different relative humidities i.e. RH50% and RH100%. All samples were divided into three groups i.e. 1) blank TPS films (without UV treatment), 2) UV treated TPS films, 3) UV treated TPS films after being soaked in sodium benzoate (SB) for three days. In literature [1, 3], sodium benzoate (SB) is mentioned as photosensitizer and showed improvement in the strength of SB soaked and UV treated TPS films (Figure 10). Based on these reports, sodium benzoate was incorporated as photosensitizer into the material to produce reactive radicals that initiate subsequent cross-linking reactions under UV irradiations. The results were according to our expectations, i.e. an increment in tensile strength after UV and UV/SB treatment. All treated TPS films showed similar patterns, the tensile strength increased in the order: UV irradiated after soaking in SB > UV irradiated > blank. That pattern and increase was more prominent at RH50% than at RH100%.

At RH50%, the maximum increase in strength was observed for 30MA.PS for both UV treated soaked and non-soaked formulations. Overall, CA plasticized or co-plasticized TPS films

showed a higher strength compared to malic acid formulated TPS films. However, strain at break gave strange results and showed following trend, UV.PS.RH50% < UV.SB.PS.RH50% < PS.RH50%. PS.RH50% had lowest strain and strength values. Overall at RH50%, CA plasticized and co-plasticized TPS films showed slightly better strength for both UV treated after soaked and non-soaked formulations. 30MA.PS had highest strength among all treated TPS films, followed by all CA plasticized and co-plasticized films.

At RH100% (Figure 9b), mechanical properties showed a similar trend, the tensile strength increased after UV treatment and soaking in SB for both malic and citric acid plasticized and co-plasticized samples. The increment followed the order: UV.SB.PS.RH100% > UV.PS.RH100% > blank. Citric acid plasticized and co-plasticized formulations showed better tensile strength compared to malic acid formulated TPS films. Only 25G.5MA.PS UV treated soaked and non-soaked in SB had equal strength as that of citric acid plasticized and co-plasticized TPS films. The strain at break followed the same trend as that at RH50%. A decrease was observed in the order: UV.PS.RH100% < UV.SB.PS.RH100% < blank.

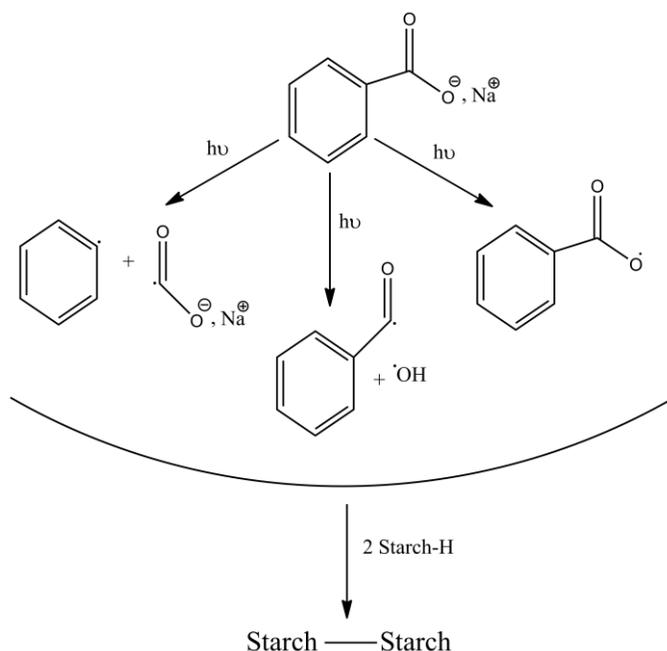


Figure 10 Mechanism involved in sodium benzoate sensitized film [1, 3].

Samples conditioned at RH50% showed higher values for tensile strength for both malic acid and citric acid plasticized and co-plasticized TPS films than at RH100%. Comparing the data found at RH50% and Rh100% shows that progressive moisture absorption lowers the mechanical properties with changes in both tensile strength and elongation. Tensile strengths reduces by moisture although moisture promotes retrogradation. The final mechanical properties for the blends are determined by the balance between crystallinity and moisture contents.

Degree of crystallinity of ultra-violet irradiation treated samples

To see whether UV cross-linking has an effect on starch crystallinity, two formulations (25G.5MA.PS and 25G.5CA.PS) were evaluated at different time intervals by XRD. The X-ray diffraction patterns of cross-linked and non-cross-linked TPS films are shown (Figure 11) for day 0 and day 7 for non-cross-linked (as blank) and day 4 for cross-linked. Analysis showed that the crystallinity of TPS films did not change because of SB/UV or UV irradiation at both relative humidities i.e. 50% and 100%. The degrees of crystallinity after cross-linking of both films i.e. 25G.5MA.PS and 25G.5CA.PS were between the crystallinity observed at day 7 and day 0. From the data shown in Figure 11, it is concluded that UV irradiation has no effect on recrystallization.

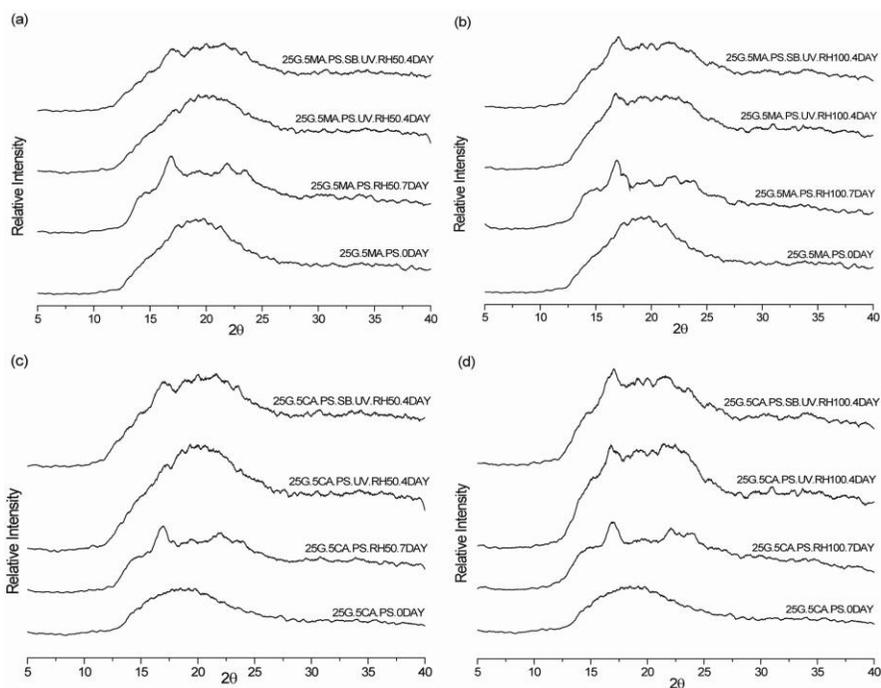


Figure 11 XRD spectra of (a) 25G.5MA.PS cross-linked film at RH50%, (b) 25G.5MA.PS cross-linked film at RH100%, (c) 25G.5CA.PS cross-linked film at RH50%, (d) 25G.5CA.PS cross-linked film at RH100%

Literature also showed no effect of cross-linking on degree of crystallinity and peak position [4, 7]. Nawapat et al. (2011) prepared photo-cross-linked rice starch-based biodegradable films by solution casting and reported UV treatment of starch did not alter the crystalline structure of starch or its gelatinization enthalpy [7].

Solubility and swelling behavior

Solubility (S) and degree of swelling (DS) of cross-linked 25G.5MA.PS and 25G.5CA.PS films were measured and are shown in Figure 12. The results were in line with literature [30, 31]. Cross-linking led to a reduction in the solubility and the degree of swelling of both TPS films. The bonding between the starch chains became stronger due to cross-linking, causing an increase in the resistance of the TPS films to swell. Cross-linking reinforced the structure of the starch films and restricted the mobility of starch chains in the amorphous region, which limits water solubility and absorption into the cross-linked starch [31].

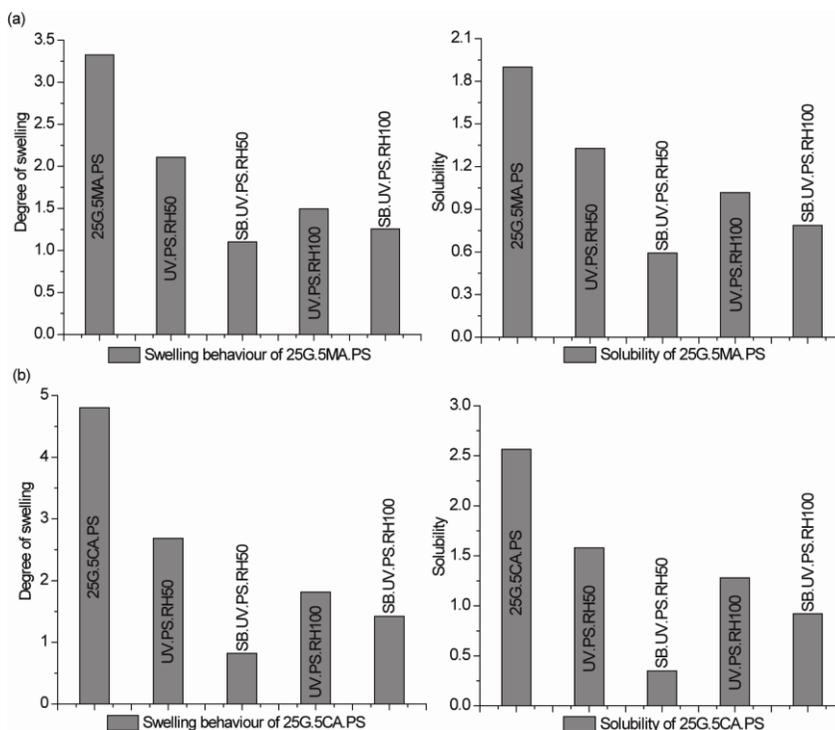


Figure 12 Degree of swelling and solubility at RH50% and RH100% of: (a) 25G.5MA.PS cross-linked film, (b) 25G.5CA.PS cross-linked film

The DS and S of cross-linked films at RH50% were lower than at RH100%. SB soaked films showed lower value of DS and S in both cases, i.e. malic acid co-plasticized and citric acid co-plasticized. These results were in line with the mechanical property data. SB soaked and RH50% conditioned films had better strength than non-soaked films and RH100% conditioned films, respectively. Citric acid co-plasticized films showed similar results. 25G.5CA.PS showed lower solubility and DS compared to 25G.5MA.PS cross-linked films at both relative humidities. Citric acid had higher number of carboxyl groups i.e. three, compared to malic acid i.e. two, so it was expected that CA co-plasticized films do stronger cross-linking and inhibited the movement of starch chains and resisted the water solubility and absorption after cross-linking compared to MA co-plasticized films.

Conclusion

Malic acid and citric acid plasticized and glycerol co-plasticized TPS films were surface cross-linked by soaking the films in a sodium benzoate aqueous solution and exposing them to UV irradiation. Totally amorphous films were produced by solution spray drying technology independent of plasticizer and varying combinations. CA and MA plasticized TPS blends had better thermal stability and hydrogen bonding interaction with starch compared to co-plasticized and glycerol plasticized blends. DSC analysis showed T_g values for all co-plasticized formulations except 20G.10CA.PS. 30MA.PS and 30CA.PS showed no T_g which may be attributed to cross-linking.

UV cross-linking improved the strength of films. When films were soaked in sodium benzoate solution the cross-linking of the films was more efficient. Cross-linking indeed decreased the degree of swelling and the solubility of films. Cross-linked films conditioned at RH50% had better strength and a lower degree of swelling compared to those conditioned at RH100%. CA plasticized and co-plasticized cross-linked films showed slightly higher strength and lower swelling compared to MA cross-linked plasticized and co-plasticized films. Decrease in solubility and degree of swelling was in order of i.e. PS.UV.SB > PS.UV. > PS. UV irradiation and SB soaking did not affect the amorphous nature of TPS films.

Adding up all the observed results (combining chapters 2-6), it is concluded that carboxylic acids act different than common plasticizers like glycerol or urea. Carboxylic acids clearly show more intensive interaction and malic acid in particular, reduces retrogradation significantly. However, lack of retrogradation also is correlated with high moisture absorption and other pathways have to be developed to reduce the effect of moisture in order to achieve and maintain better mechanical properties.

References

1. Zhou J, Zhang J, Ma Y, Tong J. Surface photo-crosslinking of corn starch sheets. *Carbohydr Polym* 2008;74(3):405-410.
2. Zhou J, Ma Y, Ren L, Tong J, Liu Z, Me L. Preparation and characterization of surface crosslinked TPS/PVA blend films. *Carbohydr Polym* 2009;76(4):632-638.
3. Delville J, Joly C, Dole P, Bliard C. Solid state photocrosslinked starch based films: a new family of homogeneous modified starches. *Carbohydr Polym* 2002;49(1):71-81.
4. Reddy N, Yang Y. Citric acid cross-linking of starch films. *Food Chem* 2010;118(3):702-711.
5. Kim M, Lee SJ. Characteristics of crosslinked potato starch and starch-filled linear low-density polyethylene films. *Carbohydr Polym* 2002;50(4):331-337.
6. Ramaraj B. Crosslinked poly(vinyl alcohol) and starch composite films: Study of their physicomechanical, thermal, and swelling properties. *J Appl Polym Sci* 2007;103(2):1127-1132.
7. Detduangchan, N., Wittaya, T. Effect of UV-treatment on properties of biodegradable film from rice starch. *WASET* 2011;81:464.

8. Yu JG, Wang N, Ma XF. The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. *Starch-Starke* 2005;57(10):494-504.
9. Shujun W. Use of X-ray diffractometry (XRD) for identification of fritillaria according to geographical origin 2005;1(4):207-211.
10. Zhang S, Zhang Y, Wang X, Wang Y. High Carbonyl Content Oxidized Starch Prepared by Hydrogen Peroxide and Its Thermoplastic Application. *Starch-Starke* 2009;61(11):646-655.
11. Peleg M. An Empirical-Model for the Description of Moisture Sorption Curves. *J Food Sci* 1988;53(4):1216-&.
12. Mali S, Sakanaka LS, Yamashita F, Grossmann MVE. Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydr Polym* 2005;60(3):283-289.
13. Yun Y, Wee Y, Byun H, Yoon S. Biodegradability of Chemically Modified Starch (RS4)/PVA Blend Films: Part 2. *J Polym Environ* 2008;16(1):12-18.
14. Shi R, Bi J, Zhang Z, Zhu A, Chen D, Zhou X, Zhang L, Tian W. The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydr Polym* 2008;74(4):763-770.
15. James BeMiller RW. *Starch: Chemistry and technology*: Elsevier, 2009.
16. vanSoest JGG, Bezemer RC, deWit D, Vliegthart JFG. Influence of glycerol on the melting of potato starch. *Ind Crop Prod* 1996;5(1):1-9.
17. Liu H, Xie F, Yu L, Chen L, Li L. Thermal processing of starch-based polymers. *PROG POLYM SCI* 2009;34(12):1348-1368.
18. Hulleman SHD, Janssen FHP, Feil H. The role of water during plasticization of native starches. *Polymer* 1998;39(10):2043-2048.
19. van den Dries IJ, van Dusschoten D, Hemminga MA, van der Linden E. Effects of water content and molecular weight on spin probe and water mobility in malto-oligomer glasses. *J Phys Chem B* 2000;104(44):10126-10132.
20. You Y, Ludescher RD. The Effect of Molecular Size on Molecular Mobility in Amorphous Oligosaccharides. *Food Biophys* 2010;5(2):82-93.
21. Chaudhary AL, Torley PJ, Halley PJ, McCaffery N, Chaudhary DS. Amylose content and chemical modification effects on thermoplastic starch from maize - Processing and characterisation using conventional polymer equipment. *Carbohydr Polym* 2009;78(4):917-925.
22. Imamura K, Sakaura K, Ohyama K, Fukushima A, Imanaka H, Sakiyama T, Nakanishi K. Temperature scanning FTIR analysis of hydrogen bonding states of various saccharides in amorphous matrixes below and above their glass transition temperatures. *J Phys Chem B* 2006;110(31):15094-15099.
23. Kurozawa LE, Morassi AG, Vanzo AA, Park KJ, Hubinger MD. Influence of Spray Drying Conditions on Physicochemical Properties of Chicken Meat Powder. *Drying Technol* 2009;27(11):1248-1257.
24. Tonon RV, Brabet C, Hubinger MD. Influence of process conditions on the physicochemical properties of acai (*Euterpe oleraceae* Mart.) powder produced by spray drying. *J Food Eng* 2008;88(3):411-418.
25. vanSoest JGG, Tournois H, deWit D, Vliegthart JFG. Short-range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier-transform IR spectroscopy. *Carbohydr Res* 1995;279:201-214.
26. Bhandari BR, Howes T. Implication of glass transition for the drying and stability of dried foods. *J Food Eng* 1999;40(1-2):71-79.
27. Walton DE, Mumford CJ. The morphology of spray-dried particles - The effect of process variables upon the morphology of spray-dried particles. *Chem Eng Res Des* 1999;77(A5):442-460.

28. Chang YP, Karim AA, Seow CC. Interactive plasticizing-antiplasticizing effects of water and glycerol on the tensile properties of tapioca starch films. *Food Hydrocoll* 2006;20(1):1-8.
29. Dangaran KL, Krochta JM. Kinetics of sucrose crystallization in whey protein films. *J Agric Food Chem* 2006;54(19):7152-7158.
30. Majzoobi M, Radi M, Farahnaky A, Jamalian J, Tongdang T. Physico-chemical Properties of Phosphoryl Chloride Cross-linked Wheat Starch. *Iran Polym J* 2009;18(6):491-499.
31. Mirmoghtadaie L, Kadivar M, Shahedi M. Effects of cross-linking and acetylation on oat starch properties. *Food Chem* 2009;116(3):709-713.

