



# The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure

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## ABSTRACT

The material compositions and the technological procedures to prepare biodegradable films with the film blowing technology based on thermoplastic starch were studied in this work. The activities were focused on the analysis of the effects of starch source (maize, potato and wheat), supplier (Roquette, Cerestar and CAMEO) and the type of plasticizers (glycerol, urea and formamide) and their content on the physical-chemical and mechanical properties. Moreover, in order to develop a film blowing technology, material composition as well as processing condition were optimized. Among 10 varieties of thermoplastic starch prepared, the combination of urea and formamide as plasticizer restrained retrogradation and improved mechanical properties. Extensional rheological properties of the thermoplastic starch films were also investigated: the results showed that the occurrence of strain-hardening behaviour in some of the investigated compositions lead to a positive effect on the film blowing process. In this study we found that the combination of high-amylose (>51%) starch and urea/formamide mixtures as plasticizer produced an homogenous film of a 50  $\mu\text{m}$  thickness and a robust film blowing process due to the good elongational viscosity, high deformability of the melt and strain-hardening behaviour.

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## 1. Introduction

The use of plastics packaging is widespread. For this reason there is a growing interest in the use of biodegradable polymers which can help to minimise the environmental impact of plastics. There are many sources of biodegradable plastics, from synthetic to natural polymers. Synthetic polymers are derived from non renewable petroleum resource while natural polymers, like polysaccharides and proteins, are available in large quantities from annually renewable sources.

Starch is a low cost polysaccharide derived from agricultural plants and it is susceptible to biological attack. Natural starch exists in granular form and it has been used as a filler in polymers. To improve starch processability, the molecular order within the granules must be destroyed. This is usually achieved by heating the granular starch mixed with plasticizers. With this process a conversion of the molecular structure to thermoplastic starch (TPS) is obtained. In this way much of the starch changes from a crystalline to an amorphous structure, even if a granular native structure or a new crystalline form induced by the process remains in the thermoplasticized material.

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The most commonly plasticizers are polyols (glycerol, sorbitol, etc.) that allow a good destructure of the starch but they usually induce recrystallization phenomena (or retrogradation) because these molecules are small and can easily separate from the starch macromolecular chains (Krogars, Heinämäki, Karjalainen, Rantanen, et al., 2003; Krogars, Heinämäki, Karjalainen, Niskanen, et al., 2003; McGlashan & Halley, 2003; Poutanen & Forssell, 1996).

In a study by Lourdin, Della Valle, and Colonna (1995) the effects on mechanical properties of different amylose contents in starch films plasticized with water and water/glycerol and unplasticized films were studied. The content of amylose was found to be an important parameter in plasticized films; the elongation and strength increased with amylose content. The effect of amylose content on the phase separation in films made from casting solution was also evaluated (Westling, Stading, & Gatenholm, 2002). With a low amylose content a phase separation between amylose and amylopectin occurred while with a high-amylose content a gelation of amylose and the formation of a continuous network took place.

Another important parameter is the plasticizer content: below 10 wt% the plasticizer-polymer interactions are weak and the material is fragile and difficult to work, while above 20 wt% there is a progressive increase in the flexibility and in the elongational properties of the films (Mylärinen, Partanen, Seppälä, & Forssell, 2002). Studies regarding the effect of molecular mass in potato

starch (van Soest, Benes, De Wit, & Vliegenthart, 1996) have shown that the thermal properties are more influenced by the water content than the molecular weight, while the elongation increases with the molecular weight.

The preparation of films based on thermoplastic starch by using the film blowing technique is a challenging technology. However, most of the studies on film blowing have been conducted on blends of thermoplastic starch with other biodegradable and non-biodegradable polymers were TPS is usually the minor component. In particular TPS were blended with PCL to adjust the rheological properties of the melt before the film blowing process (Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002). Moreover, blends of PCL/starch/LDPE were prepared with the aim of increasing the mechanical properties of PCL/starch and making the LDPE films partially biodegradable (Matzinos, Tserki, Gianikouris, Pavlidou, & Panayiotou, 2002). More recently McGlashan and Halley (2003) employed nanoclay to improve the films properties of mixtures of starch and aliphatic polyesters. With the addition of clay the film is more transparent and the process of film blowing is more stable; the exfoliation of nanoclay prevented the migration of the plasticizer.

Recent studies (Thunwall, Kuthanová, Boldizar, & Rigdahl, 2008) regarding the film blowing process of TPS were conducted on potato starch with different amylose content and modified potato starches. The increase in amylose content produced a higher stiffness and higher melt viscosity, thus the material was difficult to process and required a higher amount of plasticizers, water and glycerol.

Depending upon the plasticizer content and botanic origin of starch, materials with different properties can be prepared. Ten varieties of starch were investigated in this work in order to study the suitability of these materials to be processed in a film blowing line. Glycerol-plasticized TPS and urea/formamide-plasticized TPS were prepared and characterized by using X-ray diffractometry, SEM, FTIR, rheological and mechanical tests. The increase of the melt deformability and the elongational properties of the melt were assessed to be crucial in the film blowing process. In particular, the strain-hardening behaviour was a fundamental characteristic for this process, since it allowed tensile stresses in the bubble as a result of the extensive deformations occurring during the blowing of the films to be withstood. The extensional rheological behaviour of starch films was therefore analyzed in order to study the correlations between the material composition, the rheological behaviour in uniaxial elongation and the film blowing process.

## 2. Materials

### 2.1. Thermoplastic starch

Corn starches were purchased from Cerestar (30% amylose), Roquette (25–30% amylose; EURYLON 60, >51% amylose), Cameo (24–26% amylose). Wheat (26–28% amylose) and potato (22–23% amylose) starches were purchased from Cameo. Glycerol was supplied by Fluka, urea and formamide were supplied by Sigma-Aldrich.

Powder of natural materials, as received by the supplier, and plasticizer were premixed by hand at room temperature in order to homogenize the mixture and then subjected to temperature and shear stresses in a twin counter-rotating internal mixer (Rheomix 600, Haake, Germany) connected to a control unit for thermoplasticization. The mixing chamber (volume of 50 cm<sup>3</sup>) was filled with 50 g total mass for all experiments. During the mixing process the torque and the temperature of the melt were recorded with the aim of correlating the process parameters (temperature, speed

**Table 1**  
Starch sources and TPS compositions.

Materials	Source	Supplier	Amylose content (wt%)	Plasticizers (wt%)
Starch 1	Maize	Cerestar	25–30	–
Starch 2	Maize	Roquette	25–30	–
Starch 3	Maize	Roquette	>51	–
Starch 4	Wheat	Cameo	27–30	–
Starch 5	Maize	Cameo	25–30	–
Starch 6	Potato	Cameo	22–30	–
TPS 1	Maize	Cerestar	25–30	Glycerol (30)
TPS 2	Maize	Roquette	25–30	Glycerol (30)
TPS 3	Maize	Roquette	>51	Glycerol (30)
TPS 4	Wheat	Cameo	27–30	Glycerol (30)
TPS 5	Maize	Cameo	25–30	Glycerol (30)
TPS 6	Potato	Cameo	22–30	Glycerol (20)
TPS 7	Maize	Cerestar	25–30	Urea/formamide (30)
TPS 8	Maize	Roquette	>51	Urea/formamide (30)
TPS 9	Maize	Roquette	25–30	Urea/formamide (30)
TPS 10	Potato	Cameo	22–30	Urea/formamide (20)

of rotation, time of mixing) to the degree of thermoplasticization which affected the final structure of the TPS.

The optimal thermoplasticization conditions were 120 °C at 50 rpm for 4 min if the plasticizer was glycerol, 135 °C at 50 rpm for 4 min if the plasticizer was a urea/formamide (2:1) mixture. The ratio plasticizers/starches (w/w) was 30:70 for most of the samples except for potato starch based formulations which was 20:80 (Table 1).

## 3. Characterization

### 3.1. X-ray diffraction

X-ray diffraction analysis was performed at ambient temperature by a Philips diffractometer (model PW1710, Holland) with Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a voltage of 40 kV and 20 mA. The diffraction intensity data were collected automatically at scanning rate of 0.6°/min with a 0.01°/s steps. To study the effect of environmental humidity on recrystallization phenomena (retrogradation), the materials were stored at room temperature and 50% RH and analyzed after a storage time of 21 and 75 days (in a desiccators with saturated solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O salt).

### 3.2. FTIR spectroscopy

Infrared spectra, in ATR mode, of native starch powder and thermoplastic starch films were recorded by a Fourier Transform Infrared Spectrophotometer (Nexus, Thermo Nicolet, USA).

### 3.3. Mechanical test

Mechanical test were performed on samples prepared by compression molding. The TPS formulations prepared with the internal mixer were pressed at 20 MPa with a P300P (Collin, Germany) at 120 °C for 5 min. Mechanical tests were performed on films conditioned for 21 days at 50% RH and room temperature, by using an Instron Universal Testing Machine (model 4204, USA) according to the Standard UNI EN ISO 527-3.

### 3.4. Scanning electron microscope (SEM)

To investigate the effects of thermoplasticization on the morphological properties, native starch and liquid nitrogen fractured surfaces of TPS were analyzed with a scanning electron microscope, (Stereoscan 440, Leica, Cambridge). All the materials were vacuum coated with gold for SEM by Gold Sputtering Handscope SC500.

### 3.5. Measurements of extensional viscosity and haul off force

Measurements of elongational viscosity were performed by using a Rheometer ARES LS (Rheometric Scientific<sup>®</sup>) equipped with an extensional viscosity fixture (EVF, SER-HW-A01, XPansion Instruments, USA). The ARES-EVF design is based on the original Meissner model of the uniaxial elongation rheometer, built with rotary clamps.

To characterize the samples, measurements at different Hencky strain rates from  $10^{-4}$  to  $10^{-2} \text{ s}^{-1}$  were carried out; the testing temperature was 120 °C.

Haul off force was measured using a capillary rheometer (RH 7, Bohlin Instruments, UK) equipped with a melt strength apparatus. The barrel had a diameter of 15 mm while the capillary die diameter was of 2 mm. The polymer melt strand extruded from the capillary die was gripped between two counter-rotating wheels and the take-up speed increased with a constant acceleration. The haul off force (cN) was measured as a function of the draw ratio until the strand breaks.

The temperature of the rheometer was set at 125 °C. The polymer melt was extruded from the die at a piston speed of 25 mm/min and the take-up speed increased at a constant acceleration of  $4.5 \text{ m/min}^2$ .

## 4. Film blowing of TPS

Large amount of TPS pellets were prepared by using a counter-rotating intermeshing twin screw extruder (CTW 100, Haake, Germany). The mixtures of starch granules and plasticizer were manually fed into the extruder, having a screw length of 343 mm and a screw diameter (conical screws) of 32–25–21 mm. The screw speed was 100 rpm and the optimum temperature profile along the extruder barrel was at  $T$  (°C) = 70–110–120–120 °C when the plasticizer was glycerol, while the screw speed was 20 rpm and the temperature profile was at  $T$  (°C) = 70–110–130–130 when the plasticizer was a mixture of urea and formamide.

After the preparation described above the TPS pellets were fed in a film blowing system (E20T, Collin, Germany) having a screw diameter of 20 mm and L/D of 25; the optimal temperature profile of the four heating section of the extruder barrel was  $T$  (°C) = 100–110–120–120 and the temperature at the die was 120 °C.

## 5. Results and discussion

### 5.1. Plasticization

The thermoplasticization process of starch involves the complete and/or the partial destruction of the initial crystalline order. By applying mechanical shear stresses and heat in the presence of suitable plasticizers, the molecular chains gain mobility, favoured by the hydrogen bonding interactions with the plasticizer. The destructing process is usually accompanied by a variation of the rheological properties of the starch/plasticizer mixtures and it can be followed by monitoring the evolution of torque over time during the mixing in a Brabender chamber.

Fig. 1 reports the torque and temperature data during the thermo-mechanical destruction of three different starch/plasticizer systems: maize starch/glycerol (TPS 1), potato starch/glycerol (TPS 6) and maize starch/urea–formamide (TPS 7). It is worth to noting that the initial temperatures employed with glycerol were usually lower than with urea/formamide. In particular, it was not possible to process the starch powder below 135 °C in the presence of urea/formamide. As described in the material section (Section 2.1), the initial temperature of the mixing chamber was in this case equal to 135 °C. The melt temperature reported in Fig. 1 therefore in-

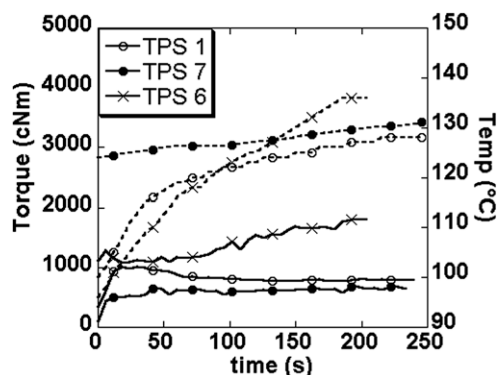


Fig. 1. Plasticization of thermoplastic starches. Torque (solid lines) and temperature (dashed lines) vs time.

creased over time and reached a final temperature that was few degrees above 130 °C. During this increase of temperature the viscosity increased in the first 10 s and then reached a constant value. In this case, the thermoplasticization occurred in the first stage and could be considered completed after the first 2 min.

When glycerol was used for the mixing experiments (TPS 1 and TPS 6), the temperature set for the mixing chamber was 120 °C, 15 °C lower than TPS 7. In this case, the temperature of the melt increased from 95 to 100 °C to values above the set  $T = 120$  °C. The fast increase of the temperature was due to the higher viscosity of the melt that resulted in higher viscous dissipation with generation of heat. The combination of higher shear stresses (higher viscosity and torque) and the increase of temperature led to a different behaviour of the torque during the mixing process. For example, in TPS 1 the values of the torque increased in the first 20 s (increase of viscosity due to thermoplasticization) and then decreased after a peak due to the increase of temperature (decrease of viscosity with  $T$ ). In the final stage, after the first 100 s, the torque reached almost a plateau. Here the slight increase of temperature is balanced by a slight increase in thermoplasticization. However, if the material is kept longer under mixing degradation phenomena occurred and the torque can increase again (data not reported here).

A different behaviour was observed in potato starch based TPS (TPS 6). In this case, the material displayed higher viscosity (higher torque) and this resulted in higher final temperatures which, at the end of the test reported in Fig. 1, was almost 140 °C. In this case, we did not observe a clear peak, as for TPS 1 and the torque increased continuously without reaching a plateau. Also in this case, longer mixing resulted in the degradation of the material.

### 5.2. X-ray analysis

X-ray diffraction is a powerful method to study the retrogradation effects on thermoplastic starch and to evaluate the difference in the hydrogen bond-forming abilities among plasticizers (Ma & Yu, 2004a). The A type structure is characteristic of a double helix in maize starch while a B type of crystallinity is present in potato starch (Myllärinen, Buleon, Lahtinen, & Forssell, 2002; van Soest, Hulleman, De Wit, & Vliegthart, 1996); the C crystallinity is an intermediate form probably due to the combination between A and B. There are also crystallinity forms induced by the thermoplasticization process called  $V_H$ ,  $V_A$ ,  $E_H$  that depend on the composition of starch, the plasticizer and the process parameters (Ma & Yu, 2004a).

Fig. 2 reports selected curves of X-ray diffraction patterns regarding native maize starch (supplier by Cerestar) and newly prepared TPS materials (TPS 1 and TPS 7). When urea and formam-

ide were used as plasticizer (TPS 7), the thermoplasticization process lead to substantially amorphous materials; the diffraction peaks, originally present in the starch granules disappeared and we did not observe the formation of new peaks which could indicate the presence of different crystalline structures induced by the thermoplasticization process. A different behaviour was observed in TPS prepared with glycerol (TPS 1). Here, the crystalline peak did not disappear. However, a new crystalline structure was developed ( $V_A$  and  $V_H$  crystalline type), as testified by the new peaks appearing in the X-ray diffractograms.

As reported in previous works (Lim, Chang, & Chung, 2001; Ma & Yu, 2004b, 2004c; Manzocco, Nicoli, & Labuza, 2002), the mixtures of urea/formamide can prevent the retrogradation phenomena of TPS. As shown in Fig. 3, where the X-ray patterns of TPS 7 stored at 50% RH for 21 and 75 days are compared to unaged materials, TPS 7 remained amorphous and no peaks developed during storage. These results are in agreement with the observations reported in the cited works where the ability of amide group to form more stable hydrogen bonds with starch than the hydroxyl group have been discussed.

### 5.3. FTIR spectroscopy

FTIR analysis is a powerful tool to analyze, in a qualitative way, the interactions between plasticizers and starch molecules. In Fig. 4, as an example, the spectrum of the sample TPS 1 is reported. The characteristics peaks of starch molecules and the possible interactions occurring with plasticizers through hydrogen bondings are described in Table 2. In particular, the peaks between 992 and 1200  $\text{cm}^{-1}$  associated with the interactions between molecules of starch and plasticizer, can be used to evaluate the thermoplasticization process with different type of plasticizers.

As reported in Table 3, a new peak appeared in all the TPS materials between 1015 and 1018  $\text{cm}^{-1}$  suggesting that new interactions and vibration modes are occurring after thermoplasticization. It is interesting to observe that the peak at

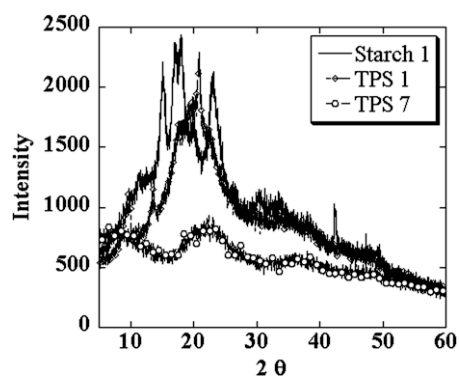


Fig. 2. X-ray patterns of native and thermoplastic starch.

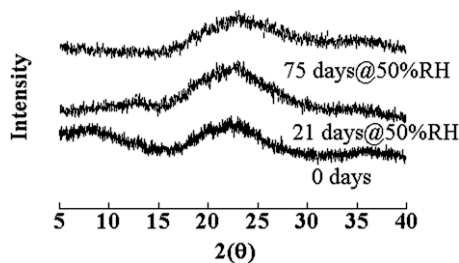


Fig. 3. X-ray patterns of urea/formamide-plasticized TPS (TPS 7) stored at 50% RH.

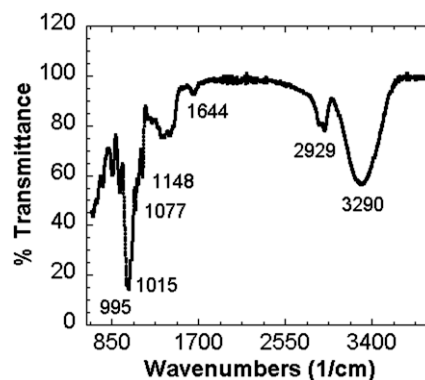


Fig. 4. The FTIR spectra of TPS 1.

Table 2

The wavenumbers and the corresponding groups of starch in the FTIR spectrum.

Wavenumbers ( $\text{cm}^{-1}$ )	Bonds	Groups of starch in the FTIR spectrum
3290	Str OH	Inter- and intra-molecular
2929	Str CH e CH <sub>2</sub>	Of the anhydroglucose ring that no takes part in the thermoplasticization
1644	H <sub>2</sub> O	In the starch and strictly bonded
1148–1077	Str CO of COH	OH group of starch takes part in the hydrogen bondformation
995–1018	Str CO of COC	Group inthe anhydroglucose ring

996  $\text{cm}^{-1}$  of native starch is reduced to 995  $\text{cm}^{-1}$  with glycerol (TPS 1) and to 993  $\text{cm}^{-1}$  with urea/formamide (TPS 7) suggesting that stronger interactions occurred with the latter system. In other systems (compare TPS 3 and TPS 8) other peaks (1016  $\text{cm}^{-1}$ , 1077  $\text{cm}^{-1}$ , 1149  $\text{cm}^{-1}$ ) were decreased with urea/formamide.

In conclusion, as already reported in previous works (Lim et al., 2001; Ma & Yu, 2004b, 2004c; Ma, Yu, & Feng, 2004; Manzocco et al., 2002) urea and formamide could form more stable hydrogen bonds with starch than glycerol.

### 5.4. Mechanical tests

The mechanical properties of the several TPS investigated are reported in Table 4. From these results it is evident that the presence of urea/formamide resulted in materials with higher elongation at break and lower Young's modulus compared to glycerol-plasticized TPS (compare TPS 1 and TPS 7, TPS 3 and TPS 8, TPS 2

Table 3

The wave numbers of starch and thermoplastic starches in the FTIR spectrum.

Materials	Source	Supplier	Plasticizers (wt%)	Wavenumbers ( $\text{cm}^{-1}$ )
Starch 1	Maize	Cerestar	–	996–1077–1150
TPS 1	Maize	Cerestar	G (30)	995–1015–1077–1148
TPS 7	Maize	Cerestar	U/F (30)	993–1015–1077–1148
Starch 2	Maize	Roquette	–	996–1077–1150
TPS 2	Maize	Roquette	G (30)	996–1018–1077–1150
TPS 9	Maize	Roquette	U/F (30)	996–1018–1077–1150
Starch 3	Maize	Roquette	–	993–1077–1149
TPS 3	Maize	Roquette	G (30)	996–1016–1077–1149
TPS 8	Maize	Roquette	U/F (30)	996–1015–1075–1147
Starch 4	Wheat	Cameo	–	996–1077–1149
TPS 4	Wheat	Cameo	G (30)	995–1015–1077–1150
Starch 5	Maize	Cameo	–	996–1077–1150
TPS 5	Maize	Cameo	G (30)	995–1018–1077–1149
Starch 6	Potato	Cameo	–	996–1077–1150
TPS 6	Potato	Cameo	G (20)	995–1018–1077–1146
TPS 10	Potato	Cameo	U/F (20)	996–1018–1077–1150



**Table 4**  
Mechanical properties of thermoplastic starches.

Materials	Source	Supplier	Plasticizers (wt%)	Deformation at break (mm/mm)	Stress at break (MPa)	Young's modulus (MPa)
TPS 1	Maize	Cerestar	G (30)	0.56 ± 0.19	2.93 ± 0.41	8.59 ± 0.53
TPS 2	Maize	Roquette	G (30)	0.68 ± 0.06	3.14 ± 0.17	9.62 ± 1.96
TPS 3	Maize	Roquette	G (30)	0.24 ± 0.032	2.04 ± 0.34	11.87 ± 3.02
TPS 4	Wheat	Cameo	G (30)	0.58 ± 0.23	1.86 ± 0.33	4.37 ± 0.78
TPS 5	Maize	Cameo	G (30)	0.68 ± 0.16	2.63 ± 0.15	6.57 ± 0.20
TPS 6	Potato	Cameo	G (20)	0.52 ± 0.16	5.42 ± 0.35	58.76 ± 7.7
TPS 7	Maize	Cerestar	U/F (30)	2.12 ± 0.39	0.77 ± 0.09	0.81 ± 0.23
TPS 8	Maize	Roquette	U/F (30)	0.97 ± 0.16	2.02 ± 0.32	9.94 ± 3.06
TPS 9	Maize	Roquette	U/F (30)	1.7 ± 0.28	0.82 ± 0.094	1.03 ± 0.32
TPS 10	Potato	Cameo	U/F (20)	0.52 ± 0.16	3.42 ± 0.35	25.76 ± 7.7

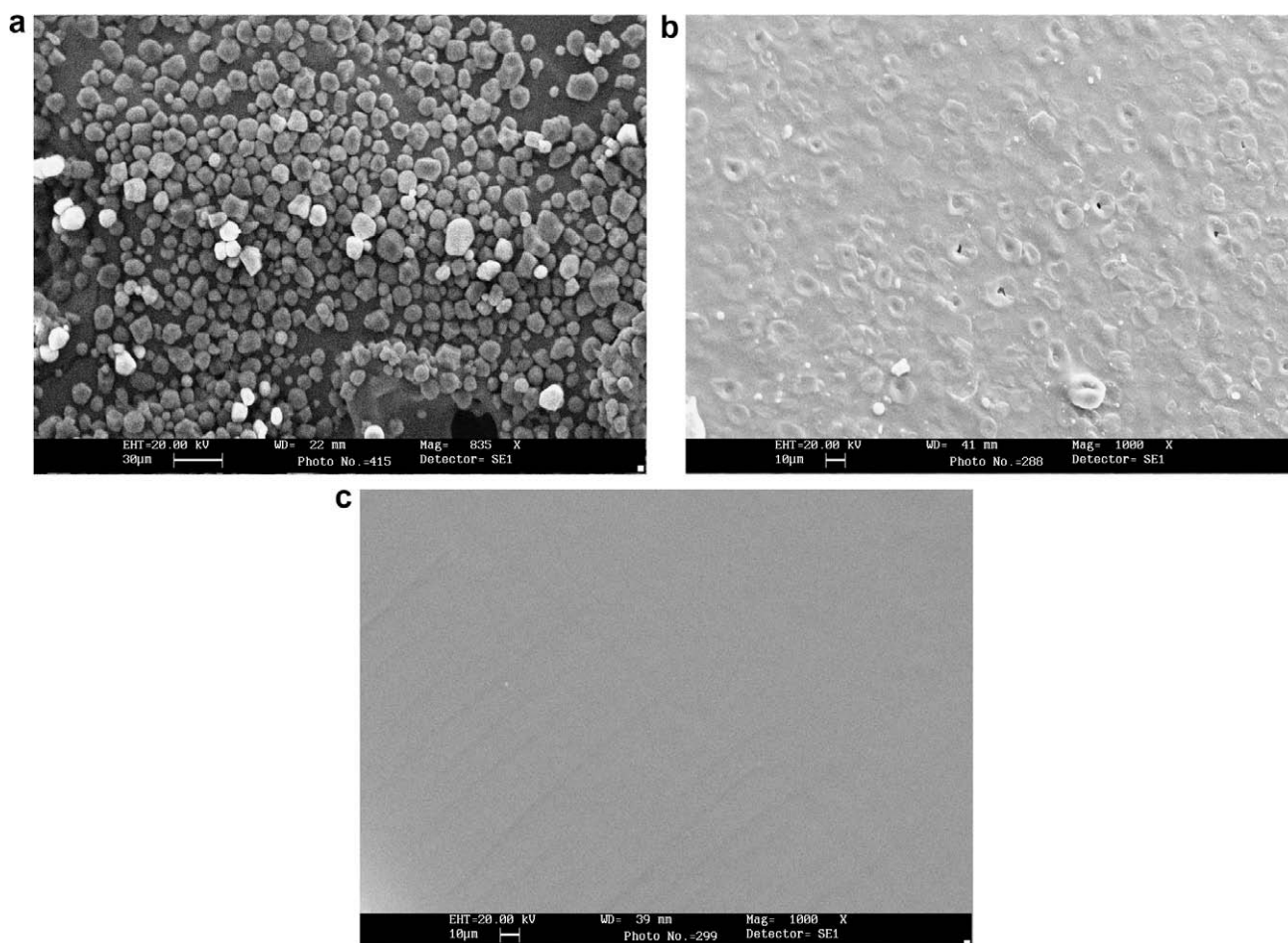
and TPS 9, TPS 6 and TPS 10). Among the maize based TPS containing urea/formamide, the highest modulus and stress at break were obtained with high-amylose starch (TPS 8). The potato thermoplastic starch (TPS 6 and TPS 10) showed the highest modulus and stress at break.

#### 5.5. Scanning electron microscope (SEM)

The SEM morphologies of native starch, glycerol and urea/formamide based TPS are compared in Fig. 5. The fracture surface of most of the TPS prepared showed a residual granular structure. However, a qualitative analysis of the micrographs revealed that samples containing urea/formamide showed a smoother surfaces which, again, can be related to a better destructure, as already confirmed by the X-ray analysis.

#### 5.6. Extensional rheology and haul off force

In many industrial processes such as film blowing and melt spinning, the molten polymer is subject to elongation. The importance of the study of the elongational properties for the processing of the materials has been widely investigated in the literature, particularly for polyethylenes (André, Demay, & Agassant, 1997; Hong, Ahn, & Lee, 2004; Kobayashi, Takahashi, Takimoto, & Koyama, 1996; La Mantia & Acierno, 1985; Laun, 2004; Micic, Bhattacharya, & Field, 1998; Spital & Macosko, 2004; Wong & Cheung, 1997). Several studies were undertaken to correlate rheological properties and molecular structure of the materials (Münstedt, Kurzbeck, & Egersdörfer, 1998) and to correlate elongational flow and film blowing process (Münstedt, Steffl, & Malmberg, 2005). It is well recognized that bubble stability, biaxial stretching, and thickness



**Fig. 5.** SEM micrographs of granule starch (a), glycerol-based TPS (TPS 3) (b) and urea/formamide based TPS (TPS 8) (c).

uniformity are very sensitive to extensional viscosity, which is strongly dependent on the average molecular weight, the molecular weight distribution and type and degree of branching (Gabriel, Kaschta, & Münstedt, 1998).

The elongational viscosity curves for several TPS films are reported in Fig. 6 at different constant strain rate  $\dot{\epsilon}_0$ . The rheological experiments were performed from  $10^{-4}$  to  $10^{-2} \text{ s}^{-1}$  since at higher strain rates an early fracture of the samples occurred. The temperature test ( $T = 120 \text{ }^\circ\text{C}$ ) was chosen to simulate the conditions employed in the film blowing process. For all materials investigated and at all applied elongational rates, the elongational viscosity defined as:

$$\mu(t) = \sigma(t) / \dot{\epsilon}_0$$

increases with time. In particular, this increasing is slight in the so-called “linear” region and became more rapid in the “strain-hardening” region of deformation.

From these results it appears that the materials showed a strain-hardening behaviour only for specific elongational rates. Similarly to what observed in most of the synthetic polymers employed for films blowing, a variation of the slope of the elongational viscosities vs time curves occurred only above a specific Hencky strain rate. However, it is worth to mention that the presence of the strain-hardening behaviour was generally observed in the urea-formamide-plasticized TPS while it was not observed in the glycerol-based TPS formulations.

For the sake of clarity, the rheological properties of several urea/formamide based TPS are compared with glycerol-plasticized TPS, all measured at the same strain rate (Fig. 7). At the strain rate of  $0.001 \text{ s}^{-1}$  the high-amylose TPS (TPS 8) displayed the highest elongational viscosity, even higher than the potato starch TPS (TPS 10) which contains 20% of urea/formamide instead of 30% as in TPS 8. This is a clear indication that at this strain rate, the strain hardening in TPS 8 is more pronounced than in TPS 10, therefore TPS 8 requires higher forces to be elongated. It is worth to note that, when

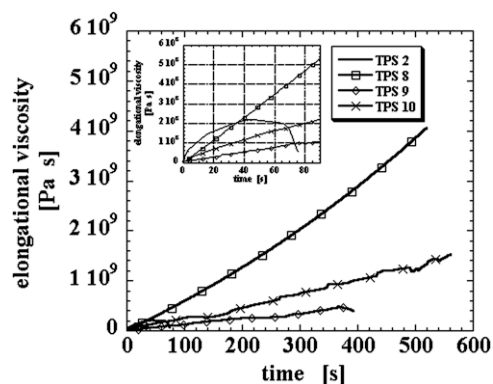


Fig. 7. Elongational viscosity of thermoplastic starches at  $0.001 \text{ s}^{-1}$ .

using the same type of starch source (compare TPS 2 and TPS 9 in Fig. 7), the maximum deformation achieved with glycerol is much lower and the sample fractured much earlier (at about 60 s) than for urea/formamide based materials.

Another way to evaluate the elongational properties, and in particular the deformability of the TPS melts, is to study the melt spinning of fibers. The melt strength analysis were used to evaluate the melt behaviour of the TPS (TPS 8 and TPS 2 are reported in Fig. 8). The high-amylose thermoplastic starch (TPS 8) showed a higher elongation and melt strength (40 cN and break at 3.5 draw ratio) respect to glycerol-plasticized TPS (TPS 2) (19 cN and break at 2.3 draw ratio). TPS 9 and TPS 10 were also tested but draw-resonance effects occurred.

5.7. Film blowing

Film blowing is a technique which consists of the extrusion of the polymer through a small annular slit die, usually vertically, to form a thin walled tube. Air is introduced via a hole in the centre

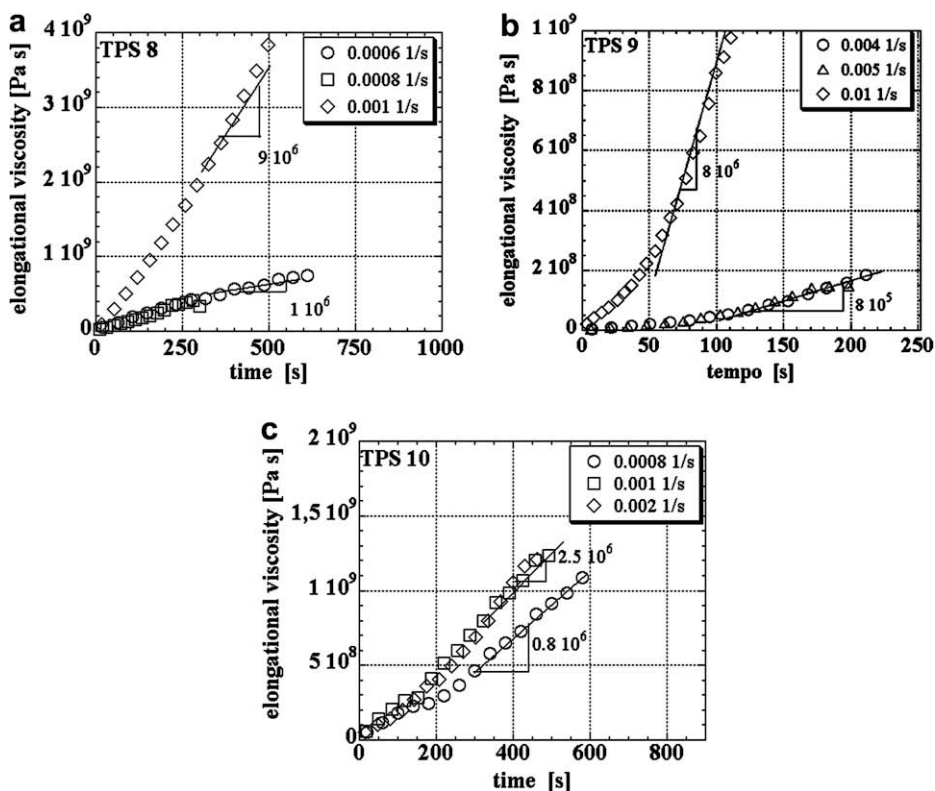


Fig. 6. Elongational viscosity of urea/formamide thermoplastic starches: (a) TPS 8, (b) TPS 9 and (c) TPS 10.

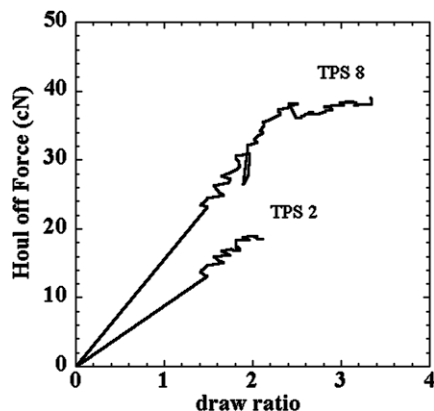


Fig. 8. Haul off force as a function of draw ratio for urea/formamide based TPS (TPS 8) and glycerol-based TPS (TPS 2).

of the die to blow up the tube like a balloon. On the top of the die an air flow is cooling the bubble. During the process the bubble cools, solidifies and can be collected by the two nip rolls (McKelvey, 1962). During the film blowing process, the molten polymer is subject to longitudinal and transverse elongational, then the molecules are stretched in both directions. These elongational effects act on the melt polymer in a region where the material can be easily deformed; above the “frost line” defined as the area above the material is in a solid state, it does not suffer any more deformation but is only transported by rolls.

In the area between the extrusion head and the frost line, the size of the bubble increases, the speed of the film vary from the extrusion ( $V_e$ ) to elongation ( $V_s$ ), the radius of the tube passes by anular die ( $R_0$ ) to the film ( $R_f$ ). We define two parameters which allow to quantify the orientation of the material in two directions:

The draw ratio:

$$DR = \frac{V_s}{V_e}$$

the ratio of bubble:

$$BUR = \frac{R_f}{R_0}$$

The two ratios determine the deformation of the molten polymer and thus the orientation of the macromolecules and then the properties of the film in the machine and transverse directions.

Several studies have been made on starch–polymer mixtures in which the starch can be used both as filler and as a thermoplastic material. Otey, Westhoff, and Doane (1987) reported on the film blowing in a pilot implant of a starch–poly (ethylene-co-acrylic acid) (EAA) mixture by adding urea and polyols as plasticizers. The addition of urea improved the starch gelatinization at low water levels and allowed direct and continuous extrusion. Uniform films were obtained from standard maize starch, high-amylose maize starch and modified maize starch using different quantities of water as plasticizer (Meadows, 1998).

The mechanical and structural properties as well as the rheological properties of the TPS reported so far suggested that the most

promising materials for film blowing were those containing urea/formamide as plasticizers. Four compositions were therefore selected (see Table 5) to correlate the film blowability to the starch structure (TPS 8 and TPS 9), starch source (potato starch in TPS 10) and finally to the type of plasticizer (glycerol in TPS 2). Starches and plasticizers were first extruded to produce a solid materials; the extrudate was then pelletized and fed in the film blowing line; the barrel temperature profile was 100, 110, 120, 120 °C and the die was 120 °C. A picture of a typical bubble during the film blowing process of TPS 8 is shown in Fig. 9.

All the thermoplastic starch materials were suitable to be blown. However, the film blowing process of high-amylose TPS thermoplasticized with urea/formamide mixture (TPS 8) was the most continuous, the bubble was stable and the minimum thickness of the film achieved was 50 μm. The surface of the film was smooth and the thickness was constant along the bubble. Moreover, the surface of the bubble prepared with this material was not sticky and the double-walled film obtained after the passage through the calendering nip was easily separated. Other general advantages resulting from the use of urea/formamide were the absence of plasticizer migration and absence of foaming during film blowing.

## 6. Conclusions

The material compositions and the technological procedures to prepare biodegradable thermoplastic starch films with the film blowing technology were studied. The activities were focused on



Fig. 9. Film blowing of urea/formamide thermoplastic starch (TPS 8).

Table 5

Processing parameters, final thickness and result of film blowing process of TPS.

TPS	Source	Supplier	Plasticizers (wt%)	Temperature profile zones 1/2/3/4/head (°C)	Minimum thickness (μm)	Notes
TPS 8	Maize	Roquette	U/F (30)	100–110–120–120–120	50	Excellent
TPS 9	Maize	Roquette	U/F (30)	100–110–120–120–120	70	Very good
TPS 10	Potato	Cameo	U/F (20)	100–110–120–120–120	150	Good
TPS 2	Maize	Roquette	G (30)	100–110–120–120–120	90	Not good

the analysis of the effects of starch source, type and content of plasticizers on the physical–chemical and mechanical properties. Moreover, in order to develop a film blowing technology, material composition as well as processing condition were optimized by taking into account the extensional rheological properties of the materials.

A variety of thermoplastic starch materials were prepared and characterized in order to evaluate the correlation between material composition, thermoplasticization conditions and extensional rheology. Better starch destructure and reduced retrogradation were obtained by using urea/formamide mixtures as plasticizer.

The best material suitable for the film blowing process was a composition based on high-amylose starch thermoplasticized with 30% of urea/formamide. This material showed good elongation viscosity, high deformability of the melt and strain-hardening behaviour. Bubbles prepared with this formulation were not sticky and they could be separated after the calendaring. Moreover, no migration of plasticizers and foaming were observed.

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