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Short communication

Aminoacids as non-traditional plasticizers of maltodextrins fast-dissolving films

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ABSTRACT

This study explored the effect of aminoacids as non-traditional plasticizers of maltodextrins fast dissolving films. 5% w/w glycine and proline decreased the glass transition temperature (T_g) of maltodextrins from 102.6 ± 2.0 °C to 73.1 ± 1.4 °C and 76.1 ± 0.7 °C, respectively; meanwhile the binary mixture made with lysine had a T_g value of 83.6 ± 2.2 °C. At the same time, all aminoacids increased the ΔC_p values. The shift of the thermal data were due to profound effect on the hydrogen bonding as evidenced by ATR-FTIR spectra since the OH stretching and scissoring bands decreased of about 15–26 cm^{-1}. A linear relationship was found (R^2 = 0.9334) between HOH scissoring wavenumbers and T_g values. The addition of glycine and proline resulted effective in reducing the elastic modulus (about 50%) and tensile strength (about three times) and, therefore, can be used to increase the film ductility.

1. Introduction

Maltodextrins (MDX) are the products of the controlled hydrolysis of starch, and are mixtures of α(1→4) linked glucose oligo- and polysaccharides with occasional α(1→6) branches (Chronakis, 1998). The degree of hydrolysis of the MDX is indicated by the dextrose equivalence (DE) value (Chronakis, 1998), which denotes the percentage fraction of reducing sugars in the sample (DE value of non-hydrolyzed starch is below 1, DE 100 is equivalent to glucose). The DE value, therefore, reflects the number-average molecular weight of the carbohydrate.

A barrier to the development of MDX based films is the brittle nature of the blends. Overcoming this issue can be accomplished with the addition of plasticizers. As plasticizers typically reflect the polarity of the polymers with which they are blended (Sears & Darby, 1982), common plasticizers for MDX include water, glycerol and propylene glycol (Cilurzo, Cupone, Minghetti, Selmin, & Montanari, 2008). A complex behavior was described as a function of the water content since the antiplasticizing and plasticizing behavior of diluents in a glassy carbohydrate depend in a sensitive manner on a balance between the molecular size and the interactions of the diluent molecules with the carbohydrate chains (Roussenova, Murith, Alam, & Ubbink, 2010). At high water content, water is a very effective plasticizer of MDX, but it evaporates easily, leaving an extremely brittle, glassy material. Glycerol, being much less volatile than water, is generally exploited to obtain workable blends which were suitable to produce fast-dissolving films loaded by different drugs (Cilurzo et al., 2010, 2011). It was evident that certain ingredients themselves can act as plasticizer. For example, nicotine or taste-masking agents affected tensile properties compromising the film integrity during the packaging procedures. A class of compounds yet to be investigated for its ability to plasticize MDX is amino acids. It was reported that proline is an exceptionally good plasticizer of standard blends of starch–glycerol (Stein & Green, 1996).

In this study, we report the effect of glycine, proline and lysine on the mechanical properties of MDX films obtained by casting. The transitions occurring during the heating of glassy carbohydrates plasticized with different amino acids were monitored by DSC in conjunction with ATR-FTIR spectroscopy in an attempt to study the molecular origin/fingerprint of the main thermodynamic transitions.

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Table 1
Composition, thickness and residual water content of MDX films amino acids as plasticizer.

Formulation code	Composition (%, w/w)						Thickness (μm)	Moisture content (%)
	MDX	GLY	SO	K	P	G		
F100	79.0	18.1	2.9	–	–	–	92.4 ± 12.8	6.47
FK95/5	74.9	17.1	3.0	5.0	–	–	90.8 ± 3.1	6.45
FP95/5	74.9	17.1	3.0	–	5.0	–	124.2 ± 3.6	7.79
FG95/5	74.9	17.1	3.0	–	–	5.0	67.4 ± 6.7	7.35

2. Materials and methods

2.1. Materials

Maltodextrin having a DE equal to 6 (Glucidex® IT6, MDX) was obtained from Roquette Frères (Lestrem, F). Lysine (K), proline (P) and glycine (G) were purchased from A.C.E.F. (I). Sorbitan monooleate (Span® 80, SO) was gifted by Uniqema (UK) and glycerol (GLY) was obtained by Carlo Erba Reagenti (I).

2.2. Preparation of binary blends

Feeds at the concentration of 5% were prepared by dissolving MDX and amino acid in the ratio 95:5% w/w in distilled water. The solutions was spray-dried by a 4M8 spray-dryer (ProCepT, B) using the following experimental condition: standard nozzle inner diameter: 0.6 mm; air speed: 0.30 m^3/min; air in temperature: 130 °C; dosing speed: 7 mL/min.

2.3. Characterization of binary blends

2.3.1. DSC

Samples accurately weighted, were sealed in pin holed aluminum pans and subject to two cooling and heating cycles from 25 to 150 °C at the cooling and heating rate of 5 K/min in a DSC 1 Stare System (Mettler Toledo, CH). Glass transition temperature (T_g) was measured on the second heating ramp.

2.3.2. TGA analysis

The residual water content was determined by thermogravimetric analyses using a TGA 2050 thermogravimetrical analyzer (TA Instruments, USA). Samples of approximately 20 mg were heated in a platinum crucible at 1 K/min under a nitrogen atmosphere and the loss of weight was recorded.

2.3.3. ATR-FTIR spectroscopy

The ATR-FTIR spectra of the sample dried were collected using a PerkinElmer Spectrum™ One spectrometer equipped with an Attenuated Total Reflectance (ATR) accessory with a resolution of 4 cm^{-1} and 32 scans in the range 4000–650 cm^{-1}.

2.4. Film preparation

MDX was dissolved in water at 80 °C, stirred for 1 h and cooled down to 40 °C. Finally, GLY, SO and amino acids were dissolved according to the composition reported in Table 1. After a rest period of at least 24 h, the dispersion was cast over a silicone release liner by a laboratory-coating unit Mathis LTE-S(M) (CH). Operative conditions: coating rate 1 m/min; drying temperature 60 °C; drying time between 15 and 20 min; air circulation speed 1800 rpm. These conditions were set to obtain films having a thickness of about 100 μm.

Films were packed in individual airtight seal packs immediately after preparation and stored at 25 ± 1 °C until use.

2.5. Film thickness

Film thickness in five different positions was measured by using a MI 1000 μm (ChemInstruments, USA). Before samples cutting, film was placed between the anvil and the presser foot of the micrometer.

2.6. Water content

The water content in 3 cm × 2 cm film sample was determined by Karl–Fischer-Titration in a V20 Volumetric KF titrator (Mettler Toledo, CH).

2.7. Tensile properties

Tensile testing was conducted according to ASTM International Test Method for Thin Plastic Sheeting (D 882-02) using an Instron 5965 texture analyzer (Instron, UK), equipped with a 50 N load cell. The film was cut into 80 mm × 15 mm strips and equilibrated at 25 ± 1 °C for 1 week.

Each test strip was longitudinal by placed in the tensile grips on the texture analyzer. Initial grip separation was 40 mm and crosshead speed was 12.5 mm/min. The test was considered concluded at the film break. The following parameters were determined.

Tensile strength (TS) was calculated by dividing the maximum load by the original cross-sectional area of the specimen.

Percent elongation at break (E%) was calculated according to the following equation:

$$E\% = \frac{L - L_0}{L_0} \times 100$$

where L_0 is the initial gage length of the specimen and L is the length at the moment of rupture.

Elastic modulus or Young's modulus (Y) was calculated as the slope of the linear portion of the stress–strain curve.

Tensile energy to break (TBE) was defined by the area under the stress–strain curve.

3. Results and discussion

3.1. Characterization of binary mixture

The residual water content in all binary mixtures was approximately 7%, which is acceptable for this class of materials.

DSC data of MDX revealed a glass transition temperature (T_g) at 102.6 ± 2.0 °C. After blending MDX with amino acids, a single T_g value at lower temperature was detected (Table 2). In particular, glycine and proline caused a drop in T_g to 73.1 ± 1.4 °C and 76.1 ± 0.7 °C, respectively; meanwhile binary mixture made with lysine had a T_g value of 83.6 ± 2.2 °C. ΔC_p at the glass transition was also considered since this parameter can be interpreted as a degree of organization in the glass (Gibbs & Di Marzio, 1958) and it accounts for the 'quality' of the hydrogen bonds between the molecules forming this glass. Generally speaking, ΔC_p decreases when strong crosslinkages, or intermolecular hydrogen bonds, or