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The effect of glycerol/sugar/water and sugar/water mixtures on the plasticization of thermoplastic cassava starch

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Abstract

The use of 2 wt% sugars as co-plasticizer in combination with glycerol was investigated for thermoplastic starch (TPS) from cassava. The results were compared to those for whole cassava root TPS, which naturally contains sugars in the same proportion. The main objective was to investigate the influence of natural sugars present in the cassava root on the properties of thermoplastic starch produced with cassava root. TPS produced with sugar and water without the addition of glycerol was also investigated. The materials were prepared by melt-processing cassava starch or ground and dried cassava root in a high-power batch mixer, Haake Rheomix 600, at 120 °C. The samples were tested by X-ray diffraction (XRD), dynamic mechanical thermal analysis (DMTA), scanning electron microscopy (SEM) and water absorption experiments. The results showed that the addition of 2 wt% sugars (glucose, fructose and sucrose) to the starch-glycerol systems causes a reduction in the glass transition temperature (Tg) of the TPS accompanied by a reduction in the storage modulus determined by DMTA and inhibits the formation of V_H-type crystal structures in the resulting TPS. The use of only sugar and water as plasticizers in the TPS causes a considerable reduction (∼60%) in the subsequent water uptake.

Keywords: Thermoplastic cassava starch; Plasticizers; Sugars; Dynamical mechanical thermal analysis (DMTA)

1. Introduction

Thermoplastic starch (TPS) for applications in biodegradable plastics has recently been the object of research in our laboratory (Carvalho, Job, Alves, Curvelo, & Gandini, 2003a; Carvalho, Zambon, Curvelo, & Gandini, 2005; Carvalho, Zambon, Curvelo, & Gandini, 2003b; Da Roz, Carvalho, Gandini, & Curvelo, 2006; Teixeira, Da Róz, Carvalho, & Curvelo, 2005) and others (Avérous, 2004; Bastiole, 1998; Follain, Joly, Dole, Roge, & Mathlouthi, 2006; Mathew & Dufresne, 2002; Shogren, Fanta, & Doane, 1993; Vilpoux & Averous, 2004) in response to the growing need for biodegradable materials. Among materials of this kind, those obtained from renewable resources are of special interest. TPS is considered one of the most attractive materials for short-life products owing to its low cost and because it is a biodegradable material obtained from renewable resources. Additionally, it can be produced by traditional processing techniques commonly used in the plastics industry. TPS is produced by the plasticization of native starch (Carvalho et al., 2003a; Forssel, Mikkilä, Moates, & Parker, 1997; Röper & Koch, 1990) in the presence of hydroxyl-rich plasticizers such as glycerol. The chemical nature of plasticizers and the amount used play an important part in TPS performance and several compounds have been investigated for this purpose, including water and polyols (Da Roz et al., 2006; Mathew & Dufresne, 2002). Other compounds such as formamide and urea (Ma, Yu, & Feng, 2004) and citric acid (Park, Chough, Yun, & Yoon, 2005) have also been used for starch plasticization.

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In a previous study (Teixeira et al., 2005) we reported that the natural sugars present in cassava (about 2 wt%) had an important influence on the mechanical properties of the TPS obtained directly from the root. It was observed that in these materials, increasing the amount of plasticizer, glycerol in that study, led to a reduction in the elongation at rupture while in general a rise in plasticizer content increases the elongation at break. This question remains incompletely understood for TPS and further investigation will be necessary to gain a better understanding of plasticization of starch.

In this paper we describe the influence of plasticizers such as glucose, fructose and sucrose on cassava starch TPS, in comparison with TPS prepared directly from the cassava root. The thermal and mechanical properties were measured by DMTA, the amount and types of crystallization by X-ray diffraction and fracture surface morphology by scanning electron microscopy.

2. Experimental

2.1. Materials

Cassava starch and cassava root, containing about 18% amylose, were kindly supplied by Corn Products Brazil. The cassava starch was used as received and the cassava root was milled and dried at 100 °C for 5 h. Both materials contained about 10% humidity and the dried root had approximately 2% of soluble sugars while the purified starch was free of sugars. Reagent grade glycerol (Synth) was used as plasticizer. The sugars employed were glucose (Synth), fructose and sucrose (Merck). The compositions of the mixtures are presented in Table 1.

2.2. Thermoplastic starch

For the preparation of TPS, the cassava starch and the milled and dried cassava root were mixed with glycerol, water and/or sugar in polyethylene bags (see Table 1 for compositions) until a homogeneous material was obtained for processing. Stearic acid (0.5 wt%) was added as processing agent to each mixture. The mixtures were processed at 120 °C in a Haake Rheomix 600 batch mixer equipped with roller rotors rotating at 60 rpm. The mixing time was fixed at 6 min. The processed samples were hot pressed at 120 °C into 1 and 2 mm thick plates.

2.3. Scanning electron microscopy (SEM)

A Leo Scanning Electron Microscope was used to examine the morphology of fractured surfaces, prepared in liquid nitrogen.

2.4. X-ray diffraction (XRD)

Diffractograms were recorded in a Rigaku diffractometer. Scattered radiation was detected in the range $2\theta = 3$–40°, at a speed of 2°/min. The extent of crystallinity was estimated after equilibrating the samples (20 days) at 53% relative air humidity (RH) and 25 ± 2 °C, by the height ratio of the diffraction peak (B-type at 16.8° and V_H-type at 19.6° and the baseline of the diffractogram, as proposed by Hulleman (Hulleman, Kabisvaart, Jabssen, Feil, & Vliegenthart, 1999). After 90 days of conditioning (aging at 53% RH and 25 ± 2 °C), the diffractograms were recorded again.

2.5. Water uptake

Water absorption experiments were conducted on circular specimens, 8 mm in diameter, cut from the hot pressed plates of TPS, which were 2 mm thick. Prior to the water absorption measurements, the samples were dried at 70 °C to constant weight. The samples were then conditioned in hermetic containers at 25 ± 2 °C with a 53% RH atmosphere in equilibrium with a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$, as stipulated in ASTM E 104. The water uptake at equilibrium (%) was computed from the gain in weight.

2.6. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were performed in a DMA 2980 TA Instrument, working in tension mode at 1 Hz with a pre-load of 0.01 N (maximum deformation of 0.025, corresponding to amplitudes in the range of 16 μm). The temperature was raised from −110 to 110 °C, and measurements carried out in steps of 5 °C per mim. The samples (35 × 5 × 1 mm) were cut from the 1 mm hot-

Table 1
Identification and composition of cassava TPS samples

Sample	Starch (%)	Glycerol (%)	Water (%)	Glucose (%)	Fructose (%)	Sucrose (%)
TPSG30	50	30	20	–	–	–
TPSG30-glu	50	30	18	2.00	–	–
TPSG30-fru	50	30	18	–	2.00	–
TPSG30-suc	50	30	18	–	–	2.00
TPSG30-sugar	50	30	18	0.67	0.67	0.67
TPSG0-sugar	50	–	25	8.30	8.30	8.30
TPSG30-root	50	30	20	–	–	–

pressed molded plates. The analyses were performed after equilibrating the samples (20 days, 25 ± 2 °C) at 53% RH.

3. Results and discussion

3.1. Morphological characterization

Micrographs of the fragile fracture surface obtained by SEM (see Fig. 1) show a homogeneous surface, indicating that the starch granules were completely disrupted. In some samples a surface roughness was seen which could be an indication of a semicrystalline material. In the TPS obtained directly from the root (TPSG30-root) the surface was more irregular, probably due to the presence of other materials such as fibers. Fig. 1f shows a very smooth surface because this sample is predominantly amorphous, in contrast to the others which show higher crystallinity (see Table 2).

3.2. X-ray diffraction analysis and water uptake

X-ray diffractograms of samples conditioned at 25 °C and 53% RH for 20 days and after additional aging up to 90 days in the same conditions are shown in Fig. 2. The characteristic peaks of starch crystallization or complexation due to V_H-type (2θ equal 19.6°) and B-type (2θ equal 16.8°) structures (van Soest & Essers, 1997; van Soest & Vliegenthart, 1997) are labeled on the figure. The crystallinity indices calculated for each sample are shown in Table 2. From these data it can be concluded that, after 20 days, the presence of sugar in TPS containing glycerol causes a small

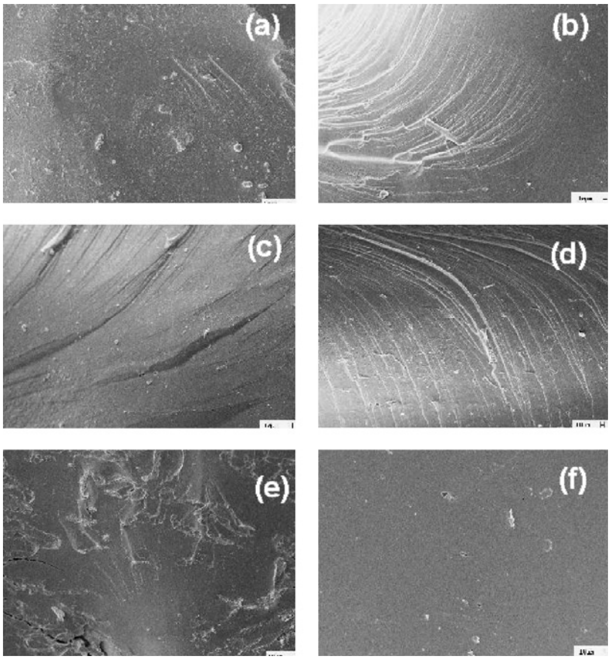

Fig. 1. SEM images of the samples: (a) TPSG30, (b) TPSG30-glu, (c) TPSG30-fru, (d) TPSG30-suc, (e) TPSG30-root and (f) TPSG0-sugar.

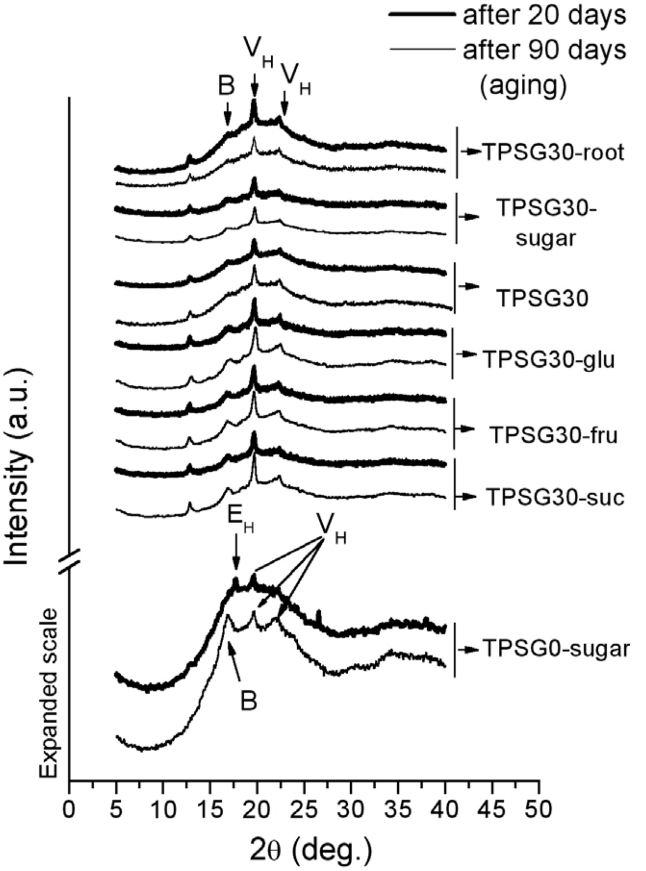

Fig. 2. X-ray diffraction patterns of the samples at equilibrium water-saturated environment (20 days) and after aging for 90 days (25 °C).

Table 2
Quantitative characterization of crystallinity and water uptake in equilibrium (after 20 day) of the plasticized TPS

Sample	$X_{c(\text{B-type})}$ ($2\theta = 16.8°$)		$X_{c(\text{V}_{\text{H-type}})}$ ($2\theta = 19.6°$)		Water*
	After 20 days	After 90 days	After 20 days	After 90 days	(%)
TPSG30	0.1	0.1	0.4	0.4	10.1 ± 0.3
TPSG30-glu	0.1	0.1	0.3	0.3	11.8 ± 0.2
TPSG30-fru	0.1	0.1	0.3	0.3	11.9 ± 0.1
TPSG30-suc	0.1	0.1	0.3	0.3	17.5 ± 0.3
TPSG0-sugar	n.d.	0.1	0.06	0.1	4.0 ± 0.5
TPSG30-sugar	0.1	0.1	0.3	0.3	10.3 ± 0.2
TPSG30-root	0.1	0.1	0.3	0.3	10.6 ± 0.2

n.d., not detected.
* Water absorption equilibrium was observed after 20 days.

decrease in V_H-type crystallinity, but no effect was observed on B-type crystallinity. This may be related to the mechanism of crystal formation. While the structures is B-type formed mainly from the short outer chains of amylopectin forming double helices with water inclusion, the V-type is a complex of single helices of amylose around lipids or other molecules such as glycerol (van Soest & Essers, 1997; van Soest & Vliegenthart, 1997). The sugar could hinder the complexation of glycerol and amylose. In TPSG0-sugar, the absence of any glycerol to be included in the amylose complexes will result in the lower V_H-type crystallinity.

After aging for 90 days, no structural changes were observed in TPS containing glycerol or glycerol and sugar were verified. Only in TPSG0-sugar the formation of E_H-type crystal (2θ equal 17.8°) was observed and, being unstable, it was converted to V_H-type (see Fig. 2) after aging by 90 days. This sample also showed the B-type structure, which was absent until 20 days of aging (Table 2).

Water uptake decreases by about 60% when no glycerol is used and increases when sucrose is used as plasticizer in addition to glycerol. In the other samples, the changes are very slight. This result shows that, except for sucrose, the sugars can be used as plasticize for starch in TPS compositions, without increasing their water uptake. The particular behavior observed for sucrose can be attributed to the fact that sucrose has a higher number of OH groups than the other sugars and so, is more hydrophilic. The lower water uptake and lower crystallinity of glycerol-free TPS (TPSG0-sugar) can be explained by the lower efficiency of sugars as plasticizers. In fact, glycerol is much more effective for this purpose, and its absence decreases dramatically the starch chain mobility, reducing the water uptake and also the molecular motion that could favor crystallization. The reason for the lower water uptake by this sample is the same as for the low crystallization. However, it is important to note that, once the TPS has crystallized, water uptake should also decrease, due to the less hydrophilic character of the crystalline regions.

3.3. Dynamic mechanical thermal analysis

The variation of the logarithm of storage modulus (E') and loss factor ($\tan\delta$) with temperature is shown in Fig. 3. The results are in good agreement with previous reported results (Avérous & Boquillon, 2004; Forssel et al., 1997). The starch plasticized with glycerol behaves as a partially miscible system with two main transitions. The first, around −55 °C, is attributed to the relaxation of the phase rich in glycerol. The second, in the 0–35 °C range, corresponds to the relaxation of plasticized starch.

It can be observed that the drop in the storage modulus with rising temperature is more pronounced for TPSG30-glu, TPSG30-fru and TPSG30-suc. This is a consequence of the lower degree of crystallinity of these materials compared to TPSG30. The absence of glycerol from the TPSG0-sugar sample makes it more rigid, resulting in a higher value for the modulus than for that of the glycerol-containing TPS. The lower chain mobility due to the absence of glycerol overcomes the effect of the more abundant crystallites in the other samples that contain glycerol as the main plasticizer. There are two opposite effects which influence the modulus, the presence of crystallites and the plasticization effect. For TPSG0-sugar, the absence of glycerol as plasticizer is the dominant effect. The values for the storage modulus in the vitreous region at ~−50 °C, and the rubbery region at ~25 °C, as well as at the glass transition temperature (Tg), are indicated in Table 3. For TPSG30-fru, a subtle transition is seen around −22 °C, which we attributed to the phase rich in hydrated fructose (Jansson, Bergman, & Swenson, 2005). It can be seen that a small addition of any of the sugars (2 wt%), combined with glycerol, reduces significantly the Tg of plasticized starch.

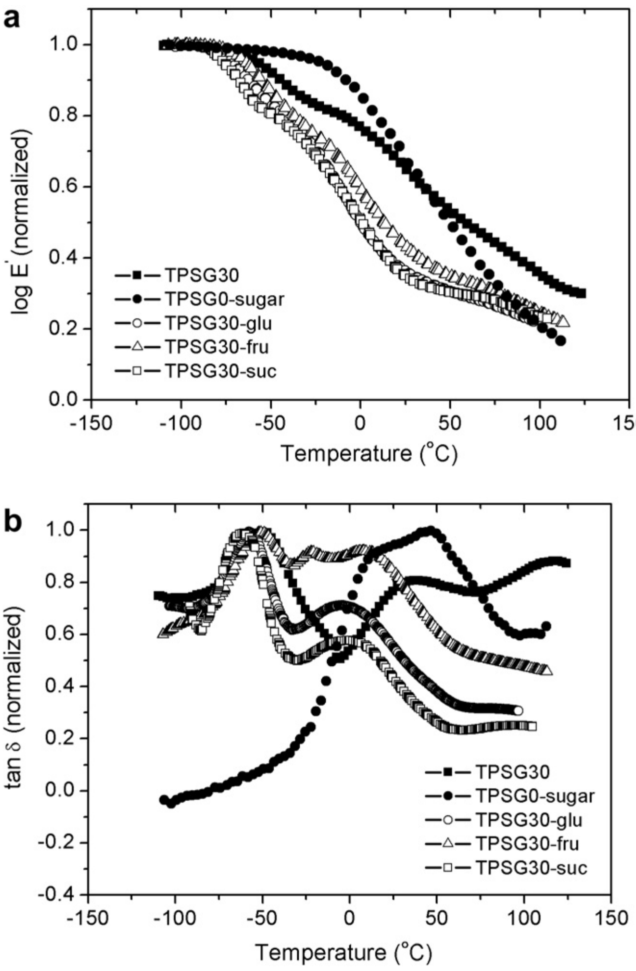

Fig. 3. (a) Logarithm of storage modulus *versus* temperature and (b) $\tan\delta$ *versus* temperature, for TPSG30, TPSG0-sugar, TPSG30-glu, TPSG30-fru and TPSG30-suc.

As TPSG0-sugar is free of glycerol, which is responsible for the transition around −55 °C, the initial drop in E' was observed only around 3 °C. The $\tan\delta$ peak for this sample is broad in comparison with the other samples, probably indicating that this material has a more heterogeneous microstructure than the others since it is plasticized by

Table 3
Log of storage modulus (E') and glass transition temperature – Tg (Tg are taken at maximum of $\tan\delta$ peak) for TPS

Sample	$\log E'_{(-50\,^{\circ}\mathrm{C})}$ (MPa)	$\log E'_{(25\,^{\circ}\mathrm{C})}$ (MPa)	Tg (°C)
TPSG30	0.92	0.65	35
TPSG30-glu	0.84	0.36	0
TPSG30-fru	0.88	0.43	8
TPSG30-suc	0.81	0.35	0
TPSG0-sugar	0.97	0.68	35
TPSG30-sugar	0.87	0.42	0
TPSG30-root	0.87	0.45	0

three distinct sugars. Above the Tg region, the TPSG30 shows a higher modulus than TPSG0-sugar, probably due to its higher crystallinity.

The effect of adding mixed sugars to cassava starch plasticized with glycerol (TPSG30-sugar) was also tested by DMTA for the purpose of comparing with TPSG30-root. The storage modulus and $\tan\delta$ results for the samples TPSG30-sugar, TPSG30-root and TPSG30 are plotted against temperature in Fig. 4.

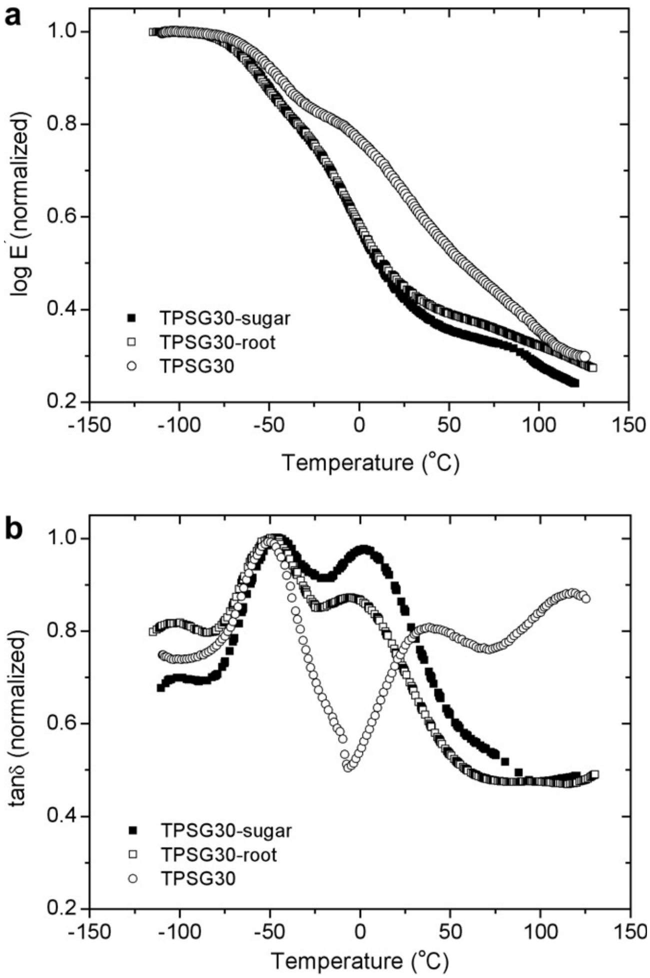

Fig. 4. (a) Logarithm of storage modulus *versus* temperature and (b) $\tan\delta$ *versus* temperature, for TPS30G-root, TPS30G-sugar and TPSG30.

TPSG30-root and TPSG30-sugar exhibited very similar values of Tg and storage modulus and it can be seen again that the presence of 2 wt% sugar as second plasticizer promotes a considerable change in the storage modulus and $\tan\delta$ curves.

Hence, the negative effect of rising glycerol content on the elongation at break in TPS produced directly with cassava root without purification as described in a previous work of this group (Teixeira et al., 2005), may be due to the additive effect of the naturally occurring sugars, which even at low contents (~2 wt%) produce significant modifications in the properties of the final material.

4. Conclusions

The TPS produced from cassava starch with addition of sugars (glucose, fructose and sucrose) was compared to that obtained directly from cassava root. A small sugar addition (2 wt%) to a starch-glycerol/water system causes a considerable reduction in the glass transition temperature and in the storage modulus of the correspondent TPS. The absence of glycerol causes the reduction of V_H-type structures. The use of sugar and water as plasticizers without glycerol causes a considerable reduction in water uptake (by about 60%) in the TPS final and results on a more amorphous material.

The presence of sugar in natural raw materials such as cassava root, even at low concentration, ought to be considered in the design of thermoplastic starch materials prepared from this raw material, owing to its influence on the plasticization process and on the mechanical properties of the end material.

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