Preparation and Characterisation of Thermoplastic Starches from Cassava Starch, Cassava Root and Cassava Bagasse

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Summary: Thermoplastic starches (TPS) based on cassava starch have been produced by extrusion at 120 °C, using glycerol as plasticizer. Three forms of cassava starch were employed, viz: cassava root (CR), cassava bagasse (CB) and purified cassava starch (PCS). The main differences between these are the presence of sugars and a few fibres in CR and high fibre concentration in CB. Conditions of processing and characteristics such as amylose and fibre content, crystallinity, water absorption and mechanical behaviour in the tension x deformation test were evaluated. The results demonstrated that the PCS and CR had amylose contents consistent with literature values (14–18%) and that CB is a material constituted mainly by amylopectin. It was found that fibres in high proportions (as in the bagasse) can confer reinforcement properties and are thus able to generate natural composites of TPS with cellulose fibre. The sugars naturally found in the root reduce the elongation of the TPS under tension. The PCS and CR TPS were stable with respect to indices of crystallinity after processing; and during a period of 90 d in a relative humidity of 53%, while the CB TPS tended to vary its crystallinity, probably because its amylose chain had low degree of polymerization.

Keywords: cassava bagasse; cassava starch; fibres; root cassava; thermoplastic starch (TPS)

Introduction

The search for new materials to substitute synthetic plastics, with the aim of minimizing the negative effects on the environment, has received considerable attention in both the academic and industrial sectors. Biodegradable plastics are one type of alternative material, and starch in particular has been the subject of much research. It can be converted to thermoplastic starches (TPS), that result from the granular disruption by a combination of temperature, shear and a plasticizer, which is usually water and/or glycerol.[1] In general, the TPS have been considered a promising material for this purpose, especially in packing materials of short useful life products, thanks to availability, low cost, renewability and biodegradability. However, the use of TPS is limited, owing to its low resistance to mechanical stress and humidity.[2] Also, the final performance of the TPS is strongly dependent on the botanical origin of the starch, since the contents of amylose, amylopectin and other constituents such as sugars, lipids and proteins vary with the plant used.[3]

The cassava (*Manihot esculenta*) is a root crop popularly grown in tropical countries such as Brazil. It is a rich source of starch, also containing proteins, lipids, fibres and sugars such as glucose, sucrose, fructose and maltose.[4] This starch is one of the most

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important substances in the food industry, but its use has been expanding recently into other sectors such as the petroliferous (lubricants), metallurgical (assisting the extraction of impurities from iron), textile (gums and reinforcement of wires) and paper industries (strength of the paper).[5,6] Most of the literature on cassava starch concentrates on modification by cross-linking reactions,[7] acetylation,[8] graft copolymerizations[9] and physics mixtures with other polymers such as polyurethane,[10] polystyrene[11] and polyethylene.[12] Cassava starch films are normally obtained by casting and not by the conventional techniques of synthetic materials processing such as extrusion.

Industrial cassava starch processing involves the elimination of soluble sugars and separation of fibres resulting in a purified starch and a solid residue called bagasse consisting basically of cellulose fibres, which represent 15 to 50% of the weight, the remainder being residual starch. Normally, this material is destined only for animal feed. This residue contains both a great deal of starch and a considerable quantity of natural fibre. These two characteristics suggest the possibility of using the bagasse as thermoplastic starch reinforced with natural fibres (composites), in the hope of reusing an industrial reject in potentially suitable materials for the biodegradable industry packing, with high added value. Matsui et al.[13] developed a composite from cassava bagasse impregnated with starch acetate and containing 10% of Kraft paper. They obtained a material resistant to humidity but with poor mechanical properties.

The aim of this work was to develop TPS consisting mainly of cassava starch and to evaluate the influence of the presence of fibres and other constituents such as sugars on the performance of these TPS. Properties such as crystallinity, water absorption and tensile strength were also investigated.

Experimental

In this work three cassava derivatives were utilized to produce TPS compositions, viz (i) cassava root (CR) (ii) cassava bagasse (CB) and (iii) purified cassava starch (PCS). These materials were kindly supplied by Corn Products Brazil. CB and PCS were used as received and the CR was milled and dried at 100 °C for 5 h. Reagent grade glycerol (Synth) was used as plasticizer. L-α-lysophosphatidylcholine (LPC) from egg yolk, obtained from Sigma, was used in determination of amylose content.

The fibre content in the samples was determined as described by Cereda.[4] About 3 mg of sample was hydrolysed successively with H_2SO_4 (1.25% w/v) and NaOH (1.25% w/v) solutions, and subsequently calcinated.

The amylose content was determined by Differential scanning calorimetry (DSC) as proposed by Mestres et al.[14] This method is based in the enthalpy of the amylose-LPC lipid complex formation. LPC solution (10 μL; 2% w/w) was added to 3 mg of accurately weighed sample in stainless-steel pans and sealed hermetically. The samples were stabilized for 1 h before analysis. A pan containing 10 μL of water was used as a reference. The readings were taken with a Shimadzu TA-50WSI calorimeter calibrated with indium and zinc and using nitrogen as purging gas. The samples were heated from 25 to 160 °C at 10 °C/min, stabilized for 2 min and cooled to 25 °C (cooling-rate 5 $°C \cdot min^{-1}$). After that the samples were reheated to 160 °C and cooled again under the same conditions. The amylose content was calculated on a dry-weight basis from the relation: % amylose $= (\Delta H_s/\Delta H_p) \times 100\%$, in which $\Delta H_s =$ measured enthalpy of the LPC-amylose complex formation (in the second scan) and $\Delta H_p =$ the enthalpy of pure potato amylose ($22.1\ J \cdot g^{-1}$).[15]

High performance size exclusion chromatography (HPSEC) analyses were performed in a Shimadzu Chromatopac C-R7A. The columns used for SEC separation were Ultrahydrogel A and Ultrahydrogel Linear, in series. The elution flow-rate was $0.8\ mL \cdot min^{-1}$ and the pressure $22\ kgf \cdot cm^{-2}$. The columns and detector were maintained at 35 °C. The

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sample (450 mg) was dissolved in 1 M sodium hydroxide solution by stirring for 2 h and heating at 70 °C. Next, to 2 mL of this solution were added 4 mL of the eluent (0.1 N $NaNO_3$; pH = 12) and the mixture filtered through a 1 μm filter (Millipore/SLPB DZ5 NZ). The injection volume was 20 μL and the standards were Pullulan with molar masses from 180 to 1.6×10^6 g · mol^{-1}.

To prepare the TPS, the starch materials and the plasticizer (glycerol), in the proportions 15, 20, 30 and 40% (dry-weight basis), were pre-mixed in polyethylene bags until a homogeneous material was obtained. 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. Stearic acid (0.5 wt.-%) was added as a processing agent. The processed samples were hot pressed at 120 °C into 2 mm thick plates.

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

Diffractograms were recorded in a Rigaku diffractometer. Scattered x-rays were detected in the range of 5–40°(2θ) at a speed of 2°(2θ) per minute. The extent of crystallinity of the CR, PCS and CB TPS was estimated (25 °C, 53% relative air humidity (RH) for 20 d) from the height ratio between the diffraction peak (V_H-type crystallinity at 19.7°; B-type at 16.8°) and the baseline of the diffractograms, as proposed by Hulleman et al.,[16] normalized by the respective starch content after water saturation. To examine the stability of the TPS, the diffractograms of the same samples after 90 d of conditioning were collected.

The tensile tests were performed with an Instron 5569 Universal Test instrument, equipped with a load cell of 50KN. The samples, previously conditioned at 53% relative humidity between 23 and 25 °C for 20 d, were tested in accordance with the ASTM D638M-96 type II requirements, using a crosshead speed of 50 mm · min^{-1}. Modulus values were calculated by the instrument software using the slope of the initial portion of the stress-strain curves.

Water absorption experiments were conducted on specimens of circular shape cut from the hot pressed plates of TPS, 8 mm in diameter and 2 mm in thickness. Prior to these measurements, the samples were dried at 70 °C to constant weight. They were then conditioned in hermetic containers at 25 ± 2 °C with 53% relative humidity, using saturated solutions of $Mg(NO_3)_2.6H_2O$, as specified in ASTM E 104. The amount of water absorbed by the samples was determined by periodical weighing, until a constant weight was attained. The water uptake (W) at time t was given by the relation

$$W(\%) = \frac{M_t - M_0}{M_0} \times 100 \qquad (1)$$

where M_t is the weight at t and M_0 the initial weight.

Results and Discussion

The composition of the original materials is shown in Table 1. It is observed that CR showed low fibre content and the presence of sugars, while CB exhibited the highest fibre content, as expected.

The DSC curves obtained for the determination of amylose content are shown in Figure 1. For all the samples,

Table 1.
Compositions of the original materials.

Sample	Moisture	Starch	Fibre	Total Sugar[4]	ΔH_s	Amylose
	%	%	%	%	J · g^{-1}	%
PCS	10	90	-	-	3.6	18.2
CR	10	85.3	2.5	2.2	2.5	14
CB	10	72.7	17.3	-	0.8	5

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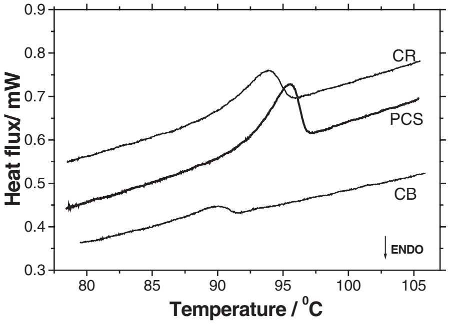

Figure 1.
DSC curves (second scan) used to determine amylose content of PCS, CR and CB.

amylose/LPC formed a complex, verified by the presence of the exothermic peak. In the case of the CB sample, this peak was relatively minor, reflecting the low amylose content of this type of material. It should also be noted that the higher the fibre content, the lower was the complexation temperature. This indicates that the presence of the fibres decreases the cohesion between amylose molecules, favouring the complexation at lower temperature.

The HPSEC results (Figure 2) showed that the PCS and CB samples exhibited a bimodal curve which is expected for samples of two components (amylose and amylopectin), corroborating the work of Carvalho et al.[17] Amylose (high amylose) and amylopectin (wax maize), both from corn starch (Corn Products Brazil) were analysed as references for the constituents. It was found that the sample of higher molar mass (amylopectin - wax maize) eluted at lower times than the main constituent of the high amylose standard. The amylose chains of PCS eluted after a longer time than amylose chains from corn, indicating a higher degree of polymerization of amylose chains from cassava starch than those from corn starch. With the CR sample, the standard bimodal curve was not observed. This was probably due to the difficulty of filtration during the sample preparation. This material produced the most viscous solution and may have caused macromolecules to be retained on the filter. However, a wide distribution of elution times can be seen indicating the presence of components with different molar masses. In CB the peak referring to amylose was relatively small compared to the peak for amylopectin. This corroborates the low amylose content in CB revealed by DSC. This suggests that in the stage of fibre separation, during the industrial processing of the cassava starch, the amylose molecules had been more damaged by degradation by the mechanical stress employed. This result is supported by the fact that the CB amylose chains elute at longer times

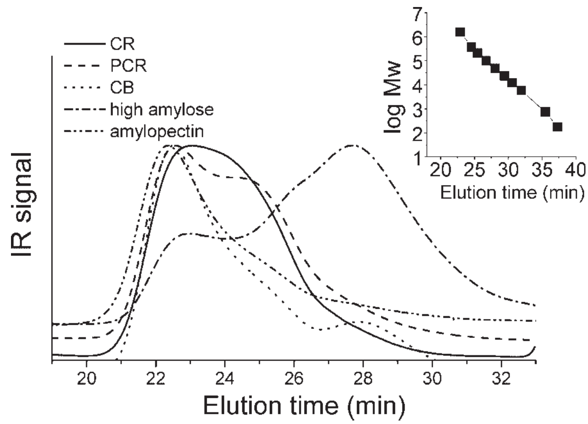

Figure 2.
HPSEC chromatograms of PCS, CR, CB and the references curves for amylose (high amylose) and amylopectin (waxy maize) (both from corn starch). Calibration curves (inset) obtained with standard Pullulan.

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than the PCS amylose chains, indicating that the former are shorter amylose chains and that CB is a material essentially constituted by amylopectin.

In the TPS preparation, the CR was the material offering the narrowest range of temperature and time of processing. This limitation is due to the degradation of sugars present in theses samples. The PCS processing was characterized by a high capacity of expansion, which was not the case for CR and CB TPS. This suggests that the presence of fibres inhibits the expansion capacity of the cassava starch. The torque curves for the samples during the TPS processing are shown in Figure 3. The samples were plasticized by the glycerol and the greater the concentration of glycerol, the lower is the maximum torque necessary to promote the plasticization. It was also observed that the maximum torque was greatest for the CB TPS, this fact being attributed to presence of fibre in sufficient quantities to hinder the mixing process. The instability of these curves was a consequence of the heterogeneity (fibres and starch) of bagasse.

The morphology of the TPS films, observed by scanning electron microscopy (SEM) (Figure 4), showed that the processing caused the complete disruption of starch granules in PCS and CR. The starch present in CB was already partially disrupted during the industrial starch process. The PCS TPS exhibited fragile fracture and had a homogeneous surface. The inhomogeneity observed in CR and CB TPS can be attributed to the presence of fibres in these materials and was most pronounced in CB TPS, due to its higher fibre content. No delamination effect was observed, indicating a strong adhesion between the cassava starch and its fibres. Thus, CR and CB TPS can be considered as optimized composites produced from a natural mixture of components (starch and fibres).

The disruption of the original starch was also evaluated by x-rays diffraction. The original materials and TPS sample diffractograms after water saturation (conditioning in RH of 53% for 20 days and 90 days) are shown in Figure 5. A complete change in the TPS profile of the diffractogram in relation to the original materials can be seen, confirming the starch granule disruption. For PCS and CR, whose characteristic pattern was C-type, after the processing the sprouting of peaks was observed in the same region of 2Θ equal to 12.6° and 22.6° (weak), and a strong peak at 19.6°. Such peaks are attributed to a type of crystallization called V_H which appears because

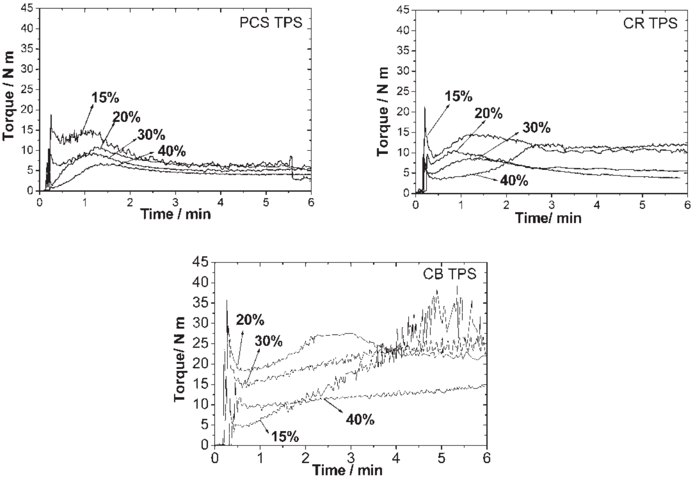

Figure 3.
Curves of torque x temperature during the processing of the TPS with various amounts of glycerol.

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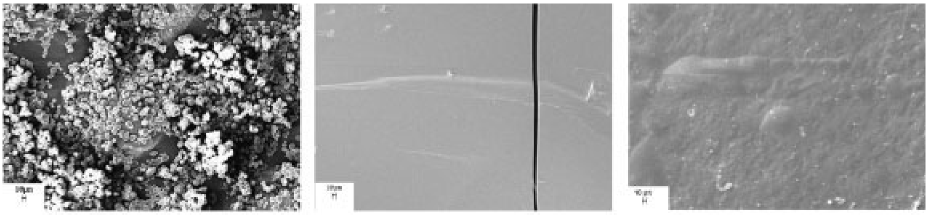
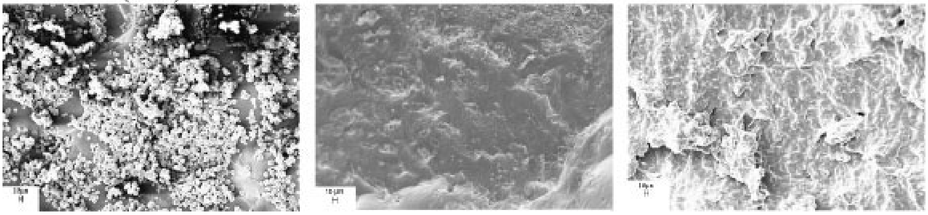

Purified Cassava Starch (PCS) PCS TPS 15% PCS TPS 40%


Cassava Root (CR) CR TPS 15% CR TPS 40%


Cassava Bagasse (CB) CB TPS 15% CB TPS 40%

Figure 4.
SEM images of PCS, CR, CB and TPS at compositions of 15% and 40% of glycerol.

the amylose recrystallizes with lipids, fatty acids and triglycerides as glycerol in simple helices after the cooling.[16,18,19] For CB, the diffraction pattern did not correspond to that normally produced by starches, indicating that the cellulose fibre crystallinity overlapped the starch crystallinity.

For the CB TPS, the processing caused the appearance of small peaks at 2Θ equal to 12.8° and 19.6° (related to V_H) since the amylose content is low in these materials. This result agrees with the behaviour observed for corn starch TPS,[15] in which the V_H crystallinity was also proportional to amylose content. The peak at 22.3° may be overlapping the peak that is also characteristic of CB (due to cellulose fibres), suggesting that, during processing, the available starch in the CB was also crystallized in the form of V_H structures similar to those in the PCS and CR TPS, although in relatively small amounts.

With regard to the evolution of the crystallinity over 90 d of conditioning (Figure 6), in agreement with that observed for other TPS made from corn[15] and potato[20], the V_H crystallinity did not increase with storage time. The CB TPS showed a small increase of this type of crystallinity with storage, suggesting that these materials possess a less stable crystalline structure with respect to conditioning. In general, increasing the glycerol content tended to produce a considerable reduction in the V_H crystallinity indicating that although glycerol is a good plasticizer for cassava starch, the cassava starch amylose chains have low mobility. This corroborates with Swinkels[3] who described the potato and cassava starch amylose molecules as having a high degree of polymerization. This would hinder the movements of this macromolecule and restrain its inter-associations and associations with other

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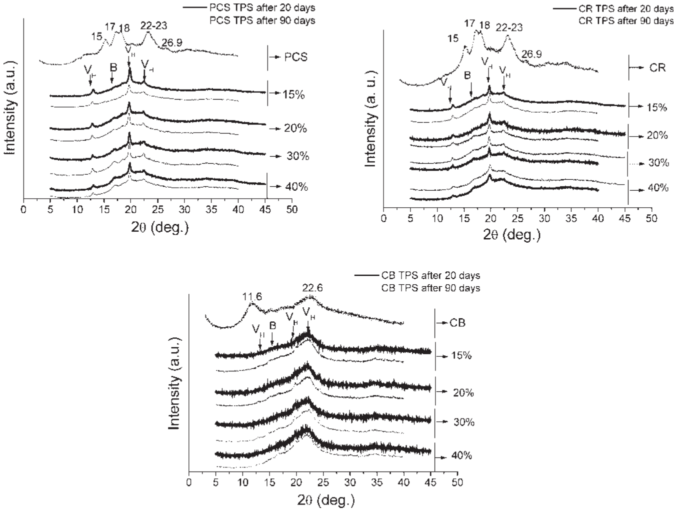

Figure 5.
X-ray diffraction patterns of pristine materials and their respective TPS after saturation by absorption of water (20 d) and the same TPS after 90 d of conditioning.

constituents such as lipids. This hypothesis is also corroborated by the chromatograms of Figure 2, whose the minor peak in the bimodal pattern of the PCS sample eluted at a lower time than the amylose peak of corn starch. With regard to B-type crystallinity, it is observed that this also did not vary for PCS and CR TPS, indicating that, possibly, the mechanical properties of these materials will be stable in these conditions of storage. Again, CB TPS showed a tendency for the B crystallinity to increase during storage. This may again be correlated with two facts: CB amyloses molecules showed a lower degree of polymerization (Figure 2) than PCS and CR and, according to Van Soest[20], fast crystallization in the B form mainly due to amylose crystallization. Secondly, the short chains present are more easily crystallized because they have greater mobility. Thus an increase in the B crystallinity was expected for CB TPS.

The water content absorbed by the TPS is shown in Figure 7. It is observed that there were no significant differences in the water absorption for the materials with the same amount of plasticizer. As glycerol content increased, the water absorption increased asymptotically due to the higher numbers of available hydroxyl groups.

The TPS mechanical properties observed in the tensile tests are shown in Figure 8. The PCS and CR TPS were relatively ductile and more tenacious than the CB TPS which proved to be highly fragile and presenting very low tenacity. The CR TPS showed an inverted elongation behaviour in response to the glycerol content, compared to PCS and CB TPS.

Figure 9 shows the behaviour of the elastic modulus, tensile strength and elongation at break of the TPS as a function of glycerol content. The increasing plasticizer content, as with synthetic polymers, causes a reduction of both the elastic modulus [Figure 9(a)] and the tension of rupture [Figure 9(b)], in all TPS samples. The reduction of the concentration of chains per volume unit due to the plasticization causes a reduction of the starch/starch interaction as the plasticizer is added. The CB TPS was slightly more resistant to this property and this was attributed to the reinforcement conferred on TPS by fibres in CB. The fibres in the CR were not sufficient to confer reinforcement on its respective TPS. In spite of the TPS composition with 15% of glycerol showing a greater modulus and tensile strength in the rupture properties, but it was a fragile material (brittle) and

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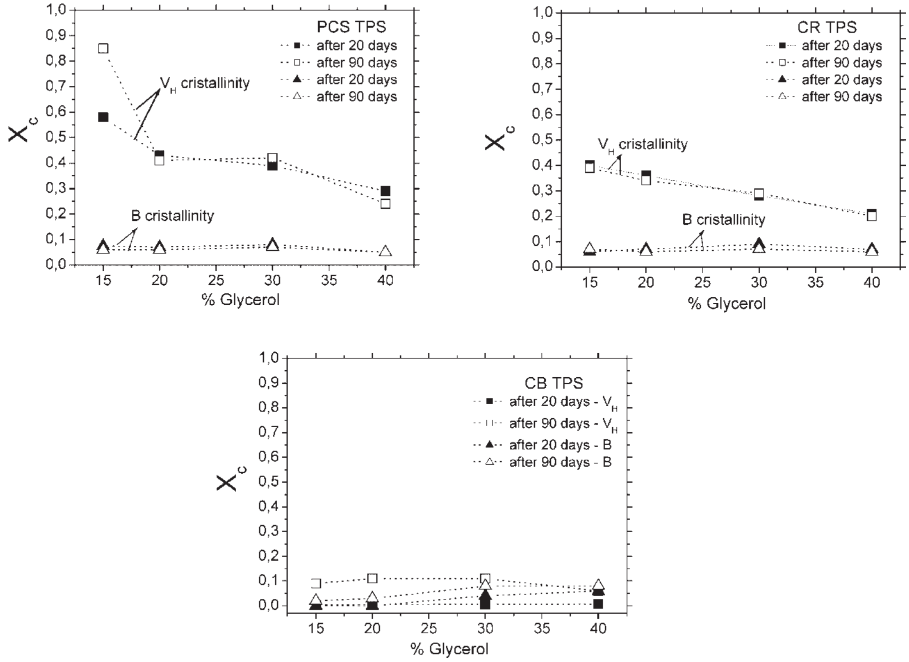

Figure 6.
V_H and B index of crystallinity (X_c) for TPS conditioned for 20 and 90 d as functions of glycerol content: PCS TPS; CR TPS, CB TPS.

hard to be processed. On the other hand, the elongation of PCS and CB TPS tends to increase with the glycerol content [Figure 9(b)], indicating that plasticization becomes more effective as plasticizer content increases. For the CR TPS, an inverse behaviour was observed, in other words, raising the glycerol content disfavours the elongation at break. This suggests an effect of antiplasticization possibly caused by sugars present in the cassava root. The effect of adding soluble sugars to starches has been reported.[21,22] In general, this effect is reflected in an increase in the gelatinization temperature and reduction in the retrogradation of starches, since the sugar molecules have the capacity to stabilize the gelatinized starch matrix. In the present study, besides glycerol, the water also behave as plasticizer and, according to literature,[22] the molecules of sugar stabilize the structure of the water, reducing the flexibility of the chains in the starch-water-sugars systems. Also, glycerol probably interacts with sugars, causing a reduction of free volume in the system and hindering the molecular movements.

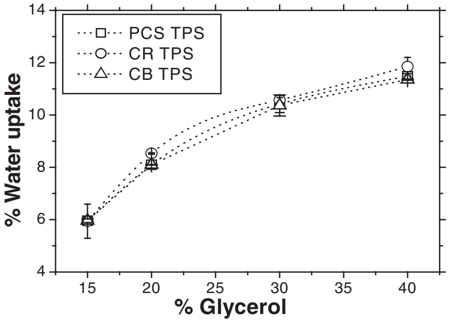

Figure 7.
Water absorption of the TPS at saturation as a function of glycerol content.

Conclusion

The results obtained in this work showed the potential of using bagasse cassava as reinforcement in the TPS and the viability

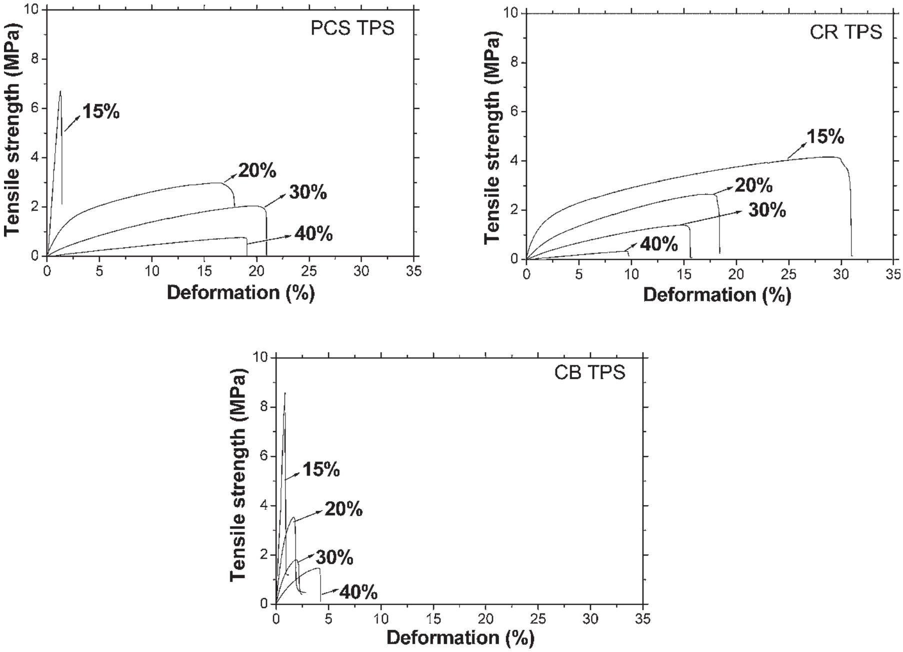

Figure 8.
Typical curves of tension *vs* deformation for all TPS.

of the direct use of cassava root in the production of these materials. In the first case, the most pronounced property was the greater elastic modulus in relation to the PCS and CR TPS. For CR TPS, it was found that the presence of sugars influenced the elongation property of the final TPS, suggesting that they generate a reduction of free volume by interacting simultaneously through hydrogen bonds with the starch chains and with glycerol and water and thus restrict the movement of the chains of TPS containing these plasticizers. An effect of antiplasticization caused by the presence of these sugars was suggested, and this should be further investigated. Increasing the glycerol content causes a reduction of the V_H-type crystallinity of the TPS, while the B type was little affected. These two types of crystallinity were revealed to be stable during storage up to 90 days suggesting that TPS made from cassava

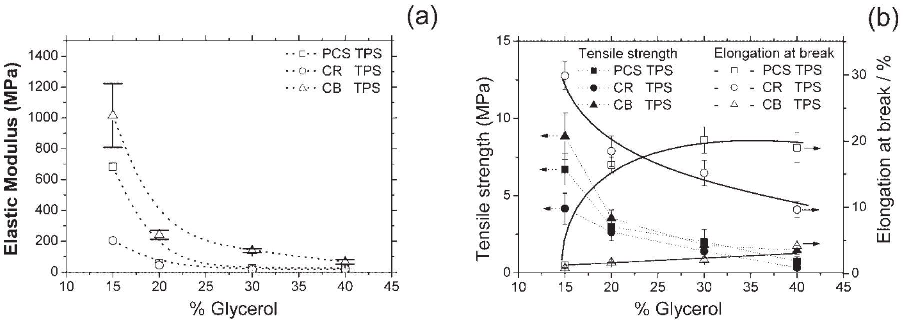

Figure 9.
(a) Elastic modulus; (b) tenxsion of rupture and elongation at break of TPS in function of glycerol content.

starch are structurally more stable than TPS produced from corn starch. Regarding the resistance to water, the various TPS behaved similarly, the resistance being diminished by an increase of the glycerol content.

Acknowledgements: The authors thank *FAPESP* for financial support and Corn Products for supplying cassava starch samples.

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