



## Primary and secondary dielectric relaxations in semi-crystalline and amorphous starch

Estrella Laredo<sup>a,\*</sup>, Dinorah Newman<sup>a</sup>, Alfredo Bello<sup>a</sup>, Alejandro J. Müller<sup>b</sup>

<sup>a</sup> Departamento de Física, Universidad Simón Bolívar, Apartado 89000, Caracas, 1080-A, Venezuela

<sup>b</sup> Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

### ARTICLE INFO

#### Article history:

Received 29 September 2008

Received in revised form 14 January 2009

Accepted 22 January 2009

Available online 1 February 2009

#### Keywords:

Starch

Dielectric relaxations

Glass transition

Moisture

Biopolymers

Amorphous phase heterogeneities

### ABSTRACT

The thermally stimulated depolarization current technique, TSDC, has been used to study the dielectric relaxations in cassava starch on semi-crystalline and amorphous samples. The A-type structure was observed by WAXS experiments and the variation of the crystallinity as a function of the moisture content,  $h$ , was followed on native starch. Retrogradation of the amorphous sample occurred at room temperature after 4 weeks in a closed vessel with a water activity 97.3%. In these conditions the humidity content reached a value of 28.5 wt% dry base and the crystallinity degree was comparable to that of the native starch. Three secondary relaxation modes were detected and attributed to short range orientations of polar groups and to main chain restricted motion. The influence of the moisture plasticization effect on the relaxation parameters of the local modes, was determined by decomposing the global TSDC curve in elementary Debye peaks with Arrhenius relaxation times. The main relaxation,  $\alpha$ , which is proposed to be the dielectric manifestation of the dynamic glass transition, sweeps a wide temperature interval around room temperature as the sample dries, shifting to higher temperatures as a result of the plasticization of the polysaccharide by water molecules. The  $\alpha$  peak deconvolution lead to the 2D relaxation time distribution and Vogel–Tammann–Fulcher parameters were obtained confirming the cooperative character of this mode. The transformed sample showed a bimodal distribution of segmental relaxation times that is interpreted as the existence of a heterogeneous amorphous phase: the mobile one which is similar to the original disordered phase present in semi-crystalline native starch and a more restricted one originated by the disruption of the crystalline lamellae during the pre-gelatinization process.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

The characterization of biodegradable materials is necessary to understand their chain dynamics which would affect their applicability in various industries. Starch is extensively used in food applications (thickening agent), in textiles (dye and sizing agent), in the paper and the chemistry industry (source of ethanol, excipients, activated carbon) and in oil wells as a component of drilling muds. Cassava (*Manihot esculenta* Crantz) is a root grown in

Africa, Latin America and Asia where it is an important part of the food intake due to its high carbohydrate content which is 60 and 27% higher than in rice and corn, respectively. In its native form, starch appears as semi-crystalline granules whose size and shape depends on their biological origin with a crystallinity degree which can vary from 20% to 45% [1]. The existence of blocklets formed by the crystalline and amorphous lamellae, which would be an intermediate between the macromolecules and the organization of the larger granule, has been proposed recently [2]. Three forms of crystalline structure have been determined, i.e., A, B and C. With some exceptions, A is most common in cereals, B in tubers and C in roots and seeds. C has been

\* Corresponding author. Tel.: +58 212 906 3536; fax: +58 212 906 3527.  
E-mail address: [elaredo@usb.ve](mailto:elaredo@usb.ve) (E. Laredo).

often considered as a mixture of A and B structures. Two polysaccharides, linear amylose and highly branched amylopectin, are the main constituents of starch. Both are based on 1 → 4 linked  $\alpha$ -D-Glucopyranosyl units, with various dipolar segments, which makes this material adequate for determining the molecular mobilities at different ranges by dielectric techniques. The variation of the glass transition temperature,  $T_g$ , in the presence of water (moisture concentration in weight %,  $h$ , calculated in wet or dry base), has been determined by differential scanning calorimetry, DSC. The  $T_g$  variation as the granular starch sample is dried from  $h = 22\%$  to  $13\%$  is +65 K for wheat, [3] and +95 K on going from  $h = 27\%$  to  $10\%$  for potato starch [4]. Chang et al. [5] reported a plasticizing-antiplasticizing effect of moisture in native tapioca starch evidenced by a  $T_g$ , that exhibited a variation in value of -145 K for a humidity weight concentration variation from 5% to 26% (plasticization) and the observation of a maximum in tensile strength, strain at break and toughness of films (antiplasticization).

Many of the possible applications are hindered by the drastic changes induced by the plasticization effect of moisture on the mechanical and dielectric properties. The molecular mobilities are strongly affected by the amount of absorbed water which exists in different forms in the amorphous and in the crystalline regions. Dynamic mechanical studies, DMA, have been frequently used on transformed starch [6] and other polysaccharides such as dextran, pullulan [7] and cellulose [8,9]. They show the existence at low temperatures of broad relaxations attributed to small entities local motions and at intermediate temperature of a strong water-induced relaxation; no glass transition was observed [7] in pullulan or amylose. Mizuno et al. [6] found by DMA a wide and weak band in the mechanical loss tangent as a function of temperature, which they attributed to the glass transition despite the behavior of the frequency of the band maximum as a function of  $1/T$ , which showed an Arrhenius dependence, typical of localized mobilities.

Broad-band dielectric spectroscopy (BBDS) [10–12], has also been widely used to study the molecular dynamics of starch, while only few works using thermally stimulated depolarization currents [13], TSDC, are available. The dielectric spectrum is a complicated one because of the presence of high intensity peaks due to water-polymer complexes whose positions and intensity depend strongly on the moisture content of the sample. Butler and Cameron [10] studied different kinds of solid native starches in a broad frequency and temperature range, with different moisture amounts ( $5\% < h < 28\%$ ). They showed that the observed modes are controlled by bound water. At high temperatures, their  $\alpha$  mode is related to the gelatinization process of starch in the presence of moisture. Around room temperature a mode, labeled  $\beta$ , is observed whose position is highly correlated with  $h$  and is attributed to be the segmental mobility of the amylose and amylopectin molecules, i.e., the dielectric manifestation of the glass-rubber transition of starch. At lower temperatures,  $\gamma$  secondary relaxations are detected which are also affected by the presence of water molecules and attributed to short range motions of the main chain and to rotations of the lateral

methylol groups. Other previous works by BBDS have reported dielectric data,  $\epsilon''(\omega, T)$ , on a variety of polysaccharides [14], such as starch, viscose, dextran and cellulose [15], where at least five relaxations are identified. The so-called  $\beta$  mode, which occurs well below room temperature, is attributed to a segmental motion and a  $\beta_{\text{wet}}$ -relaxation, at higher temperature than the  $\beta$  mode, appears in samples with low moisture contents [15]. The relaxation plots on a variety of polysaccharides resulted in either Arrhenius dependences of the average relaxation times,  $\tau(1/T)$ , for all the modes identified, or in a not well defined trend.

The objective of this work is to study by TSDC technique, samples of semi-crystalline native and amorphous transformed cassava starch with different moisture contents so as to contribute to the identification of the origin of the different modes and to try to find in the complicated dielectric spectrum, well resolved by TSDC, the elusive dielectric manifestation of the glass transition temperature.

## 2. Experimental

### 2.1. Materials

Cassava starch granular powder is a commercial product used without additional purification. It was obtained from Agroindustria Mandioca CA (Monagas, Venezuela). The amylose to amylopectin abundance ratio is 30/70. For the WAXS experiments on native cassava starch, the powder was equilibrated for 3 weeks in closed vessels over saturated atmospheres of different salt solutions with decreasing water activities ( $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{SrCl}_2$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgCl}_2$ ,  $\text{LiCl}$ ) [16]. Sorption curves of water in cassava were obtained and the total humidity content in the cassava sample for these water activities, at different temperatures, could be calculated [17]. The samples for the TSDC tests were disks of 20 mm in diameter and less than 1 mm thick obtained with the following procedure: the native powder was equilibrated for 1 month over saturated  $(\text{NH}_4)_2\text{SO}_4$  atmosphere at 25 °C (water activity 0.806) and then the powder was compression molded into disks at 50 °C, and 3500 psi for 8 min. The temperature was decreased to 30 °C in 9 min with the sample kept under pressure. The disks were extremely fragile and once in the measuring cell they could not be handled further. During the drying process they became brittle and often broke between the measuring electrodes.

The transformed samples were made by mixing the granular starch with water to reach a concentration of 25%. The dispersion was thoroughly mixed before compression molding in a hydraulic press at 140 °C and 3700 psi for 20 min and cooled under pressure to 30 °C in 5 min. Pressure was released after 3 min. Transparent disks (20 mm in diameter and about 0.5 mm thick) were obtained. The state of the samples after treating the native starch with this procedure was checked by Differential Scanning Calorimetric experiments in excess water.[17] The absence of any residual gelatinization endotherm guaranteed that the samples had been completely transformed to the amorphous state during the compression molding procedure.

Download English Version:

<https://daneshyari.com/en/article/1400827>

Download Persian Version:

<https://daneshyari.com/article/1400827>

[Daneshyari.com](https://daneshyari.com)