NMR AND SEM INVESTIGATION OF EXTRUDED NATIVE CORN STARCH WITH PLASTICIZERS

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The biodegradable packing of native corn starch samples with different ratios of glycerol and water were prepared. Their crystalline/amorphous changes, after extrusion process, were investigated by NMR (relaxation, ^{13}C CP/ MAS) and SEM methods. The composition having starch/glycerol/water 68/17/15 mass % ratio was found to have a dominant amorphous character and very similar features as a commercial specimen used for the package.

Key words: starch, plasticizers, NMR relaxation, ^{13}C CP/MAS NMR, SEM.

1. INTRODUCTION

Starch is one of the most studied biopolymer. The structural aspects involving the arrangement of the amylose and amylopectin component molecules inside of many starchy materials are intensely investigated [1–4]. The starch is used as the main component of biodegradable packaging materials used in the textile and the food industries [1, 5].

The native starch has a granular structure with an internal architecture characterized by concentric rings involving semi-crystalline shell (thickness 120–400 nm) separated by essentially amorphous regions. The semi-crystalline shells consist of regular alternating amorphous and crystalline lamellae repeating at 9–10 nm. In this structural organization, parallel double helices of amylopectin side chains are assembled into radially oriented clusters [4].

The component molecules of starch consist of $\alpha(1-4)$ linked D-glucose units, amylose being essentially linear, whereas amylopectin is a highly branched polymer due to 5–6% of $\alpha(1-6)$ links [1–3]. The physical-chemical properties of starch as viscosity, gelation power, adhesion etc., are strongly influenced by the amylose / amylopectin ratio [1, 6].

The plasticizing/antiplasticizing effect of some plasticizers (water, glycerol etc.) on various corn starch types was investigated by vibrational [4, 7] and NMR [8, 9] spectroscopies as well as by XRD, ESM and DCS methods [10–13]. The presence of both amorphous and crystalline structural phases was evidenced in pure native corn starch and also in the samples containing plasticizers [4, 7, 8].

The native starch materials used in the packaging process must to have a high content of amorphous phase and biodegradability at natural agents [5, 14]. Besides the presence of plasticizers, the extrusion process disrupts and transforms the semi-crystalline structure of starch granules in a homogeneous amorphous material. In this way there is an increase of biodegradability [15–17].

In this paper, the NMR (relaxation, ^{13}C CP/MAS) and SEM methods are used to analyse crystalline/amorphous changes in native corn starch as function of the plasticizers (water, glycerol) content, after an extrusion process.

2. MATERIALS

The commercial corn starch, having 21 wt % amylose and 10.8 wt % water content with a density of 0.561 g/cm^3, was obtained from SC Amylon SA (Sibiu, Romania). The glycerol used in sample preparation has a concentration of 99.5% and a density of 1.262 g/cm^3. The ratio starch/glycerol of $\cong 4$ during preparation was maintained constant, while the added water content increased from 0 up to 15% (0; 2.5; 5; 7.5; 10; 12.5; 15). The starch, glycerol and water were putted directly into the extruder. An extruded specimen obtained from FT International USA (http://www.fpintl.com/application-bible.htm), was also investigated by us in order to compare their properties with the prepared samples.

From the set of seven prepared samples, only three of them having starch / glycerol / water ratios: 78/19.5/2.5 (a), 72/18/10 (b), 68/17/15 (c) were investigated in addition to the commercial extruded specimen (d).

3. METHODS

The ^1H NMR relaxation measurements were obtained using the Bruker Minispec spectrometer with the 10 mm probe-head working at 19.688 MHz Larmor frequency. For the T_1 spin-lattice relaxation times measurements, 10 pulses were used for the magnetization saturation with a decremented inter-pulse time. The re-magnetization time was increased in 72 unequal steps with a 1.1 multiplication factor from 1 ms up to 956 ms. For the T_2 spin-spin relaxation times measurements the pulse length was 8.5 μs and 1000 CPMG echoes were recorded with 64 scans and a recycle delay of 0.5 sec. In all measurements the temperature was set at 35 ^{o}C. The CPMG decays and saturation recovery curves were analyzed

using the UPIN algorithm, which perform a Laplace inversion of the measured data [18]. In this way the T_1 and T_2 distributions as function of samples composition were analyzed.

The ^{13}C solid state cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded on a Bruker Avance III wide-bore spectrometer operating at 125 MHz Larmor frequency for ^{13}C, using a 4 mm double resonance probe head. Standard ^{13}C CP/MAS experiments were analyzed at room temperature, using a spinning frequency of 14 kHz and a [1]H 90° pulse of 2.3 µs. The spectra were acquired under two-pulse phase-modulated (TPPM) ^{1}H decoupling at 100 kHz by averaging 4000 scans, with a recycle delay of 5 s, and a 2 ms contact pulse. The ^{13}C CP/MAS spectra were calibrated using the [13]CH_3 line in TMS through an indirect procedure which uses the carboxyl NMR line in α-glycine.

Scanning electron microscopy (SEM) images were obtained with a FEI QUANTA 3D FEG dual beam in high vacuum using EDT detector (Everhart Thornley Detector). In order to amplify the secondary electrons signal a conductive Pt-Pd coating was applied to the specimens into an Agar Automatic Sputter Coater, in Ar atmosphere.

A co-rotating intermeshing twin-screw extruder ZK 25 (Collin, Germany) with six independent heating and cooling areas was used to conduct the extrusions. The screw has a diameter of 25 mm and a length to diameter ratio of 30:1. A die plate with one orifice of 3 mm was used. The starch was fed into the extruder hopper with a twin-screw volumetric feeder (Model DSV 020D, Definitive Inovation, Italy). The plasticizers were added into the working area through a pipe connection located at 170 mm from axis of the supply hopper with a peristaltic pump (Model SP 311/12, VELP, Italy). The screw speed was 150 rpm and the barrel temperatures (from the feeding port to the die section) 30, 50, 80, 100 and 120 ^{0}C, respectively. Finally, the extruding product was collected and cooled to room temperature.

4. RESULTS AND DISCUSSION

4.1. NMR RELAXATION DATA

The distributions of the spin-lattice relation time T_1, that give the information about the morphology and the crystallization degree [14, 19] are shown in Fig. 1. The main and small peaks for sample (c) having (68/17/15) composition are located at $T_1 \cong 90$ ms, and at $T_1 = 15$ ms, respectively. For the samples (a) and (b) these are situated at lower T_1 values, *i.e.* at $T_1 \sim 65$ ms and $T_1 \sim 5$ ms, respectively. These data suggest an increased amorphous content for sample (c).
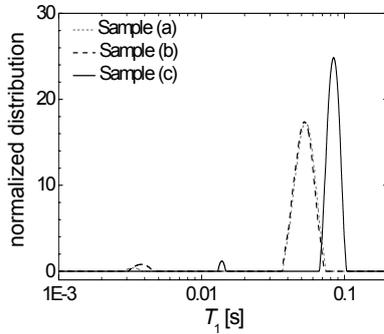
Fig. 1 – The distribution of spin-lattice relaxation time T_1 of (a) to (c) extruded samples.
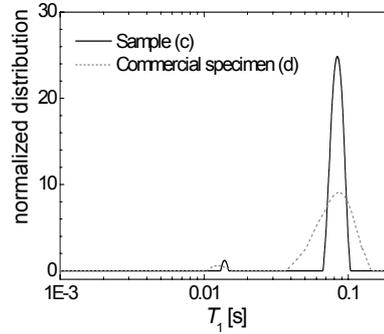
Fig. 2 – The distribution of spin-lattice relaxation time T_1 of (c) and (d) extruded samples.

Fig. 2 shows the normalized distribution of the T_1 relaxation time for the package obtained from the extruded sample (c) and the commercial extruded one (d). For both materials prevail the amorphous phase as showed by the peak at $T_1 \sim 90$ ms. The commercial extruded specimen is more heterogeneous compared with sample (c) as evidenced by comparing their line widths.
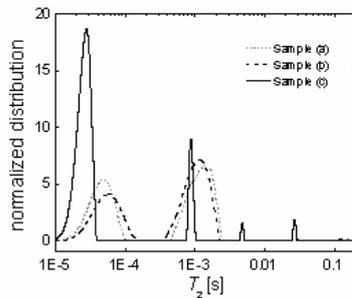

Fig. 3 – The distribution of spin-spin relaxation time T_2 of (a) to (c) extruded samples.
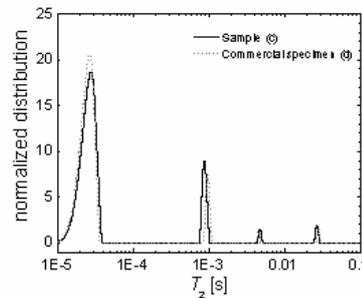
Fig. 4 – The distribution of spin-spin relaxation time T_2 of (c) and (d) extruded samples.

Figs. 3 and 4 show the normalized distributions of the spin-spin relaxation time, T_2. The peaks characteristic ($T_2 \sim 0.1$ s) of mobile region (amorphous), are very small for samples (a) and (b) – Fig. 3. These peaks are more pronounced for sample (c) having $T_2 \sim 4.7$ ms and $T_2 \sim 26.6$ ms which satisfies the required conditions for antishock filling packages. The samples (a) and (b) are more rigid, features observed also from the smaller values of T_2 relaxation time (two major peaks in the range of $T_{2,max} \sim 4.7 - 5.7$ μs and $T_{2,max} \sim 1.1 - 1.5$ ms). There is also a rigid core at sample (c), characterized by a peak at $T_2 \cong 27$ μs.

The comparison between extruded (c) and commercial specimen (d) shows that the four peaks have identical location and area, so a similar behaviour is suggested [8, 19].

4.2. THE ^{13}C CP/MAS NMR MEASUREMENTS

The ^{13}C CP/MAS NMR spectra of the sample (c) and commercial specimen (d) are shown in Fig. 5. The crystalline behaviour of a starch granule can be attributed to amylopectin content. According to Thérien-Aubin and Zhu [20], there are three types of crystalline starch structures: A, B, which are both formed by double helices of amylose and amylopectin, and V-type, composed of single helice. Their contributions can be determined from the spectra [20–23].
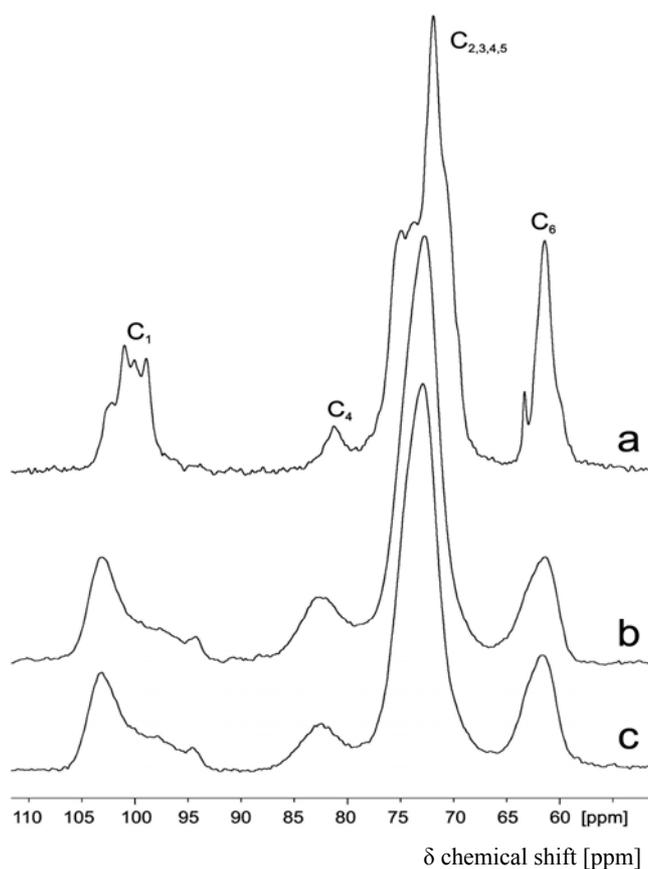

Fig. 5 – The ^{13}C CP/MAS NMR spectra of starch / glycerol / water [mass %] formula with 68/17/15 ratio, a – before and b – after extrusion and c – commercial extruded product, recorded at room temperature and 14 kHz spinning speed.

The ^{13}C CP/MAS spectrum of the sample (c) before extrusion evidences the presence of A, B and V – types structures. In the region of the characteristic glucose unit C_1 NMR resonance, there is an overlap of the triplet centered around $\delta = 101$ ppm characteristic to the A type phase with the doublet at $\delta = 101$ ppm characteristic of B type structure and also with a singlet at $\delta = 104$ ppm of the V- type structure – Fig. 5a. The strong $C_{2,3,4,5}$ quadruplet signal from $\delta = 73$ ppm is characteristic of A – type phase, whereas the intense C_6 absorbtion region ($\delta = 62$ ppm) is due to contributions from A, B, and V – types crystalline phases – Fig. 6.
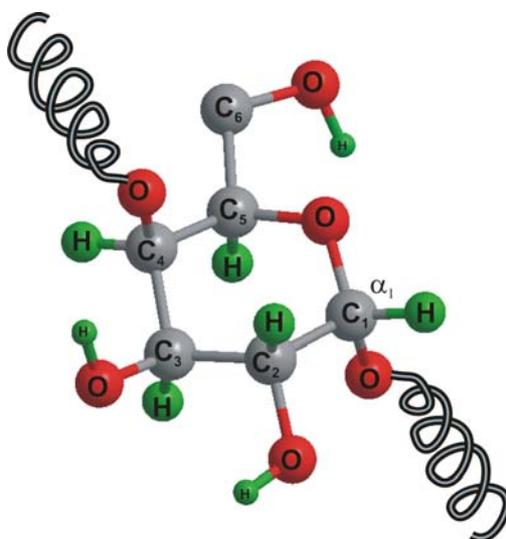

Fig. 6 – The $\alpha(1 - 4)$ glucopyranose structure and the labeling of carbon atoms.

The sharp ^{13}C line at $\delta = 64$ ppm belongs to glycerol, and suggests the formation of a complex between native starch and glycerol, most probably stabilized by hydrogen bonds.

The presence of a small amorphous phase in the sample (c) is suggested by the weak and broad NMR resonances at $\delta = 104$ ppm (C_1), $\delta = 83$ ppm (C_4) and $\delta = 61$ ppm (C_6). In contrast with these results, the NMR spectra from Figs. 5b and 5c of the extruded samples show that the amorphous phase prevails. Both spectra are similar with the ^{13}C CP/MAS NMR spectra already reported for amorphous starch samples [20, 22].

4.3. SEM (SCANNING ELECTRON MICROSCOPY)

Scanning electron micrographs of the investigated starch samples in cross and longitudinal – sections are shown in Fig.7. Some structural changes may be

observed as function of composition. The changes of holes form and the increase of their sizes can be observed with the decrease of glycerol and increase of water contents, till a limit which provides a useful product for filling packages.
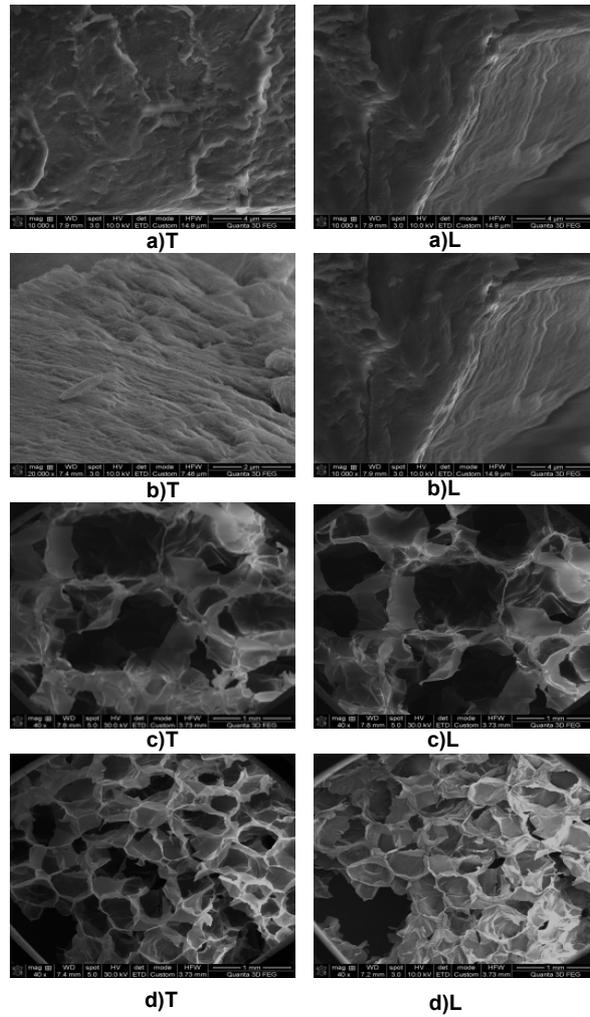

Fig. 7 – The SEM images of extruded samples from (a) to (d).
T means transversal section; L means longitudinal section.

The extruded samples (a) and (b) are very compact, the pores are small, elongated and little open – Fig.7. The pores are open and large, homogeneously distributed in cross and longitudinal planes and separated by thin walls in the case of sample (c). The extruded sample (c) and the commercial specimen (d) have a

similar form of the pores although the commercial specimen has a greater number of pores with a smaller dimensions.

5. CONCLUSION

The ^{1}H NMR T_1 and T_2 relaxometry measurements show that the ratio of starch / glycerol / water is the main factor determining morphology and polymer dynamics and also the macroscopic properties of the extruded samples. The sample (c) with 68/17/15 starch / glycerol / water (mass %) ratio shows similar features as the commercial specimen.

The ^{13}C CP/MAS NMR spectra evidence that the crystalline phases (A, B, V – type) prevail in the sample (c) before extrusion. After extrusion process the amorphous phase becomes dominant in both starch material (c) and commercial specimen (d).

Similar conclusion is also suggested by scanning electron micrographs of the investigated starch samples in cross and longitudinal sections. Very alike form of the pores, large and homogeneously distributed in cross and longitudinal planes and separated by thin walls were evidenced for both extruded sample (c) and commercial specimen (d).

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