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WATER ABSORPTION AND DEGRADATION OF PACKAGES BASED ON NATIVE CORN STARCH WITH PLASTICIZERS

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ABSTRACT. The starch in native forms or chemically modified is found as the main component of biodegradable packaging materials. Regarding this the water can produce a fast degradation, of the order of days, of such materials. Four types of packaging materials, one witness and three with different starch, glycerol and water ratios were subjected to natural degradation after absorption of distilled water. The degradation process was monitored by various NMR relaxometry methods based on the measurement of CPMG (Carr-Purcell-Meiboom-Gill) decays with a T_1 filter to exclude the signal from free water. The analysis of NMR signal decays was performed using a Laplace inversion algorithm and the dynamic components were identified from the T_2 transverse relaxation times distributions. We found that the best package with 68/17/15 ratios between starch/glycerol/water is extremely degraded after just one day forming a colloid substance. After that in time we observe a quasi-solid precipitation at the bottom of NMR tube. The reduction of dynamics is observed also in the T_2–distributions measured for 5 days. The most resistant package (78/19.5/2.5) was that with a large content of starch but which was also reaching the swallow limit in five days and start to be decomposed.

Keywords: *starch, plasticizers, extrusion, degradation, NMR relaxation*

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INTRODUCTION

Biodegradable polymers represent a promising solution to the environmental problem of plastic waste disposal [1]. Among the candidates polymers, the starch presents interest for the products which require rapid degradation [2,3]. The target of recent investigations in the field of bioplastics is to obtain commercial packaging material produced from pure starch, a natural polymer, and to exclude synthetic polymers from the formulation [4]. Native starches are non-plastic due to the intra- and intermolecular hydrogen bonds between the hydroxyl groups in starch molecules, which represent their crystallinity. Native starch exists in a semi-crystalline granule and is comprised of two major polysaccharides: amylose and amylopectin. Amylose consists of α-(1-4)- linked D-glucose and amylopectin that has the same backbone as amylose but with myriad α-(1-6)-linked branch points [5,6].

To obtain loose fill packaging, thermal and mechanical processing should disrupt semi-crystalline starch granules using extrusion, a conventional technology used in synthetic plastic manufacture. Because the melting temperature of pure starch is substantially higher than its decomposition temperature, it is necessary to use plasticizers. According to the literature glycerol is most commonly used plasticizer [7]. If the total thermal and mechanical energy provided to the starch is insufficient, the product will show unmelted starch granules of clear crystallographic structure. Similarly, the proportion of plasticizer and its chemical nature, influence strongly the physical properties of the processed starch by controlling its destructuration and depolymerisation and by affecting the final properties of the material. An insufficient amount of plasticizer may result in an incomplete destruction of the crystallographic structure of starch [8,9].

Abiotic hydrolysis is the most important reaction for initiating the environmental degradation of biopolymers [10]. Polymer hydrolytic degradation, as abiotic disintegration, may be defined as the scission of chemical bonds in the polymer backbone by the attack of water to form oligomers and finally monomers. In the first step, water contacts the water-labile bond, by either direct access to the polymer surface or by imbibition into the polymer matrix followed by bond hydrolysis. The hydrophilic and hydrophobic nature of polymeric materials influences their degradation rate, and the susceptibility to hydrolysis follows this order: (1) hydrophilic with hydrolysable bonds, (2) hydrophobic with hydrolysable bonds, (3) hydrophilic with no hydrolysable bonds, and (4) hydrophobic with no hydrolysable bonds [11]. All biodegradable polymers contain hydrolysable bonds, such as glycosides, esters, orthoesters, anhydrides, carbonates, amides, urethanes, ureas, etc. [12]. Polymers with strong covalent bonds in the backbone (like C-C) and with no hydrolysable groups require longer times to degrade [13].

The hydrophilic nature of starch plays an important role in initiating biodegradation process [14]. The degradation of starch-based packaging includes the disintegration into their monomers. Therefore unstable and hydrolysable linkages are required, where chemical, biological or photochemical reactions can take place [15].

A number of non-destructive techniques can be used to obtain information about the degradation mechanism of biopolymer. These include: Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD), contact angle measurements and water uptake [10]. For the structures within starch und starch-based products, both ^{1}H and ^{13}C high resolution NMR spectroscopy can be used to identify and quantify branch points and end groups [16,17]. Although reducing ends of starch molecules can be determined chemically and non-reducing ends can be determined by the difference in reducing power before and after debranching, ^{1}H NMR is the method of choice for quantifying the degree of branching based on the ratio of intensities observed for anomeric proton signals for (1-6)- and (1-4)-linked residues [16, 18].

This paper presents the results of water absorption and ^{1}H NMR investigations obtained for four types of packaging materials, one witness and three with different starch, glycerol and water ratios subjected to natural degradation after absorption of distilled water.

RESULTS AND DISCUSSION

Fig.1. presents the normalized mass of the swallowed water absorbed during five days by three packages based on native corn starch with different formula presented in Table 1. The experiment was performed for four packages, if we consider also the control specimen, but one of our products, which present the formula with the lowest starch content or lowest starch/water ratio (4.53 – sample 3), was degraded after one day. The hardest sample, with lowest water content (sample 1 with 78/19/2.5 starch/glycerol/water ratio) absorbed the lowest quantity of water (~ 50 % from sample's mass in day 5) with a smallest velocity. If the water content of formulas increases, then the quantity of absorbed water after 5 days increases to ~ 66 %. Moreover the absorption velocity is much higher, and as one can observe from Fig. 1 in 1 day the sample 2 (72/18/10) absorbed already water of ~ 60 % from sample mass. If the water content in the production formula of package increases as for the sample 3, which is the best package, the sample looses is integrity and become a colloid. The control package, which as we will see below is similar with package 3, absorbs a large quantity of distilled water ~ 1586 % from

sample mass. The swallowed water must be accommodated between amylose and/or amylopectin polymer chain segments modifying their dynamics. One can observe that the percentage of more mobile components associated with lateral branches is reduced and becomes more mobile while the additional

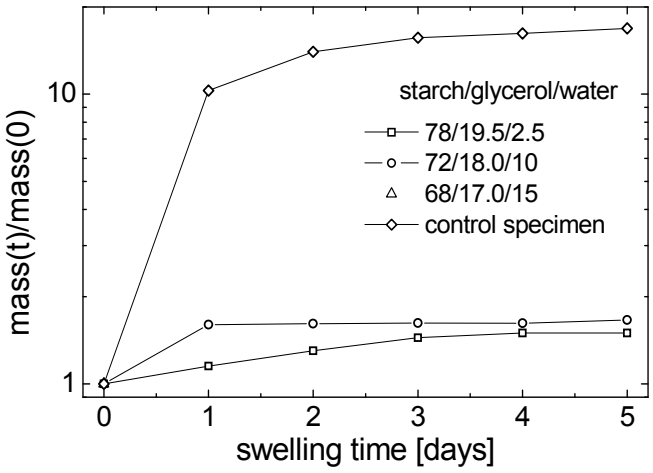


Figure 1. The normalized mass uptake during five days by three packages samples with 4:1 starch: glycerol constant ratio compared with a control specimen. The package with starch/glycerol/water 68/17/15 was degraded after 1 day. The lines are drawn to guide the eyes. The errors are under 5% error limits.

water content leads to a largest immobilization of amylopectin polymer chain segments in the core packed branches [19]. Therefore such changes can be well monitored by NMR relaxometry.

Fig. 2 presents the decays of the CPMG echoes trains for package sample 1 (78/19.5/2.5) and 3 (68/17/15). The curves recorded at 1 – 5 days are compared with the CPMG decays curves recorded for dry sample (contain only the water introduced in the manufacturing process). As expected, in both cases, the CPMG curve measured for the dry samples decay much faster than for the sample packages with water. Large differences between samples can be observed for the CPMG curves recorded during the monitoring of degradation process. While the sample 1 (with a low water content in the production formula – see Table 1) maintains is integrity and starting with day 2 present a reduced decay of CPMG curve indicating that the components (among them the amylose and amylopectin polymer chain segments) becomes more mobile, the sample 3 present a different behavior. First of all, the CPMG

decay decays much slowest (in 4 s compared with ~ 320 ms for sample 1) since the measurement was performed not for the package sample per se but for the colloidal solution resulted from the degradation of package in water. In the same time, the dissolution process of the (best) package in water continues for ~ three days (see the CPMG echoes represented with triangle with top down in Fig. 2b which decays the slowest) then a precipitation process can be intuited from the increased decay of the CPMG curves corresponding to days 4 (diamond) and five (stars).

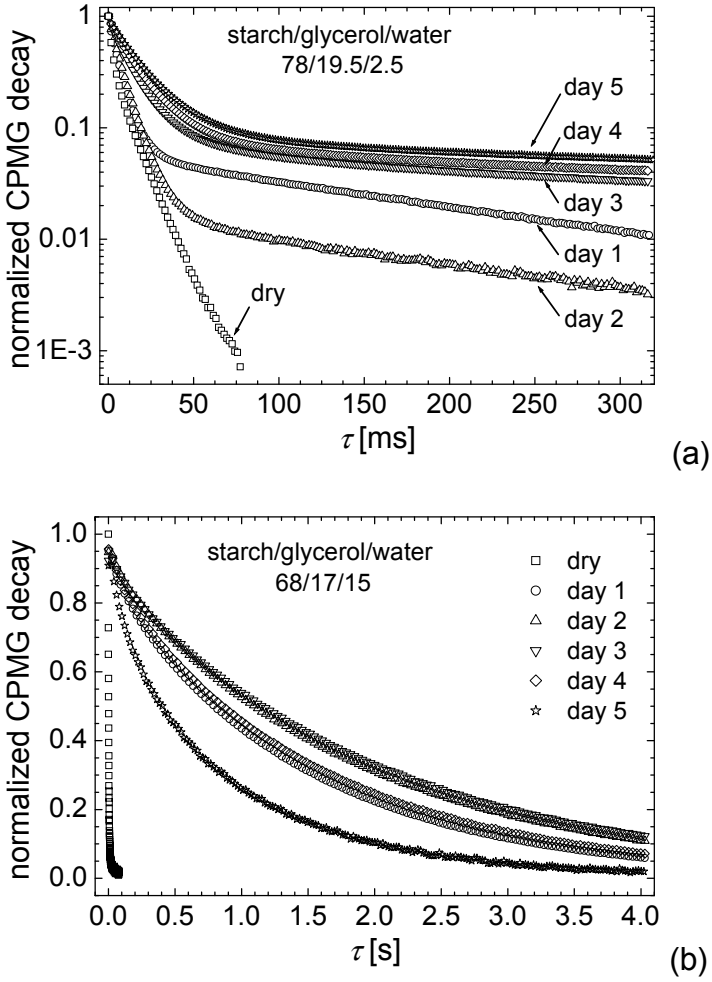


Figure 2. Compared CPMG decays during 5 days and dry samples for mixtures of starch/glycerol/water: 78/19.5/2.5 (a) and 68/17/15 (b).

A much better interpretation of the CPMG curves can be obtained if we will analyze the normalized T_2 relaxation times distributions obtained by Laplace inversion of the measured curves. Such normalized T_2–distributions are presented in Figs. 3 and 4 separately first for samples 1 and 2 which could maintain their structural integrity during the five days of water absorption and then for samples 3 and 4 which were measured as colloid.

In Fig. 3a the normalized T_2–distributions recorded for sample 1 with the largest starch/water ratio (small water content in the initial formula) show the most dramatically changes in the dynamics of components.

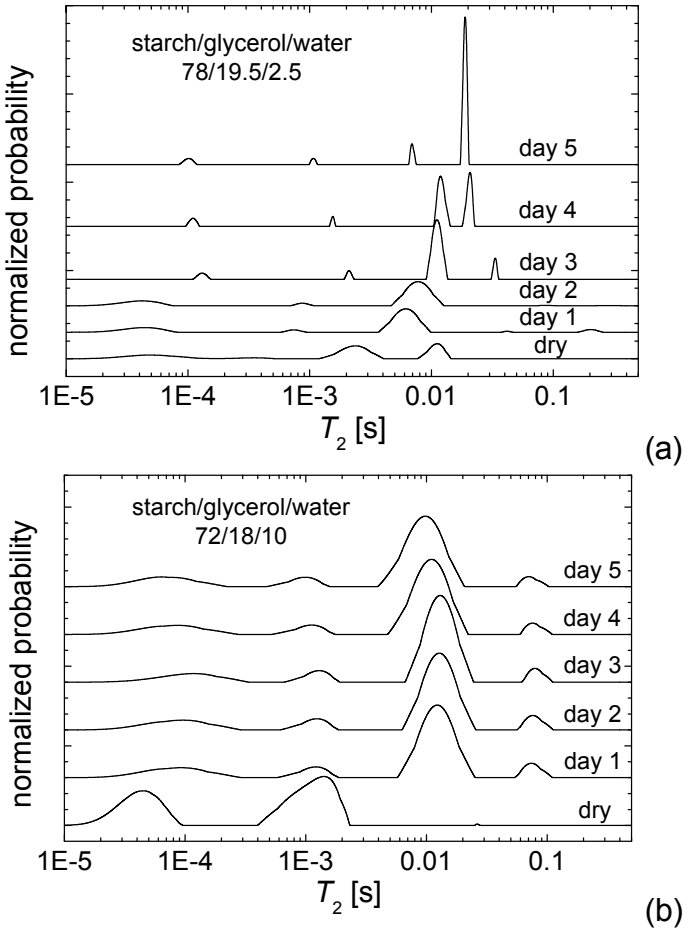
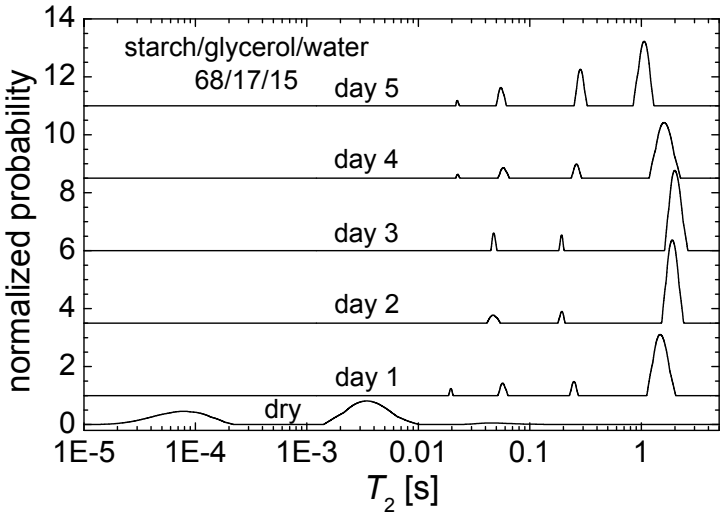


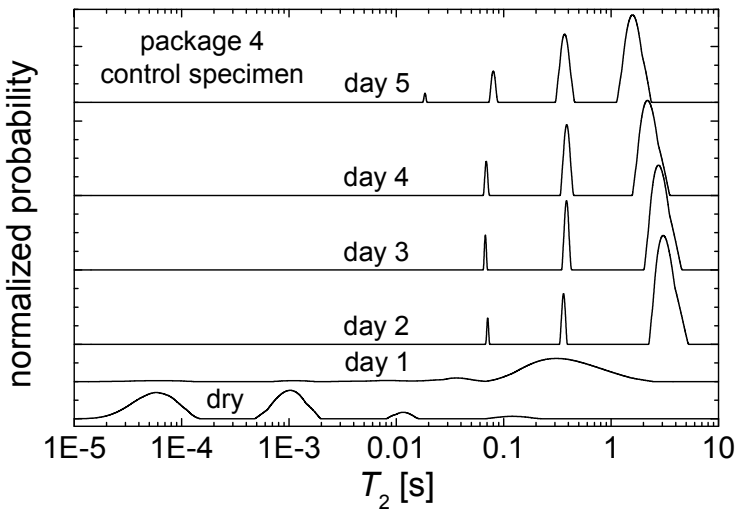
Figure 3. The normalized T_2 relaxation times distributions of packages samples with starch/glycerol/water: 78/19.5/2.5 (a) and 72/18/10 (b) for 5 days water absorption compared with dry samples.

For the dry sample the majority of ^{1}H reservoirs are characterized by T_2 values of ~2.5 ms and ~11 ms which can be considered as semi-mobile, and a small ^{1}H reservoirs is characterized by T_2 values of ~50 μs located into a rigid region (probably in the junctions of lateral branches with the amylopectin polymer backbone). One day of water absorption lead to the conservation of the rigid component but a collapse of the peaks located at T_2 values of the order of milliseconds to a unique peak located at T_2 values of ~ 6.3 ms. In the same time two new peaks appears at largest T_2 values (~ 41.3 ms and ~ 210 ms) indicating a largest mobility associated with the ^{1}H from these reservoirs. After another day (2) of water swallowing maintains the new composition observed in day 1 with a slight increase of mobility observed form the shift of T_2 values to largest numbers. A dramatically changes can be observed starting with day 3. First of all, one can observe that the peaks in the normalized T_2–distributions becomes more narrow indicating a reduced distribution compared dray sample or with not so degraded sample (first two days). While first three peaks (T_2 ~0.13 ms, ~2 ms and ~10.9 ms) are shifted to larger T_2 values compared with the values measured in day 2, the most mobile peak (T_2 ~ 33.6 ms) contain a larger ^{1}H reservoir but is moved to smaller T_2 value. In the next two days of water absorption, with the exception of the main peak (which present the largest area under the peak) which is moving slowly towards a larger T_2 value the rest of peaks are moving to smaller T_2 value. This is an indication that the excess of water lead also to a stiffening of some components (more mobile but also more rigid) of this package formula. Among all samples, sample 2 (72/18/10) once swallow the initial amount of water become more stable in time (see Fig. 3b). The dry sample is characterized by two relative rigid components. These are observed also for degraded sample but into a much smaller percentage. The largest ^{1}H reservoirs are found at T_2 values ~ 11 ms and ~ 75 ms. For this package one can observe also a slight increase of the T_2 values up to the day 3 then a slight decay of the T_2 values in days 4 and 5. The same conclusion, of some component stiffening after day 3 as in the case of the previous sample can be underlined.

Despite of the different condition of measurement (the state of sample in colloidal solution) a similar behavior can be observed in the case of the sample 3 of which normalized T_2–distributions are presented in Fig. 4a. For the dry sample the T_2–distributions is characterized by T_2 values smaller than 10 ms. In one day, the sample 3, of which formula contain the largest amount of water (the starch/glycerol ratio being the same in all formulas), is degraded to a colloidal stage characterized by T_2 values larger than 10 ms. Three of four distinct dynamic components are observed in this case. In the same time one can observe a degradation which continues in the first 3 days but starting with day 4 a precipitation was visual observed and is validated by the decrease of the main peak (more mobile – with the largest T_2) T_2 values towards lower values, then with a reduced mobility.



(a)



(b)

Figure 4. The normalized T_2 relaxation times distributions of packages samples with starch/glycerol/water: 68/17/15 (a) and a control specimen (b) for 5 days water absorption compared with dry samples.

The degradation behavior of the control specimen is similar with the behavior of the sample 3, the best package formula, with some minor differences. The control specimen reaches the largest degradation effects not in one day as in the case of sample 3 but in two days. From this point (day two) the control specimen starts to precipitate, as easily observed by visual inspection, but also denoted, as in the case of sample 3, by the decrease of the main peak T_2 values towards lower values starting from T_2 ~3 s to ~ 1.5 s.

CONCLUSIONS

A series of formulas were tested in order to obtain packages based on native corn starch with plasticizers with a reduced time of degradation while swallowed in water and are compared with the performances of a control sample. The swallowing capabilities were estimated from inflation (water uptake) and the degradation a process was monitored from the analysis of normalized T_2–relaxation times distributions measured during five days of observations. We observe that with the decrease of the starch/initial-water ratio the samples becomes more and more soluble in water and for a certain formula (starch/glycerol/water: 68/17/15) the tested sample is degraded under in less that one day. Nevertheless, in all cases a degradation process continues slowly in time but starting with day 3 part of each package start to precipitate. This behavior is observed also in the case of the control specimen with slightly different timing.

EXPERIMENTAL SECTION

The normal corn starch used in this study was obtained from SC Amylon Sibiu, Romania, having water content on wet basis (wt.b) of 10.76 %, a density of 0.561 g/cm^3. The amylose content was 21%. The glycerol used in formulas was purchased from SC Nordic Invest SRL Cluj Napoca and had a concentration of 99.5% and a density of 1.262 g/cm^3. The water used was from the water supply system. Table1 shows the ratio of the components in the used formulas.

Table 1. The content and ratio of starch-glycerol-water components in the used formulas

Sample	Starch [%]	Glycerol [%]	Water [%]	Starch/ Glycerol	Starch/ Water
1	78	19.5	2.5	4	31.2
2	72	18	10	4	7.2
3	68	17	15	4	4.53
4	control specimen with unknown values				

The packages samples were cut to fit into a 10 mm diameter NMR tube and 1 cm^3 of distilled water was added. For samples 1 and 2 each day the excess water was removed and the water uptake was measured using an AGN 200 C analytical balance with a precision of 0.0001 mg. For samples 1 and 2 one cm^3 of distilled water was added after NMR measurements. Sample 3 and 4 being largely degraded after 1 and 2 days, respectively, were measured by NMR relaxometry in the state of colloid. The mass uptake for sample 4 was measured for another part that the part used in the NM measurements.

The ^1H NMR relaxation measurements was performed using the Bruker Minispec spectrometer with the 10 mm probe-head. The Larmor frequency was 19.688 MHz and the temperature was set to 35 ^oC. For the T_2 spin-spin relaxation times measurements the pulse length was 10.1 μs and 4000 CPMG echoes were recorded with 256 scans and a recycle delay of 0.5 sec which acts as a T_1 filter to reduce the contribution of the free water. In order to find the T_2 spin-spin relaxation times distributions, the CPMG decays curves were analyzed using the UPIN algorithm, which perform a Laplace inversion of the measured data [20].

A corotating intermeshing twin-screw extruder ZK 25 (Collin, Germany) 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 0C, respectively. Finally, the extruding product was collected and cooled to room temperature.

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