Macromol. Symp. **2014**, 340, 65–72 DOI: 10.1002/masy.201300134

Porous Biodegradable Starch-Based Polymer: Effects of Plasticizers on the Physical Properties

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Summary: The effect of the plasticizer content (mixture of water and glycerol) on the cellular structure of the considered material and its influence on the resulting properties, such as mechanical stiffness, are investigated by means of optical microscopy, X-ray diffraction, thermogravimetry and standard mechanical testing. Adding glycerol leads to larger cell walls and smaller pores but it does not significantly affect the elastic tangent modulus and strength under compression for deformations up to 50%; only a tendency to promote elastic recovery is observed.

Keywords: biodegradable; foam extrusion; macroporous polymers; starch; structure-property relations

Introduction

Petrochemical based polymers predominate in the plastic industry due to their easy processing and low cost. However, there is currently an increasing interest in replacing these by more sustainable materials to follow the global ecological need.[1] Renewable polymers are obtained either from natural biopolymers such as starch or by polymerization of bio-based monomers.[2] Starch is highly water soluble, bio- sourced and could be treated thermo-mechanically to produce a bio-plastic by adding plasticizers.[3] Plasticizers such as water, glycerol, sorbitol, xylitol and glycol are common plasticizers used in producing biodegradable plastics[4] and each has its specific plasticization abilities.[5] Plasticizers under concern in this study are water and glycerol. We specifically concentrate on the effect of the amount of glycerol, which, added to starch during the processing of films, is known to play a major role at many levels: (i) it influnces the processing of plastic films since the amount of glycerol directly affects the gelatinisation temperature of the starch-water mixture and thus dictates the processing conditions for producing homogeneously gelatinized materials;[6] (ii) concerning material characteristics such as specific heat capacity,[7] storage modulus (a measure of the energy stored during a cycle) and water vapor permeability, the properties change substantially when increasing glycerol;[8] (iii) concerning the molecular organization (crystallinisation, amorphisation), cereals such as the native wheat starch exhibits an A- type crystalline structure while the plasticized starches exhibits three crystalline structures V_H, V_A or E_H in which they forms during the extrusion,[9,10] V_h-type structures tend to disappear when reducing glycerol amount and amorphisation takes place when replacing glycerol by sugar and water;[11] (iv) concerning the mechanical properties: from a general point of view, the addition of glycerol increases the elongation at break[12] and, as a result, corollary facilitates the efficiency of processing films (which involves large deformations); it can also, up to a certain content, increase the tensile strength or, above this content, decrease this strength;[13,14] local damage

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in the form of microcracks in films can also be related to the concentration of glycerol which, because it is only partially miscible with starch, can induce phase separation mechanisms in the film.[15]

All of the above mentioned studies and, to the best of our knowledge, the large majority of the studies on the effect of glycerol content in glycerol-starch systems deal with materials in the form of films. Few (see e.g.[16–19]) concern porous expanded materials, which correspond to another stable quasi-solid state of a plasticizer-starch mixture. This type of starch-based material is our concern in this study, with the objective to pave the road for a comprehensive characterization of the relationships between processing conditions and mechanical properties. This paper first presents, the material, its processing conditions and the different methods for analyzing it; this is then followed by the discussion of material content and the crystallization after processing, the microstructural morphology and the mechanical properties.

Materials and Methods

The starch used was provided by Roquette (France). It is a wheat based starch coming from a cereal grain with a high gel temperature (85 °C), a low viscosity and a short texture. It has particle sizes of < 200 microns. The conditions of extrusion (screw speed, diameter etc..) and the composition of the initial mixture (water/starch ratio) play an important role on the expansion of the system. In this work, we have used a single screw extruder MUPLAST E/30-25D. With this equipment, the expansion was obtained at 160 °C (extrusion temperature) with a screw speed of 140 rpm. These conditions were kept fixed when processing different expansion with different initial percentage of glycerol. These include glycerol contents of 5% (material a), 5% after mechanical testing (material b), 10% (material c) and 15% (material d). All had a water content of 15%. An expansion of E = 271% was obtained according to the calculation of the expansion index given by $E=D/D_0$ (where D and D_0 are, respectively, the average diameter of the specimens and the diameter of the die at the exit of the extruder). Figure 1 shows two examples of such expanded materials corresponding to 5 and 15% of initial plasticizer content. As we increase the glycerol content of the initial composition, the softness and the transparency of the expansion increased. The expanded material is prone to rapid drying, about which particular attention needs to be paid, especially to avoid large variation scattering of mechanical properties from specimen to specimen.

Optical microscopy was performed by using a Nikon OPTIPHOT-2 microscope connected to a micro-camera (Sony,

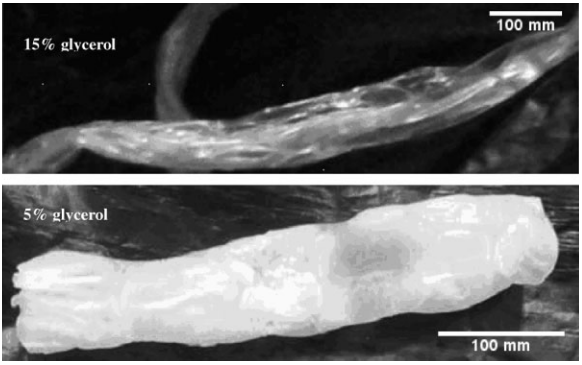

Figure 1.
Samples obtained after extrusion with a content of glycerol of 5% and 15% (w/w) before extrusion process.

CCD-IRIS). For this analysis, samples have been polished and sprinkled with gold powder for a better reflection and contrast. The morphology of the samples was tested by X-ray diffraction using a Bruker D8 Advance wide angle X-ray diffractometer. X-ray diffraction patterns were obtained for the powder of the samples with different percentage of glycerol. Experiments were carried out with Co Kα radiations ($\lambda = 1.78897$ nm), the scattering angle (2θ) covered the range from 10° to 35° (θ is the Bragg angle) with a step of 0.05° and a sampling interval of 0.5 s. Thermal degradation studies were performed using thermogravimetric measurements (Netzsch TGA 209 balance, Germany). The measurements were carried out in a nitrogen atmosphere from 20 to 600 °C at a heating rate of 10 °C/min. Finally, compression tests were carried out by using a Zwick/Roell machine. These tests were performed in atmospheric conditions using a strain rate of 0.0028 s^{-1}. An experimental protocol had to be developed for the mechanical testing in order to ensure the results were representative and the reproducible, in particular regarding the material's drying. This protocol is presented in the section dedicated to these results.

Results and Discussion

The thermogravimetric curves obtained on the same series of samples are reported in Figure 2. All these curves show the same global characteristic with two significant mass losses. The first mass loss occurs at about 100 °C while the second mass loss is centered at 300 °C. The first mass loss is related to the evaporation of water (100 °C) presented at in the initial composition of the mixture before the thermal processing and to the evaporation of the glycerol (120 °C). Similar results have been reported with a conclusion that water and glycerol can evaporate at approximately the same temperature.[20–23] Thus it is nearly impossible to determine the amount of water and/or glycerol molecules which are engaged in this evaporation process. This is why; we evaluate only the combined evaporation of plasticizers. We obtained, for the mass loss at 100 °C, a loss of 10% for the sample with the smaller content of plasticizer. After mechanical compression, the thermogravimetric curve has given the same amount of mass too which indicates that mechanical deformation has not changed the sample global composition. For the sample initially with 25% of plasticizer, the mass loss is 15%, for the material with 30% of plasticizer, the evaporation concerns 20% of the initial mass. The measures also indicate that the process of expansion associated to the content of plasticizer leads to a maximum of plasticizer remaining inside the expanded material which cannot be greater than 10%. The second mass loss observed is at a higher temperature and corresponds to the degradation of the starch itself. The mechanical compression has no effect on the thermal stability of these materials. Table 1 summarizes the mass loss percentage for the processed materials and their degradation temperature according to the percentage of added plasticizers.

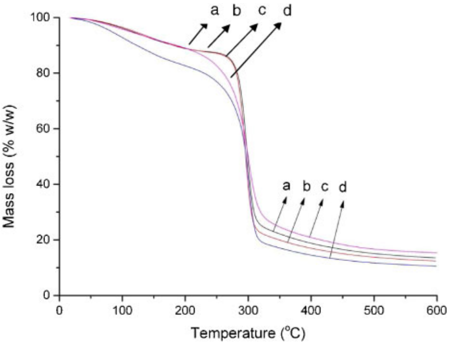

Figure 2.
Influence of the Glycerol content over the thermal stability of the materials: samples a (5% glycerol), b (5% glycerol) after compression, c (10% glycerol) and d (15% glycerol).

To summarize these results, it appears that the expanded materials are chemically stable for temperature below 100 °C. We will also have to keep in mind that the content of glycerol given here, corresponds to the initial composition before expansion

Table 1.
The mass loss of the material and the thermal stability in relation to the plasticizers content.

Materials	Mass loss (%) at 100 °C	Plasticizers Composition After Processing	Degradation Temperature (°C)	Residual Mass After Degradation (%)
a	10%	5%	290 °C	17%
b	10%	5%	290 °C	17%
c	15%	10%	280 °C	18%
d	20%	10%	270 °C	16%

and that the expansion is the result of the evaporation of both water and glycerol molecules. As a result, it is expected that we have more gas released during expansion for the sample having an initial content of plasticizer of 30% than for the sample having a composition of 25% of plasticizers, for example.

It is known that the morphology of starch based thermoplastics is very sensitive to the composition (mainly the water content) and to the method and conditions used to process the final material.[24,25] Figure 3 shows the X-ray diffraction patterns for materials a, b, c and d initially with 20%, 25% and 30% of plasticizer. It can be seen from the plot of relative intensity versus the angle 2 theta (2θ) that the normal agglomerated wheat starch has sharp peaks for $2\theta \approx 15°$, 23° and 26° for all the samples which shows the presence of V_H (Orthorhombic system) and E_H (Hexagonal system) crystalline structures.[9,10] More precisely, the materials c and d exhibit an extra peak at $2\theta \approx 20°$ which characterizes the presence of the A- crystalline structure of native starch. The existence of the "A" structure proves that the native wheat starch granules have not completely melted by extrusion. For the results concerning the sample tested after compression, it appears that the crystalline pattern is the same as the one obtained before compression. In other words, the compression does not change the crystalline structure, and as a consequence since the structure depends upon the content of plasticizer, the compression does not change drastically the composition of the material neither for the diffusion nor segregation of plasticizer. The different values of the diffraction peaks are presented in Table 2. This table also reports the calculation of the degree of crystallinity, determined by measurements of the surface under the peaks according to the method already presented in the literature.[26,27] The degree of crystallinity varies from 24 to 35% and depends upon the initial content of plasticizer with the following behavior: greater the initial content of glycerol, greater is the crystallinity of the final expanded material. This range of crystallinity is in agreement with what has been reported in the literature.[28,29]

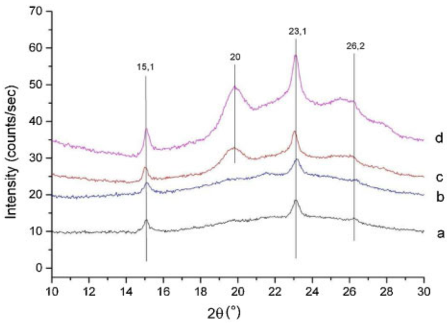

Figure 3.
X-ray diffraction patterns of wheat starch products for different glycerol contents: samples a (5% glycerol), b (5% glycerol) after compression, c (10% glycerol) and d (15% glycerol).

Figure 4 provides typical micrographs of cell wall sections for samples a, c and d. At this scale of observation, there is no qualitative effect of the glycerol content. From these images, the distribution of wall thickness, and the cavity size have been determined.

The distribution of the wall sizes are reported on figure 5. Two different families of walls were detected depending on the position of the measurement on the cell wall. Close to the junction of three cell walls, the thickness (called Thickness 2) is

Table 2.
The crystalline structures and crystallinity degree of the material according to the glycerol content.

Material (Glycerol %)	Diffractogram Parameters			
	≈ 2 θ/o	Type	Crystallinity	Intensity
a (5%)	16	E_H	24%	Medium
	24	V_H		Medium
	27	V_H		Weak
b (5%)$_{\text{compressed}}$	16	E_H	23%	Medium
	24	V_H		Medium
	27	V_H		Weak
c (10%)	16	E_H	31%	Medium
	20	A		Medium
	24	V_H		High
	27	V_H		Weak
d (15%)	16	E_H	35%	Medium
	20	A		High
	24	V_H		Very High
	26	V_H		Weak

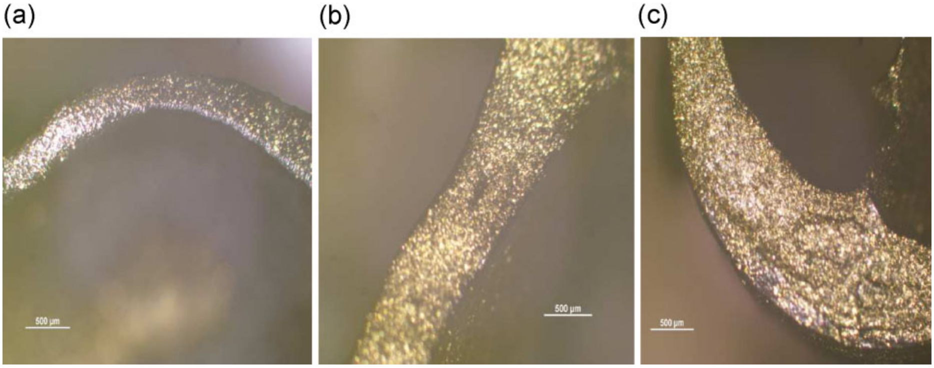

Figure 4.
Sectional view of the pore boundaries for different glycerol contents (samples a, c and d); magnification at 500 µm.

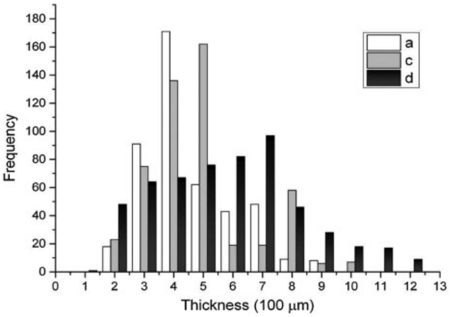

Figure 5.
Boundary thickness distribution for different glycerol contents: samples a (5% glycerol), c (10% glycerol) and d (15% glycerol).

larger than what is obtained in the middle of a cell wall (called Thickness 1). These values are reported in Table 3. Using the maximum in the distribution of thickness, we observe that greater the initial content of glycerol and whatever the position of the measurement, greater is the size of the cell walls. The size of the variation is larger for the initial high content of glycerol, and shows a narrow distribution for the lower initial content of glycerol. Thus, in spite of the fact that the content of plasticizer is the same after expansion for the two samples for which the content of glycerol was initially the highest, it appears clearly that

Table 3.
Wall thickness and pore size measurements according to the glycerol content.

Microstructure Characterization	a	c	d
Thickness 1 (μm) Near three-cell-junction	400	500	700
Thickness 2 (μm) At cell wall middle	700	800	1100
Pore diameter (mm)	4.6	4.1	–

the morphologies of the porous starch are not the same.

As can be seen, when the initial content of glycerol is high, the final expanded material tends to have thicker pore walls and less expansion. We have to notice that the material with initially 15% of glycerol, has no tubular form and consequently, it was not possible to calculate the cavity size for this composition. The cavity size is found to approximately be constant for the other compositions tested.

Mechanical tests consisted in compressing and unloading pile-ups of cylinders in a rigid box (Fig. 6) at a given strain rate. The length, number and spatial arrangement of cylinders have been set in order to minimize the scattering of measures of compressive stress from specimen to specimen. Once a pile-up has been built and before it is subjected to the compression test, it is preformed in a rigid box with fixed dimensions and stored at constant temperature and hygrometry for about 24 hours. With this protocol, specimens with identical dimensions and pre-stressing history are obtained, which enables to induce (i) reproducibility of tests from a specimen to specimen and (ii) compare results with different compositions. However, a small dispersion of results remains observable from one test to another. As a result, a given material was systematically characterized by means of at least three tests on three virgin specimens. Responses were then averaged over all the tests performed in the same conditions of loading. Figure 7 presents the stress-strain responses of materials a and c (5 and 10% glycerol in the initial composition) subjected to up to 50% compression at the strain rate 0.0028 s^{-1}. The engineering strain is considered, i.e. the current specimen height over its initial height. From a qualitative viewpoint, the constitutive

Figure 6.
Pile-up of 10 × 10 cylinders in a rigid box during compression.

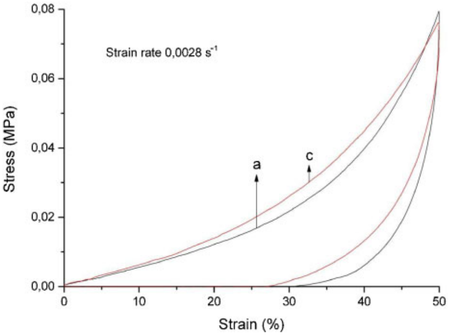

Figure 7.
Stress-strain curves for loading/unloading during compression tests of materials: samples a (5% glycerol) and c (10% glycerol).

Table 4.
Main characteristics of mechanical properties according to the glycerol content: samples a (5% glycerol) and c (10% glycerol).

Mechanical Properties	Compressive Strength at 50% imposed strain	Tangent Moduli at 0% strain	Elastic Recovery after 50% compression
Material a (5% gly)	0.079 MPa	1.5. 10^{-3} MPa	33%
Material c (10% gly)	0.075 MPa	1.5. 10^{-3} MPa	44%

behavior is quasi-linear up to 15% strain and then gradually hardens, which can be related to the process of densification of the material, arising as cell walls come into contact with each other under compression. It is worth nothing that the typical first two stages of deformation of large cell foams, namely characterized by deformation of cell walls followed by walls buckling, cannot be distinguished. This means that the material is too soft to enable the walls to support a stress of the order of the critical buckling stress corresponding to this thickness of the walls. Table 4 presents the main quantitative characteristics of the responses.

The materials exhibit similar compressive strengths and tangent moduli. The distinctive difference is the elastic recovery (i.e. the percentage of the maximum imposed strain which is recovered during unloading), which tends to increase with increasing the content of glycerol. In other words, increasing the glycerol would increase the ability of back stress elasticity to induce recovery, which is consistent with the main observations made from film materials.[30]

Conclusion

Different initial compositions in terms of water and glycerol have been used to process starch foam-like polymers with an expansion of the order of 300%. The obtained materials have been characterized in terms of thermogravimetry, optical microscopy, X-Ray analysis and mechanical testing. A dedicated experimental protocol had to be respected in order to inhibit any source of scattering. As plasticizers content is increased in the initial composition, their content in the product material saturates at a maximum of 10% in weight; the main effect of initial glycerol content on the product material's composition concerns the native starch granules: their melting during processing is inhibited by glycerol, as shown by the A crystalline structure in the X-Ray diffraction patterns. Concerning the microstructural morphology, thicker cell walls and smaller pores (i.e. smaller pores volume fraction) are obtained from larger glycerol content. There is a small effect of the composition on the strength and tangent moduli measured from compressive tests. This means that, for identical microstructural morphology in terms of cells and pore sizes, the higher the glycerol content, the softer the material. A tendency of glycerol to enhance back stress elasticity to dominate recovery has been shown. Further analyses will enable more precise charatrization of the elasto-visco-plastic nature of the constitutive behavior through cyclic compressive tests at different strain rates.

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