ORIGINAL PAPER

Preliminary XRD and IR investigation of some starch based biodegradable systems

MIHAI TODICA[1], NICOLAE CIOICA[2], LOREDANA ELENA OLAR[3], IONEL PAPUC[3], CONSTANTIN COTA[2], EUGEN MARIN[2], DRAGOŞ MANEA[2], ELENA MIHAELA NAGY[2*]

[1] *"Babes-Bolyai", University, Faculty of Physics, 1 Kogalniceanu str, Cluj-Napoca, Romania*
[2] *INMA Bucharest, Branch Cluj-Napoca, 59 Al. Vaida Voevod str., Cluj Napoca, Romania*
[3] *USAMV, Departments: I Preclinic and III Paraclinic,3-5 Manastur route, Cluj-Napoca, Romania*
[*] *Corresponding author: Elena Mihaela Nagy, E-mail: nagy@inma.ro*

Abstract

New biodegradable materials, with applications in packaging, can be obtained by plasticization of starch with glycerin and water. The physical properties of new materials are different from those of the initial components, and some properties of the initial components are subject to modifications during the synthesis process. Such modifications were investigated by XRD and IR spectroscopy. For this aim some new types of packaging materials with different starch, glycerin and water (mass %) ratios were prepared and investigated after extrusion process. XRD measurements indicate a progressive degradation of the ordered phase of the starch in function of glycerin and water content of samples. It can be observed that increasing of water concentration leads to a progressive degradation of the ordered structure of pure starch, (samples P1 and P2), until a completely amorphous phase that appears at highest water concentration (sample P3 having starch/glycerin/ water 68/17/15 mass % ratio). These modifications can be correlated with the IR observations.

1. Introduction

The manufacturing of biodegradable packaging is one of the challenges of our times requested by the necessity of reducing the pollution generated by the enormous quantity of residual wastes produced daily by the humanity. Many materials are used for this purpose, such as paper, wood, cellulose, plastics, but each of these materials gives some disadvantages. The products obtained from cellulose and wood can be destroyed by burning or putrefaction, but both methods are pollutant. On the other hand the production of these materials leads to excessive exploitation of the forests, with negative effects on the climate and environment. The oil based plastics can be easy obtained but their recycling is expensive and leads to collaterally pollutants emissions and extensively exploitation of oil resources. An alternative is the use of regenerative materials obtained from crops or other vegetables which can be recycled naturally, with low potential of pollution. Starch is one of the most promising materials for this purpose, which offer some advantages compared with other materials. It can be easier obtained at low costs from many plants, corn, potatoes, etc. and has the advantage of wide availability from agricultural exploitations, and total recycling without toxic residues, (F. XIE &.al. [1], H.LIU & al. [2], N.CIOICA & al. [3]). However, starch, in the natural state, cannot be used for packaging, due to its low mechanical properties and low resistance to water. Improvement of its qualities can be obtained by blending with different plasticizers. According to the literature glycerin is the most commonly used for this purpose (H.LIU & al. [2]). The challenge is to find the best composition of starch/plasticizer to ensure enough

mechanical resistance requested for the use as packaging material, and on the other hand the possibility to recycle it using the simplest ways, burning or hydration. Starch, in its natural state, and the pure glycerin can be easy destroyed or recycled without pollutant effect of the environment. However, during the plasticizing process modification of the physical and chemical properties of the components can occur, with negative effects on the recycling process. Our interest is to know if the initial properties of the components were modified during this process and what are the properties of the new material obtained. For this purpose we prepared many systems with different composition of starch/glycerin/water, and we analyzed theirs properties by XRD and IR spectroscopy.

2. Materials and Methods

We prepared using extrusion method, three samples with different starch/glycerin/water content, as presented in Table 1, named P1-P3. We used corn starch manufactured by SC Amylon Sibiu, Romania, with 21 % amylase, 10.76 % (wt. b) water content, particle sizes between 2.3 and 37.3 μm and density of 0.561 g/cm^3, glycerin with 99.5% purity and density of 1.262 g/cm^3, and distilled water. For homogenization, the components were thoroughly mixed and stored in sealed containers for 24 hours before performing the tests.

Table 1. The ratio of starch/glycerin/water components in the developed formulas

Sample	Starch [%]	Glycerin [%]	Water [%]	Starch/ Glycerin ratio	starch/water ratio
P1	78	19.5	2.5	4	31.2
P2	72	18	10	4	7.2
P3	68	17	15	4	4.53

To conduct the extrusion process, it was used a corotating intermeshing twin-screw extruder ZK 25 Collin with a die plate with one orifice of 3 mm. The extruder screws has a diameter of 25 mm and a length to diameter ratio of 30:1. The screws speed was 150 rpm and the cylinder temperatures (from the feeding point to the die) were 30, 50, 80, 100 and 120 ^{o}C, respectively. The XRD measurements were performed with Brucker X-ray diffractometer with Cu Kα (λ = 0,154 nm) at 45 KV and 40 mA. The 2θ range of 10 - 90º was recorded with 0.1 º resolution. The FTIR absorption spectra were recorded in 400 - 4000 cm^{-1} spectral range with JASCO FTIR 4100 spectrometer.

3. Results and Discussions

XRD analysis

The native starch is a semi-crystalline material which contains mainly two chemical compounds: the amylase, which is a linear structure, and the amylopectin which is a branched structure. Physically, it contains both amorphous and crystalline regions (H.LIU & al. [4], JANE [5], R. F. TESTER & al. [6]). The crystalline region is determined mainly by the amylase and branching points of amylopectin, while the amorphous phase is associated to the

short-branched chains of amylopectin. During the plasticizing process the native starch is combined with glycerin and water and submitted to a mixing-shearing processes at high temperatures (90° - 180°C) (CIOICA [7]). Such operations involve many physical changes such as water diffusion, granular expansion, gelatinization, decomposition, melting and crystallization (H.LIU & al. [2]), followed by the modification of the local structure of the composition. The character and the intensity of such modifications depend on the initial composition of the melt and can be observed by XRD technique. Our samples were submitted to the same experimental protocol, but theirs compositions were different. The diffractogram of pure starch shows a broad region between 10° and 27° with some distinctively peaks, (Fig. 1). The shape of the spectrum suggests the superposition of amorphous and crystalline phases. As presented previously the amorphous phase is associated to the short-branched chains of amylopectin. The main peaks are observed at $2\theta = 11.4°$; $15.3°$; $17.4°$; $18.3°$; $20°$ and $23.17°$. A broad peak with low amplitude is observed between $19.7°$ and $20.7°$. Some differences between the diffractograms appear after the introduction of the glycerin and water in the composition. As in the case of pure starch, the diffractograms of samples P1 to P3 contain a broad region in the $10° - 25°$ domain and some peaks superposed on this broad signal. These peaks are more or less intense depending on the composition of the samples. For the sample P3 the diffractogram is almost entirely dominated by this broad region without clear distinctive peaks, whereas the samples P1 and P2 contain some clearly peaks. The position of these peaks is shifted compared with the pure starch, and their amplitude decreases when the concentration of the starch decreases, (Fig. 1). For instance the peak at $11.4°$ for pure starch cannot be seen at this angle in the difractograms of samples P1 and P2. This peak is shifted to $12.9°$ for these samples. The shift towards greater diffraction angles means a structure with smaller interplanar distance (M.TODICA & al [8]). In the presence of water, due to the increasing of the local molecular mobility, the starch has the tendency to adopt a more compact structure with smaller interplanar distances. The intense peaks at $15.3°$, $17.4°$ and $18.3°$ of pure starch cannot be seen in the difractograms of samples P1 to P3.
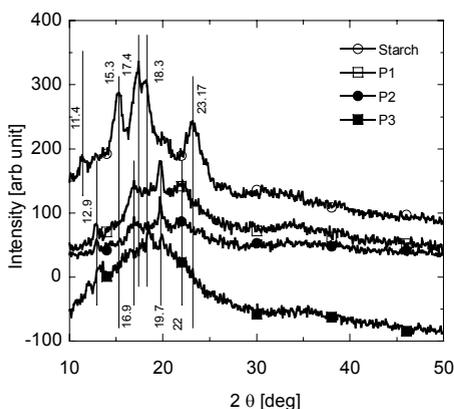

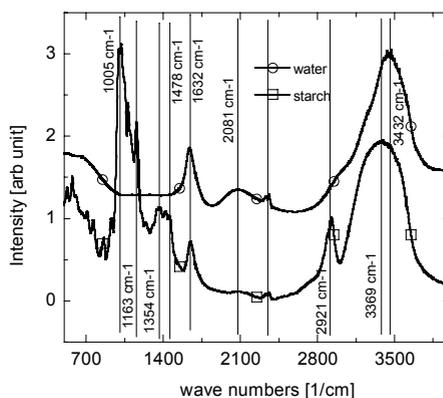**Fig. 1**. The XRD pattern of pure starch and P1, P2 and P3 samples

Fig. 2. The IR spectra of pure water and pure starch

These three peaks are correlated with the diffraction on three distinctive crystalline planes of pure starch and they are replaced by a peak at 16.9° in the spectra of P1 and P2 samples and they are almost absent in the spectrum of P3. That means a progressive degradation of the ordered structure of pure starch depending on the water concentration (samples P1 and P2), until a completely replacement by an amorphous phase at high water concentration (sample P3). The large peak between 19.7° and 20.7° of pure starch becomes narrow and can be seen at 19.7° in the spectra of P1 to P3 samples. The peak at 23.17° can be seen at 22° in the spectra of P1 and P2 and it is absent for P3. During the extrusion process, and in function of the water content, the amylose can recrystallize more rapidly than the amylopectin, fact that could explain the particularities of the diffractograms in this region (V. M-.F. LAI & al. [9]). For P1 to P3 samples the concentration of starch and glycerol deceases and the concentration of water increases continuously, but the ratio starch/glycerin remains constant (this ratio is 4). The progressive attenuation and the shift of the peaks of the pure starch can be attributed the slower crystallization process of amylopectin at high water concentration (K. J. ZELEZNAK & al. [10]).

IR analysis

The structural modifications induced by the composition and synthesis process of the samples could have effects on the vibrations of the molecular bonds. Such modifications can be revealed by IR measurements. We compared the spectra of P1 – P3 samples with the spectra of pure starch, pure glycerin and distilled water. The water molecules have a small moment of inertia allowing a multitude of possible rotation-vibration combinations, but in the liquid state the rotations are restricted by the hydrogen bonds which give rise to the librations. The resulting spectrum is a superposition of the individual lines of the librations, but the spectral distance between them is very small and the final spectrum is broad. Even in this situation some bands appear distinctively on the spectrum. We can see a well defined band at 1632 cm^{-1} that corresponds to symmetric stretch (v_1) of OH bonds, a small band at 2081 cm^{-1} assigned to combination of bend (v_2)+ libration, and a large and high band at 3432 cm^{-1} determined by symmetric stretch (v_1), asymmetric stretch (v_3) and overtone of bend (v_2), (Fig. 2). The spectrum of pure starch contains many broad bands, some of them appearing at the same wave numbers as in the spectrum of the water. For instance the band at 1632 cm^{-1} of water appears distinctively and without shifting in the spectrum of starch. The band at 2081 cm^{-1} appears as a shoulder with low intensity and without shifting. The large band 3432 cm^{-1} of water appears almost with the same width and the same amplitude in the spectrum of the starch, but shifted at 3369 cm^{-1}. The presence of these bands demonstrates the existence of some amount of water in the pure starch. However some vibrations of water are restricted in the starch, fact that explains the shift of the band at 3369 cm^{-1}. Other bands can be seen at 1005, 1080 and 1163 cm^{-1}. As shown by other authors the bands in this interval are sensitive to changes in crystallinity of the starch. The intensity of these bands is correlated with the orientation in intermolecular H-bonding of OH and CH_2 in CH_2OH (M. KACURAKOVA & al. [11], J. J. G. VAN SOEST & al. [12]). The superposed bands in the region of 1354 cm^{-1} and 1478 cm^{-1} may be assigned to conjugated carbonyl and carboxyl groups and C–O vibrations (M. H. NUOPPONEN & al. [13], L. G. THYGESEN & al. [14]).
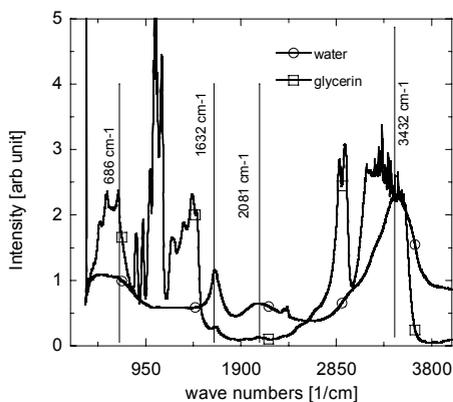
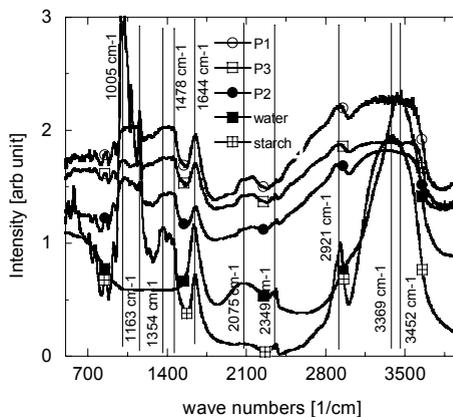**Fig. 3**. The IR spectra of pure water and pure glycerin

Fig. 4. The IR spectra of pure water, pure starch and P1 and P3 samples

A well defined band appears at 2921 cm^{-1}. A similar band was observed at 2930 cm^{-1} for other kind of starch of fresh tortilla by other authors and was assigned to vibrations of CH$_2$, (A. FLORES-MORALES & al. [15]). The IR spectra of P1-P3 samples contain the vibration bands of the starch, water and glycerin with amplitudes depending on their concentration (Fig. 4). For better comparison we presented in Fig. 3 the spectra of pure water and pure glycerin and in Fig. 5 the IR spectra of pure starch and pure glycerin. We observed that the spectra of starch and glycerin contain a lot of vibration bands located at the same wave number. Other bands can be observed for pure glycerin at 665 cm^{-1}, 848 cm^{-1}, 922 cm^{-1}, 1213 cm^{-1}, 1321 cm^{-1}, 1412 cm^{-1} and 3112 cm^{-1}. In Fig. 4 are presented the IR spectra of P1 to P3 samples. We can clearly see the band at 1644 cm^{-1} of pure water with an amplitude depending on the water concentration. P1 sample with 19.5% water gives the most intense band, and P3 sample with 10% water gives the weakest signal.
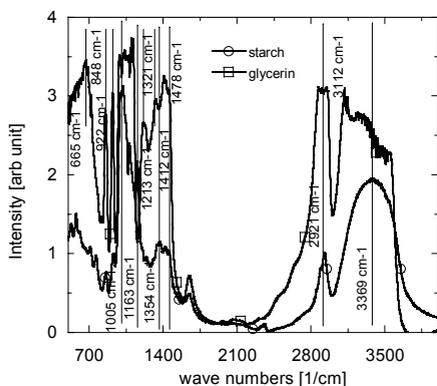

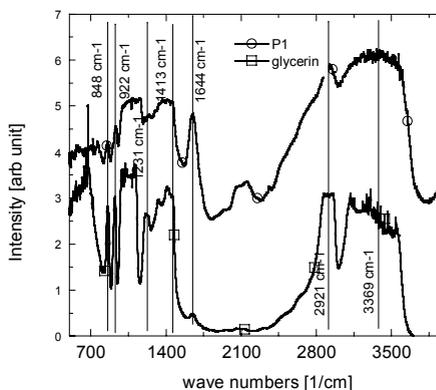**Fig. 5.** The IR spectra of pure starch and pure glycerin

Fig. 6. The IR spectra of pure Glycerin and sample P1

The large band of water around 3452 cm^{-1} appears in the spectra of P1 – P3 samples but it is broad and its centum is shifted towards lower wave numbers due to the superposition with the band at 3369 cm^{-1} of pure starch. The bands of pure starch between 1005 cm^{-1} and 1163 cm^{-1} cannot be seen separately but they merge into a large band with amplitude monotonically depending on the starch concentration for P1 – P3 samples. Same situation concerns the bands between 1354 cm^{-1} and 1478 cm^{-1}. The band at 2921 cm^{-1} appears unshifted but its amplitude is proportional with the starch concentration in these samples. The presence of glycerin in the samples is responsible for the large band between 922 cm^{-1} and 1231 cm^{-1}. Other large bands associated to the glycerin are centered at 1431 cm^{-1}. The band at 2921 cm^{-1} of pure glycerin can be clearly seen, without shifting, but with reduced intensity, at the same wave number. For easier comparison we presented in Fig. 6 the spectra of pure glycerin and of P1 sample.   For easier comparison we presented in Fig. 6 the spectra of pure glycerin and of P1 sample. The spectra of samples P2 and P3 are very close to this one. Generally the spectra of samples P1-P3 are smoothest than the spectra of pure glycerin, effect determined by the presence of starch and water in these samples, which mask a part of the bands of glycerin. The hiding effect is more pronounced when the concentration of glycerin decreases (samples P2 and P3). However a lot of vibrations of the glycerin molecules are not perturbed by the presence of the starch and water, fact confirmed by the presence of the vibration band of pure glycerin at the same wave numbers in the spectra of samples.

4. Conclusions

New system with applications in the packaging can be obtained by the plasticization of starch using glycerin. The XRD investigation reveals the existence of two phases, the crystalline and the amorphous one. The crystalline region is determined mainly by the amylase and branching points of amylopectin, while the amorphous phase is associated to the short-branched chains of amylopectin. Some modifications of the structural organization of starch appear in the presence of glycerin and water. Increasing of water concentration leads to a progressive degradation of the ordered structure of pure starch (samples P1 and P2), until a completely amorphous phase appears at high water concentration (sample P3).   The progressive attenuation and the shift of the peaks of the pure starch can be attributed to the low degree of crystallization of amylopectin at high water concentration. However these structural modifications are not followed by major modifications of the vibrations of the molecular bonds. This behavior is confirmed by the IR investigation. The spectrum of pure starch contains some bands which can be seen also in the spectrum of pure water at the same wave numbers, which indicates the presence of some amount of water trapped into the structure of starch. However some vibrations of water are restricted due to the crystalline phase of the starch, fact that explains the shift of the band at 3369 cm^{-1}. The modification of the intensity of the bands at 1005, 1080 and 1163 cm^{-1} is correlated with the orientation of intermolecular H-bonding of OH and CH_2 in CH_2OH of starch. The vibrations bands of pure components, starch, water and glycerin, can be seen in the spectra of samples P1-P2 with small modifications. Only some bands of pure starch appear shifted in the spectra of samples P1-P3, meaning a modification of some local vibration of starch molecules determined by the changes of the crystallinity. These observations are in accordance with the XRD measurements.

5. Acknowledgments

References

1. F. XIE, P. J. HALLEY, L. AVÉROUS, Rheology to understand and optimize processibility, structures and properties of starch polymeric materials, *Progress in Polymer Science*, 37, 595– 623 (2012);
2. H. LIU, F. XIE, L. YU, L. CHEN, L. LI, Thermal processing of starch based polymers, *Progress in Polymer Science*, 34, 1348-1368 (2009);
3. N. CIOICA, R. FECHETE, R. CHELCEA, C. COTA, M. TODICA, C. V. POP, O. COZAR, Water absorbtion and degradation of packages based on native corn starch with plasticizers, *Studia UBB Chemia, LX*, 1, 45-55 (2015);
4. H. LIU, L. YU, F. XIE, L. CHEN, Gelatinization of cornstarch with different amylose/amylopectin content, *Carbohydrate Polymers*, 65, 357–363 (2006);
5. J. JANE, Current Understanding on Starch Granule Structures, *Journal of Applied. Glycoscience*, 53: 205-213 (2006);
6. R. F. TESTER, J. KARKALAS, X. QI, Starch - composition, fine structure and architecture, *Journal of Cereal Science*, 39, 151–165 (2004);
7. NICOLAE CIOICA, Extrudere alimentare cu un melc scurt cu autoincalzire. Solutii de imbunatatire a parametrilor de lucru, Ed. Terra Nostra, Iasi, (2013)
8. M. TODICA, T. STEFAN, D. TRANDAFIR, S. SIMON, ESR and XRD investigation of effects induced by gamma radiation on PVA-TiO2 membranes, *Central European Journal of Physics*, 11, 7, 928-935 (2013);
9. V. M-.F. LAI, S. LU, C.-Y. LII, Molecular Characteristics Influencing Retrogradation Kinetics of Rice Amylopectins, *Cereal Chem.*, 77, 272-278 (2000);
10. K. J. ZELEZNAK, R. C. HOSENEY, The role of water in the retrogradation of wheat starch gels and bread crumb, *Cereal Chem.*, 63, 407-411 (1986);
11. M. KACURAKOVA, M. MATHLOUTHI, FTIR and laser-Raman spectra of oligosaccharides in water: characterization of the glycosidic bond, *Carbohydrate Research*, 284, 145–157 (1996);
12. J. J. G. VAN SOEST, D. DE WIT, H. TOURNOIS, J. F. G. VLIEGENTHART, Retrogradation of Potato Starch as Studied by Fourier Transform Infrared Spectroscopy, *Starch/Stärke*, 46, 453–457 (1994);
13. M. H. NUOPPONEN, H. I. WIKBERG, G. M. BIRCH, A. S. JÄSKELAÏNEN, S. L. MAUNU, T. VUORINEN, D. STEWART, Characterization of 25 tropical hardwoods with Fourier transform infrared, ultraviolet resonance Raman, and ^{13}C-NMR cross-polarization/magic-angle spinning spectroscopy, *Journal of Applied Polymer Science*, 102, 810–819 (2006);
14. L. G. THYGESEN, E. M. LØKKEY, L. MICKLANDER, O. B. ENGELSEN, Vibrational microspectroscopy of food. Raman vs. FT-IR, *Trends in Food Science & Technology*, 14, 50–57 (2003);
15. A. FLORES-MORALES, M. JIMENEZ-ESTRADA, R. MORA-ESCOBEDO, Determination of the structural changes by FT-IR, Raman, and CP/MAS ^{13}C NMR spectroscopy on retrograded starch of maize tortillas, *Carbohydrate Polymers*, 87, 61– 68 (2012);