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FT – IR INVESTIGATION OF THE PLASTICIZERS EFFECTS ON THE NATIVE CORN STARCH MACROSTRUCTURE

O. COZAR[a,b,c], C. COTA[b], N.CIOICA[b], E.M. NAGY[b], L. ŢIBRE[a]

ABSTRACT. The influence of the water and glycerol in various contents and ratios on the native corn starch is investigated by FT-IR spectroscopy. The changes in intensity of the bands from 1000 cm^{-1} region characteristics of amylose and amylopectin are correlated with the amorphous – crystalline forms of the studied starch samples. The increase of water and glycerol content until 10 – 12% leads to the prevalence of the amorphous phase.

Keywords: *starch, water, glycerol, FT-IR*

INTRODUCTION

Starch is a biopolymer with a very complex structure, formed by glycosidic linkages between glucose units, and presenting functional properties which make the polymer very helpful for the paper industry, the textile industry, and mainly the food industry. The ratio between amylose and amylopectin is fundamental in determining the functional properties of the starch [1,2].

Amylose is a molecule which is essentially linear, formed by D-glucose residues linked by α(1–4) bonds in a helicoidal structure; inside the helix it contains hydrogen atoms, which characterizes amylose as a hydrophobic species. This hydrophobic characteristic is very important in the biological medium, and allows the complexation with free fatty acids, and also with alcohols or iodine. On the other hand, amylopectin is a highly branched polymer formed by D-glucose units linked in an α(1–4) fashion, and containing only 5–6% α(1–6) bonds in the structure [1-3].

Many physical-chemical characteristics and properties of starch as viscosity, gelation power, adhesion etc., are strongly influenced by the amylose to amylopectin ratio [4].

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[a] *Babes-Bolyai University, Faculty of Physics, RO-400084 Cluj-Napoca, Romania*

[b] *National Institute of Research - Development for Machines and Installations designed to Agriculture and Food Industry-INMA Bucuresti – Cluj-Napoca branch, RO-400458 Cluj-Napoca, Romania*

[c] *Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094, Bucharest, Romania*

The vibrational spectroscopic techniques, such as IR spectroscopy and Raman spectroscopy are successfully used in the quantitative investigation of control analysis of starch for the food industry, characterization of some medical polysaccharides and quantitative investigation of amylose and amylopectin content in different starch samples [5-12].

Fechner et al. [5] have investigated the retrogradation of untreated wild-type starches (potato, corn and wheat) by employing Raman spectroscopy. The studies of potato starch retrogradation were also made by FT-IR spectroscopy [6]. Zhbankov et al. [7] characterized some medical polysaccharides, including amylose and amylopectin, by FT-IR and FT-Raman spectroscopy, whereas Schuster et al. [8] presented a novel approach to monitor starch hydrolysis by FT-Raman spectroscopy.

Flores-Morales et al. [9] determined the structural changes on retrograded starch of maize tortillas by FT-IR, Raman and CP/MAS ^{13}C NMR spectroscopy.

Iizuka and Aishima [10] directly observed some changes related to the gelation process of starch by using FT-IR / ATR spectroscopy.

Kizil et al. [11] applied FT-IR and FT-Raman methods, as well as discriminant analysis, for the rapid characterization and classification of selected irradiated starch samples. Sohn et al. [12] employed FT-Raman and near-IR reflectance spectroscopy to compare calibration models for determination of rice cooking quality parameters such as apparent amylose and protein.

Most native starches are non-plastic due to their crystallinity of about 20- 45% [2]. Amylose and the branching points of amylopectin form amorphous regions. The short-branched chain in the amylopectin is the main crystalline component in granular starch. Crystalline regions are present in the form of double helices with a length of ~5nm. The amylopectin segments in the crystalline regions are all parallel to the axis of the large helix. The molecular weight of amylopectin is about 100 times higher that of amylose. The ratio of amylose / amylopectin depends upon the source and age of the starch.

Thermoplastic extrusion is a thermo-mechanical processing used to disrupt and transform the semi-crystalline structure of starch granules to form a homogeneous and amorphous material. This transformation is usually accomplished by small amounts of molecular substances commonly known as plasticizers. The most used plasticizes are water, a volatile plasticizer and glycerol, a non-volatile plasticizer [13, 14].

The plasticizing – antiplasticizing effects of water and glycerol contents on starch samples and also the amylose / amylopectin ratios were recent investigated by various methods [15-18].

FT – IR investigation of various ratios contents of the water and glycerol on the macrostructure of native corn starch is also reported in this paper.

RESULTS AND DISCUSSION

Figs.1 and 2 show the characteristic IR spectra of starch samples with different amounts of volatile (water) and non-volatile (glycerol) plasticizer agents. The representative bands are situated in the following five regions: 3300 cm^{-1}, 2900 cm^{-1}, 1610 cm^{-1}, 1300 cm^{-1} and 1000 cm^{-1}. The two bands at 3300 cm^{-1} and 1610 cm^{-1} are ascribed to water stretching and bending vibrations [9, 10]. The other three absorptions are originated mainly from the vibrational modes of the amylose and amylopectin, the principal components of starch [9].

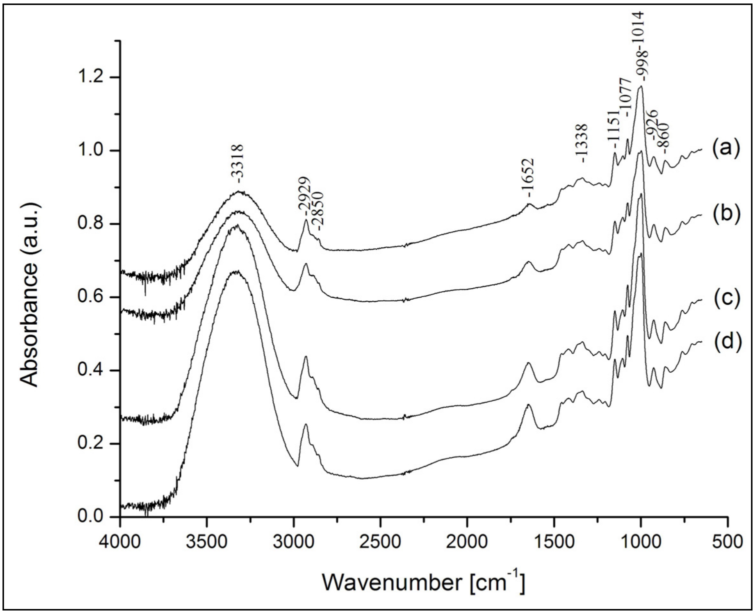

Figure 1. FT-IR spectra of samples with 4:1 starch:glycerol constant ratio and various water contents: 0%(a); 2.5%(b); 10%(c), 15%(d).

The two absorption bands from at 2930 cm^{-1} and 2850 cm^{-1} are assigned to vibrations of CH_2 groups [9]. The absorptions from 1350 cm^{-1} region are due to bending modes of O-C-H, C-C-H and C-O-H angles from amylose and amylopectin formations [19].

The strong absorption peaks appeared in the 1150 – 900 cm^{-1} region are assigned to C-C and C-O stretching vibrations [20]. The bands at 1000 cm^{-1} and 850 cm^{-1} are sensitive to changes in crystallinity and the intensity of 1000 cm^{-1} band determines the orientation in intermolecular H – bonding of CH and CH_2 in CH_2OH [9, 21].

It can be seen that the main intensity variations of the absorption bands without those of water 3318 cm^{-1}, 1652 cm^{-1}, with the content and ratio of the added plasticizers appear in the 1000 cm^{-1} region. These changes may by related with crystalline – amorphous forms ratio of the corn starch in the investigated samples. In principle, the amorphous regions are determined by amylose and branching points of amylopectin, while crystalline component by the short-branched chains from amylopectin [2].

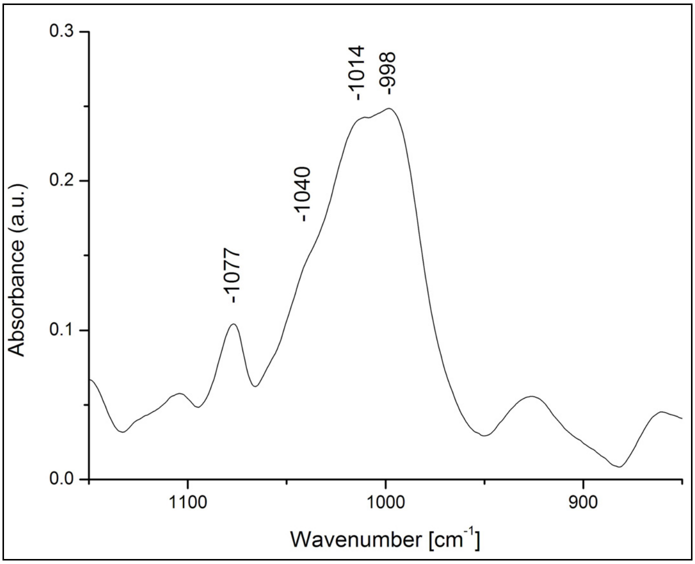

Figure 2. Extended region of 1000 cm^{-1} absorbtion of (b) IR spectrum from Figure 1.

On the other hand very little changes appear in the 2930–2850 cm^{-1} and 1350 cm^{-1} region bands with the modifications of the plasticizers content in the starch samples.

Taking into account the small changes in the intensity of 2928 cm^{-1} band for all the samples, the ratios of 998 / 2928 cm^{-1} and 1014/2928 cm^{-1} band intensities versus water and glycerol content are shown in Figs. 3 and 4, respectively.

According to Capron et al. [18] the intense absorption from 998 cm^{-1} may be assigned to hydrated crystalline domains whereas the band at 1014 cm^{-1} reveals the amorphous contribution of plasticizers in starch formulas. Iizuka and Aishima [10] mentioned also that the absorption peaks from 1000 cm^{-1} region assigned to C-C and C-O stretching modes of the polysaccharide backbone of amylose and amylopectin, increase in intensity with temperature, being closely related with gelatinization process.

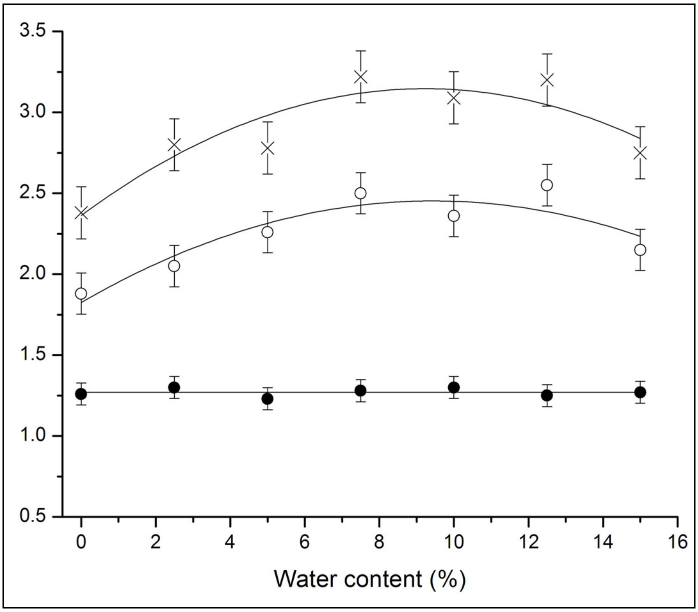

Figure 3. The dependence of 998 / 2929(x), 1014/2929(o) and 998/1014(•) ratios band intensities versus water content. (The errors bars are under 5% error limits)

A simultaneously increase of the 998 and 1014 cm^{-1} bands intensities with the increasing of water content until 10% and then a decreasing is observed in Fig. 3 for the samples with a fixed ratio of 4:1 between starch and glycerol (17-20%).

In agreement with NMR relaxation measurements [26] this fact suggested the appearance of new interactions between amorphous components at a larger spatial distance, which finally lead to a collapse of these components into a single amorphous phase for the studied starch samples. Also no change in the intensity of ratio 998 / 1014 cm^{-1} was observed (Fig. 3.) with varying water content suggesting an absence of structural order at the FTIR observation range. A similar situation is also mentioned for the 1000 / 1022 cm^{-1} ratio in the case of extruded starch and granular starch with water content fewer than 20% [18].

Many correlations between changes in the some band intensities from the 1000 cm^{-1} region (994, 1000, 1022, 1040, 1047, 1053 cm^{-1}) and the crystalline and amorphous phases (forms) of different starches are given in papers [6,9,17,18].

Analog results were also obtained in the case of samples where ratio between starch and water (12.5-15%) remains constant (5.66:1) and the glycerol increases from 0 to 16.5% (Fig. 3). The little increase of the 998 / 1014 cm^{-1} ratio versus glycerol content may be attributed to the reaching of the double helices on a more ordered structure [18].

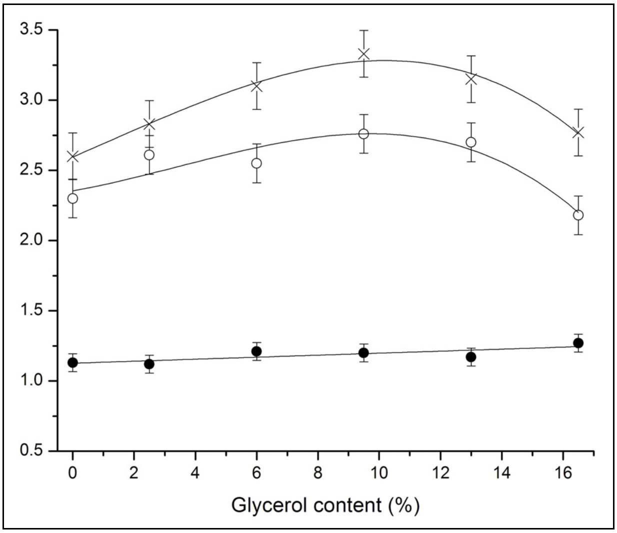

Figure 4. The dependence of 998/2929(x), 1014/2929(o) and 998/1014(•) ratious band intensities versus glycerol content. (The errors bars are under 5% error limits)

NMR relaxation data show also for these samples an increase content of lateral branches and free – end chain segments correlated with the decrease content of less mobile segments located in amylopectin core banches. In the same time the content of segments adjacent to junctions seems to be less affected by the increase of glycerol content.

The changes of the band intensities from 1000cm^{-1} region may be related with plasticizing – antiplasticizing effects of water and glycerol in function of their content in the studied starch samples. An analogous behavior amorphous – crystalline function of glycerol content in these samples was also emphasized in paper [26]. Raman and MAS-NMR data on these samples and their processing are in progress.

CONCLUSIONS

FT-IR spectra of the native corn starch with water and glycerol in various ratios and contents show the changes in intensity of the bands from 1000 cm^{-1} region characteristics to C-C and C-O stretching modes of the polysaccharide backbone from amylose and amylopectin.

These changes are correlated with the amorphous – crystalline forms of the investigated starch samples in function of plasticizers (water, glycerol) content.

In agreement with our NMR relaxation data on these starch samples results that the amorphous phase prevail until 10 – 12% water and glycerol content. The additional increasing of plasticizes content leads to the appearance of the crystalline form.

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 and an amylose content of 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.

Table 1 shows the ratio of the components in the used formulas. For homogenization, the components were thoroughly mixed and stored in sealed containers for 24 hours before performing the tests.

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

Sample	Starch [%]	Glycerol [%]	Water [%]	Starch/ Glycerol	Starch/ Water
1	100	0	0	-	-
2	80	20	0	4	-
3	78	19.5	2.5	4	31.2
4	76	19	5	4	15.2
5	74	18.5	7.5	4	9.87
6	72	18	10	4	7.2
7	70	17.5	12.5	4	5.6
8	68	17	15	4	4.53
9	71	16.5	12.5	4.3	5.68
10	74	13	13	5.69	5.68
11	77	9.5	13.5	8.1	5.68
12	80	6	14	13.33	5.68
13	83	2.5	14.5	33.2	5.68
14	85	0	15	-	5.68

FT-IR/ATR spectra were recorded at room temperature on a conventional Equinox 55 (Bruker, Germany) spectrometer equipped with a DTGC detector, coupled with an ATR sampling device (Miracle, Pike Techn.). The resolution was of 2 cm^{-1}. The ATR crystal is of ZnSe and we made 40 acquisitions for obtaining IR spectra.

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