RESEARCHES TO IMPROVE THE PHYSICAL - MECHANICAL PROPERTIES AND STRUCTURE OF THE BIODEGRADABLE PACKAGING MATERIALS FROM INDIGENOUS RAW MATERIALS

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OVERALL OBJECTIVE

The overall objective of this project is the development of knowledge by fundamental research, advanced researches for resolving some frontier complex issues, which suppose aninterdisciplinary approach in physics-chemistry-biology-engineering. By controlling nanostructural level phenomena, the projects aims to improve physical and mechanicalproperties and structure of biodegradable packaging materials made of local raw materials.

SPECIFIC OBJECTIVES

- Characterize physicochemical features of raw materials and investigate the effects of plasticizer on the structure and properties of local raw material combinations ofdifferent types and proportions.
- Study the processing behaviour of the recipes based on local raw materials forachieving biodegradable packaging materials.
- Structural and physical and mechanical characterization of biodegradable packagingmaterials made of local raw materials.
- Comparative study of results obtained
- Elaboration of some PhD theses

PROJECT STAGES

STAGE 1: 2011

OBJECTIVES

1. Research and evaluation of producing methods and characterization of thebiodegradable packaging

ASSOCIATED ACTIVITIES

1.1. Scientific documentation regarding the methods and techniques anticipated to be used in the whole project
1.2. Establish working methodologies

1.3. Development of a WEB page.

STAGE 2: 2012

OBJECTIVES

1. Experimental physicochemical characterization of raw materials

ASSOCIATED ACTIVITIES

1.1. Synthesis and acquisition of necessary components
1.2. Spectroscopic investigations on raw materials purchased

2. Investigation of the effects of the plasticizers on structure and properties of combination of indigenous raw materials by different types and proportions

ASSOCIATED ACTIVITIES

2.1. Identification of phase transformations to heating in the presence of plasticizers
2.2.Identification of phase transformations at heating and shear in the presence of plasticizers
2.3. Making rheometric measurements at different temperatures, shear stress and shear rate
2.4. Making measurements at the microscopic level (NMR) on viscoelastic behavior
2.5. Registration of IR and Raman spectrum
2.6. Mathematical and physical description of the process of "flow" for the polymer chains
2.7. Establishing the optimal protocol to investigate the effect of plasticizer on the structure and the properties of the analyzed combinations

3. Experimental study of processing behavior of the indigenous raw materials to achieve the biodegradable packaging materials

ASSOCIATED ACTIVITIES

3.1. Experiments to make packaging at different configurations of the screws
3.2. Experiments to make packaging at different rpm of the screw
3.3. Experiments to make packaging at different flow rat

3.4. Experiments to make packaging at different temperatures in the extruder zones and rolling cylinders

4. Reporting and disseminating the scientific results

ASSOCIATED ACTIVITIES

4.1. Presenting the results in 2 international conferences
4.2. Develop and submit for publication of 2-3 papers in ISI journals

STAGE 3:2013

OBJECTIVES

1. Structural and physico-mechanical characterization of the biodegradable packaging materials made from indigenous raw materials (Part 1)

ASSOCIATED ACTIVITIES

1.1.The microscopic structural characterization by IR, Raman, RES and NMR
1.2.Investigations of the surface by SEM
1.3.Physical characterization: degree of expansion, density, thermal analysis, stability

2. Reporting and dissemination of the scientific results

ASSOCIATED ACTIVITIES

2.1. Presentation of results at an international conference
2.2. Elaboration and submitting for publicationof 1-2 worksat international journals ISI rated

STAGE4: 2014

OBJECTIVES

1. Structural and physico-mechanical characterization of the biodegradable packaging materials made from indigenous raw materials (Part 2)

ASSOCIATED ACTIVITIES

1.1.Mechanical characterization: tensile strength, compressive strength, resilience
1.2. The study of biodegradability in water by measurements of viscosity and NMR

2. Reporting and dissemination of the scientific results

2.1. Presentation of results at an international conference
2.2. Elaboration and submitting for publication of one work at international journals ISI rated

STAGE 5: 2015

OBJECTIVES

1. Comparative study of the results obtained

ASSOCIATED ACTIVITIES

1.1.Study on the influence of components nature and proportion on characteristics of packages

1.2.Analysis of influence of working regime parameters on packages characteristics

2. Reporting and dissemination of scientific results (Part I)

ASSOCIATED ACTIVITIES

2.1. Presentation of results at an international conference

2.2. Elaboration and submitting for publication of one work at international journals ISI rated

3. Study on optimal variants which could improve the structure and physical and mechanical features of materials designed to biodegradable packages made of autochthonous raw materials (Part I)

ASSOCIATED ACTIVITIES

3.1.Analyzing and interpreting results.

STAGE 6: 2016

OBJECTIVES

1. Study on optimal variants which could improve the structure and physical and mechanical features of materials designed to biodegradable packages made of autochthonous raw materials (Part II)

ASSOCIATED ACTIVITIES

1.1. Optimizing the working characteristics and parameters

2. Reporting and dissemination of scientific results (Part II)

ASSOCIATED ACTIVITIES

2.1. Presenting the results at an International Conference

2.2. *Elaboration and submitting for publication of 2 works at international journals ISI rated*

PROJECT ABSTRACT

The main purpose of this project is the development of knowledge by fundamental research, advanced researches for resolving some complex frontier issues, which suppose an interdisciplinary approach in physics-chemistry-biology-engineering. The choice of project is justified by the need to improve the structure and physical and mechanical properties of packaging made of indigenous starch, which have an amylose content of max. 25%. Special emphasis is put on correlation between the structure of starch, the recipe used, working regime at processing by extrusion and rolling (configuration of the screw, rpm, flow rate,temperature) and the structure and physical and mechanical properties of the packaging obtained. The effect of heat, mechanical and chemical treatment during the processing will be

pursued both by appropriate physical methods, rheometry, viscoelastic methods, endurance, resistance to different solvents, through surface optical microscopy and through microscopic methods, which provide information on atomic and molecular level: RAMAN, IR, ESR, NMR. By controlling phenomena at nanostructural level will be possible to improve physical and mechanical properties and structure of biodegradable packaging materials made of local raw materials. The achievement of these objectives will lead to the extension of the knowledge base and the increase of the research capacity in the addressed areas, with favourable implications on the international competitiveness of the Romanian research.

RESULTS

STAGE 1

Stage 1 of the project took place between October-December 2011, aimed to research and evaluate the producing methods and characterize the biodegradable packaging, and it was structured on three activities as follows:

1.1. Scientific documentation regarding the methods and techniques anticipated to be used in the whole project
1.2. Establish working methodologies
1.3. Development of a WEB page.

Scientific conclusions of the report were:

- It was accomplished a scientific documentation about the methods and techniques applied or potentially applicable to manufacturing and characterization of biodegradable materials, especially those used as loose fill packaging
- The researches carried out worldwide highlight the fact that processing natural polymers, particularly the starch, is much more complicated and harder to control than at synthetic polymers because involves many physical changes and chemical reactions such as water diffusion, granular expansion, gelatinization, decomposition, melting and crystallization
- Our researches will consider especially the gelatinisation mechanism, which is the most important between these phase transformations, being the basic phenomenon that ensures the quality of finished product.
- The methodology which will be used will allow identification of transformations on heating and shearing, by extrusion of the starch, in the absence and presence of plasticizers. This identification will be achieved by instrumental thermal analysis. Rheometric measurements will be carried at different temperatures, shear stress and stress rate. To obtain information about the mixture structure at molecular and atomic level, will be performed measurements by microscopic methods (NMR, IR and Raman).
- The project website will provide stakeholders information on the results obtained throughout the project.
- The results obtained during stage 1 / 2011 have a theoretical value and will be used as a scientific basis in the following stages of the project.

STAGE 2 of the project took place from January to December 2012 and had the following ***objectives:***

l.Experimental physical-chemical characterization of the raw materials

2. Investigation of the effects of the plasticizers on structure and properties of combination of indigenous raw materials of different types and proportions

3. Experimental study of processing behavior of the indigenous raw materials to achieve the biodegradable packaging materials

4.Reporting and dissemination of scientific results

Components used in the studied recipes in this stage were starch as raw material and *glycerol and water* as plasticizers. We used local native starch, produced by Amylon SA Sibiu, glycerol purchased from SC Nordic Invest Ltd ClujNapoca and water from water supply system.

In order to experimentally characterize ***physical-chemical features of raw materials*** were performed chemical analyses and *spectroscopic investigations.*

Starch water content, determined by oven-drying method ISO 1666:1996, was 10.76% and amylose content determined using the method of hydration, centrifugation, vacuum concentration and precipitation with methanol was 21%.

Glycerol has a concentration of 99.5% and a density of 1.262 g/cm^3.

FT-IR/ATR spectra were performed at room temperature on a conventional Equinox 55 (Bruker, Germany) spectrometer equipped with a DTGC detector, connected with an ATR sampling device (Miracle, Pike Techn.). The resolution was of 2 cm^{-1}.

FT-Raman spectra were performed with a resolution of 2 cm^{-1} in a backscattering geometry with a Bruker FRA 106/S device equipped with a nitrogen-cooled germanium detector. The 1064 nm Nd:YAG laser was used as an excitation source and the laser power measured at the sample position was 350 mW.

The bands determined by this spectometric investigations, for raw materials, were used as a standard for *investigating the effects of plasticizers on structure and properties of combinations of raw materials.*

We used 14 combinations of starch, glycerol and water. One of the samples was the native starch with water content indicated above, and, the other combinations were resulted by adding to it water and glycerol in various proportions. At seven of them the starch/ glycerol ratio remained constant to 4/1 and water content was changed from 0 to 31.2%, while to the other six, remained constant the starch/water ratio to 5.7/1 and we changed the glycerol content from 0 to 33.2%. For this combinations we performed DSC, RMN, IR and Raman measurements and rheometry measurements.

The DSC measurements were performed on a Mettler-Toledo DSC1/700/227 differential scanning calorimeter, equipped with liquid nitrogen-cooling accessory, and have allowed the *identification of phase transformations when heating in the presence of plasticizers.* It resulted a decrease of glass transition temperature T**g**and melting temperature M**1** of the mixtures, these being 72^{0}C and 120^{0}C for the mixture with the highest plasticizers content, lower by 10^{0}C, and 30^{0}C than those of native starch.

To identify *the phase transformations at heating and shear in the presence of plasticizers* were performed DSC analyses of the products obtained from these combinations through shearing and heating into extruder. Although in this case, T**g**and M**1** are somewhat higher, however, especially the melting temperature, which is required to be as low as possible, is maintained at a much lower value than for the native starch.

To *make rheometric measurements at different temperatures, shear stress and shear rate* we used a Brookfield centrifugal viscometer, type DV-II+PRO over a range of share rates between 0 and 3.66 s^{-1}, at temperatures between 40 and 70 C. It was found that at low temperatures (t = 40 ^{0}C) there is a dependence of viscosity of the starch/glycerol/water depending on shear rate which does not comply with the Newtonian model. If the temperature increases (t = 50 ^{0}C), the viscosity continues to have a non-newtonian dependence of share rate, but its values decrease. If the temperature keeps growing (t = 60, 70 ^{0}C), this dependence tends to linearity.

The relaxometry^{1}H NMR measurements at the microscopic level on the viscoelastic behavior were performed using the BrukerMinispec spectrometer with the 10 mm probe-head, working at 19.688 MHz Larmor frequency.

The distributions of spin-lattice relaxation times T**1** have shown an oscillatory behavior of the degree of crystallinity according to glycerol content and a linear behavior along with of water content increment in the starch-water-glycerol mixtures used in the

manufacture of biodegradable packaging materials by extrusion. The distribution of spin-spin relaxation times T_2 of native starch and its combination with water present three dynamic components. Combining starch with glycerol leads to a distribution with four peaks, while remaining a significant part rigid enough, the other peaks being in the area with dynamic soft-solid behavior and similar to liquid. For the mixture of starch with glycerol and water are kept four peaks in the distribution of T_2but there is a more pronounced shift toward higher T_2times, the three major components being in the area with soft -solid and liquid-like behavior. It can be concluded that the addition of glycerol in the recipe leads to increased polymer chain mobility.

Registration of *IR and Raman spectra* of the mixtures was performed according to the methodology and equipment presented in characterization of the raw materials.The FTIR spectra of the mixtures, show changes in the intensity of bands in the 1000 cm^{-1} area, characteristics to C-C and C-O stretching modes of the main polysaccharide chain from amylose and amylopectin. These changes are correlated with the change of amorphous and crystalline phase ratio depending on the content of plasticizers. It was found that increasing the plasticizer content up to 10 - 12% leads to an increase of amorphous phase, over this content appearing the crystalline phase.

The Raman spectra of the analyzed mixtures showed a slight increase in intensity of the bands 940 cm^{-1} and 850 cm^{-1}, bands sensitive to changes in crystallinity compared to native starch,. It was found an increase in the proportion of starch amorphous phase, at plasticizers adding, up to 10%. At *mathematical and physical description of the process of "flow "for the polymer chains* of the mixtures, was found that equations of the form:

$$\sigma = a(\phi)\cdot\eta(T,\dot{\gamma})\cdot\dot{\gamma}\text{, where } a(\phi)\text{=ct. For a given concentration, and}$$

$$\eta(T,\dot{\gamma}) = \eta_0(T) + b(T)\cdot(\dot{\gamma})^{1.17}$$

where: $\eta_0(T)$resulting at the intersection of experimental curves with ordinate axis,
1,17 is the coefficient of the exponential equation that gives the best approximation of each curve, at a given temperature
$b(T)$ determined using Kaleidagraph software.
describes correctly in terms of mathematics and physics the polymer chains flow process, of the mixtures.

Based on the results obtained to achieve this objective, that shows that the methods used are applicable for highlighting processes and transformations that take place at plasticizers action on starch, was established *the optimal protocol to investigate the effect of plasticizer on the structure and properties of the analyzed combinations.* This protocol includes working methodology and manner of processing and interpretation of data for each investigation: differential scanning calorimetry (DSC) - to identify phase transformations on heating in the presence of plasticizers without and with shear; rheometry - to investigate flow properties; nuclear magnetic resonance (NMR)-for measuring at microscopic level and determining viscoelestic behavior; infrared spectroscopy (IR) and Raman - two different techniques which by different capacity to seize the molecular vibration give complementary indications on the starch structure mixed with plasticizers.

In order to study ***the processing behavior of the indigenous raw materials to achieve the biodegradable packaging materials, experiments*** were done on an 'ZK 25'extruder , manufactured by Collin GmbH, Germany with twin co-rotating modular screws. There were made loose-fill packaging withthree configurations andthree different screw speeds. Also, were made experiments withthree different feed flow rates, three different temperatures in die area and three different ranges of temperatureson extruder length.

In the next stages of the project will be made structural and physical-mechanical characterization of the products obtained from these experiments and will determine the optimal variants that lead to improve structure and physical-mechanical properties of biodegradable packaging materials made from local raw materials.

The results of the researches conducted in this stage of the project were ***disseminated*** *through papers presented at three international conferences and 2 published in international ISI journals.*

Papers published in ISI indexed journals

- O. Cozar , C. Cota, N.Cioica, E.M. Nagy, L. Tibre, FT - IR investigation of the plasticizers effects on the native corn starch macrostructure, Studia Univ. Babes-Bolyai, Chemia, LVII, 4, 23-32, (2012)
- N.Cioica, R. Fechete, C. Cota, E.M. Nagy, O. Cozar , L. David , NMR relaxation Investigation of the native corn starch structure with plasticizers, Journal of Molecular Structure, 1044, 128-133 (2012)

Papers published in ISI indexed proceedings of international conferences

- N. Cioica, M. Tomoaia-Coti§el, C. Cota, M. Fene§an, A. Mocanu, E. M. Nagy, The influence of plastifiants' content on rheology, microstructure and expansion index of corn starch - basedpacking peanuts, Procedings of the 40th International Symposium „Actual Tasks on Agricultural Engineereing", Opatija, Croatia, 395-402 (2012).
- N.Cioica, R. Fechete, C. Cota, E.M. Nagy, O. Cozar, L. David , NMR investigation of the structure of corn starch with plasticizers used to obtain loose fill packing, 31st European Congress on Molecular Spectroscopy, Cluj-Napoca, Romania, Poster PS1-13 si Book of Abstracts, 170 (2012).
- N.Cioica, R. Fechete, C. Cota, E.M. Nagy, O. Cozar , C.V.Pop, Structural changes of the corn starch from Romania used to make biodegradable packaging, Procedings of the 41th International Symposium „Actual Tasks on Agricultural Engineereing", Opatija, Croatia, 398-404 (2013).

Papers published in IDB indexed journals

- N.Cioica, R. Fechete, O. Cozar, C. Cota , Investigate the effect of some plasticizers on the macrostmcture of corn starch used to obtain biodegradable packaging, INMATEH - Agricultural Engineering, Tome 36, 6972, (2012)

STAGE 3 of the project took place from January to December 2013. This stage had the following ***objectives:***

1. Structural and physico-mechanical characterization of biodegradable packaging materials made of indigenous raw materials (Part 1)
2. Reporting and disseminating the scientific results

At the first objective microstructural characterization was performed through IR, Raman, ESR and NMR, investigation of surfaces microstructure in cross and longitudinal section of the samples by SEM and physical characterization in terms of the expansion index, density, thermal analysis and stability of biodegradable packaging made in the previous stage, of indigenous raw materials, were performed.

Besides the effective characterization was made an analysis of changes during the experiments and, on this basis, for the most successful product obtained from experiments, were compared its characteristics with those of a standard product manufactured by FP International, USA.

FT-IR/ATR and Raman investigations were performed at room temperature on the equipment and in conditions described in stage 2.

Absorption bands at 2930 cm^{-1} and 2860 cm^{-1} are attributed to the vibrations of CH_2 groups. Absorption in the region 1338 cm^{-1} are caused by the angles bending modes O-C-H, C-C-H and C-O-H from amylose and amylopectin formations.

The strong peaks of absorption appeared in the region 1150 - 900 cm^{-1} are assigned to C-C and C-O stretching vibrations. Bands in the region 1000 cm^{-1} are sensitive to changes in crystallinity and the intensity of the 1000 cm^{-1} band determines the orientation in the intermolecular hydrogen bond of CH and CH in CH_2OH.

We can make correlations between changes in intensity of some bands in the region of 1000 cm^{-1} (999, 1015 cm^{-1}) and the crystalline and amorphous phases of the various extruded samples. Thus, the intense absorption at 999 cm^{-1} can be attributed to the hydrated crystalline domains, whereas the band at 1015 cm^{-1} reveals the amorphous contribution of the plasticizers in extruded samples. Meanwhile, for the extruded samples, the 1015 cm^{-1} band is more intense than the 999 cm^{-1}band, resulting, thus, that in extruded samples the amorphous domain prevails.

Decreased intensity of the bands at 3300 cm^{-1} and 1645 cm^{-1} is related to the amount of water lost during processing, the greater this amount being, the more processed mixture contained a higher amount of plasticizer relative to starch content . The ratio of bands around 1000 cm^{-1} (1017/991), which are directly related to the crystallinity degree of packaging, decreases with increasing plasticizers content of the recipe, in the case of packaging of best quality the two phases, crystalline and amorphous, having very close weights. Also, the absorption bands in the 1150 cm^{-1} and 1078 cm^{-1} zone decrease in intensity, which indicates an increase in the influence of plasticizers on the packaging structure.

FT-IR spectra of the mixture, with a ratio of starch/ glycerol/water: 68/17/15 before and after extrusion and of the standard product show the existence of two bands of 3000 cm^{-1} and 1650 cm^{-1} which are attributed to stretching and bending vibrations of the water. The other absorptions derived from vibrational modes of the amylose and amylopectin, the main components of starch.

In the case of *Raman spectras,* intensity changes observed in absorption band 2902 cm^{-1}, 1460 cm^{-1} , 1335 cm^{-1}, 1120 cm^{-1}, 850 cm^{-1} and 474 cm^{-1} with total content and the different ratio of plasticizer indicate changes in the crystalline-amorphous ratio of extrudates. Basically the amorphous part of the extrudates is determined by amylose and amylopectin linear branches and the crystaline part is determined by branched chains of amylopectin.

Since the ratio of amylose and amylopectin remains constant, it follows that the ratio between the amorphous part and crystalline part of extrudate depends on the number of hydrogen bonds that are responsible for its hardening.

FT-IR and Raman analyzes allowed the interpretation of the influence of plasticizer content on extruded products according to the amount and ratio of plasticizers in the formula but did not occurred significant changes of the spectra depending on processing conditions used in the experiments.

In order to characterize by *Electron Spin Resonance (ESR),* packaging samples were exposed to y radiation from a ^{60}Co source (GAMMA CHAMBER 900) in ambient conditions. ESR spectra were recorded at room temperature with a spectrometer JEOL-JES-3B operating in the X-band (~ 9.5 MHz) with a 100 kHz field modulation, equipped with a computer acquisition system. Simulated -computer analysis of spectra to obtain the magnetic parameters features has been done using a program that is available on the Internet (http://alfred.niehs.nih/LMB).

For the packaging sample obtained by processing the mixture starch/glycerol/water 68/17/15, ESR spectra of irradiated sample consists of a triplet and a doublet heavily centered around g value= 2.0035. Triplets can be attributed to radical CH_2OH and OH radical doublet of starch structure. Hyperfine splitting in the triplet case is 26.1 G and for doublet is 32 G.

*^{1}HNMR relaxometry*measurements on viscoelastic behavior of the samples were performed at room temperature with equipment and in conditions described in 2-nd stage. The outcome measurements for spin-lattice relaxation time, T**1,** provided information on the morphology and degree of crystallization of the samples. There was an increase in the amorphous component for the packaging represented by the sample obtained through extruding mixtures with a ratio starch/glycerol/water 68/17/15 where high peak is located at T_1 ~ 90 ms and lower peak is located at T_1 ~ 15 ms compared with the other samples, where high peak stands at T1 ~ 65 ms and peak lower in T_1 ~ 5 ms.

For the standard product has been also found that high peak is located at T_1 ~ 90 ms, which may be associated with the amorphous phase.

From the distribution of spin-spin relaxation times T**2** was observed that, for the sample mentioned above, that had best met the conditions imposed on a loose fill packaging, peaks have been more pronounced in the mobile zone.

^{13}C CP /MAS NMR spectra of the same extruded samples were obtained on a BrukerAvance III at room temperature, using a spin frequency of 14 kHz. Analysis of the spectra showed that the most pronounced crystalline behavior appears in the spectrum of the mixture before extrusion.

Microstructure of the extruded samples analyzed with previous methods too, and of the standard sample, as cross-sectional and longitudinal section, were analyzed by *scanning electron* microscopy (SEM) using a microscope manufactured by FEI Company, the Netherlands, with a secondary electron detector Everhart Thornley (ETD).

Analyzing the images of selected samples was observed that with the decrease in glycerol content and increasing water content up to a limit that ensures a product that can be used as loose fill packaging, there is a change in pores shape and an increase of their size. This move from closed elongated and quite small pores, to semi-open greater pores with a balanced form in the three directions. In addition, at the sample with the optimum content of plasticizers the pores are separated from each other by thin bridges.

Changes in the structure of the analyzed samples allow to explain the difference between the *expansion index* (min.5, 6% / max.25%) and *apparently density* (max. 0,560 g/cm /min.0,012 g/cm^3) of the samples.

Thermal stability of the extruded samples was investigated by differential thermal analysis (TG-DTA) using a DTG 60H analyzer manufactured by Shimadzu, Japonia. It was observed that up to ~ 50 ^{o}C the sample loses initial weight. Further on, the sample weight remains constant until ~ 210 ° C after which great weight loss due to degradation of components, mainly of starch take place. Between 50 ° C and 210 ° C, the samples analyzed are thermally stable.

Reporting and disseminating the scientific results

Papers published in ISI journals

- O. Cozar, N.Cioica, C. Filip, C. Cota, *Structural FT-IR and ^{13}C CP/MAS NMR investigation of native starch with plasticizers before and post extrusion process,* Studia Univ. Babes-Bolyai, Chemia, LVIII, 4, 275-283 (2013)

Papers published in ISI indexed proceedings of international conferences

- O. Cozar, C. Filip, N.Cioica, C. Cota, C. Tripon, E.M. Nagy, *Determination of the Structural Changes by Raman and ^{13}C CP/MAS NMR Spectroscopy on Native Corn Starch with Plasticizers,* AIP Conference Proceedings 1565, 39-42 (2013)

Papers published in IDB journals

- G. Fodorean, C. Cota N. Cioica, *Influence of rotation speed during extrusion to the properties and morphology of biopolymers blend,* ActaTechnicaNapocensis, Series: Applied Mathematics and Mechanics Vol.56, Issue III, 493-496 (2013)

STAGE 4 - of the project was developed during December 2013-December 2014. This stage had the following *objectives*:

1. Physico-mechanical and structural characterization of biodegradable packaging materials made from local raw materials (Part 2)
2. Reporting and dissemination of research results

Within this objective the mechanical characterization was performed in terms of tensile strength, compressive strength and resilience as well as the water biodegradability study by viscosity measurements and NMR.

And to this objective,besides the effective characterisation was made an analysis of the evolution of the results during the experiments and, on this basis, for the most successful product obtained at experiments, were compared its characteristics with those of a standard product, manufactured by FP International, SUA (http://www.fpintl.com/application-bible.htm).

The physico-mechanical activity was performed on specimens of biodegradable starch based material and consisted in tensile tests, compression tests and tests of resilience.

The mechanical tests were performed on a tensile-compression testing machine INSTRON-3366.

The results of traction application were centralized in the Bulletin of measurements presented in Table 1.

Table 1 Values obtained at the tensile test

Test specimen	Maximum force N_{max} [kgf]	Initial sectional area A_0 [mm^2]	Breakingtension $\sigma_{rt}= N_{max}/ A_0$ [kgf/mm^2]	Total elongation Δl [mm]	Specific deformation $\varepsilon=\Delta l/l$ [%]	Active length of the test specimen l [mm]
INMA packaging	1.65	201.06	0.0082	14.2	129.09	11
Standard packaging	1.5	154.46	0.0097	15.1	137.27	11

The results obtained from the compressive stress were centralized in the Bulletin of measurements presented in the Table 2.

Table 2 Values obtained at the compressive test

Test specimen	Maximum force N_{max} [kgf]	Initial sectional area A_0 [mm^2]	Breaking tension to compression $\sigma_{rt}= N_{max}/ A_0$ [kgf/mm^2]	Shortening Δl [mm]	Specific deformation $\varepsilon=\Delta l/l$ [%]	Length l [mm]
INMA packaging	34.0	201.06	0.1691	22.5	90.00	25
Sample packaging	19.5	154.46	0.1262	39.5	94.04	42

For the resilience calculationwas used the method ofthe ratio of the mechanical work of breakingto the breaking-sectional area.

$$KCU=L / A \ (J / mm^2)$$

where L is the mechanical work consumed to break test specimen,

A –the breaking sectional area, (mm^2)

The mechanical work consumed was determined by measuring with a laboratory apparatus type CHARPY pendulum. It has the measurement range between 0 and 0.4 J.

The results are shown in the Table 3

Table 3 Values obtained at the resilience test

Test specimen	Mechanical work [J]	Breaking sectional area A_0 [mm^2]	Resilience KCU= L/A [J/mm^2]
INMA packaging	0,08	121,25	$6,59 * 10^{-4}$
Sample packaging	0,084	121,25	$6,92 * 10^{-4}$

The study of the biodegradability in water was done both by viscosity measurements and by NMR

The viscosity measurements were performed with a Brookfield DV-III Ultra programmable rheometer with a range of rotational speeds between 0.01-250 rot / min. To determine the viscosity at different temperatures the samples were heated in a recirculating bath type TC 150SD Brookfield with digital controller, with a measuring range of 10-150 °C. The viscosity was measured for 3 packing samples with the ratio of starch / glycerol / water differently, at four different temperatures (30,40,50 and 60 °C) and at rotational speeds ranging between 5-200 rot / min for each of the samples. The viscosity was measured after the

samples have absorbed the maximum amount of distilled water and were completely degraded. After each measurement was verified the total mass (container, sample and water) and the water loss due to the evaporation were completed to achieve the initial weight (Table 4).

Table 4 The amounts of sample and distilled water used for the rheological measurements

Sample of packaging	The ratio 78/19/2.5 starch / glycerol / water	Mass of dry sample [g]	Mass of distilled water [g]	Initial mass container, sample and water [g]
1	78/19/2.5	24.49	39.19	86.11
2	72/18/10	13.93	39.19	77.43
3	68/17/15	0.80	20.00	48.36

With the increasing of temperature (60 °C) the viscosity variation with the speed no longer corresponds to the Newtonian model.The transition from a non-Newtonian behavior to a Newtonian behavior indicates that the conglomerates of polymer structurestransform intosmaller elementswith spherical symmetry,characteristics to the simple Newtonian liquids - clear evidence of the degradation.

The study of biodegradability in water by *NMR measurements* was made on four types of products: a standard product and three products with different ratios of starch, glycerol and water, shown in Table 5, which have been subjected to the natural degradation after the absorption of distilled water. The normalized mass of water absorbed within the five days by the three packing samples based on native corn starch with different formulas is shown in Fig.1. The packaging samples with the ratio starch / glycerol / water of 68/17/15 was degraded after 1 day.

Table5 - The ratio of componentsstarch-glycerol-water in recipes

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	Standard product with unknown formula				

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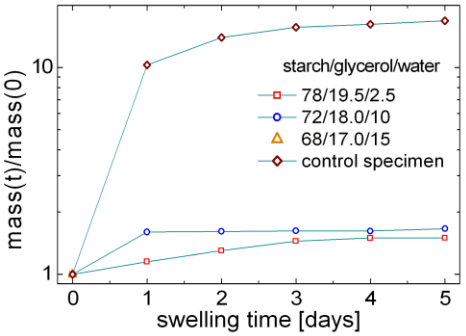

Fig.1.The normalized mass absorbed during of 5 days by the 3 packaging sampleswith constant ratio of 4: 1 starch / glycerol compared with the standard sample

The hardest sample, with a lower water content (sample 1) has absorbed thelowest quantity of water (around 50% from sample`s massin day 5) with the lowest speed. If the water content in the formula increases, then the amount of water absorbed and the absorption speed increase (Figure 1)

To monitor the degradation in distilled water of the four types of packaging materials have been made at this stage, relaxometry measurements^{1}H NMR. For the samples 3 and 4 that have been degraded very fast after the day 1 and 2, were made NMR measurements in colloidal state.

The ^{1}H RMN relaxation measurements were made using the MinispecBruker spectrometer. Larmor frequency was 19.688 MHz and the temperature was set to 35° C. For the T_2 spin-spin relaxation time measurements the pulse lenght was of 10.1 µsand 4000 CPMG echoes were recordedwith 256 scans and a recycle delay of 0.5 sec, which acts as a filter $T_1$to reduce the contribution of 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. In Fig. 2 are presenting the CPMG echoes for the packaging samples 1 and 3.The curves recorded at 1-5 days are compared with the CPMG decay curves recorded for the dry sample.

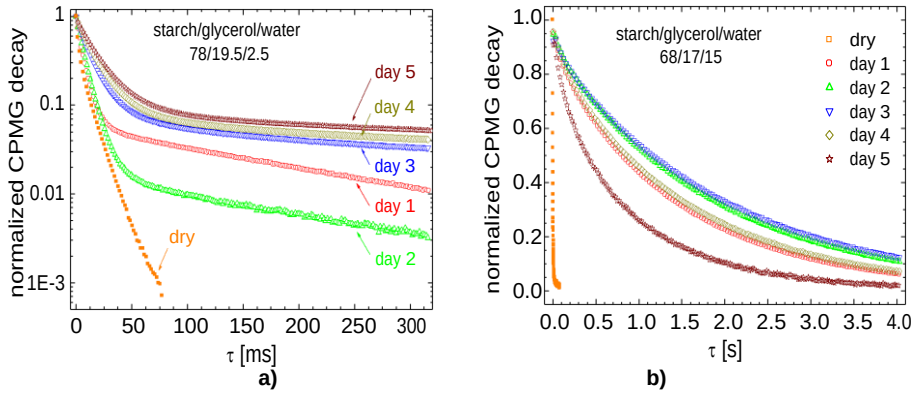

Fig.2. CPMGdegradationcurvesduringthe 5 daysof the testcompared to thedrysample for the mixtures ofstarch/ glycerol/water78/19.5/2.5 (a) and 68/17/15 (b).

In both cases the CPMG curve measured for the dried samples decreases much faster than for the packaging samples with absorbed water. For the dry sample 1 - Fig. 3a),most of the reservoirs^{1}Hare characterized by values of T_2 of approx. 2.5 msand 11 ms which can be considered as semi-mobile, and a small^{1}H reservoir characterized by values of T_2 of approx.50µslocated in a rigid area(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 to a collapse of the peaks located at T_2 values of the milliseconds order to a unique peak located at T_2 values of about 6.3 ms.

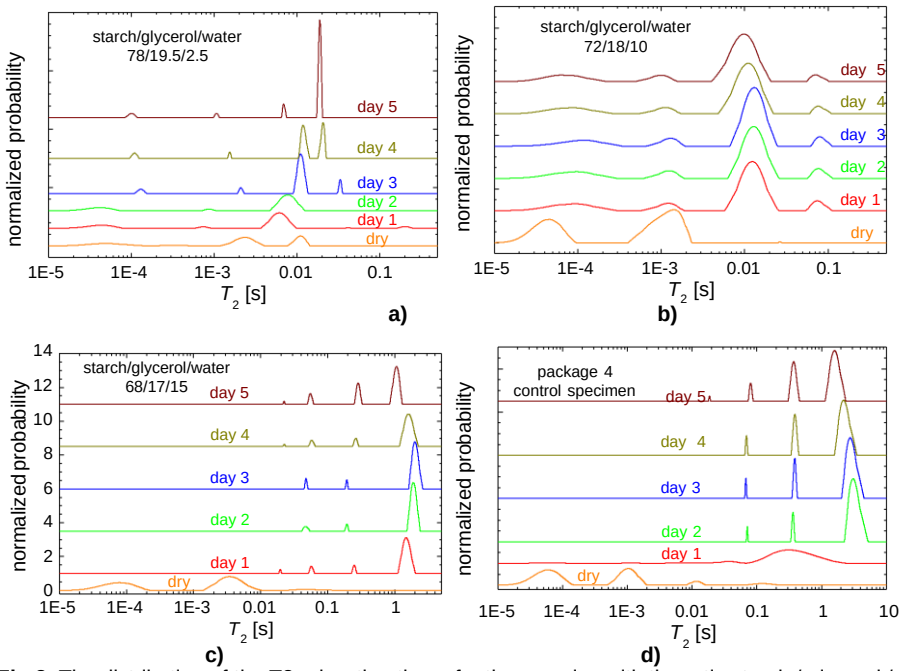

Fig.3. The distribution of the T2 relaxation times for the samples with the ratio starch / glycerol / water 78/19.5/2.5 (a), 72/18/10 (b), 68/17/15 (c) and the standard sample (d) for 5 days of water absorption and dried samples

Major changes are observed starting with the 3rd day. While the 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 the 2nd day, the majority of the mobile peaks (T_2 ~33.6 ms) contain a larger ^{1}H reservoir which is shifted to lower T_2 values.
In the next two days of water absorption, except the main peak which slowly moves towards a larger value T_2, the other peaks shifted to lower T_2 values. This is an indication that the excess of water also leads to a stiffening of the components of this package formula. The sample 2 (72/18/10) once it has absorbed the initial amount of water becomes more stable over time (Figure 3 b). The dry sample is characterized by two relatively rigid components, also observed for the sample degraded, but in a much smaller proportion. The largest ^{1}H reservoirs are found at values of T_2 of ~11 msand~75ms. For this type of packaging can be seen also, a slight increase of T_2 values up to the 3rd day after which a slight decrease of T_2values on days 4 and 5. Can be emphasized the same conclusion as in the case of the previous sample. A similar behavior is observed for the sample 3 for which the normalized T_2 distribution is shown in Figure 3 c). For the dry sample the T_2 distribution is characterized by values of T_2 of less than 10 ms. In a single day, the sample 3 is degraded up to the colloidal stage characterized by T_2 values larger than 10 ms.The degradation behavior of the standard sample (Figure 3 d) is similar to the behavior of sample 3. Starting with the the 2nd day the control sample starts to precipitate (visually observed) and, as in the case of the sample 3, by the decrease of the T_2 values of the main peak compared to the lower values starting from T_2 ~3 to ~ 1.5 s.

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- C. Cota, N. Cioica, E.M. Nagy, C. Filip, R. Fechete, O. Cozar., *Spectroscopic Investigation of Structural Changes in Native Corn Starch with Plasticizers*, The Third International Conference on Analytical and Nanoanalytical Methods for Biomedical and Environmental Sciences "IC-ANMBES 2014", Brasov, Romania , 13 – 15 Iunie, Book of Abstracts, pg 137
- N. Cioica, R. Fechete, R. Chelcea, C. Cota, M. Todica, C.V. Pop and O. Cozar, *Water absorption and degradation of packages based on native corn starch with plasticizers*, The fifth conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems. 5- th BioNanoSpec/ Cluj-Napoca, 07-10 sept. 2014, pg 73

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STAGE 5- of theproject was developed during December 2014 – December 2015 and had the following ***goals:***

1. Comparative study of the results obtained

2. Study on optimal variants which could improve the structure and physical and mechanical features of materials designed to bio-degradable packages made of autochthonous raw materials (Part I)

3. Reporting and disseminating the scientific results (Part I)

In order to*find outthe influence of components nature and proportion on characteristics of packages,* three representative samples noted with a), b) and c) were chosen among the 14 recipes tested within the project.

Sample symbol	Starch [g]	Glycerine [g]	Water [g]
a	78	19,5	2,5
b	72	18	10
c	68	17	15

The starch from recipes wasautochthonous starch having an amylose content of 21%, density of 0.561 g/cm^3 and humidity reported to humid substance, 10.76 %. Glycerine had a concentration of 99.5% and a density of 1.262 g/cm^3.

FTIR spectra of mixes have indicated intensity modifications of bands depending on components percentage, noticing especially in area of 3318 cm^{-1} band an increment of band's intensity along with water content growth in the network.. The same thing was noticed in area of 1000 cm^{-1} band, which is appropriate to vibrations of extension of groups C-C and C-O of main polysaccharide chain from the two components of starch, namely amylose and amylopectin. Thus, intense absorptions starting from 998 cm^{-1} can be associated to hydrate crystal field of mixture and the band from 1014 cm^{-1} indicates plasticizer contribution to amortisation.

Spectra FTIR of packages have shown a diminishing of intensity of bands from 3300 cm^{-1} and 1645 cm^{-1} after extruding, more important according to processed mixture plasticizer quantity comparing to starch content. Intensity decrease of absorption bands from area of 1150 cm^{-1} and 1078 cm^{-1} has also indicated a growth of plasticizer content influence on package structure.

Raman spectra of the three mixtures analyzed have also shown a slighter increase of bands intensity along with plasticizer content growth in the network. Modification of bands intensity of 940 cm^{-1} and 850 cm^{-1}, indicates the crystallinity change, namely a certain increase of proportion of amorphous phase from starch along with growth of plasticizer share.

At Raman spectra for packages, it has noticed intensity changes of bands with plasticizer proportion, especially for absorption bands 2902 cm^{-1} and 474 cm^{-1}, which indicate modifications in crystalline-amorphous stage of extrusions.

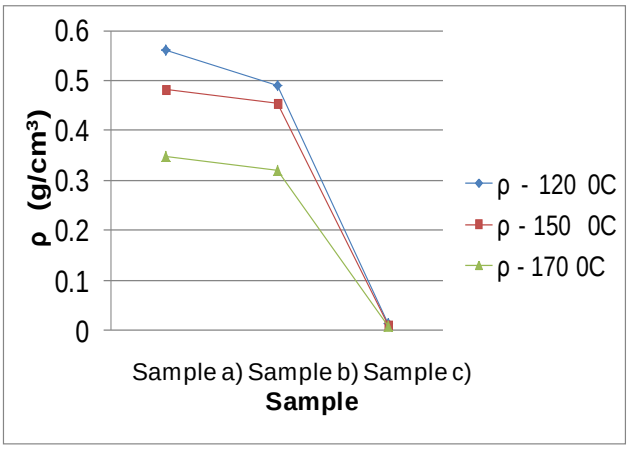
Comparing the results of relaxometry^{1}H RMN it has noticed modifications of viscoelastic behaviour of the three mixtures before and after extrusion. Therefore, from the distribution relaxing spin time-network T_1 can be noticed a progress of peaks intensity when plasticizer content grows..

For the packages, distributions T_1indicate an increase of amorphous component according to plasticizer content growth.

Distribution of transversal relaxing time T_2, of mixtures has shown that along with plasticizer content growth, a displacement of peaks to bigger time T_2 , so to the area with solid-soft behaviour similar to liquids, due to increase of polymer chains mobility. As for packages the relaxing time distribution spin-spin T_2, shows that peaks from mobile area are more stressed when plasticizer content increases.

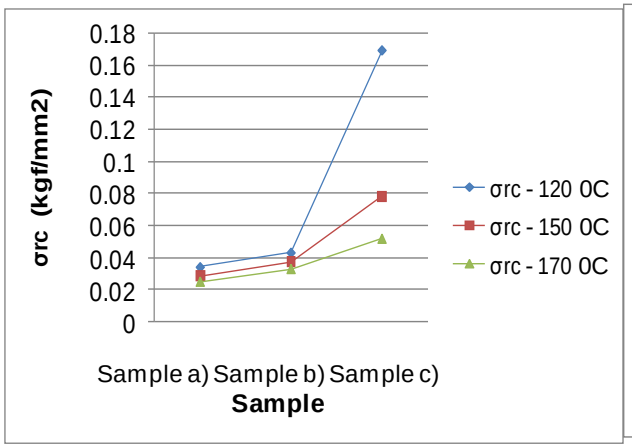
Analysis of influence of working regime parameters on packages characteristics has shown that parameters which influence the most the packages features are the plasticizer content and working temperature in the five areas of extruder and in matrix. The three repartitions of temperature on the extruder's length were: 30/50/80/100/120/120 ºC, 30/60/100/130/150 ºC and 30/70/120/150/170 ºC.

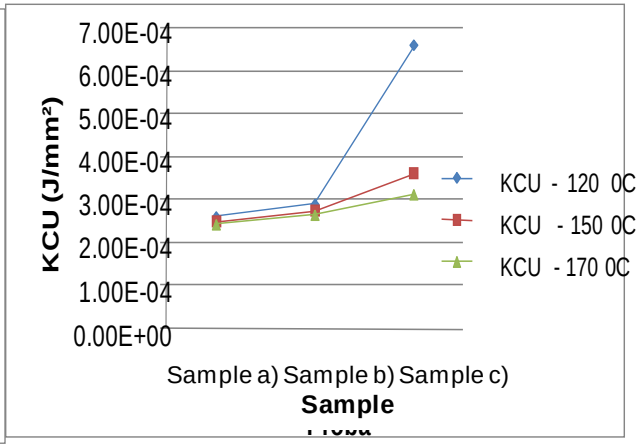
Density and transversal expanding index are two characteristics placed in reversed ratio one from the other, an increase of the expanding ratio leading to a decrease in the density of the package. Package density increases along with increasing the starch based water content in thesubjected to extrusion, due to the high quantity of water which evaporates from



for a certain content of plasticizers in the recipe takes place a decrease in package density and an increase of the transversal expanding index along with increasing the processing temperatures on the length of the five areas of the extruder and in the matrix, on one hand due to a more intensified plasticization of the mixture, and on the other hand, due to the higher pressure in the matrix and the atmospheric pressure when the material exits the matrix.

Both the compressive strength resistance and the package resilience increase with increasing the content of plasticizers in the network, but decrease with increasing the temperature.





This is explained by the greater elasticity of the walls that separate alveoli of the extruded with a higher expansion degree.

2. *Analysis and interpreting results* performed within the **second objective** gives indications regarding the optimal options that lead to improving the structure and the physical-chemical properties of material for biodegradable packages made from indigenous raw materials.

By comparing the FTIR spectra of the packages obtained by extruding mixtures containing different shares of starch and plasticizers with the FTIR spectra of the same mixtures before extrusion, changes in the intensity of the vibrating bands are noticed. These modifications show the change of the distance between the atoms of the molecules of the angle between the links depending on the nature and the share of plasticizers, with direct effect on the characteristics of packages.

Raman spectrometry also indicates changes of band intensity in the spectrum characteristic to mixtures before and after extrusion. Thus is noticed a slight increase in the intensity of packages bands along with increasing the content of plasticizers in the mixture.

This is caused by the fact that by adding plasticizers and through thermomechanical processing by extrusion, a share of the polymeric chains rupture, becoming shorter and more mobile, and a share of the temporary knots loosen, allowing a greater mobility for the polymeric chains. This way, the number of chemical bonds involved in vibrations increases, and thus, the intensity of corresponding peaks also increases. However, new vibrating bands do not appear after extrusion, and the ones existing in the raw mixtures remain approximately at the same wavelength, because the rupture of polymeric chains did not induce changes in the chemical structure of the polymer.

^{1}H RMN spectra of the mixtures before and after extrusion also give important information regarding the influence of the components ratio on the molecular structure and dynamics of the packages obtained. Thus, from the distribution of the longitudinal relaxation time T_1 is noticed an increase of the amorphous component of the package as the content of plasticizers increases in the recipe, and from the distribution of the transversal relaxation time T_2 is noticed, in the same conditions, the presence of important peaks in the area of soft solid behaviour similar to liquids. Both changes of the spectra indicate an increase in mobility for the polymeric chains of packages obtained from a mixture with a higher content of plasticizers.

All these information at molecular and atomic level explain the behaviour of mixtures based on autochthonous starch during processing and the variation of expansion and mechanical characteristics of the corresponding packages obtained.

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STAGE 6- of the project was carried out during December 2015-october 2016 and had the following objectives:

1. *Study on optimal variants which could improve the structure and physical and mechanical properties of materials for biodegradable packages made from local raw materials* (Part II)
2. *Reporting and dissemination of scientific results (Part II)*

In the first objective, based on the comparative study, analysis and interpretation of the results obtained during the development of the preceding phases of the project, it was made the *optimization of characteristics and working parameters* leading to improved structure and physico-mechanical properties of materials for biodegradable packaging made from local raw materials.

Final product characteristics considered when choosing the optimal were: microstructure, density, compressive strength, resilience, thermal stability and biodegradability.

The working parameters of the combination which resulted in this embodiment were: the formula, feed rate, screw speed and the temperatures on the length of the extruder and of the die.

The formulas used in the experiments included: local native starch manufactured in Amylon SA Sibiu, with 21% amylose content, density of 0.561 g / cm3 and humidity on the ash wet, 10.76%; glycerin with a concentration of 99.5% and a density of 1.262 g / cm3, acquired from SC Nordic Cluj-Napoca, and water from the water supply system.

Investigation of the effect of plasticizers on the properties of combinations of raw materials and finished products obtained, showed an interactive plasticizer- anti-plasticizer effect of water and glycerol.

Thus, from DSC measurements result, when using of a single plasticizer, a higher degree of influence of glycerol versus water in reducing the glass transition temperature T_g, and when using both plasticizers a different influence depending on the ratio of glycerol / water in the formula, there are areas where occurs the decreasing of the T_g temperature even in conditions of increasing water / starch ratio.

Changes in the intensity of the absorption bands in the 1000 cm $^{-1}$ of the FTIR spectra, characteristic of amylose and amylopectin which are correlated with the amorphization ability of plasticizers indicates changes of crystalline-amorphous ratio of the mixture of starch and plasticizers in the formula depending on the ratio starch / glycerin / water. Were also noted changes in the intensity of the Raman spectra bands and ^{13}CCP / MAS NMR of studied formulas, indicating the increase or decrease the proportion of the amorphous phase in the formulas composition depending on the content of water and glycerol as plasticizers.

The variation curve of the spin-lattice relaxation time, T_1 determined by ^{1}H NMR relaxometry measurements show that by adding 15% water the sample becomes 100% amorphous and by adding 20% glycerol leads to destruction of the crystalline phase, resulting in 88.1% amorphous phase and 11.9% highly mobile phase.

These investigations have shown that, of the 14 proportions of the components studied, the formula that leads to the best results in terms of plasticizers effect is one that contains *68% starch, 17% glycerin and 15% water.*

The experiments showed that parameters used in extrusion influence also, largely, morphology, density, mechanical characteristics and degradability of the final product.

Thus, the lower the feed rate is and higher the speed of screws is, the degree of mixing and mechanical processing of formula components is higher due to higher time of stay in the extruder, respectively, a higher rate of shear of mixture made by special items of screws intended for that purpose. The higher temperature values on the length of the extruder, increase the specific consumption of electricity for heating but lead to a lower viscosity of the melt and thereby to a lower specific consumption of electricity for driving the screws. As mold temperature is higher the degree of expansion of extruded finished product is higher.

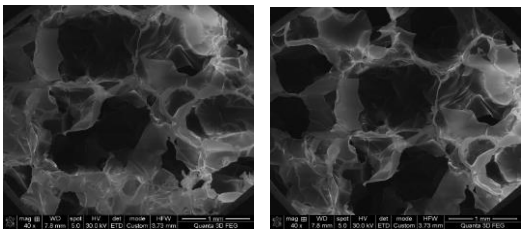
For the formula chosen *the working parameters of the extruder* that gave the best results in terms of quality of finished product, in terms of using an extruder type "ZK 25", production Collin GmbH, Germany, with two modular corotating screws, with screw diameter: D = 25 mm and length: L = 30xD, were as follows:

- *Starch feed rate: 0.5 kg / h;*
- *Screw speed: 150 rev / min;*
- *Temperature gradient in five zones of the extruder: 30/50/80/100/120 ^{o}C.*

The resulting final product characteristics were:

Microstructure: semi-open pores with a balanced form in three directions, separated by thin bridges between them (Fig.46).

Thermal stability: between 50 ° C and 210 ° C, the sample analyzed is thermally stable (Fig.47).



(a) (b)

Fig.46 SEM images of the extrudate obtained from mixtures with a ratio of starch / glycerol / water [% by weight]: 68/17/15 (a) = cross section; (b) = in longitudinal section

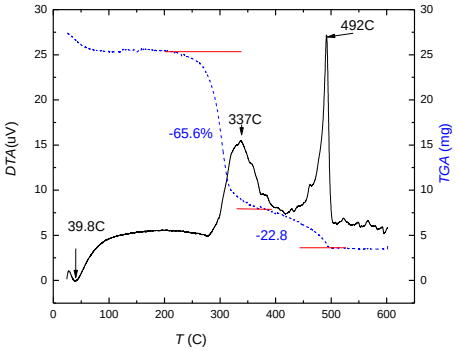


Fig. 47 TG DTA thermogram of extrudate obtained from the mixture with a ratio starch / glycerol / water [% by weight] 68/17/15

Density: 0.012 g / cm 3 at a transverse swelling index of 25%.
Compressive strength: 0.1691 kgf / mm2
Resilience: 6.59 * 10-4 J / mm²
Degradability: viscosity measurements and ^{1}H NMR showed that after one day the samples degrade until to colloidal state.

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