



**ELECTRONIC
JOURNAL
OF POLISH
AGRICULTURAL
UNIVERSITIES**

**2005
Volume 8
Issue 4
Topic
AGRICULTURAL
ENGINEERING**

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WÓJTOWICZ A. , VAN DER GOOT A. 2005. THE INFLUENCE OF WATER AND GLYCEROL ADDITION ON THERMAL PROCESSING, RHEOLOGY AND MICROSTRUCTURE CHANGES OF POTATO STARCH **Electronic Journal of Polish Agricultural Universities**, Agricultural Engineering, Volume 8, Issue 4.

Available Online <http://www.ejpau.media.pl/volume8/issue4/art-51.html>

THE INFLUENCE OF WATER AND GLYCEROL ADDITION ON THERMAL PROCESSING, RHEOLOGY AND MICROSTRUCTURE CHANGES OF POTATO STARCH

Agnieszka Wójtowicz¹, Atze Jan van der Goot²

¹ *Department of Food Process Engineering, Agricultural University in Lublin, Poland*

² *Food and Bioprocess Engineering Group, Wageningen University, The Netherlands*

ABSTRACT

In the present paper the influence of glycerol and water addition to potato starch during thermo-mechanical treatment was observed. The shearing-heating treatment was realised on the new designed equipment – Shear Cell – based on the cone and plate rheometer device. The measurement of rheological changes during processing showed that water and glycerol addition lowered the shear stress and the shear rate values. Also the influence on intrinsic viscosity was observed: higher level of water and glycerol added, the lower values of intrinsic viscosity was observed. Microstructure changes during processing confirming these results.

Key words: potato starch, glycerol, Shear Cell, shearing, thermal treatment, intrinsic viscosity, microstructure.

INTRODUCTION

Thermoplastic starch (TPS) is the most popular biopolymer useful for production of packaging materials in selected areas of food industry but also to the biomedical and cosmetic industries in gels, foams, films and membrane forms. Different types of processing based on disruption and melting the semi-crystalline structure of starch may be used to transformation of native starch to form a bioplastic starch. Thermo-mechanical treatment that combines temperature and shear stress, like extrusion or injection moulding, is able to transform granular starch into TPS.

Water is most often used as a plasticizer during starch transformation and minimum moisture content required for starch gelatinization is around 33%. There are many studies about the transformations of different starchy materials to thermoplastic forms with intermediate and high water level. It is mostly visible in the energy context, because specific mechanical energy (SME) values decrease with increasing water level in raw material. High water content also influences the onset temperature, glass transition temperature and rheological properties of molten material [4, 11, 13, 17]. Also other plasticizers were examined i.e. monoglycerides or glycerol, as a flexibility improvers [15]. Addition of glycerol is the reason of increasing the gelatinization onset temperature by an increase in the activation energy of the melting of the starch crystallites and than higher glass transition temperatures and higher interactions forces between glycerol and starch polymers [5, 16, 17, 18, 21]. The onset melting temperature of starch-water-glycerol mixture before extrusion process is approximately 100°C and peak temperature –120°C, so process conditions 120-135°C from a melting point of view are too low to complete destruction of starch granules. But the extrusion process takes place at high shear stress and high value of energy input, and onto these conditions melting process may be enhanced [16]. Different types of starchy materials were investigated with different combinations of starch – glycerol – water contents using DSC or X-ray wide-angle diffractometry. Most often corn or waxy corn and wheat or barley starch was investigated as basic thermoplastic raw material [1, 2, 3, 8, 12, 13, 19, 20, 22].

The melting of crystalline parts of starch is time and temperature dependent; also the shearing intensity should be taken into account [6]. The increasing the process time, increasing the breakdown and degree of macromolecular degradation was observed [7]. But the results of tests on different equipment with similar temperature and treating time shows that breakdown is more intensive when higher shear forces are present. Shearing forces are influenced on increase in cold water solubility [10]. There are noted in literature many differences between the results of starch modifications during heating-shearing treatment depended on investigation method, starch origin and treatment conditions. Most popular method used is DSC evaluation of melting enthalpy, but it provides incomplete description of starch modifications [23]. Also different types of rheometers were used to simulate the thermo-mechanical conditions (i.e. extrusion-cooking process). Properties of obtained product are similar to those after extrusion by WAXS or intrinsic viscosity measurement [1]. The shear rates, temperature profile, residence time influenced simultaneously on native starch in the presence of water content. Also in these research results the changes in properties in excess of water were observed. Most studies were carried in the presence of high water content, but it is well known, that extrusion-cooking processes are industrially collected in a presence of low or medium water content (10-30%). Product behaviour and properties after extrusion with high level of water content are not always acceptable because of i.e. water droplets inside the starchy-glycerol pellets, too high moisture level in products or changes in crystallinity, retrogradation and stress-strain properties of the materials (tensile strength, elongation) [18].

In these study investigations results on potato starch-glycerol mixtures with limited water addition (below 30%) subjected on the heating and shearing behaviour are presented. The purpose of the treatment was to use special designed shearing device – Shear Cell for obtains a starchy molten phase under thermo-mechanical processing similar to extrusion. This new equipment is based on the cone and plate rheometer ideology. There is possibility to isolate singular parameters during processing like temperature, rotation speed (i.e. shear rate) or shear stress in this equipment [7].

MATERIAL AND METHODS

Materials. Potato starch was a commercial product with initial moisture contents 16% from Łomża, Poland. Glycerol an analytical grade at 99.5% purity and 0.5% moisture content was used. The samples were prepared one day before testing to allow equilibrium of water over the starch. Potato starch-glycerol mixtures were prepared using bakery mixer with content 20%, 22.5% and 25% of glycerol (w/w). Moisture content of starch and mixtures was allowed by drying in 130°C by 2 hour in an air dryer. Mixtures were stored in closed plastic bags at room temperature before

testing. Deionised water was used to prepare mixtures with starch-glycerol raw material with 5, 10, 15 and 20% amount of added water (w/w). Also for comparing of plasticizer influence on starch-glycerol mixtures behaviour during treatment it was prepared mixtures with replaced glycerol by water (80% of starch and 20% of water) and also deionised water was added in the similar amounts of plasticizers as with starch-glycerol mixtures.

Methods. Transformation of starch-glycerol-water mixtures was made using the Shear Cell by mechanical shearing and heating conduction from the walls of equipment realised by heating – cooling system. Temperature of the product was measured with thermocouple sensors inside the chamber and in the cone of equipment, respectively.

Shear Cell tests. The Shear Cell device was based on the cone and plate rheometer on a pilot scale (fig. 1). The shearing device details are described by Einde et al. (2004). View of the working equipment is presented on the figure 2.

Figure 1. Shear Cell equipment: 1 – shearing zone, 2 – heating elements, 3 – rotating plate, 4 – non-rotating cone, 5 – thermocouple, 6 – torque measurement point.
Cone angle = 100° , shear zone angle = 2.5° , $R = 0.1$ m, $H = 0.082$ m

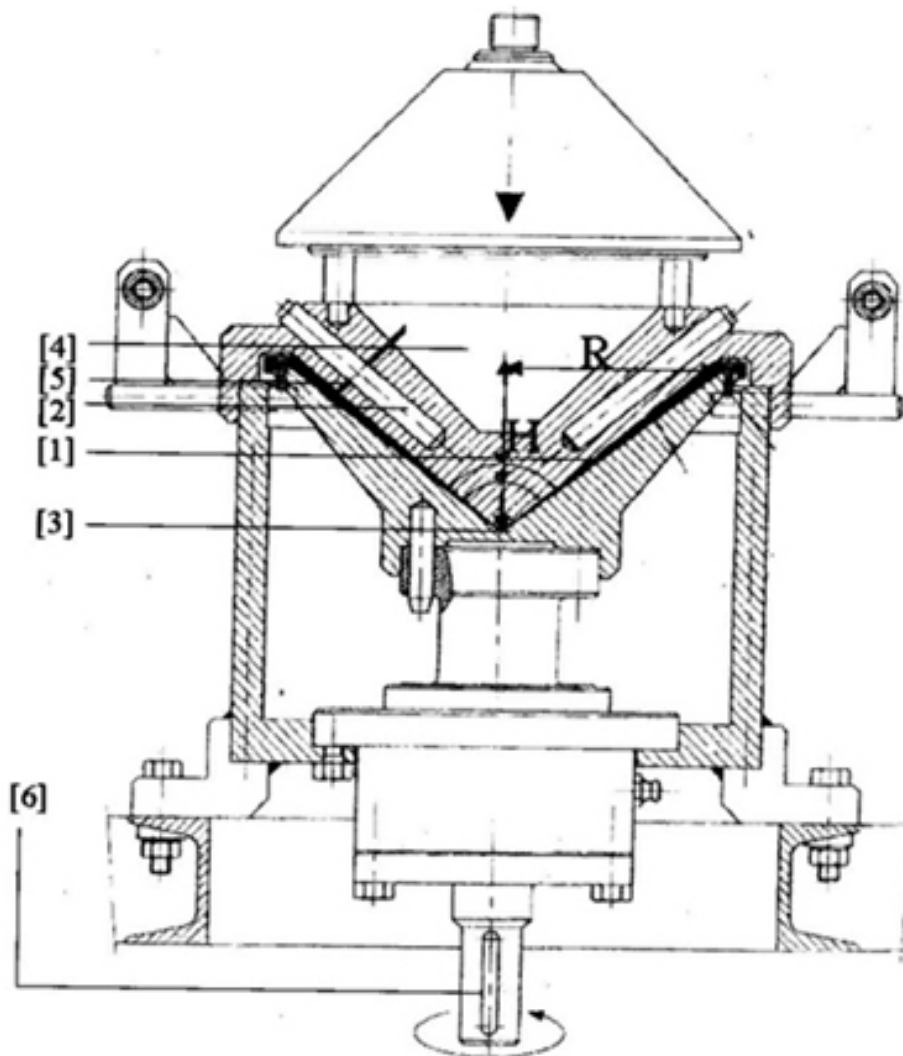


Figure 2. Working Shear Cell device



In all the experiments sample size was 150 g. Mixture sample was put on the plate at a uniform rate (fig. 3a), covered by the cone element and closed precisely because of the pressure increase during heating – shearing process. Temperature was selected on 85°C for samples with 15 and 20 % of water added, 88°C for samples with 5 and 10% of water added and 115°C for starch-glycerol mixtures. During starch-water mixtures 85°C was used. The engine was started immediately after the temperature set point was reached. The rotation speed was 10 rpm (equivalent to a shear rate of 24 s^{-1}) during first 2 minutes, increased simultaneously to 100 rpm (240 s^{-1}) during 3 minutes and continuation of shearing process until 10 minutes. Only for starch-glycerol mixtures the maximum rotation speed was lower range – 85 rpm to avoid circular flow of samples with low moisture content at higher rotation speed, what was observed during first tests with 100 rpm. Temperatures and times are summarised in the table 1. After tests the Shear Cell was opened (fig. 3b), samples were cooled and collected in plastic bags at room temperature.

Figure 3. Starch-glycerol mixtures before (a) and after (b) shearing-heating process

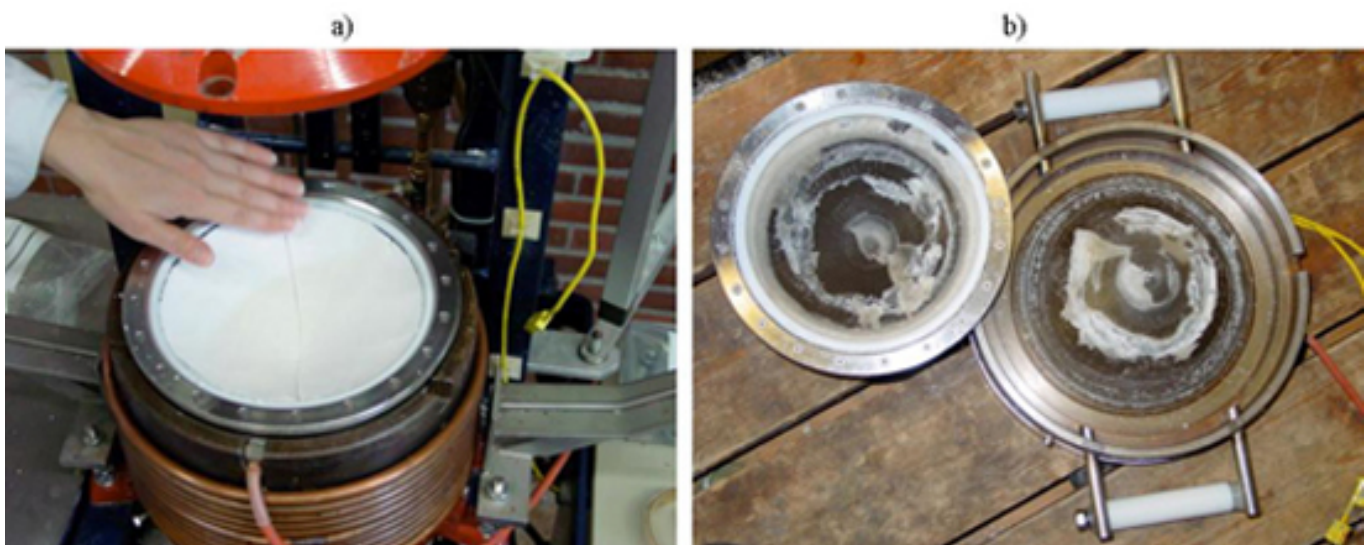


Table 1. Time and temperature changes profile during thermo-mechanical treatment of starch-water-glycerol mixtures in Shear Cell

Starch – Glycerol ratio	Water (%)	Moisture content (%)	Rotation speed (rpm)	Treatment temp. (°C)	Total process time (s)	Melting start time (s)	Melting start temp. (°C)	Melting start rotation speed (rpm)	Max. temp. (°C)
100-0 ¹⁾	-	29.9	100	85	660	480	84	90	90
	5	36.4	100	85	420	150	89	80	90
	10	39.1	100	85	420	132	88	40	91
	15	42.5	100	85	480	108	88	40	91
	20	43.8	100	85	480	64	88	40	91
80-20	-	13	85	115	960	810	115	85	117
	5	20	100	88	960	510	92	100	112
	10	22.5	100	88	960	360	91	90	106
	15	27.5	100	85	680	240	91	80	92
	20	30	100	85	620	210	89	100	92
77.5-22.5	-	19	85	115	700	720	114	85	118
	5	20	100	88	960	330	92	100	115
	10	26	100	88	640	240	92	90	95
	15	29	100	85	610	240	89	100	92
	20	32.5	100	85	640	330	84	100	94
75-25	-	21	85	115	820	740	113	80	114
	5	23	100	88	980	270	92	100	112
	10	27.5	100	88	700	350	89	100	92
	15	31	100	85	680	315	88	100	91
	20	34	100	85	680	210	89	70	101

¹⁾Glycerol was replaced by water (80% of starch – 20% of water)

The torque changes during the treatment were recorded using calibrated measurement device and used to further calculations. The shear stress (τ), shear stress multiplied by time ($\tau \cdot t$) and SME values were calculated and analysed depending glycerol and water level in tested mixtures.

Intrinsic viscosity measurements. The intrinsic viscosity (η) is very sensitive for thermomechanical treatment and the degradation of molecular weight compounds in starch, therefore it can be used as a method to molecular weight measurement. Intrinsic viscosity of native starch and sheared-heated samples was measured according the Ubbelohde viscometer method [7] at 25°C. Samples were collected in closed plastic bags after treatment at room temperature. Before measurements they were frozen in liquid nitrogen and directly ground with electrical mill with intensive cooling system. Ground samples were kept in an oven at 30°C overnight and sieved by 335 μ m opens. Samples were dissolved in 1 M KOH during 30 minutes in six concentrations in the range of 0.5-2 mg/ml. The flow time during capillary system of Ubbelohde viscometer (Labovisco b.v., the Netherlands) was measured. The time it takes a volume of sample solution to flow through a thin capillary was compared to the time for a solvent flow. It turns out that the flow time for either is proportional to the viscosity and inversely proportional to the density. After the flow time measurement of each tested sample, intrinsic viscosity was calculated as specific viscosity related to sample concentration. Values of intrinsic viscosity measurements were in duplicate.

Microstructure changes. Samples after cooling were tested on optical microscope Axioskop (Zeiss West Germany) with polarised light. Microscope was equipped with camera. Photos were recorded on computer. Photos were made with zoom 320×.

RESULTS AND DISCUSSION

On figure 4 there are shown potato starch-glycerol (80-20) mixtures behaviours with different water addition during treatment in the Shear Cell. Mixtures with low amount (5%) of water added showed the highest values of torque and increasing the water content led to lower torque values during the treatment. It means that water becomes a plasticizer for starch, which is in accordance with previous reports [16]. Quite similar results were observed for (77.5-22.5) starch-glycerol mixtures during treatment (fig. 5).

Figure 4. Influence of water addition on torque value during thermo-mechanical treatment of potato starch-glycerol (80–20) mixtures in the Shear Cell

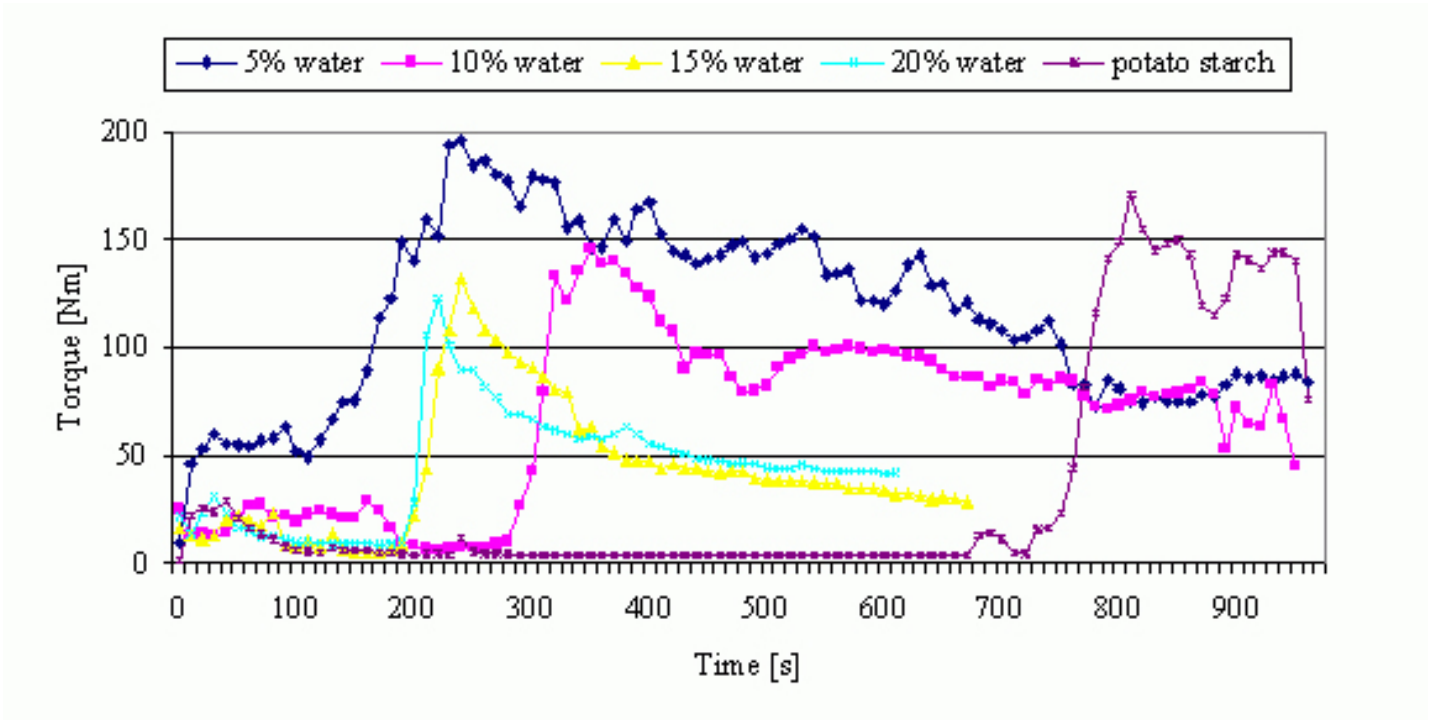
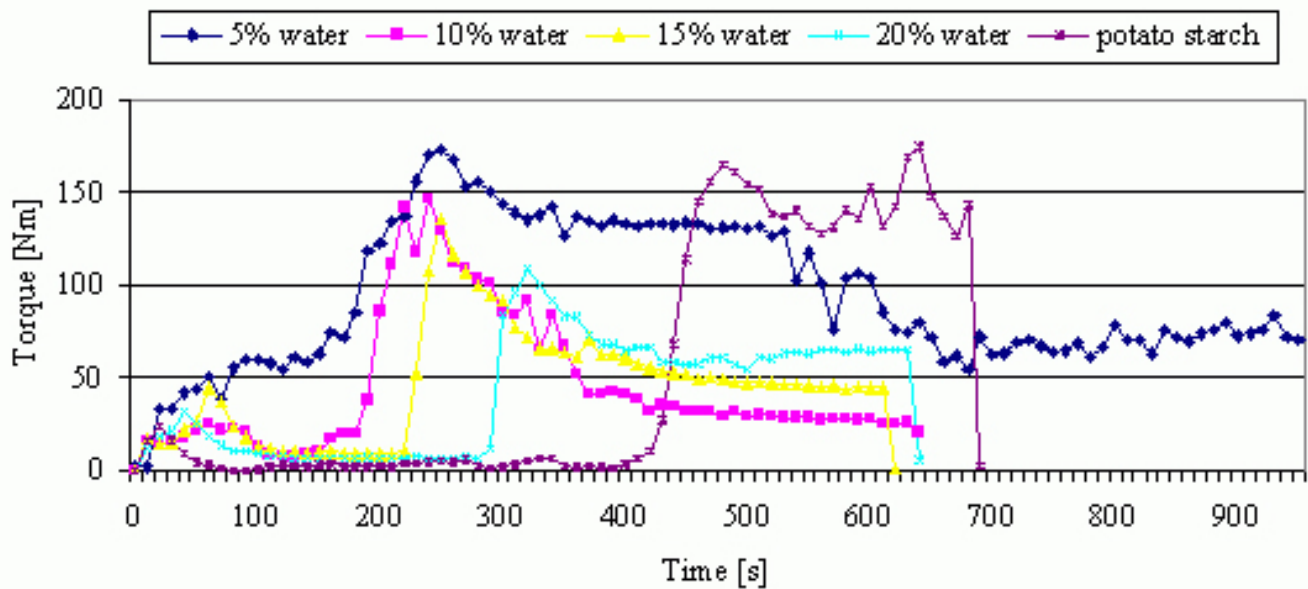


Figure 5. Influence of water addition of torque values during shearing-heating of potato starch-glycerol (77.5–22.5) mixtures in the Shear Cell device



During intensive thermo-mechanical treatment in the Shear Cell short time required to starting changes inside the structure was observed. It may be explained by high shear stress during shearing-heating in Shear Cell. After tests in Shear Cell it was known that start-melting temperature for the recipe without water addition to starch-glycerol mixtures was about 115°C and the time for the beginning of the melting was much longer than for others samples (tab. 1).

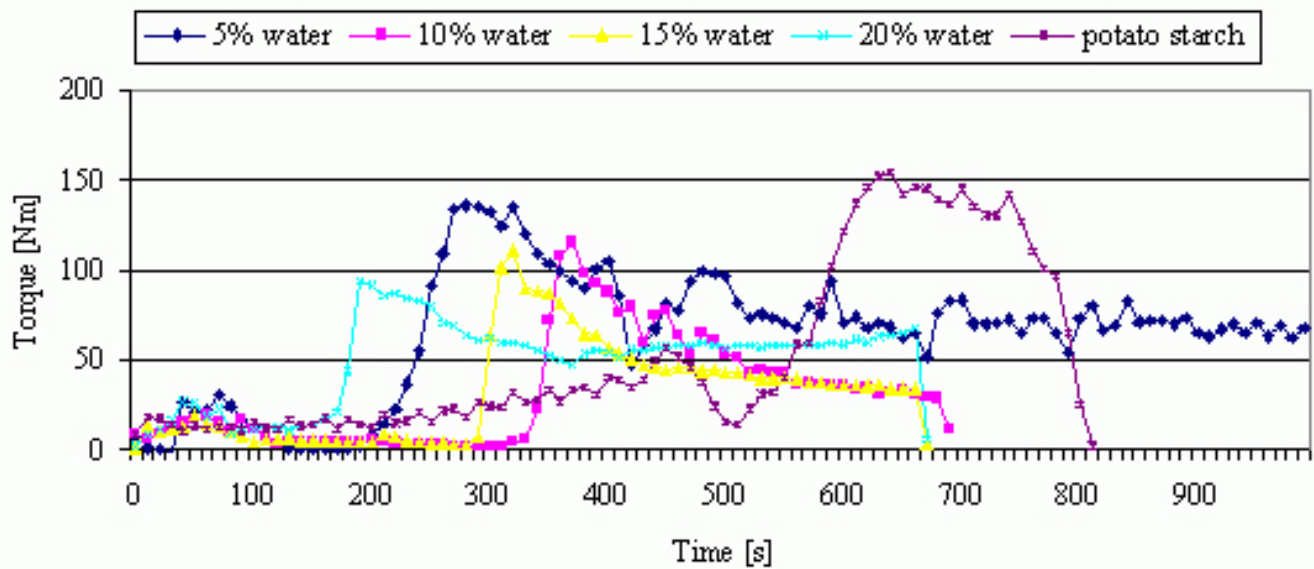
It's shown on figures that for potato starch-glycerol mixtures without water addition were not easy to treat using Shear Cell equipment. It was very hard to control the process conditions after initiation of melting and gelatinisation process, because of big variations in the pressure values and in rotation speed (engine is equipped with safety system able to slowing rpm under to high pressure and torque values).

Increasing the water addition resulted in a lower maximal shear stress, reducing the macromolecular degradation, but here the influence of the temperature on starch-water mixtures takes place [7]. Della Valle et al. [5] reports that increase in moisture content increase of SME values induced decrease of macromolecular weight measured by intrinsic viscosity.

There are some differences between potato and cornstarch during extrusion as reported by Della Valle et al. [5]. The molten potato starch at the same conditions exhibits higher melt viscosity, early melting inside the extruder and high energy requirements. It may be caused by the higher molecular weight of potato starch and early melting require transition temperature lower than the value for cereal starches. It has been founded that increasing extrusion temperature an increase in the molecular degradation effect was observed, but also influence of SME should be taken into account [5].

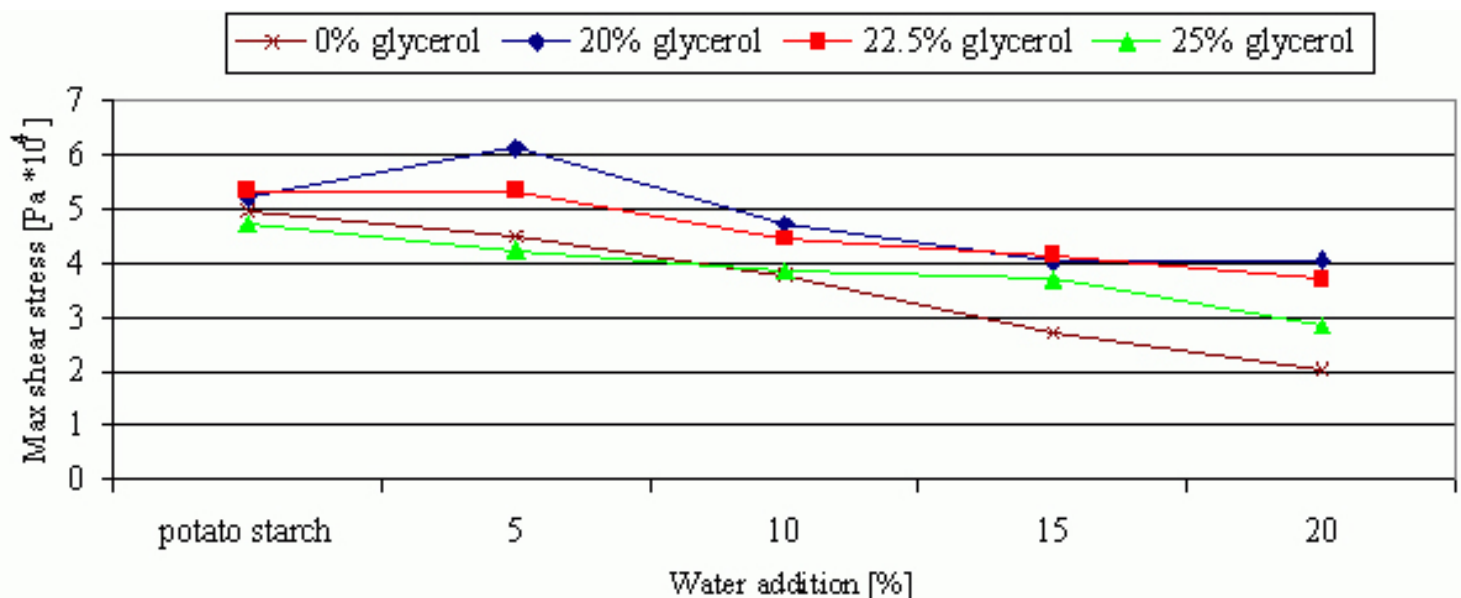
Nashed et al. [13] reported through DSC that glycerol behaves as an anti-plasticizer because of hindering the gelatinization process and linear increase of onset temperature with increasing glycerol content was observed during treatment of wheat starch-water-glycerol mixtures. During thermo-mechanical treatment of starch-glycerol mixtures it was clear that higher glycerol addition resulted in decreasing melting or gelatinization time and temperature and also decrease of torque values during treatment. It was most visible comparing torque values between starch-glycerol-water mixtures, but also for starch-glycerol mixtures without water addition (tab. 1).

Figure 6. Influence of water addition of torque values during shearing-heating of potato starch-glycerol (75–25) mixtures in the Shear Cell device



During the samples treatment in the Shear Cell its hard tendency observed to decrease torque values with the increasing glycerol content in mixtures from 200 Nm for sample with 20% of glycerol and 5% of water added and 170 Nm for starch with glycerol only (fig. 4.) to 135 Nm and 153 Nm for glycerol content 25% (fig. 6), respectively. Also the influence of shearing-heating treatment on mechanical parameters calculated on the torque base was observed. Comparison of achieved data with results during treatment of corn and waxy cornstarch [7] shows the higher values of maximal shear stress during measurement for potato starch without or with small amount of water, and almost similar values for initial moisture content range 30-34%. With increasing of water addition values of maximal shear stress decreased and also increasing of glycerol content influenced on decrease of this parameter values (fig. 7).

Figure 7. Influence of glycerol and water addition on maximum shear stress during treatment of starch-glycerol-water mixtures in the Shear Cell



There are also some unexpected results for starch-glycerol mixtures without water addition. Almost all parameters calculated for these samples showed the lower values than with 5% added water (tab. 2). Much lower values of SME and shear stress multiplied by time was noted (fig. 8). But during treatment in the shear cell lower rotation speed and higher temperature of heating was used (tab. 1) According to previous data [7] it may be concluded that increasing the moisture content will lower the maximum shear stress and thus should reduce the macromolecular degradation. It can be confirmed by intrinsic viscosity measurement.

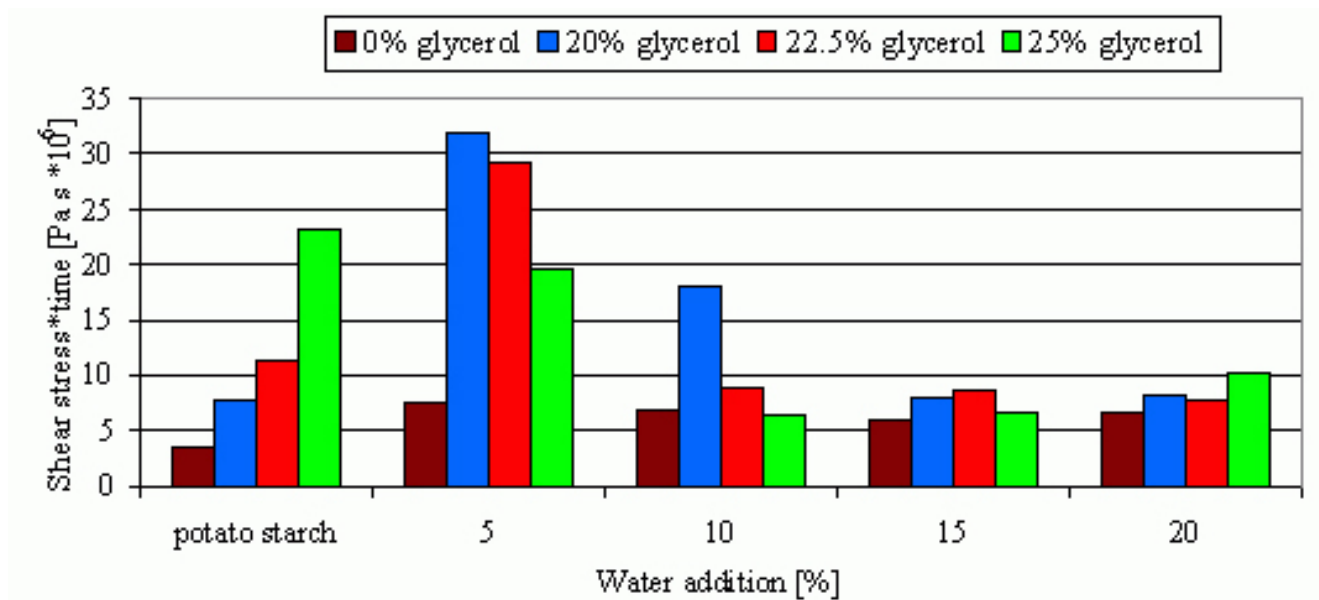
Table 2. Results of main parameters calculated for potato starch-glycerol-water mixtures processed in the Shear Cell

Starch - Glycerol ratio	Water (%)	Max torque (Nm)	Max shear stress (Pa)	Max SME (kJ/kg)	Shear stress multiplied by time (Pa*s)	Intrinsic viscosity (ml/g)
100-0 ¹⁾	-	162.65	4.96*10 ⁴	0.69*10 ⁴	3.44*10 ⁶	217
	5	172.59	5.26*10 ⁴	1.26*10 ⁴	6.96*10 ⁶	167
	10	123.93	3.78*10 ⁴	1.15*10 ⁴	6.95*10 ⁶	181
	15	88.78	2.70*10 ⁴	1.06*10 ⁴	5.92*10 ⁶	157
	20	74.87	2.28*10 ⁴	0.65*10 ⁴	6.70*10 ⁶	162
80-20	-	170.80	5.21*10 ⁴	1.02*10 ⁴	7.82*10 ⁶	155
	5	200.79	6.13*10 ⁴	6.38*10 ⁴	31.98*10 ⁶	142
	10	155.20	4.74*10 ⁴	3.76*10 ⁴	17.95*10 ⁶	108
	15	132.12	4.03*10 ⁴	1.66*10 ⁴	8.06*10 ⁶	159
	20	132.82	4.05*10 ⁴	1.78*10 ⁴	8.28*10 ⁶	138
77.5-22.5	-	175.00	5.34*10 ⁴	2.12*10 ⁴	11.22*10 ⁶	157
	5	174.71	5.33*10 ⁴	5.10*10 ⁴	29.19*10 ⁶	125
	10	146.16	4.46*10 ⁴	1.27*10 ⁴	8.79*10 ⁶	165
	15	135.78	4.14*10 ⁴	1.79*10 ⁴	8.62*10 ⁶	149
	20	121.92	3.72*10 ⁴	1.66*10 ⁴	7.78*10 ⁶	145
75-25	-	155.44	4.74*10 ⁴	3.91*10 ⁴	23.19*10 ⁶	215
	5	138.85	4.24*10 ⁴	4.39*10 ⁴	19.67*10 ⁶	116
	10	126.47	3.86*10 ⁴	1.38*10 ⁴	6.48*10 ⁶	168
	15	121.65	3.71*10 ⁴	1.42*10 ⁴	6.61*10 ⁶	160
	20	93.90	2.86*10 ⁴	2.11*10 ⁴	10.18*10 ⁶	140

¹⁾Glycerol was replaced by water (80% of starch – 20% of water)

But anti-plasticizer behaviour of glycerol can be concluded, because of lower values of almost all measured parameters during shearing-heating treatment mixtures with replaced glycerol by water in the same amount. Especially big differences were observed for the melting start time measured in the moment of increasing torque values (tab. 1) and the shear stress multiplied by time values (fig. 8).

Figure 8. Influence of glycerol and water addition on shear stress multiplied by time values during treatment of starch-glycerol-water mixtures in the Shear Cell

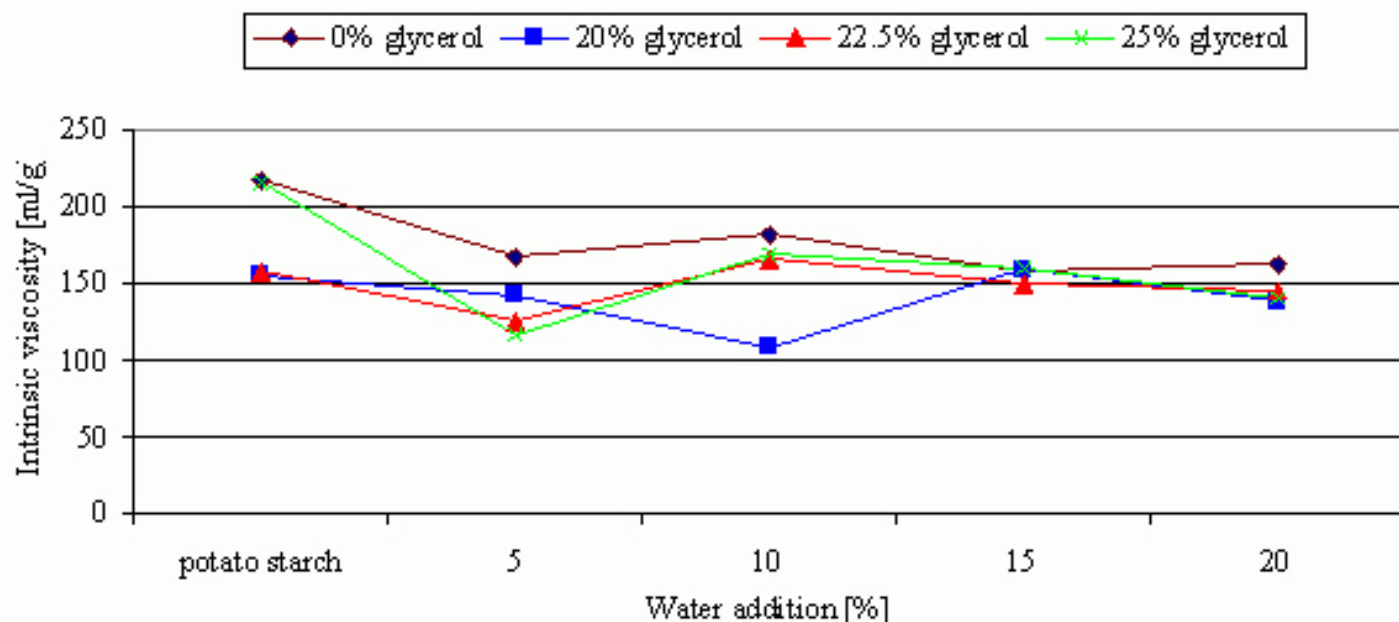


It was also expected high level of gelatinized starch in these samples with high amount of water added. It was achieved completely transparent and glassy appearances for all the samples with glycerol replaced by water, but the initial moisture content of these samples were much higher. It was also observed tendency to easily become hard and crispy properties after cooling to ambient temperature. All samples with addition of glycerol had visibly transparent glassy-like appearance and smooth surface, in worm stage they were easy to elongation and showed rubbery properties and they were longer present after cooling to room temperature.

Intrinsic viscosity of native potato starch was 369.8 ml/g. All achieved results were much lower than for native starch and average values variation was between 111 and 219 ml/g (tab. 2). It means that during shearing-heating treatment in Shear Cell high macromolecular degradation taken place. It's with accordance with Fujio et al. [9] for potato, corn and wheat starches, Einde et al. [6] for cornstarch and also Rushing and Hester [14] for polymers. Intrinsic viscosity is very sensitive especially on thermo-mechanical degradation. Low values of shear stress influenced on lower intrinsic viscosity of treated starch-glycerol mixtures.

Higher amount of glycerol and also water in the mixture influenced on decreasing molecular degradation of starch granules and intrinsic viscosity values were a little bit higher, but the differences are not easy to explanations. With the increase of water content from 10 to 20%, average intrinsic viscosity was around 20 ml/g lower in all tested samples. It means that more starch molecules were broken. But different behaviour was observed during viscosity measurement in samples with 5% water added: they had lower values of intrinsic viscosity than sample without water addition and with 10% of water added (fig. 9).

Figure 9. Influence of water addition and glycerol content on intrinsic viscosity of potato starch-glycerol-water mixtures after shearing-heating treatment



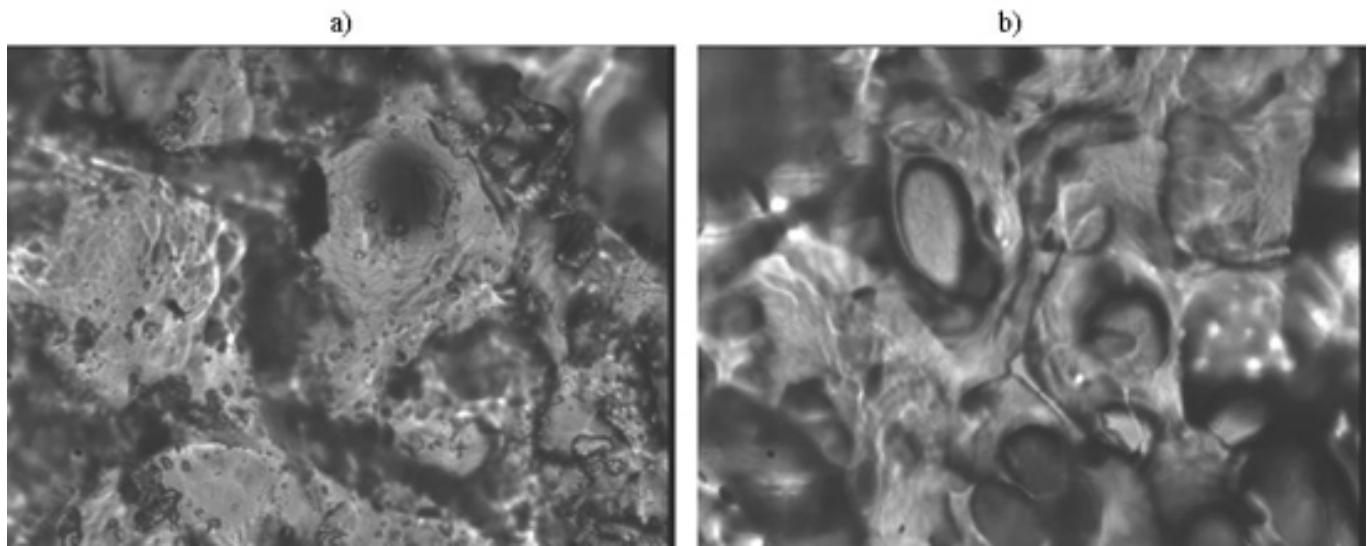
Intrinsic viscosity values were slightly dependent on glycerol content in mixtures (fig. 9) and with increasing glycerol content decrease of intrinsic viscosity was observed inside potato starch-glycerol-water mixtures treated in the Shear Cell under similar conditions. Only for samples without extra water addition opposite tendency was observed and intrinsic viscosity increased with increasing of glycerol content in the mixture (tab. 2). But in all cases variations between intrinsic viscosity are quite small and it can be concluded that almost the same degree of starch molecules degradation was noted. In comparing with native starch intrinsic viscosity value it means that over 50% of residue starch molecules was broken by thermo-mechanical treatment.

There was also difficult to conclude the influence of water content on intrinsic viscosity. On the figure 9 there are shown the changes of intrinsic viscosity values after treatment starch-glycerol-water mixtures in Shear Cell.

Intrinsic viscosity of samples with higher amount of water added (15 and 20%) was almost the same, it may be concluded that in the presence of these amounts of water degree of starch molecules degradation was the same, independent on starch-glycerol ratio. Higher differences were observed after treatment of samples with small or without water addition (fig. 9). By comparing those data with data generated by Eide et al. [7], it can be concluded that potato starch is less thermostable than corn starch. The low thermostability of potato starch makes interpretation of Shear Cell data very complicated, because it can't be separated the effects of shear, time and temperature, but it can also explain the changes in final product properties over time. This complicates not only the Shear Cell experiments (the time between mixing and Shear Cell should be constant) but also it can't be exclude a significant effect at room temperature at prolonged storage times.

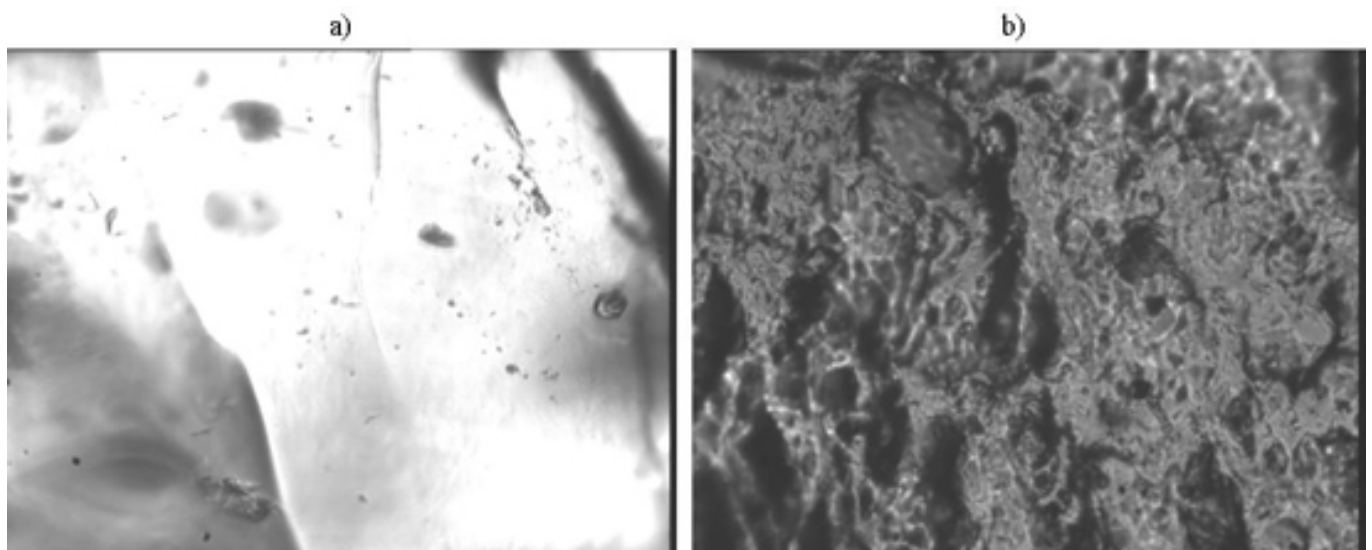
Microstructure changes. Samples from potato starch-glycerol mixtures treated on the shear cell without water addition shows many of untreated starchy granules inside the structure. In the proposed temperature – screw speed profile, water content included in starch is not enough for the starch gelatinization process. Also visual observation confirm this. Product was not transparent, not elastic and it was visible singular untreated starch particles in samples showed on the figure 10a and 10b.

Figure 10. Microstructure of potato starch-glycerol-water treated on the Shear Cell without water addition: a) 20% of glycerol, b) 25% of glycerol



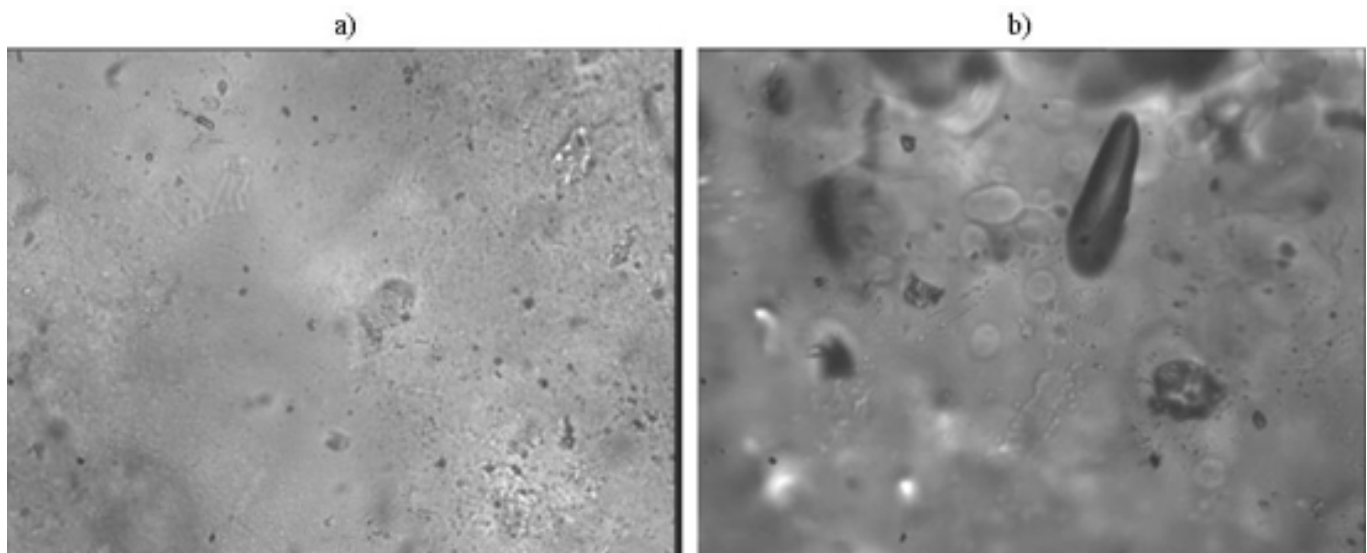
Behaviour of starch-glycerol samples with 5% of added water was different and, as it is shown on the figure 11a and 11b, had different influence on the inside structure of samples. Less level of glycerol caused better homogeneous of the mixture than with 25% of glycerol. Inside this sample there are visible singular starch granules but most of the product is transformed to compact mass with small amount of gas bubbles.

Figure 11. Microstructure of potato starch-glycerol-water treated on the Shear Cell with 5% of water added: a) 20% of glycerol, b) 25% of glycerol



On the figure 12a and 12b it is shown the structure of starch-glycerol mixtures with 10% of water added. It is clearly visible, comparing with the figure 10. That means the starch gelatinization process became. There are only a few visible starch granules inside the smooth homogenous network inside the samples. They start to be transparent and the milky like colour disappears. Lower glycerol content caused more stable structure. Inside the samples with higher amount of glycerol singular parts of glycerol are present as transparent bubbles on the figure 12b.

Figure 12. Microstructure of potato starch-glycerol-water treated on the Shear Cell with 10% of water added: a) 20% of glycerol, b) 25% of glycerol



The higher than 10% of water influenced on starch gelatinization. It was observed swelled starch granules in the samples with 15% of water added (fig. 13a and 13b) inside the gelatinized starch network. But 20% of added water influenced on smooth and homogenous structure inside all the samples after shearing process (fig. 14a and 14b).

Figure 13. Microstructure of potato starch-glycerol-water treated on the Shear Cell with 15% of water added: a) 20% of glycerol, b) 25% of glycerol

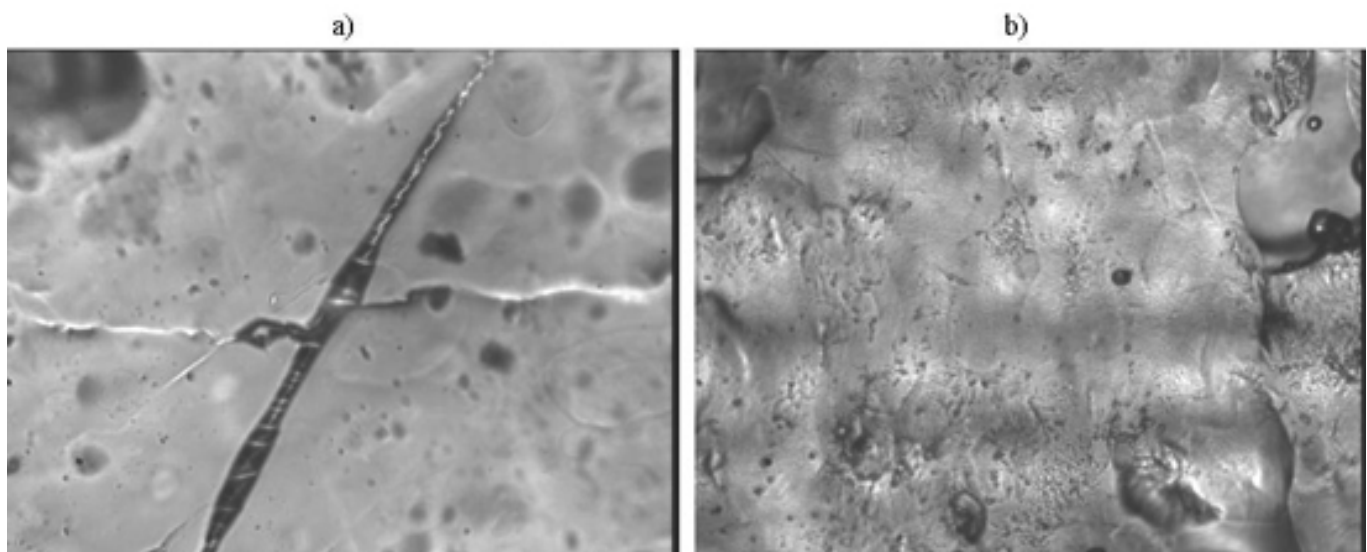


Figure 14. Microstructure of potato starch-glycerol-water treated on the Shear Cell with 20% of water added: a) 20% of glycerol, b) 25% of glycerol

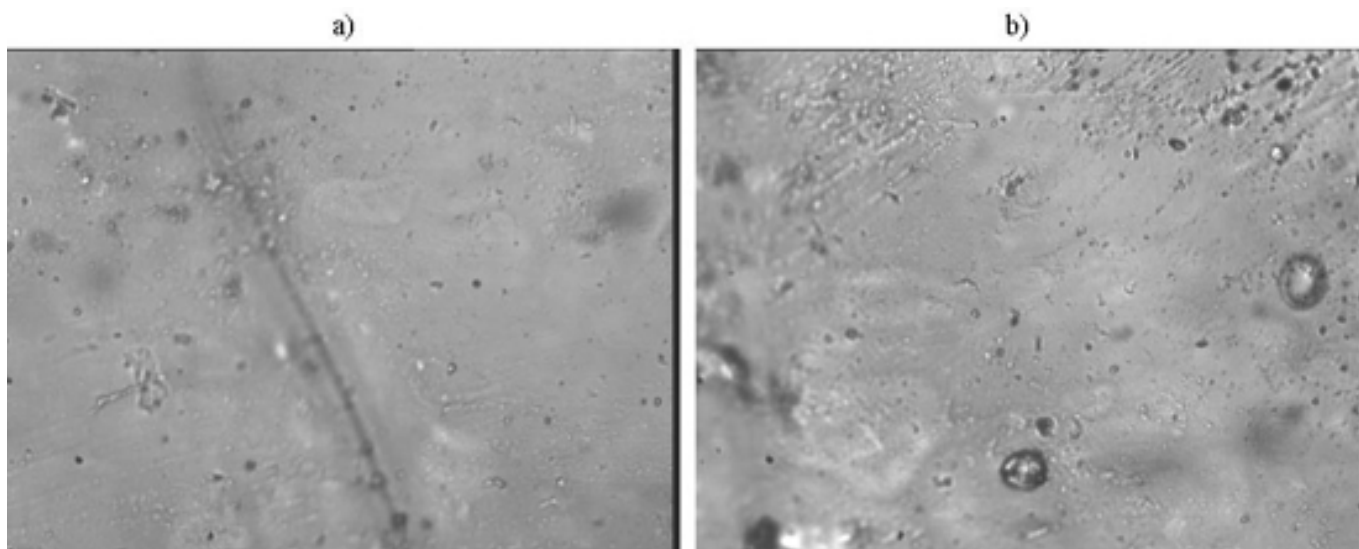
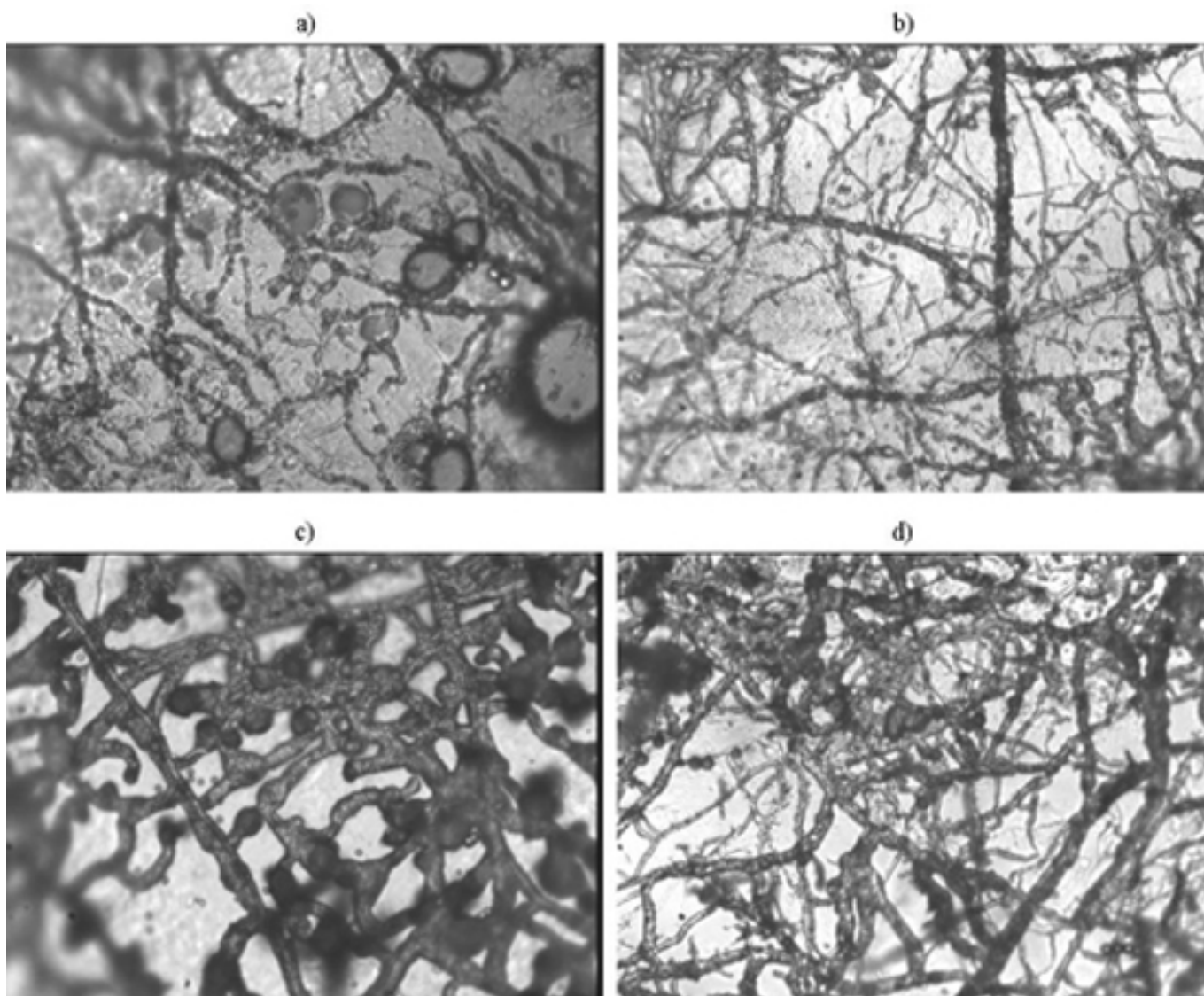


Figure 15. Microstructure of potato starch-water mixtures treated on the Shear Cell with different water addition: a) 5%, b) 10%, c) 15%, d) 20%



Samples without glycerol behave quite different during the shearing process. They were easy to melt, melting process started with 40 to 70 rpm (tab. 1) and with lower temperature. But, as it shown on the Figure 15, it wasn't observed starch gelatinization. In our opinion inside structure shows the amylopectine chains with singular starch granules which starts to disappear in products with higher water level (fig. 15d), however this is hypothetical statement due to

magnification used. Product was completely transparent and looks like glass, it was flexible and elastic but after few days storing became harder and no more flexible.

CONCLUSIVE REMARKS

Results of the experiment shows that the treatment needed to gelatinization process of thermoplastic potato starch was depended on water and glycerol content. Higher water and glycerol contents resulted in earlier and complete gelatinization. Water and glycerol content influenced also on the shear stress: higher level of water and glycerol caused lower shear stress values. Higher rotation speed during heat-shear treatment influenced higher breakdown of starch expressed lower intrinsic viscosity level after treatment. Microstructure pictures shows that completely gelatinization process can be easy realise with 25% of glycerol and 10-20% of water added to potato starch using suggested parameters of thermal shearing.

ACKNOWLEDGEMENT

Presented studies were partly supported by International Agricultural Centre in Wageningen under the scientific fellowship programme of Netherlands Ministry of Agriculture, Nature and Food Quality for Dr. ir. A. Wójtowicz in 2003.

Thanks to Prof. dr. ir. R.M. Boom for kind permission for tests and measurements in the laboratory of Food and Bioprocess Engineering Group Wageningen University.

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Department of Food Process Engineering,
Agricultural University in Lublin, Poland
44 Doświadczalna Street, 20-236 Lublin, Poland
phone: (+48 81) 461 00 61 ext. 118,
fax: (+48 81) 461 06 83
email: agnieszka.wojtowicz@ar.lublin.pl

Atze Jan van der Goot
Food and Bioprocess Engineering Group,
Wageningen University, The Netherlands
Bomenweg 2, 6703 HD, Wageningen, The Netherlands
phone: +31 (0)317 482884 / 482954
fax: +31 (0)317 482237
email: atzejan.vandergoot@wur.nl

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