



Modification of rheological, thermophysical, textural and some physical properties of corn starch by tribomechanical treatment

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ABSTRACT

The aim of this research was to examine the effect of tribomechanical micronization and activation (TMA treatment) on rheological, thermophysical, textural and some physical properties of corn starch. In this work, samples were treated using laboratory equipment for tribomechanical micronization and activation (TMA equipment). Before and after the TMA treatment, analysis of the particle size and particle size distribution was carried out, in addition to micrography. The results showed that the TMA treatment causes a significant decrease in particle size, and change in particle size distribution of powdered corn starch. Micrography showed obvious impact of TMA treatment on structure and size of starch granules. TMA treatment caused disrupting of starch granules by mechanical forces and made the granule more permeable to water during the heating step. Because, statistically significant increase in solubility and swelling power was observed. TMA treatment caused significant lowering of the beginning gelatinization temperatures, which indicated an earlier state of granule swelling during heating. Also, TMA treatment has affected a significant increase of starch suspension viscosity. Results of differential scanning calorimetry measurements are showing decrease in enthalpy of gelatinization. The texture profile analyses of the starch gel prepared with suspension of TMA treated corn starch presented higher hardness, adhesiveness, cohesiveness, springiness and gumminess when compared with untreated suspension.

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1. Introduction

In the year 1998, the process of tribomechanical micronization and activation (TMA), as well as the appropriate equipment, was patented under number PCT/PB 99P/00757 in the International Bureau of the WPO PCT Receiving Office in Geneva (Lelas, 1998).

The TMA equipment is made up of housing and two rotor discs placed against each other. Each disc is furnished with 3–7 concentric circles – rings of teeth projecting from the surface of the disc – with specially constructed hard metal elements. The discs rotate in opposite directions at the same angular rate. The starting material enters the equipment through the central part of the rotor system by ventilator air streaming. Therefore the particles are accelerated and, because of repeated changes in the direction of motion, collide, causing friction over short time intervals (less than 0.001 s).

The investigation with tribomechanical activation (TMA) as a technique concerned with the study of phenomena appearing during fine milling under dynamic conditions has been primarily

focused on inorganic materials (Bhushan, 2000; Lelas, 1998), but recently investigations were directed to organic materials such as powdered whey proteins and have established that application of this technique caused changes in physicochemical and functional properties of treated materials offering potential to commercialization (Herceg, Lelas, Brnčić, Tripalo, & Ježek, 2004a,b; Herceg, Lelas, & Krešić, 2005; Lelas, 2006). Despite the modification of functionality of food macromolecules, the advantages of these techniques are expressed in milling, resulted in obtaining the particles of equable size while the shortening of process time with lower process temperature and lower energy costs is also remarkable using this technique in emulsification and homogenization (Lelas & Herceg, 2002; Lelas, Herceg, & Rimac-Brnčić, 2003).

Starch products are used nowadays for many applications in food technology industry to achieve particular technological properties such as e.g. solubility, viscosity properties in solution, swelling and pasting properties, digestibility, which are produced from native starches by partial degradation. Starch is an useful polymer not only because it is a cheap, natural material but also because possibility of its physicochemical properties that can be

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altered through chemical or enzyme modification and/or physical treatment. (Che, Li, Wang, Chen, & Mao, 2007a; Che et al., 2007b).

Physical and structural properties of macromolecules can sometimes be exchanged by mechanical means.

Previous investigations have shown that TMA treatment, besides breaking up developed agglomerates, may significantly change structural characteristics of proteins and its reactivity (Krešić, Lelas, Režek Jambrak, Herceg & Rimac Brncić, 2008). Because of such effects on the physical and structural properties of proteins, it is to be expected that the procedure of TMA treatment can cause similar changes on starches.

The purpose of this research was to establish a possible significant influence of TMA treatment on rheological, thermophysical, textural and some physical properties of corn starch. The examinations of the influence of TMA treatment on the morphological characteristic of the corn starch were also performed.

2. Materials and methods

Powdered corn starch sample (commercial name: Maisita 21,000) has been used which composition has been declared by manufacturer (Agrana Starke GmbH, Wien, Austria) as follows: water 11.11%, starch 88.89%.

2.1. Tribomechanical micronization

Corn starch was laboratory treated in the equipment for TMA (Fig. 1).

The laboratory TMA device is capable of treating samples within a wide range of rotor speeds (from 10,000 rpm up to the maximum rotor speed of 22,000 rpm). The TMA treatment was carried out at rotor speed (20,000 rpm) and at ambient temperature. Corn starch was treated using the TMA equipment under atmospheric pressure. Overheating of the materials was prevented by water cooling of the equipment through its housing. Intake of the material for treatment was continuous at 1 kg/min.

2.2. Particle size distribution and specific surface area

The particle size distribution of the powdered corn starch before and after TMA treatment was measured using a laser light scattering instrument, the Malvern Mastersizer 2000 (with a lens of 100 mm focal length). For analysis of the results obtained, MIE

theory was applied (Bohren & Huffman, 1983). Each analysis was made in triplicate and the mean values were taken.

2.3. Micrography of corn starch model systems

Previously prepared and treated 10% w/w corn starch suspensions were photographed using digital camera (Olympus DP 12, Japan) that is attached on the microscope (Olympus BX 51, Japan). Magnification was 1000×. Pictures were computerized with computer software program analysis Image Processing Olympus (Olympus, Japan).

2.4. Solubility index and swelling power determination of corn starch model systems

Solubility and swelling power of corn starch model systems were determined in triplicate according to the method of Leach, McCowen, and Schoch (1959). Aqueous suspensions of 2% starch (w/w) were heated in a water bath at constant temperatures and shaken, for 30 min. Each suspension was cooled and centrifuged at 3000g for 15 min; the decanted was weighed and the supernatant was placed in a vacuum stove at 120 °C for 4 h.

Solubility index, SI (%) has been calculated according to the equation:

$$SI = (W_s/W_0) \times 100 \quad (1)$$

W_s – percentage of the dry matter in supernatant (%); W_0 – percentage of the dry matter in the starting suspension (%).

Swelling power, SP (g of hydrated molecules / g starch dry matter) is calculated according to:

$$SP = W_G/W_{GDM} \quad (2)$$

W_G – gel mass (g); W_{GDM} – mass of gel dry matter (g).

2.5. Determination of rheological properties of corn starch model systems

Rheological properties of corn starch suspensions were determined according to the method of Hagenimana and Ding (2005). Corn starch suspension of 10% (w/w) in 100 mL volume was directly placed into a stainless steel measuring bowl of a Brabender Micro Visco Amylo-Graph (Duisburg, Germany). System operating at 250 rpm was then heated from 30 to 93 °C, with heating rate of 7.5 °C. Samples were held for 1 min at 52 °C and 5 min at maximal temperature of 93 °C. The following parameters: maximum viscosity, decrease in viscosity during cooling, increase in viscosity during heating and beginning of gelatinization (°C) were derived from the Viscoamylograph.

2.6. Differential scanning calorimetry of corn starch model systems

Gelatinization properties were analyzed using a differential scanning calorimeter DSC 822e (Mettler Toledo) equipped with STARE software. An empty pan was used as a reference. Prepared and TMA treated corn starch suspensions were weighed into standard aluminum pan (40 µL). The pans were sealed and equilibrated for 24 h at room temperature before heat treatment in the DSC. The starch slurry was gelatinized in the DSC using a heat rate of 10 °C/min from 25 to 95 °C. After the heat treatment, the samples were cooled to 25 °C and removed from DSC. The changes in enthalpy (ΔH in kJ kg⁻¹ of dry starch), onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) for gelatinization were obtained from the exothermal DSC curves. The experiments were run in triplicates.



Fig. 1. Laboratory equipment for tribomechanical micronization and activation (TMA equipment).

2.7. Gel preparation and determination of textural properties corn starch gels

Prepared corn starch model systems of 10% (w/w) before and after TMA treatment have been used for gel preparation. Gel preparation has been conducted by heating the suspensions placed in 150 mL glass beaker at 80 °C for 15 min in water bath with constant stirring. After heating, samples were rapidly cooled at room temperature by immersing the beaker in icy water and are kept at 4 °C for further analysis. Textural properties were determined 24 h after gel preparation. Gel hardness has been conducted by texture analyzer (Texture analyzer HD+, Stable Micro System, Godalming, Great Britain). Speed of measuring probe was 1 mm/s. Depth of measurement was 10 mm. According to the measuring curves, during two measuring cycles following properties have been derived: hardness, cohesiveness, adhesiveness, springiness and gumminess. Gel hardness has been defined as maximal applied force (N).

2.8. Statistical analyses

The whole study was repeated and each value represents the mean of three measurements from three independent ultrasound treatments. The effect of tribomechanical treatment on tested parameters was determined by analysis of variance, using statistical analyses with SPSS for Windows version 13.0 (SPSS Inc., Chicago, IL). Analysis of variance (One-Way ANOVA), significant level used was 5% ($\alpha = 0.05$). The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

3. Results and discussion

Solutions for the construction of equipment for fine dynamic milling and micronization make significant energy savings possible, as the losses of energy during milling are smaller than with the classic methods where a significant amount of energy is spent on rubbing. With this newly constructed equipment, striking hammers and ventilation paddles placed on rotating discs have the task of producing turbulent movement in the materials being treated, and in this way tested material particles collide and rub against each other in short time intervals (less than 0.001 s), which saves a considerable amount of energy when milling (Herceg, Lelas, Brncic, Tripalo, & Ježek, 2004a).

Powdered corn starch for tribomechanical micronization and activation (TMA) was placed in appropriate equipment (Fig. 1) (Lelas, 1998). The inlet temperature of the corn starch was 20.1 °C, and the outlet temperature was 23.4 °C. This temperature difference achieved during TMA treatment is, in spite of the high friction and collision occurring among the particles, the consequence of cooling the housing of the equipment, and the very short time required for the material to pass through the equipment.

During TMA treatment, corn starch is exposed to the strong mechanical forces that cause collision between particles over short time intervals. The results obtained in this research have shown a significant decrease in particle size of corn starch (Fig. 2). TMA treatment is rupturing and mechanically damages the starch granules by the strong mechanical forces that induces collision between particles and changes their size and shape (Figs. 2 and 3). These causes shear forces that are capable of breaking the chains of polymers and damaging granules that is also influenced by chemical affects caused by TMA treatment (Boldyrev, 1995). The procedure of TMA treatment significantly changes the physical characteristics of the treated material (Krešić, Lelas, Režek Jambrak, Herceg, & Rimac Brncic, 2008).

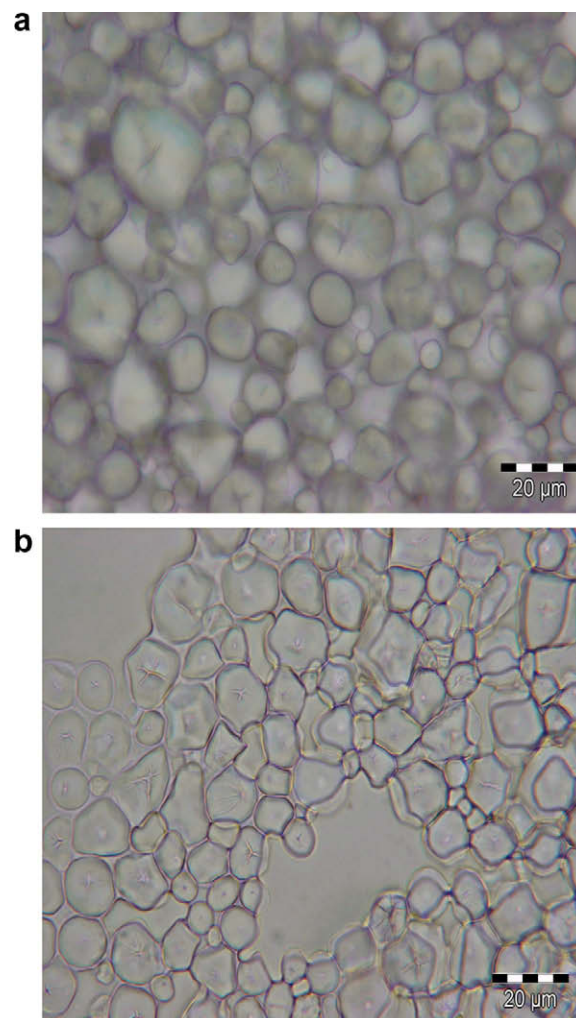


Fig. 2. Microphotographs of samples – K (a), KA (b).

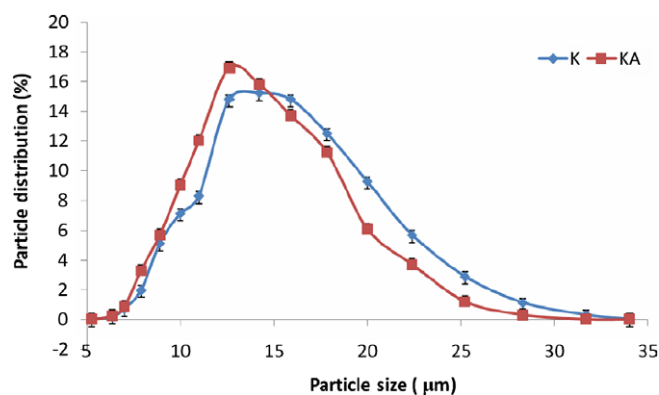


Fig. 3. Particle size distribution of powdered corn starch before and after tribomechanical treatment. K – untreated, KA (TMA treatment).

The solubility index and swelling power of the corn starch were analyzed in order to obtain information about the structural differences and molecular arrangement of the granules. The solubility index (SI) and swelling power (SP) of the starch gel prepared with suspension of TMA treated corn starch had higher values when compared with untreated suspensions (Table 1). It is caused by disruption of starch granules and molecule by TMA treatment. The increase in swelling power is associated with the water absorption

Table 1

Values of solubility index (%) and swelling power for native and modified corn starch suspensions after TMA treatment.

Sample	Determination conditions	Solubility index (%)	Swelling power (g of hydrated molecules / g starch dry matter)
K	20 °C/ 5 min	0.20 ± 0.01 ^a	1.633 ± 0.010 ^a
	20 °C/ 15 min	0.08 ± 0.01 ^a	2.021 ± 0.009 ^a
	70 °C/ 5 min	4.49 ± 0.10 ^a	2.672 ± 0.010 ^a
	70 °C/ 15 min	4.41 ± 0.14 ^a	11.045 ± 0.011 ^a
KA	20 °C/ 5 min	5.02 ± 0.13 ^b	2.752 ± 0.011 ^b
	20 °C/ 15 min	5.21 ± 0.12 ^b	2.589 ± 0.012 ^b
	70 °C/ 5 min	7.75 ± 0.14 ^b	3.953 ± 0.009 ^b
	70 °C/ 15 min	7.72 ± 0.11 ^b	11.998 ± 0.08 ^b

K – untreated, KA (TMA treatment). The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

capacity and the solubility of corn starch granules, respectively. The molecular arrangement, which depends on the present amount of amylose and amylopectin, allows an estimation of the kind of organization occurring in the interior of the granule. The higher facility for water entrance in corn starch granule is due to TMA treatment disruption of granule which is leading to higher water uptake and retention (Kim et al., 2006; Sandhu & Singh, 2007). The major impact on starch granule disintegration is caused

by the strong mechanical forces. These causes shear forces that are capable of pitting the starch granule and breaking the chains of polymers by disrupting covalent bonds. The crystalline molecular structure of corn starch is broken and the water molecules are bonded to the free hydroxyl groups of amylose and amylopectin by hydrogen bonds, which could cause an increase in solubility and swelling power (Singh, Kaur, Singh Sandhu, Kaur, & Nishinari, 2006; Singh, Singh, Kaur, Sodhi, & Gill, 2003). Increase in solubility and swelling power when applying TMA treatment are also significant higher for samples at higher temperature (70 °C) than at 20 °C.

TMA treatment caused significant lowering of the beginning gelatinization temperatures, which indicated an earlier state of granule swelling during heating (Table 2). Such behavior is consistent with mechanical activation's increasing the amorphous regions of the starch granules while weakening and decreasing the crystalline regions of the starch (Hagenimana & Ding, 2005; Huang, Lu, Li, & Tong, 2007; Iida et al., 2008). The onset temperature reflects the first measurable swelling of the starch granules as reflected by the appearance of an increasing viscosity, and the gelatinization temperature reflects the beginning of granule distortion or disruption after the granular structure can no longer support continued swelling. TMA treatment has affected a significant increase of starch suspension viscosity (Fig. 4). TMA treatment caused disrupting of starch granules by strong mechanical forces and crystalline region of molecule being more weakened causing

Table 2

Viscosity of corn starch suspensions.

Sample	Maximum viscosity (BU)	Decrease in viscosity during cooling (BU)	Increase in viscosity during heating (BU)	Beginning of gelatinization (°C)
K	659 ± 1.1 ^a	201 ± 1.1 ^a	428 ± 1.1 ^a	73.0 ± 0.1 ^a
KA	1245 ± 1.3 ^b	505 ± 1.1 ^b	678 ± 1.1 ^b	70.6 ± 0.2 ^b

K – untreated, KA (TMA treatment at 20,000 rpm). The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

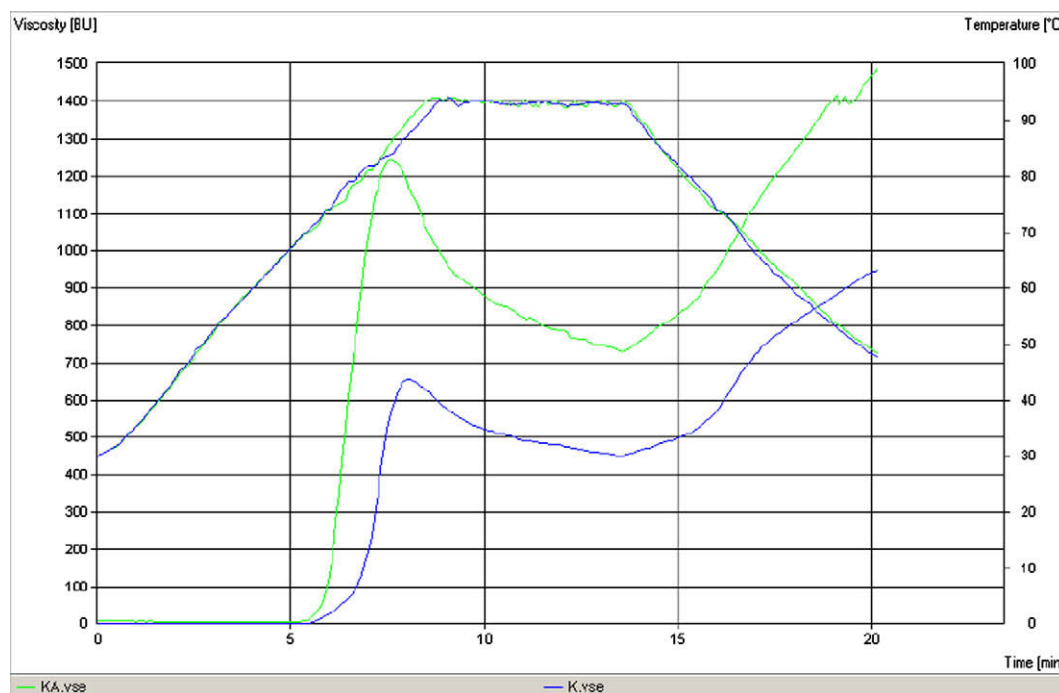


Fig. 4. Viscosity of corn starch suspensions for K and KA samples. K – untreated, KA (TMA treatment).

Table 3

DSC parameters of native and modified corn starch suspensions after TMA treatment.

Sample	T_o (°C)	T_p (°C)	T_e (°C)	ΔT (°C)	ΔH (kJ/kg)
K	66.49 ± 0.25 ^a	71.09 ± 0.24 ^a	74.93 ± 0.14 ^a	8.54 ± 0.12 ^a	12.978 ± 0.24 ^a
KA	66.27 ± 0.16 ^a	70.96 ± 0.21 ^a	74.45 ± 0.26 ^a	8.28 ± 0.15 ^a	10.266 ± 0.25 ^b

K – untreated, KA (TMA treatment at 20,000 rpm). The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

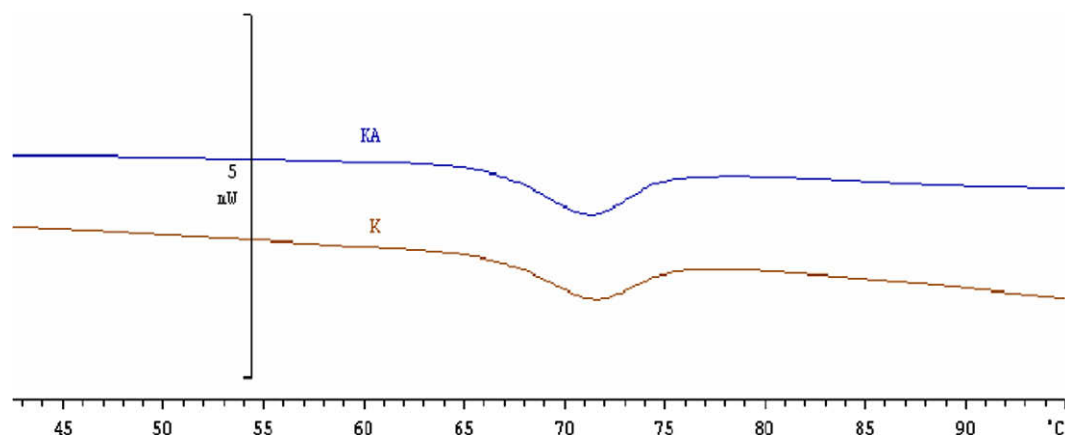


Fig. 5. Gelatinization DSC curves of native and TMA modified corn starch suspensions. K – untreated, KA (TMA treatment).

Table 4

Texture parameters of native and TMA modified corn starches.

Sample	Hardness (N)	Adhesiveness (N/mm)	Cohesiveness	Springiness	Gumminess
K	0.22 ± 0.12 ^a	0.117 ± 0.112 ^a	0.575 ± 0.101 ^a	0.927 ± 0.104 ^a	0.147 ± 0.104 ^a
KA	0.59 ± 0.15 ^b	0.228 ± 0.101 ^b	0.684 ± 0.103 ^b	0.935 ± 0.106 ^a	0.405 ± 0.103 ^b

K – untreated, KA (TMA treatment). The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

more water entrapped within molecule leading to higher viscosity and therefore better homogenization of the whole system (Phillips & Williams, 1995).

The gelatinization temperature of TMA treated corn starch was not statistically higher as compared to the gelatinization temperatures of native corn starch (Table 3). Lower gelatinization temperature for TMA treated corn starch indicate that the beginning of gelatinization requires less energy ($\Delta H_{\text{gel}} = 10.266 \text{ kJ kg}^{-1}$) as compared to the untreated corn starch ($12.978 \text{ kJ kg}^{-1}$), respectively. Obtained variation of gelatinization energy could be explained by differences amongst the bonding forces of the double helix forming the amylopectin crystallography, which resulted in different alignments of the hydrogen bonds within the starch molecules. Loss of double-helical order is considered to be responsible for the enthalpic transition in the thermograms (Fig. 5) (Sandhu & Singh, 2007; Singh et al., 2006). Heat-gelatinization is a phase transition of granules from an ordered state to a disordered one during heating in excess water. It involves melting of ordered regions, both on the crystallite and on the level of double-helical order. TMA treatment of corn starch distorts the crystalline region in starch granules prior to a reversible hydration of the amorphous phase, which results in the destruction of the granular structure.

The texture properties of the corn starch gels were determined by a texture analyzer and are shown in Table 4 and Fig. 6. The gel firmness is mainly caused by the starch gel retrograding, which is associated with the syneresis of water and amylopectin crystallization loss (Miles, Morris, & Ring 1985). Starch gels presenting high stiffness tend to have high amylose content and long amylopectin

chains (Mua & Jackson, 1997a). The texture profile analyses of the starch gel prepared with suspension of TMA treated corn starch (KA) presented higher hardness, adhesiveness, cohesiveness, springiness and gumminess when compared with untreated suspensions (K) (Table 4). It can be explained that starch molecule is degraded and chains of amylose and amylopectin are disrupted and reorganized. There is statistically significant changes in texture properties of gels prepared with TMA treated corn starch suspension as compared to untreated ones.

4. Conclusions

The application of tribomechanical micronization and activation gives opportunity to modify and to improve rheological, thermophysical, textural and some physical properties of corn starch. TMA treatment is causing significant changes in starch granule size and structure and observed decrease in size and, consequently, changes in the starch granules physical properties. TMA treatment caused disrupting of starch granules by mechanical forces and made the granule more permeable to water during the heating step. Because, statistically significant increase in solubility and swelling power was observed. TMA treatment caused significant lowering of the beginning gelatinization temperatures, which indicated an earlier state of granule swelling during heating. Also, TMA treatment has affected a significant increase of starch suspension viscosity. Results of differential scanning calorimetry measurements are showing decrease in enthalpy of gelatinization. The texture profile analyses of the starch gel prepared with suspension of

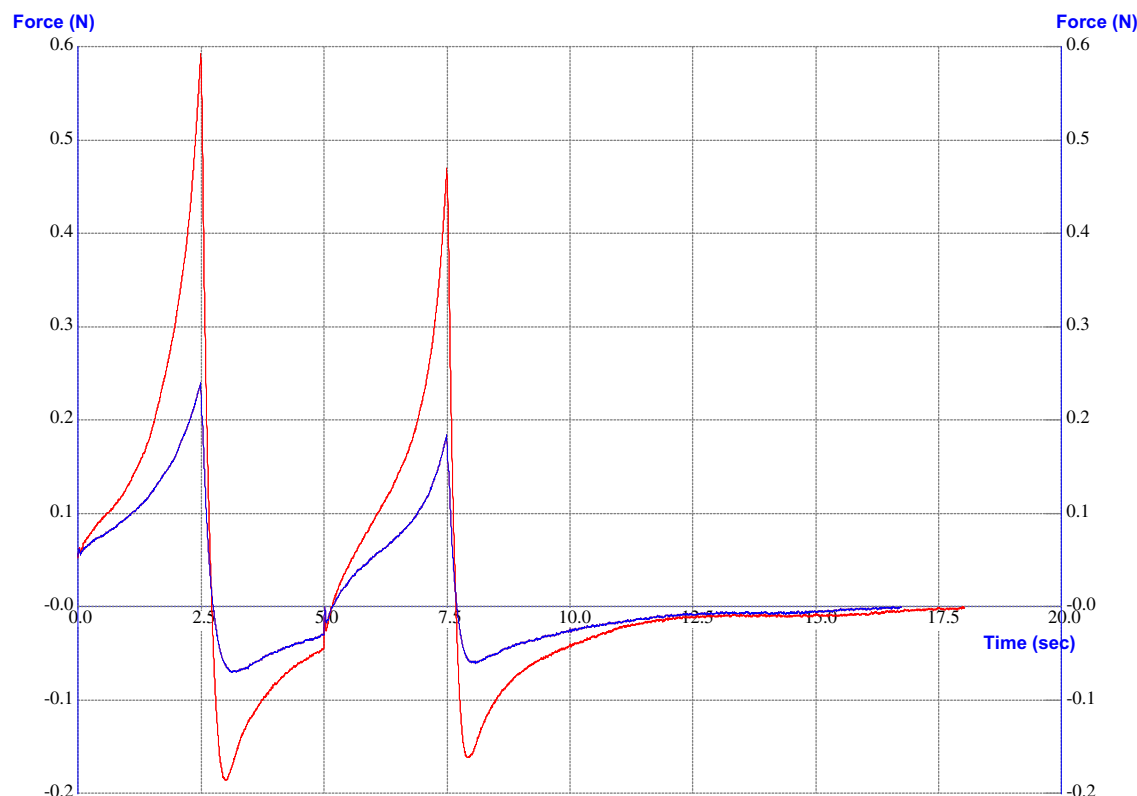


Fig. 6. Texture profile analysis of corn starch gel (K – blue, KA – red). (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

TMA treated corn starch presented higher hardness, adhesiveness, cohesiveness, springiness and gumminess when compared with untreated suspension.

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