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Ultrasound effect on physical properties of corn starch

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ABSTRACT

High power ultrasound (HPU) represents a non-thermal processing method that has been rapidly researched and used in the last 10 years. The application of power ultrasound offers the opportunity to modify and improve some technologically important compounds which are often used in food products. One of them is starch. The aim of this research was to examine the effect of the high power ultrasound of 24 kHz frequency on rheological and some physical properties of corn starch. Various ultrasound treatments were used; an ultrasound probe set with different intensities (34, 55, 73 W cm^{-2}) and treatment times (15 and 30 min) and ultrasound bath of 2 W cm^{-2} intensity and treatment times (15 and 30 min). Rheological parameters, turbidity and swelling power of corn starch suspensions were determined for native and ultrasonically treated corn starch suspensions. Differential scanning calorimetry was used in order to examine the pasting properties of corn starch. The results have shown that the ultrasound treatment of corn starch distorts the crystalline region in starch granules. The results of differential scanning calorimetry measurements have shown a decrease in enthalpy of gelatinization. A significant decrease in consistency coefficient (k) has also been observed. The consistency coefficient decreases stepwise jointly with the increasing ultrasound power. The increase in the swelling power is associated with water absorption capacity and corn starch granules solubility, respectively.

1. Introduction

Starch products are nowadays used for many applications in food processing to achieve particular technological properties such as solubility, viscosity properties in solution, swelling and pasting properties, digestibility, produced from native starches by partial degradation. As starch molecule is composed of an amorphous region (amylose) and crystalline region (amylopectin). Ratio and proportion of amylose and amylopectin are from 20% to 25% for amylose and from 75% to 80% for amylopectin. The proportion depends on the source of starch, either plan or tuber. The size of a starch granule also depends on the source, and the potato starch granules are the largest granules of all sources. When heated, in the presence of excess water, starch granules lose their crystallinity, absorb large amounts of water, and leach out amylose, which impart viscosity to the starch/water system (Che, Li, Wang, Chen, & Mao, 2007b; Che et al., 2007a; Evans & Haisman, 1979).

Ultrasound is the sound that is above the threshold of the human ear (above 18 kHz). Ultrasound is typically divided into three regions of frequency. Power ultrasound is in the region from 16 to 100 kHz (1 Hz is 1 cycle/s), high-frequency ultrasound is from 100 kHz to 1 MHz and diagnostic ultrasound is from 1 to 10 MHz. Ultrasound is generated with either piezoelectric or magnetostrictive transducers that create high-energy vibrations. These vibrations are amplified and transferred to a sonotrode or probe, which is in direct contact with the fluid. Some known applications of high power ultrasound in food processing include the following: extraction (release of plant material), emulsification, homogenization, crystallization (formation of smaller ice crystals in freezing), filtration, separation, viscosity alteration, defoaming, and extrusion. Ultrasound inactivates enzymes and bacteria by breaking the cell membranes due to the violence of cavitation and due to the formation of free radicals. Cavitation is the formation of cavities filled with gas or vapor as the pressure decreases, and their collapse as soon as the pressure increases again (Mason, 1998).

The viscosity of starch solution of moderate concentration (5–10%) can be reduced to about two orders of magnitude to 100 mPa s by ultrasonic irradiation for 30 min. The ultrasonic process has been confirmed to be applicable to many kinds of starches (corn, potato, tapioca, and sweet potato) and polysaccharides (Iida, Tuziuti, Yasui, Towata, & Kozuka, 2008). The effects of 360 kHz ultrasound on an aqueous solution of chitosan and starch have been studied. This treatment is an efficient procedure for the reduction of molecular weight of both polysaccharides. It has been demonstrated that at the applied ultrasound frequency, degrada-

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tion of starch molecule is caused both by OH radicals and mechanochemical effects (Czechowska-Biskup, Rokita, Lotfy, Ulanski, & Rosiak, 2005).

The aim of this research was to examine the effect of a high power ultrasound of 24 kHz frequency on rheological and some physical properties of corn starch. Various ultrasound treatments were used; an ultrasound probe set with different intensities (34, 55, 73 W cm^{-2}) and treatment times (15 and 30 min) and the ultrasound bath of 2 W cm^{-2} intensity and treatment times (15 and 30 min).

2. Materials and methods

2.1. Sample preparation

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

Suspensions have been prepared by stirring the appropriate amount of corn starch powder and distilled water as stated in Table 1 so that suspension contains 10% of dry matter (w/w). Suspensions prepared in this way have been homogenized on magnetic stirrer and labeled as described in Table 2. Suspensions labeled as K1, K2, K3, K4, K5, K6, K7, K8, and K9 have then been treated with ultrasound as described in Table 2. Treated and untreated (K1) suspensions have been used for the determination of rheological parameters, turbidity measurements, swelling power and for gelatinization properties using a differential scanning calorimeter, as well.

2.2. Ultrasound treatments of corn starch model systems

2.2.1. Ultrasound treatment with 24 kHz probe

Prepared samples for ultrasound treatment with probe (24 kHz) of 500 mL volume were placed in a flat bottomed conical flask. Samples were treated for 15 and 30 min with power ultrasound of 100, 300, and 400 W of nominal power with constant amplitude of 100%. High intensity and low frequency 24 kHz probe (UP 400S, "Dr. Hielscher" GmbH, Teltow, Germany) was attached to the transducer. Probe had a vibrating titanium tip of 7 mm in diameter and was immersed in the liquid and the liquid is irradiated with an ultrasonic wave directly from the horn tip.

2.2.2. Ultrasound treatment with 24 kHz bath

Prepared samples of 500 mL volume were placed directly in the ultrasound bath and treated with ultrasound bath of 24 kHz frequency. Samples were treated for 15 and 30 min (Model designed at Faculty of Mechanical Engineering and Naval Architecture, HF-Pk-power 300 W – overall dimensions: 370 × 175 × 250 mm; internal dimensions: 300 × 150 × 150 mm, Zagreb, Croatia). Ultrasonic transducers were attached to the bottom of the outer surface of the liquid container and the liquid was irradiated with ultrasonic waves from the surface of the liquid container.

Table 1
Composition of corn starch suspensions.

Sample	Corn starch (g)	Water (g)
10% (w/w) suspension[c]	11.25	88.75
1% (w/w) suspension[a]	1.12	98.88
2% (w/w) suspension[b]	2.25	97.75

[a] Used for turbidity measurements.
[b] Used for swelling power measurements.
[c] Used for rheological properties.

Table 2
Labels of samples, intensity, and treatment times.

Sample	Treatment	Intensity (W cm^{-2})	Time (min)
K1	Untreated	–	–
K2	Ultrasound bath	2	15
K3	Ultrasound bath	2	30
K4	Ultrasound probe	34	15
K5	Ultrasound probe	34	30
K6	Ultrasound probe	55	15
K7	Ultrasound probe	55	30
K8	Ultrasound probe	73	15
K9	Ultrasound probe	73	30

2.2.3. Determination of ultrasound power and intensity

Ultrasonic power, which is considered as mechanical energy, would be partly lost in the form of heat when ultrasound passes through the medium (Thompson & Doraiswamy, 1999). Since the ultrasonic irradiation of a liquid produces heat, recording the temperature as a function of time leads to the acoustic power estimation (in W) by the equation (Margulis & Malt'sev, 1969; Margulis & Margulis, 2003).

$$P = m \cdot c_p \cdot \left(\frac{dT}{dt}\right) \quad (1)$$

where m is the mass of the sonicated liquid (g), c_p is the specific heat of medium at a constant pressure dependent on composition and volume of medium (J $(g\,K)^{-1}$), dT/dt is the slope at the origin of the curve.

Ultrasound intensity is expressed in watts per unit area of the emitting surface (W cm^{-2}), or in watts per unit volume of the sonicated solution (W cm^{-3}).

Ultrasonic intensity is measured by calorimetry by thermocouple (model: HI 9063, Hanna Instruments Ltd., Leighton, Buzzard LU7 4AD, UK) and expressed in W cm^{-2}.

2.3. 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 reference. Prepared and ultrasound treated corn starch suspensions were weighed in standard aluminum pans (40 μL). The pans were sealed and equilibrated for 24 h at room temperature before heat treatment in DSC. The starch slurry was gelatinized in DSC using a heat rate of 10 °C/min from 25 to 95 °C. After 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.

2.4. Determination of rheological properties of corn starch model systems

Torque measurements were carried out on the 10% (w/w) model systems using a Rheometric Viscometer (Model RM 180, Rheometric Scientific, Inc., Piscataway, USA) with the spindle (No. 3; Ø = 14 mm; l = 21 cm). Shear stress against the increasing shear rates from the lowest value of 0 to 1290 s^{-1}, as well as downwards was applied. Volume of the beaker was 32 mL. The samples were kept in a thermostatically controlled water bath for about 15 min before measurements in order to attain the desirable temperature of 20 °C. Measurements were done in triplicates for each sample. The shear rate versus shear stress was interpreted using the Rheometric computer program. The values for n and k were obtained

Table 3
Temperature of corn starch suspensions after ultrasound treatment (K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), K5 (ultrasound probe – 100 W–30 min), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min)).

Sample	Initial sample temperature (°C)	Temperature of sample after treatment (°C)
K1	18.1 ± 0.1[a]	18.1 ± 0.2[a]
K2	18.2 ± 0.1[a]	20.3 ± 0.2[a]
K3	18.2 ± 0.1[a]	21.4 ± 0.2[a]
K4	18.2 ± 0.1[a]	40.2 ± 0.2[b]
K5	18.2 ± 0.1[a]	50.0 ± 0.2[b]
K6	19.6 ± 0.1[a]	37.2 ± 0.2[b]
K7	19.6 ± 0.1[a]	42.2 ± 0.2[b]
K8	19.1 ± 0.1[a]	49.4 ± 0.2[b]
K9	19.1 ± 0.1[a]	56.4 ± 0.2[b]

The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

from plots of log shear stress versus log shear rate, according to the power law equation:

$$\log \tau = logk + nlog\gamma \quad (2)$$

where τ is the shear stress (Pa); γ is the shear rate (s^{-1}); n is the flow behaviour index, and k is the consistency index (Pa s^n).

Apparent viscosity (η_{app}) was calculated at 1290 s^{-1} using Newtonian law, in addition with linear least square method for regression analysis:

$$\tau = \eta_{app} \cdot \gamma \quad (3)$$

2.5. Turbidity measurements of corn starch model systems

A 1% aqueous suspension of corn starch (native, ultrasound treated) near neutral pH was heated at 90 °C in a boiling water bath for 1 h with constant stirring (mild shear forces). After the suspension was cooled for 1 h at 30 °C, the turbidity was determined by measuring the absorbance at 640 nm against a water blank in 1 cm path length cuvettes with a UV–visible spectrophotometer (Helios-b, Pye Unicam Ltd., Cambridge, UK). The development of turbidity was followed by storing samples for 5 day at 4 °C. The absorbance of the suspension was measured every day by a spectrophotometer. The absorbance was read initially, after what the turbidity was calculated using the following formula:

$$T = 2303 \cdot A/I \quad (4)$$

where T is the turbidity, A is the absorbance at 640 nm, and I is the path length of cuvette (m).

2.6. Swelling power of corn starch model systems

Granule disintegration was determined using a method to measure the swelling power of starch. The swelling power was 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 shaking for 30 min. Each suspension was cooled and centrifuged at 3000 rpm for 15 min; the decanted was weighed and the supernatant was placed in a vacuum stove at 120 °C for 4 h. The data obtained were used to calculate the swelling power of starch granules.

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

$$SP = W_G/W_{GDM} \quad (5)$$

where W_G is the gel mass (g) and W_{GDM} is the mass of gel dry matter (g).

2.7. Micrography of corn starch model systems

Previously prepared and treated 10% w/w corn starch suspensions were photographed using a digital camera (Olympus DP 12, Japan) which was attached to the microscope (Olympus BX 51, Japan). Magnification was l000×. Photographs were computerized with the computer software program analySIS Image Processing Olympus (Olympus, Japan).

2.8. Statistical analyses

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

3. Results and discussion

3.1. Differential scanning calorimetry of corn starch model systems

The gelatinization temperature (Table 4) of sonicated corn starch has not been statistically higher as compared to the gelatinization temperatures of native corn starch (74.99 °C). In corn starch lower gelatinization temperature for K2 and K3 samples indicates that the beginning of gelatinization requires less energy

Table 4
DSC parameters of native and modified corn starch suspensions after ultrasound treatment (K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), K5 (ultrasound probe – 100 W–30 min), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min)).

Sample	T_o (°C)	T_p (°C)	T_e (°C)	ΔT (°C)	ΔH (kJ kg^{-1})
K1	66.44 ± 0.25[a]	71.07 ± 0.24[a]	74.99 ± 0.14[a]	8.55 ± 0.12[a]	12.966 ± 0.24[a]
K2	66.69 ± 0.16[a]	71.06 ± 0.21[a]	74.69 ± 0.26[a]	8.00 ± 0.15[b]	8.733 ± 0.25[b]
K3	66.60 ± 0.27[a]	71.03 ± 0.19[a]	74.68 ± 0.18[a]	8.08 ± 0.16[b]	8.733 ± 0.29[b]
K4	66.73 ± 0.21[a]	71.25 ± 0.23[a]	75.42 ± 0.17[a]	8.69 ± 0.08[b]	11.973 ± 0.31[b]
K5	66.57 ± 0.13[a]	71.16 ± 0.18[a]	74.76 ± 0.21[a]	8.19 ± 0.07[b]	10.455 ± 0.24[b]
K6	66.62 ± 0.17[a]	71.36 ± 0.24[a]	75.27 ± 0.27[a]	8.65 ± 0.10[b]	11.666 ± 0.26[b]
K7	66.88 ± 0.16[a]	71.11 ± 0.27[a]	75.04 ± 0.25[a]	8.16 ± 0.14[b]	11.000 ± 0.21[b]
K8	66.63 ± 0.13[a]	71.91 ± 0.16[a]	74.82 ± 0.23[a]	8.19 ± 0.15[b]	10.333 ± 0.20[b]
K9	68.65 ± 0.14[a]	71.71 ± 0.18[a]	75.24 ± 0.22[a]	6.59 ± 0.17[b]	7.466 ± 0.19[b]

The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

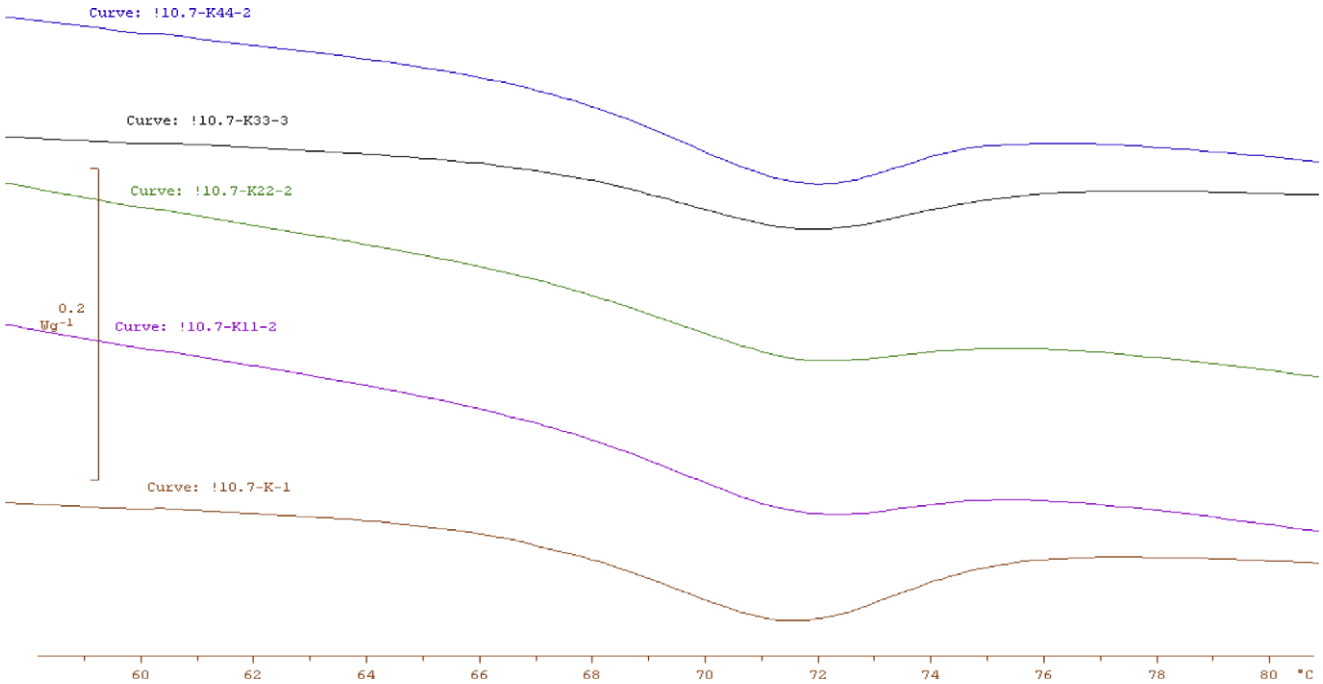

Fig. 1. Gelatinisation DSC curves of native and ultrasonically modified corn starch suspensions (K1, K2, K3, K4, and K5). K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), and K5 (ultrasound probe – 100 W–30 min).

(ΔH_{gel} = 8.733 kJ kg^{-1}) as compared to the untreated corn starch (12.966 kJ kg^{-1}), respectively. The greatest decrease in enthalpy is for ultrasonically treated K9 sample (7.466 kJ kg^{-1}) which indicates that it requires the least energy for gelatinization as compared to the native and other ultrasonically treated samples. The obtained variation of gelatinization energy could be explained by differences amongst the bonding forces of the double helix forming the amylopectin crystallography, which has resulted in different alignments of the hydrogen bonds within the starch molecules (Sandhu & Singh, 2007). The loss of double-helical order is considered to be responsible for the enthalpic transition in the thermograms (Figs. 1 and 2) (Altay & Gunasekaran, 2006; Liu, Bao, Du, Zhou, & Kennedy, 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. Ultrasound 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 (Blaszczak et al., 2007; Rubens & Heremans, 2000). Ultrasound causes a

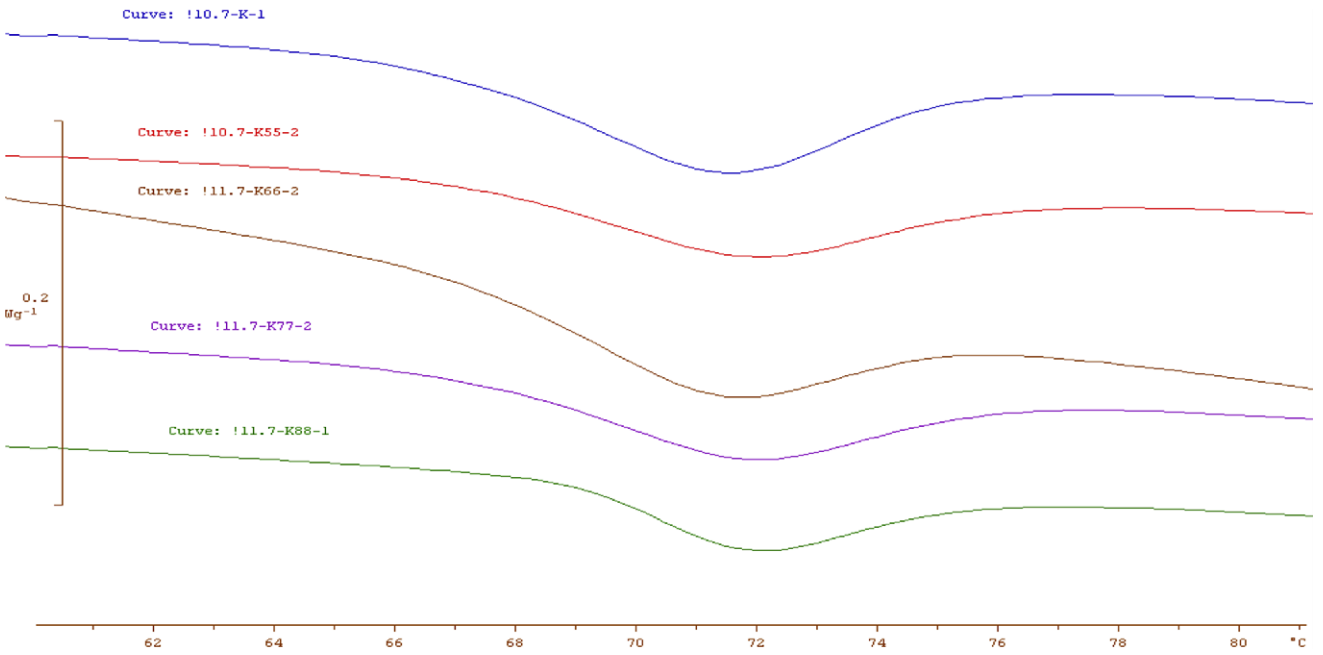

Fig. 2. Gelatinisation DSC curves of native and ultrasonically modified corn starch suspensions (K1, K6, K7, K8, and K9). K1 (untreated), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min).

Table 5
Rheological parameters of corn starch suspensions at temperature of 20 °C (K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), K5 (ultrasound probe – 100 W–30 min), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min)).

Sample	Apparent viscosity* μ (Pa s)	Consistency coefficient k (μPa s)	Flow index n	Determination coefficient R^2
K1	0.8722 ± 0.1262[a]	27.31 ± 0.20[a]	1.733 ± 0.147[a]	0.9929
K2	0.8740 ± 0.1368[a]	27.44 ± 0.21[a]	1.792 ± 0.167[b]	0.9948
K3	0.8832 ± 0.1348[a]	28.64 ± 0.19[a]	1.789 ± 0.135[b]	0.9968
K4	0.8789 ± 0.1186[a]	27.74 ± 0.18[a]	1.767 ± 0.167[a]	0.9988
K5	0.8647 ± 0.1678[a]	25.78 ± 0.16[b]	1.736 ± 0.198[a]	0.9995
K6	0.8643 ± 0.1698[a]	24.11 ± 0.19[b]	1.822 ± 0.168[b]	0.9963
K7	0.8507 ± 0.1476[a]	20.07 ± 0.22[b]	1.891 ± 0.210[b]	0.9972
K8	0.8254 ± 0.1205[b]	19.57 ± 0.17[b]	1.834 ± 0.186[b]	0.9976
K9	0.7603 ± 0.1068[b]	17.12 ± 0.15[b]	1.839 ± 0.123[b]	0.9974

The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).
* Apparent viscosity is calculated at shear strain of 1290 s^{-1}.

Table 6
Turbidity parameters of native and modified corn starch suspensions after ultrasound treatment (K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), K5 (ultrasound probe – 100 W–30 min), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min)).

Sample	Time (h)				
	0	24	48	72	96
K1	365.25 ± 1.11[a]	360.64 ± 1.11[a]	338.77 ± 1.21[a]	284.88 ± 1.18[a]	278.89 ± 1.16[a]
K2	360.65 ± 1.11[a]	311.24 ± 1.13[b]	277.34 ± 1.19[b]	233.44 ± 1.16[b]	210.34 ± 1.13[b]
K3	368.43 ± 1.12[a]	298.54 ± 1.14[b]	210.62 ± 1.18[b]	180.36 ± 1.15[b]	158.94 ± 1.14[b]
K4	362.37 ± 1.13[a]	209.80 ± 1.09[b]	176.17 ± 1.17[b]	66.55 ± 1.13[b]	37.76 ± 1.16[b]
K5	359.47 ± 1.12[a]	195.52 ± 1.09[b]	75.22 ± 1.13[b]	17.83 ± 0.18[b]	6.67 ± 0.17[b]
K6	359.73 ± 1.11[a]	32.47 ± 0.10[b]	8.98 ± 0.12[b]	3.45 ± 0.19[b]	3.45 ± 0.18[b]
K7	350.21 ± 1.12[a]	2.07 ± 0.11[b]	1.38 ± 0.16[b]	1.15 ± 0.17[b]	0.69 ± 0.19[b]
K8	348.66 ± 1.10[a]	3.14 ± 0.13[b]	1.99 ± 0.15[b]	1.41 ± 0.16[b]	1.02 ± 0.16[b]
K9	340.49 ± 1.09[a]	2.97 ± 0.14[b]	1.88 ± 0.14[b]	1.67 ± 0.15[b]	0.70 ± 0.15[b]

The values not statistically different are accompanied by the letter (a) and the values statistically different with the letter (b).

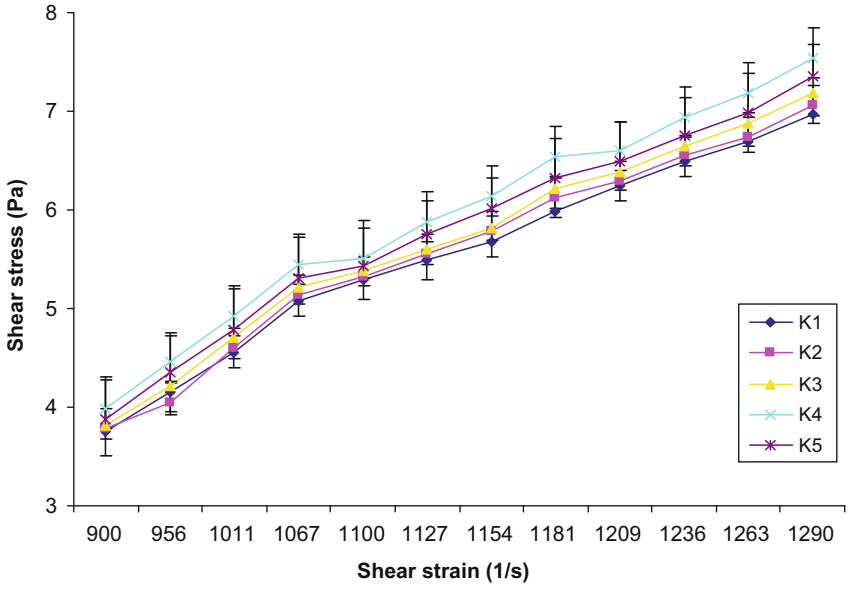

Fig. 3. Relationship between shear stress and shear strain of native (K1) and ultrasonically modified corn starch suspensions (K2, K3, K4, and K5). K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), and K5 (ultrasound probe – 100 W–30 min).

higher increase in samples temperature when increasing ultrasound power and applying higher intensity (Table 3). The highest increase from the native sample temperature (18.1 °C) is for K9 treatment (56.4 °C) by applying ultrasound power of 400 W for 30 min. The destruction of inter-helix interactions under ultrasound conditions results in decreasing gelatinization enthalpy by applying high ultrasound power. Obviously, the main effect is cavitation and ultrasound disrupting of starch granules, because the treatment temperature did not exceed 60 °C. A higher temperature would generally result in more starch breakdown. Heat treatment at temperatures 110 °C in study of Van den Einde, Akkermans, Van der Goot, and Boom (2004) induced only a small amount of starch degradation within 15 min, which can probably be neglected in short-time experiments. The heating experiments showed that

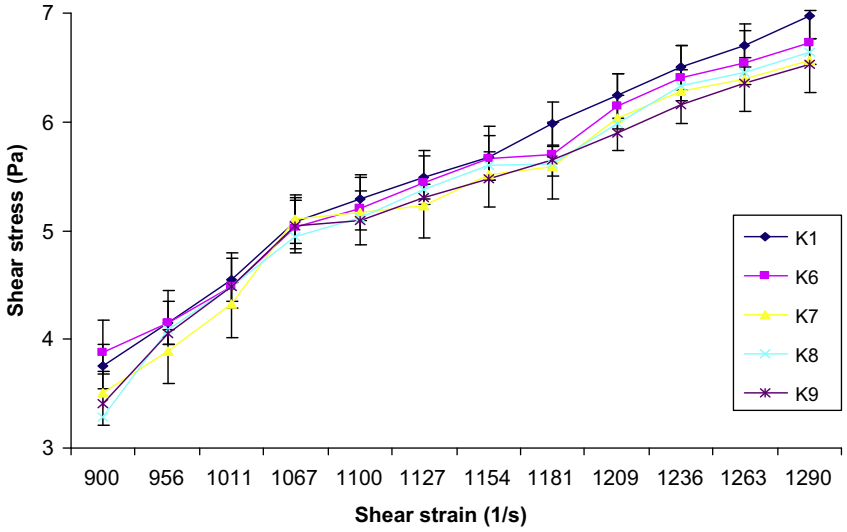

Fig. 4. Relationship between shear stress and shear strain of native (K1) and ultrasonically modified corn starch suspensions (K6, K7, K8, and K9). K1 (untreated), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min).

thermal effects on starch granules play a role within 15 min at temperatures higher than 110 °C. Water reactivity is also increased during cavitation and elevated pressures that enhance the process of water diffusion into starch granules, especially into the amorphous phase. Cavitation disrupts starch granules and the diffusion of water leads to breaking of the crystal structure.

3.2. Rheological properties of corn starch model systems

The results of measuring the rheological parameters of corn starch suspensions are shown in Table 5. From data one can observe statistically significant decrease in consistency coefficient (k) as compared to the untreated sample (27.31 μPa s). The highest decrease is obtained for K8 (19.57 μPa s) and K9 (17.12 μPa s) samples that are ultrasonically treated with ultrasound probe set of 400 W power. It is obvious that the consistency coefficient is decreasing stepwise jointly with increasing ultrasound power. The ultrasound induced degradation of starch might be mainly attributed to the violent shear force encountered by starch molecule in the shearing valve. Czechowska-Biskup et al. (2005) have postulated that a shear induced degradation occurs in a non-random manner (breakage near the mid-point of the chain is preferred), and that there is a definite minimum chain length limiting the degradation process. When it is reached, no further chain disruption is observed. It is reasonable to assume that there is a definite minimum apparent viscosity corresponding to the minimum chain length. From the data it can be seen that there is no statistically difference in the results of apparent viscosity (μ) of ultrasound treated samples as compared to untreated (native) starch (0.8722 Pa s), but statistically different data have been observed for K8 and K9 samples (0.8254 and 0.7603 Pa s) that are treated with maximum power and intensity (400 W, 73 W cm^{-2}). The starch molecule chains get shorter and shorter with increasing ultrasound intensity and progressively approach the minimum chain length (Table 6).

The flow behavior of corn starch samples are dominated by the disrupted starch molecules. The flow behavior indices of these corn starch samples are all higher than 1 ($n > 1$) which indicates that they exhibit a time-independent non-Newtonian character which should be considered as dilatant properties. The relationship between shear stress and shear rate for native and ultrasonically treated samples are shown in Figs. 3 and 4.

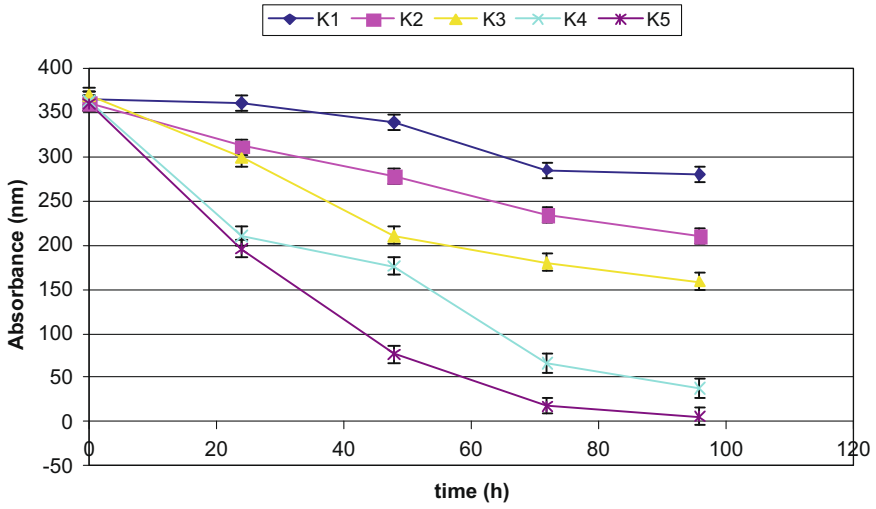

Fig. 5. Relationship between absorbance and storage time of native (K1) and ultrasonically modified starches (K2, K3, K4, and K5). K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), and K5 (ultrasound probe – 100 W–30 min).

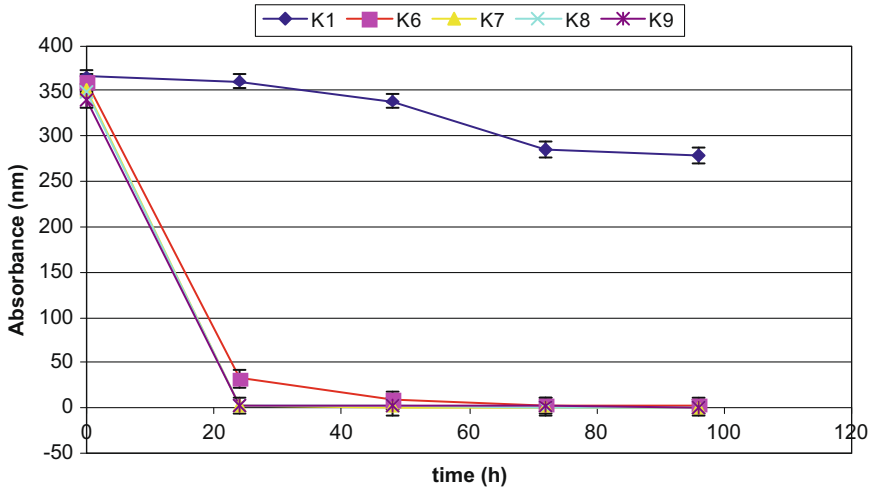

Fig. 6. Relationship between absorbance and storage time of native (K1) and ultrasonically modified starches (K6, K7, K8, and K9). K1 (untreated), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min).

3.3. Turbidity of corn starch model systems

The reduction in turbidity of ultrasound treated corn starch suspensions is not statistically different compared with the untreated samples (Table 5). But with storage, the turbidity of samples decreases rapidly. The greater the decrease is when applying more and more ultrasound intensity and is remarkably observed for K6, K7, K8, and K9 samples for 24, 48, 72, and 96 h storage time. That is, the greatest decrease in turbidity when corn starch suspensions were treated with 300 W and 400 W ultrasound probe set. Turbidity further decreases with the prolonging of storage time. The graphical overview of the absorbance values with time are shown in Figs. 5 and 6. It can be observed that, as mentioned before, the greatest decrease in absorbance and consequently in turbidity is when applying ultrasound probe set with the greatest intensity. Values of absorbance and turbidity are decreased also for samples that were ultrasonically treated with 24 kHz bath but not as remarkably as when applying probe. As the temperature is increased (Table 3), when applying higher intensity ultrasound, the molecules absorb translational energy and gradually lose their hydration resulting in the lowering of viscosity as mentioned before (Table 5) (Sarkar & Walker, 1995).

3.4. Swelling power of corn starch model systems

The swelling power of the corn starch was analyzed in order to obtain information on the structural differences and molecular arrangement of the granules. From the results in Table 7 one can observe an increase in the swelling power with increasing ultrasound power and intensity. Values for swelling power for ultrasonically treated corn starch suspensions K4 (13.533 g of hydrated molecules/g starch dry matter), K5 (12.412 g of hydrated molecules/g starch dry matter), K6 (15.431 g of hydrated molecules/g starch dry matter), and K7 (15.867 g of hydrated molecules/g starch dry matter) at 70 °C are higher than for untreated (11.055 g of hydrated molecules/g starch dry matter) and for 24 kHz bath treated corn starch suspensions (K2 – 11.877 g of hydrated molecules/g starch dry matter and K3 – 11.744 g of hydrated molecules/g starch dry matter). The increase in swelling power, when applying ultrasound is also higher for samples at higher temperature (70 °C) than at 20 °C. The swelling power (SP) is directly correlated to the increase in temperature. The increase in swelling power is associated with the water absorption

Table 7
Values of swelling power for native and modified corn starch suspensions after ultrasound treatment (K1 (untreated), K2 (ultrasound bath – 15 min), K3 (ultrasound bath – 30 min), K4 (ultrasound probe – 100 W–15 min), K5 (ultrasound probe – 100 W–30 min), K6 (ultrasound probe – 300 W–15 min), K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min)).

Sample	Preparation	Swelling power (g of hydrated molecules/g starch dry matter)
K1	20 °C/5 min	1.621 ± 0.012[a]
	20 °C/15 min	2.011 ± 0.011[a]
	70 °C/5 min	2.662 ± 0.008[a]
	70 °C/15 min	11.055 ± 0.009[a]
K2	20 °C/5 min	2.017 ± 0.010[b]
	20 °C/15 min	2.123 ± 0.011[b]
	70 °C/5 min	2.733 ± 0.007[a]
	70 °C/15 min	11.877 ± 0.010[a]
K3	20 °C/5 min	2.123 ± 0.011[b]
	20 °C/15 min	2.054 ± 0.009[a]
	70 °C/5 min	2.922 ± 0.012[b]
	70 °C/15 min	11.744 ± 0.011[a]
K4	20 °C/5 min	2.613 ± 0.008[b]
	20 °C/15 min	2.219 ± 0.011[b]
	70 °C/5 min	2.901 ± 0.010[b]
	70 °C/15 min	13.533 ± 0.011[b]
K5	20 °C/5 min	2.413 ± 0.012[b]
	20 °C/15 min	2.233 ± 0.013[b]
	70 °C/5 min	3.018 ± 0.016[b]
	70 °C/15 min	12.412 ± 0.014[b]
K6	20 °C/5 min	2.624 ± 0.013[b]
	20 °C/15 min	2.858 ± 0.014[b]
	70 °C/5 min	3.978 ± 0.010[b]
	70 °C/15 min	15.431 ± 0.008[b]
K7	20 °C/5 min	2.643 ± 0.009[b]
	20 °C/15 min	2.526 ± 0.008[b]
	70 °C/5 min	6.313 ± 0.010[b]
	70 °C/15 min	15.867 ± 0.013[b]
K8	20 °C/5 min	2.781 ± 0.011[b]
	20 °C/15 min	2.640 ± 0.009[b]
	70 °C/5 min	3.023 ± 0.010[b]
	70 °C/15 min	12.736 ± 0.013[b]
K9	20 °C/5 min	2.752 ± 0.011[b]
	20 °C/15 min	2.589 ± 0.012[b]
	70 °C/5 min	3.953 ± 0.009[b]
	70 °C/15 min	11.998 ± 0.08[b]

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 a corn starch granule is due to the ultrasound disruption of the granule leading to a higher water uptake and retention (Kim, Lee, & Yoo, 2006; Sandhu & Singh, 2007). The major impact on starch granule disintegration is caused by the cavitation forces. The sudden collapse of cavitation bubbles induces high pressure gradients and high local velocities of liquid layers in their vicinity which 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 bounded to the free hydroxyl groups of amylose and amylopectin by hydrogen bonds, which could cause an increase in swelling power (Singh, Singh, Kaur, Sodhi, & Gill, 2003).

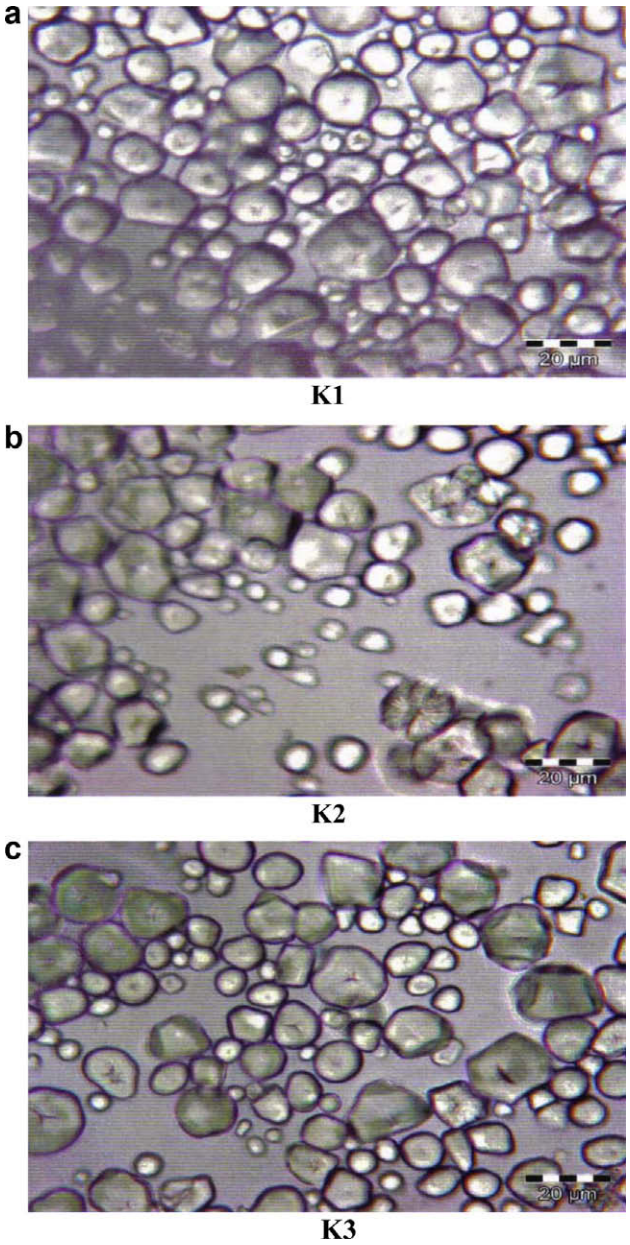

Fig. 7. Microphotographs of corn starch samples – K1 (a), K2 (b), and K3 (c). K1 (untreated), K2 (ultrasound bath – 15 min), and K3 (ultrasound bath – 30 min).

3.5. Micrography of corn starch model systems

Pictures from micrography are shown in Figs. 7–9. From the pictures one can see the obvious impact of ultrasound on the structure and size of starch granules. Ultrasound treatment is rupturing and mechanically damages the starch granules by collapse of cavitation bubbles that induces high pressure gradients and high local velocities of liquid layers in their vicinity, which causes shear forces that are capable of breaking the chains of polymers and damaging granules. Water is also partially decomposed into OH radicals and H atoms in the collapsing cavitation bubbles. Some of these radicals diffuse out of the cavities to the surrounding

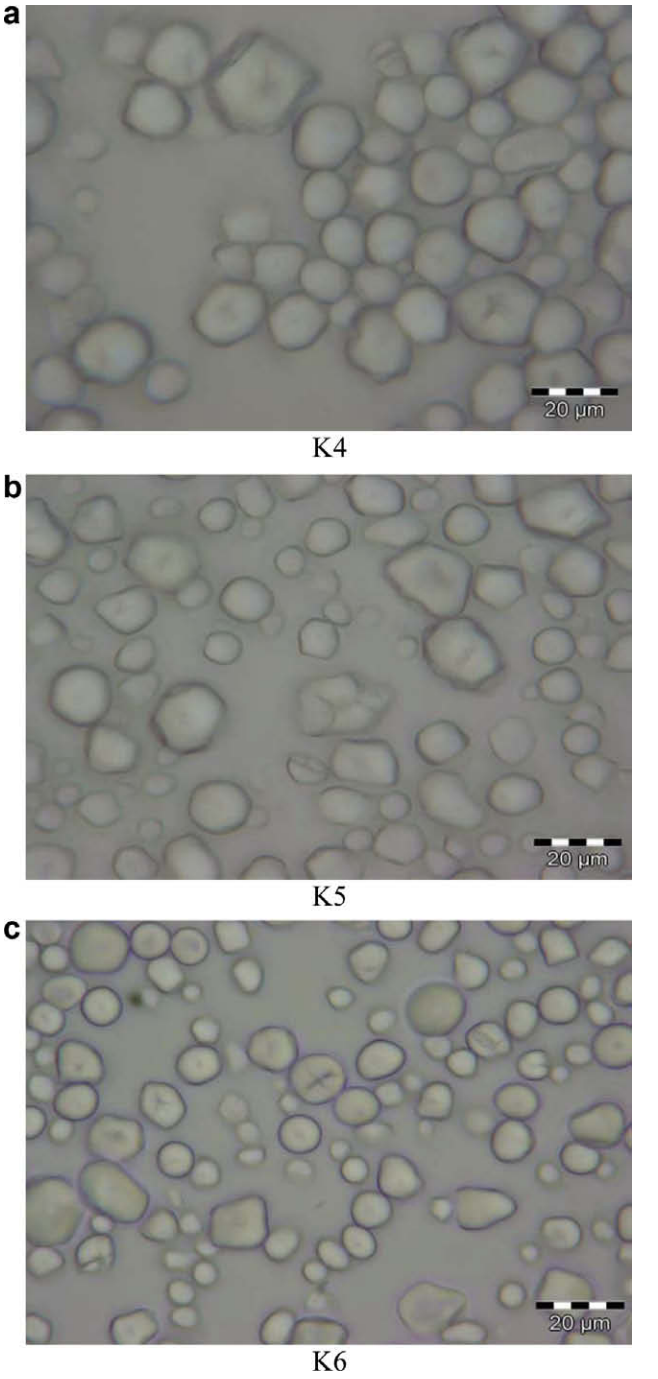

Fig. 8. Microphotographs of corn starch samples – K4 (a), K5 (b), and K6 (c). K4 (ultrasound probe – 100 W–15 min), K5 (ultrasound probe – 100 W–30 min), and K6 (ultrasound probe – 300 W–15 min).

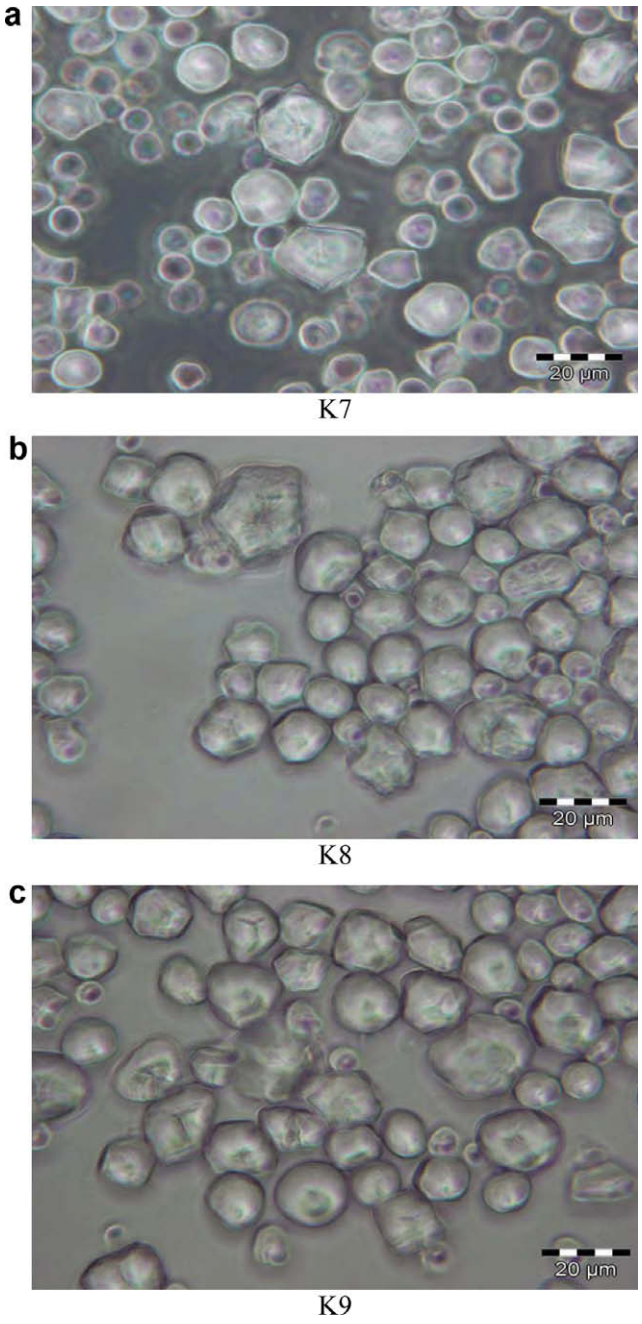

Fig. 9. Microphotographs of corn starch samples – K7 (a), K8 (b), and K9 (c). K7 (ultrasound probe – 300 W–30 min), K8 (ultrasound probe – 400 W–15 min), and K9 (ultrasound probe – 400 W–30 min).

liquid and then react with solute molecules causing polymer degradation (Czechowska-Biskup et al., 2005). It is widely known that the shape and size of starch granules varies (Tester & Karkalas, 2005) with botanical source. Form the pictures it is obvious that there are no significant changes in the size of granules when suspension are treated with ultrasound bath, but the size of granules is dramatically decreased and changed when applying ultrasound probes. The ultrasound process with 100 and 300 W probes (K4, K5, and K6) has highest impact on the size of the granules and its reduction. With further applying the power, starch granules tend to agglomerate becoming larger in shape and size due to liberated bonds that offer the opportunity to connect linkages between polymers. Ultrasound causes changes in the starch granule size and decrease in size and, consequently, changes in the physical–chemical properties of starch.

4. Conclusions

Ultrasound 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 potential of applying ultrasound for starch modification is in the fact that starch granule can be changed by cavitational forces. Ultrasound uses much less energy input and the treated medium has a lower temperature increase than conventional procedures that are used to modify starches that are used in food products. The ultrasound induced degradation of starch can be mainly attributed to the violent shear force encountered by starch molecule in the shearing valve. The results of differential scanning calorimetry measurements show a decrease in enthalpy of gelatinization. A statistically significant decrease in consistency coefficient (k) has also been observed. The consistency coefficient decreases stepwise jointly with increasing ultrasound power. The increase in swelling power is associated with the water absorption capacity and the solubility of corn starch granules, respectively. The higher facility for water entrance in corn starch granule is due to ultrasound disruption of granule which leads to a higher water uptake and retention. Micrography has shown an obvious impact of ultrasound on the structure and size of starch granules. Ultrasound treatment is rupturing and it mechanically damages the starch granules by the collapse of cavitation bubbles that induces high pressure gradients and high local velocities of liquid layers in their vicinity.

Several researches should be done to observe not only the positive effect of the ultrasound treatment but also the negative side effects of processing. The effect of ultrasound treatments on the specific food components have not been jet studied enough to surly claim about degradation effect of ultrasound treatment. Ultrasound frequency, ultrasound power, temperature, processing time and other parameters should be optimized to outdo or reduce the negative effect of free radicals produced by the implosion of the cavitation bubbles.

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