

Effect of Tribomechanical Micronisation and Activation Treatment on Textural and Thermophysical Properties of Wheat and Potato Starch Gels

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Summary

The aim of this study is to determine various textural properties of heat-induced gels prepared from wheat and potato starch suspensions (10 %) treated with tribomechanical micronisation and activation (TMA). Particle size measurements showed that the TMA treatment caused a significant decrease in particle size and change in particle size distribution of powdered starches. Scanning electron microphotographs showed an obvious impact on the structure and size of starch granules. The effect of TMA treatment on the texture profile of wheat and potato starch gels was assessed by measuring their textural properties, such as hardness, adhesiveness, cohesiveness, springiness and gumminess. The texture profile analyses of the TMA-treated wheat and potato starch gels showed lower hardness and gumminess; however, adhesiveness, cohesiveness and springiness were higher when compared with untreated suspensions. TMA treatment caused no significant lowering of the initial gelatinization temperatures. Results of differential scanning calorimetry measurements showed a decrease in the enthalpy of gelatinization. This can be explained by the disruption of starch granules by mechanical forces during the TMA treatment, which made the granules more permeable to water during the heating step of differential scanning calorimetry analysis.

Key words: wheat starch, potato starch, tribomechanical micronisation and activation, textural properties, thermophysical properties

Introduction

Starch is used in many foods because it contributes greatly to their textural properties, as well as having many industrial applications including as a thickener, colloidal stabilizer, gelling agent, bulking agent, water retention agent and adhesive. Textural properties of starch gels are very important as they are used as evaluation criteria for the performance of starch in food systems. As an exam-

ple, Ji *et al.* (1) used a texture analyzer for studying gel properties of starches from selected corn lines and found significant differences among them. Starch is a useful polymer not only because it is a cheap and natural material but also because it is possible to alter its physicochemical properties through chemical or enzyme modification and/or physical treatment (2,3). Tribomechanics is an area of physics linked with the phenomena that appear during fine milling under dynamic conditions. In 1998,

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the process of tribomechanical micronisation and activation (TMA), as well as the appropriate equipment, was patented under number PCT/1B99/00757 at the International Bureau of the WIPO (Patent Cooperation Treaty Receiving Office) in Geneva (4). With this newly constructed equipment, striking hammers and ventilation paddles placed on rotating discs produce turbulent movement in the treated materials. As a result, particles of the tested material collide and rub against each other at short time intervals (less than 0.001 s), which saves a considerable amount of energy. Compared to the classical milling methods where a significant amount of energy is spent on rubbing, the energy loss during the TMA process is significantly lower (5). Many studies have shown that tribomechanical micronisation can modify the physical, structural and functional properties of materials (5–12). Studies on TMA have mainly been conducted on inorganic materials (4,6), but recently investigations have been directed to organic materials such as powdered whey proteins. Krešić *et al.* (11) showed that TMA treatment, besides breaking up agglomerates, significantly changes the structural characteristics of proteins and their reactivity. The same was discovered by Herceg *et al.* (12), who studied the effect of TMA treatment on the physical and structural properties of corn starch. Because of the pronounced effects on the physical and structural properties of proteins and corn starch, it is highly likely that TMA treatment can also cause changes in the textural properties of wheat and potato starch gels. The purpose of this research is to study the effects of tribomechanical micronisation and activation treatment on the textural and thermophysical properties of wheat and potato starch gels.

Materials and Methods

Samples of powdered potato starch (labelled with P; Potato Starch Superior®) and wheat starch (labelled with W; C-gel 20006) were provided by Palco d.o.o., Zagreb, Croatia. The composition of the starches was declared by the manufacturer (Cargill Benelux BV, Ghent, the Netherlands) as follows: for potato starch 17.86 % moisture and 82.14 % starch, and for wheat starch 12.60 % moisture and 87.40 % starch.

Tribomechanical micronisation and activation

The TMA equipment consists of a housing and two rotor discs placed against each other (Fig. 1). Each disc is equipped with three or four concentric rings of teeth projecting from the surface of the disc, which are secured with specially constructed hard metal elements. The discs rotate in the opposite directions at the same angular rate. The feed (starting material) enters the equipment through the central part of the rotor system and is accelerated by air convection (a fan). Because of repeated changes in the direction of the motion, particles collide and induce friction over short time intervals (less than 0.001 s). Although the 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 treatment of potato and wheat starches was carried out at a rotor speed of 20 000 rpm, at ambient temperature and atmospheric pressure. Overheating of the materials was pre-

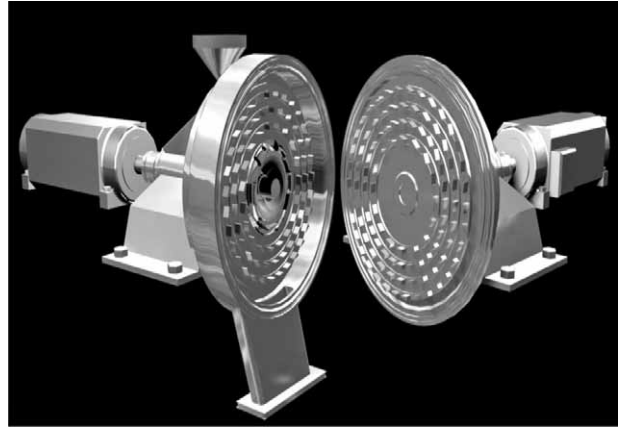


Fig. 1. Laboratory equipment for tribomechanical micronisation and activation (TMA)

vented by water cooling of the equipment through its housing. Intake of the feed was continuous at 1 kg/min.

Particle size distribution

The particle size distribution of the powdered potato and wheat starches before and after the TMA treatment was measured using laser light scattering (Malvern Mastersizer 2000 with a lens of 100-mm focal length, Malvern Instruments Ltd., Malvern, UK). The results were analysed by applying Mie theory (13). Settings were optimised for the refractive index of starch in water and an average of three consecutive measurements is reported.

Morphological properties

Scanning electron microphotographs of starch were taken with a scanning electron microscope (Philips XL30 ESEM Volfram, Philips, Eindhoven, the Netherlands). Images were recorded using the following procedure: after preparing a starch suspension (1 %) in ethanol, one drop of the suspension was placed on an aluminium stub and coated with gold. An accelerating potential of 25 kV was used during the imaging.

Gel preparation and determination of textural properties of starch gels

Untreated and TMA-treated starch suspensions (10 %, by mass) were used for gel preparation. Gels were prepared by heating the suspensions in 15-mL glass beakers in a water bath with constant stirring on the magnetic stirrer at 80 °C for 15 min. After heating, the samples were rapidly cooled to room temperature by immersing the beakers in ice water, and were held at 4 °C for further analysis. Textural properties were determined 24 h after the gel preparation. Gel hardness analysis was conducted using a texture analyzer (Texture Analyzer HD+, Stable Micro System, Godalming, UK). The speed of the measuring probe was 1 mm/s. Depth of measurement was 10 mm. During two measuring cycles, the following properties were derived from the generated curves: hardness, cohesiveness, adhesiveness, springiness and gumminess. Gel hardness was defined as the maximal applied force (in N).

Differential scanning calorimetry of potato and wheat starch model systems

Gelatinization properties were analyzed using a differential scanning calorimeter DSC822e (Mettler Toledo, Twente, the Netherlands) equipped with STARe software. An empty pan was used as a reference. Untreated and TMA-treated potato and wheat starch suspensions (10 %, by mass) were placed into a standard aluminium pan (40 μ L). The pans were then sealed and equilibrated for 24 h at room temperature before heat treatment in the calorimeter. The starch slurry was gelatinized in the calorimeter using a heat rate of 10 $^{\circ}$ C/min from 25 to 95 $^{\circ}$ C. After the treatment, the samples were cooled to 25 $^{\circ}$ C and removed from the DSC. The enthalpy (ΔH in kJ per kg of dry starch), onset temperature (t_o), peak temperature (t_p), and conclusion temperature (t_c) of gelatinization were obtained from the exothermal differential scanning calorimetry (DSC) curves. The experiments were run in triplicate.

Statistical analyses

All experiments in this study were repeated at least three times, thus all the data are presented as mean values of three independent tribomechanical treatments \pm standard deviation. Comparison among data for different processing conditions was performed with a one-way analysis of variance (ANOVA) followed by a *post-hoc* Scheffe test for comparison between groups (STATISTICA v. 6.0, StatSoft Inc., Chicago, IL, USA). A statistically significant difference was assumed at $p < 0.05$. The values not statistically different are denoted with the letter a and the values statistically different with the letter b in superscript.

Results and Discussion

Wheat and potato starches were processed by tribomechanical micronisation and activation (TMA, Fig. 1) (4). The inlet temperature of the wheat starch was 20.7 $^{\circ}$ C and the outlet temperature was 22.6 $^{\circ}$ C. The inlet temperature of the potato starch was 19.8 $^{\circ}$ C and the outlet temperature was 21.7 $^{\circ}$ C. Although the instrument was cooled, the slight temperature increase during TMA treatment was a consequence of friction and collisions among the particles.

The results presented in Figs. 2a and 2b show a significant decrease in the particle size of starches treated with TMA. Both figures show a bimodal distribution of granule size in the potato and wheat starches. Native potato starch contained a high percentage of large granules with peak values of 39 μ m. Wheat starch had a high percentage of 20- μ m particles. The potato granule size after tribomechanical treatment ranged from 2 to 100 μ m with the peak value of 31 μ m. Clearly, TMA treatment is rupturing and mechanically damaging the starch granules by strong mechanical forces that induce collision between particles and cause change in their size and shape (Figs. 3a–3d). These in turn cause shear forces to break the polymer chains and damage the granules (5,8,11,12).

The wheat granule size after tribomechanical treatment ranged from 3 to 32 μ m with a peak value of 18

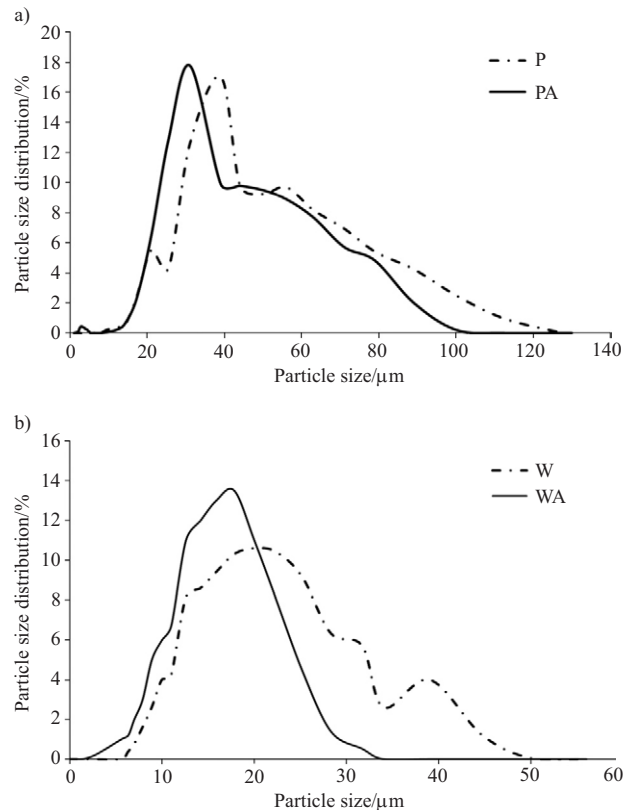


Fig. 2. Particle size distribution of powdered starch before and after tribomechanical micronisation and activation (TMA) treatment: a) potato starch (P=untreated, PA=TMA-treated) and b) wheat starch (W=untreated, WA=TMA-treated)

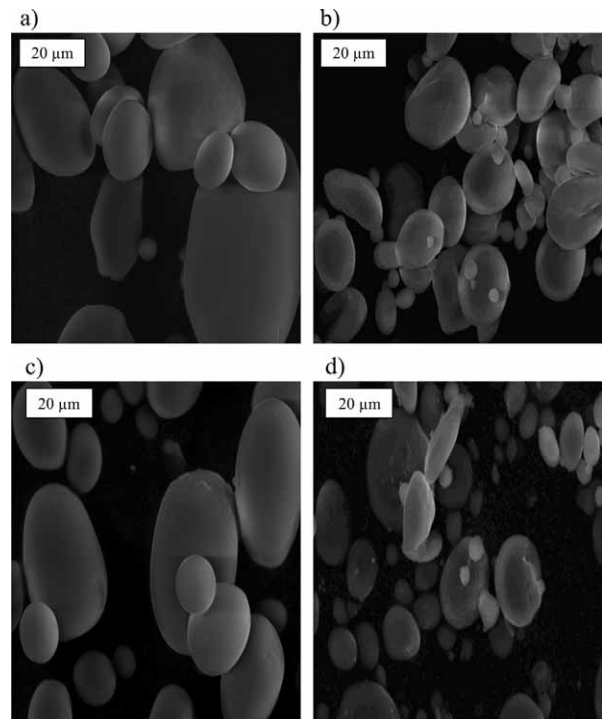


Fig. 3. Scanning electron microphotographs of untreated and tribomechanical micronisation and activation (TMA)-treated samples: a) untreated potato starch, b) TMA-treated potato starch, c) untreated wheat starch, and d) TMA-treated wheat starch

μm . It is well known that wheat starch is composed of two types of granules, large A-type granules (diameter $> 9.9 \mu\text{m}$) and small, spherical B-type granules (diameter $< 9.9 \mu\text{m}$) having somewhat different physical, chemical, and functional properties (14). Differences in these two starch granule types result in different industrial and food applications, because starch composition, gelatinization, rheological and pasting properties, swelling properties, and overall processing are strongly influenced by the starch granule size distribution (15–18). In this work, the fraction of wheat starch granules $< 50 \mu\text{m}$ and $> 8 \mu\text{m}$ was 97 % of the total number, which indicated that the wheat starch sample was made up primarily of A-type granules. SEM images of the untreated surfaces of potato and wheat starch granules are shown in Figs. 3a and 3c. According to Tang *et al.* (16), potato starch granules are relatively resistant to TMA, due to their crystallinity and thicker blocklets on the surface. Singh *et al.* (19) found that potato starches are characterized by high hardness of starch granules. The effect was attributed to the presence of a high percentage of large granules and low amylose content. However, some authors have suggested that potato starch granules with a lower amylose content compared with normal starch granules are more susceptible to physical deterioration and are readily damaged by milling (20,21). SEM images in Figs. 3b and 3d show an obvious impact of TMA treatment on the structure and size of potato and wheat starch granules. Clearly, the treatment increased both the number of damaged granules and the extent of damage of individual granules. The susceptibility of granules to the damaging forces depends on the distribution of granular size, together with the variations in granular composition (amylose/amylopectin ratio and lipid content), architecture, crystallite size and spacial location within granules, crystalline/amorphous ratio and surface area to volume ratio. Additionally, damaged granules are easily hydrated and have higher swelling factors than the intact granules in cold water. Such behaviour is consistent with mechanical activation, increasing the amorphous regions of the starch granules, while weakening and decreasing the crystalline regions (22–24).

The texture properties of the potato and wheat starch gels were determined by using a texture analyzer and are shown in Table 1 and Figs. 4a and 4b. The texture profile analyses of both starch gel suspensions after TMA treatment revealed lower hardness and gumminess values when compared to untreated gels (Table 1). However, cohesiveness, adhesiveness and springiness of gels prepared with TMA-treated starches are statistically much higher than those of the gels prepared with untreated starches (Table 1).

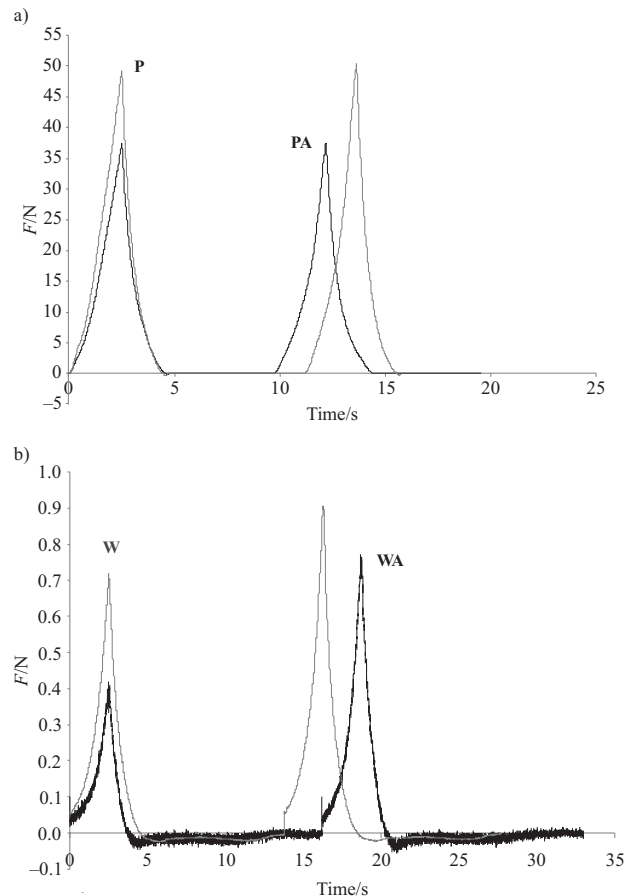


Fig. 4. Texture profile analysis of untreated and tribomechanical micronisation and activation (TMA)-treated starch gel during two measuring cycles: a) potato starch (P=untreated, PA=TMA-treated) and b) wheat starch (W=untreated, WA=TMA-treated)

The mechanical properties of starch gels depend on various factors, including the rheological characteristics of the amylose matrix, the volume fraction and the rigidity of the gelatinized starch granules, as well as on interactions between the dispersed and continuous phases of the gel (25). These factors are in turn dependent on the amylose content and the structure of the amylopectin (25). After intensive TMA treatment, changes occur mostly in the amorphous regions of starch granules such as hydrolysis of amorphous layers. The consequence of the aforementioned changes is lower gel hardness for both starches in comparison with untreated gels. This can be explained by the degradation of starch biopolymers and the disruption of mobility chains of amylose

Table 1. Texture parameters of native and tribomechanical micronisation and activation (TMA)-modified potato and wheat starches

Sample	Hardness/N	Adhesiveness/(N/mm)	Cohesiveness	Springiness	Gumminess
P	(49.37±0.18) ^a	(0.02±0.04) ^a	(0.88±0.07) ^a	(0.99±0.10) ^a	(43.74±0.17) ^a
PA	(37.34±0.20) ^b	(0.03±0.03) ^b	(0.95±0.12) ^b	(1.04±0.09) ^a	(35.63±0.24) ^b
W	(0.70±0.09) ^a	(0.13±0.09) ^a	(1.20±0.11) ^a	(1.03±0.07) ^a	(0.85±0.11) ^a
WA	(0.38±0.07) ^b	(0.15±0.11) ^b	(1.89±0.11) ^b	(1.09±0.11) ^a	(0.73±0.09) ^b

P=untreated potato starch, PA=TMA-treated potato starch, W=untreated wheat starch, WA=TMA-treated wheat starch
^avalues are not statistically different, ^bvalues are statistically different

Table 2. Differential scanning calorimetry (DSC) parameters of native and modified potato and wheat starch suspensions after tribomechanical micronisation and activation (TMA) treatment

Sample	$t_o/^\circ\text{C}$	$t_p/^\circ\text{C}$	$t_e/^\circ\text{C}$	$\Delta H_{\text{gel}}/(\text{kJ}/\text{kg})$
P	$(61.45 \pm 0.04)^a$	$(65.44 \pm 0.03)^a$	$(72.17 \pm 0.04)^a$	$(52.19 \pm 0.02)^a$
PA	$(60.54 \pm 0.02)^a$	$(65.01 \pm 0.01)^a$	$(72.64 \pm 0.01)^a$	$(50.01 \pm 0.01)^b$
W	$(55.53 \pm 0.06)^a$	$(59.76 \pm 0.06)^a$	$(64.52 \pm 0.13)^a$	$(24.19 \pm 0.08)^a$
WA	$(55.42 \pm 0.07)^a$	$(60.05 \pm 0.02)^a$	$(64.84 \pm 0.08)^a$	$(22.15 \pm 0.02)^b$

t_o =gelatinization onset temperature ($^\circ\text{C}$), t_p =gelatinization peak temperature ($^\circ\text{C}$), t_e =gelatinization conclusion temperature ($^\circ\text{C}$), ΔH_{gel} =enthalpy of gelatinization per dry starch mass (kJ/kg of dry starch); P=untreated potato starch, PA=TMA-treated potato starch, W=untreated wheat starch, WA=TMA-treated wheat starch

^avalues are not statistically different, ^bvalues are statistically different

and amylopectin. As a result of degradation of starch molecules, interactions between polymer molecules will be weakened and the strength of the gels will be reduced. NMR studies have shown that TMA significantly reduces the firmness of starch gels without altering their chemical structure (26). The reduction in molecular mass of starches after TMA treatment was confirmed by Fourier transform infrared spectroscopy. The effect was explained by an increase in the number of free, mobile polymer molecules separated from the starch granules (27).

The gelatinization temperatures (t_p and t_e) of TMA-treated potato and wheat starches were not statistically

different from the gelatinization temperatures of native starches (Table 2). A lower gelatinization temperature indicates that the beginning of gelatinization requires less energy ($\Delta H_{\text{gel}}=50.01$ kJ/kg for potato starch, $\Delta H_{\text{gel}}=22.15$ kJ/kg for wheat starch) as compared to the untreated potato starch ($\Delta H_{\text{gel}}=52.19$ kJ/kg) and the untreated wheat starch ($\Delta H_{\text{gel}}=24.19$ kJ/kg).

Thermal 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 in the crystallite and at the level of double-helical order. It is possible that the minute differ-

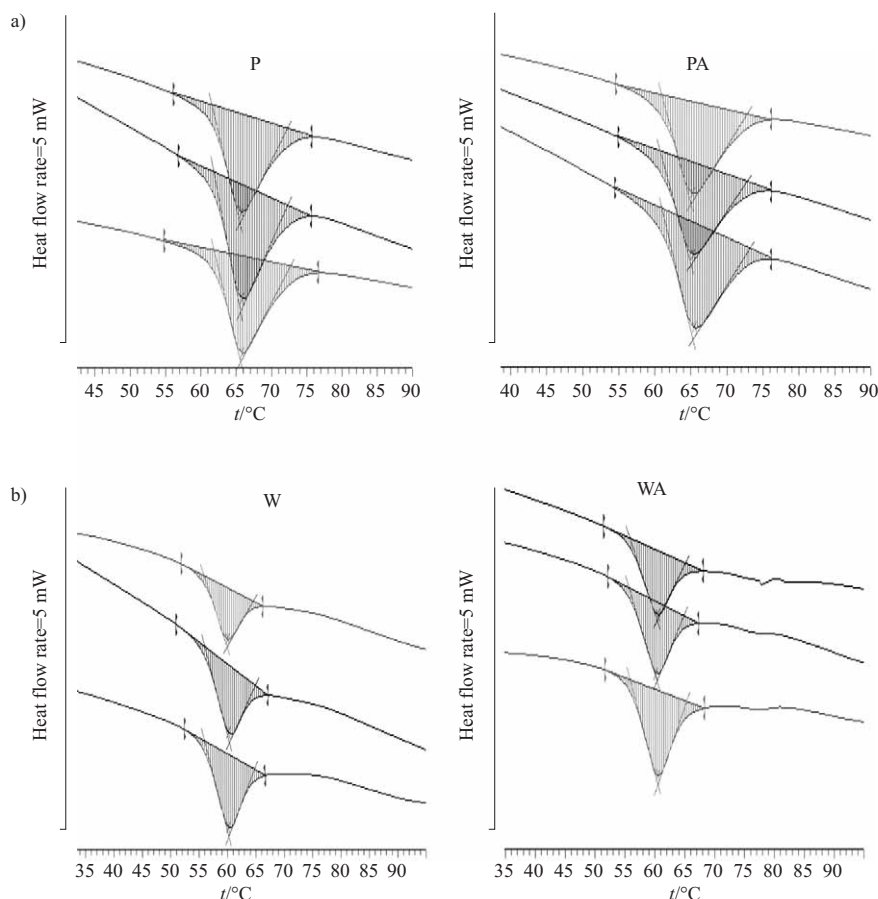


Fig. 5. Differential scanning calorimetry (DSC) curves for three replicate measurements of untreated and tribomechanical micronisation and activation (TMA)-treated starch suspensions: a) potato starch (P=untreated, PA=TMA-treated) and b) wheat starch (W=untreated, WA=TMA-treated)

ences in gelatinization energy observed between the native and the treated starches are related to the differences in the bonding forces of the double helix forming the amylopectin crystallography, *i.e.* different alignments of the hydrogen bonds within the starch molecules (28). Although this hypothesis cannot be proven without further investigation, the loss of the double-helical order is suggested as a possible explanation for the enthalpic transition observed in thermograms shown in Figs. 5a and 5b (29).

Conclusions

TMA treatment caused significant changes in the size, structure and physical properties of starch granules. Statistically significant decreases in the hardness and gumminess of potato and wheat starch gels were observed. The texture profile analyses of the starch gels prepared with the suspensions of TMA-treated potato and wheat starches showed higher adhesiveness, cohesiveness and springiness when compared to the untreated suspensions. TMA treatment caused no significant lowering of the initial gelatinization temperatures. Results of differential scanning calorimetry measurements showed a statistically significant decrease in the enthalpy of gelatinization. This can be explained by the disruption of starch granules by mechanical forces during TMA treatment, which made the granules more permeable to water during the heating step of DSC analysis.

References

1. Y. Ji, K. Wong, J. Hasjim, L.M. Pollak, S. Duvick, J. Jane, P.J. White, Structure and function of starch from advanced generations of new corn lines, *Carbohydr. Polym.* 54 (2003) 305–319.
2. L.M. Che, D. Li, L.J. Wang, X.D. Chen, Z.H. Mao, Micronization and hydrophobic modification of cassava starch, *Int. J. Food Prop.* 10 (2007) 527–536.
3. L. Che, D. Li, L. Wang, N. Özkan, X.D. Chen, Z. Mao, Effect of high-pressure homogenization on the structure of cassava starch, *Int. J. Food Prop.* 10 (2007) 911–922.
4. T. Lelas, Device for the micronisation of materials and possible new applications of these materials. *Patent PCT/1B99/00757*, WIPO, Geneva, Switzerland (1998) (in German).
5. Z. Herceg, V. Lelas, M. Brncic, B. Tripalo, D. Jezek, Fine milling and micronization of organic and inorganic materials under dynamic conditions, *Powder Technol.* 139 (2004) 111–117.
6. B. Bhushan: *Modern Tribology Handbook, Vol. 2: Nanoscale Tribophysics and Tribomechanic*, CRC Press, Boca Raton, FL, USA (2000).
7. V. Lelas, Z. Herceg, Influence of tribomechanical treatment on the phase transition temperatures of whey proteins model systems, *Proceedings of the International Conference on Innovation in Food Processing Technology and Engineering*, Bangkok, Thailand (2002) pp. 24–34.
8. Z. Herceg, V. Lelas, M. Brnčić, B. Tripalo, D. Jezek, Tribomechanical micronization and activation of whey protein concentrate and zeolite, *Sādhanā*, 29 (2004) 13–26.
9. Z. Herceg, V. Lelas, G. Krešić, Influence of tribomechanical micronization on the physical and functional properties of whey proteins, *Int. J. Dairy Technol.* 58 (2005) 225–232.
10. V. Lelas, Novel food processing technologies, *Mljekarstvo*, 56 (2006) 311–330 (in Croatian).
11. G. Krešić, V. Lelas, A. Režek Jambrak, Z. Herceg, S. Rimac Brnčić, Influence of novel food processing technologies on the rheological and thermophysical properties of whey proteins, *J. Food Eng.* 87 (2008) 64–73.
12. Z. Herceg, V. Batur, A. Režek Jambrak, M. Badanjak, Modification of rheological, thermophysical, textural and some physical properties of corn starch by tribomechanical treatment, *Carbohydr. Polym.* 80 (2010) 1072–1077.
13. C.F. Bohren, D.R. Huffman: *Absorption and Scattering of Light by Small Particles*, Wiley, New York, NY, USA (1983).
14. R.P. Ellis, M.P. Cochrane, M.F.B. Dale, C.M. Duffus, Starch production and industrial use, *J. Sci. Food Agr.* 77 (1998) 289–311.
15. P. Meredith, Large and small starch granules in wheat – Are they really different?, *Starch*, 33 (1981) 40–44.
16. H.J. Tang, T.H. Mitsunaga, Y. Kawamura, Molecular arrangement in blocklets and starch granule architecture, *Carbohydr. Polym.* 63 (2006) 555–560.
17. R.B.K. Wong, J. Lelievre, Rheological characteristics of wheat starch pastes measured under steady shear conditions, *J. Appl. Polym. Sci.* 27 (1982) 1433–1440.
18. S.M.J. Langeveld, R. van Wijk, N. Stuurman, J.W. Kijne, S. de Pater, B-type granule containing protrusions and interconnections between amyloplasts in developing wheat endosperm revealed by transmission electron microscopy and GFP expression, *J. Exp. Bot.* 51 (2000) 1357–1361.
19. N. Singh, L. Kaur, K.S. Sandhu, J. Kaur, K. Nishinari, Relationships between physicochemical, morphological, thermal, rheological properties of rice starches, *Food Hydrocoll.* 20 (2006) 532–542.
20. X.Z. Han, O.H. Campanella, N.C. Mix, B.R. Hamaker, Consequence of starch damage on rheological properties of maize starch paste, *Cereal Chem.* 79 (2002) 897–901.
21. M.J. Ridout, M.L. Parker, C.L. Hedley, T.Y. Bogracheva, V.J. Morris, Atomic force microscopy of pea starch granules: Granule architecture of wild-type parent, r and rb single mutants, and the rrb double mutant, *Carbohydr. Res.* 338 (2003) 2135–2147.
22. A. Hagenimana, X. Ding, A comparative study on pasting and hydration properties of native rice starches and their mixtures, *Cereal Chem.* 82 (2005) 70–76.
23. Z.Q. Huang, J.P. Lu, X.H. Li, Z.F. Tong, Effect of mechanical activation on physico-chemical properties and structure of cassava starch, *Carbohydr. Polym.* 68 (2007) 128–135.
24. Y. Iida, T. Tuziuti, K. Yasui, A. Towata, T. Kozuka, Control of viscosity in starch and polysaccharide solutions with ultrasound after gelatinization, *Innov. Food Sci. Emerg. Technol.* 9 (2008) 140–146.
25. J.P. Mua, D.S. Jackson, Relationships between functional attributes and molecular structures of amylose and amylopectin fractions from corn starch, *J. Agric. Food Chem.* 45 (1997) 3848–3854.
26. X. Wang, W.Y. Gao, L. M. Zhang, P.G. Xiao, Study on the morphology, crystalline structure and thermal properties of yam starch acetates with different degrees of substitution, *Sci. China B: Chem.* 51 (2008) 859–865.
27. B. Vidić, T. Vukušić, I. Ljubić Herceg, D. Šubarić, Đ. Ačkar *et al.*, Influence of high intensity ultrasound on physical and textural properties of wheat starch, *Croat. J. Food Technol. Biotechnol. Nutr.* 4 (2011) 134–140.
28. K.S. Sandhu, N. Singh, Some properties of corn starches II: Physicochemical, gelatinization, retrogradation, pasting and gel textural properties, *Food Chem.* 101 (2007) 1499–1507.
29. H. Liu, J.G. Bao, Y.M. Du, X. Zhou, J.F. Kennedy, Effect of ultrasonic treatment on the biochemophysical properties of chitosan, *Carbohydr. Polym.* 64 (2006) 553–559.