Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 68 (2007) 128–135
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Effect of mechanical activation on physico-chemical properties and structure of cassava starch

Zu-Qiang Huang, Jian-Ping Lu, Xuan-Hai Li, Zhang-Fa Tong *

School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

Received 28 May 2006; received in revised form 18 July 2006; accepted 18 July 2006
Available online 30 August 2006

Abstract

Cassava starch was mechanically activated with a stirring ball mill and subsequently studied for cold-water solubility and rheological characteristics. In addition, the crystal structure, thermal properties, functional groups, granular morphology and size distribution of the activated cassava starch were further characterized using granularity analysis, scanning electron microscopy, X-ray diffractometry, Fourier transform infrared spectroscopy and differential scanning calorimetry. It was found that the crystal structure and granular morphology of cassava starch were significantly altered. Specifically, the crystalline structure of the cassava starch was significantly degraded, and the resulting amorphous particles were seen to agglomerate during the process of mechanical activation. Also, the gelatinization temperature and enthalpy, apparent viscosity and shear thinning of cassava starch were reduced, resulting in enhancement of cold-water solubility of the starch. Infrared spectroscopy showed no new functional groups produced during the mechanical activation process.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Cassava starch; Mechanical activation; Modification; Structure; Physico-chemical property

1. Introduction

Starch is a morphologically complex polymer substance, consisting of loose amorphous regions that are interspersed with highly regular crystalline regions, resulting from the formation of hydrogen bonds between the starch molecules. The crystalline composition consists of around 15–45% of the starch granules (Christopher, 1997; Tang, Mitsunaga, & Kawamura, 2004). The scope of starch application is both enhanced and limited by its unique molecular structure. For instance, the compact arrangements of molecules in the crystalline regions inhibit water or chemical reagents from making contact with the molecules in the crystalline region. As a result, the gelatinization temperature is higher and chemical reactivity of starch is decreased. Meanwhile, the relative large molecular weight and the extensive network formed by hydrogen bonds lead to high gelatinization temperature and lower fluidity. For many purposes, the market prefers starch with less extensive crystalline regions, resulting in improved physico-chemical properties and increased reactivity for planned applications. Therefore, there is great interest in methods to modify the structure in the crystalline region, or decrease the size of crystalline regions (Fiedorowicz, Tomasik, & Lii, 2001; Liang, Zhang, Yang, & Gao, 2004). The main methods of decreasing starch crystalline regularity include chemical processes, such as acidolysis (Nakazawa & Wang, 2003), oxidation (Wang & Wang, 2003), enzymatic degradation processes (Zhang & Oates, 1999) and physical processes, such as heat-moisture treatment (Gunaratne & Hoover, 2002), radioactive degradation (Bertolini, Mestres, Colonna, & Raffi, 2001), microwave degradation (Lewandowicz, Jankowski, & Fornal, 2000), ultrasonic degradation (Renata, Bozena, Salah, Piotr, & Janusz, 2005) and extrusive degradation processes (Cai, Diosady, & Rubin, 1995). In addition, mechanical activation refers to the use of friction, collision, impingement, shear or other mechanical actions to modify the crystalline structures and properties of the starch granules. During

---

[*] Corresponding author. Tel.: +86 771 3233728; fax: +86 771 3233718.
E-mail addresses: bioche@gxu.edu.cn, zhftong@sina.com (Z.-F. Tong).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.07.017

mechanical activation the chemical reactivity is enhanced because some mechanical energy is converted into internal energy of the substance (Boldyrev, 1986). Currently, mechanical activation is used in a variety of applications, including nanomatrix composites, dispersed alloy materials, metallic refinery, ore treatment, waste disposal and synthesis of organic materials (Mulak, Balaz, & Chojnacka, 2002; Ren, Yang, & Shaw, 1999; Sim, Xue, & Wang, 2004; Suryanarayana, Ivanov, & Boldyrev, 2001; Takacs, 1998). In this paper, we report on the application of mechanical activation in modification of starch.

The study involved the use of a customized high-efficiency stirring mill to activate cassava starch, followed by investigation of the crystalline structures and physico-chemical properties of the resulting mechanically activated cassavas starch (MACS). The cold-water solubility and viscosity of the MACS were determined. Further characterization of the MACS's crystal structure, thermal properties, granular morphology and size distribution were studied using granularity analyzer, scanning electron microscopy (SEM), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The mechanism of activation was also explored.

2. Experimental

2.1. Ball mill used in the mechanical activation of cassava starch

The mechanical activation in this study was achieved with a customized stirring mill driven by a commercial available drill press equipped with a variable speed motor. The motor turned a shaft that was fitted with four paddles for mixing the cassava starch (acquired from Mingyang Biological Inc. Ltd, Guangxi, China) and 6 mm mill balls inside a stainless 1200 ml steel chamber whose temperature was maintained at constant level. The mill was stopped and the balls removed after the designated time. The resulting samples were sealed for storage and analysis immediately.

2.2. Cold-water solubility

An approximately 2.0000 g (dry weight basis) sample of MACS was dissolved in 100 ml deionized water. Then the solution was heated to a constant temperature (30 °C or 40 °C) for 20 min, with continuous stirring in order to avoid agglomeration. The solution was centrifuged at 3000 rpm for 20 min. The supernatant was removed and evaporated to dryness at room temperature. The resulting residue was placed in a drying oven at 110 °C until constant was obtained. The solubility of the starch was calculated by the weight of the resident divided by the original starch weight × 100%.

2.3. Rheological properties

The rheological properties were determined by adding deionized water to an accurately sample of starch to form 10% (w/v) starch paste. The paste was heated in boiling water bath for 15 min, and then cooled to room temperature. An aliquot of sample was analyzed using a rotational viscosity meter (Precise Scientific Instrument Co. Ltd., Shanghai, China) for its apparent viscosity at different shear rates.

2.4. Granule size distribution

Alcohol, as dispersing reagent, was added to a MACS sample which was then ultrasonically dispersed for 2 min. The particle size distribution was then determined using a granularity analyzer (SA-CP3 granularity analyzer, Shimadzu, Japan).

2.5. Scanning electron microscopy

The starch sample was fixed on a sample bench using a double glue tape for spraying gold powder. The morphological changes of the sample were examined using a SEM (S-570 SEM, Hitachi, Japan) before and after mechanical activation.

2.6. X-ray diffractometry

The X-ray diffraction patterns of the starch samples were measured using a Rigaku D/MAX 2500 V diffractometer (Japan) under the following conditions: Cu-Kα radiation, Ni filter disk, 40 kV, 30 mA and measurement range $2\theta = 3$–40°.

2.7. IR spectroscopy

KBr-pelletized starch samples analyzed using a Nicolet Nexue 470 FTIR (Nicolet Co., USA).

2.8. Differential scanning calorimetry

The starch samples were studied using a DSC-6200 differential scanning calorimetry (Perkin-Elmer Co., USA). A 4.0 mg (dry basis) sample was placed in an aluminum case and deionized water added to obtain a starch/water ratio of 1:4 by weight. The sample was sealed and equilibrated for 4 h. Then it was scanned from 30 °C to 150 °C using a scanning rate of 10 °C/min, while nitrogen gas flowed through the sample chamber at the rate of 30 ml/min. The characteristic temperatures of the transitions were recorded as onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c).

3. Results and discussion

3.1. Cold-water solubility

The effect of mechanical activation on the cold-water solubility of cassava starch is shown in Fig. 1. The data show that the longer the mechanical activation time, the

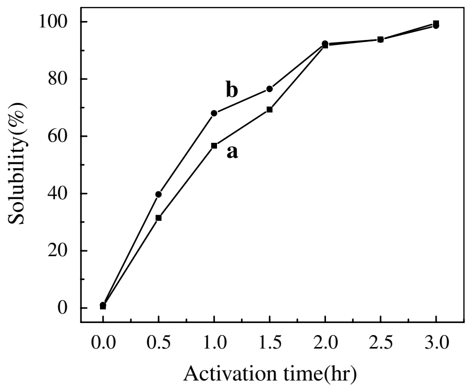

Fig. 1. Solubility of MACS at different dissolving temperatures: (a) 30 °C and (b) 40 °C.

greater the cold-water solubility. As revealed in Fig. 1, the influence of the activation time on the solubility is much larger than that of temperature. The solubilities of the non-activated starch are 0.48% and 0.97% when the temperatures are 30 °C and 40 °C, respectively. However, the solubilities at these temperatures of starch activated for 2 h are 93.76% and 93.86%, respectively. Interestingly, activation beyond 2 h had little further effect on the solubility. The observed increase in cold-water solubility of starch with increased duration of activation time is consistent with the model that mechanical agitation is capable of degrading the crystalline regions of the starch and allowing greater entry of water into the interior of the granule.

3.2. Rheological properties

Fig. 2 summarizes the effect of mechanical activation on the viscosity of MACS. At a constant shear rate, the apparent viscosity of MACS decreases as the activation time increases. Further, the apparent viscosity decrease is generally greatest with the initial period of activation, reaching essentially zero viscosity at 2 h. These data suggest that the crystal structure of starch is damaged through the mechanical agitation, so that the intramolecular affinities in the starch are diminished. As a result, the resistance between molecules movement dwindles, and the apparent viscosity decreases. This interpretation and these data agree with the picture presented by the effect of mechanical activation on the cold-water solubility of starch in the previous section.

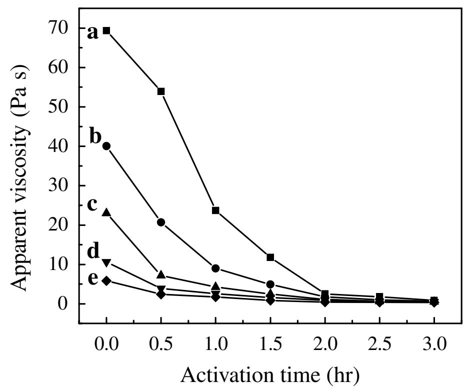

Fig. 2. Apparent viscosity of MACS with different shear rates: (a) 0.05 s^{-1}, (b) 0.25 s^{-1}, (c) 1.00 s^{-1}, (d) 2.50 s^{-1}, and (e) 5.00 s^{-1}.

The significant decrease of the apparent viscosity with the increase of the shear rates demonstrates that shear thinning nature exists (Josef, 1992; Marcotte, Ali, & Ramaswamy, 2001; Yang, Zhang, Gu, & Fang, 1999). Note that the shear thinning nature of MACS decreases as the activation time increases and essentially disappears after two hours' activation. These data are consistent with the model of the MACS consisting of chains of macromolecules that are intertangled with each other, resulting in higher apparent viscosity values. In this model under the shear action the tangled molecules are forced to straighten out, which reduces the shear force between fluid layers, thereby resulting in the decrease of viscosity. However, this arrangement becomes highly regular with the enhancement of shear rates, the apparent viscosity tends to be higher and higher when the rate increases. In this circumstance, the apparent viscosity reaches a constant, suggesting that the starch molecules do not have enough time to align themselves or align themselves completely. Therefore, its viscosity is maintained as a constant. The crystalline structure and hydrogen bonds of cassava starch are damaged during the mechanical activation, its structure becomes lose, degradation happens as well. This reduces the opportunities for the molecules to combine each other, which induces the decline of the shear thinning effect.

3.3. Size distribution and morphology

The size and morphological changes of cassava starch during the mechanical activation can be seen in Fig. 3. The untreated cassava starch granules are essentially spherical. When subjected to mechanical activation, the starch granules appear to be fractured and swollen, agglomerating into larger more amorphous particles. Some of the agglomerates are impacted to be prolate again and become powder during the activation, while some coalesce to form granule. Finally, congregates consisting of tiny granules are obtained when starch experiences cracking, cold welding, structural change from irregulate agglomerates to layered grains.

The size distribution data of MACS are presented in Table 1. After 1 h activation, the MACS particles show evidence of swelling and agglomeration, with a definite shift to larger particle size. These data are consistent with mechanical activation's fracturing the crystalline regions of the starch, allowing for greater water penetration (swelling) and agglomeration via the interaction between the resulting greater amorphous regions.

After 2 h activation, the size distribution broadens a bit more, while there is an appearance of small particles below 2 μm (possibly fracture fragments), but with an overall shift to larger particle size associated with further agglomeration. This suggests that dynamic equilibrium is achieved with agglomerates cracked whilst grains combined after 2 h activation.

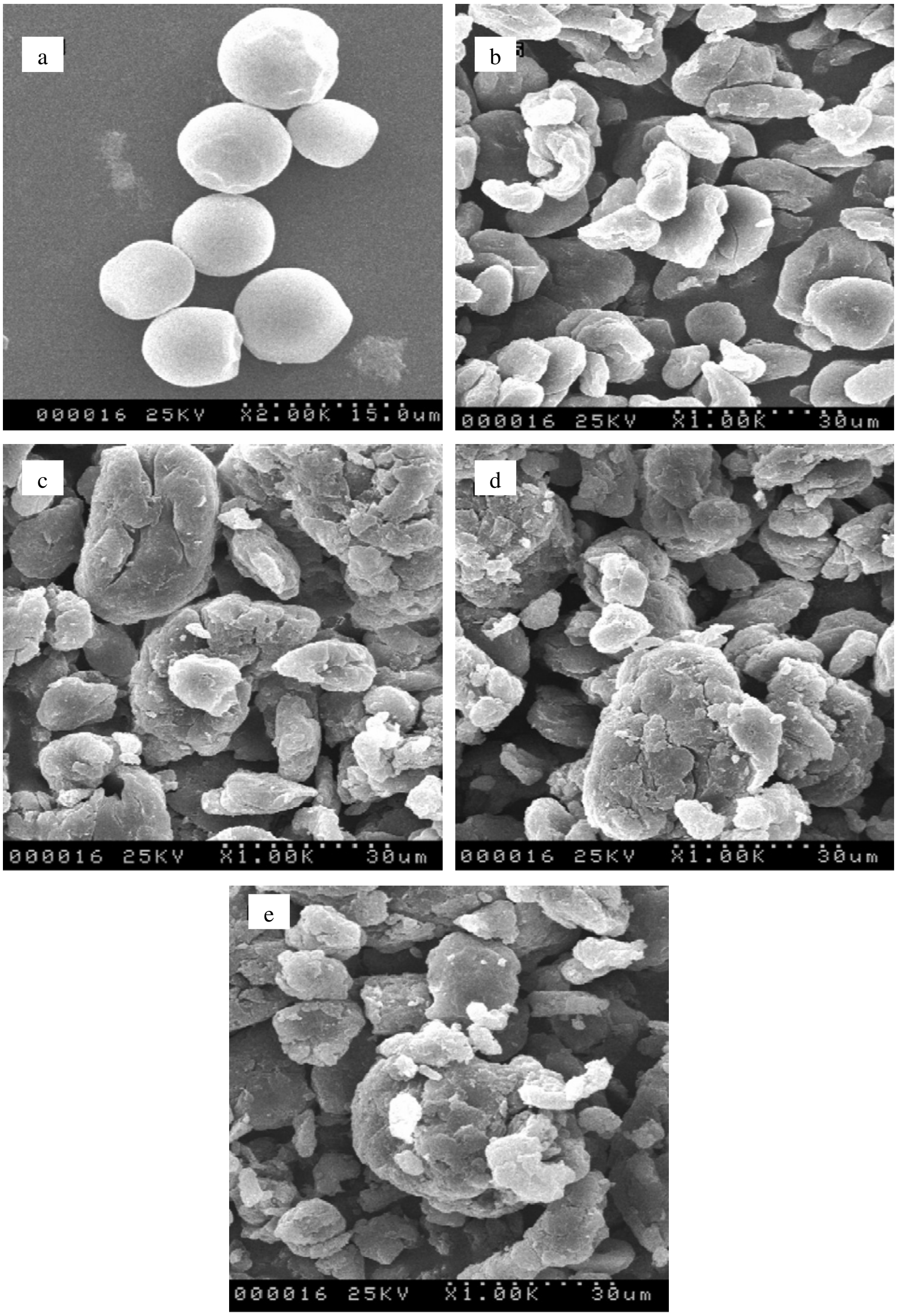

Fig. 3. Scanning electron microphotographs of MACS with different activation time: (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 3.0 h.

Consequently, granule sizes attain uniform. This is in the agreement with the observations from SEM. Above results illuminate that starch transits from tough to brittle at first when it is broken and minified under the mechanical activation. The new generated surfaces are activated by the mechanical strength. The new grains possess even higher reactivity. The strength of van der Waal's force and electrostatic force among these grains is large enough to bring out local plastic transformation and penetrates each other between their boundaries. Therefore, these grains start to form congregates called second granules (Boldyrev, Pavlov, & Goldberg, 1996).

3.4. X-ray diffractometry

X-ray diffraction spectra of MACS with the various activation time are presented in Fig. 4.

The spectrum of the untreated starch sample shows definite diffraction peaks that presumably reflect crystalline regions in the starch. The occurrences of peaks at $2\theta = 15.3°$, 17.3°, 18.3° and 23.5° explain that the structure of cassava starch is C pattern. As the activation time increases and the regions of amorphism is becoming larger and larger at the expense of the crystalline regions, the diffraction pattern

Table 1
Granule size distribution of MACS with different activation time

Activation time (h)	Granule size distribution (%)										Median diameter (μm)
	0–2 μm	2–5 μm	5–10 μm	10–15 μm	15–20 μm	20–30 μm	30–40 μm	40–50 μm	50–60 μm	60–80 μm	
0	–	0.8	6.1	35.0	41.1	7.7	3.7	2.2	1.5	1.9	15.99
0.5	–	1.0	4.0	14.5	23.4	25.6	12.4	8.0	4.9	6.2	22.78
1.0	–	1.1	3.4	11.3	12.6	24.6	15.6	10.8	14.8	5.8	28.73
2.0	0.3	1.5	2.5	13.4	13.1	25.8	16.1	10.1	2.1	15.1	27.39
3.0	0.6	2.6	4.6	10.2	11.1	24.7	18.4	11.1	7.3	9.4	28.46

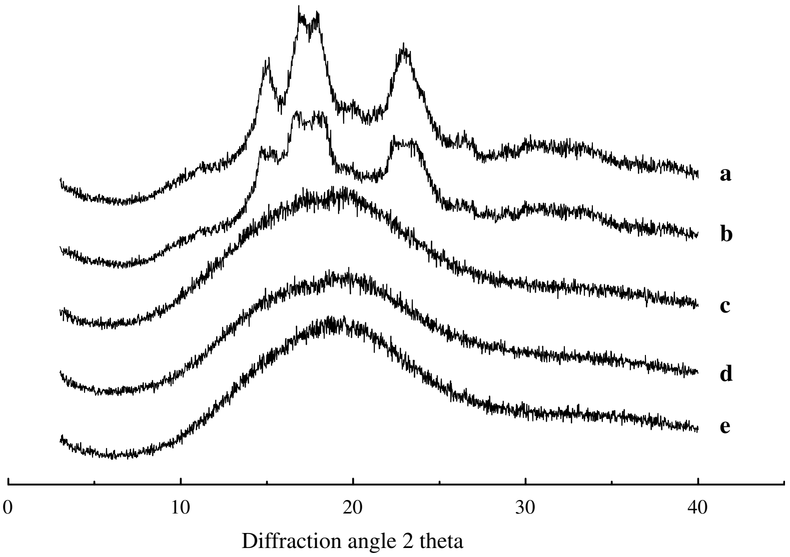

Fig. 4. X-ray diffraction patterns of MACS with different activation time: (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 3.0 h.

decreases. After 2 h, the peak diffraction disappears completely, implying that cassava starch has been converted largely into non-crystalline states. Consequently, the diffraction spectrum shows a broad, featureless peak that is a typical spectrum of amorphism. The degree of conversion to the non-crystalline state by this mechanical activation method is greater than that observed through heat-moisture treatment (Gunaratne & Hoover, 2002), radiation degradation (Bertolini et al., 2001), microwave degradation (Lewandowicz et al., 2000), and ultrasonic degradation (Renata et al., 2005).

3.5. Thermal properties

The DSC curves of MACS samples shown in Fig. 5 are consistent with the foregoing interpretation of the X-ray diffraction data. There are two endothermic peaks between 30 °C and 150 °C whose parameters are listed in Table 2. T_o represents onset temperature, T_p peak temperature, T_c conclusion temperature, ΔH endothermic enthalpy of gelatinization and SG the degree of gelatinization [SG (%) $= (1 - \Delta H_{1M}/\Delta H_{1raw}) \times 100$, where ΔH_{1M} is the gelatini-

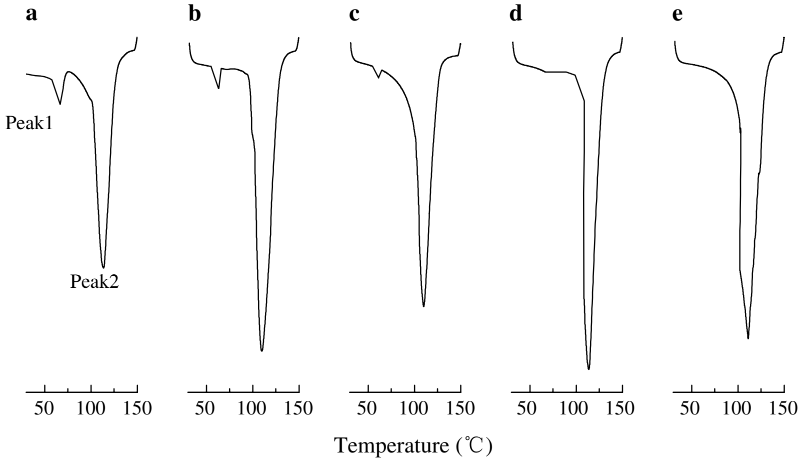

Fig. 5. Differential scanning calorimetry thermograms of MACS with different activation time: (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 3.0 h.

Table 2
Thermal properties of MACS with different activation time by differential scanning calorimetry

Activation time (h)	Peak 1				Peak 2				SG[a] (%)
	T_{o1} (°C)	T_{p1} (°C)	T_{c1} (°C)	ΔH_1 (J/g)	T_{o2} (°C)	T_{p2} (°C)	T_{c2} (°C)	ΔH_2 (J/g)	
0	57.9	66.5	69.9	11.5	100.3	113.5	125.6	1036	0
0.5	55.1	64.1	66.0	5.8	100.6	109.8	127.9	1567	49.6
1.0	54.8	61.2	63.5	1.8	99.8	110.0	124.5	1457	84.3
2.0	No endotherm detected				101.0	113.3	129.6	1521	100
3.0	No endotherm detected				100.4	110.9	132.2	1542	100

[a] SG, degree of gelatinization of MACS.

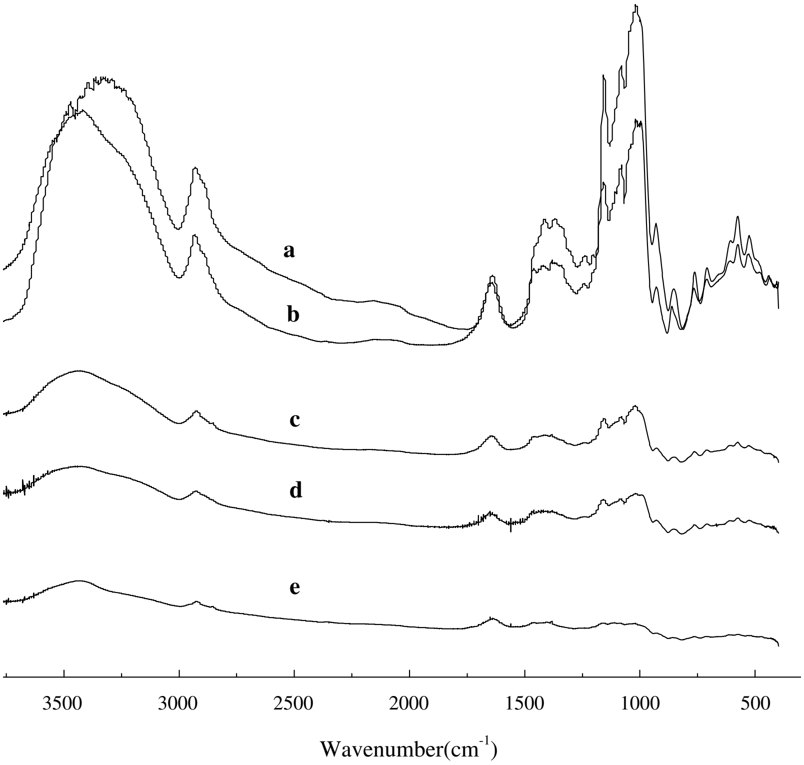

Fig. 6. Infrared spectra of MACS with different activation time: (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 3.0 h.

zation enthalpy of MACS and $\Delta H_{1\mathrm{raw}}$ is the gelatinization enthalpy of untreated cassava starch (Lai, 2001)]. The endothermic peak 1 appears to reflect the transformations of both from poly crystalline states to non-crystalline states and from granule to gelatinized states happened when cassava starch was heated.

Peak 2 with a high endothermic ΔH value appears around 100 °C, the boiling point of water and presumably reflects the vaporization of water in the MACS sample and the destruction of the crystalline structure between water and starch (Zhang, Xu, Yang, & Gao, 2001).

As revealed by the data in Table 2, as the activation time increases, three temperatures of MACS' T_o, T_p and T_c for peak 1 decrease continuously, corresponding to a decrease in the enthalpy of gelatinization and an increase in SG. These data are consistent with the cassava starch's crystalline structure being damaged by the mechanical strength from activation process. After the activation time is over 2 h, the endothermic peak 1 from gelatinization phase transformation disappeared. The SG reaches 100%, indicating that cassava starch has become a completely non-crystalline state. This result is in accordance of that observed in XRD. The somewhat erratic increase in the intensity of peak 2 can be related to the increasing easy with which water molecules can penetrate into starch molecules when the starch crystalline structure is reduced by mechanical activation.

3.6. IR spectroscopy

The spectra of MACS with different activation time are shown in Fig. 6. The following peaks are evident in the treated starch: 3426 cm^{-1} (O–H hydrogen bonding stretching vibration), 2931 cm^{-1} (C–CH$_2$–C asymmetric stretching vibration), 1636 cm^{-1} (H_2O bending vibration), 1158 cm^{-1} (C–O–C asymmetric stretching vibration) and 700–1100 cm^{-1} region (D-glucopyran band and stretching vibration of C–O with the attachment of OH in infrared spectrum).

The MACS does not show any obvious new peaks. This suggests that no new functional groups were produced during the activation. However, as the activation time increases, the peak of 3426 cm^{-1} becomes wide and its intensity decreases. This behavior could be a reflection of that the mechanical activation's decreasing the number of hydrogen bonds in the crystalline phase, with the result that there are more free OH groups in the amorphous phase. The peak of 1636 cm^{-1} is the water freed from starch. The peak width shrinks and intensity decreases, which illustrates the water content in starch is gradually reducing as the mechanical activation progresses. Actually, the measured water contents in non-activated cassava starch and MACS after 3 h activation are 12.72% and 7.91%, respectively. The intensities of other peaks in the spectra show significant decrease and their widths increase as well, which are related to the decrease of crystallization degree.

3.7. Modification process of cassava starch by mechanical activation

In order for activation to occur, it is necessary that two conditions be fulfilled. First, particles should be smaller than the size of tough-brittle transition. If the initial material does not contain sufficiently small particles, they will be produced by breakage. The time needed to generate such particles represents the induction period of the process. Second, the activating stress should be higher than the yield stress, which depends on particle size. If impacts in a device are weak, activation is impossible. Nevertheless, one can change the operational mode of the device in such a manner that the strength of impacts becomes higher. This change may result in activation taking place above this so-called "threshold effect" (Boldyrev et al., 1996; Pavlukhin & Boldyrev, 1988).

Based on the experimental results shown in this paper, it appears that two processes occurred during the mechanical activation. In the first process, between 0 h and 1 h, the impact, shear and friction operating between grinding matrix and starch causes the granules to break into smaller "fine" pieces. This action breaks atomic and hydrogen bonds in the granules, which reduces the size of the crystalline region and creates defects in crystalline structure, including lattice shifts. At this moment, the surfaces of some granules are spontaneously activated so that agglomerates are produced, resulting in a shift to large particle size. However, some tiny granules are also generated. The granule size distribution becomes broader and more uniform.

In the second process over 1 h, a certain value of granularity reaches, starch granules become tougher and harder. They are difficult to break. Destroying these granules becomes impossible, only plastic transformation could happen. Thus, the regularity of the crystal lattice disappears, resulting in the crystal defects. The substitution of crystalline structure by layered non-crystalline structure, the layer becoming thicker and thicker with the progress of grinding, finally drives granules to become amorphous.

In addition, Schoene (1969) thought that the productions of crystal defects, crystalline pattern transformation and non-crystalline formation for an object subjected to grinding, together with formation of unsaturated bonds from the breakage of some bonds on its surface and generation of free ions and electrons, conduce the energy of crystal lattice to increase. The rapid occurrence of interstices inside an object makes its surface temperature and pressure increase. The surface temperature possibly reaches higher than 1000 °C. It is possible that the local intensive heat generated from mechanical activation makes starch degrade and its water content reduces.

4. Conclusion

This study shows that mechanical activation decreases the gelatinization temperature, enthalpy of gelatinization, apparent viscosity and shear thinning of cassava starch, and increases its cold-water solubility. 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. Compared with other methods of bringing about such changes, mechanical activation has the advantages of being a simple process, presenting minimal environmental problems and subject to convenient operation. These features make it possible to envision different degrees of degradations for cassava starch for different applications.

Acknowledgements

This work was financed by the National Natural Science Foundation of China (Grant No. 20366001) and Natural Science Foundation of Guangxi (Grant No. 0640006), China. The authors wish to express their gratitude to Dr. Donald Barnes, guest professor of Guangxi University, for helpful discussion and edition in grammar.

References

Bertolini, A. C., Mestres, C., Colonna, P., & Raffi, J. (2001). Free radical formation in UV- and gamma-irradiated cassava starch. *Carbohydrate Polymers, 44*, 269–271.

Boldyrev, V. V. (1986). Mechanical activation of solid and its application to technology. *Journal de Chimie Physique, 83*, 821–829.

Boldyrev, V. V., Pavlov, S. V., & Goldberg, E. L. (1996). Interrelation between fine grinding and mechanical activation. *International Journal of Mineral Processing, 44–45*, 181–185.

Cai, W., Diosady, L. L., & Rubin, L. J. (1995). Degradation of wheat starch in a twin-screw extruder. *Journal of Food Engineering, 26*, 289–300.

Christopher, G. O. (1997). Towards an understanding of starch granule structure and hydrolysis. *Trends in Food Science & Technology, 8*, 375–382.

Fiedorowicz, M., Tomasik, P., & Lii, C. Y. (2001). Degradation of starch by polarised light. *Carbohydrate Polymers, 45*, 79–87.

Gunaratne, A., & Hoover, R. (2002). Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydrate Polymers, 49*, 425–437.

Josef, L. (1992). Effect of starch structure on starch rheological properties. *Food Technology, 3*, 82–87.

Lai, H. M. (2001). Effects of hydrothermal treatment on the physicochemical properties of pregelatinized rice flour. *Food Chemistry, 72*, 455–463.

Lewandowicz, G., Jankowski, T., & Fornal, J. (2000). Effect of microwave radiation on physico-chemical properties and structure of cereal starches. *Carbohydrate Polymers, 42*, 193–199.

Liang, Y., Zhang, B. S., Yang, L. S., & Gao, D. W. (2004). Chemical reaction activity of tapioca starch with non-crystallized granule state. *Journal of Zhengzhou Institute of Technology (China), 25*, 9–13.

Marcotte, M., Ali, R. T. H., & Ramaswamy, H. S. (2001). Rheological properties of selected hydrocolloids as a function of concentration and temperature. *Food Research International, 34*, 695–703.

Mulak, W., Balaz, P., & Chojnacka, M. (2002). Chemical and morphological changes of millerite by mechanical activation. *International Journal of Mineral Processing, 66*, 233–240.

Nakazawa, Y., & Wang, Y. J. (2003). Acid hydrolysis of native and annealed starches and branch-structure of their Naegeli dextrins. *Carbohydrate Research, 338*, 2871–2882.

Pavlukhin, Y. T., & Boldyrev, V. V. (1988). Mechanical activation of closed-packed inorganic crystals. *Reviews of Solid State Science, 2*, 603–621.

Renata, C. B., Bozena, R., Salah, L., Piotr, U., & Janusz, M. R. (2005). Degradation of chitosan and starch by 360-kHz ultrasound. *Carbohydrate Polymers, 60*, 175–184.

Ren, R. M., Yang, Z. G., & Shaw, L. L. (1999). Synthesis of nanostructured chromium nitrides through mechanical activation process. *Nanostructured Materials, 11*, 25–35.

Schoene, R. (1969). Increasing the activating of the surface of crystals by bombardment with solid particles. *Chemie Ingenieur Technik, 41*, 282–288.

Sim, M. H., Xue, J. M., & Wang, J. (2004). Layer structured calcium bismuth titanate by mechanical activation. *Materials Letters, 58*, 2032–2036.

Suryanarayana, C., Ivanov, E., & Boldyrev, V. V. (2001). The science and technology of mechanical alloying. *Materials Science and Engineering*, 151–158.

Takacs, L. (1998). Solid state reactions induced by ball milling. *Hyperfine Interactions, 111*, 245–250.

Tang, H., Mitsunaga, T., & Kawamura, Y. (2004). Relationship between functionality and structure in barley starches. *Carbohydrate Polymers, 57*, 145–152.

Wang, Y. J., & Wang, L. F. (2003). Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. *Carbohydrate Polymers, 52*, 207–217.

Yang, H. G., Zhang, H., Gu, H. C., & Fang, T. N. (1999). Study on the thixotropy simulation of shear-thinning suspensions. *Journal of Chemical Engineering of Chinese Universities (China), 13*, 506–510.

Zhang, T., & Oates, C. G. (1999). Relationship between α-amylase degradation and physico-chemical properties of sweet potato starches. *Food Chemistry, 65*, 157–163.

Zhang, B. S., Xu, L. H., Yang, L. S., & Gao, D. W. (2001). Study on the melting characters of starch crystal. *Journal of Zhengzhou Institute of Technology (China), 22*, 15–18.