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Starch nanoparticle formation via reactive extrusion and related mechanism study

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ABSTRACT

In this study, starch nanoparticles were prepared by a reactive extrusion method. The mechanism of starch nanoparticle formation during extrusion was investigated. The effects of extrusion conditions, including temperature (50–100 °C), screw speed, torque, starch water content and crosslinker addition, on particle size were studied. The results indicate that, with the addition of appropriate crosslinkers, the starch particles with an average size about 160 nm could be obtained. The morphology, crystalline property, and rheological properties of starch nanoparticles were also characterized.

1. Introduction

Starch is polysaccharide existing as energy reserve in various plants. Starch is composed of two different components, linear amylose and branched amylopectin. Normally, there are 20–30% amylose and 70–80% amylopectin in starch, depending on the species of source. The size and shape of starch granules vary in different plant species. Starch granules have a semi-crystalline structure with a typical crystallinity around 15–45% (Zobel, 1988). As an abundant natural polymer, starch has many attractive properties such as biodegradability and biocompatibility. Since starch is a low-cost versatile biopolymer, it has been widely used in food and many industrial applications (Jobling, 2004; Song, Zhao, Dong, & Deng, 2009).

In recent years, preparation and application of biodegradable nanocrystals/nanoparticles have been attracting more research interests. As a typical biodegradable natural polymer, starch is a good candidate for nanocrystals/nanoparticles. Recently, Le Corre, Bras, & Dufresne (2010) published a comprehensive review on starch nanoparticle preparation, characterization, and applications. Starch nanoparticles or nanocrystals have many potential applications in various aspects, such as plastic fillers (Angellier, Molina-Boisseau, & Dufresne, 2005; Angellier, Putaux, Molina-Boisseau, Dupeyre, & Dufresne, 2005; Kristo & Biliaderis, 2007), food additives, drug carriers (Simi & Emilia Abraham, 2007), implant materials (Thielemans, Belgacem, & Dufresne, 2006), biodegradable composites (Chen et al., 2008), coating binders (Bloembergen, McLennan, Lee, & Leeuwen, 2008), adhesives (Bloembergen et al., 2005), and so on. Starch nanoparticles also have a great potential for use in papermaking wet end, surface sizing, coating and paperboard as a biodegradable adhesive for substitution of petroleum based adhesives. In addition, starch nanoparticles have many advantages over traditional cooked starch, due to its unique properties such as low viscosity of the suspension even at very high solid concentration (up to 30 wt%), and higher bonding strength (Bloembergen et al., 2005, 2008).

Starch nanocrystals/nanoparticles can be prepared by three different ways, including acid or enzymatic hydrolysis, regeneration, and mechanical treatment (Le Corre et al., 2010). Acid hydrolysis is a typical way to generate starch nanocrystals (Dufresne, 2008; García, Ribba, Dufresne, Aranguren, & Goyanes, 2011; Namazi & Dadkhah, 2010; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). With acid hydrolysis, platelet-like starch nanocrystals with a length of 20–40 nm and a thickness of 4–7 nm were obtained (Dufresne, 2008; Putaux et al., 2003). The method of acid hydrolysis is difficult for practical application due to its low yield, long treatment period, and use of acid. Nanosized starch particles can be generated by precipitating starch solution with some organic solvents (Ma, Jian, Chang, & Yu, 2008; Valodkar & Thakore,

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2010). Ma et al. (2008) used ethanol as a precipitant to precipitate pre-cooked native starch, and starch nanoparticles at 50–100 nm were obtained. By using a combination of complex formation with *n*-butanol and enzymatic hydrolysis, Kim & Lim (2009) prepared starch nanoparticles with a size of 10–20 nm. Bastioli et al. (2009) filed a patent for producing starch nanoparticles by complexing modified starch with complexing agents followed by mixing with a hydrophobic polymer. Starch nanoparticles can also be prepared by processing starch granules with mechanical and thermal treatment. Liu, Wu, Chen, & Chang (2009) proposed a simple and environmental friendly mean using high pressure homogenization method for preparing starch nanoparticles. Experimentally, 5% starch slurry was passed through a specially designed microfluidizer several times under high shear pressure. They found the starch particle size could be reduced from 3–6 μm to 10–20 nm after 20 passes. By combining high-pressure homogenization technique with miniemulsion cross-linking, Shi, Li, Wang, Li, & Adhikari (2011) prepared sodium trimetaphosphate (STMP)-cross-linked starch nanoparticles. As a pure mechanical treatment process within a water system, the higher pressure homogenization method is environmentally friendly. However, as only low concentration starch slurry could be processed for homogenization, the yield is still not high. Another environmental friendly mechanical method is extrusion. Giezen, Jongboom, Gotlieb, & Boersma (2000) filed a patent of preparing starch nanoparticles via reaction extrusion. Basically, the premixed starch and plasticizer were loaded into a twin screw extruder, and reversible crosslinkers, such as glyoxal, was added. The extruded starch particles with a size less than 400 nm were obtained, and the starch nanoparticle dispersion at 10% solid content demonstrated a low viscosity of 26 MPa at a shear rate of 55 s^{-1} at room temperature. As the extrusion is conducted under semi-dry conditions (around 65% solid content), therefore the yield is high. The starch nanoparticles prepared by reactive extrusion were also considered as “regenerated starch” nanoparticles because of the crosslinking step (Le Corre et al., 2010). Based on this technology, commercial product, Eco-Sphere is produced by Ecosynthetix. However, the mechanism of starch nanoparticle formation during extrusion was not reported.

Starch extrusion has been widely investigated by many researchers, particularly in food industry. During extrusion, starches are subjected to relatively high pressure, heat and mechanical shear. As a result, significant structural changes, including gelatinization, melting, and fragmentation might occur. The physicochemical change of starch during extrusion was reviewed by Lai & Kokini (1991). It was noted that, during extrusion, complete gelatinization would not occur because of the limited water content in starch. However, at high extrusion temperatures, starch granules soften and melt, and become more mobile. The softened and melted starch granules were physically torn apart by shear force so that faster transfer of water into the interior starch molecules can be achieved. Such mechanical disruption of the molecular bonds by the intense shear force may cause the loss of crystallinity during extrusion. It was found by X-ray diffraction that partial or complete destruction of the crystalline structure of the raw starch granule occurred. This is a good evidence of starch fragmentation during extrusion. During extrusion, hydrogen bonds between linear amylose and branched-chain amylopectin can be broken under high shear force and temperature (Lai & Kokini, 1991). It was found that the molecular weight (Mw) decreased exponentially when the specific mechanical energy input increased (Xie, Yu, Liu, & Chen, 2006). However, no starch particle size measurement was involved in these studies.

The objective of this study is to investigate the mechanism of starch nanoparticle formation via reactive extrusion. The effects of extrusion conditions, such as temperature, screw speed, crosslinker and water content on starch extrusion process and starch particle size were systematically studied. The transitional properties of starch particles, including morphology, crystallinty structure, and rheological properties, at different size levels were also characterized.

2. Materials and methods

2.1. Materials

Native corn starch (B200) was provided by Grain Process (Muscatine, IA, USA). Glycerol (99% pure) and glyoxal (40% aqueous solution) were purchased from Aldrich USA, and were used as plasticizer and crosslinker, respectively.

2.2. Process of nano starch preparation

The nanostarch was prepared using the method described in the patent (Giezen et al., 2000) with minor modification. Giezen used a continuous feeding extruder with 9 heat zones. In our study, a batch feeding extruder with one single heat zone was used. Native corn starch granules were premixed with water and glycerol using a lab blender at a ratio of 100:22:23 (starch:water:glycerol). The well mixed mixture was sealed into a plastic bag, and stored in a refrigerator at around 2 °C for 24 h. A co-rotating twin-screw extruder (HAAKE Minilab) was used to extrude the starch premix. The screw speed range is 100–360 rpm. Amount of starch used for each test is 5 g. 10% glyoxal aqueous solution was added in the starch premix or at the chemical addition point of the extruder (downstream hopper) at a dosage level of 0.5–3% pure glyoxal (based on dry starch amount). The extrusion was conducted within 55–110 °C. The starch samples could be directly flushed out through a die, or cycle inside for longer residence time. The torque was monitored and recorded by a reading screen, and the peak value was reported and used for comparison. In Giezen’s patent, the extrudates were ground and sieved, followed by dispersing the starch particles in water. In our study, no grinding and sieving were conducted, and the starch extrudates were simply cut into small pieces (around 0.3 cm) and immersed in water for 1 h. The starch pieces were further broken by an Ultra Turrax homogenizer (IKA T18 BASIC) at a speed of 16,000 rpm for 30 min, producing starch particle suspension.

The prepared starch particle suspension was diluted, and used for particle size measurement and rheological tests. Part of suspension was freeze dried, and the dried powder was used for determining starch crystalline structure.

2.3. Characterization

The particle size and zeta potential of starch particles were measured using a Malvern Zetasizer 3000. The viscosity of prepared starch particle suspension was measured using a MCR 300 rheometer in rotating model with couette geometry. The morphology of starch particles was observed using a scanning electron microscopy (SEM LEO 1530). The crystalline structure of freeze dried starch powders was determined using a wide angle X-ray diffractometer (PANalytical X’Pert PRO) with Cu Kα radiation ($\lambda = 0.154$ nm). The scanning was conducted at 40 kV with a rate of 0.5° per minute. The diffraction data from 5 to 35° were collected.

3. Results and discussion

3.1. Characterization of extruded starch rods and particles

Premixed starch samples (starch with plasticizer) were loaded into the extruder and processed under different conditions, including temperature, screw speed, crosslinker dosage and starch water

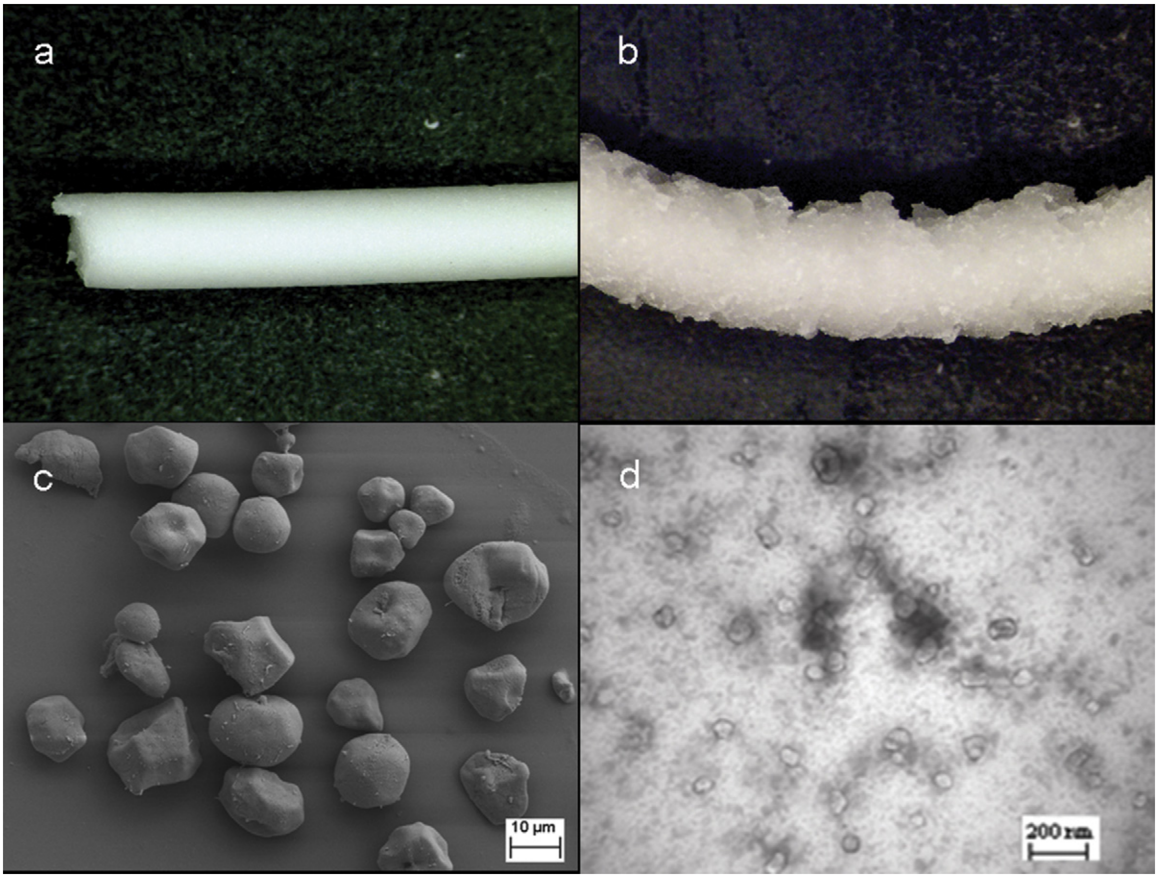

Fig. 1. Microscope pictures of extruded starch rods and starch particles (a) optical microscope picture of extruded starch rods without glyoxal at 70 °C; (b) optical microscope picture of extruded starch rods with 2% glyoxal at 60 °C; (c) SEM picture of original starch granules; (d) SEM picture of extruded starch particles at 85 °C with 2% glyoxal at 200 rpm). Scale bar for *c* is 10 μm and for *d* is 200 nm.

content. In this study, glyoxal was used as the crosslinker for starch. As a dialdehyde compound, glyoxal has two carbonyl groups on its molecules which can react with hydroxyl groups in starch molecules (Yang, Dou, Liang, & Shen, 2005). Acetalization reaction can occur, i.e. acetal bonds are formed between the hydroxyl groups and aldehydes, as shown below.

$$R_2C{=}O + R'OH \rightleftarrows R_2C(OH)OR'\text{(Hemiacetal Formation)}$$

$$R_2C{=}O + 2R'OH \rightleftarrows R_2C(OR')_2 + H_2O\text{(Acetal Formation)}$$

Heat is required to initiate reactions and achieve curing. The impact of the crosslinker on the extrusion process and starch particle size will be discussed.

The starch rods with a diameter of 2–3 mm were extruded. However, different appearance of extruded starch rods was observed for different extrusion conditions. Starch rods with smooth surface were obtained when no crosslinker was added (Fig. 1a), and the color of rods changed from white to translucent with the increase of extrusion temperature. When crosslinker (2% glyoxal) was added, the surface of the extruded rods became rough even at a low extrusion temperature of 60 °C (Fig. 1b), indicating some pattern of damage which might be attributed to high shear force during extrusion. This will be further discussed later.

The extruded starch rods were cut into small pieces and immersed in water. After 30-min high speed stirring, a well dispersed starch particle suspension was obtained. The size and morphology of starch particles were characterized with SEM. The morphology of original starch particles was shown in Fig. 1c. It can be seen that most of the granules are spherical, and the average size is around 10–15 μm. After extrusion at 85 °C without crosslinker, the average starch particle size was reduced to 1–2 μm. On contrary, at the same extrusion temperature (85 °C), when 2% glyoxal was added during extrusion, nano sized starch particles with a size around 160 nm were obtained (Fig. 1d).

SEM images can provide visual comparison of starch particles at different size levels. In order to obtain a statistical result, the number intensity distribution of the particle size was determined using the light scattering method. For extrusion without crosslinkers, the starch particle size decreased with the increase of extrusion temperature, as shown in Fig. 2. The size distribution also changed with

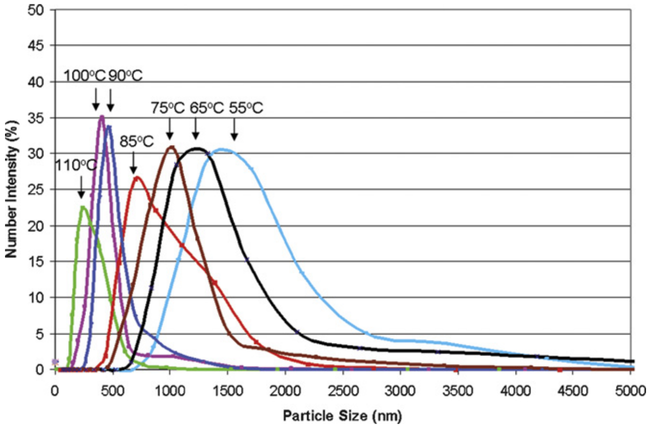

Fig. 2. Starch particle size distributions for extruded starch particles at different temperatures measured in deionized water (no crosslinker, 300 rpm).

the temperature. At a low extrusion temperature, for example 55 °C, the size distribution is very broad, at a range of 500–5000 nm. At a higher extrusion temperature of 90 °C or above, a much narrower size distribution was presented.

The size change of extruded starch particles with 2% glyoxal is shown in Fig. 3. With the increase of extrusion temperature, the particle size decreased sharply initially, and then kept at a low level around 100–200 nm at 75–100 °C. At low temperatures (55 and 65 °C), the size distribution was broad. At higher extrusion temperatures (>70 °C), a narrower size distribution could be achieved.

It was also found that at the same extrusion temperature, the size of starch particles extruded with crosslinker (2% glyoxal) is much smaller than that without crosslinker. For example, at 65 °C, the average size of starch particles without crosslinker is around 1.3 μm, while the average size of starch extruded with 2% glyoxal is about 300 nm. These results suggest that the crosslinker (glyoxal) can facilitate the reduction of particle size during extrusion, which agrees well with the literature (Giezen et al., 2000). The mechanism of how the crosslinker addition can reduce the particle size and the size distribution will be discussed later.

The zeta potential of extruded starch particles at different size was also measured. For starch extrusion with and without crosslinkers, the zeta potential increased (the absolute values decreased) with the decrease of particle size. In contrast, Liu et al. (2009) reported that for high pressure homogenization treatments, the smaller the starch particle size, the lower the zeta potential. This is because the high pressure homogenization is a pure physical tear-apart process which releases more free hydroxyl groups on starch particle surface when particle size is decreased. However, extrusion conducted in this study is a complicated process including starch gelatinization, melting, fragmentation or even crosslinking. During the process of fragmentation (i.e., tear-apart), melting would also occur, and the released free hydroxyl groups might form hydroxyl bonds again at particle surface, resulting a higher zeta potential (smaller absolute values).

In order to investigate the effect of extrusion on starch crystal structure, X-ray patterns were determined for different starch samples. As a native cereal starch, original corn starch granule has A-type crystallinity, i.e. showing strong diffraction peaks at around 15°, 17°, 18° and 23° (Fig. 4a), which agrees with the literature (Bhatnagar & Hanna, 1994; Cheetham & Tao, 1998; Sívoli, Pérez, Lares, & Leal, 2009; Zobel, 1988). During the extrusion process, starch granules were exposed to high temperature and high shear force so that the particle size decreased. As a result, the crystalline structure would also change. Fig. 4 shows, the diffraction peaks diminished or even disappeared for extruded starch particles (Fig. 4b and c). The peaks at 15°, 18° and 23° totally disappeared, and only a small peak at 17° exists after extrusion, which suggests that the extrusion, i.e. combination of heat and shear force, caused a significant change on starch crystal structures. Farhat, Mitchell, Blanshard, & Derbyshire (1996) reported that the crystallinity of extruded starch is only 2–4%. Liu et al. (2009) also reported that the degree of crystallinity of starch particles decreased with the reduction of particle size during high pressure homogenization treatment. They argued that both amorphous and crystalline part of starch granules were broken into much smaller particles under mechanical treatment. In addition, Fig. 4 also shows that the X-ray patterns of extruded starch without or with crosslinker did not show significant difference. The results indicate that the crosslinking reaction itself did not change the crystal structure of starch, which agrees with previous results in literature (Sívoli et al., 2009; Yoon, Chough, & Park, 2007).

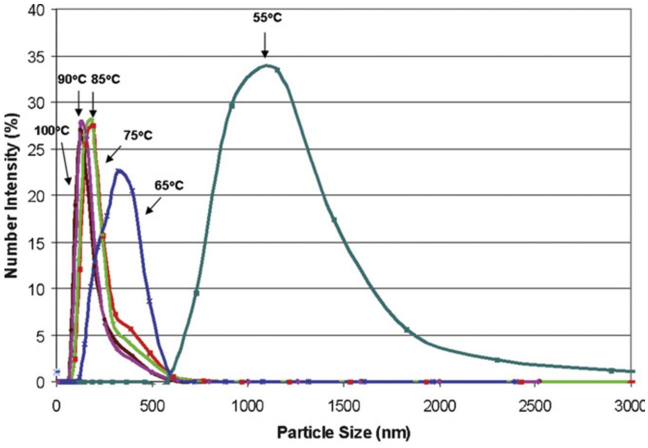

Fig. 3. Starch particle size distributions for extruded starch at different temperatures measured in deionized water (2% glyoxal, 300 rpm).

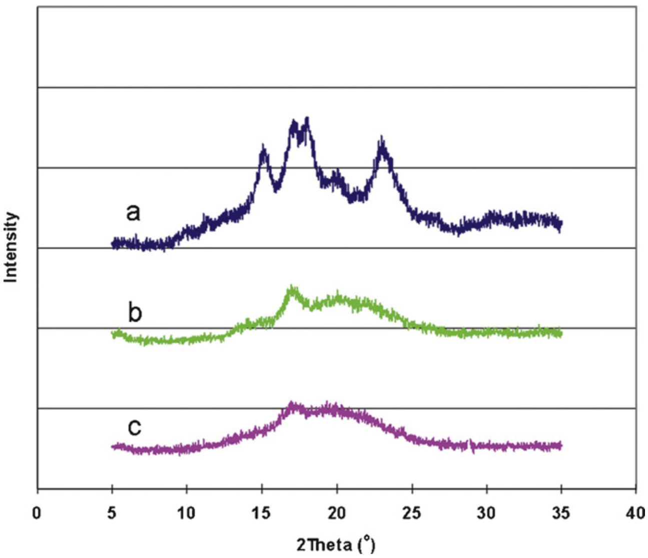

Fig. 4. X-ray pattern of starch (a) starch granules; (b) extruded starch without glyoxal (300 nm); (c) extruded starch with 2%glyoxal (300 nm).

3.2. Mechanism of starch nanoparticle formation

During extrusion, starches are subjected to high temperature and high shear force. Essentially, starch gelatinization, melting and fragmentation occur, resulting in the decrease of starch particle size. Klingler, Meuser, & Niediek (1986) proposed that both the thermal and mechanical energy applied to starch during extrusion may cause the breakdown of covalent bonds and hydrogen bonds between starch molecules. Colonna, Doublier, Melcion, Monredon, & Mercier (1984) found that the average molecular weight of amylose and amylopectin significantly decreased after extrusion. With the breakdown of those bonds, starch granules might be easily torn apart into smaller particles, even to nanosize. In this study, the contribution of heat, shear and chemicals was identified by investigating starch extrusion at different combinations of processing conditions.

The extrusion temperature or thermal energy usually has strong impact on polymer morphology, crystallinity and chemical compositions. To study the extrusion temperature effects on the starch particle size, a fixed screw speed at 300 rpm with different temperatures were employed. For the extrusion tests without crosslinkers, the starch particle size decreased with the increase of extrusion temperature (Fig. 5 the upper solid line). However, the torque during extrusion was decreased with the increase of temperature. This is because at higher temperatures, a higher extent of starch softening and melting will require less energy (shear force) to push starch through the extruder. Therefore, a decreased torque was observed. On the other hand, the highly softened and melted starch granules are easier to be torn apart into smaller particles even at a small torque of 120 N cm. That means the reduction of starch size with temperature increase is likely due to heat effect, i.e. thermal energy effect.

When crosslinker (2% glyoxal) was added, the starch particle size was sharply decreased when temperature increased from 55 to 75 °C after extrusion. A further increase of temperature only lowered the particle size slightly. It is interested to note that the dependence of torque on the temperature is totally different for the starch system with and without crosslinker. As shown in Fig. 5 (dash lines), the torque increased with the temperature when crosslinker was added, but it decreased for the system without crosslinker. Generally speaking, the higher temperature will results in a decrease of the viscosity for melted starch so a decrease in toque should be observed. However, for the extrusion of starch in presence of crosslinker (glyoxal), the crosslinked starch network is formed, which has a negative impact on the softening and melting of starch. As a result, a higher toque is needed during extrusion, and a smaller starch particle size can be reached, compared to extrusion without a crosslinker. Furthermore, raising temperature can result in an increase of the crosslinking rate, and an increase in torque.

In order to study the effect of mechanical energy, the extrusion temperature was fixed and the extrusion at different screw speeds were conducted, which corresponds to the different shear forces applied. It was shown in Fig. 6 (dash lines) that for a given temperature regardless of using crosslinker or not, the faster the screw speed, the higher the torque. Furthermore, a much higher torque could be achieved when crosslinker (glyoxal) was added. For example, at a screw speed of 360 rpm, the torque for the extrusion with 2% glyoxal at 75 °C was about 390 N cm, while a much lower torque (around 140 N cm) was measured for the extrusion without crosslinker. As we discussed before, the high torque was attributed to the crosslinking effect during extrusion.

Fig. 6 (solid lines) shows that at a given extrusion temperature, the starch particle size was decreased with the increase of screw speed, i.e. torque values, which suggests that the shear force is critical for the reduction of starch particle size during extrusion. It has been known that fragmentation of starch during extrusion is attributed to mechanical energy (SME) (Klingler et al., 1986; Seker & Hanna, 2005). Furthermore, it can be seen in Fig. 6 (solid lines) that even at a low extrusion temperature (65 °C), the particle size of extruded starch with crosslinkers (2% glyoxal) is much smaller than that of the starch extruded without crosslinker at a high temperature of 90 °C. This is mainly because a higher torque was achieved during extrusion with crosslinker.

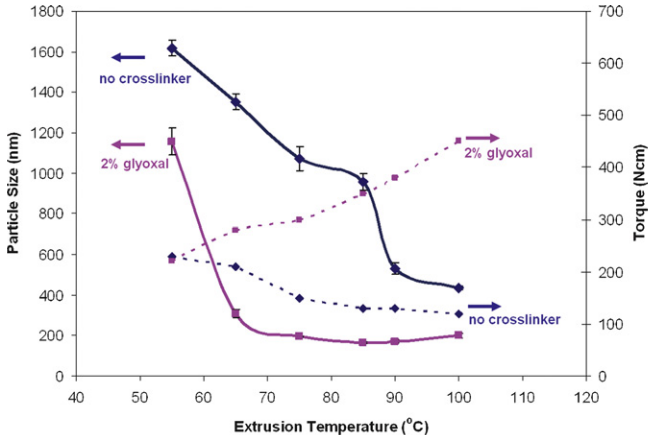

Fig. 5. Particle size (solid lines) and torque values (dash lines) at different extrusion temperatures.

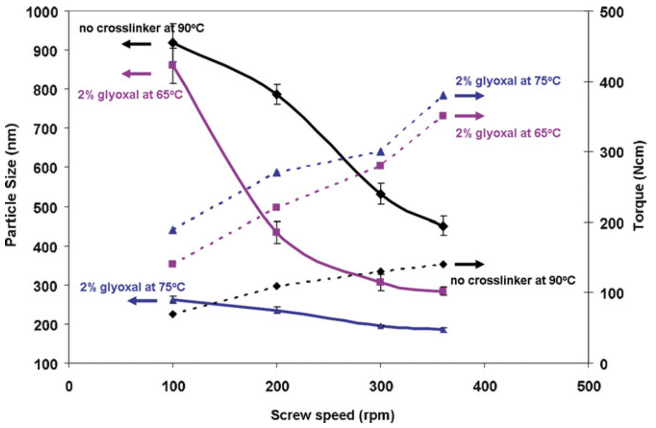

Fig. 6. Particle size (solid lines) and torque values (dash lines) at different extrusion screw speeds.

Fig. 6 also shows that for extrusion with 2% glyoxal at a low temperature (65 °C), starch particle size decreased sharply with the increase of torque. The results suggest that, at low temperatures, the softening and melting of starch granules are limited, and the resultant particle size is highly dependent on the mechanical energy induced. However, at higher temperatures (75 °C), the particle size was reduced to a low level and almost kept constant at different torques. During the extrusion at high temperatures, both heat and shear force are important. First of all, a high extent of starch softening and melting could be realized, and it is much easier to tear starch granules apart into smaller particles. At the same time, a crosslinked starch network was formed due to the induction of glyoxal. When crosslinked starch was going through the screws, a high torque (>200 N cm) was reached, even at a low screw speed (100 rpm). At such a high torque, the softened, melted and crosslinked starch could be easy to be torn apart into nanosized particles. However, a further increase of torque could only slightly decrease the particle size.

Starch extrusion with different crosslinker dosages was also conducted, and the corresponding torque and size was summarized in Fig. 7. It can be seen that the higher the crosslinker dosage, the higher the torque, and the lower the resultant particle size. This result further proved that crosslinker addition could increase the shear force during extrusion which facilitates the reduction of particle size.

Starch softening and melting occurs at high temperatures. The effect of starch softening and melting on particle size of extruded starch is complicated. Under high shear force, softened and melted starch can be broken into smaller particles easily. On the other hand, starch softening and melting normally can reduce the viscosity of starch, and therefore reduce the shear force. The degree of softening and melting is highly dependent on water contents of starch. In this study, different levels of water content of premixed starch were chosen, e.g. 30, 35, 40, 45%. For extrusion without crosslinker, as expected, the higher the water content, the lower the torque. However, it was found that, although the torque decreased with the increase of water content of starch, the actual particle size was decreased. The reduction of size for this case is mainly attributed to enhanced starch swelling and softening at higher water content, though the torque values decreased. For the extrusion with crosslinker (2% glyoxal), the torque decreased with the increase of water content, and the particle size was increased. The results suggest that, for the extrusion with crosslinker, the effect of torque reduction overtook the contribution of starch swelling and softening.

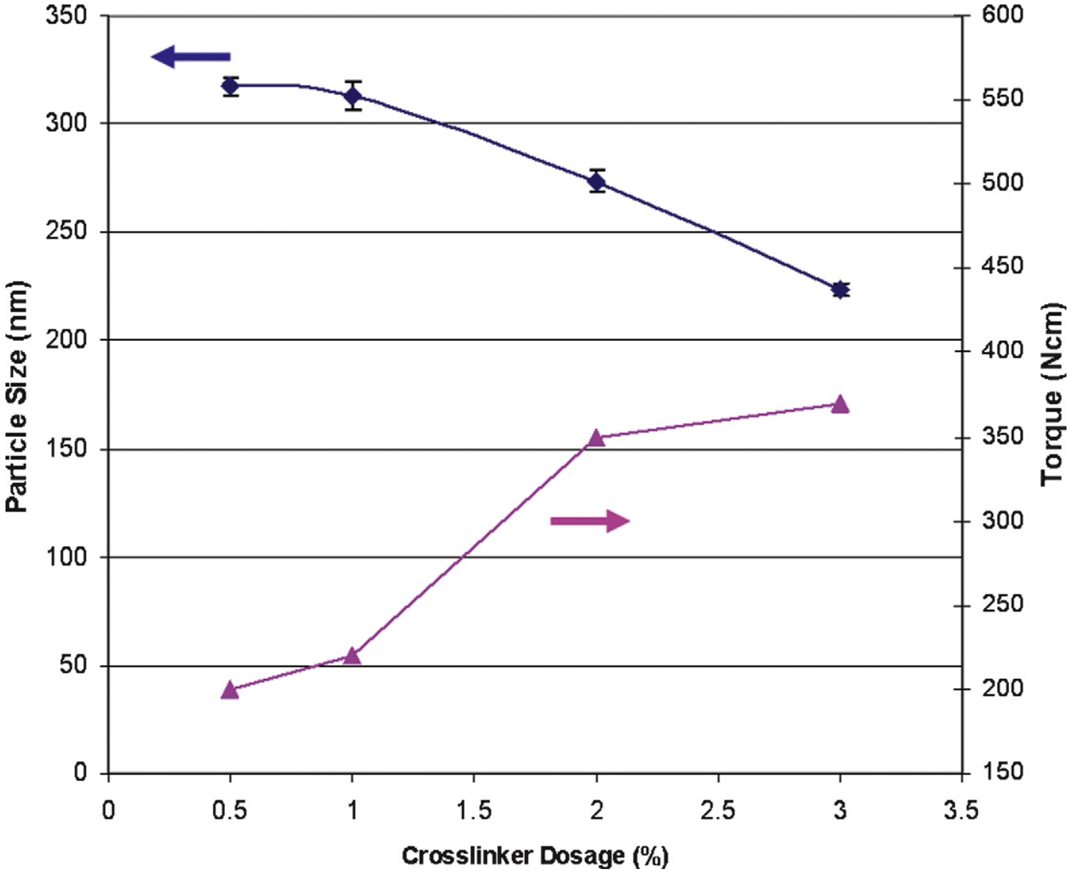

Fig. 7. Effect of crosslinker dosage on particle size and torque (at 90 °C and 300 rpm).

3.3. Rheological properties of starch nanoparticle suspension

The viscosity of a particle suspension depends on many factors such as particle numbers, size, aggregation status and the interaction forces of particle–particle and particle–solvent. Highly swelled particles usually have a higher viscosity. Fig. 8 shows that for a given shear rate, the viscosity significantly increased with the decrease of particle size, particularly when the size is reduced to 600 nm or lower. This is because, for a given mass concentration, the smaller the particle, the more particles in the solution, and the higher interaction between the particles, resulting in a higher viscosity of suspension. When starch particle size is higher than 1 μm, the viscosity of starch suspension kept constant while changing shear rates. For starch particles with small size around 600 nm or lower, the suspension shows shear thinning phenomenon, i.e. viscosity decreased with the increase of shear rates.

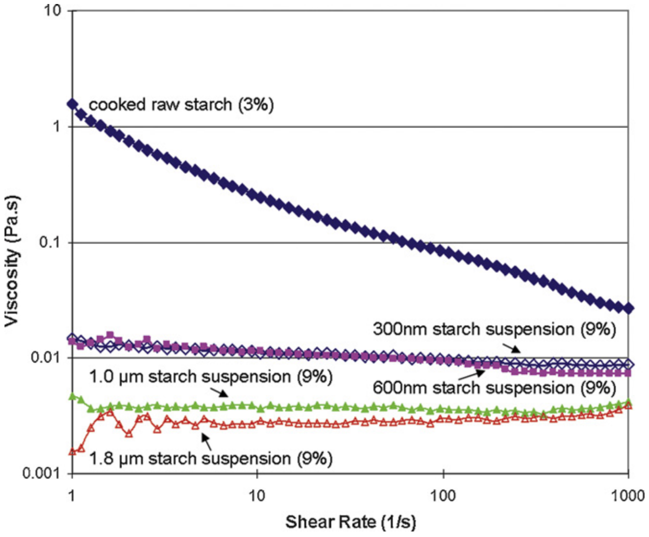

Fig. 8. Viscosity of starch particle suspension and cooked starch at room temperature.

The viscosity of starch nanoparticle suspension and cooked starch solution was also compared in Fig. 8. At a high shear rate of 1000 s^{-1}, the viscosity of 300 nm starch particle suspension at 9% is lower by around 70% than that of cooked starch at a low solid content of 3%. A low viscosity at high solid contents is a great advantage of starch nanoparticles for industry applications.

4. Conclusions

In this study, the mechanism of starch nanoparticle formation during extrusion was investigated. The results indicate that after extrusion at 100 °C without crosslinker, the starch particles with a size of 300 nm were obtained. With the addition of appropriate crosslinkers, the starch particle size could be further reduced to around 160 nm, even at a lower extrusion temperature of 75 °C. The temperature and torque are two important factors. The addition of crosslinkers could significantly increase the shear force (torque), and therefore facilitate the reduction of particle size. The dependence of torque on the temperature for the starch systems with and without crosslinker is totally different. The torque decreases with the increase of temperature for the system without crosslinker, however, it increases quickly with the increase of the temperature if crosslinker was added to the starch system. Compared to original starch granules, the crystallinity of the extruded starch nanoparticles is lower as indicated by X-ray pattern. The prepared starch nanoparticle suspension had a much lower viscosity than the cooked starch.

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