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Factors influencing the properties of hydroxypropylated potato starches

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Abstract

Starches separated from four potato cultivars were hydroxypropylated and their physico-chemical, morphological, thermal and rheological properties were compared. The extent of hydroxypropylation measured as molar substitution differed significantly among the starches from different potato cultivars. Kufri Jyoti hydroxypropylated starch showed highest molar substitution, while Kufri Chandermukhi hydroxypropylated starch showed the lowest. The hydroxypropylated starches showed higher swelling power, solubility, solubility in dimethyl sulphoxide (DMSO) and paste clarity than their counterpart native starches. Light transmittance of hydroxypropylated starches did not change significantly during refrigerated storage while a substantial decrease in the same was observed for native starches. SEM pictures showed that the hydroxypropylated starch granules from all the potato cultivars differed in shape and size from the native starch granules, and showed the presence of slight fragmentation and a distinct groove in their central core region along the longitudinal axis. Hydroxypropylation treatment showed more pronounced effect on large size granules than small size granules. The extent of granule disruption was observed to be higher for hydroxypropylated starch gels that later developed numerous rod shaped or fuzzy clustered microfibrils with diameters ranging from 15 to 20 μm, after 30 days of refrigerated storage. The studies on the phase transitions associated with gelatinization of starches showed lower gelatinization parameters (T_o, T_p, T_c, and ΔH_{gel}) among the hydroxypropylated starches in which Kufri Jyoti and Kufri Sindhuri starches were the most affected. Hydroxypropylated potato starches exhibited higher peak G', G'' and lower tan δ during rheological measurements on the dynamic rheometer. Whereas the native starches did not possess freeze-thaw stability, upon hydroxypropylation there was a pronounced decrease in the tendency towards syneresis.

Keywords: Hydroxypropylation; Potato starch; Freeze-thaw; Morphological; Thermal; Rheological; Retrogradation

1. Introduction

Starch is a typical homopolysaccharide, it is one of the major polysaccharides used for energy storage and is widely distributed in seeds, roots, and tubers as well as in stems, leaves, fruits and even pollen. The unique physical and chemical characteristics and nutritional quality of starch sets it apart from all other carbohydrates. Various physico-chemical, thermal, rheological and retrogradation properties have been significantly correlated with the average granule size of the starches (Chiotelli & Meste, 2002; Sahai & Jackson, 1996; Singh, Singh, Kaur, Sodhi, & Gill, 2003; Singh & Singh, 2001, 2003; Sodhi & Singh, 2003; Whistler & BeMiller, 1997). Potato starch is a good texture stabilizer and regulator in food systems (Cousidine, 1982), but limitations like low shear stress resistance, thermal resistance, thermal decomposition and high retrogradation have limited its use in some industrial food applications. Starch modification, which involves the alteration of the physical and chemical characteristics of the native starch to improve its functional characteristics, can be used to tailor the starch to a particular process (Hermansson & Svegmark, 1996). Chemical modification of native granular starches by etherification profoundly alters their gelatinization, pasting and retrogradation behaviour (Choi & Kerr, 2003; Kim, Hermansson, & Eriksson, 1993; Liu, Ramsden, & Corke, 1999; Perera & Hoover, 1999; Seow & Thevamalar, 1993). The chemical and physical properties achieved when modifying starch depend on e.g. reaction

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conditions, type of substituent, molar substitution and distribution of substituents (Kavitha & BeMiller, 1998; Richardson, Nilsson, Bergquist, Gorton, & Mischnick, 2000; Rutenberg & Solarek, 1984; Steeneken & Woortman, 1994). Food-grade starches are mainly hydroxypropylated to increase paste consistency and clarity, and to impart freeze-thaw and cold-storage stabilities (Liu et al., 1999; Perera & Hoover, 1999; Shi & BeMiller, 2002; Tuschhoff, 1986; Wu & Seib, 1990; Xu & Seib, 1997). The hydroxypropyl groups introduced into the starch chains are said to be capable of disrupting inter- and intra-molecular hydrogen bonds, thereby weakening the granular structure of starch leading to an increase in motional freedom of starch chains in amorphous regions (Choi & Kerr, 2003; Seow & Thevamalar, 1993; Wooton & Manatsathit, 1983). Choi and Kerr (2003) studied the effects of hydroxypropylation on water sorption isotherms and molecular mobility of both starch and water molecules using pulsed ^{1}H-MMR techniques and reported that the water absorption capacity of hydroxypropylated wheat starch increases with increasing degree of molar substitution of hydroxypropylated group in a specific water activity range. Microscopy has played an important role in improving the understanding of the granular structure of starches. It has also been used to detect structural changes caused by chemical modifications is the most substituted regions of starch granules. Kim, Hermansson, and Eriksson (1992) have used light microscopy for hydroxypropylated potato starches and suggested that hydroxypropylation mainly takes place at the central region of the granules. Many researchers have studied the pasting properties of hydroxypropylated starches using viscoamylograph and Rapid Visco-Analyzer (RVA) and reported that the alteration in the pasting properties is mainly due to the decrease in associative forces within the starch granule (Kim et al., 1992; Liu et al., 1999; Shi & BeMiller, 2000; Yeh & Yeh, 1993). The objective of the present study was to study the effect of hydroxypropylation on physico-chemical, morphological, thermal, rheological and retrogradation properties of starches from different potato cultivars.

2. Materials and methods

2.1. Materials

The tubers of *Solanum tuberosum* L. cv. Kufri Jyoti, Kufri Sutlej, Kufri Sindhuri and Kufri Chandermukhi were procured from the Government Potato Seed Farm, Mattewara, Punjab, India from the 2002 harvest. Uniform sized tubers were selected from each cultivar and washed thoroughly. Analytical grade propylene oxide and deuterium oxide (for NMR spectroscopy) was procured from MERCK-Schuchardt, Hohenbrunn, Germany, while the alpha-amylase was purchased from HiMedia Laboratories Ltd, Mumbai (India). All other chemicals were analytical grade.

2.2. Methods

2.2.1. Starch isolation

Starch was isolated from the four potato cultivars as described earlier (Singh & Singh, 2001).

2.2.2. Preparation of hydroxypropyl potato starches

Etherification of potato starches with propylene oxide was carried out in the presence of NaOH and $Na_2\,SO_4$ at pH 11.3 by slightly modifying the procedure outlined by Perera and Hoover (1999). Double jacketed glass bottles (300 ml) in which water was circulated at 40 °C were used to carry out the reaction. The starch (15 g, dry basis) from each potato cultivar was suspended in distilled water (35 ml) containing $Na_2\,SO_4$ (1.5 g) with mild stirring and the pH was adjusted to 11.3 with 0.5 N NaOH. Propylene oxide was added at 0, and 10% levels, based on dry weight of starch. The reaction vessel was sealed and the reaction was continued for 24 h with stirring. The starch suspensions were then neutralized to pH 5.5 with dilute HCl (0.1 N). The hydroxypropylated samples were isolated as described by Perera and Hoover (1999). Each reaction was replicated three times.

2.2.3. Determination of molar substitution

The molar substitution (MS) (hydroxypropyl) was determined by ^{1}H-NMR as described by Xu and Seib (1997).

2.2.4. Physico-chemical properties

2.2.4.1. Moisture content (%). Moisture content of the starches was determined in triplicate using Halogen Moisture Analyzer (Mettler, Switzerland).

2.2.4.2. Amylose content (%). Amylose content of the native starches was determined in triplicate using the method of Williams, Kuzina, and Hlynka (1970).

2.2.4.3. Swelling Power (g/g) and solubility (%). Swelling power and solubility of the starches were determined using 2% (w/v) aqueous suspension of starch at 90 °C by the method of Leach, McCowen, and Schoch (1959).

2.2.4.4. Transmittance (%). Transmittance of the starches was measured as described by Craig, Maningat, Seib, and Hoseney (1989). A 1% (w/v) aqueous suspension of starch near neutral pH from each potato cultivar was heated in a water bath at 90 °C for one hour with constant stirring at 75 rpm. The suspension was cooled for one hour at 30 °C. The samples were stored for five days at 4 °C in a refrigerator and transmittance was determined every 24 h by measuring absorbance at 640 nm against a water blank with a Spectronic-20D (Milton Roy Company, USA).

2.2.4.5. Solubility (%) and transmittance (%) in DMSO. The solubility of the native and modified starches in anhydrous dimethyl sulphoxide (DMSO) was measured using the method of Yeh and Yeh (1993). The transmittance of the starch suspensions (1%, w/v) in DMSO was measured at 640 nm against a DMSO blank with a Spectronic-20D (Milton Roy Company, USA). The starch suspensions were shaked for 24 h to keep starch granules continually suspended and transmittance was measured after specified shaking times (0, 4, 8, 12, 16, 20 and 24 h).

2.2.5. Morphological properties

2.2.5.1. Granule size analysis. Granule size distributions of the native starches were determined using an automated digital image analyzer, equipped with an image acquisition and computer processor. Granules were washed with 100% acetone and air-dried, were suspended in 99.5% (v/v) glycerol and subsequently imaged under a light microscope. The images were later analyzed using USB digital scale software that determined the major axis of each granule. Percent distributions were formed from the data. Five hundred granules were observed for each sample. Starch granules touching the edge of the field of view were eliminated from analysis and not counted.

2.2.5.2. Scanning electron microscopy of starches. Scanning electron micrographs of native and hydroxypropylated starches were obtained as described earlier (Kaur, Singh, & Sodhi, 2002).

2.2.5.3. Scanning electron microscopy of starch gels. The specimen preparation of freshly prepared and stored (up to 10th day at 4 °C) potato starch gels for SEM was carried out as described by Perera and Hoover (1999). A 2% (w/v) aqueous suspension of potato starch near neutral pH was heated in a boiling water bath for one hour with constant stirring at 75 rpm and then cooled for one hour at 25 °C. The paste was stored for ten days at 4 °C. The gels were then freeze-dried and the samples were examined and photographed in a JEOL JSM- 6100 scanning electron microscope (Jeol Ltd, Tokyo, Japan). An accelerating potential of 20 kV was used during micrography.

The stored starch suspensions (30th day at 4 °C) were filtered through a 0.45 μm filter membrane (Millipore (India), New Delhi), air dried at ambient temperature, and stored in a desiccator over phosphorus pentaoxide. An untreated membrane and the membranes that had been subjected to all preparation steps were then sputter coated and examined under the scanning electron microscope using the same operating conditions as for the gel micrography.

2.2.6. Thermal properties

Thermal properties of native and hydroxypropylated potato starches were analyzed using DSC-821^e (Mettler Toledo, Switzerland) equipped with a thermal analysis data station. Starch (3.5 mg, dwb) was weighed into a 40 μl capacity aluminium pan (Mettler, ME-27331) and distilled water was added with the help of Hamilton microsyringe to achieve a starch–water suspension containing 70% water. Pans were hermetically sealed and allowed to stand for 1 h at room temperature before heating in DSC. The DSC analyzer was calibrated using indium and an empty aluminum pan was used as reference. Sample pans were heated at a rate of 10 °C/min from 20 to 100 °C. Onset temperature (T_o); Peak temperature (T_p); Conclusion temperature (T_c); Enthalpy of gelatinization (ΔH_{gel}) and gelatinization temperature range (R) were calculated.

2.2.7. Rheological properties

A small amplitude oscillatory rheological measurement was made for starches from each potato cultivar, with a dynamic rheometer (Carri-Med CSL^2-100, TA Instruments Ltd, Surrey, England) equipped with parallel plate system (4 cm dia.). The gap size was set at 1000 μm. The strain and frequency were set at 0.5% and 1 Hz, respectively, for all determinations. The dynamic rheological properties such as storage modulus (G'), loss modulus (G'') and loss factor (tan δ) were determined for starches from different potato cultivars. Starch suspensions of 15% (w/w) concentration were loaded on the plate of the rheometer and the edges of the sample covered with a thin layer of low-density silicon oil (to minimize evaporation losses). The starch samples were subjected to temperature sweep testing and were heated from 30 °C to 75 °C at a rate of 2 °C/min.

2.2.8. Retrogradation properties

2.2.8.1. Syneresis (%). Starch suspensions (2%, w/v) were heated at 90 °C for 30 min in a temperature controlled water bath with constant stirring at 75 rpm, followed by rapid cooling in an ice water bath to room temperature. The starch sample was stored for 1, 2, 3, 4,and 7th days at 4 °C. Syneresis was measured as % amount of water released after centrifugation at 3000 g for 15 min.

2.2.8.2. Freeze-thaw stability. An aqueous starch slurry (5%, w/v) was heated at a rotation speed of 75 rpm from 30 to 90 °C, at a rate of 1.5 °C/min, held for 20 min. at 90 °C, then cooled at 50 °C at a rate of 1.5 °C/min in Brabender Viscoamylograph (Brabender OHG Duisburg, Germany). The cooked paste was weighed (20 g) accurately into polypropylene centrifuge tubes, and centrifuged at 1000 g for 15 min. The supernatant (free water) was decanted and the remainder was subjected to successive freeze-thaw cycling by placing them at −20 °C in a freezer for 24 h, followed by thawing in a water bath at 30 °C for 4 h and centrifuged. The weight of the supernatant was determined and the extent of syneresis was expressed as the percentage of liquid separated per total weight of sample in the centrifuge tube. In this study, 10 freeze-thaw cycles were performed.

Table 1
Molar substitution (MS) of hydroxypropylated and amylose content of native potato starches

Starch source	MS (Hydroxypropylated)	Amylose content (%) (Native)
Kufri Chandermukhi	0.098^{a}	19.4^{a}
Kufri Sutlej	0.106^{a}	22.7^{b}
Kufri Jyoti	0.122^{c}	26.9^{d}
Kufri Sindhuri	0.118^{b}	24.1^{c}

Values with similar superscripts in a column do not differ significantly ($p < 0.05$).

2.2.9. Statistical Analysis

The data reported in all the tables are an average of triplicate observations. The data were subjected to statistical analysis using Minitab Statistical Software (Minitab Inc., USA).

3. Results and discussion

3.1. Physico-chemical properties

The amylose content of the native starches from all the potato cultivars ranged from 19.38 to 26.97% (Table 1). Amylose content was higher for Kufri Jyoti and Kufri Sindhuri native starches. The size and shape of the potato starch granules determines significantly the amylose content of the starches (Kaur et al., 2002; Singh et al., 2003; Singh & Singh, 2003). The extent of hydroxypropylation as represented by molar substitution varied considerably among the different starches. The higher the amylose content of starch the greater the MS Kufri Jyoti starch showed highest molar substitution (MS 0.122), while Kufri Chandermukhi starch showed the least (Table 1). It has been reported that during hydroxypropylation, the hydroxypropyl groups in the starch chains are primarily introduced in the amorphous regions composed mainly of amylose (Blanshard, 1987; Hood & Mercier, 1978). Kavitha and BeMiller (1998) and Shi and BeMiller (2000) have also confirmed that amylose is modified to a greater extent than amylopectin in hydroxypropylated corn and potato starches and the modification of amylopectin occurs close to the branch points, presumably because amorphous regions are more accessible to the modifying reagent. So, it can be concluded that the variation in the amylose content ultimately led to varied degrees of molar substitution for the starches from different cultivars.

The swelling power, solubility and light transmittance (%) of native and hydroxypropylated starch pastes varied to a greater extent (Table 2, Fig. 1). Kufri Chandermukhi and Kufri Sutlej native starches with lower amylose content showed higher swelling power, while Kufri Sindhuri and Kufri Jyoti showed the least. The behaviour of the starch granule during heating is that water penetrates into the more accessible amorphous region of the starch granule, resulting in hydration and limited swelling (Liu et al., 1999). The differences among the swelling power, solubility (%) and light transmittance (%) of native starch pastes could also be attributed to the variation in the granule size distribution among the starches from different cultivars (Singh et al., 2003). The hydroxypropylated starch pastes showed a considerably higher swelling power, solubility and light transmittance (%) than their native counterpart starches. The higher the MS of the hydroxypropylated starches, the more the swelling power, solubility and transmittance (%) increased. Kufri Jyoti and Kufri Sutlej starches showed highest increment in the swelling power and light transmittance (%) after hydroxypropylation.

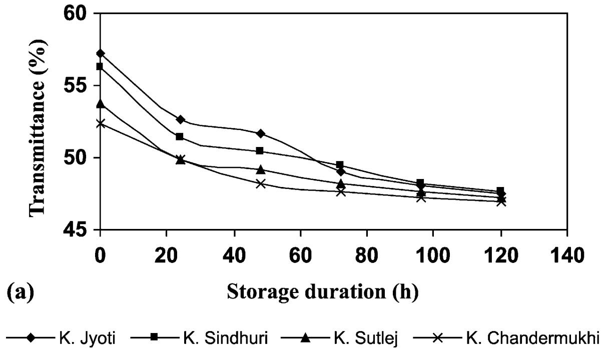
The solubility in DMSO of native and hydroxypropylated starches increased significantly with time (data not shown). Among the native and the modified starches, Kufri Sindhuri and Kufri Jyoti starches were observed to be more soluble in DMSO. Sahai and Jackson (1996) reported that the extent of starch solubilization in methyl sulphoxide varies significantly within a population of different starch granule sizes, presumably reflecting inherent structural hetrogeneity within the granules. The hydroxypropylation treatment resulted in a significant increase in the solubility of the starches. After 12 h, all the hydroxypropylated starches were found to be more than 80% soluble in

Table 2
Swelling power and solubility of native and hydroxypropylated potato starch pastes

Starch source	Native		Hydroxypropylated	
	Swelling power (g/g)	Solubility (%)	Swelling power (g/g)	Solubility (%)
Kufri Chandermukhi	31.4^{c}	3.2^{a}	33.8^{a}	5.1^{a}
Kufri Sutlej	30.2^{b}	5.9^{c}	36.1^{b}	7.4^{c}
Kufri Jyoti	29.3^{a}	5.0^{b}	38.6^{c}	8.2^{d}
Kufri Sindhuri	28.0^{a}	6.1^{c}	33.7^{a}	6.8^{b}
Control*	30.5^{b}	3.6^{a}	–	–

*Kufri Chandermukhi native potato starch was used as control. Values with similar superscripts in column do not differ significantly ($p < 0.05$).

Values with similar superscripts in a column did not differ significantly ($p < 0.05$).



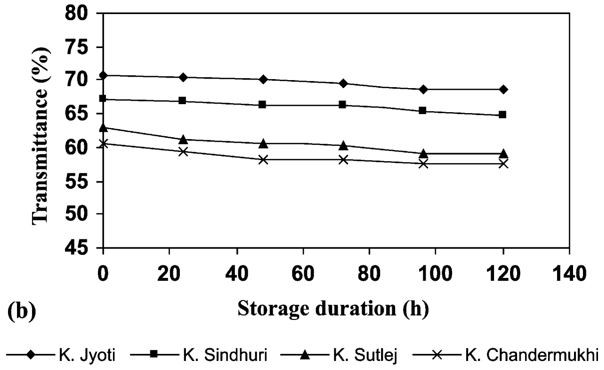


Fig. 1. Effect of storage duration (at 4 °C) on the light transmittance (%) of (a) native, (b) hydroxypropylated starch pastes prepared from different potato starches.

DMSO, while the native starches dissolved up to 75% after 24 h (Figs. 2 and 3).

The observed effects of hydroxypropylation on the physico-chemical properties of starches are consistent with an overall reduction in bonding between the starch chains and a consequent increase in the ease of hydration of the starch granule.

3.2. Morphological properties

Fig. 4 illustrates the size distributions of the native starch granules from different potato cultivars. The potato starch granules separated from all the cultivars showed a wide distribution from 5–60 μm except Kufri Sutlej that had nearly 10% of the granules in the range of 60–85 μm. The starch granules from Kufri Sindhuri and Kufri Jyoti showed the highest proportions of large size granules in their starches (Fig. 4a and b). The native and hydroxypropylated starches from different potato cultivars varied considerably in size and shape (Fig. 5a and b). The control starch granules showed a similar structure as observed for the native starch granules (not shown), suggesting that the reaction conditions did not cause any detectable structural change. The treatment of the starch granules with propylene oxide resulted in an altered granule morphology. The affected granules appeared as folded structures with their outer sides drawn inwards, assuming the shape of a doughnut. Many of the less affected starch granules were observed to develop a depression that later resulted in slight fragmentation, indentation and formation of a deep groove in the central core region, along the longitudinal axis as observed for highly affected granules. These regions were found to be apparently larger in the large size granules compared to the small size granules in all the potato starches, which may be due to the differences in the granule architecture and fragility of the granules. The results are in agreement with those reported by Kim et al. (1992), who suggested that most of the structural changes take place at the relatively less organized central region of the starch granule i.e. where the hydroxypropyl groups are most densely deposited. The ‘pushing apart effect’ exerted by the bulky hydroxypropyl groups, especially in the central region of the granule, might lead to an alteration in the granule morphology upon hydroxypropylation. Huber and BeMiller (2001) also reported that the starch material within the inner regions of potato starch granules was more susceptible to reaction than the outer granule shell. Also, the potato starch granules do not possess channels, therefore, the reagent diffuses inward through the exterior granule surfaces and propylene oxide being less reactive tends to diffuse into the granule matrix prior to reacting (Huber & BeMiller, 2001). The peripheral regions and also the outer membrane of the less

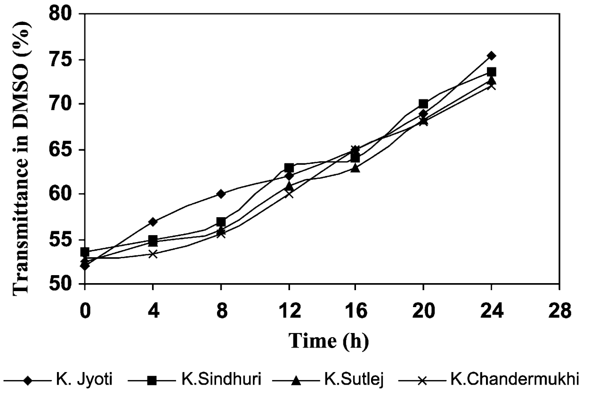


Fig. 2. Changes in the light transmittance (%) (in dimethyl sulphoxide) of native starch suspensions with time.

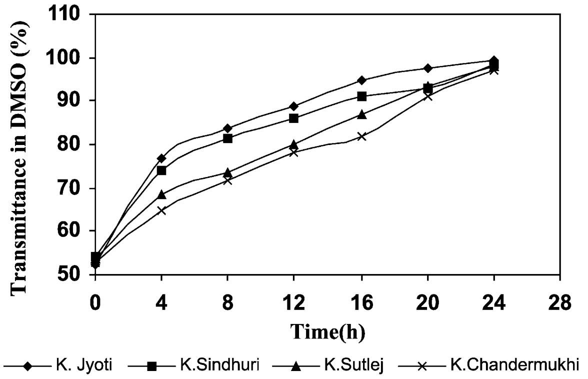


Fig. 3. Changes in the light transmittance (%) (in dimethyl sulphoxide) of hydroxypropylated starch suspensions with time.

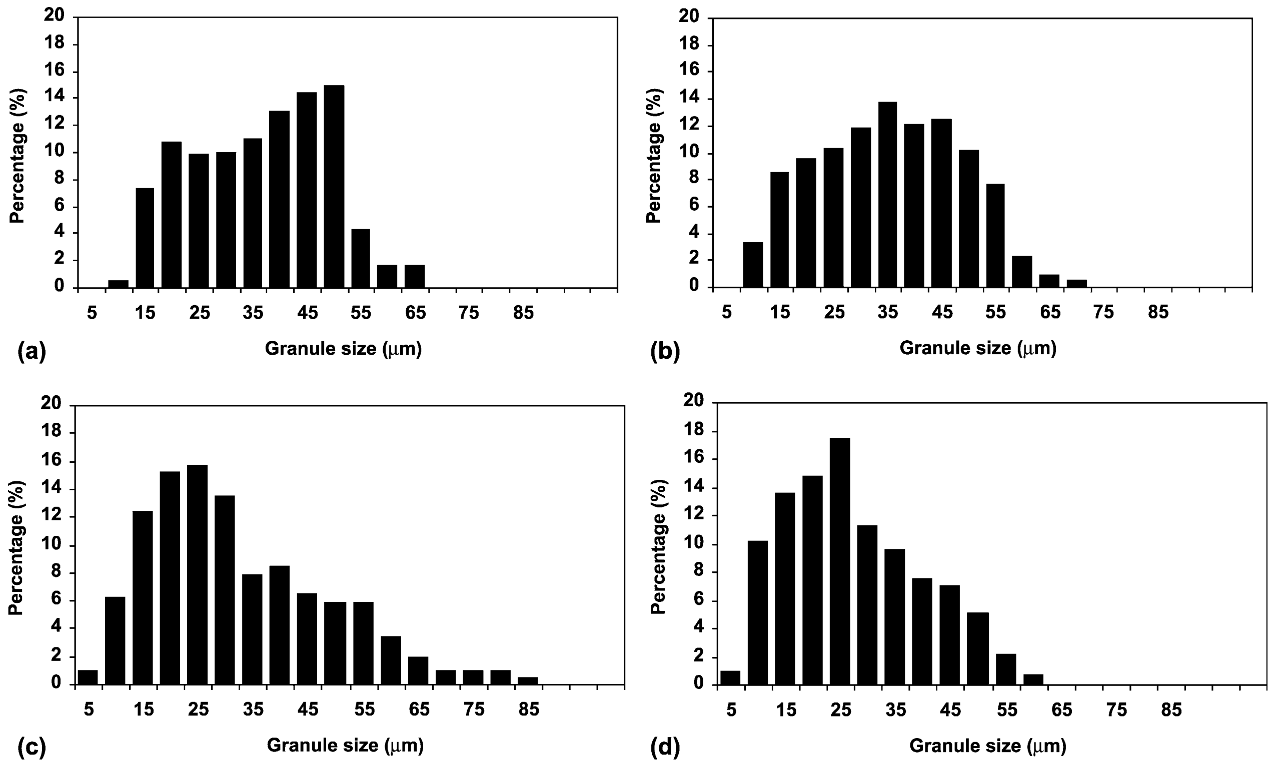


Fig. 4. Granule size distribution of native starches (a) Kufri Jyoti, (b) Kufri Sindhuri, (c) Kufri Sutlej, (d) Kufri Chandermukhi.

affected granules remained unaltered and the changes remained confined to the central core regions as observed for Kufri Chandermukhi and Kufri Sutlej starch granules, whereas the highly affected granules from Kufri Jyoti and Kufri Sindhuri developed blister like appearances, cracks and small protuberances on the surface along with the development of a deep groove in the central core region, which suggests that some reaction started at the granule periphery during the later stages. From these observations, it may be concluded that the peripheral regions and the outer membrane of the granules are the last to be modified. The granule structure was substantially altered, when the reaction was carried out with a higher concentration of propylene oxide (15%) as compared to 10% in other experiments. These highly affected granules appeared as if gelatinized, loosened their boundaries and fused together to form a gelatinized mass (Fig. 5c). This effect was again observed to be more pronounced in the large-size granules as compared to the small-size granules.

Scanning electron micrographs of fresh and stored native and hydroxypropylated potato starch gels are shown in Figs. 6 and 7. The morphology of the granule remnants of both freshly gelatinized native and hydroxypropylated starches differed considerably. The fresh gels showed a uniform network of disrupted starch granule fragments. Compared to the native fresh starch gels, the extent of granule disruption was seen to be considerably higher for hydroxypropylated fresh starch gels. Contrary to the large-size, leaflet like granule remnants of native starch gels, hydroxypropylated fresh starch gels appeared to have more planar structure. The reasons may include loosened structure of starch granules due to weak inter- and intra molecular hydrogen bonding, thereby leading to more granular disruption during gelatinization. As it is clearly revealed by the SEM micrographs, the hydroxypropylated starch gels maintained well this planar structure throughout storage of 10 days, whereas the stored gels from native starches showed extensive aggregation of the granule remnants. Similar observations for hydroxypropylated starch gels have been reported earlier (Perera & Hoover, 1999; Yeh & Yeh, 1993).

Numerous rod-shaped or irregular fuzzy clustered microfibrils appeared in all the hydroxypropylated starch gels (after 30 days of storage at 4 °C) that were easily distinguishable from the other starchy material (Fig. 8). These rod-shaped microfibrils had an average length and width of 15–20 and 3–5 µm, respectively. These fuzzy clustered structures may have formed due to the extensive phase separation that occurred during long-time refrigerated storage. The slow cooling has also been reported to enhance the formation of crystalline non-spherulitic morphologies in the starch gels (Nordmark & Ziegler, 2002).

3.3. Thermal properties

The native starches with high amylose content were observed to gelatinize at a higher temperature but needed

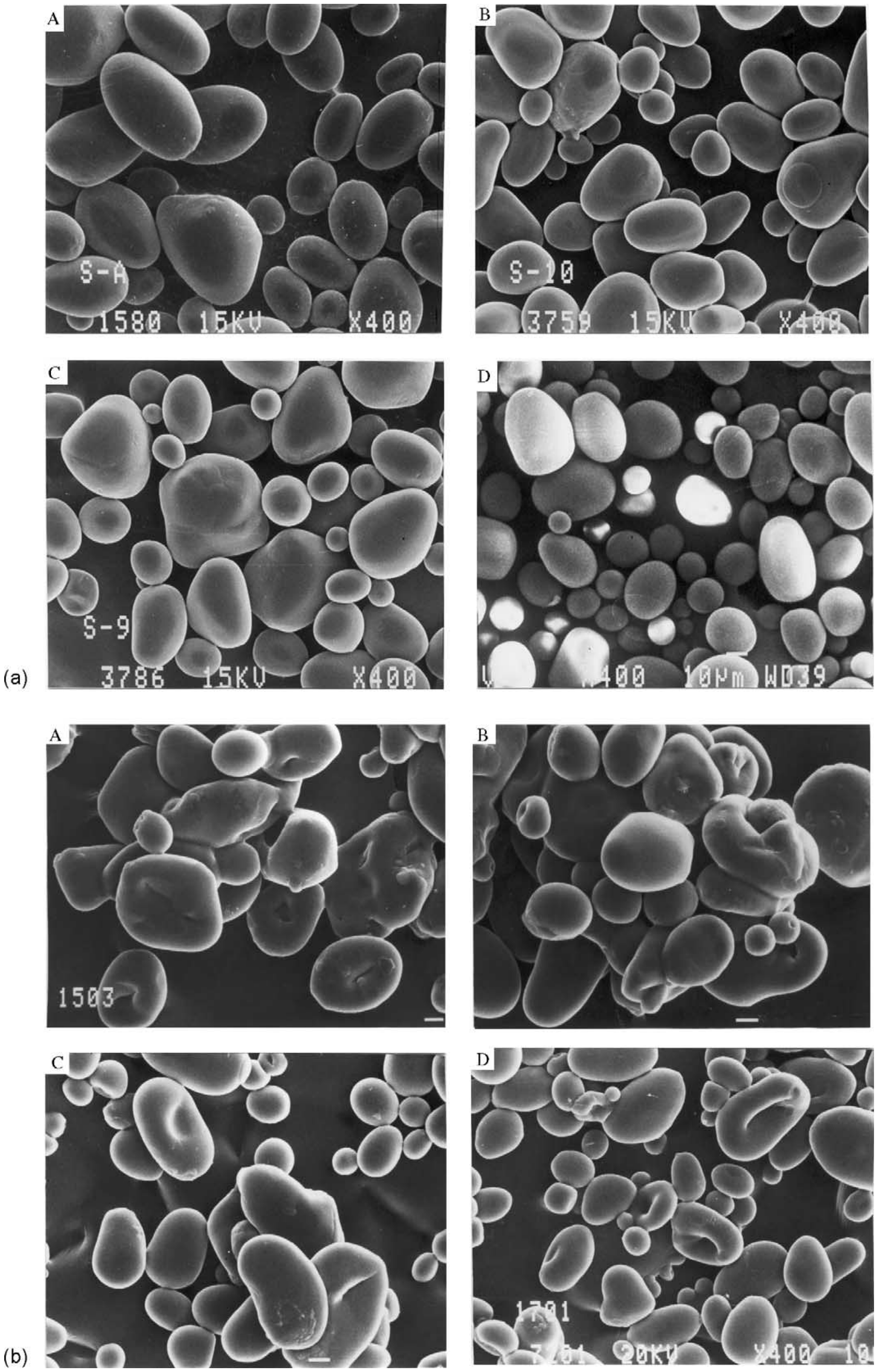


Fig. 5. (a) Scanning electron micrographs (SEM) of native potato starches (A) Kufri Jyoti, (B) Kufri Sindhuri, (C) Kufri Sutlej, (D) Kufri Chandermukhi (× 400, Bar = 10 μm). (b) Scanning electron micrographs (SEM) of hydroxypropylated potato starches (A) Kufri Jyoti, (B) Kufri Sindhuri, (C) Kufri Sutlej, (D) Kufri Chandermukhi (× 400, Bar = 10 μm). (c) Effects of increased concentration of propylene oxide (15%) on the starch granular structure during hydroxypropylation, (A) Starch granules with gelatinized mass like appearance, (B) Highly disintegrated starch granule.

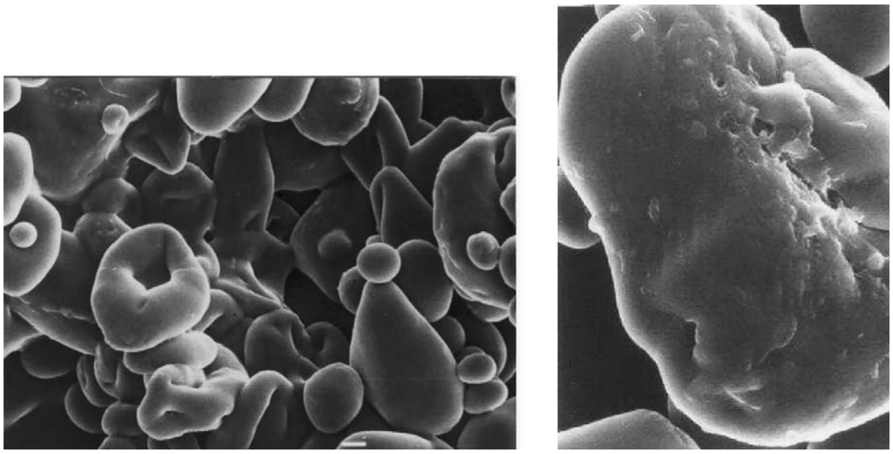


Fig. 5 (*continued*)

a lower enthalpy and vice-versa (Table 3). Among the native potato starches, Kufri Jyoti starch showed highest ΔH_{gel} value (12.9 J/g) and Kufri Chandermukhi starch showed the lowest (11.67 J/g). Kufri Chandermukhi starch had highest T_o (59.2 °C), followed by Kufri Sutlej starch (58.3 °C) while it was lowest for Kufri Jyoti starch (57.2 °C). This correlation indicates that the starch with higher amylose content has more amorphous region and less crystalline, thereby lowering the gelatinization temperatures (Flipse, Keetels, Jacobson, & Visser, 1996; Sasaki, Yasui, &

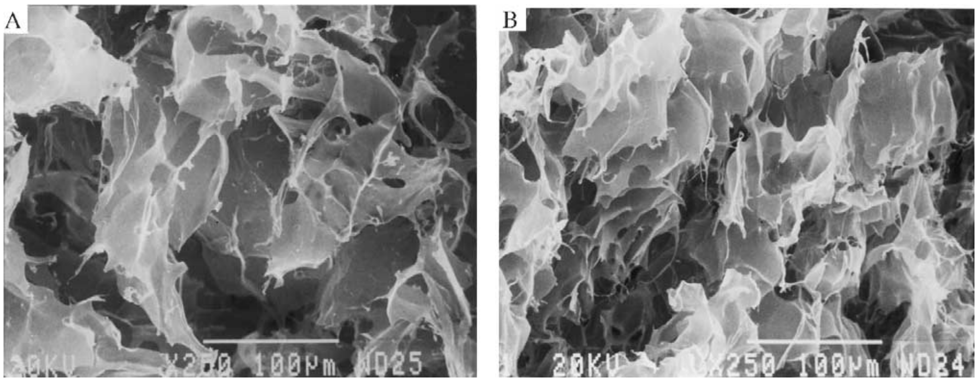


Fig. 6. Scanning electron micrographs (SEM) of fresh pastes of native and hydroxypropylated potato starches (A) fresh native (Kufri Chandermukhi) starch; (B) fresh hydroxypropylated (Kufri Chandermukhi) starch. *Artifacts produced by freeze-drying are being observed and do not necessarily represent structures present in the gel before freeze-drying.

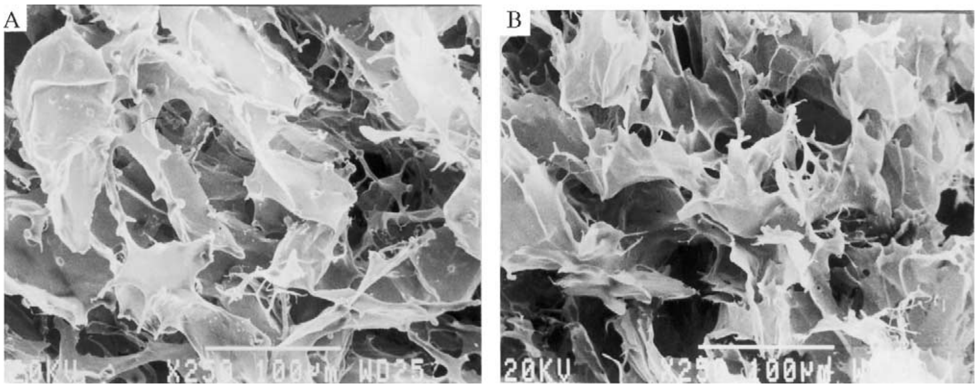


Fig. 7. Scanning electron micrographs (SEM) of stored pastes of native and hydroxypropylated potato starches (A) native (Kufri Chandermukhi) starch; (B) hydroxypropylated (Kufri Chandermukhi) starch. *Artifacts produced by freeze-drying are being observed and do not necessarily represent structures present in the gel before freeze-drying.

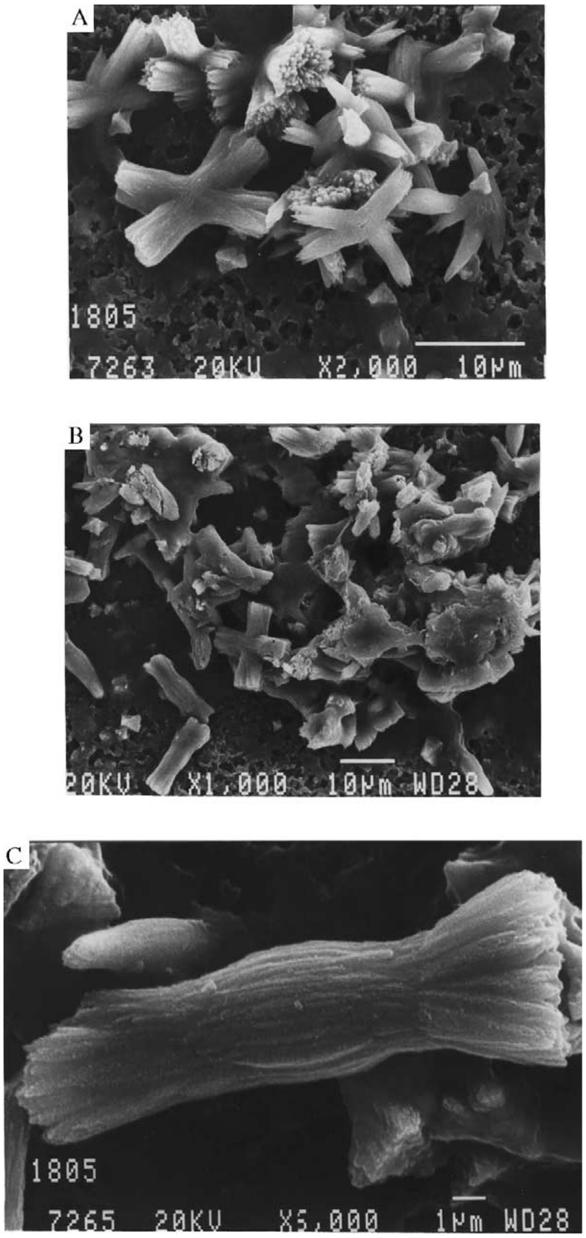


Fig. 8. Formation of rod-shaped microfibrils during long term refrigerated storage of gelatinized starch paste, (A, B) Fuzzy clustered microfibrils, (C) A microfibril showing longitudinal arrangement of crystalline structures.

Matsuki, 2000). ΔH_{gel} provides an overall measure of crystallinity (quality and quantity) and is an indicator of the loss of molecular order within the granule (Cooke & Gidley, 1992). The lower ΔH_{gel} suggests a lower percentage of organized arrangements or a lower stability of the crystals (Chiotelli & Meste, 2002).

A decrease was recorded for the transition temperatures and enthalpy of gelatinization (ΔH_{gel}) of all the starches upon hydroxypropylation (Table 3). The higher the MS of the starch the larger the decrease in thermal parameters. Decreases in the thermal parameters are consistent with fewer crystals being present after modification and with a cooperative melting process enhanced by added swelling (Jenkins & Donald, 1998; Liu et al., 1999; Nurul Islam & Mohd Azemi, 1994; Rutenberg & Solarek, 1984; Seow & Thevamalar, 1993). The gelatinization range (R) of hydroxypropyl potato starches was observed to be slightly broadened than their native counterparts, which may probably be due to the increased inhomogeneity within both the amorphous and crystalline regions of the starch granules (Seow & Thevamalar, 1993). This extent of alteration in the gelatinization range was found to be in accordance with the molar substitution of the hydroxypropylated starches.

3.4. Rheological properties

The rheological parameters G', G'' and tan δ varied considerably among the native and hydroxypropylated potato starches (Fig. 9a and b). Rheological behaviour of native starch pastes was observed to be strongly influenced by the granule size distribution, granule shape and amylose content (Kaur et al., 2002; Morikawa & Nishinari, 2002; Singh et al., 2003; Singh and Singh, 2001, 2003). The control starch showed the rheological properties that differed somewhat from those of the native potato starches (Table 4). These differences may be ascribed to the structural changes of starch granules taking place due to the alkali treatment. The hydroxypropylation of the potato starches resulted in increased peak G', G'' and decreased peak tan δ of the starch pastes (Table 4). This increase in peak G' and G'' may have occurred due to

Table 3
Thermal properties of native and hydroxypropylated potato starches during heating

Starch source	Native					Hydroxypropylated				
	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g)	R	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g)	R
Kufri Chandermukhi	59.2^{c}	63.3^{c}	67.7^{c}	11.7^{a}	8.52^{c}	55.9^{d}	59.2^{c}	64.5^{d}	10.7^{b}	8.60^{b}
Kufri Sutlej	58.3^{b}	62.4^{ab}	66.7^{b}	12.1^{ab}	8.46^{c}	54.3^{c}	58.0^{b}	62.8^{c}	10.9^{b}	8.53^{b}
Kufri Jyoti	57.2^{a}	61.6^{a}	64.4^{a}	12.9^{b}	7.15^{b}	51.8^{a}	56.2^{a}	59.5^{a}	10.9^{b}	7.74^{a}
Kufri Sindhuri	58.1^{b}	61.7^{a}	64.7^{a}	12.5^{b}	6.59^{a}	53.1^{b}	56.8^{a}	60.8^{b}	10.0^{a}	7.65^{a}
Control*	59.3^{c}	63.5^{c}	67.6^{c}	11.7^{a}	8.35^{c}	–	–	–	–	–

T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_{gel}, Enthalpy of gelatinization (dwb, based on starch weight); R, Gelatinization temperature range ($T_c - T_o$). *Kufri Chandermukhi native potato starch was used as control. Values with similar superscripts in column do not differ significantly ($p < 0.05$).

Values with similar superscripts in a column did not differ significantly ($p < 0.05$).

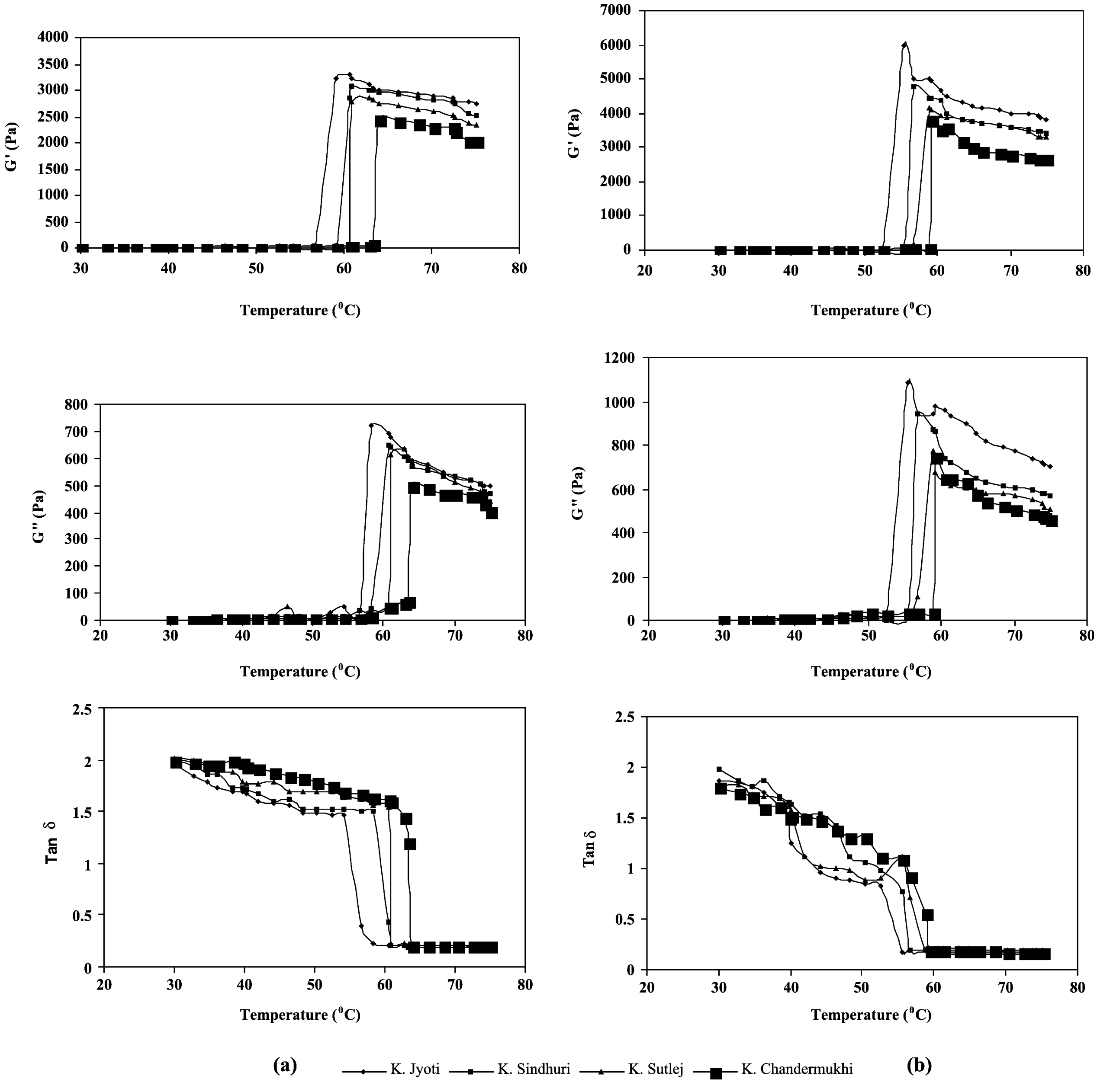


Fig. 9. (a) Storage modulus (G'), loss modulus (G''), and loss factor (tan δ) of native potato starches during heating. (b) Storage modulus (G'), loss modulus (G''), and loss factor (tan δ) of hydroxypropylated potato starches during heating.

Table 4
Rheological properties of native and hydroxypropylated potato starches during heating

Starch source	Native			Hydroxypropylated		
	Peak G' (Pa)	Peak G'' (Pa)	Peak tan δ	Peak G' (Pa)	Peak G'' (Pa)	Peak tan δ
Kufri Chandermukhi	2456^{b}	500^{a}	0.203^{a}	3789^{a}	743^{a}	0.196^{b}
Kufri Sutlej	2854^{b}	635^{b}	0.222^{b}	4152^{b}	776^{a}	0.187^{a}
Kufri Jyoti	3288^{d}	693^{c}	0.211^{ab}	5951^{d}	1083^{c}	0.182^{a}
Kufri Sindhuri	3140^{c}	640^{b}	0.204^{a}	4765^{c}	943^{b}	0.198^{b}
*Control	2518^{a}	524^{a}	0.208^{a}	–	–	–

*Kufri Chandermukhi native potato starch was used as control. Values with similar superscripts in column do not differ significantly ($p < 0.05$).

Values with similar superscripts in a column do not differ significantly ($p < 0.05$).

Table 5
Syneresis (%) of native and hydroxypropylated potato starch pastes

Starch source	Syneresis (%)						
	Native					Hydroxypropylated	
	1st day	2nd day	3rd day	4th day	7th day	6th day	7th day
Kufri Chandermukhi	4.48^{a}	4.87^{a}	5.89^{a}	6.12^{a}	9.43^{a}	2.66	3.12
Kufri Sutlej	6.58^{bc}	6.74^{b}	6.82^{b}	7.21^{b}	10.53^{b}	0.88	1.57
Kufri Jyoti	6.74^{c}	7.8^{c}	8.25^{d}	8.4^{c}	11.14^{c}	–	–
Kufri Sindhuri	6.15^{b}	7.02^{b}	7.12^{c}	7.55^{b}	10.45^{b}	0.54	1.91

Values with similar superscripts in a column do not differ significantly ($p < 0.05$).

the decrease in associative forces within the starch granules due to hydroxypropylation that resulted in an increased penetration of water during heating that ultimately resulted in an increased G'. The increase in viscosity of the potato starches after hydroxypropylation has also been reported earlier (Kim et al., 1992; Liu et al., 1999; Reddy & Seib, 1999; Shi & BeMiller, 2000). The reaction conditions, method and the starch source are the critical factors that govern the rheological behaviour of starches after hydroxypropylation (Reddy & Seib, 1999; Woo & Seib, 1997; Yeh & Yeh, 1993). Kufri Jyoti and Kufri Sindhuri hydroxypropylated starches showed comparatively higher increase in peak G', G'' during heating, than hydroxypropylated starches from other sources.

3.5. Retrogradation properties

The retrogradation tendency of gels prepared from native and hydroxypropylated potato starches was measured by determining syneresis (%) during storage at 4 °C (for 7 days) and at −20 °C (10 freeze-thaw cycles). The native potato starch gels started to retrograde after 24 h, which increased progressively with storage (Table 5). Hydroxypropylation considerably diminished the syneresis in starch gels and no retrogradation in the hydroxypropylated starch gels was observed even after 5 days of storage at 4 °C. Compared to native potato starch gels, which turned into sponge like material after only one freeze-thaw cycle, the gels from modified starches had improved freeze-thaw stability (Fig. 10). Native starches started yielding separated water after two freeze-thaw cycles. Hydroxypropylated starch gels did not yield any separated water even after five freeze-thaw treatments and exhibited better freeze-thaw stability (depending on the MS). Kufri Sindhuri and Kufri Jyoti hydroxypropylated starches were observed to show very little syneresis even after seven freeze-thaw treatments. The retrogradation properties of starches are indirectly influenced by the structural arrangement of starch chains with in the amorphous and crystalline regions of the ungelatinized granule, which in turn, influence the extent of granule breakdown during gelatinization and the interactions that occur between starch chains during gel storage (Perera & Hoover, 1999). The freeze-thaw treatment results implies that the amount of mingled amylose and amylopectin in hydroxypropylated starch gels is the main factor that plays a vital role in influencing the retrogradation properties. When the amylose molecules carrying hydroxypropyl groups are mingled with amylopectin, the hydroxypropyl groups sterically hinder the aggregation of amylopectin, resulting in lower retrogradation (Kim et al., 1993).

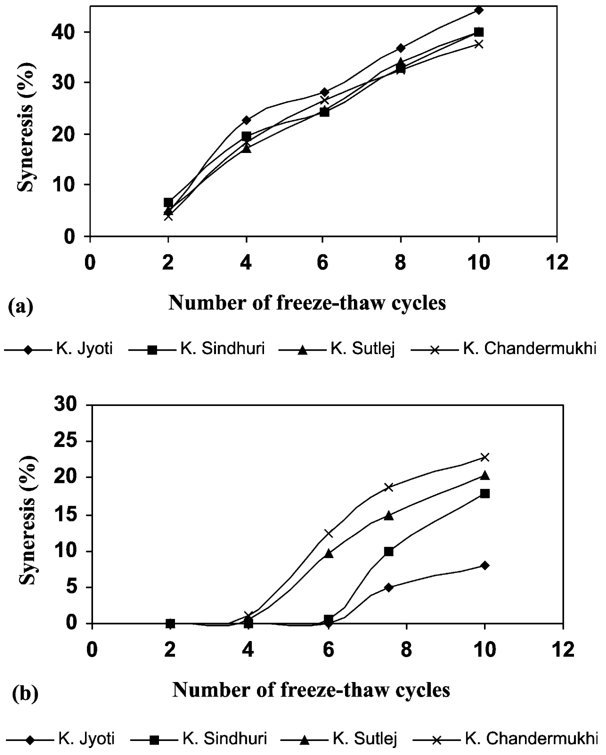


Fig. 10. Syneresis (%) during freeze-thaw cycles for (a) native, (b) hydroxypropylated starch pastes.

4. Conclusion

The changes in the starch properties due to hydroxypropylation have been observed to be associated with the amylose content and granule morphology of native starch. The Larger the granule size of the starting population, higher is the extent of hydroxypropylation on starches. A longer period of refrigerated storage of hydroxypropylated starch gels resulted into the formation of many rod like fuzzy clustered microfibrils. Hydroxypropylated potato starches with desirable properties and molar substitution can be prepared by critically considering native starch from a suitable cultivar.

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