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Effect of granule organisation on the behaviour of starches in the NMMO (N-methyl morpholine N-oxide) solvent system

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ABSTRACT

The response of starches of different botanical origin to heating in 78% N-methyl morpholine N-oxide (NMMO) is compared with their behaviour in water. For all starches studied an exothermic transition is obtained in the NMMO system rather than the endothermic transition in water. In NMMO the transition temperatures are lower for A-type starches (wheat, rice and tapioca) than the C-type starches (sago and pea) and also potato which has a B-type polymorph. Observations using a hot stage microscope show two different types of initial behaviour in NMMO; erosion of the granule from the surface or disruption into fragments. In both cases the final outcome is dissolution but for the most resistant C-type starches (pea and sago) some intact granules could be seen following heating at 95 °C in 78% NMMO and subsequent precipitation in ethanol. The results are discussed in terms of what is known from previous structural studies on these six starches and the behaviour of maize starch in NMMO and ionic liquids. The work is relevant to the co-dissolution of starch and cellulose to form novel polysaccharide based materials.

1. Introduction

Native starches from different botanical origins have their own unique properties. Physical and chemical characteristics such as granule size, amylose and amylopectin contents, branch chain lengths, phosphate group and lipid content vary substantially depending on botanical origin and genetic background (Swinkels, 1985). The behaviour of starches when heated in water is central to many applications particularly in the food industry. Although less directly related to applications there have been extensive studies on the behaviour of starch in other solvent systems. These include dimethyl sulfoxide (DMSO), concentrated salt solutions and sugar solutions (Jane, 1993; Perry & Donald, 2000). Recently several studies have been reported on starches in ionic liquids (Liu & Budtova, 2012; Mateyawa et al., 2013). These solvents have received considerable interest partly because of their ability to dissolve cellulose. Thus it is possible to prepare mixed products from solutions of starch and cellulose in NMMO.

The solvent NMMO is used industrially to prepare cellulose fibres and films through dissolution and subsequent regeneration of cellulose in water. Although it was reported that NMMO could dissolve starch more than thirty years ago there has been relatively little subsequent published work on starch in NMMO (Chanzy, Chumpitazi, & Peguy, 1982). There are two reasons why these mixtures are of interest. Firstly dissolution behaviour can provide further insight into the structure of starch which is complementary to measurements of order by spectroscopic and microscopic methods. Secondly it will be possible to co-dissolve starch and cellulose in NMMO and in ionic liquids and produce shaped products containing both polysaccharides on regeneration in water (Liu & Budtova, 2012). To develop and optimise such process, it is important to increase our understanding of the behaviour of starch in NMMO.

The behaviour of maize starches in NMMO has been studied previously (Koganti, Mitchell, Ibbett, & Foster, 2011). In particular the structural changes occurring on heating in different concentrations of NMMO in water have been examined. For normal maize starch when the NMMO concentration was increased to 70%, the endothermic response observed when starch was heated in water changed to an exotherm. This exotherm was interpreted in terms of the accessibility of the starch crystalline and amorphous structures within the granule to the solvent and allowing further dissolution. Dynamic rheology results revealed the dominant viscous behaviour ($G'' > G'$) of starch–NMMO solutions representative of a polymer solution rather than a particle suspension. Therefore, it was concluded that NMMO, at an appropriate concentration can dissolve maize starch. This approach has now been applied to starches from different botanical sources. Of particular interest is to determine

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whether there is a relationship between the polymorphic form of the starch granule and this behaviour. For this reason three A-type starches (rice, tapioca and wheat), a B-type starch (potato) and two C-type starches (pea and sago) were selected.

2. Materials and methods

2.1. Materials

Potato (Avebe FOOD, The Netherlands), tapioca (Cargill, The Netherlands), wheat (Witwood Food Products, UK), rice (Bene remy, Belgium), pea (Roquette) and sago (Thailand) starches used in this study were obtained from suppliers and used without any further treatment.

2.2. Methods

2.2.1. Preparation of samples

The 78% NMMO mixture has a melting point slightly higher than that of a 2.5 hydrate NMMO (39 °C), so it was heated to bring it to the liquid state before use. Starch powder was then dispersed in the liquid and thermal and rheological measurements initiated before any signs of NMMO recrystallisation (significant for the 78% NMMO system only) were observed. 5% (w/w) starch samples were used for all measurements except for the DSC where the concentration was 10%. All samples were prepared immediately prior to measurements. Higher dissolution temperatures for longer times particularly in the presence of metallic ions can lead to exothermic decomposition of NMMO and in extreme cases may cause a fire hazard. Propyl gallate (0.01%) is used as an anti-oxidant to decrease the radical degradation of NMMO and starch.

2.2.2. Precipitation of NMMO–starch samples

All dissolved starches in NMMO obtained at the end of the RVA process, at 50 °C, were precipitated into ethanol at room temperature in the presence of shear. The starch samples were separated from the NMMO–ethanol solution by centrifugation at 2000 rpm for 20 min and underwent repeated washings (3–4 times) in ethanol to remove residual NMMO present in the sample. The resulting precipitated starches were dried in the vacuum oven at 35 °C overnight. The same process was also performed for water gelatinised starches. All samples were stored over P_2O_5 for further measurements.

2.2.3. Differential scanning calorimetry (DSC)

Thermal analysis was carried out using a differential scanning calorimeter (model 823e Mettler Toledo, UK Ltd.). Appropriate amounts of starches and the solvents (78% NMMO and distilled water) were weighed in stainless steel pans according to their weight concentrations. The samples were heated from 20 °C to 140 °C at a rate of 5 °C/min followed by cooling at a rate of 20 °C and reheating at the same heating rate. An empty stainless steel pan was used as the reference. The onset, peak and conclusion temperatures associated with gelatinisation/dissolution were obtained from the thermograms.

2.2.4. Rapid viscosity analysis

Pasting properties of the starches in deionised water and 78% of NMMO were measured using a Rapid Visco Analyser (RVA, Newport Scientific). The following temperature profile was used: the suspension was held at 50 °C for 10 min, ramped to 95 °C at 5 °C/min, held at 95 °C for 15 min, cool to 50 °C at 5 °C/min and held at 50 °C for 10 min. The suspension was continuously stirred at 160 rpm throughout the profile. The onset, peak viscosities, and the final viscosities were recorded. All samples were run in triplicate.

2.2.5. Light microscopy

Polarised light microscopy (Leitz) equipped with a hot stage was used to visually distinguish and compare the structural changes of starch granules during gelatinisation and dissolution both in water and 78% of NMMO. 5% (w/w) starch was dispersed in the solvent at room temperature and a small drop of sample was placed between two cover slips to form a layer. The edges of the cover slips were sealed in order to avoid evaporation of the water from the sample. Temperature was controlled from 40 °C to 100 °C at a heating rate of 5 °C/min. A series of micrographs were taken every 2 °C rise in temperature at 400× magnification over the temperature range of granule swelling, gelatinisation and dissolution, using Linksys data capture software.

2.2.6. X-ray diffraction

The crystallinity of starch powders was measured using a X-ray diffractometer (Bruker AXS D5005) equipped with a copper tube operating at 40 kV and 50 mA produced Cu Kα radiation of 0.154 nm wave length. Data was recorded over a 2θ angular range of 4–45° with an angular interval of 0.05°, and a rotation speed of 60 rpm. The crystallinity of the measured samples was calculated by using the method described by Hermans and Weidinger (1948) with the following equation.

$$\%\,\text{Crystallinity} = \frac{\text{crystalline scattering area}}{\text{total scattering area}} \times 100$$

2.2.7. Scanning electron microscopy (SEM)

Starch samples were dried in the vacuum oven at 35 °C overnight and stored over P_2O_5 to ensure the sample was dry before performing SEM. Samples were mounted on aluminium stubs and coated with gold to about 25 nm thickness using sputter coater (Leica EM SCD005 Sputter Coater–Ion). Images of samples were captured using a JEOL 6060L variable pressure scanning electron microscope (Jeol, UK Ltd.) and an automatic software system. Images at several magnifications were recorded. Magnification is shown by a calibrated bar on the figures.

2.2.8. Fourier transformed infrared spectroscopy (FTIR)

The FTIR spectra of starch powders were recorded using a Bruker Tensor 27 spectrometer with a DTGS detector and equipped with a 45° incidence angle ATR single reflectance cell with a diamond crystal (golden gate cell, Graseby-Space Ltd., Orpington, UK). For each measurement, the spectrum obtained was the average of 128 scans at a resolution of 4 cm^{-1} against an empty background. Spectra were base line corrected in the region of 1200–800 cm^{-1} and deconvolution was carried out using the OPUS 3.0 software (Bruker, UK). IR absorbance values 1047, 1022, 995 cm^{-1} were extracted from the spectra after data processing.

3. Results and discussion

3.1. The effect of starch granule structure: solubility of native starches from different botanical sources in NMMO

The sizes and shapes of granules for the starches used in this study are summarised in Table 1. Potato starch has the largest while rice starch has the smallest granules among the starches studied here. The starch granules are oval and irregular in shape in potato, tapioca and sago starches and much larger in size than in the cereal starches, wheat and rice. Wheat starch granules have a bimodal granule size distribution (Baum & Bailey, 1987) consisting of large disc or lenticular shaped granules (A-type) and small spherical granules (B-type), while for rice, granules are angular shaped. Pea starch has irregularly shaped granules. Amylose content of starches was determined using the Megazyme method. Pea starch had the

Table 1
Morphological parameters and amylose contents of the native starches studied (Baum & Bailey, 1987; Hoover, 2001; Jane, Kasemsuwan, Leas, Zobel, & Robyt, 1994).

Starch	Type	Size, diameter (μm)	Morphology	Amylose (%)
Potato	Tuber	5–110	Oval/spherical irregular	20.5 ± 1.1
Wheat	Cereal	1–45	Disc like/round lenticular	24.3 ± 1.7
Rice	Cereal	3–8	Angular/polygonal	18.4 ± 0.7
Tapioca	Root	4–40	Oval/round truncated	20.9 ± 0.9
Pea	Seed	2–40	Oval spherical/elliptical	29.2 ± 2.6
Sago	Pith	15–65	Oval truncated	26.3 ± 3.7

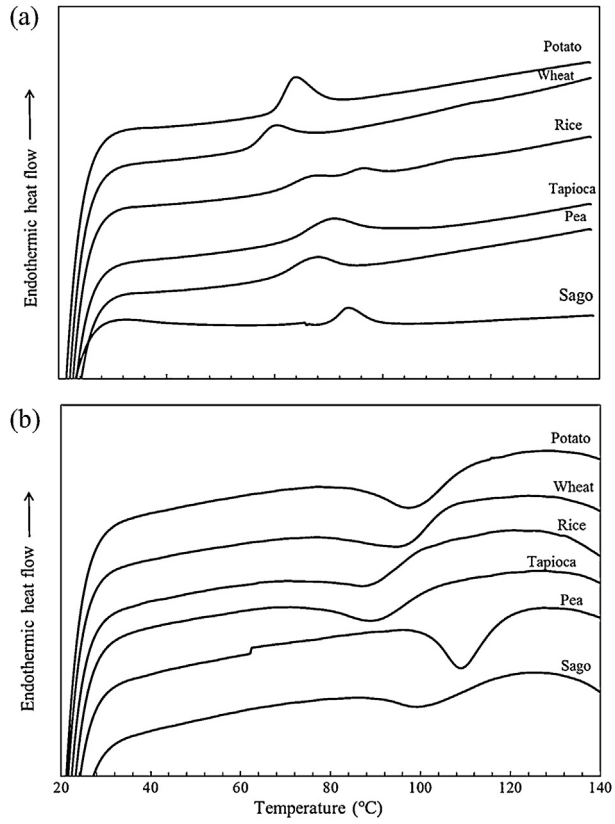

Fig. 1. DSC thermograms show the effect of starches from different botanical sources in (a) water and (b) 78% NMMO as a function of temperature.

highest content of amylose followed by Sago, with rice having the lowest.

Thermograms of starches from different botanical sources in water and in 78% NMMO are presented in Fig. 1 and corresponding transition temperatures and enthalpy values are summarised in Table 2. Dispersions of different starches (10%) in water show gelatinisation endotherms as expected, which is attributed to the disruption of crystalline order in the starch granules (Biliaderis, Maurice, & Vose, 1980; Donovan, 1979). The transition temperatures and gelatinisation endotherm enthalpies are related to the characteristics of the starch granule, such as degree of crystallinity (Krueger, Knutson, Inglett, & Walker, 1987). It has been suggested that the gelatinisation enthalpy (ΔH) is a measure of the overall crystallinity of the amylopectin, i.e. the quality and quantity of starch crystals (Tester & Morrison, 1990). However Cooke and Gidley reported that enthalpy values of DSC primarily reflect the melting of double helices rather than loss of crystalline order over different distance scales (Cooke & Gidley, 1992). Among all the starches, sago starch had a higher onset of gelatinisation at 70 °C, which is in agreement with previously published data (Ahmad et al., 1999). It has been reported that a high transition temperature is a consequence of a higher degree of crystallinity, which provides structural stability and makes the granule more resistant towards gelatinisation (Singh, Singh, Kaur, Singh Sodhi, & Singh Gill, 2003). Endothermic enthalpy values are highest in potato followed by tapioca starch, whereas other starches, exhibited relatively lower enthalpy values. Particularly in cereal starches, this might be due to the presence of free lipids which form helical inclusion complexes with the amylose molecules during heating. This complex formation is an exothermic process which could reduce the enthalpy value of endothermic gelatinisation (Eliasson, 1986). Potato and tapioca starches, which do not contain any native lipids, exhibited higher enthalpies than cereal starches.

Table 2
DSC parameters of starches from different botanical sources in water and 78% NMMO.

Sample	T_o (°C)	T_p (°C)	T_e (°C)	ΔH (J/g)
Potato in water	58	64	71	16.3
Wheat in water	57	59	70	10
Rice in water	64	70	78	10
Tapioca in water	62	70	79	16.2
Pea in water	58	64	76	9
Sago in water	70	73	78	7
Potato in 78% NMMO	85	98	112	−17
Wheat in 78% NMMO	82	96	104	−15
Rice in 78% NMMO	78	88	98	−11
Tapioca in 78% NMMO	78	90	102	−16
Pea in 78% NMMO	98	110	118	−14
Sago in 78% NMMO	90	99	113	−12

All starches exhibited exotherms in 78% NMMO, which has been interpreted as a sign of strong polymer–solvent interaction and further dissolution of starch granules as explained in Koganti et al. (2011). It can be seen that all starches had higher onset temperatures in 78% NMMO than in water. Comparatively cereal starches had early transitions in 78% NMMO compared to the other starches. Potato, pea and sago starches exhibited higher peak and conclusion temperatures which may be attributed to a greater resistance to dissolution in 78% NMMO. An interesting observation was that starches belonging to B and C polymorphs, except sago had a lower onset of gelatinisation in water and exhibited higher onset temperatures in 78% NMMO, corresponding to their resistance towards the solvent. The higher accessibility of A-type cereal starches to solvent could be explained by the porous structure of the granule (Leach & Schoch, 1961) or structural heterogeneity within the granule with resistant regions separated by more open and accessible areas (Leach & Schoch, 1962). The dissolution pattern of starches in NMMO shows some relationship to the susceptibility to enzyme hydrolysis of starches of different polymorphic types. It has been shown that the B- and some C-type starch granules are resistant to enzyme hydrolysis, whereas the A-type starch granules are easily hydrolysed (Jane et al., 2003).

Fig. 2a and b shows the RVA pasting properties of native starches in both water and 78% NMMO respectively. The RVA onset and viscosity parameters are summarised in Table 3. RVA pasting temperatures of all starches in water are higher than the DSC onset gelatinisation temperatures and considerable differences were not found for cereal starches. This may be associated with the limited swelling due to the small size and rigid structure of cereal starch

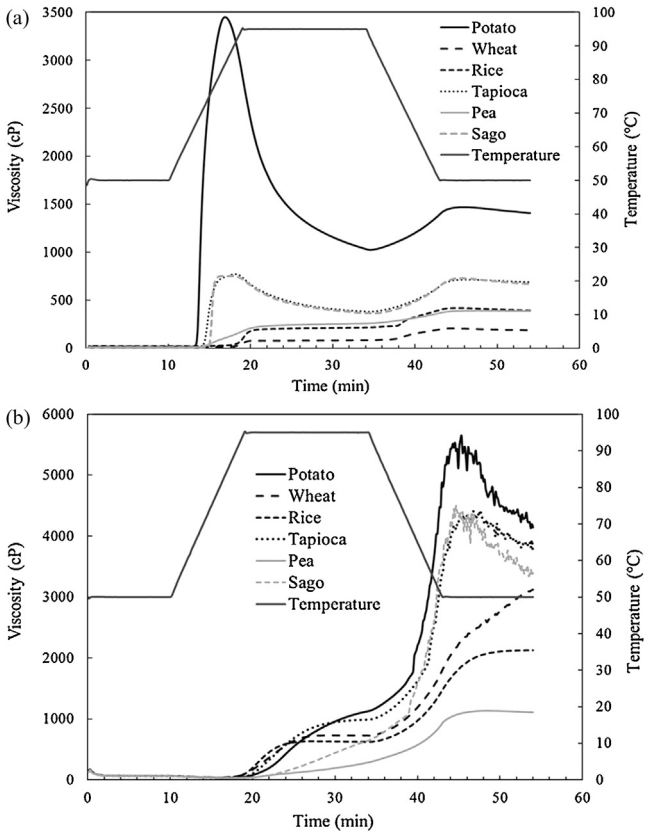

Fig. 2. RVA pasting profiles of 5% native starches of different botanical origin in (a) water and (b) 78% NMMO.

granules. As shown in Fig. 2a, potato starch had lower onset and highest peak and final viscosities while wheat shows the lowest viscosities. The higher swelling and viscosity of the potato may be due to the large size of granules, positive charged groups present and low content of amylose-lipid complexes. Tester and Morrison (1990) reported that amylopectin contributes to the swelling of starch granules whereas amylose and lipids inhibit the swelling (Tester & Morrison, 1990). Another explanation for the higher swelling of potato starch is the presence of mono phosphate esters covalently bound primarily to the amylopectin (Jane, Kasemsuwan, Chen, & Juliano, 1996; Swinkels, 1985). According to the literature, wheat granules swell up to 30–40 times to their original volume, whereas potato granules swell 100 times (Singh & Kaur, 2004). After potato, the highest peak and final viscosities were shown by tapioca and sago. It was suggested that, increasing amylose contents along with higher levels of lipids and phospholipids considerably increase starch pasting temperature and decreases the peak and final viscosities. Pea starch has higher amylose content than wheat and rice but exhibited lower onset and higher peak and final viscosities, which may be due to lack of lipids. Cereal starches exhibited higher onset and lower peak, final viscosities, which may be attributed to their higher levels of lipids and phospholipids. However, the influence of amylose content on the gelatinisation temperature is not fully understood, as many contradictory results are reported in the literature (Fredriksson, Silverio, Andersson, Eliasson, & Aman, 1998; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003).

Table 3
Pasting properties of starches from different botanical sources in water and 78% NMMO.

Sample	Onset temperature (°C)	Peak viscosity (cP)	Final viscosity (cP)
Potato in water	64	3450	1408
Wheat in water	82	78	188
Rice in water	75.3	196	394
Tapioca in water	65.2	773	690
Pea in water	65	227	387
Sago in water	69	753	669
Potato in 78% NMMO	86.7	1120	4143
Wheat in 78% NMMO	81	729	3121
Rice in 78% NMMO	77.56	632	2128
Tapioca in 78% NMMO	84	972	3714
Pea in 78% NMMO	95	–	1109
Sago in 78% NMMO	93.5	–	3394

For all starches final viscosities are much higher in 78% NMMO than in water. Unlike water, starches in 78% NMMO do not have a viscosity profile with a sharp gelatinisation peak, which may be due to restricted swelling of granules followed by immediate dissolution. The DSC also shows that the endotherm appears at a higher temperature than 95 °C which is the highest temperature in the RVA. When compared with the calorimetric data, the pasting onset temperatures were higher for starches in 78% NMMO as observed for starch–water systems; however the differences between these two temperatures were much lower in NMMO than in water. Interestingly, pea and sago starches had considerably higher onset of pasting temperatures in 78% NMMO, which was strongly correlated with the calorimetric data. Since the maximum temperature used in the RVA profile is 95 °C, but the DSC completion temperatures of starches in NMMO exceeded 95 °C and are as high as 118 °C, this indicates that starches need higher temperatures to dissolve completely. To understand this more clearly, structural changes of starches upon heating at the same heating rate as used for the DSC and RVA experiments, were monitored using hot stage microscopy.

Hot stage microscopy using polarised light was performed for all starches in NMMO but the data is shown for only potato and pea starches. Micrographs presented in Fig. 3, clearly illustrate the differences between the gelatinisation and dissolution behaviour of potato starch in water and NMMO, respectively. During heating in water, starch granules start to swell and lose their characteristic 'Maltese Cross' or birefringence. This process was followed by break up of granules and pasting. In agreement with both the DSC and RVA, some granules started to break up at 58 °C and a few granules remained intact up to 62 °C. The break up temperature varied from granule to granule. Granular disruption and pasting took place at 70 °C. Unlike in water, neither of the starches have shown significant swelling in 78% NMMO. Previously similar behaviour was observed for waxy maize starch in ionic liquid, whereas waxy mazie starch dissolved in 1-ethyl-3-menthylimidazolium acetate (EMIMAC) without swelling (Liu & Budtova, 2013). Potato starch granules showed completely different behaviour in 78% NMMO upon heating. The starch granules remained visibly intact even at 85 °C, above which the granules started to have erosion from outside of the granule without considerable swelling. The dissolution process seemed to start on the periphery of the granule. A progressive detachment/dissolution of external layers was observed. Granules remained intact and optically birefringent until they dissolved completely. This is in contrast to the previously reported maize starch dissolution in NMMO, where the dissolution seemed to start both at the hilum and the periphery as the granules become fragmented into 3–4 small pieces. This was followed by complete dissolution. For maize the breaking of the granule provides a larger surface area for solvent access to the starch. For potato, fragmentation of the granule is not observed. Gradually the granule decreased in size in NMMO undergoing on an erosion like process in NMMO. Similar behaviour has been reported for potato starch in 90% DMSO (Leach & Schoch, 1962), but the dissolution process was much slower compared to NMMO which takes place within minute. It seems potato starch has its own distinctive solvation process. One other difference was that maize granules completely

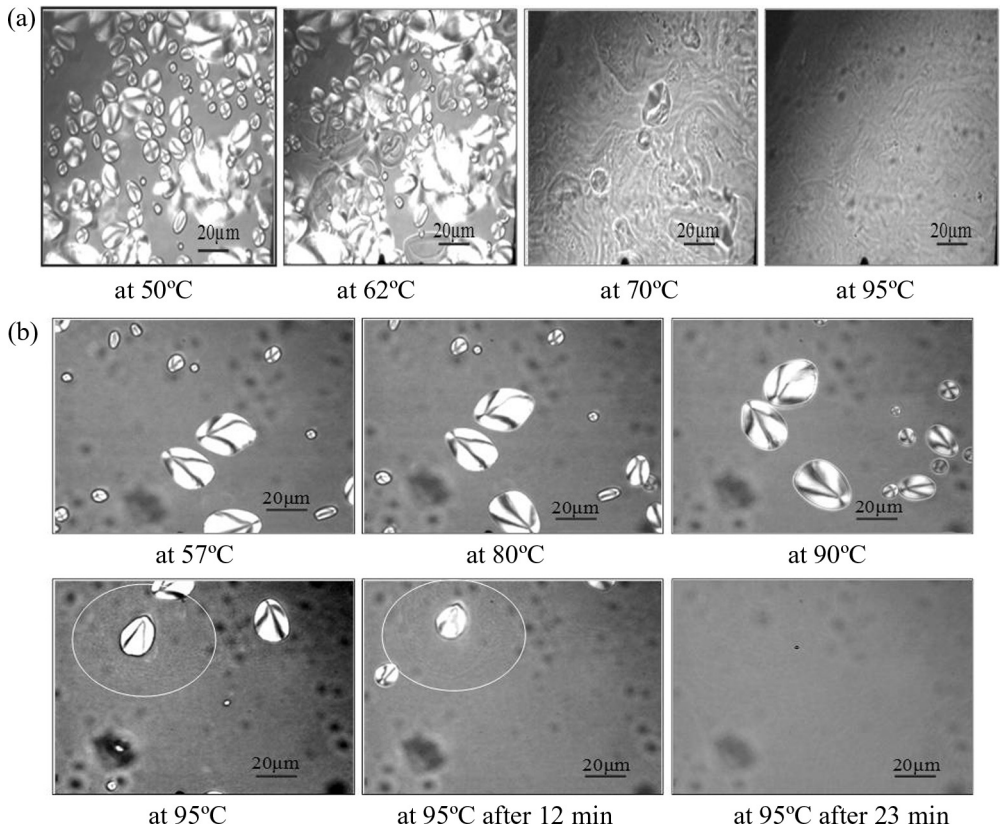

Fig. 3. Gelatinisation and dissolution patterns of native potato starch in (a) water and (b) 78% NMMO observed using a polarised light microscope equipped with a hot stage.

dissolved when the temperature reached 95 °C, in the hot stage microscope. However, in the case of potato undissolved granules were found even after holding for 15 min at 95 °C. This observation supports the data obtained from calorimetry, as the conclusion temperature of potato in 78% NMMO was 112 °C. This suggests that compared to maize, potato starch granules are more resistant to dissolution in NMMO. When heating is continued in the hot stage, after 20 min at 95 °C, nearly all the granules disappear. This again indicated the process is kinetically controlled, as found for maize starch and reported in Koganti et al. (2011).

In agreement with the thermograms, pea starch granules in NMMO remained undissolved even at 100 °C as shown in Fig. 4. Granules exhibit erosion and slight fragmentation in 78% NMMO during heating in the hot stage microscope. Sago starch showed the same type of dissolution process as pea. When rice, wheat and tapioca starches were heated at 95 °C, they gradually dissolved completely after 20 min unlike pea and sago. All starch–NMMO solutions obtained at the end of RVA were centrifuged. Sediments were found for both pea and sago. Partially dissolved and very few intact granules were observed in the sedimented sample when viewed in the microscope. Other starch solutions were clear as it appears the shear applied in the RVA helps in the dissolution process. It has been suggested that applying shear could lower the activation energy for thermal bond rupture (Bueche, 1960).

When the microscopy and DSC data are considered together, it can be seen that starches with high amylose contents are more resistant to solvent ingress, opposing dissolution. Leach and Schoch (1962) made similar observations for native starches during enzyme treatment and dissolution in 90% DMSO, and suggested that fragmentation of maize starch during dissolution may be due to some sort of structural heterogeneity within the granule with resistant regions separated by more accessible areas. Whereas, for the starches which are resistant to solvent, it was suggested that they had a more homogeneous granule structure with respect to distribution of internal bonding forces (Leach & Schoch, 1962). Stevenson, Biswas, Jane, and Inglett (2007), studied the behaviour of corn, rice, wheat and potato starches in ionic liquids and reported that the treatment significantly reduced the amylopectin molecular weight of all cereal starches compared to potato starch, where much lower degradation was observed (Stevenson et al., 2007). They suggested this may be due to phosphoesters present in the potato starch, which are negatively charged and can covalently link to the imadazolium rings. Another explanation is that the B-type structure has a lower packing density of crystalline amylopectin double helices, where as cereal starches contain densely packed A-type helices, so the solvent can diffuses into and be accommodated in the potato starch structure without severe degradation compared to cereal starches.

3.2. Precipitation of starch–78% NMMO solutions and characterisation

As shown in Fig. 5, all starches lost their granular structure during dissolution process and showed agglomerated structures with rough surfaces when viewed under the SEM after precipitation. In agreement with DSC and microscopy, pea and sago still had few granules which were not completely dissolved in 78% NMMO. According to the X-ray diffractograms (data not shown), the starches used in this study characterised into A, B and C polymorph types as displayed in Table 4. It has been stated that the crystal type of starch depends on packing of the helices in the crystal (Ratnayake & Jackson, 2009; Zobel, 1988b). Hizukuri studied 20 starches from different botanical origins and found that there was a close association between average chain length of amylopectin and the crystal type of starch. A-type starches have shorter chain

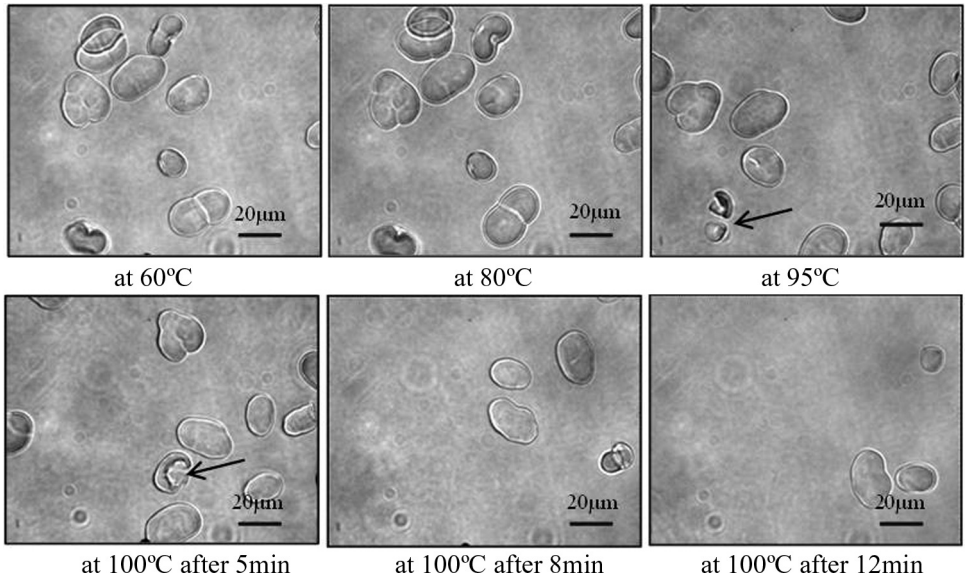

Fig. 4. Micrographs showing structural changes observed for pea starch in 78% NMMO using a light microscope equipped with a hot stage. Arrows in the micrographs indicate the fragmentation of the granules.

lengths compared to B-type, while C-type has intermediate length chains (Hizukuri, 1985).

Cereal starches, rice and wheat and tapioca exhibited an A-type pattern with major diffraction peaks at 15, 17, 18 and 23° 2θ, where as potato starch showed a B-type pattern with major peaks at 17, 22 and 24 2θ (Cheetham & Tao, 1998; Zobel, 1988a). Tapioca, pea and sago starches showed C-type which is a mixture of both A- and B-type polymorphs with intermediate behaviour. As illustrated in Table 4, the crystallinity of the sago starch is higher than other starches, which could be associated with its higher amylopectin content, which in turn is responsible for the crystalline structure in starch. Dissolution caused loss of order in all starches since all precipitated starches lost their characteristic diffraction peaks and showed an amorphous structure. Precipitated pea and sago starches exhibited slightly sharp diffractograms compared to other starches, which could be associated with the partially disrupted starch granules during dissolution. Precipitated sago starch had highest crystallinity while potato had the lowest crystallinity. According to DSC, RVA and microscopy, it appears that A-type cereal starches are more susceptible to and B- and C-type starches are more resistant to 78% NMMO. Tapioca starch also has an A-type polymorph and shows similar low melting temperatures to the cereal starches however unlike the two cereal starches it develops viscosity more slowly as can be seen form the time dependence of the viscosity and the lack of reversibility on the preheat. A possible reason for this slightly anomalous behaviour could be due to differences in the extent of order on the granule's surface. Some support for this is given by the ratio of the intensity of the IR bands at 1047–1022 cm^{-1} shown in Table 5 for the native starches. It has previously been proposed that this ratio increases with crystallinity portion present in the sample. In addition to this, factors like different sizes of the granules and non-carbohydrate component present on the starch granule may influence the dissolution kinetics and may cause restricted dissolution which lead to granule ghosts in the solution.

The FTIR spectra of starches have shown three major distinct bands at 1047, 1022 and 995 cm^{-1} in the region of 960–1060 cm^{-1} (data not shown). The bands at 1047 and 1022 cm^{-1} are related to the ordered and amorphous structures of the starch respectively, whereas the band at 995 cm^{-1} was associated with water content (Sevenou, Hill, Farhat, & Mitchell, 2002; Vansoest, Dewit, Tournois, & Vliegenthart, 1994). Both native pea and sago starches had a relatively less pronounced band at 1022 cm^{-1} compared to the other starches. The band at 1047 cm^{-1} is very prominent in tapioca, followed by pea and sago, which could be attributed to the more ordered structure on the surface of the starch granule. For all native starches the peaks were slightly shifted from 1022 cm^{-1}. The ratios of the absorbance peaks 1047/1022 cm^{-1} were calculated and presented in Table 5. In agreement with X-ray crystallinity values, sago starch had highest 1047/1022 cm^{-1} value, where as potato showed the lowest value. The less pronounced bands at 1047 cm^{-1} for all precipitated starches indicated that the ordered structure was destroyed and increase in the intensities of the bands at 1022 cm^{-1} illustrates the increased amorphous structure of samples. Precipitated sago and pea starches, which showed slightly sharper X-ray diffractograms, have also shown higher intensities at peak 1047 cm^{-1} for precipitated pea is higher followed by precipitated sago which might be attributed to the remaining ordered structure. Precipitated pea and sago starches

Table 4
Crystallinity values of native and regenerated starches.

Source	Type	Native granule crystallinity (%)	Precipitated starch crystallinity (%)
Potato	B	21.3	0.8
Wheat	A	24.79	1.66
Rice	A	29.85	1.04
Tapioca	A	33.33	1.82
Pea	C	25	2.43
Sago	C	35.47	3.04

Table 5
FTIR ratio values for the absorbances 1047/1022 cm^{-1} obtained for native and regenerated starch powder.

Source	Native starch IR ratio 1047/1022 cm^{-1}	Regenerated starch IR ratio 1047/1022 cm^{-1}
Potato	0.64	0.525
Wheat	0.67	0.536
Rice	0.66	0.526
Tapioca	0.82	0.528
Pea	0.78	0.63
Sago	0.83	0.58

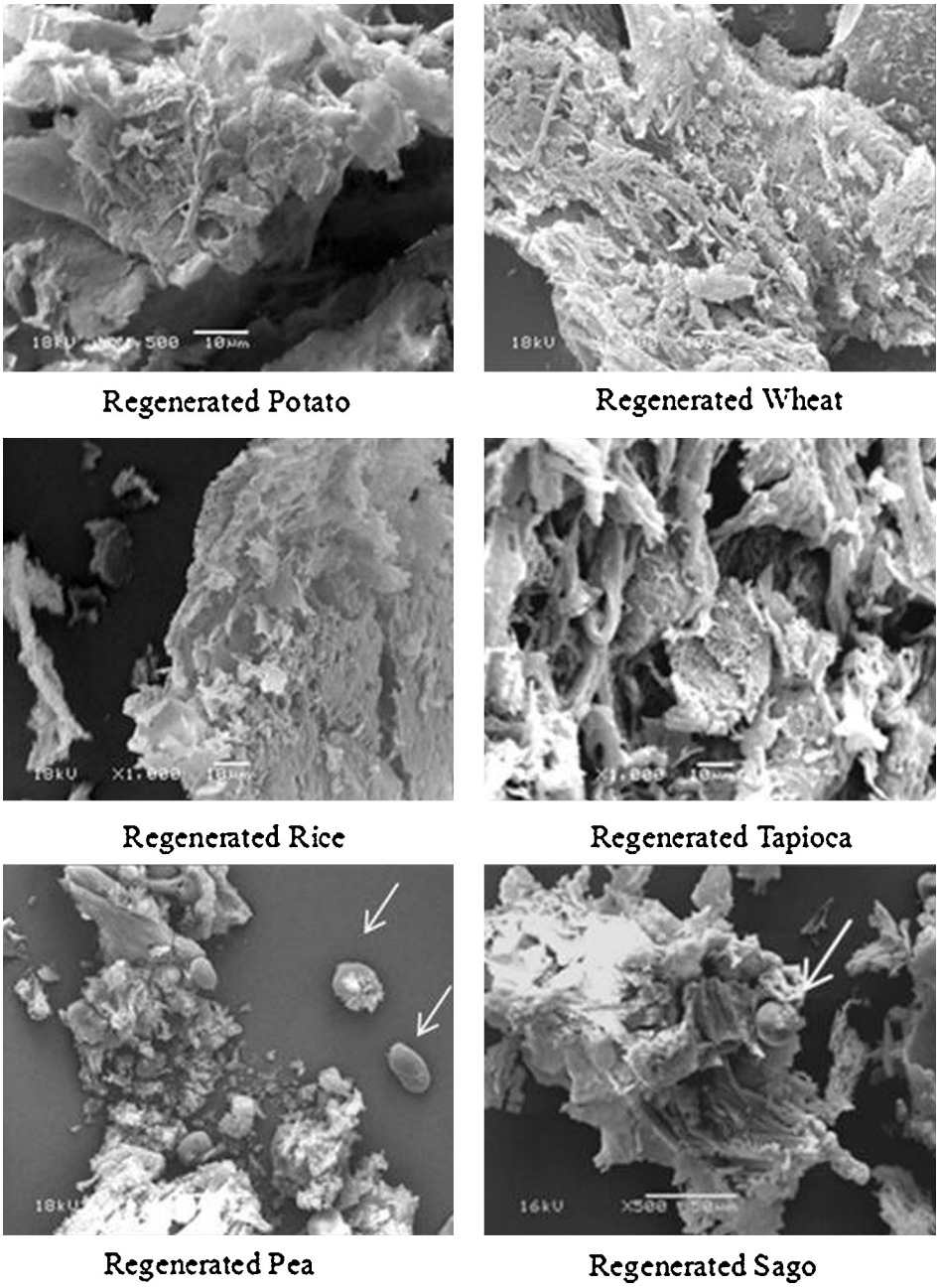

Fig. 5. Scanning electron micrographs of regenerated starches of different botanical origins. The arrows in the micrographs of regenerated pea and regenerated sago indicates undissolved or partially damaged granules.

had highest 1047/1022 cm^{-1} ratio value followed by precipitated sago, where as potato showed lower value which is strongly correlated with X-ray crystallinity data. This data indicate that the starches belong to C-type polymorphism even more resistant to solvent that B-type.

4. Conclusions

Native starches from different botanical sources show variation in physical organisation and resistance towards solution. These differences could be attributed to differences in molecular architecture of starch granules. 78% NMMO can dissolve cereal starches which belong to A-type, completely and rapidly. In contrast B- and C-type starches are more resistant to 78% NMMO suggesting morehomogeneous granules with respect to distribution of internal bonding forces. Cereal starches showed progressive fragmentation of the granules into small pieces. Starches with high amylose content showed a much slower granule disruption, with no fragmentation of the granule. Particularly in potato, most of the granules remained intact and optically birefringent until they were dissolved completely, although the outer layers of the granule were dissolved. Tapioca starch behaves slightly anomalously dissolving more slowly than the other A-type starches although having relatively low DSC onset temperatures. The information on the dissolutions of starches in NMMO shows some relationship to the susceptibility to enzymatic attack. Thus in addition to contributing to the understanding of mixed cellulose starch products prepared by co-dissolution in NMMO and also possibly ionic liquids this study may provide another approach to obtaining information on starch granule structure.

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