Drug Development and Industrial Pharmacy, 2009; 35(11): 1389–1406

informa
healthcare

ORIGINAL ARTICLE

Evaluation of the material and tablet formation properties of modified forms of *Dioscorea* starches

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Abstract

Starches obtained from four different *Dioscorea* species—namely, White yam (*Dioscorea rotundata*), Bitter yam (*Dioscorea dumetorum*), Chinese yam (*Dioscorea oppositifolia*), and Water yam (*Dioscorea alata*)—were modified by cross-linking, hydroxypropylation, and dual modification—cross-linking followed by hydroxypropylation. The physicochemical, material, and tablet properties of the modified starches were investigated with the aim of understanding their properties to determine their potential use for different applications. The tablet formation properties were assessed using 3D modeling, the Heckel equation, and force-displacement profiles. The analyzed tablet properties were elastic recovery, compactibility, and disintegration. The result indicates that the modifications generally increased the swelling power for all the starches in the rank order hydroxypropyl > hydroxypropylated cross-linked > cross-linked (CL) while the solubility did not show a clear-cut pattern. This indicates that hydroxypropylation generally showed the strongest effects on swelling. Furthermore, hydroxypropylation improved the hot water swelling of the CL starches. The modifications did not cause any detectable morphological change in the starch granules shape or size although slight rupture was observed in some granules. CL starch had the lowest water sorption capacity and hydroxypropylation increased the sorption capacity of the CL starches. The material property results indicate that hydroxypropylation and cross-linking did not significantly improve the flowability and compressibility but improved bonding, which resulted in an increased compaction and higher tablet crushing force even though they all disintegrated rapidly. Thus, the modified *Dioscorea* starches showed potentials for development as new excipients in solid dosage form design, and they could be useful as disintegrants or for Soft tableting.

Key words: *Cross-linking;* Dioscorea *starches; hydroxypropylation; modified starch; tableting; yam*

Introduction

Native starches have inherent properties that could be extended by physical and chemical modification techniques to produce functionally tailored starches with a wide range of functional properties to meet specific applications[1]. Chemical modification involves the introduction of functional groups into the starch molecule, resulting in markedly altered physicochemical properties. The properties of starch derivatives obtained depend on the kind of starch bases used and their basic properties. The physicochemical properties achieved also depend on factors such as the chemical nature of the reagent, the degree of substitution (DS), starch type, reagent concentration, pH, reaction time, and temperature[1,2]. Chemically modified starches are used for a variety of value-added products and account for one-sixth of all starch solids[2,3].

Hydroxypropylation and cross-linking are two widely used methods of preparing chemically modified starches[4]. Hydroxypropylated starches are generally prepared by etherification of native starch with propylene oxide in the presence of an alkaline catalyst. The hydroxypropyl (HP) groups are hydrophilic in nature, and when introduced into starch chains, they weaken or disrupt the internal bond structure that holds the granules together

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(Received 3 Nov 2008; accepted 7 Apr 2009)

ISSN 0363-9045 print/ISSN 1520-5762 online
DOI: 10.3109/03639040902960185

and alter their physicochemical and application properties[5]. Hydroxypropylation increases the freeze–thaw stability, decreases gelatinization and pasting temperatures, and increases paste clarity of starches[2,6–8]. Cross-linking treatment is intended to add chemical bonds at random locations in a granule. Cross-linking reinforces, stabilizes, and strengthens the relatively tender starch granules; makes them more resistant toward acidic medium, heat, and shearing; and provides more stable pastes at high temperature and low pH[9,10]. Dual modification may be employed to obtain the desired combination of properties. Cross-linking followed by hydroxypropylation has been shown to alter the physicochemical properties of the parent starches to yield starches with desirable functional properties, providing a wider range of potential applications[2,4,8,11]. Cross-linking reduces the degree of subsequent hydroxypropylation, and hydroxypropylation increases the degree of subsequent cross-linking[12].

Most studies on the production of chemically modified starches have been limited to widely available starches such as maize, potato, wheat, tapioca, and rice[5,7,13,14]. Chemical modification of starches from other botanical sources may yield starches with desirable functional properties that could be valuable in the food and pharmaceutical industries. Knowledge of the physicochemical properties of these new starch derivatives is important for manufacture in terms of quality by design, quality control, and criteria for selecting starches capable of imparting specific requirements[3]. Furthermore, the derived starches may have better properties as tablet excipients especially in direct compression manufacture of pharmaceutical tablets.

Tropical yam tubers are a potential starch source that could be explored commercially because of their high starch content (70–80% dry basis) and cheap cost[14]. Recent studies have shown the potential of starches obtained from four different tropical *Dioscorea* (yam) species as direct compression excipients for pharmaceutical tablets. However, native *Dioscorea* starches generally exhibited poor flow and compaction properties, and some of the starches did not form intact tablets except at high densification and high compression pressures[15]. Chemical modification of the native *Dioscorea* starches may yield starches with improved properties that will provide an alternative to the existing starches. So far, no work has been carried out on the chemical modification of *Dioscorea* starches.

Thus, in this study, starches from four *Dioscorea* species—namely, White yam, *Dioscorea rotundata*; Bitter yam, *Dioscorea dumetorum*; Chinese yam, *Dioscorea oppositifolia*; and Water yam, *Dioscorea alata*—were modified by cross-linking, hydroxypropylation, and dual modification—cross-linking followed by hydroxypropylation. Four species of *Dioscorea* were evaluated to determine the relative applicability of the starches of the four species. The physicochemical, thermal, morphological, and material properties of the modified starches were investigated with the aim of understanding their properties to determine their potential use for different applications in solid dosage form and especially tablet design. The tablet formation properties were assessed using the 3D modeling parameters, the Heckel equation, and the force-displacement profiles, whereas the properties of the starch tablets were evaluated using the elastic recovery (ER), compactibility plots, and disintegration test.

Materials

Tubers of four different *Dioscorea* species—namely, White yam, *Dioscorea rotundata* L.; Bitter yam, *D. dumetorum* Kunth; Chinese yam, *D. oppositifolia* L.; and Water yam, *D. alata* L. DIAL2—were obtained from local farmers in Ibadan, Nigeria, and authenticated. The starches were extracted from the relevant tubers using established procedures[16]. From hereon, only the abbreviations White, Bitter, Chinese, and Water will be used for the starches. All materials and tablets were equilibrated, produced, and stored at 23 ± 1°C and 45 ± 2% relative humidity (RH).

Methods

Production of modified starches

Preparation of cross-linked *Dioscorea* starch

Cross-linking of the starches was performed using established methods[17]. Native starch (300 g) was suspended in 600 mL of distilled water containing sodium trimetaphosphate (15 g, STMP), sodium hydroxide (1.8 g), and sodium carbonate (9 g). The starch suspension was stirred at room temperature for 3 hours and then adjusted to pH 6.5 with 0.2 N HCl to terminate the reaction. The cross-linked (CL) starch slurry was washed five times with distilled water, dried in a hot air oven for at 40°C for 24 hours, and then powdered using a laboratory mill. All the starches were passed through a 125-µm mesh sieve. Phosphorus content was determined from the starch ash. The starch was mixed with 1% (w/w) sodium carbonate and ignited in a furnace at 550°C. The phosphorus content in the ash was determined colorimetrically according to the method described by Murphy and Riley[18]. The DS was calculated using the following equation by Paschall[19]:

$$\mathrm{DS} = \frac{162P}{3100 - 102P}, \tag{1}$$

where P = % phosphorus (dry basis) of phosphorylated starch.

Preparation of hydroxypropyl starch

Starch hydroxypropylation was carried out as described by Leegwater and Luten[20] with a little modification. Native starch (200 g db, equivalent to 40% starch solid slurry) was suspended in distilled water containing sodium sulfate (30 g, 15% dry starch basis) with mild stirring to make a uniform slurry. The pH was adjusted to 10.5 using sodium hydroxide solution (5%). After 10 minutes of reaction, propylene oxide (12%, v/w, of starch solid) was added, and the reaction was continued at 40°C for 24 hours with shaking. The reaction was neutralized with 0.2 M HCl and the pH adjusted to 5.5. The starch cake was washed five times with distilled water, dried in a hot air oven at 40°C for 24 hours, and then powdered using a laboratory mill. The hydroxypropyl content was determined by the spectrophotometric method[21] and expressed in terms of molar substitution (MS) defined as moles of substituent per mole of anhydroglucose unit[1]. The results are means of three determinations.

Preparation of hydroxypropylated cross-linked starch

Dual modification of starch was carried out by first reacting starch with propylene oxide followed by a mixture of phosphate salt [2% STMP and 5% sodium tripolyphosphate (STPP)] according to the method of Saowakon[22]. Starch (200 g) was hydroxypropylated as previously described for 24 hours. The cross-linking agents (2% STMP and 5% STPP) were added to the slurry. The reaction was allowed to proceed for 2 hours at 40 ± 2°C with continuous stirring. The pH of the starch slurry was adjusted to 5.5 with 0.2 M HCl solution to terminate the reaction. The starch was washed five times with distilled water, dried in a hot air oven at 40°C for 24 hours, and then powdered using a laboratory mill. All the starches were passed through a 125-µm mesh sieve.

Physicochemical material properties

Swelling power and solubility

The swelling and solubility properties of the starches in cold water (22 ± 1°C) and hot water (85 ± 1°C) were assessed using established methods[23]. Starch suspensions (1%, w/w) were prepared in a flask and heated to appropriate temperature for 30 minutes with shaking for every 5 minutes and left to cool at room temperature and centrifuged for 15 minutes at 3000 × g. The supernatant was decanted and dried in an oven for 2 hours at 130°C. The residue obtained after drying the supernatant represents the amount of starch solubilized in water at that particular temperature. The solubility was calculated as 100 grams per gram of sample on dry weight basis. The residue obtained was weighed to obtain the swelling of the starch. All determinations were done in triplicate.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were performed on a DSC 200 (Netzsch Gerätebau GmbH, Selb, Germany) using sealed stainless steel pans. The sample pan (20%, w/w, dispersion of starch in water) and the reference pan were heated from 25°C to 160°C at a scanning rate of 10 K/min, held for 2 minutes at 160°C, and cooled to 60°C at 10 K/min. The gelatinization enthalpy ($\triangle H$), onset temperature (T_o), the peak temperature (T_p), and the endset temperature (T_c) of each sample were then determined. All analyses were performed in triplicate.

X-ray powder diffraction

The X-ray diffraction pattern was recorded with Co-Kα_1 X-ray radiation (STOE STADI-MP diffractometer; STOE & Cie GmbH, Darmstadt, Germany). The starch powders tightly packed in a sample holder were exposed to X-ray beam at 40 kV and 30 mA. The scanning region of the diffraction angle (2θ) was from 3° to 50°. The total run time was 100 minutes.

FT-Raman spectroscopy

The modified starches were analyzed using FT-Raman spectroscopy. The spectra were collected on a Bruker RFS 100/S FT-Raman spectrometer (Bruker Optik GmbH, Ettlingen, Germany) using a diode-pumped Nd : YAG with an operating wavelength of 1064 nm. Typical spectra were acquired with 200 scans and a laser power of 200 mW at the sample location. The interferograms were apodized with the Blackman–Harris four-term function and subjected to Fourier transformation to give spectra with a resolution of 4 cm^{-1}.

Powder-technological material properties

Scanning electron microscopy

The starch powders and tablets (upper surface and breaking surface) were analyzed using scanning electron microscopy (SEM) (ESEM 30; Philips, Kassel, Germany) at an accelerating voltage of 5 keV.

Water content

The water content was determined by thermogravimetric analysis using TGA 209 in triplicate (Netzsch Gerätebau GmbH). The powder was heated with 10 K/min from 20°C to 150°C and the water loss determined.

Sorption isotherms

The sorption isotherms were determined gravimetrically after equilibrating the samples over saturated salt solutions for 7 days in triplicate at 21 ± 1°C[24]. Dynamic sorption isotherms showed that the starches equilibrated after 3–4 days. The powders were equilibrated at specific RH, and after equilibration, the powders were weighed and transferred to the next higher RH starting at 32% RH and up to 90% RH. Desorption was performed by placing the powders in the next lower RH up to 0% RH (phosphorous pentoxide). The water content was calculated on the dry powder weight basis at 0% RH.

Particle size determination

Particle size distribution was determined by laser light diffraction using a dry powder feeder (Malvern Instruments, Worcester, UK, Series 2600c, 63 mm focal length, beam length 10 mm). The software from Malvern was used to calculate the mean particle size (D_{50}), the particle size distribution with parameters for 10% (D_{10}) and 90% (D_{90}) particle size, and the specific surface area of the powder. Determinations were done in quadruplicate, and results are given as mean and standard deviation.

Apparent particle density

The apparent particle density of all equilibrated starches was determined by Helium pycnometry (Accupyc 1330; Micromeritics, Norcross, GA, USA) in triplicate[24].

Bulk and tap density

Bulk and tap density were determined in a 250-mL cylinder using a volumeter (Stampfvolumeter STAV 2003; J. Engelsmann AG, Ludwigshafen, Germany). Determinations were performed in triplicate according to the European Pharmacopoeia[25].

Powder flowability

The flowability of the starches was assessed using the Hausner ratio and the Carr index[26].

Tablet production

Tableting

Tableting was performed on an instrumented eccentric tableting machine (EK0/DMS, No. 1.0083.92; Korsch GmbH, Berlin, Germany) using 11 mm diameter flat-faced punches (Ritter GmbH, Hamburg, Germany). Equal volumes of the substances based on apparent particle density were tableted to the graded maximum relative densities ($\rho_{\mathrm{rel,max}}$) of the tablets 0.75, 0.80, 0.85, 0.90, and 0.95 (precision 0.001). The amount of material necessary for each tablet with a given $\rho_{\mathrm{rel,max}}$ was calculated. The tablet height at maximum densification under load was held constant at 3 mm, and the filling depth was held constant at 13 mm. Displacement of the punch faces was measured using an inductive transducer (W20 TK; Hottinger Baldwin Messtechnik, Darmstadt, Germany). Displacement was corrected for elastic deformation of the punches. Elastic deformation was measured by punch-to-punch deformation. The powder was manually filled into the die, and one compaction cycle was performed. The production rate was 10 tablets/min. No lubricant was used to avoid its influence.

Ten single tablets were produced at each condition, and data acquisition was performed by a DMC-plus system (Hottinger Baldwin Messtechnik). Data were stored by BEAM Software (AMS, Flöha, Germany). Force, time, and displacement of the upper punch were recorded for each compaction cycle. Tableting was performed in a climate-controlled room, which was set to 23 ± 1°C and 45 ± 2% RH.

Data analysis

For analyzing tableting data, only data greater than 1 MPa were used. For all compaction cycles of each material, normalized time, pressure, and $\ln(1/1{-}D_{\mathrm{rel}})$ according to Heckel[27] were calculated.

3D model

The recorded data were analyzed using the 3D model. All three calculated parameters were presented in a 3D data plot to which a twisted plane was fitted by the least-squares method according to Levenberg–Marquardt (Matlab)[28].

$$z=\ln\left(\frac{1}{1-D_{\mathrm{rel}}}\right)=\left[(t-t_{\max})(d+\omega\cdot p_{\max}-p)\right]+(e\cdot p)+(f+d\cdot t_{\max}), \tag{2}$$

where D_{rel} = relative density, t = time, and p = pressure;

$$d=\frac{\delta\ln(1/(1-D_{\mathrm{rel}}))}{\delta t}, e=\frac{\delta\ln(1/(1-D_{\mathrm{rel}}))}{\delta p},$$

$$f=\ln\left(\frac{1}{1-D_{\mathrm{rel}}}\right),$$

where $t_{\max}$ = time at maximum pressure, $p_{\max}$ = the maximum pressure, and ω = twisting angle at $t_{\max}$.

The plane is twisted at $t = t_{\max}$. Time plasticity (d) describes the plastic deformation with respect to time. Increasing time plasticity indicates faster deformation during tableting. Pressure plasticity (e) describes the relationship between density and pressure. Large pressure plasticities are observed with materials that require only a small amount of pressure for deformation. The twisting angle (ω) is a measure for the elasticity of the material. Elasticity decreases with increasing ω. Thus, fast elastic decompression is the inverse of ω. Time plasticity (d), pressure plasticity (e), and the twisting angle (ω) of all compaction cycles at each tableting condition (material and a given $\rho_{\mathrm{rel,max}}$) were obtained, and the means and standard deviations were calculated.

Heckel function

Heckel describes the decrease of porosity with pressure by first-order kinetics[27]. The slope of the Heckel equation was calculated from the compression (linear) portion of the plot, which was determined by building the second derivation of the compression curve. The correlation coefficient was set to $R \geq 0.999$. The slope provides information on the total deformation of the starches during the compression phase.

Force-displacement profiles

Force-displacement profiles are used to calculate the different types of energy used for tableting[28]. The analysis includes the compression and decompression of the powder in the die. The area between compression and decompression curve is defined as the area of compaction energy (E2). The area between maximum displacement and decompression curve is defined as the area of elastic energy (E3). E2 and E3 values were calculated and normalized for tablet weight. The normalized energies $E2_{norm}$ and $E3_{norm}$ are presented.

Tablet properties

Elastic recovery

ER after tableting was calculated using the equation of Armstrong and Haines-Nutt[29]:

$$\mathrm{ER}\,(\%) = 100\,\frac{H_1 - H_0}{H_0}, \tag{3}$$

where ER = elastic recovery, H_1 = height of the tablet after 10 days, and H_0 = minimal height of the tablet under load. Ten tablets were analyzed, and the means and standard deviations were calculated.

Crushing force

The crushing force of the tablets was determined with the crushing force tester (TBH 30; Erweka GmbH Heusenstamm, Germany). Five tablets were analyzed 10 days after tableting in all cases, and the means and standard deviations were calculated.

Disintegration

The disintegration times of the tablets were determined using an Erweka ZT 2 disintegration tester (Erweka Apparatebau GmbH, Heusenstamm, Germany) coupled with a water bath (GFL GmbH, Burgwedel, Germany). Determination was performed for six tablets.

Statistical analysis

Statistical analysis was carried out using analysis of variance using a computer software GraphPad Prism® 4 (GraphPad Software Inc. San Diego, CA, USA). Tukey–Kramers multiple comparison tests were used to compare the material and tablet properties of various starches. At 95% confidence interval, P-values less than or equal to 0.05 were considered significant.

Results and discussion

Physicochemical properties

The functional properties of starches have been shown to be affected by their chemical composition[30]. The phosphorus and hydroxyl content of the modified starches and their DS are presented in Table 1. The results showed that different levels of substitution were achieved for the various starches and the DS varies slightly from one starch to the other. Hydroxypropylation increased the degree of subsequent cross-linking of the dual modified starch. This is in agreement with the result of other workers[2,11]. However, the degree of MS obtained was low. It has been suggested that granular starches must be hydroxypropylated with high amount of propylene oxide to obtain an MS between 0.1 and 0.3[31]. Low

Table 1. Phosphorus and hydroxyl content, degree of substitution, and molar substitution of modified *Dioscorea* starches (mean ± SD, $n = 3$).

Starch	Modification	Molar substitution (MS)	Degree of substitution (DS)	Hydroxypropyl content (%, mol/mol)	Phosphorus content (%, mol/mol)
White	CL		0.003	—	0.052 (0.001)
	HP	0.001	—	0.027 (0.003)	—
	HPCL	0.002	0.004	0.064 (0.002)	0.076 (0.002)
Chinese	CL		0.003	—	0.064 (0.002)
	HP	0.001	—	0.041 (0.003)	—
	HPCL	0.003	0.004	0.080 (0.001)	0.082 (0.000)
Bitter	CL		0.004	—	0.084 (0.000)
	HP	0.001	—	0.036 (0.001)	—
	HPCL	0.003	0.006	0.073 (0.001)	0.110 (0.001)
Water	CL		0.004	—	0.072 (0.25)
	HP	0.001	—	0.030 (0.003)	—
	HPCL	0.003	0.005	0.068 (0.002)	0.100 (0.002)

degree of MS suggests that the hydroxypropylation inside the starch granules was hindered[12]. An important factor that affects the extent of cross-linking is the granule size and granule size distribution of starch granules[32]. During cross-linking, small-sized granules have been reported to be derivatized to a greater extent than large-sized granules[33].

The swelling power and solubility properties of the starches in cold (22.0 ± 1.0°C) and hot water (85.0 ± 1.0°C) are given in Table 2. The swelling power and solubility of the starches were generally low at low temperatures but increased significantly ($P < 0.01$) at 85°C, which is in agreement with the properties observed for other modified starches[2]. The ranking for swelling of the starch sources was Chinese > White > Water > Bitter, whereas the ranking for solubility was Chinese > Bitter > White > Water. Thus, Chinese starch that showed the highest swelling and solubility in its native form also showed the highest effects when modified[15]. The swelling power of the modified starches was higher than those earlier reported for the native forms of the same starches. This may be because of the introduction of the hydrophilic group in the hydroxypropylated starch and the higher phosphate cross-linking inside the granules of the CL starches[34]. This indicates that the modifications generally increased the swelling power for all the starches. The ranking of the swelling for the types of modification was generally HP > hydroxypropylated cross-linked (HPCL) > CL while the solubility did not show a clear-cut pattern. Thus, hydroxypropylation generally showed the strongest effects on the swelling properties of the starches. The repulsion between adjacent starch molecules caused by the negatively charged phosphate groups may have reduced the interchain associations and gave increased levels of hydrated swollen molecules, which resulted in increased swelling power of the CL starches[35]. On the other hand, the increased swelling power of the hydroxypropylated starches has been attributed to the reduction of interactions between starch chains because of the increased hydrophilicity of starch that results from the introduction of HP groups. In addition, inter- and intramolecular hydrogen bonds in the starch chains are disrupted. Thereby the granular structure of starch is weakened and the motional freedom of starch chains in amorphous regions is increased, as described by Kaur et al.[13] and Choi and Kerr[36]. In addition, hydroxypropylation improved the hot water swelling of the CL starches.

The X-ray powder diffraction patterns of native and modified forms of Water, which are representative of the difference in spectra for the other *Dioscorea* species, are presented in Figure 1. The X-ray diffraction pattern shows that the cross-linking and hydroxypropylation did not induce a transition in the crystal type of the starch. This is similar to the result obtained by other workers[31]. The diffraction pattern of native *Dioscorea* starches have been interpreted as intermediate between A and B polymorphs, which are referred to as C-type diffraction pattern, which are amorphous and not true crystalline polymorphs[15].

The FT-Raman spectra of native and modified Bitter starches, which are representative of the difference in spectra for the other *Dioscorea* species, are presented in Figure 2 while the FT-Raman bands are shown in Table 3. The Raman fingerprints of the modified starches are characteristic of granular starches although the chemical modifications caused some shift in the Raman band position and shape. There was a slight shift in the α-1,4

Table 2. Swelling and solubility properties of modified *Dioscorea* starches (mean ± SD, $n = 3$).

		Cold water (22 ± 1°C)		Hot water (85 ± 1°C)	
Starch	Modification	Swelling (g/g)	Solubility (%, m/m)	Swelling (g/g)	Solubility (%, m/m)
White	Native	1.04 (0.16)	1.02 (0.20)	12.24 (1.59)	4.77 (0.33)
	CL	2.02 (0.30)	2.22 (0.49)	14.62 (0.93)	6.57 (0.46)
	HP	1.48 (0.13)	1.59 (1.70)	17.23 (1.90)	3.2 (0.68)
	HPCL	1.64 (0.21)	2.98 (0.20)	17.10 (0.77)	8.43 (0.57)
Chinese	Native	1.53 (0.04)	1.06 (0.03)	16.30 (2.16)	7.10 (1.02)
	CL	3.27 (0.53)	1.45 (0.28)	22.19 (2.02)	12.00 (0.61)
	HP	2.29 (0.26)	1.18 (0.16)	24.56 (2.21)	17.38 (0.70)
	HPCL	2.03 (0.11)	2.22 (0.95)	23.11 (2.48)	15.56 (0.55)
Bitter	Native	1.72 (0.48)	2.52 (0.31)	10.80 (1.37)	6.01 (1.14)
	CL	2.95 (0.16)	2.82 (0.53)	9.49 (0.35)	8.77 (0.72)
	HP	2.17 (0.16)	1.59 (0.31)	11.99 (1.20)	8.15 (0.93)
	HPCL	2.65 (0.21)	2.00 (0.89)	10.03 (1.07)	5.91 (0.78)
Water	Native	0.97 (0.14)	1.04 (0.06)	13.43 (1.11)	9.97 (1.88)
	CL	2.02 (0.23)	1.87 (0.25)	14.40 (0.75)	4.05 (0.72)
	HP	1.42 (0.33)	1.87 (0.11)	14.93 (0.28)	3.88 (0.63)
	HPCL	2.08 (0.91)	1.31 (0.18)	16.69 (0.83)	3.33 (0.22)

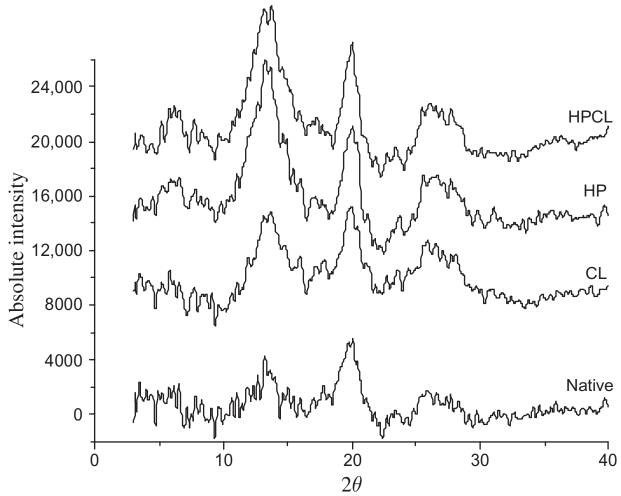

Figure 1. X-ray powder diffraction pattern of modified Water starches.

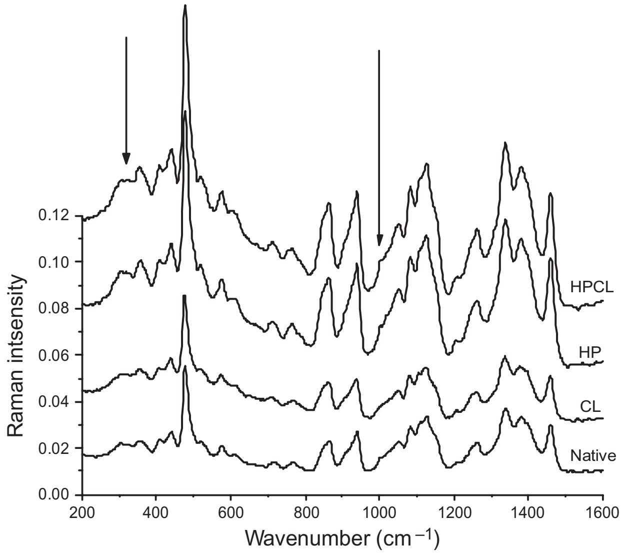

Figure 2. FT-Raman spectroscopy pattern of native and modified Bitter starches.

glycosidic linkages assigned to the band at 940 cm^{-1}. The COH deformation at 1052 cm^{-1} for the native starches appeared as a shoulder in the modified starches probably because of the different substituents[37].

DSC results of the modified starches are given in Table 4. Hydroxypropylation and cross-linking resulted in a decrease in the values of T_o, T_p, T_c, and $\triangle H_{gel}$ of the modified starches when compared to the values obtained for the native forms of the starches[15]. Gelatinization enthalpy reflects the energy required to disrupt the granule structure, whereas $\triangle H_{gel}$ provides an overall measure of crystallinity (quality and quantity) and is an indicator of the loss of molecular order within the granules[14,38]. Yeh and Yeh[8] have reported that starch granules could have been swollen or damaged because of alkali treatment during cross-linking and hydroxypropylation which results in loosening of the granular structures, and therefore less heat is required for gelatinization of the starches. This results in lower values of gelatinization temperatures and enthalpy for the modified starches than the native forms of the starches. Furthermore, the ranking of the gelatinization temperature for the modified starches was Bitter > Water > White > Chinese. The difference in gelatinization temperature between the various *Dioscorea* starches has been attributed to the differences in molecular organization within the starch granules[39]. Similar results have been obtained for hydroxypropylated potato[40] and hydroxypropylated rice[41] starches.

Table 3. Raman bands of native and modified Bitter yam starch.

Assignment	Native starch	CL starch	HP starch	HPCL starch
Skeletal modes of pyranose ring	440	438	440	440
	477	474	476	477
	577	573	575	577
	614	—	—	—
CH and CH_2 deformation	864	862	864	864
Skeletal mode involving -1,4-glycosidic linkage (COC)	940	938	939	939
COH deformation	1052	Shoulder	Shoulder	Shoulder
	1126	1125	1124	1126
CH_2OH (side chain)-related mode	1262	1260	1261	1262
CH_2 twist, COH bending	1339	1337	1339	1337
CH_2 scissoring, CH and COH deformation	1387	1391	1388	1389
CH_2 sym. deformation	1460	1458	1460	1458
CH stretching modes	2910	2904	2912	2910
OH modes				

In summary, the modification of the various *Dioscorea* starches resulted in improved swelling properties but decreased gelatinization temperatures and enthalpy. Substitution of starch granules occurs mainly in the amorphous regions, which promotes swelling in these regions and thus disrupts the crystalline portion that melts at a lower temperature than the native starches[41].

Material properties

The SEMs of the modified starches are shown in Figure 3. The granules of the modified starches were similar to the morphology of the native starch granules[15], suggesting that the modification did not cause any detectable morphological changes in the starch granules shape or size, although slight rupture was observed in some granules probably because of the strong alkaline conditions

Table 4. Thermal properties of modified *Dioscorea* starches (mean and SD, $n = 3$).

Starch	Modification	T_o (°C)	T_P (°C)	T_c (°C)	ΔH_{gel} (J/g)
White	CL	71.47 (0.23)	75.53 (0.42)	83.10 (0.36)	10.87 (1.17)
	HP	72.63 (0.51)	76.33 (0.51)	83.03 (0.12)	15.13 (1.09)
	HPCL	71.80 (0.20)	75.43 (0.21)	81.50 (0.44)	8.07 (0.44)
Chinese	CL	69.23 (0.42)	73.57 (0.38)	80.87 (1.10)	10.27 (0.51)
	HP	70.33 (0.55)	74.73 (0.40)	81.53 (0.92)	8.13 (1.21)
	HPCL	70.23 (0.21)	74.50 (0.20)	81.60 (0.52)	9.57 (0.34)
Bitter	CL	78.80 (0.26)	82.43 (0.42)	86.70 (0.72)	6.67 (0.55)
	HP	76.27 (0.32)	79.63 (0.40)	84.57 (0.68)	8.85 (0.27)
	HPCL	78.23 (0.06)	81.50 (0.00)	86.30 (0.26)	5.63 (0.63)
Water	CL	76.03 (0.50)	80.13 (0.86)	86.03 (1.26)	9.23 (1.48)
	HP	76.27 (0.67)	80.17 (0.85)	86.03 (1.70)	10.23 (1.07)
	HPCL	75.80 (0.35)	79.73 (0.51)	84.57 (0.72)	13.12 (0.73)

during the modification process. Similar observation has been made in hydroxypropylated potato starch[13] and some starches from other botanical sources[9,12].

The parameters D_{10}, D_{50} (median particle size), and D_{90} and the specific surface area as obtained from the particle size distribution analysis using the laser diffractometry are given in Table 5. The granule sizes varied considerably among the various starches. However, there were no significant differences in the granule size of the native and modified forms of the starches. The specific surface area was in the rank order of Chinese > Bitter > Water > White.

The water content of the starches determined by thermogravimetric analysis is summarized in Table 6. The water content of the equilibrated modified starches ranged between 10% and 13% (w/w) when stored at 23°C and RH of 43%. The ranking of the water content was HPCL > HP > CL. Thus, HPCL showed the highest water content values and the CL showed the lowest. This value is within the limit prescribed for safe storage of starches by most starch-producing countries[16]. Higher levels of water can lead to microbial spoilage and subsequent deterioration in starch quality. Furthermore, water has been known to affect the flow and mechanical properties of starches[15]. The sorption isotherms of the modified White are shown in Figure 4. For all four starches, the water content determined by thermogravimetric analysis corresponds with the water content measured during sorption. The result shows that the water content increased with the RH. The ranking of the water content at the highest RH (90%) was HPCL > HP > CL. Thus, hydroxypropylation appears to increase the water sorption capacity of the starches probably because of the introduction of hydroxyl group. CL starch had the lowest water sorption capacity, and hydroxypropylation was shown to increase the sorption capacity of the CL starches. Thus, the HPCL starches had the highest water content at specific RH. Furthermore, CL starch showed lower water content than those reported for the native forms of the starches[15] while HP and HPCL showed higher values. Thus, cross-linking could be used to improve the stability of the starches to water sorption. In contrast to other materials, no range can be defined in which water content remains almost constant. Thus, the RH during tablet production and storage should be carefully controlled to obtain powders with optimum flow and compaction properties and also to prevent the deterioration of the tablets.

The powder-technological properties of the starches are presented in Table 6. The particle density of the modified starches was in the rank order of Chinese > Bitter > White > Water, whereas the ranking was White > Water > Chinese > Bitter for the bulk and tap density values. The values of the bulk and tap densities provide information on the flowability of powders and are used to calculate the Carr index, which is a measure of the flowability and compressibility of a powder. The lower the Carr index of a material, the better the flowability, but the poorer the compressibility[26]. The Carr index was in the rank order of Bitter > Chinese > Water > White. All the modified Bitter and Chinese starches had values higher than 21 and therefore exhibited poor flow properties. However, all the modified White starches and HP Water showed Carr index of 21 or less, indicating fair flow properties. The ranking of Carr index was generally CL > HPCL > HP. Thus, CL starches showed the highest compressibility while HP showed the lowest values. However, the modified starches did not flow through a funnel, indicating poor flowability similar to what has been reported for the native forms of the starches. This result is confirmed by the Hausner ratio, which was generally higher than 1.25. There were no significant ($P > 0.05$) differences in the flowability and compressibility of the native and modified starches. Thus, hydroxypropylation and cross-linking did not significantly improve the flowability and compressibility of the starches, indicating that the chemical modification did not affect the physical properties of the granules.

Thus, the morphology and flow properties of the various starches were not affected by chemical modification. However, the RH during tablet production and storage should be carefully controlled.

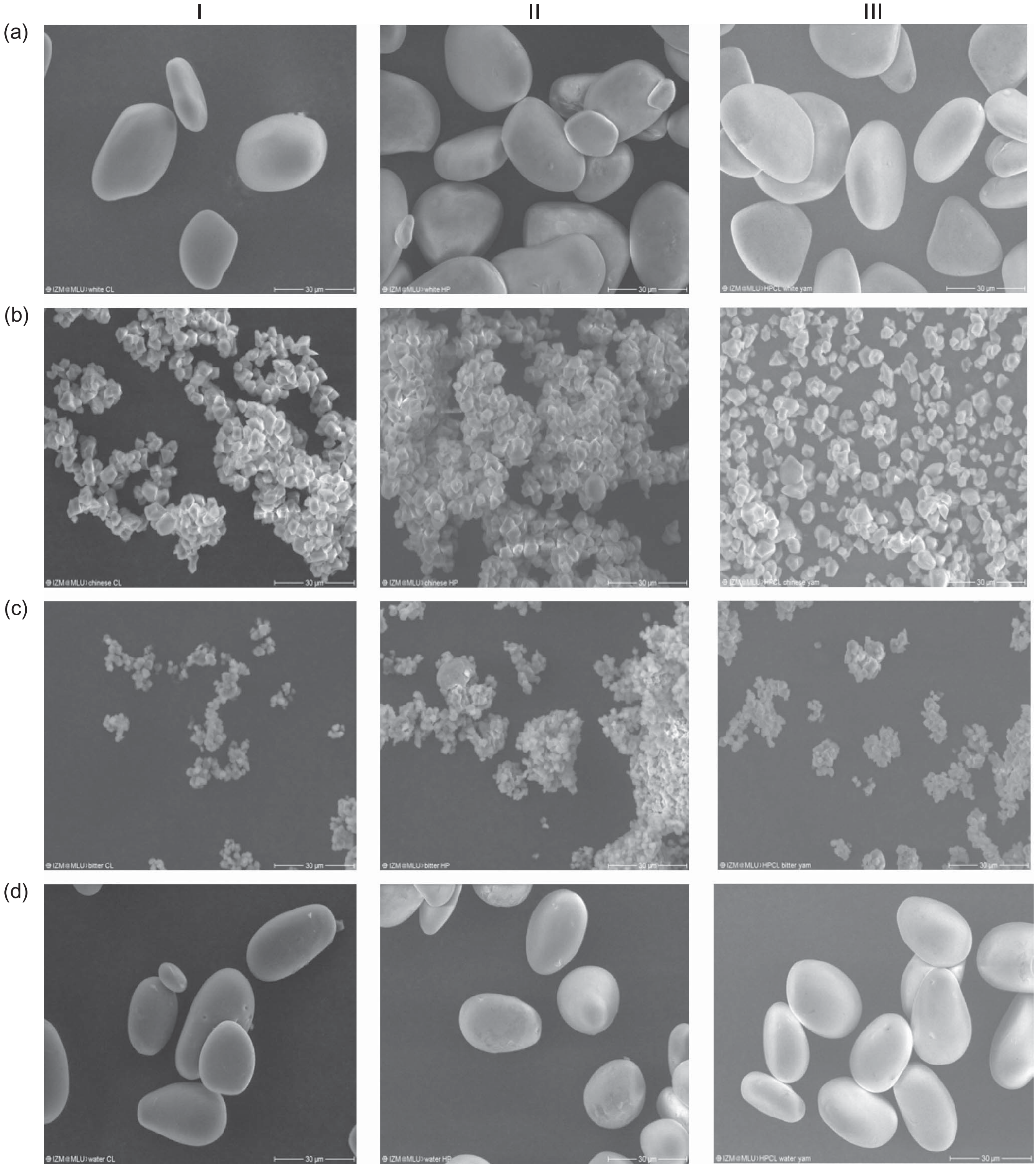

Figure 3. SEM of modified *Dioscorea* starches: I, cross-linked; II, hydroxypropylated; and III, hydroxypropylated cross-linked. (a) White, (b) Chinese, (c) Bitter, and (d) Water.

Tableting and tablet properties

The 3D modeling technique that allows the simultaneous evaluation of the three most important tableting process variables (normalized time, pressure, and density) was used to study the deformation of the modified starches during tableting. To these data a twisted plane is fitted, which is characterized by three parameters, d, e, and ω. The time plasticity (d) describes the plastic deformation with respect to time, the pressure plasticity (e) describes the relationship between density and

Table 5. Particle size distribution and specific surface area of modified *Dioscorea* starches (mean and SD, $n = 4$).

Starch	Modification	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Specific surface area (m^2/cm^3)
White	CL	20.74 (0.11)	30.60 (0.03)	42.59 (0.11)	0.21 (0.00)
	HP	19.97 (0.88)	30.29 (0.03)	44.52 (0.70)	0.13 (0.04)
	HPCL	20.60 (0.12)	30.04 (0.07)	46.01 (0.07)	0.21 (0.00)
Chinese	CL	2.49 (0.06)	6.43 (0.79)	190.46 (0.91)	1.15 (0.08)
	HP	2.50 (0.09)	6.80 (1.15)	183.80 (2.11)	1.11 (0.09)
	HPCL	2.63 (0.01)	11.99 (0.29)	220.09 (2.71)	0.90 (0.01)
Bitter	CL	2.76 (0.03)	28.23 (0.58)	209.89 (1.05)	0.80 (0.02)
	HP	2.78 (0.17)	42.35 (1.45)	214.05 (2.37)	0.72 (0.03)
	HPCL	4.75 (0.17)	11.58 (1.19)	248.62 (3.34)	0.37 (0.01)
Water	CL	15.86 (0.20)	23.29 (0.05)	32.44 (0.06)	0.29 (0.00)
	HP	17.44 (0.75)	24.53 (0.31)	33.49 (0.38)	0.35 (0.04)
	HPCL	19.90 (0.15)	25.78 (0.11)	35.06 (0.76)	0.25 (0.01)

Table 6. Powder-technological properties of modified *Dioscorea* starches (mean and SD, $n = 3$).

Starch	Modification	Water content (%)	Apparent particle density (g/cm^3)	Bulk density (g/cm^3)	Tap density (g/cm^3)	Carr index (%)	Hausner ratio
White	CL	11.54 (0.02)	1.517 (0.003)	0.711 (0.006)	0.910 (0.001)	21.80 (0.00)	1.28
	HP	12.03 (0.04)	1.514 (0.001)	0.715 (0.008)	0.894 (0.002)	20.00 (0.00)	1.25
	HPCL	12.20 (0.01)	1.512 (0.001)	0.714 (0.005)	0.895 (0.002)	20.26 (0.00)	1.25
Chinese	CL	11.49 (0.04)	1.541 (0.005)	0.437 (0.003)	0.654 (0.003)	33.14 (0.00)	1.50
	HP	11.57 (0.05)	1.532 (0.001)	0.479 (0.003)	0.694 (0.002)	30.89 (0.00)	1.45
	HPCL	11.66 (0.08)	1.521 (0.001)	0.418 (0.008)	0.608 (0.008)	31.31 (0.00)	1.46
Bitter	CL	10.88 (0.07)	1.539 (0.004)	0.480 (0.003)	0.728 (0.007)	34.03 (0.00)	1.52
	HP	10.96 (0.05)	1.521 (0.001)	0.506 (0.001)	0.746 (0.003)	31.54 (0.00)	1.46
	HPCL	10.86 (0.08)	1.534 (0.001)	0.490 (0.008)	0.717 (0.000)	31.62 (0.00)	1.46
Water	CL	11.90 (0.02)	1.510 (0.001)	0.683 (0.003)	0.939 (0.001)	27.28 (0.00)	1.38
	HP	12.25 (0.02)	1.509 (0.001)	0.681 (0.002)	0.853 (0.009)	20.15 (0.00)	1.25
	HPCL	12.77 (0.03)	1.497 (0.001)	0.630 (0.004)	0.861 (0.001)	26.90 (0.00)	1.37

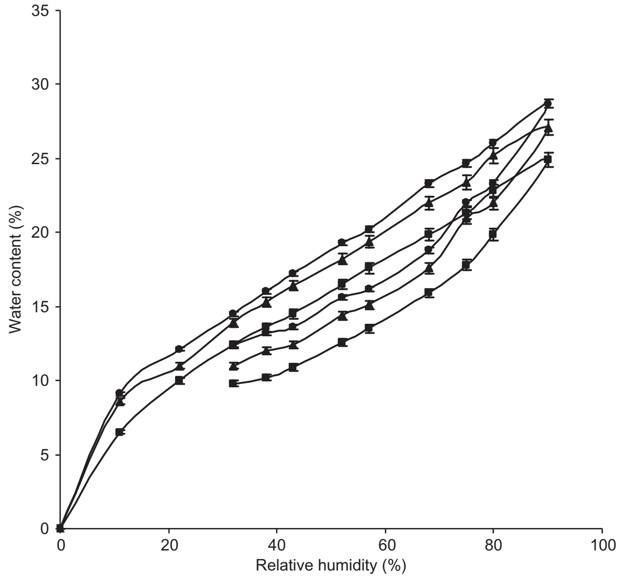

Figure 4. Sorption isotherm of modified White yam starches: ■, cross-linked; ▲, hydroxypropylated; and ●, hydroxypropylated cross-linked (mean and SD, $n = 3$).

pressure, and the angle of torsion (ω) is a measure of the material's elasticity. The 3D parameter plots for the starches are given in Figure 5 while the parameters and their standard deviations are shown in Table 7.

For all the starches, the time plasticity (d) increased with increasing $\rho_{\text{rel,max}}$, which indicates faster deformation during tableting. The d-values of the modified starches were comparable to those of the native forms[15] with the exception of the CL starches, which showed increased d-values and thus faster deformation than the other starches. Especially the d-values for higher $\rho_{\text{rel,max}}$ were strongly increased. A similar behavior has been reported for maize starch[42]. The modification of the starches caused different changes in the pressure-dependent deformation. For modified Bitter, Chinese, and White, the e-values were slightly lower than those of the native starches, while for Water, e-values were lower compared to the native forms of the starches and was about 0.003, which indicates less easy deformation[15]. All modified *Dioscorea* starches exhibited deformation because of pressure comparable to modified celluloses[43]. The ranking of e for the various *Dioscorea* species was Water > White > Chinese > Bitter while for the modified

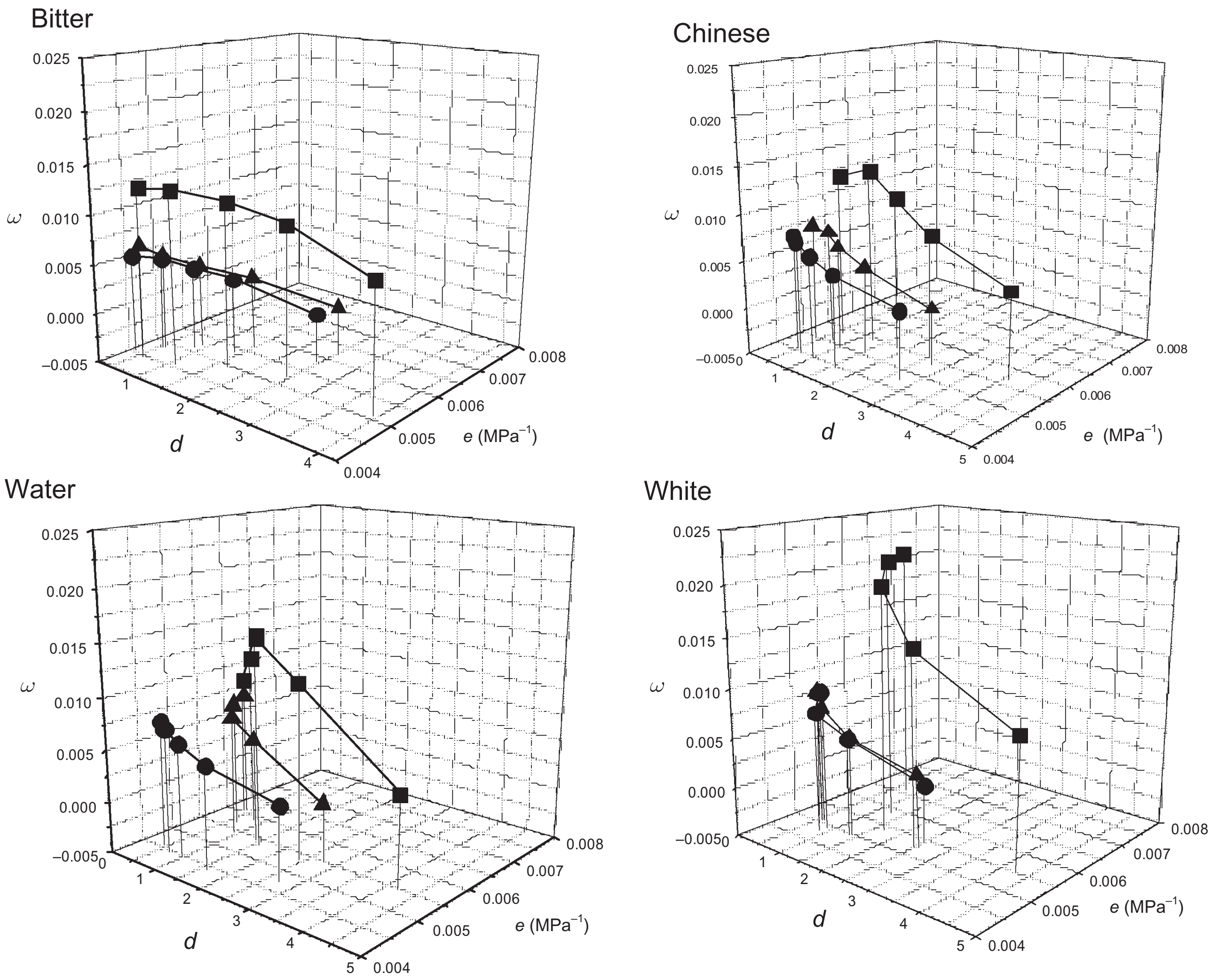

Figure 5. 3D parameter plot for modified *Dioscorea* starches: ■, cross-linked; ▲, hydroxypropylated; and ●, hydroxypropylated cross-linked.

Table 7. The 3D modeling parameter of modified *Dioscorea* starches (mean and SD, $n = 5$).

Starch	Modification	$\rho_{\text{rel.max}}$	d	e	ω
Bitter	CL	0.75	0.5997 (0.0056)	0.0044 (0.0000)	0.0124 (0.0001)
		0.80	1.1212 (0.0035)	0.0045 (0.0001)	0.0129 (0.0001)
		0.85	1.6672 (0.0033)	0.0050 (0.0000)	0.0117 (0.0001)
		0.90	2.4662 (0.0094)	0.0052 (0.0000)	0.0103 (0.0002)
		0.95	3.9214 (0.0437)	0.0051 (0.0001)	0.0077 (0.0006)
	HP	0.75	0.3255 (0.0023)	0.0047 (0.0001)	0.0058 (0.0001)
		0.80	0.5555 (0.0041)	0.0049 (0.0000)	0.0048 (0.0001)
		0.85	0.9103 (0.0055)	0.0052 (0.0001)	0.0037 (0.0002)
		0.90	1.4555 (0.0060)	0.0057 (0.0000)	0.0024 (0.0002)
		0.95	2.5232 (0.0372)	0.0060 (0.0001)	0.0001 (0.0008)
	HPCL	0.75	0.3173 (0.0036)	0.0046 (0.0001)	0.0050 (0.0002)
		0.80	0.5457 (0.0014)	0.0049 (0.0001)	0.0045 (0.0001)
		0.85	0.8806 (0.0057)	0.0051 (0.0000)	0.0036 (0.0001)
		0.90	1.3939 (0.0062)	0.0054 (0.0001)	0.0028 (0.0001)
		0.95	2.4565 (0.0203)	0.0058 (0.0001)	0.0001 (0.0001)

(*Continued*)

Table 7. (*Continued*).

Starch	Modification	$\rho_{\mathrm{rel.max}}$	*d*	*e*	ω
Water	CL	0.75	0.3630 (0.1274)	0.0061 (0.0001)	0.0089 (0.0036)
		0.80	0.7513 (0.2132)	0.0059 (0.0002)	0.0119 (0.0042)
		0.85	1.5906 (0.0379)	0.0053 (0.0001)	0.0154 (0.0003)
		0.90	2.4282 (0.0240)	0.0053 (0.0001)	0.0119 (0.0004)
		0.95	4.2022 (0.0944)	0.0055 (0.0001)	0.0040 (0.0005)
	HP	0.75	0.3813 (0.0081)	0.0061 (0.0001)	0.0072 (0.0004)
		0.80	0.5966 (0.0048)	0.0057 (0.0001)	0.0072 (0.0001)
		0.85	0.8895 (0.0034)	0.0054 (0.0001)	0.0067 (0.0001)
		0.90	1.3935 (0.0171)	0.0054 (0.0000)	0.0051 (0.0003)
		0.95	2.7295 (0.3426)	0.0055 (0.0001)	0.0006 (0.0012)
	HPCL	0.75	0.3983 (0.0035)	0.0075 (0.0002)	0.0077 (0.0002)
		0.80	0.6199 (0.0006)	0.0068 (0.0001)	0.0085 (0.0001)
		0.85	0.9026 (0.0119)	0.0063 (0.0000)	0.0084 (0.0002)
		0.90	1.4253 (0.0066)	0.0062 (0.0001)	0.0054 (0.0001)
		0.95	2.5973 (0.0229)	0.0066 (0.0001)	0.0007 (0.0004)
Chinese	CL	0.75	0.6339 (0.0056)	0.0053 (0.0000)	0.0129 (0.0001)
		0.80	1.2272 (0.0035)	0.0054 (0.0001)	0.0138 (0.0001)
		0.85	1.7398 (0.0033)	0.0055 (0.0000)	0.0112 (0.0001)
		0.90	2.5230 (0.0094)	0.0055 (0.0000)	0.0082 (0.0002)
		0.95	4.0838 (0.0437)	0.0057 (0.0001)	0.0044 (0.0006)
	HP	0.75	0.4499 (0.0021)	0.0049 (0.0001)	0.0077 (0.0001)
		0.80	0.6813 (0.0054)	0.0051 (0.0000)	0.0071 (0.0002)
		0.85	1.0022 (0.0043)	0.0050 (0.0001)	0.0061 (0.0001)
		0.90	1.5535 (0.0087)	0.0051 (0.0001)	0.0044 (0.0001)
		0.95	2.7318 (0.0702)	0.0054 (0.0001)	0.0010 (0.0009)
	HPCL	0.75	0.4707 (0.0021)	0.0046 (0.0001)	0.0075 (0.0001)
		0.80	0.6836 (0.0052)	0.0045 (0.0001)	0.0072 (0.0001)
		0.85	1.0195 (0.0061)	0.0044 (0.0001)	0.0062 (0.0001)
		0.90	1.5962 (0.0135)	0.0044 (0.0001)	0.0050 (0.0002)
		0.95	2.7295 (0.0322)	0.0047 (0.0001)	0.0023 (0.0001)
White	CL	0.75	0.7650 (0.0536)	0.0066 (0.0001)	0.0213 (0.0015)
		0.80	1.2149 (0.0206)	0.0059 (0.0001)	0.0213 (0.0007)
		0.85	1.6683 (0.0171)	0.0054 (0.0000)	0.0197 (0.0003)
		0.90	2.4974 (0.0137)	0.0052 (0.0001)	0.0147 (0.0004)
		0.95	4.2829 (0.0737)	0.0055 (0.0001)	0.0082 (0.0011)
	HP	0.75	0.3866 (0.0023)	0.0052 (0.0001)	0.0085 (0.0001)
		0.80	0.5810 (0.0044)	0.0050 (0.0001)	0.0085 (0.0001)
		0.85	0.8827 (0.0057)	0.0049 (0.0000)	0.0076 (0.0000)
		0.90	1.4347 (0.0114)	0.0050 (0.0001)	0.0052 (0.0001)
		0.95	2.5403 (0.0316)	0.0053 (0.0001)	0.0023 (0.0005)
	HPCL	0.75	0.3817 (0.0076)	0.0052 (0.0001)	0.0082 (0.0001)
		0.80	0.5684 (0.0087)	0.0051 (0.0001)	0.0086 (0.0002)
		0.85	0.8837 (0.0230)	0.0048 (0.0001)	0.0074 (0.0000)
		0.90	1.3813 (0.0088)	0.0049 (0.0001)	0.0051 (0.0002)
		0.95	2.5147 (0.0715)	0.0054 (0.0001)	0.0011 (0.0003)

starches, the ranking was CL > HP > HPCL. Furthermore, the starches showed different deformation because of pressure. Pressure plasticity (e) increased with increasing $\rho_{\mathrm{rel,max}}$ for Bitter and Chinese while it decreased for Water and White. Increasing pressure plasticity indicates greater pressure-dependent deformation while decreasing pressure plasticity indicates more resistance of the materials to the increase in pressure. The difference in pressure-dependent deformation can be attributed to the different particle sizes and shapes as presented in Figure 3 and Table 5. This indicates a change in the nature of the particles of modified White and Water compared to the native forms of the starches and may be responsible for the improved swelling properties and decreased gelatinization temperatures. In general, the angle of torsion (ω) for all modified *Dioscorea* starches was quite low, which indicates high elasticity of these materials[43]. The ranking of ω was CL > HP > HPCL, which indicates that HPCL showed the highest elastic deformation while CL showed the lowest. The 3D plots appeared flatter compared to the native *Dioscorea* starches, which indicate homogenous bonding facilitating deformation, and this behavior is similar to the behavior of other well-known tableting materials such as microcrystalline cellulose[28,43]. It is notable that the CL starches showed slightly steeper plots and thus less homogeneous deformation compared with HP and HPCL. In summary, the modified starches exhibited higher elasticity and improved deformation compared to the native forms supported by the fact that the materials deformed more homogenously. This more homogenous deformation is similar to pregelatinized starches[43,44].

The slope of the Heckel plots indicates the total deformation of a material, and deformation increases with increasing slope of the Heckel equation[27]. The Heckel slopes of the modified starches are presented in Figure 6. The Heckel slope stayed almost constant at lower $\rho_{\text{rel,max}}$ but generally increased with increase in $\rho_{\text{rel,max}}$ at higher $\rho_{\text{rel,max}}$ as for the native *Dioscorea* starches[15]. The Heckel slope was lower for HP and HPCL compared to the native forms of the starches but similar to the CL forms. The ranking of the Heckel slope for the modified starches was CL > HP > HPCL except for Water for which the value was reversed. The ranking of the Heckel slope for the various *Dioscorea* species was in the order Water > White > Chinese > Bitter yam starch. Thus, the various forms of Water showed the highest deformation while those of Bitter exhibited the lowest values. This order is the same as for pressure plasticity (e) and supports the results obtained by 3D modeling.

The compaction and elastic energies determined by force-displacement profiles give an insight into the energies consumed during tablet formation. The results are shown in Figure 7. The order of the normalized compaction energy, $E2_{\text{norm}}$ (Figure 7a), for the modified starches was generally CL > HP > HPCL while the

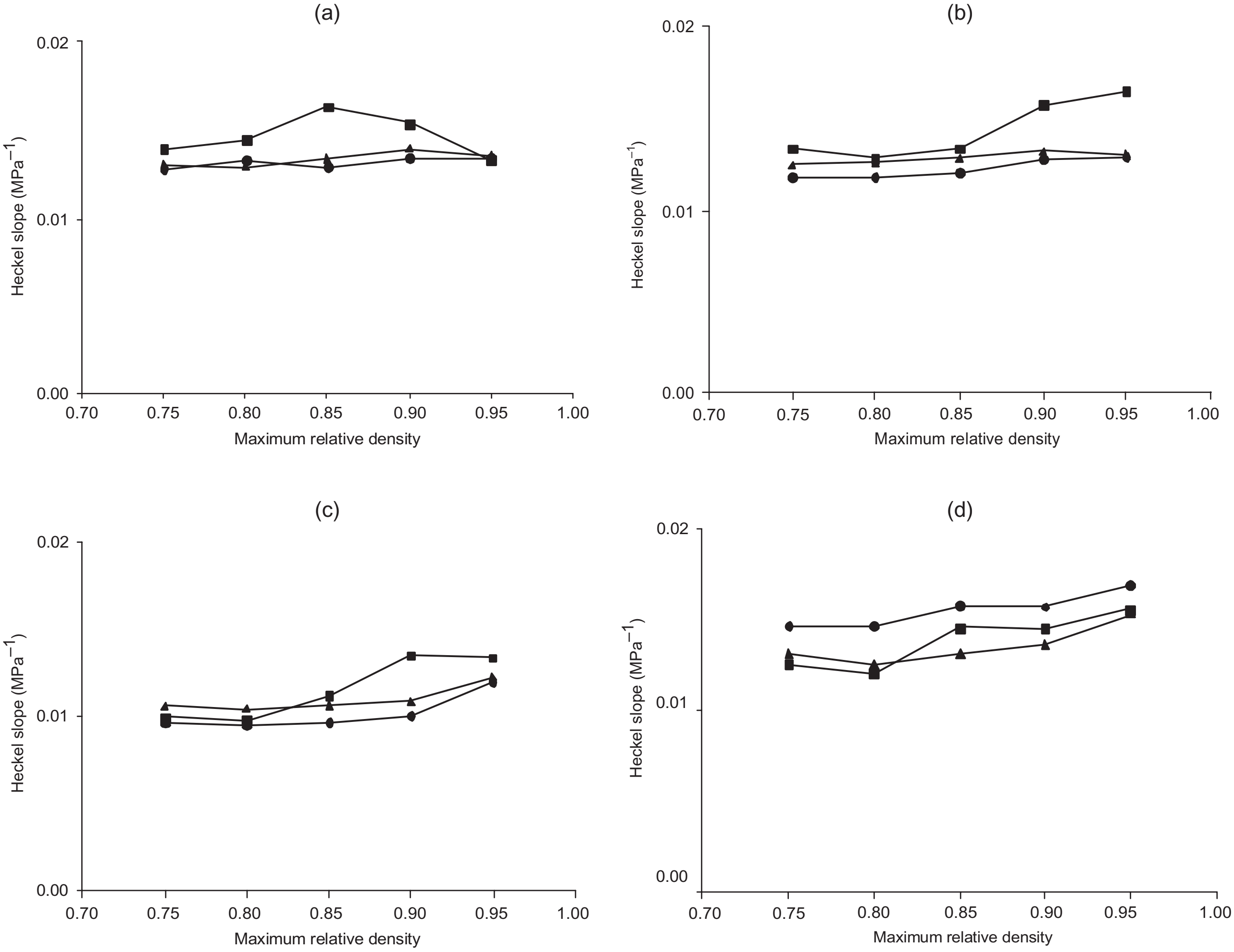

Figure 6. Heckel slope at different maximum relative densities of modified *Dioscorea* starches: ■, cross-linked; ▲, hydroxypropylated; and ●, hydroxypropylated cross-linked. (a) White, (b) Chinese, (c) Bitter, and (d) Water.

normalized elastic energy, $E3_{norm}$ (Figure 7b), was in the reverse order. This indicates that more compaction energy was involved in tablet formation for CL starches than for HPCL starches while more elastic energy was involved in HPCL starches. In addition, HPCL appears to be the most elastic material that is in agreement with the results from 3D modeling (ω-values).

The ER can be divided mainly into two parts, first, the ER between maximum compression until lifting of the upper punch from the tablet (fast ER) and, second, the ER during storage. To obtain an overview of when relaxation of the tablets occurred and when it was finished, the ER of the tablets was determined at various times, and the results are presented in Table 8. Generally, the modified starches showed complete elastic relaxation after 10 days, and the ER of the modified starches after this time was between 14% and 21%. The ER is high compared to the values obtained for the native forms of the starches[15] and indicates higher elasticity of the modified materials as already observed during tableting analysis. Furthermore, the fast ER increased with increasing $\rho_{rel,max}$, and the ER of the starch tablets increased with storage. The ER of the tablets varied considerably depending on the *Dioscorea* species and the

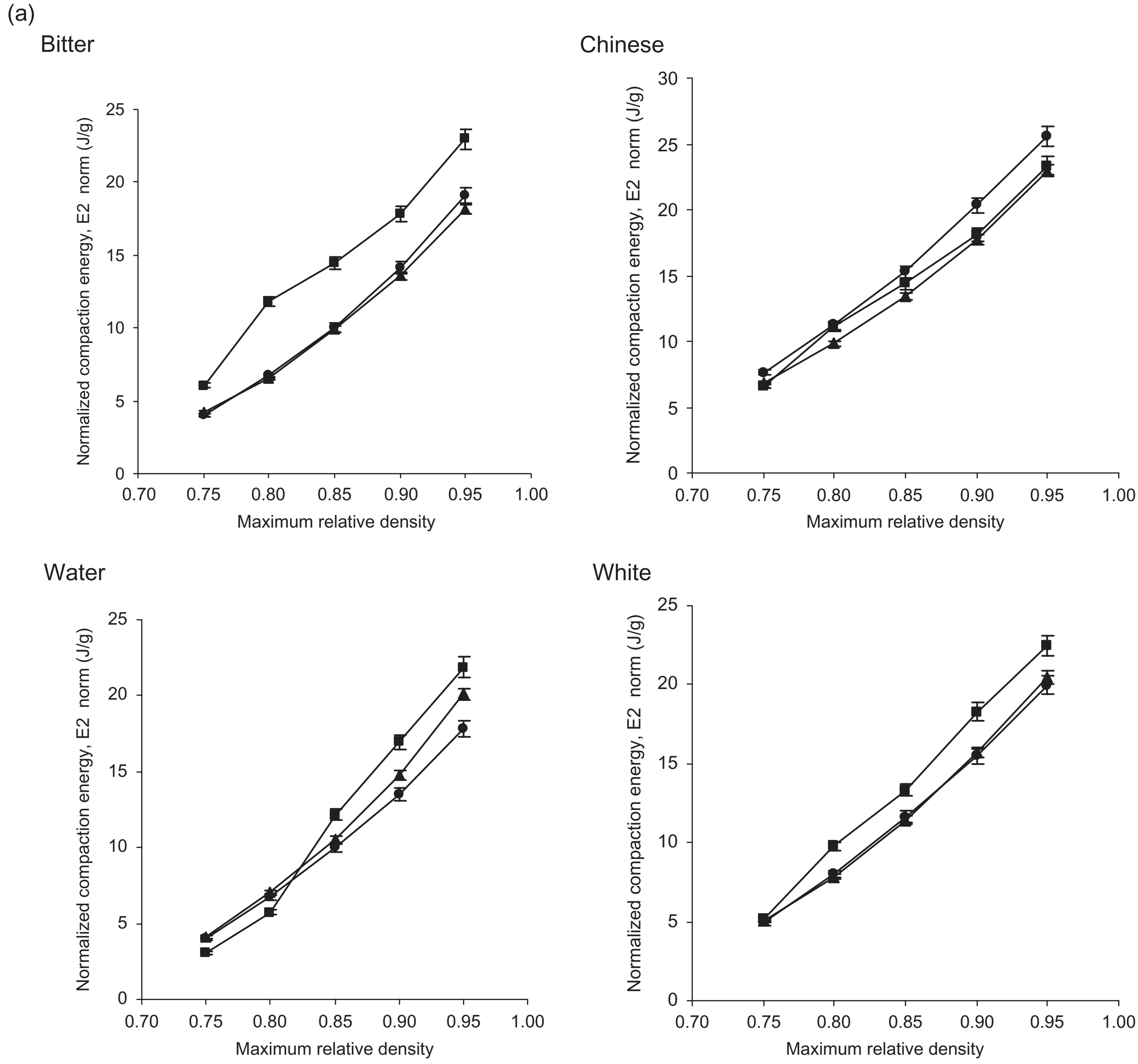

Figure 7. (a) Normalized compaction energy, E2, and (b) normalized elastic energy, E3, calculated from force-displacement profiles at different maximum relative densities for *Dioscorea* starches: ■, cross-linked; ▲, hydroxypropylated; and ●, hydroxypropylated cross-linked.

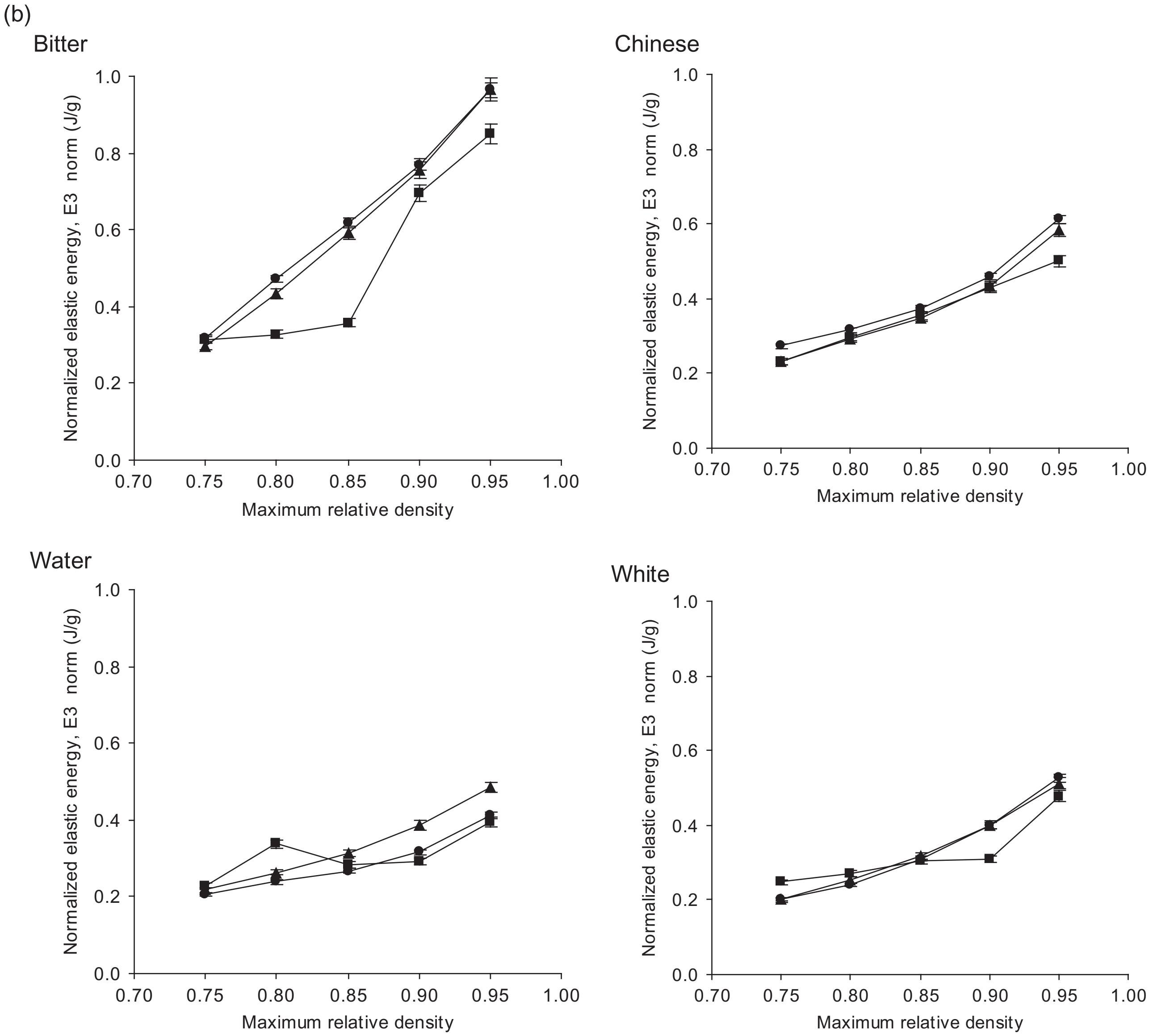

Figure 7. (*Continued*).

Table 8. Elastic recovery (ER) at different $\rho_{\mathrm{rel,max}}$ of modified *Dioscorea* starches (mean and SD, $n = 10$).

Starch	Modification	$\rho_{\mathrm{rel.max}}$	Fast ER (%)	ER after ejection (%)	ER after 1 hour (%)	ER after 10 days (%)
Bitter	CL	0.75	3.65 (0.50)	12.38 (0.18)	13.91 (0.13)	14.90 (0.78)
		0.80	3.86 (0.30)	13.59 (0.20)	15.30 (0.21)	16.70 (0.07)
		0.85	4.97 (0.03)	14.30 (0.20)	16.20 (0.18)	17.70 (0.12)
		0.90	5.54 (0.10)	14.71 (0.15)	16.60 (0.16)	18.24 (0.24)
		0.95	6.01 (0.07)	15.16 (0.30)	16.86 (0.28)	18.52 (0.06)
	HP	0.75	3.57 (0.56)	12.92 (0.29)	14.73 (0.33)	15.80 (0.40)
		0.80	4.18 (0.35)	14.04 (0.16)	16.04 (0.13)	17.30 (0.16)
		0.85	4.78 (0.33)	14.70 (0.12)	16.76 (0.09)	18.14 (0.09)
		0.90	5.15 (0.40)	15.35 (0.14)	17.38 (0.08)	18.82 (0.19)
		0.95	5.45 (0.37)	15.88 (0.24)	17.75 (0.12)	19.10 (0.19)
	HPCL	0.75	3.60 (0.56)	11.57 (0.15)	13.18 (0.13)	14.58 (0.13)
		0.80	4.34 (0.35)	12.76 (0.15)	14.60 (0.15)	16.09 (0.15)

(*Continued*)

Table 8. (*Continued*).

Starch	Modification	$\rho_{rel.max}$	Fast ER (%)	ER after ejection (%)	ER after 1 hour (%)	ER after 10 days (%)
		0.85	4.77 (0.33)	13.59 (0.08)	15.48 (0.12)	17.34 (0.29)
		0.90	5.04 (0.40)	14.12 (0.14)	16.05 (0.16)	17.98 (0.36)
		0.95	5.25 (0.37)	14.65 (0.16)	16.56 (0.18)	18.37 (0.20)
Water	CL	0.75	3.73 (0.05)	—	—	—
		0.80	4.14 (0.03)	—	—	—
		0.85	3.33 (0.03)	14.75 (0.35)	—	—
		0.90	2.95 (0.04)	15.08 (0.29)	17.45 (0.31)	—
		0.95	3.28 (0.03)	15.51 (0.33)	17.46 (0.19)	—
	HP	0.75	3.40 (0.06)	13.61 (0.17)	15.55 (0.25)	16.30 (0.31)
		0.80	3.31 (0.05)	14.16 (0.25)	16.15 (0.15)	16.94 (0.24)
		0.85	3.14 (0.03)	14.31 (0.23)	16.34 (0.17)	17.26 (0.12)
		0.90	2.89 (0.03)	14.00 (0.26)	15.95 (0.30)	17.02 (0.17)
		0.95	2.82 (0.07)	13.65 (0.30)	15.15 (0.26)	16.08 (0.22)
	HPCL	0.75	3.35 (0.05)	11.89 (0.26)	13.18 (0.16)	14.34 (0.39)
		0.80	3.33 (0.03)	11.85 (0.19)	13.40 (0.19)	14.25 (0.23)
		0.85	3.19 (0.03)	11.84 (0.25)	13.37 (0.18)	13.93 (0.14)
		0.90	2.83 (0.04)	11.73 (0.12)	13.32 (0.15)	13.93 (0.08)
		0.95	2.77 (0.03)	11.56 (0.24)	12.83 (0.19)	13.34 (0.10)
Chinese	CL	0.75	3.18 (0.06)	12.69 (0.23)	14.16 (0.15)	15.18 (0.18)
		0.80	3.39 (0.05)	13.18 (0.29)	14.86 (0.21)	15.69 (0.78)
		0.85	3.47 (0.03)	13.35 (0.26)	15.05 (0.17)	15.93 (0.12)
		0.90	3.62 (0.10)	13.72 (0.98)	15.07 (0.25)	15.88 (0.17)
		0.95	3.53 (0.07)	13.02 (0.17)	14.74 (0.18)	15.68 (0.11)
	HP	0.75	2.99 (0.04)	12.25 (0.56)	13.79 (0.28)	14.57 (0.20)
		0.80	3.23 (0.09)	12.73 (0.37)	14.36 (0.31)	15.07 (0.23)
		0.85	3.20 (0.13)	12.87 (0.16)	14.56 (0.15)	15.36 (0.06)
		0.90	3.02 (0.10)	12.85 (0.18)	14.49 (0.15)	15.32 (0.17)
		0.95	3.11 (0.17)	12.51 (0.22)	13.99 (0.29)	15.19 (0.41)
	HPCL	0.75	3.26 (0.04)	11.79 (0.21)	13.47 (0.31)	14.24 (0.21)
		0.80	3.17 (0.11)	12.01 (0.18)	13.85 (0.16)	14.99 (0.15)
		0.85	3.06 (0.04)	12.01 (0.18)	13.96 (0.22)	15.12 (0.11)
		0.90	3.06 (0.02)	12.15 (0.20)	13.79 (0.28)	15.07 (0.36)
		0.95	3.27 (0.03)	11.65 (0.22)	13.31 (0.13)	14.57 (0.14)
White	CL	0.75	5.03 (0.06)	16.19 (0.26)	18.01 (0.34)	—
		0.80	4.72 (0.05)	17.65 (0.30)	20.26 (0.19)	—
		0.85	4.74 (0.03)	17.79 (0.24)	20.30 (0.25)	21.22 (0.81)
		0.90	4.02 (0.02)	17.64 (0.35)	20.04 (0.29)	21.19 (0.19)
		0.95	4.57 (0.01)	16.70 (0.26)	18.90 (0.21)	20.28 (0.15)
	HP	0.75	3.22 (0.02)	14.86 (0.26)	16.88 (0.23)	16.00 (0.39)
		0.80	3.30 (0.03)	15.45 (0.29)	17.72 (0.27)	18.76 (0.54)
		0.85	3.30 (0.03)	15.84 (0.15)	17.92 (0.23)	19.13 (0.12)
		0.90	3.20 (0.10)	15.31 (0.29)	17.22 (0.26)	18.49 (0.28)
		0.95	3.20 (0.03)	14.66 (0.32)	16.47 (0.39)	17.51 (0.13)
	HPCL	0.75	3.12 (0.05)	14.90 (0.23)	16.85 (0.13)	-
		0.80	3.00 (0.05)	15.45 (0.35)	17.90 (0.34)	19.12 (0.42)
		0.85	3.03 (0.03)	15.45 (0.30)	18.17 (0.20)	21.00 (0.81)
		0.90	3.08 (0.04)	15.22 (0.34)	17.68 (0.28)	19.04 (0.21)
		0.95	3.16 (0.02)	14.92 (0.64)	16.88 (0.32)	19.00 (0.16)

type of modification carried out on the starches. The modified White starches generally showed higher ER after 10 days while modified forms of Bitter showed the lowest values. CL Water did not form intact tablets except at high $\rho_{rel,max}$, and the tablets were highly friable and tend to crumble after 24 hours.

The compactibility profiles of the starch tablets are shown in Figure 8. The results showed that the crushing

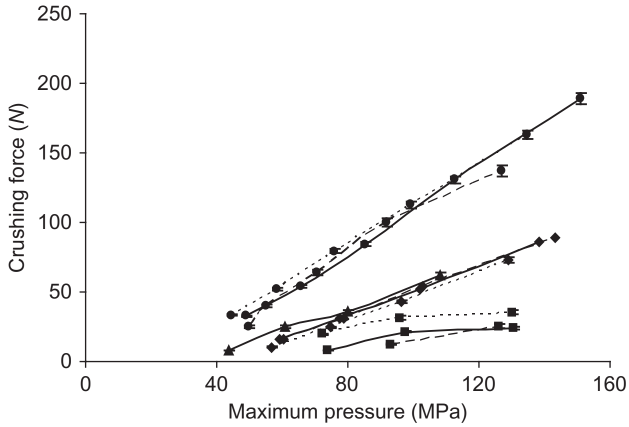

Figure 8. Compactibility plot of tablets made from (_ _ _ _) cross-linked, (----------) hydroxypropylated, and (____) hydroxypropylated cross-linked *Dioscorea* starches. ▲, Water yam; ◆, Bitter yam; ●, Chinese yam; and ■, White yam (mean and SD, $n = 5$).

force increased with compression pressure. Compared to the native forms of the starches[15], there was a significant increase in the crushing force of the tablets, indicating improved compaction properties of the modified starches. There were significant ($P < 0.01$) differences in the compactibility of the various starches. The crushing force at $\rho_{\mathrm{rel,max}}$ of 0.90, which is representative of commercial tablets, is shown in Table 9. The crushing force varied depending on the species and the type of modification carried out on the starches. Generally, the modified forms of Chinese showed the highest crushing force.

The disintegration time of the starch tablets at $\rho_{\mathrm{rel,max}}$ of 0.90 is also shown in Table 9. The ranking of disintegration time for the modified starches was HP > HPCL > CL while for the species, the ranking was Bitter > Chinese > White > Water. Modified White and Water disintegrated fast in less than 1 minute. However, modified Chinese and Bitter tablets disintegrated rapidly even though their crushing forces were very high, and the European Pharmacopoeia limit of 15 minutes for disintegration was not exceeded by all the starches. Thus, these results suggest that the starches could be used as disintegrants in tablet formulations.

Table 9. The crushing force and disintegration time (minutes) of modified *Dioscorea* starches at $\rho_{\mathrm{rel,max}}$ of 0.9 (mean ± SD, $n = 6$).

Starch	Modification	Crushing force (*N*)	Disintegration time (minutes)
White	CL	12.80 (4.44)	0.22 (0.00)
	HP	31.42 (2.88)	0.48 (0.28)
	HPCL	21.40 (1.82)	0.28 (0.02)
Chinese	CL	99.80 (1.30)	4.78 (0.32)
	HP	112.60 (1.79)	9.98 (0.97)
	HPCL	130.80 (1.79)	9.43 (0.15)
Bitter	CL	54.20 (3.70)	7.23 (0.24)
	HP	43.20 (1.30)	10.79 (0.62)
	HPCL	51.80 (1.48)	8.56 (0.40)
Water	CL	—	—
	HP	—	—
	HPCL	36.40 (1.31)	0.07 (0.01)

—, Not measurable.

Conclusion

The results obtained indicate that the physicochemical and material properties of the *Dioscorea* starches were affected by the chemical process of hydroxypropylation and cross-linking. The swelling properties of the starches were improved by the chemical treatment, and gelatinization temperatures and enthalpy were changed. The results of the sorption analysis show that cross-linking decreased the water sorption capacity of the starches while hydroxypropylation was shown to increase the sorption capacity of the CL starches. The powder-technological properties were similar to the native forms of the *Dioscorea* starches. The analysis of the tablet formation process by 3D modeling indicated that tableting materials with improved deformation properties were obtained by the modification of the starches. While being more elastic, the modified starches showed more homogenous deformation and thus bonding was facilitated. The improved bonding observed during tableting resulted in an increased compaction and thus higher crushing force even though all tablets disintegrated rapidly. This behavior was most expressed for Chinese. The HPCL forms of the starches exhibited the highest elasticity, and more elastic energy was involved in tablet formation.

In summary, the modified *Dioscorea* starches exhibited different physicochemical properties and water sorption capacity that influenced their tablet formation properties. The materials showed potentials for development as new excipients in solid dosage form design, and they could be useful as disintegrants or for soft tableting.

Acknowledgments

We gratefully acknowledge the Alexander von Humboldt Foundation for a Georg Forster Fellowship awarded to O.A. Odeku.

Declaration of interest: The authors report no conflicts of interest.

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