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Effect of high-pressure homogenization on structural, thermal and rheological properties of bambara starch complexed with different fatty acids

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The effect of high-pressure homogenization (HPH) on the degree of complexation of different fatty acids with bambara starch was studied. HPH significantly increased the complexation of bambara starch with palmitic, stearic, oleic and linoleic acids. However, saturated fatty acids generally showed higher complexing ability than unsaturated ones. For all fatty acids, bambara starch showed a higher complex index than corn and potato starches, which could be associated with the variation in amylose contents (22.5–31.5%). The formation of V-amylose crystalline materials was confirmed by XRD with peaks at 2θ = 7.4, 12.9 and 19.9°. Bambara starch–fatty acid complexes displayed significantly higher melting temperatures (95.74–103.82 °C) compared to native uncomplexed starch (77.32 °C). Homogenized bambara starch complexes were non-gelling while unhomogenized complexes produced weak gels, with $G' > G''$ in the range of 0.1–10 Hz. Complexation of bambara starch with fatty acids using HPH may be employed in the production of modified starch with non-gelling properties and higher thermal stability suitable for certain industrial applications.

Introduction

Starches are modified to make them suitable for most industrial applications. Modification improves starch resistance to extreme processing conditions such as shear and heat that are usually encountered in industry. Over the last few decades, starch has been modified by physical, genetical, enzymatic and chemical methods.[1,2] Chemical modification of starch seems to be the most widely used.[2] But most of these chemicals, for example, propylene oxide, are synthetically derived.[3] Currently, natural alternatives, such as the use of lipids, are being sought to produce clean label starches.

The structural and functional properties of a starch–fatty acid complex may vary with fatty acid type and concentration,[4–6] as well as processing conditions such as gelatinization time and temperature.[7–9] The interaction between added lipids such as fatty acids and starch as revealed by X-ray diffraction studies results in distinct V-type crystalline structure known as V-amylose complex.[10] Exarhopoulos and Raphaelides[6] studied the morphological and structural studies of thermally treated starch–fatty acid systems. The presence of fatty acids effectively retarded gelatinization process of maize starch, high amylose starch and pea starch.[6] Several starch modification processes using lipids such as fatty acids have been reported to improve starch functionality.[4,6,11,12] For example, rice starch showed restricted granule swelling, reduced solubility and lower rate of retrogradation with stearic acid addition.[4] Furthermore, starch–lipid complexes showed improved thermal stability compared to their native counterparts.[13,14] These changes in starch functionality are associated with the formation of amylose–inclusion complexes with added lipids. The rheological behaviour of starch complexed with fatty acid was investigated by Singh *et al.*[15] Stearic acid addition reduced the storage modulus (G') in corn starch and increased the same parameter in potato starch. However, the addition of myristic acid decreased the G' in both starches.[15] Thus, the rheological behaviour of various starches may depend on the starch source and fatty acid type.

Different methods have been explored in the preparation of starch–fatty acid complexes.[3,7–9] The main purpose for using these methods is to increase the degree of complexation of starch with fatty acids. D'Silva *et al.*,[3] found that the degree of complexation of teff starch with 0.25% stearic acid increased by approximately 83% when the holding time was increased from 5 to 120 min during starch pasting. The increase in complexation was attributed to prolonged interaction between the starch and stearic acid.[3] A promising method for increasing the degree of complexation of lipids with starch is the application of high-pressure homogenization (HPH) to gelatinized starch–fatty acid complexes. Previous research documented that the use of HPH

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can enhance the interaction between lipids and starch, resulting in better complexation.[16–20] Meng *et al.*,[17] found that HPH enhanced complexation of corn starch with fatty acids. Corn starch–fatty acid complexes prepared by HPH displayed higher complex index (almost double) compared to those prepared without homogenization.[17] However, the melting temperature of the complexes was not significantly affected by HPH.[17]

Most of the studies on V-amylose complex formation have focused on conventional sources of starch like maize[7,12,17,18] and potato.[13,15] However, pulse starches such as pea and bambara groundnut (*Vigna subterranea*), which are generally high in amylose are also promising base material for the formation of V-amylose complexes. Unlike pea starch, which has been reported to show some potential for industrial utilization,[6,21,22] starch from bambara have not been well researched. Bambara groundnut has potential for application in the industry, since it is a good source of starch (22–46%).[23–26] Depending on source and variety, the amylose contents of bambara starch have been found to vary between 20 and 35%.[23,26–28] A recent study conducted in our laboratory showed that pasting bambara starch with stearic acid, linoleic acid and lysophosphatidylcholine produced type I V-amylose complex which was confirmed by XRD.[29] However, the preparation of bambara starch–fatty acid complexes using HPH is not known. Complexing bambara starch with fatty acids using HPH may be important to enhance its industrial potential and further promote utilization. Hence, this study investigated the effect of high-pressure homogenization on physicochemical properties of bambara starch complexed with different fatty acids.

Materials and methods

Experimental materials

Bambara groundnut was obtained from Markathini Research station, Jozini KwaZulu-Natal province, South Africa. Potato starch was obtained from Sigma-Aldrich (St. Louis, MO). Corn starch and fatty acids: palmitic, stearic, oleic and linoleic acids were purchased from Aladdin Chemistry Company (Shanghai, China).

Starch extraction and amylose contents determination

Starch was extracted from bambara flour as described by Oyeyinka *et al.*[23] The amylose contents of extracted bambara starch and those of corn and potato starches were 31.5%, 22.5% and 24.6% respectively, as determined by iodine binding method.[30]

Preparation of starch–fatty acid complexes by high-pressure homogenization

Starch–fatty acid complexes were prepared as previously reported by Meng *et al.*,[18] except that fatty acids were added in concentration of 0, 1, 2, 3 and 4% to bambara starch (dry weight basis). Starch–fatty acid mixtures were heated with constant stirring in a water bath at 95 °C for 20 min. The resulting starch–fatty acid pastes were homogenized using high-pressure homogenizer (APV2000 SPX, Germany) at 100 MPa for three passes. A portion of homogenized starch–fatty acid pastes was freeze-dried, while another portion was used for rheological measurement. Unhomogenized complexes were prepared in the same way as homogenized complexes but without homogenization. Corn and potato starches were included as reference samples.

Analyses

Complex index

The extent of complex formation between starch and fatty acids were determined as previously reported.[18] The complex index (CI), which is a measure of reduction in iodine binding capacity, was evaluated using eqn (1). The CI was determined at different fatty acid concentrations. After establishing the range of fatty acids for maximum complexation, structural; XRD, thermal and rheological properties of starch–fatty acid complexes were determined at 4% fatty acid concentration as described in sections below.

$$\mathrm{CI}\% = \frac{100 \times (\text{absorbance of reference} - \text{absorbance of sample})}{\text{absorbance of reference}} \tag{1}$$

reference: starch samples without fatty acids, sample: starch with fatty acids.

X-ray diffraction

X-ray diffraction (XRD) of starch–fatty acid complexes was conducted using Empyrean PANalytical diffractometer (Netherlands). The diffractometer operated at 40 kV with a target current of 40 mA. Scanning was done from 5° to 30° (2θ) with an exposure time of 16 min 14 s, step size of 0.026° and a time/step ratio of 229.5 s.[12]

Thermal properties of dried starch–lipid complex

Thermal properties of starch–fatty acid complex were examined as previously described.[20] Briefly, pasted freeze-dried complexed starch (3 mg) was directly weighed into the aluminum DSC pan and distilled water (9 µl) added. Pans were hermetically sealed and equilibrated for 24 h. Equilibrated pan containing the samples were directly heated from 20 to 140 °C at a rate of 10 °C min^{-1}. An empty pan was used as reference.

Rheology

The viscoelastic properties of starch gels were determined as previously reported.[20] Briefly, the viscoelastic properties of the gels were measured at 25 °C and a strain of 1% which was in the range of the linear viscoelastic region using a Rheometer (KNX2210 Malvern, UK). The spectra was obtained by recording storage modulus (G') and loss modulus (G'') as a function of angular frequency in the range 0.1 to 10 Hz.

Statistical analysis

All analyses were conducted in triplicate. Data were analyzed using analysis of variance (ANOVA) and means were compared using Fischer's Least Significant Difference Test ($p < 0.05$).

Results and discussion

Complex index

Complex index (CI) of gelatinized bambara starch–fatty acid complexes, generally increased with increasing fatty acid concentration, reaching a plateau between 2 and 4% (Fig. 1A and B). The degree of complexation of bambara starch with fatty acids was affected by high-pressure homogenization (HPH) and fatty acids types. Homogenized bambara starch–fatty acid complexes displayed significantly higher CI (Fig. 1A) than

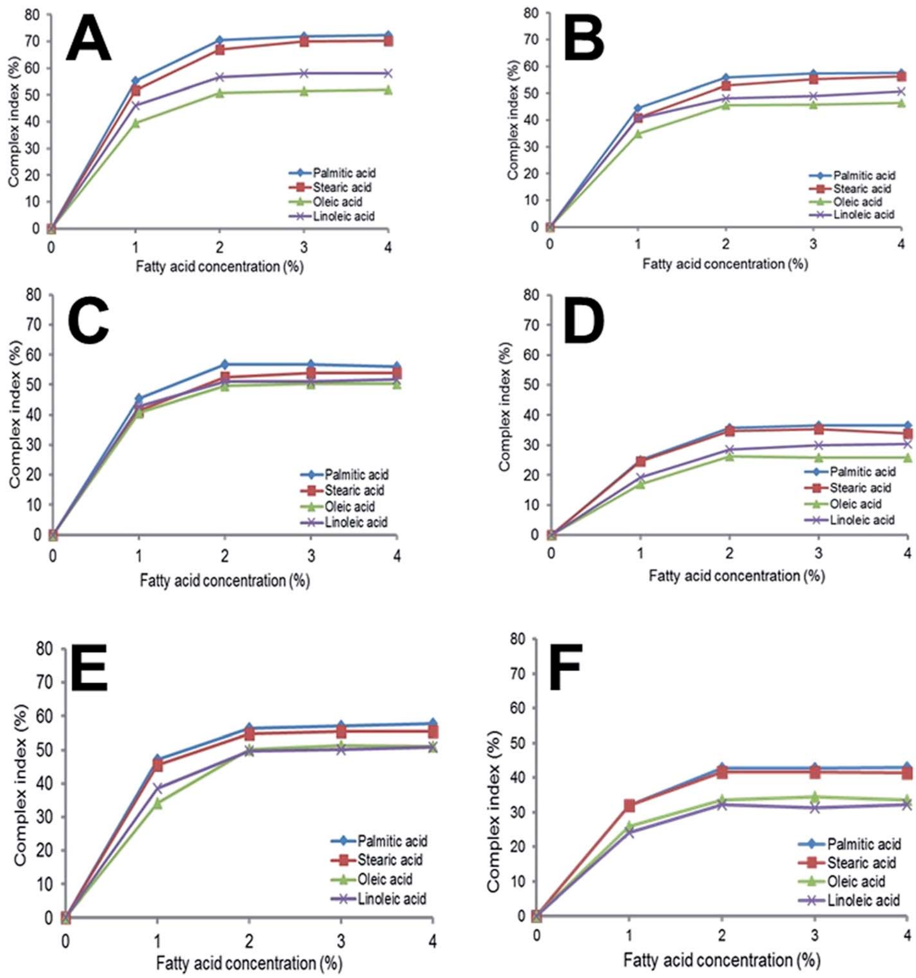

Fig. 1 Complex index of gelatinized bambara, corn and potato starches complexed with different fatty acids. (A): homogenized bambara starch–fatty acid complex, (B): unhomogenized bambara starch–fatty acid complex, (C): homogenized corn starch–fatty acid complex, (D): unhomogenized corn starch–fatty acid complex, (E): homogenized potato starch–fatty acid complex, (F): unhmogenized potato starch–fatty acid complex.

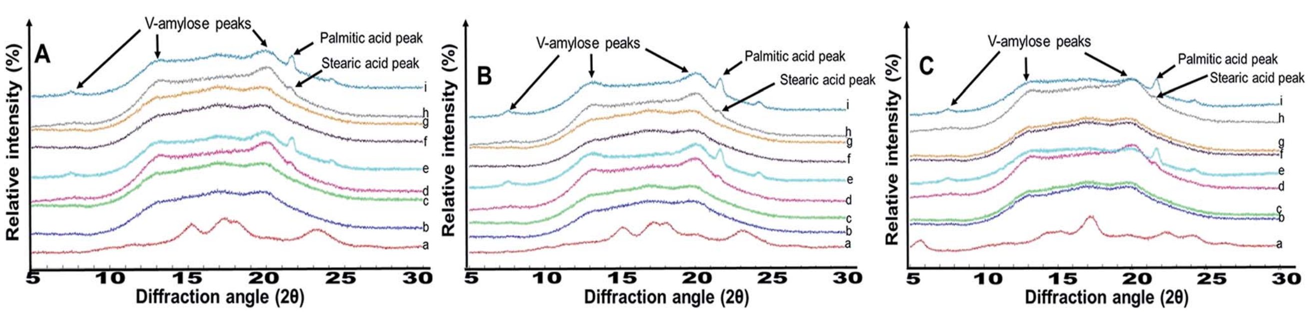

Fig. 2 XRD of gelatinized bambara, corn and potato starches complexed with different fatty acids. (A): bambara starch, (B): corn starch, (C): potato starch, (a): native starch, (b): oleic acid, (c): linoleic acid, (d): stearic acid, (e): palmitic acid (unhomogenized complexes), (f): oleic acid, (g): linoleic acid, (h): stearic acid, (i): palmitic acid (homogenized complexes).

unhomogenized ones (Fig. 1B). This could be attributed to better dispersion of lipid in starch suspension during homogenization.[17,18,20] Furthermore, saturated fatty acids, palmitic and stearic showed higher CI than unsaturated fatty acids (*i.e.* oleic and linoleic acids), even when unhomogenized. Molecular rigidity introduced by the presence of double bonds in unsaturated fatty acids have been reported to hinder access to the amylose helix[4,19] and thus reducing CI as observed for bambara-starch–fatty acid complexes. Our result is in agreement with previous research where *cis*-unsaturated fatty acids complexed poorly with amylose.[4,5,29] Homogenized corn (Fig. 1C) and potato (Fig. 1E) starch–fatty acid complexes showed similar CI trend. However, the CI values of corn and potato starches were lower than those of bambara starches. The amylose content of

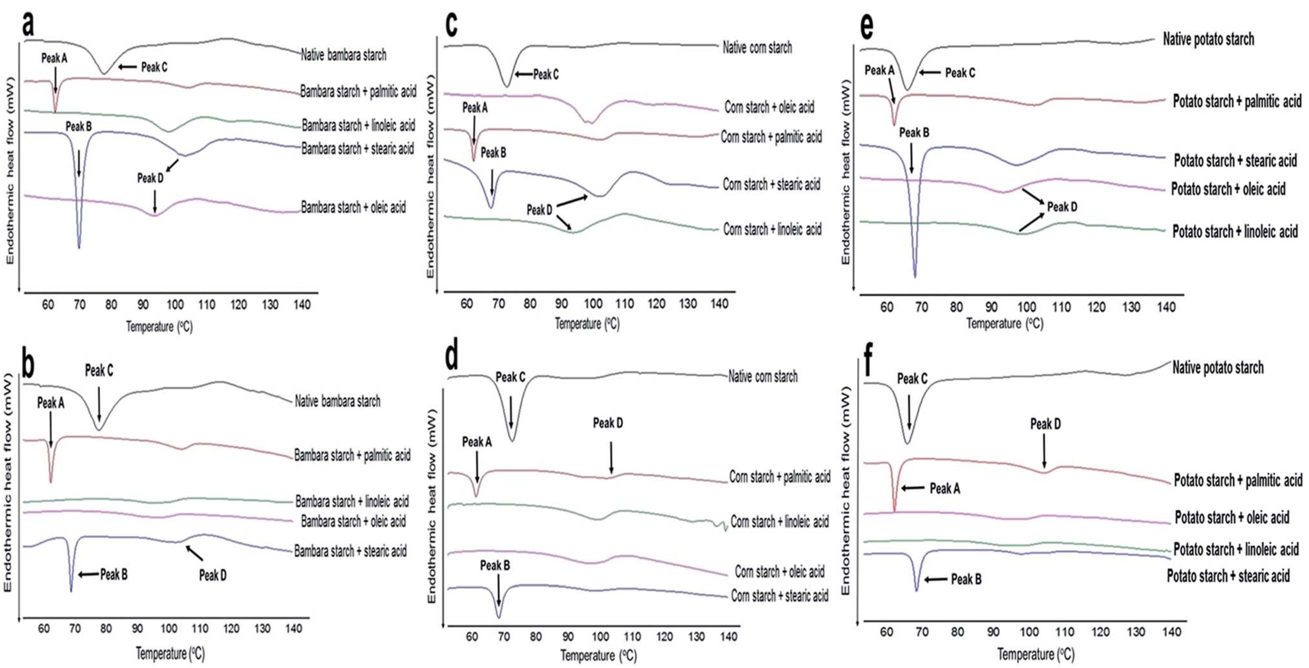

Fig. 3 Thermograms of gelatinized bambara, corn and potato starches complexed with different fatty acids. (a): homogenized bambara starch, (b): unhomogenized bambara starch, (c): homogenized corn starch, (d): unhomogenized corn starch, (e): unhomogenized potato starch, (f): homogenized potato starch.

Table 1 Thermal properties of gelatinized bambara, corn and potato starch–fatty acid complexes[a]

	Unhomogenized				Homogenized			
Fatty acid	T_o (°C)	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})	T_o (°C)	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})
Bambara starch								
Palmitic	$89.55^{bc} \pm 0.85$	$103.82^{a} \pm 0.71$	$107.69^{a} \pm 1.30$	$1.94^{a} \pm 0.06$	$95.21^{b} \pm 0.04$	$103.62^{a} \pm 0.46$	$108.26^{a} \pm 0.19$	$6.77^{a} \pm 0.04$
Stearic	$92.13^{b} \pm 0.01$	$101.81^{ab} \pm 0.94$	$106.96^{ab} \pm 0.62$	$1.63^{ab} \pm 0.54$	$95.97^{a} \pm 0.11$	$103.67^{a} \pm 0.26$	$112.02^{a} \pm 0.18$	$6.52^{a} \pm 0.02$
Oleic	$89.14^{bc} \pm 0.18$	$95.74^{c} \pm 2.02$	$104.22^{c} \pm 0.79$	$1.34^{abcd} \pm 0.71$	$85.72^{g} \pm 0.70$	$93.35^{d} \pm 0.04$	$100.10^{i} \pm 0.06$	$5.11^{b} \pm 0.14$
Linoleic	$89.04^{bc} \pm 0.17$	$97.34^{c} \pm 0.23$	$103.09^{d} \pm 1.38$	$0.86^{d} \pm 0.03$	$90.55^{d} \pm 0.04$	$97.83^{bc} \pm 0.09$	$106.14^{e} \pm 0.30$	$5.69^{b} \pm 0.01$
Corn starch								
Palmitic	$87.83^{cd} \pm 0.49$	$102.41^{ab} \pm 0.60$	$106.75^{abc} \pm 0.51$	$1.57^{abc} \pm 0.07$	$90.01^{de} \pm 0.16$	$102.39^{a} \pm 0.39$	$107.13^{d} \pm 0.17$	$6.76^{a} \pm 0.06$
Stearic	$90.04^{bc} \pm 0.11$	$97.99^{bc} \pm 0.47$	$105.22^{bcd} \pm 1.56$	$1.27^{bcd} \pm 0.02$	$92.35^{c} \pm 0.15$	$101.25^{a} \pm 0.19$	$109.06^{b} \pm 0.11$	$6.55^{a} \pm 0.06$
Oleic	$87.19^{cd} \pm 1.79$	$94.39^{c} \pm 1.42$	$104.24^{d} \pm 0.49$	$0.97^{cd} \pm 0.06$	$84.93^{h} \pm 0.02$	$92.56^{d} \pm 2.35$	$103.82^{g} \pm 0.74$	$5.41^{a} \pm 0.14$
Linoleic	$87.93^{cd} \pm 0.29$	$98.31^{bc} \pm 0.98$	$104.51^{cd} \pm 0.55$	$0.92^{d} \pm 0.08$	$91.69^{c} \pm 0.31$	$99.48^{b} \pm 0.27$	$105.03^{f} \pm 0.29$	$5.45^{b} \pm 0.05$
Potato starch								
Palmitic	$95.60^{a} \pm 0.59$	$103.86^{a} \pm 0.45$	$108.43^{a} \pm 0.04$	$1.63^{ab} \pm 0.04$	$90.40^{b} \pm 0.72$	$102.24^{a} \pm 0.28$	$105.24^{f} \pm 0.02$	$5.87^{b} \pm 0.06$
Stearic	$92.28^{b} \pm 0.05$	$97.94^{bc} \pm 0.35$	$104.88^{bcd} \pm 0.28$	$1.43^{abcd} \pm 0.01$	$86.74^{f} \pm 0.04$	$96.27^{c} \pm 0.43$	$106.48^{de} \pm 0.03$	$5.64^{b} \pm 0.24$
Oleic	$85.64^{d} \pm 1.29$	$95.74^{c} \pm 1.02$	$103.22^{d} \pm 0.62$	$0.82^{d} \pm 0.02$	$84.75^{h} \pm 0.04$	$92.78^{d} \pm 0.16$	$101.14^{h} \pm 0.76$	$4.81^{c} \pm 0.01$
Linoleic	$89.22^{bc} \pm 0.75$	$95.49^{c} \pm 1.06$	$103.72^{d} \pm 0.33$	$0.83^{d} \pm 0.01$	$89.74^{e} \pm 0.21$	$98.29^{b} \pm 0.08$	$106.48^{de} \pm 0.06$	$4.68^{c} \pm 0.05$

[a] Mean ± SD. Mean with different superscript letters along a column are significantly different ($p < 0.05$). T_o, T_m, T_c and ΔH_m are onset temperature, melting temperature, conclusion temperature and melting enthalpy respectively.

bambara starch (31.5%) was higher than those of corn (22.5%) and potato (24.6%) starches respectively. The variation in CI among these starches could be due to differences in their amylose contents.[31] Other factors such as the degree of polymerization of amylose[32,33] may also influence the degree of complexation.

XRD

The XRD pattern of native bambara starch showed the A-type crystallinity pattern with strong peaks at 15° (2θ), a doublet at 17° and 18° (2θ) and a single peak at 23° (2θ) (Fig. 2A). However, when bambara starch was gelatinized with fatty acids, XRD analysis showed peaks at $2\theta = 7.4$, 12.9 and 19.9° (Fig. 2A–C), which is in agreement with the XRD peaks observed for V-amylose in previous studies.[5,6,10,29] Similar V-amylose peaks were observed for corn (Fig. 2B) and potato (Fig. 2C) starch–fatty acid complexes. The peaks corresponding to V-amylose crystalline types were significantly ($p < 0.05$) higher for the homogenized starch–fatty acid complexes (Fig. 2A–C), further suggesting better complexation with HPH. Peaks at $2\theta = 22°$ and $2\theta = 24°$ were observed in bambara, corn and potato starches complexed with palmitic and stearic acids (Fig. 2A–C).

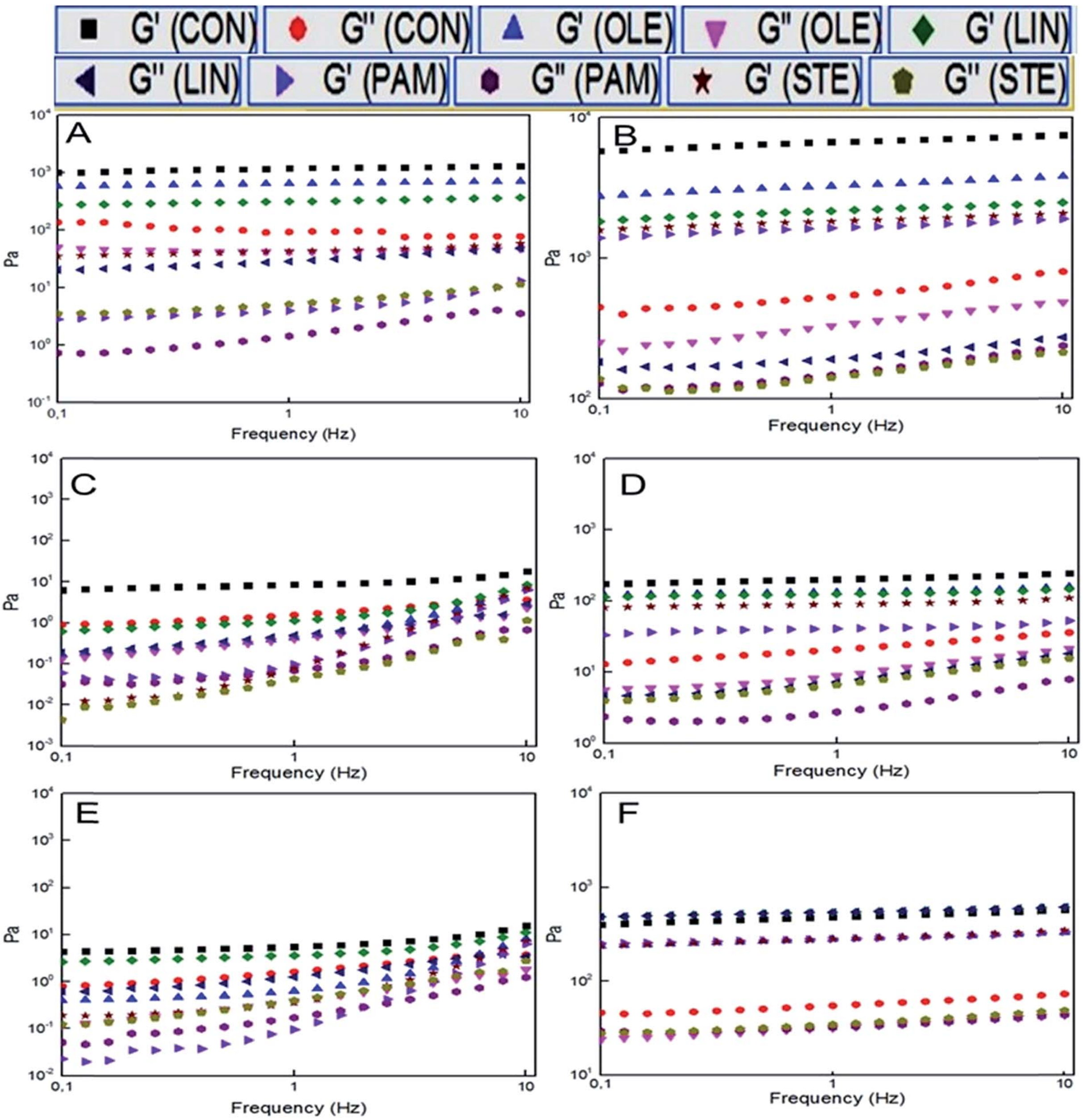

Fig. 4 Effect of high-pressure homogenization on viscoelastic properties of gelatinized bambara, corn and potato starch–fatty acid complexes, CON: control starch, OLE: starch + oleic acid, LIN: starch + linoleic acid, PAM: starch + palmitic acid, STE: starch + stearic acid, (A): homogenized bambara starch, (B): unhomogenized bambara starch, (C): homogenized corn starch, (D): unhomogenized corn starch, (E): homogenized potato starch, (F): unhomogenized potato starch.

These peaks suggests the presence of free fatty acid aggregates.[7,9,11,12]

DSC

The melting temperatures (T_m) of bambara starch complexed with fatty acids were generally higher than their native counterparts (Fig. 3a and b). Corn and potato starches displayed similar trend (Fig. 3c–f). Homogenized starch–fatty acid complexes displayed broader transitions than unhomogenized samples (Fig. 3). The T_m of bambara starch–fatty acid complexes varied from 93.35 to 103.82 °C (Table 1), which corresponds to the melting temperature of type I V-amylose complex.[34,35] According to Kawai *et al.*,[13] T_m represents the helical length of V-amylose complexes and indicates their physical stability. Homogenized bambara starch–fatty acid complexes including those of corn and potato reference samples displayed substantially higher ΔH_m values (4.68–6.77 J g^{-1}) than the unhomogenized ones (0.82–1.94 J g^{-1}) (Table 1). Previous studies reported that ΔH_m values of V-amylose complexes corresponds to the amount of complex and the degree of order within the complex.[13,36] The ΔH_m result is in agreement with the CI (Fig. 1) and XRD (Fig. 2). Fatty acid type significantly influenced the thermal stability of V-amylose complexes. Bambara starch complexed with saturated fatty acids (palmitic and stearic) displayed significantly ($p < 0.05$) higher thermal stability (*i.e.* > T_m) than those complexed with unsaturated fatty acids (oleic and linoleic). Differences in thermal stability could be linked to the double bonds of unsaturated fatty acids, which give a kink and allow for partial inclusion into the amylose helix cavity.[13,29,37]

Bambara, corn and potato starches complexed with palmitic and stearic acid showed additional transitions at approximately 62 °C (peak A) and 68 °C (peak B) respectively (Fig. 3a–f). These transitions may be attributed to the melting of free uncomplexed fatty acid. XRD results from this study (Fig. 2) also indicated the presence of free fatty acids. Similar results have been reported in the literature.[7,11,12]

Rheology

The viscoelastic behaviour of bambara starch gels was affected by HPH and complexation with fatty acids (Fig. 4A and B). The storage moduli (G') of bambara starch gels were generally greater than their loss moduli (G'') (Fig. 4A and B) in the frequency range of 0.1–10 Hz. Both G' and G'' showed a minor dependency on frequency. These results suggest that complexation produced weak gel structure, which is in agreement with previous studies.[38] Bambara starch–fatty acid complexes produced gels with reduced G' and G'' compared to their native starch gel counterparts. The reduction in G' and G'' in the presence of lipids has been associated with the formation of V-amylose complex.[15,20,39] Singh *et al.*,[15] also observed a reduction in G' and G'' of corn and potato starches complexed with myristic acid. In general, saturated fatty acids showed greater reduction in G' and G'' of bambara starch gels when compared to the unsaturated types. This could be linked to better complexation of bambara starch with saturated fatty acids as indicated by the CI (Fig. 1). Furthermore, bambara starch complexed with saturated or unsaturated fatty acids were non-gelling when prepared under homogenized condition. The non-gelling behaviour of starch paste with added lipids have also been observed in earlier studies.[3,20,40] Amylose–fatty acid complexes have been suggested to either prevent the formation or increase the spacing between junction zones. We hypothesize two major influence of HPH on the rheological behaviour of starch–fatty acid gels. First, the applied pressure during homogenization enhances better interaction with fatty acid. Also, the higher level of starch disintegration during HPH may also slow down the association of amylose during short term storage. Similar rheological behaviour were recorded for corn and potato starch gels. But the G' and G'' of bambara starch gels were generally higher than the reference starches. Pulse starches are generally characterized by stronger gels compared to cereal and tuber starches. For instance, cowpea starch showed higher gel strength and higher G' and G'' compared to corn and potato starches, which was attributed to the presence of longer amylose chains in cowpea starch.[41,42] Differences in amylose contents (22.5–31.5%) may also have influenced the rheological behaviour of studied starches. Biliaderis and Tonogai,[43] attributed the substantially higher G' of legume starch (pea and garbanzo bean) gels (with or without lipids) to their high amylose contents compared to rice and wheat starch gels.

Conclusions

High-pressure homogenization improved the degree of complexation of bambara starch with fatty acids. Bambara starch seemed to complex better with fatty acids than did corn and potato starches. Saturated fatty acids showed higher complexing ability with bambara, corn and potato starches than unsaturated fatty acids. Bambara starch formed type I V-amylose complexes with fatty acids. Starch–fatty acid complexes prepared under unhomogenized condition formed weak gels, while homogenized samples were non-gelling. Complexation of bambara starch with fatty acids using HPH may be employed to produce modified starch with improved thermal stability and non-gelling behaviour, that are more suitable for certain industrial applications.

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