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Research Paper

Improvement of Amphiphilic Properties of High and Low Amylose Rice Starch through Chemical and Physical Modification and its Functionality in an Emulsion System

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Abstract

Native rice starch has functional limitations such as poor solubility, heat tolerance, and emulsifying properties, which restrict its industrial applications. To address these deficiencies, this study investigated the modification of rice starch using octenyl succinic anhydride (OSA), followed by physical modifications like pre-gelatinization (PG) and granular starch (GS) treatments. High amylose (HA) and low amylose (LA) rice starches were sourced, modified, and characterized. The degree of substitution (DS) analysis revealed higher substitution in HA-OSA starch (0.012 ± 0.001%) than in LA-OSA starch (0.009 ± 0.001%). Functional properties like oil and water absorption, and water solubility were enhanced in PG starches compared to GS starches. Emulsion stability tests demonstrated that OSA-modified starches effectively stabilized oil-in-water emulsions, with HA-PG showing the highest elastic properties and stability due to its robust three-dimensional network formation. Light and confocal microscopy confirmed the complete covering of oil droplets by starch molecules, enhancing emulsion stability through steric hindrance. These findings suggest that OSA-modified rice starch, particularly HA-PG, is a promising alternative to synthetic emulsifiers, offering a green solution for the food, pharmaceutical, and personal care industries.

Keywords: Amylose, Emulsion, Functional properties, Granular rice starch, Pre-gelatinization

Introduction

The octenyl succinic anhydride (OSA) modification is a widely used modification that imparts hydrophobic properties by weakening the internal bonding that keeps granules together (Bhosale & Singhal, 2007). The hydroxyl groups of glucose molecules are substituted by the OSA groups in an aqueous medium, producing esters with both hydrophilic and hydrophobic molecules, incorporating them amphiphilic properties (Agama-Acevedo & Bello-Perez, 2017). The most attractive application of OSA starches may be as an emulsifier due to the structures of OSA starches play an important role in stabilizing the emulsion.

Modified starches, particularly OSA-modified starches, play a key role in various industries due to their ability to emulsify in complex systems. This modification process alters the starch molecule, making it a valuable emulsifier ingredient. Emulsions require the stable dispersion of oil and water, and OSA starches offer a natural, multifunctional alternative to traditional emulsifiers. They can act as emulsifiers, thickeners, stabilizers, and texture enhancers, making them ideal for formulators seeking versatile ingredients. The use of OSA starches extends beyond food to pharmaceuticals, cosmetics, and industrial applications. Their compatibility with various conditions and their natural origin makes them a desirable choice for formulators creating stable and high-performing emulsions that meet consumer demand for clean-label products.

The main objective of this research is to improve the stability and quality of food products by enhancing the uniform dispersion of oil and water phases in oil in water emulsion. The use of double modified starch as an emulsifier has seen limited exploration in published research. However, this novel approach holds significant potential for enhancing emulsion stability and functionality in food products.

Materials and Methods

Materials

'Pathum thani 1' is a high amylose (27.13%) (high amylose categorized 25-33%) rice cultivar and Jasmin rice is a low amylose (13.89%) (low amylose categorized 12-20%) rice kindly supplied by Watcharewan green farm, Thailand. Octenyl succinic anhydride (OSA) was purchased from Siam modified starch Pvt Ltd, Pathum Thani, Bangkok, Thailand.

Rice starch extraction

Rice starch was extracted following the procedure of Ranathunga *et al.* (2023a). Briefly, the alkaline steeping method was used using 0.2% NaOH aqueous solution for continuous stirring around 16 hrs. After several washing and centrifugation, residual starch pellet was neutralized. Finally, the resultant whitish starch pellets were dried at 45 °C for reaching moisture content around 10-12%. The dried starch sample was ground and sieved using 100 mesh size.

Chemical and physical starch modifications

Starch was chemically modified using octenyl succinic anhydride (OSA) followed by physical modification, cold water granular starch and pre-gelatinization,

by the method explained by Ranathunga & Suwannaporn (2023b). Briefly, OSA at a concentration of 3% based on the dry weight of starch was added stepwise in four equal portions at 15 min intervals. Throughout the modification process, the pH of the starch solution was maintained using 1M NaOH. The reaction was allowed to run for 6 hr followed by neutralization using 1M HCl. The resultant starch modified further in to cold-water granular starch with reacting with 3M aqueous NaOH solution. After several washing with alcohol followed by neutralization resulting a cold-water granular starch. Pregelatinized starch was produced by boiling of 10% starch solution in a water bath at 100°C for two and half hours followed by freeze drying. The modified starch samples were coded as high amylose octenyl succinic anhydride modified pre gelatinized starch (HA_OSA_PG), high amylose octenyl succinic anhydride modified granular starch (HA_OSA_GS), low amylose octenyl succinic anhydride modified pre gelatinized starch (LA_OSA_PG) and low amylose octenyl succinic anhydride modified granular starch (LA_OSA_GS)

Characteristics of starch

Degree of substitution (DS)

The degree of substitution of modified starch (only HA-OSA and LA-OSA starches) was measured using a chemical method following the procedure of Song *et al*. (2006). Procedure and calculation of degree of substitution was done accordingly.

Water solubility of Pregelatinized (PG) and Granular starch (GS)

The cold-water solubility was determined following the procedure of Chen *et al*. (2020) with some modifications. Precisely measured distilled water (100 mL) was added to the laboratory blender and 1 g of starch sample was added when the blender works at lowest speed for 30 sec. Then, the starch mixture was run at highest speed for 2 min. The mixture was transferred into a 250 mL centrifuge bottle and centrifuged at 3000 × g for 15 min. The supernatant (25 mL) was transferred to a pre-weighted stainless steel moisture evaporating dish. The mixture was dried in an oven at 120 °C until it gets constant weight. The water solubility was determined using the following Equation 1.

$$\text{Cold Water Solubility \%} = \frac{(\text{Weight (g) of solid in supernatant} \times 4)}{\textit{(Weight (g) of sample)}} \times 100 \quad (1)$$

Oil and water absorption capacity of PG and GS

The oil/water absorption of the modified samples was determined following the procedure of Ahmad, *et al*. (2020) with minor modifications. The starch samples (1 g) were mixed with 10 mL of sunflower oil/distilled water and continuously stirred for 30 min at room temperature. The slurry was centrifuged (Allerga X-22R, Beckman Coulter, City name, Country name) at 3000 × g for 10 min. The supernatant was decanted, and centrifuged tubes turn upside down to drain off free water and oil.

$$\text{Oil/water absoption capacity} \left(\frac{g}{g}\right) = \frac{(m_2 - m_1)}{m_2} \quad (2)$$

Where: m_2 is the residual weight (g), m_1 is the dry starch weight (g)

Emulsifying properties of starch

Preparation of emulsion

OSA starch was used in two forms granular and fully gelatinized for emulsion preparation. PG and GS starch suspensions were prepared at a concentration of 240 mg mL^{-1} (oil) with sodium azide as a preservative (0.02% as the weight of starch). The oil in water emulsion (O/W) with 25% sunflower oil was mixed with hand homogenizer (Ultra-Turrax T25, IKA-Werke GmbH & Co. Staufen, Germany) at 15,000 revolution per minute for 1 min. Then, it passed through a high-pressure homogenizer (HU-3.0, Delta Instruments lab homogenizer, City name, Taiwan) at 120 bars for 2 min. The emulsions were coded as HA-GS O/W, HA-PG O/W, LA-GS O/W, and LA-PG O/W, respectively.

Light and confocal laser scanning micrograph

The emulsion was diluted ten times and placed a drop of emulsion onto a glass slid and covered with a cover slip preventing trapping of air bubbles, and observed using light microscopy (Axioskop 2 plus, Cal Zeiss AG, Jena, Germany) at 20x magnification. The emulsions were observed through confocal microscopy (LAS × 5.1, Leica, Wetzlar, Germany). The dyes used to stain the samples were Nile red (CAS No. 7385-67-3, Sigma-Aldrich Co., St. Louis, MO, USA) with a concentration of 1 mg mL^{-1} in isopropyl alcohol for the oil phase, and Nile blue (CAS No. 3625-57-8, Sigma-Aldrich Co., St. Louis, MO, USA) 1mg/mL in Milli-Q water for OSA starch, respectively. The Nile red and Nile blue excitation wavelengths were set at 488 nm and 633 nm, respectively (Ge *et al*., 2017).

Particle size

The particle size distribution of the O/W emulsion was determined using a static light scattering instrument (Mastersizer 3000, Malvern Instruments Ltd., Worcestershire, UK). The relative refractive index of sunflower oil was set to 1.46. The absorbance value of the starch particles was 0.001. Each sample was run in triplicates.

Rheological properties of O/W emulsion

The emulsion rheology was measured using a stress-controlled rheometer (MCR302, Anton Paar, Graz, Austria). The geometry of 50 mm diameter stainless-steel parallel plate with 1 mm gap size. Emulsions (2.4 mL) were added to the "G" plate and rested for 10 min to equilibrate the temperature at 25 °C before starting the analysis. The gap was covered with low-density silicon oil to prevent dehydration. The measurements were taken as triplicates for each sample.

Small amplitude oscillatory shear (SAOS)

The SAOS analysis was carried out within the linear viscoelastic region (LVE). The frequency sweep was measured with a frequency ranging from 0.1 to 20 Hz at a constant strain of 1%. This was followed by an amplitude sweep test to find out the LVE region, using strain 0.1-1000% ramp logarithmic mode with a constant frequency of 1Hz at 25 °C.

Large amplitude oscillatory shear (LAOS)

The non-linear visco-elastic regime of oil in water emulsion was evaluated using LAOS. The oscillation amplitude was varied in the range of 0.1-1000 % at constant frequency

(1 Hz) at 20 °C. Lissajous plots were used to analyze the response of the emulsions. The viscos and elastic Lissajous plots calculated using the equation of Ewoldt *et al*., 2008.

Statistical analysis

All results were reported as the mean and standard deviation of three replicates. Analysis of variance (ANOVA) was performed using a completely randomized design. The difference in mean was determined by Duncan's multiple range test ($p < 0.05$) (IBM SPSS Statistics for Windows, Version 26.0, IBM Corp., City name, NY, USA)

Results and Discussion

Degree of substitution of starch

The degree of substitution (DS) is a key metric used to measure the extent of modification in starches, specifically indicating the number of hydroxyl groups replaced by other substituents. In a study employing the titration method, it was found that HA-OSA starch had the highest DS at 0.012 ± 0.001% , compared to LA-OSA starch, which had a DS of 0.009 ± 0.001%. This variation is attributed to the amylose content in the starch. Amylose, a major component of starch, plays a significant role in the substitution process. Previous research has shown that the amorphous regions of starch, which are less organized and less crystalline, are more easily substituted than crystalline regions (No *et al*., 2019).

Oil and water absorption and cold-water solubility

The oil absorption capacity (OAC) of PG and GS starches with high and low amylose content is illustrated in Table 1. There were insignificant differences in OAC between the two amylose groups for PG starch, with values of 4.20 ± 0.17 g oil/g dry starch for LA-PG and 4.24 ± 0.04 g oil/g dry starch for HA-PG. However, GS starches exhibited lower OAC than PG starches. This difference is attributed to the complete separation and fragmentation of starch molecules in PG, which increases the number of active sites for oil absorption. In contrast, the intact starch granules in GS restrict oil binding. HA-GS starch had a higher OAC (1.66 ± 0.05 g oil/g dry starch) than LA-GS starch (1.19 ± 0.02 g oil/g dry starch), related to the degree of substitution (DS) of OSA molecules, with higher DS in HA starches indicating a positive relationship between amylose content and OSA esterification (No *et al.*, 2019).

Table 1. Functional properties of starch

Starch types	Oil absorption Capacity (g/g)	Water absorption Capacity (g/g)	Water Solubility (%)
HA-PG	4.24 ± 0.04a	10.04 ± 0.08b	73.61 ± 0.78b
LA-PG	4.20 ± 0.17a	19.26 ± 0.13a	78.86 ± 1.38a
HA-GS	1.66 ± 0.05b	8.58 ± 0.01c	53.34 ± 1.06c
LA-GS	1.19 ± 0.02c	8.44 ± 0.25c	46.76 ± 1.32d

a-d different letter in the same column of the sample indicated significant difference ($p \leq 0.05$).

Water absorption capacity (WAC) reflects a starch's water-holding ability and viscosity. PG starches exhibited significantly higher WAC than GS starches, with LA-PG showing higher WAC (19.26 ± 0.13 g/g dry starch) than HA-PG (10.04 ± 0.08 g/g dry starch). GS starches had similar WAC values (8.44 ± 0.25 g/g dry starch and 8.58 ± 0.01 g/g dry starch). The higher WAC in PG starches is due to the fragmentation of starch granules, allowing more water absorption and higher solubility, unlike GS starches, where intact granules hinder water binding (Montesinos-Herrero *et al*., 2006). Contrarily, other research indicated that GS starches could exhibit higher water absorption due to structural changes (Li *et al*., 2014).

Water solubility varied significantly among modified starches, with the highest solubility in LA-PG starch (78.86 ± 1.38 %), followed by HA-PG starch (73.61 ± 0.78 %), HA-GS starch (53.34 ± 1.06 %), and LA-GS starch (46.76 ± 1.32 %). Cold-water solubility is influenced by molecular weight, branching degree, and amylose-to-amylopectin ratio (Singh & Kaur, 2004). Fragmentation during gelatinization enhances water absorption and solubility in PG starches compared to GS starches. While amylose content impacts cold-water solubility (Jivan *et al.*, 2014), other factors also contribute to starch solubility based on these findings.

Emulsifying properties of PG and GS

Light and confocal laser scanning microscopy

The light microscopy images of emulsion are illustrated in Figures 1A, B, C, and D. It was clear that all the fat globules of emulsion are covered with thick and viscous starch gels, which prevent the coalescence, hence producing the stable emulsion system.

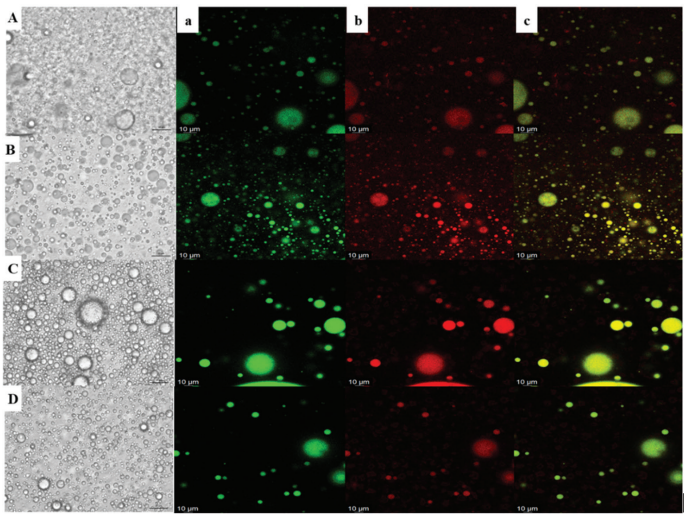

Figure 1. Microstructure images under the light microscope (50x); (A) HA OSA PG, (B) LA OSA PG, (C) HA OSA GS, and (D) LA OSA GS and Confocal laser scanning microscope (CLSM) images of a 25% sunflower oil O/W emulsion stabilized by modified starches. (a) The oil was stained with Nile red coded as green, (b) the starch phase was stained Nile blue and was coded red and (c) overlapping starch-rich and oil-rice regions appear yellow

Figures 1A, B and C show the confocal microscopic images of O/W emulsions stabilized by PG and GS. It was clearly seen that fat globules are completely covered with the viscous and thick continuous gel medium of emulsions in PG starch. The fat globules are trapped within the starch molecules which increases the stability through steric hindrance by the OSA-PG layer on the surface of oil droplets. The OSA-GS has intact starch granules which surrounded the oil droplets as in pickering emulsion. However, both type of starch is cold water soluble and the starch molecules in the continuous phase led to a developed three-dimensional network that retard the movement of fat droplets. A similar observation was reported by Hedayati *et al*. (2020). Since OSA-PG is more amphiphilic than the OSA-GS (results of water absorption and Oil absorption), when oil droplets were dispersed in the aqueous phase by homogenization, both types of starch first adsorbed to the oil/water interface to stabilize the oil droplets, and excess was dispersed in the aqueous phase. In these images, Nile blue was used to stain OSA-starch (PG and GS) and is denoted as red colour. Nile red was used for the oil phase and is coded as green colour. The overlay of images a and b presented as yellow colour in the image confirmed that oil droplets are covered completely by the starch particles. It is clearly seen in the overlay images that starch particles occupied the interface of the oil in water (Figure 1c). Therefore, the emulsions are highly stable due to steric hindrance by the starch molecules and higher viscosity of aqueous phase (Jo *et al*., 2021).

Particle size distribution of emulsion

Figure 2 reveals a key finding: emulsions stabilized with low amylose (LA) starches, regardless of modification (granular starch, GS; pre-gelatinized, PG), produced significantly smaller droplets compared to high amylose (HA) starches. Notably, LA-GS emulsions recorded the lowest droplet size (average diameter of 15.4 µm), followed by LA-PG (16.2 µm). This phenomenon can be attributed to the higher viscosity of LA starches. Their dominant amylopectin content creates a more viscous environment, effectively trapping oil droplets and hindering their movement and potential expansion. This trapping mechanism contributes to the smaller droplet size observed in LA starch emulsions.

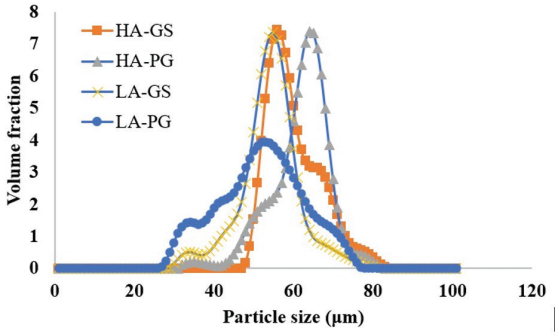

Figure 2. Droplet size distribution of O/W emulsion stabilized with 6% modified starch concentration

HA starches, on the other hand, HA-GS and HA-PG emulsions displayed nearly double the droplet size compared to their LA counterparts (31.4 μm and 36.1 μm, respectively). While this might seem disadvantageous of having large droplet size, it is important to consider potential benefits of HA starches. Their high amylose content could contribute to improved emulsion stability, a crucial factor for long-term product quality. It is important to acknowledge that the emulsification process itself can also influence droplet size. The high energy used during processing can lead to the degradation of starch molecules, potentially affecting their emulsifying properties (Nilsson & Bergenståhl, 2006). Optimizing processing conditions to minimize starch degradation could be a future area of exploration to achieve smaller droplet sizes while maintaining the potential benefits of HA starches.

SAOS measurements of O/W emulsion

This study investigated the rheological properties of oil-in-water (O/W) emulsions stabilized by different starches, focusing on their behavior within and beyond the linear viscoelastic (LVE) regime. Small amplitude oscillatory shear (SAOS) measurements revealed valuable insights into the elastic and viscous contributions of these starches. The frequency sweep revealed that key finding lies in the superior elastic properties exhibited by emulsions stabilized with high amylose (HA) starches, particularly HA-PG. Under LVE conditions (1% strain), HA-PG emulsions displayed the highest elastic modulus (G') compared to all other emulsions, exceeding 100 Pa (Figure 3A). This signifies a more rigid and structured system. Interestingly, HA-PG even surpassed HA-GS emulsions (around 80 Pa), highlighting the crucial role of amylose content. The HA-PG starch showed larger LVE region compared to HA-GS starch incorporated emulsion system (Figure 3B).

SAOS measurements not only quantified elasticity but also shed light on the interaction between starch and emulsion droplets. HA-PG emulsions demonstrated a stronger interaction, with oil droplets acting as “active fillers”. These droplets actively participate in the gel network formed by HA-PG, further enhancing its rigidity. This behavior likely stems from the formation of amylose-lipid inclusion complexes within HA-PG, which facilitate stronger interactions with the oil phase. Furthermore, the higher water absorption capacity (WAC), oil absorption capacity (OAC), and water solubility of HA-PG compared to HA-GS contribute to its superior performance. These properties enable HA-PG to form a more extensive and robust network within the emulsion.

In contrast to HA starches, LA-PG emulsions exhibited a distinct rheological profile in frequency sweep and amplitude sweep measurement (3 A1 and 3 B1). They displayed a higher viscous modulus (G'') compared to G', indicating a more viscous and energy-dissipating character (Figure 3A1). This suggests that LA-PG acts as an “inactive filler”, with minimal interaction between the starch and oil droplets. The lower amylose content and dominance of amylopectin in LA-PG likely contribute to this behavior, as amylopectin possesses a more branched structure with less network-

forming potential. LA-GS emulsions, however, presented a more balanced profile (Figure 3B1). They displayed higher G' compared to G'', indicating some elastic character. This could be attributed to the amphiphilic nature of intact LA-GS granules, allowing them to absorb both oil and water and become embedded within the network formed by leached-out starch molecules.

This study underscores the importance of amylose content in starch for designing emulsions with superior elasticity. HA starches, particularly HA-PG, promote the formation of a rigid network through active filler interactions and amylose-lipid complex formation. On the other hand, LA-PG exhibits a more viscous character due to its limited network-forming ability. By understanding these rheological differences, researchers can select the most suitable starch type to achieve desired functionalities in O/W emulsions.

Large amplitude ocsillatory shear (LAOS) of emulsions

The non-linear viscoelastic (NLVE) regime is used to simulate processing conditions during industrial applications because materials undergo significant deformation. As strain increases beyond the linear viscoelastic (LVE) limit, the ellipsoidal shape of the stress-strain curve distorts to become nearly quadrilateral. This shift indicates a change from elastic-dominated behaviour to viscous-dominated behaviour. This phenomenon can be attributed to the destruction of the material's microstructure and altered flow characteristics (Liu *et al.*, 2021).

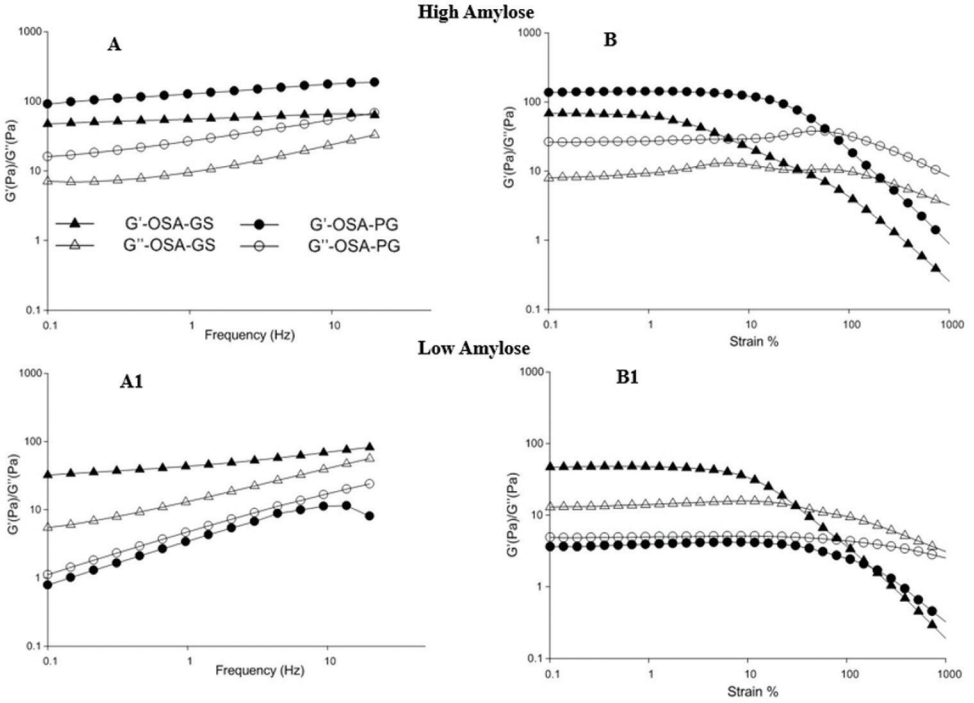

Figure 3. SAOS measurements of emulsions stabilized with GS and PG starches; Frequency sweep (A, A1), Amplitude sweep measurements (B, B1)

Large amplitude oscillatory shear (LAOS) offers various techniques to assess these changes in materials. These techniques include Lissajous plots, stress-strain deformation analysis, and Fourier-transform rheology. Each technique can help separate the structural properties and flow behaviour of the material as a function of non-linear stress (Liu *et al*., 2021). In this study, Lissajous plots were employed to elucidate the changes observed in the NLVE regime of the emulsions.

The HA-PG and GS emulsions exhibited weakly overshooting behaviour (Figure 3B), which was not observed in the LA starch emulsions (Figure 3B1). The sudden hike of G'' of the amplitude sweep test (overshoot) phenomenon arises from the formation and destruction of clusters or new bonds during shearing within a colloidal suspension. However, this thickening effect is temporary. In HA starches, amylose molecules play a crucial role in developing these network structures, which is absent in LA starches. LA starches displayed type I non-linear behaviour, where both G' (elastic modulus) and G'' (loss modulus) decrease with increasing strain (Figure 3B1).

The elastic Lissajous plots (Figures 4 A1-2, 4 B2) revealed an ellipsoidal shape for all emulsions except LA-PG (Figure 4 B1) at low strain (0.67% and 3.31%),

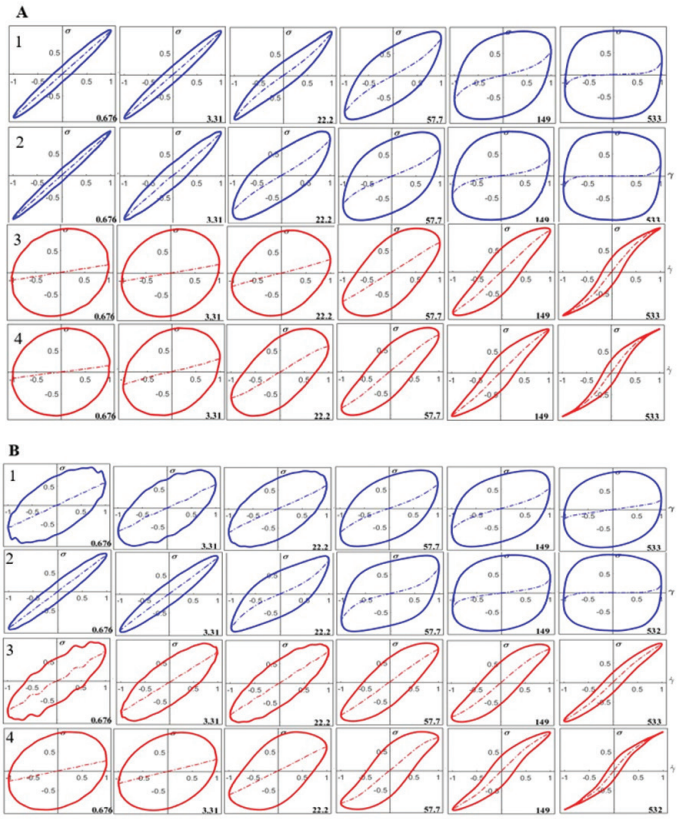

Figure 4. Normalized Lissajous curves of A 1 and 3, A 2 and 4 for elastic and viscous curves of HA -PG and HA- GS emulsions and B 1 and 3, B 2 and 4 for elastic and viscous curves of LA -PG and LA- GS elastic and viscous Lissajous plots at 0.68%, 3.31%, 22.2%, 57.7%, 149% and 533% at 20 °C of O/W emulsion stabilized by modified starches

indicating elastic dominance. In contrast, the LA-PG-O/W emulsion displayed a more expanded oval shape at low strain, suggesting viscous dominance (Figure 4 B1). This could be attributed to the higher water absorption capacity of LA-PG starch, leading to a weaker structure due to the lack of amylose molecules and its inability to form a rigid network. Additionally, LA-PG starch behaves as an inactive filler, lacking strong interactions with both oil droplets and other starch molecules.

As strain increases, the Lissajous plot shape progressively transitions from elliptical to rhomboidal and finally to a more rectangular shape, signifying plastic flow behaviour. However, HA-PG exhibited a narrower loop with minimal strain hardening compared to the other emulsions. This observation suggests that the higher amylose content in HA starches facilitates the development of a rigid three-dimensional network within the continuous phase. The middle dashed line in the plots represents the elastic contribution to the total stress. At the minimum strain, the slope of this line approaches zero, indicating the destruction of the material's microstructure.

The viscous Lissajous plots (Figures 4 A3-4, 4 B3-4) depict the viscous contribution to the total stress. At lower shear rates, all emulsions except the LA-PG starch stabilized emulsion exhibited a round shape, signifying elastic dominance. As the shear rate increased, the shape transformed into a sigmoidal shape, indicating a more viscous or shear-thinning behaviour at high shear rates.

Conclusions

Modifying starch with OSA, especially high amylose OSA-PG, creates a powerful natural emulsifier for oil-in-water mixtures. These starches form a stable network around oil droplets, resulting in emulsions with smaller droplet size and elastic texture. Compared to other starches, HA-OSA-PG showed the best performance. This research suggests OSA-modified starches, particularly HA-OSA-PG, hold promise as a sustainable substitute for synthetic emulsifiers in food and cosmetics. Further studies are needed to confirm long-term stability and effectiveness in complex food systems.

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