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Dynamic rheological and morphological properties of Phosphorylated, hydropropylated and dual modificated wheat starch

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Abstract

In this study, dynamic rheological properties of wheat starch gels as a function of starch chemical modification (Phosphorylation, hydroxypropylation and dual modification) were studied. The hydroxypropyl-phosphorylated and hydroxypropylated wheat starch gels had higher dynamic modulus (storage modulus (G') and loss modulus (G")) compared to the native and Phosphorylatedwheat starches. All of treatments showed higher elastic modulus than those for control that led to lower tangent values than 1. Unlike the native and phosphorylated wheat starches samples which exhibited an intermediate behavior between a weak and an elastic gel, the hydroxypropylated and hydroxypropyl-phosphorylated samples relatively showed an elastic gel behavior. The results of creep-recovery test illustrated that the stronger starch gel samples, which had greater resistance to deformation had smaller, creep compliance values. The results explained that the hydroxypropylated and hydroxypropyl-phosphorylated wheat starches had specific dynamic rheological properties which make it different for applied in different gel-like foods.

Keywords: Wheat starch, hydroxypropylation, phosphorylation, dynamic rheological properties, Creep-recovery test.

Introduction

Starches are known as the major reserve substance of plant sources and are found in leaves, flowers, fruits, seeds, different types of stems and roots. The major industrial sources of starch are maize, tapioca, potato, and wheat. Starches have an importance role in the food industry for its nutritional value and broad technological functionality [1]. Native starches have limited application in industrial operations because they have restricted solubility in water, highly resistant to enzymatic hydrolysis and consequently lacking in functional properties. Native starches are frequently modified to develop functional properties such as solubility, texture, adhesion and tolerance to the heating temperatures used in food processing [2,3]. Several methods had been developed to produce modified native starches with a variety of characteristics and applications. Modifications of starch include physical, chemical and enzymatic methods [4]. The physical modification methods involve the treatment of native starch granules under different temperature/moisture combinations, pressure, shear, irradiation, and mechanical attrition [5]. The most common chemical modification processes are acid-modified, oxidation, esterification, etherification, crosslinking, and enzymatic modification is mainly based on the use of starch hydrolyzing enzymes such as α-amylase, pullulanase and glucoamylase [2,6,7]. Cross-linking and hydroxypropylation are two widely used methods for making preparation of modified starches [8]. Cross-linking is generally performed by treating starches with reagents capable of forming either ether or ester linkages between hydroxyl (–OH) groups on starch molecules. Multifunctional chemical reagents such as phosphorus oxychloride (POCl3), sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), had been commonly used to cross-link starches [2,9]. The phosphorylation provides more stable pastes at high temperature and at low pH [10,11].

The phosphorylation reaction may be produced either monostarch phosphates via substitution or distarch phosphates via cross-linking [12]. In general, monostarch phosphate can be obtained by esterification of native starch using sodium tripolyphosphate (STPP) sodium, and distarch phosphate can be obtained using sodium tripolyphosphate [13]. Hydroxypropylation is one of the commonly methods used in the chemical modification of the native starch. Hydroxypropyl groups are being substituted to the native starch in alkaline environments and increases freeze-thaw stability and cold water solubility, decreases gelatinization and pasting temperatures, compared with native starch [11,14,15]. Cross-linking of starch is often combined with hydroxypropylation [7]. Dual chemical modification introduced two kinds of functional groups, the functional properties benefits from each individual modification [16]. Many researchers had been studied the rheological properties of various modified starches treated with different chemical reagents, including Phosphorylatedcorn [17], sweet potato [8,11], oat [18], rice [19], and wheat [20]. Investigations on dual modification by cross-linking and hydoxypropylation had been reported by Wattanachant et al. [21] for sago starch, Van Hung and Morita [22] for wheat starch and Woggum et al. [16] for rice starch. In particular, there is a few information on the dynamic rheological properties of modified starches [11,23,24]. Therefore, the main objective of the current study was to investigate the dynamic rheological properties of hydroxypropylation, cross-linking, and hydroxypropylation with Phosphorylation wheat starch.

Materials and methods

The Native wheat starch (NWS) was a commercial product obtained from Ardineh Company (Isfahan, Iran). Propylene oxide, sodium triphosphate (STP), and sodium tripolyphosphate (STPP) and other chemical materials including NaOH, HCl were in analytical grade and provided from Merck (Germany).

Preparation of modified wheat starch

Hydroxypropylation

The preparation of hydroxypropylated wheat starch was performed according to the method reported by Chung et al. [25]. Wheat starch slurry (100g, dry basis) was suspended in 150 ml distilled water. Then, 10 mL propylene oxide was injected to the slurry and vigorously shaken. After adjusting the pH to 11.5 with NaOH (0.1M), the mixture was stirred at 40°C for 40 h using an incubator shaker. The reaction was terminated by adjusting pH 6.0–6.5 with HCl (1M). The hydroxypropylated starch washed three times with 500mL distilled water, oven-dried at 40–45°C.

Phosphorylation

The preparation of phosphorylated wheat starch was performed by the method reported by Chung et al. [25]. Phosphorylation was prepared by adding STP/STTP mixture (4g, 99:1%w/w) to a slurry with pH 11. Subsequently, the mixture was stirred for 3h at 45°C. The starch slurry pH was adjusted to 5.5–6.0 with HCl (1M) and washed three times with 500mL distilled water (in each time) and then dried overnight at 40°C.

Hydroxypropyl-phosphorylation

Firstly, hydroxypropylated wheat starch was prepared by using the method described, and then the phosphorylation was conducted of the hydroxypropylated wheat starch based on the method described to prepare hydroxypropyl-phosphorylated wheat starch [26].

Phosphoryl - hydroxypropylation

Firstly, phosphorylated wheat starch was prepared by using the method described, and then the hydroxypropylation was perfomed based on the method described to prepare phosphoryl- hydroxypropylated wheat starch.

Dynamic shear rheological properties

Dynamic shear rheological properties include storage modulus (G′), loss modulus (G″), and tan δ (G″/G′) of native and modified wheat starch were determined on a strain controlled Physica MCR 301 Rheometer (Anton Paar). It was equipped with a measuring system and the Reoplus software, as well as a spindle Plate and Plate PP40/S (the gap of 1 mm). System temperature was controlled by a Peltier.

Dynamic strain sweep

Dynamic amplitude sweeps were employed for the determination of the critical strain of the testing wheat starch gels in this test; the frequency was kept constant (1 Hz), but the strain was raised from 10-3 to 103 until a breakdown of the structure, which corresponded to the critical strain. In the present study, the critical strain was identified as the largest G' which was followed by decreasing G' with increasing the strain values. The decrease in G' was due to the disturbance of the structure. Subsequent to the critical strain, G' was decreased with the strain. Dynamic amplitude test was also conducted on one sample. After the beginning of the test, the amplitude test was carried out at 100 s-1 for 30 sec and this followed G' by this test. The dynamic amplitude sweep test was ended within 5 min.

Frequency sweep measurements

Frequency sweep test was done by subjecting the samples to oscillatory measurements at a frequency range of 0.01– 100 Hz and a constant strain at linear viscoelastic region (strain of 0.1%). Accordingly, the mechanical spectra were characterized by values of G' and G" (Pa) and loss tangent (tan δ) as a function of frequency at 25°C. The relationships between the rheological parameters can be represented here:

$$G' = \frac{\sigma_0 \cos\delta}{\varepsilon_0} \qquad (1)$$

$$G" = \frac{\sigma_0 \sin\delta}{\varepsilon_0} \qquad (2)$$

$$\tan\delta = \frac{G"}{G'} \qquad (3)$$

Temperature sweep measurements

The viscoelastic properties of the samples affected by temperature (5–70 °C) were determined at a strain of 0.1% and 1Hz frequency.

Creep-recovery test

Creep tests were performed by imposing a sudden step shear stress (1 Pa) in the linear viscoelastic region for 440 s. The stress was suddenly removed and the creep recovery was followed for a further 440 s to recover the elastic (instantaneous and retarded) part of the deformation. Results of a creep test are generally expressed as a time-dependent function of creep compliance, (J_t), which is defined as the strain divided by the stress applied (maintained constant during the creep test). The parameters obtained were: maximum creep compliance (J_{max}) and residual compliance corresponding to the permanent deformation (J_∞). In addition, to calculate the final percentage recovery of the entire system, the following equation has been proposed [27]. All rheological measurements were performed in triplicate.

$$\%R = \left[\left(\frac{J_{Max} - J_\infty}{J_{Max}}\right)\right] \times 100 \qquad (4)$$

Starch granule morphology

SEM micrographs were obtained with a Hitachi S-4800 cold field emission SEM 148 (Tokyo, Japan) operated at an accelerating voltage of 3.0 kV. The samples were added to double-sided adhesive tape mounted on an aluminum stub and coated under vacuum with a thin film of platinum.

Results and discussion

Frequency sweep analysis

The dynamic storage modulus (G') is a measure of the energy stored in the material and recovered from it per cycle of sinusoidal deformation and representing the elastic behaviour of a sample, while the loss modulus (G") is a measure of the energy dissipated or lost per cycle and representing the viscous behaviour of a sample [28]. The ratio of the energy lost to the energy stored (G"/G') for each cycle can be defined as tan δ. Loss tangent (tan δ) is the phase difference between the applied sinusoidal strain and the resulting sinusoidal stress. Values of tan δ <1 and tan δ >1 indicate predominantly elastic and viscous behaviors, respectively [29,30]. Figure 1 and Figure 2 shows changes in storage modulus (G'), loss modulus (G"), and loss tangent (tan δ) as a function of frequency at 25°C for the native and modified starches. As shown in Figure 1 G' and G" were almost independent of frequency, thereby displaying the typical strong gel-like behavior of all samples. Among the different modified starches in the whole range of frequencies, G' were much greater than G", showing that the samples exhibited rheological behaviors more like a solid and therefore the deformations will be essentially elastic and recoverable. Similar behavior has also been reported for other starch gels such as hydroxypropylated potato starch; native, and phosphorylated corn starches; cross-linked potato starch; rice starch; and hydroxypropylated sweet potato starch [11,24,31,32].

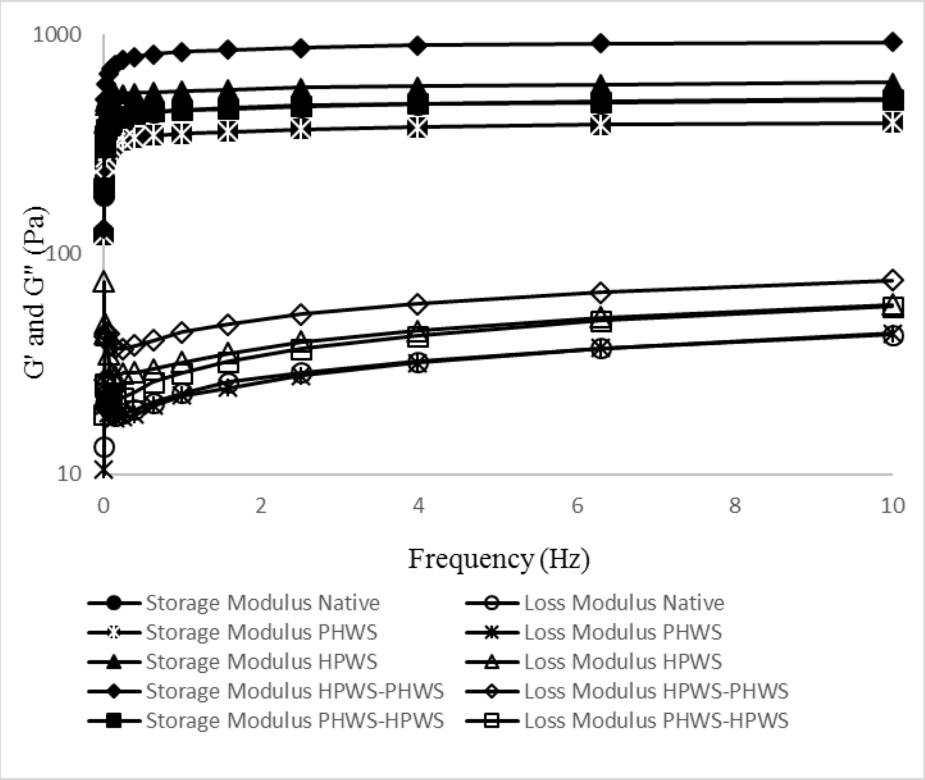

Figure (1) Frequency sweep native (NWS), Phosphorylated(PHWS), hydroxypropylated (HPWS), hydroxypropyl-phosphorylated (HPWS-PHWS), and phosphoryl-hydroxypropylated (PHWS-HPWS) wheat starch. at a strain amplitude 1%

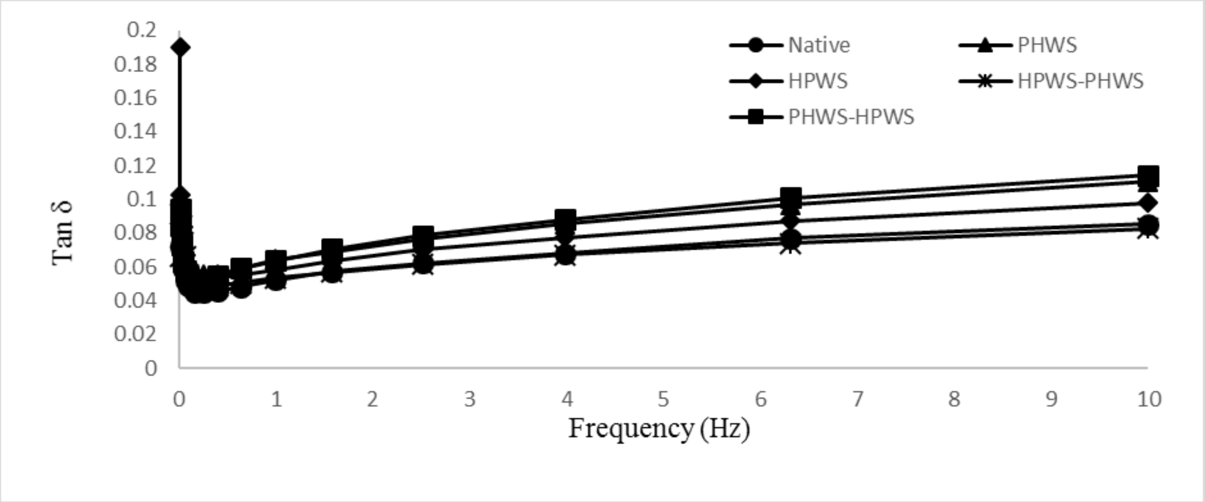

Figure (2) The Tan δ of native (NWS), Phosphorylated(PHWS), hydroxypropylated (HPWS), hydroxypropyl-phosphorylated (HPWS-PHWS), and phosphoryl-hydroxypropylated (PHWS-HPWS) wheat starch

The hydroxypropyl- Phosphorylation led to a great increase of dynamic values. Hydroxypropylation increases the degree of subsequent cross-linking and this leads to the formation of a strong gel network structure by the introduction of phosphate cross-links. Cross-linking followed by hydroxypropylation has been reported to yield starches that are more shear stable than the native starch. This may be due to the structural change in the granules after the first modification (cross-linking). Cross-linking reduces the degree of subsequent hydroxypropylation. Strengthening bonding between starch chains by cross-linking will increase resistance of the granules towards swelling and resulting in lower G' value [21]. The decrease in associative forces within the starch granules due to hydroxypropylation results the increase in peak in G' and G" of modified starch. Morikawa and Nishinari [32] also indicated that the G' value of the hydroxypropylated potato starch pastes was primarily governed by the volume fraction of the granules induced by heating. As can be seen in Figure 2, the tan δ (ratio of G"/G') values of all samples were found to be less than one, showing that the mixtures were more elastic rather than viscous. In contrast, the tan δ values of the PHWS-HPWS were higher, as compared with others; this revealed that PHWS-HPWS pastes had a higher proportion of sticky ingredients and the more viscous properties, in comparison to other pastes.

Temperature sweep measurements

Figure 3 show the changes in G' and G" of native and modified wheat starches, during a heating cycle. The Storage (G') and loss modulus (G") of hydroxypropylated, Phosphorylated and dual modified starches progressively increased. The increase in G' can be attributed to granule swelling. Granules may swell to fill the entire available volume of the system [33], and inter-granular contact might then result in the formation of a three-dimensional network of swollen granules [34,35]. As seen in Figure 3, dual modified wheat starches showed greater values of G' and G" under heating, confirming their lower tendency to retro gradate. The increases in the storage and loss modulus peak of hydroxypropylated starches during heating occurs, due to the decrease in associative forces within the starch granules. Hydroxypropyl groups introduction results in greater water penetration and swelling and a consequent increase in G'. Similar results had been reported by Kaur et al. [23] who stated that Hydroxypropylated potato starches exhibit higher peak G' and G" during heating than do the native starches. Dual-modification resulted in starch pastes with higher peak viscosity and greater stability than those of native starch pastes [36]. The result shows that hydroxypropylation followed by Phosphorylation made the native starch heat stable. This may be due to the structural change in the granules after modification, caused during hydroxypropylation followed by Phosphorylation. Reports revealed that hydroxypropylation increases the degree of subsequent cross-linking.

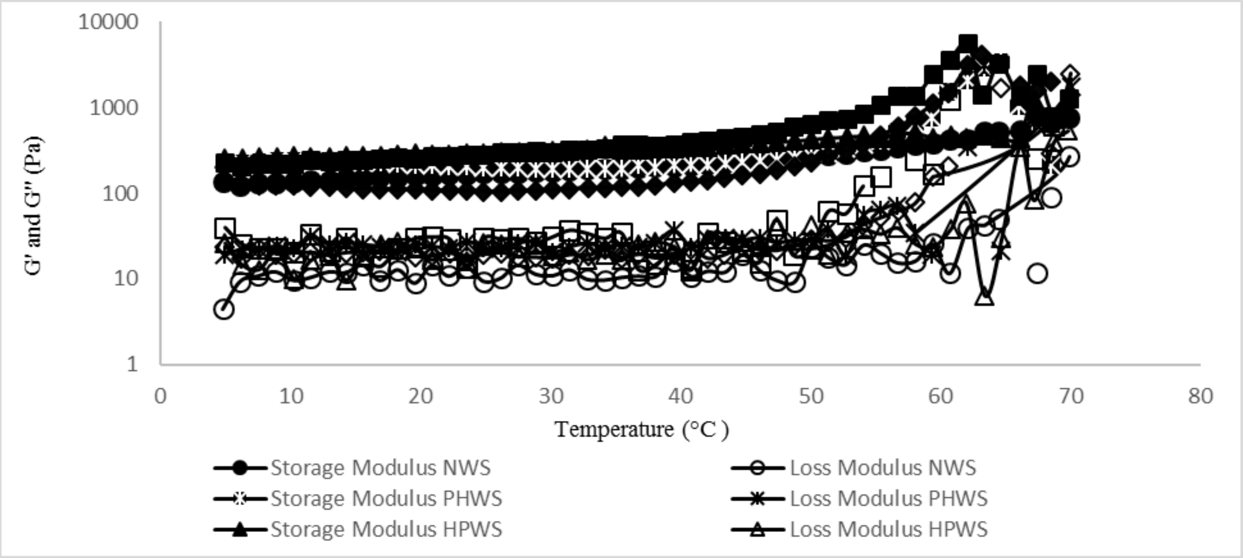

Figure (3) Temperature sweep of native (NWS), Phosphorylated(PHWS), hydroxypropylated (HPWS), hydroxypropyl-phosphorylated (HPWS-PHWS), and phosphoryl-hydroxypropylated (PHWS-HPWS) wheat starch. at a strain of 0.1% and 1Hz frequency

Creep-recovery test

The creep-recovery test is an alternative for obtaining the viscoelastic properties of a material. This test provides information about the network formations and structural changes on the molecular level inside the material that presented an important elastic behavior as showed by mechanical spectra. The complete creep-recovery curves, J=f(t), for native and modified wheat starch gels were showed in Figure 4. It can be seen that the creep recovery patterns are consistent with the normal behaviors of viscoelastic materials that combine both elastic and viscous components. When stress was applied, immediate compression of the gels, the instantaneous elastic deformation [37], was observed because of the elastic component. Then creep compliance increased with time because of viscous and elastic components [37]. When stress was removed after 440 s gels sprang back to a certain strain due to elastic recovery. Hydroxypropyl-phosphorylated wheat starch exhibited lower compliance values in both creep and recovery phases. Among starches, Phosphorylatedstarch displayed higher compliance values than other starch, which is in agreement with the low consistency (low viscoelastic moduli) of PHWS observed in the mechanical spectra. The maximum creep compliance (J_{max}), residual compliance (J_{∞}) and recovery (%) values are shown in Table 1.

Table 1- Jmax, J∞ and R(%),values of samples

Samples	J_{max} (pa^{-1})	J_{∞} (pa^{-1})	R(%)
NWS	0.0381	0.0254	33.33
PHWS	0.0494	0.0219	55.67
HPWS	0.0133	0.0048	63.83
HPWS-PHWS	0.00932	0.00188	79.83
PHWS-HPWS	0.0133	0.0048	63.83

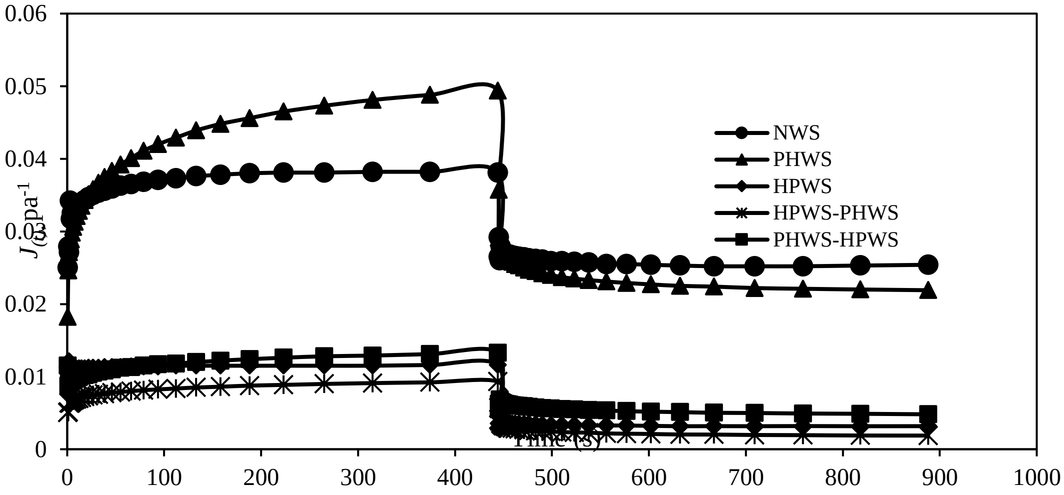

Figure (4) Creep- recovery curve of (NWS), Phosphorylated(PHWS), hydroxypropylated (HPWS), hydroxypropyl-phosphorylated (HPWS-PHWS), and phosphoryl-hydroxypropylated (PHWS-HPWS) wheat starch

Results show that the starch modification decreases the values of J_{∞} which means an improvement in the elasticity of samples. The stronger starch gel samples which had greater resistance to deformation had smaller J_{∞} values. The highest R% values of Hydroxypropyl-phosphorylated wheat starch, was more elastic than the others, corroborating the G' data, demonstrating that the Phosphorylation followed by hydroxypropylation allows the formation of stronger and more elastic gels. The greater rigidity of the hydroxypropyl-phosphorylated wheat starch gel can again attribute to the higher three-dimensional structure and stronger intermolecular interactions.

Starch granule morphology

The SEM micrographs of native and modified starches are shown in Figure 5. The native starch granules showed a smooth surface with different sizes and shapes and no cracks (Figure 5A). Phosphorylated starch (Figure 5B) had similar morphological characteristics as those of native starch. On the other hand, Hydroxypropylated starch had reduced smoothness and the appearance of cracks in Compared with native starch (Figure 5C). Hydroxypropylation disrupts inter- and intra-molecular hydrogen bonds, weakening the granular structure of starch [38]. Kaur et al. [23] reported that the treatment of potato starch granules with propylene oxide alters granule morphology. Hydroxypropyl-phosphorylated starch granules (Figure 5D) lost their structural integrity, in order to destruction of crystalline structure by the disruption of hydrogen bonds [39]. In addition, several large granules were present, which may be formed through the Phosphorylation of starch molecules. The swollen granules were observed in phosphorylate-hydroxypropylated starch (Figure 5E), demonstrating that the native starch undergoes apparent damage after phosphorylate-hydroxypropylated, which can influence paste properties.

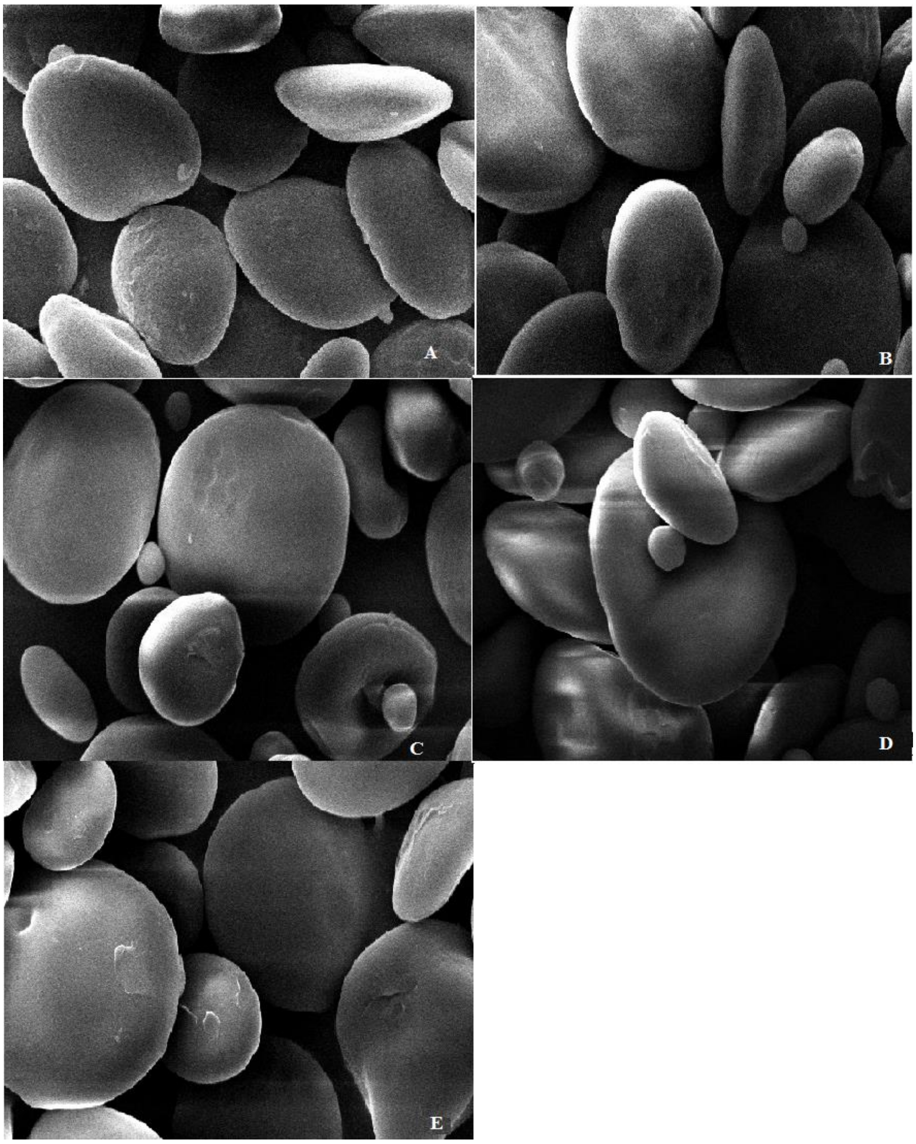

Figure (5) Effects of chemical modification on the granule morphology of native (NWS) (A), Phosphorylated(PHWS) (B), hydroxypropylated (HPWS) (C), hydroxypropyl-phosphorylated (HPWS-PHWS) (D), and phosphoryl-hydroxypropylated (PHWS-HPWS) (E) wheat starches

Figure 6 shows the granule size distribution of native and modified starch samples, and provides average sizes. The granule size distribution of the native and modified starches was obtained by analysis of SEM images using ImageJ software. According to the Figure 6, the modification process significantly changed the average size of wheat starch granules. The higher cell size (8.00 µm) in the Phosphorylated starch with STMP/STPP is due to the substitution by phosphate groups inside the modified granules, building certain repulsive forces that increase the sizes of inter- and intra-molecular spaces, allowing more water molecules to be absorbed [37]. Bertolini et al.

[40] declared that during cross-linking, small size granules derivatized to a greater extent than the large size granules. Also, Hydroxypropylation enlarged granule size. Granule size increased significantly from ≈6.7 to 7.1 µm. Hydroxypropyl groups in the neighboring starch chains prevent interchain association and they facilitate water molecules to penetrate into the granules and thereby increase swelling.

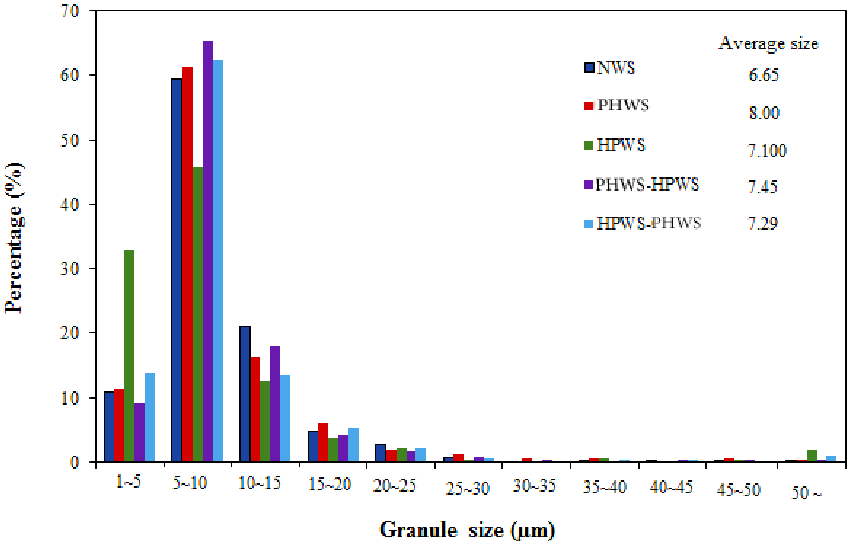

Figure (6) Effects of chemical modification on the granule size of native (NWS), Phosphorylated(PHWS), hydroxypropylated (HPWS), hydroxypropyl-phosphorylated (HPWS-PHWS), and phosphoryl-hydroxypropylated (PHWS-HPWS) wheat starches

Conclusions

Hydroxypropylated, phosphorylated, hydroxypropyl-phosphorylated, and phosphoryl-hydroxypropylated starches were achieved through chemical modification. The results of frequency sweep tests revealed that viscoelastic moduli had very low frequency dependency, indicating all the gels are a cross-link network. The results were also shown a typical weak-gel behavior for the all samples, which among them the hydroxypropyl-phosphorylated ones indicated more elasticity. During the heating, starch granules swell during the process of gelatinization. Soluble polymer molecules leach from the swollen granules and the rheological properties, such as storage modulus (G') and loss modulus (G") of the starch increase to a maximum. The creep recovery curves of all samples exhibited a typical viscoelastic behaviour combining both viscous fluid and elastic responses. SEM micrographs revealed that phosphorylated starch granules retained their relative integrity, while some cracks appeared on the surface of hydroxypropylated and hydroxypropyl-phosphorylated starch granules. The starch granule size was increased due to the chemical modification. Therefore, by appropriate choice of the type of chemical modification, and type of the modifying reagent, modified starches with very useful rheological properties can be obtained.

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