Journal of Food Process Engineering

WILEY

Journal of
Food Process Engineering

ORIGINAL ARTICLE OPEN ACCESS

Investigation of Morphological, Structural, Rheological and Digestibility Characteristics of Common Buckwheat Starch Modified via Physical and Chemical Methods

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Received: 8 August 2025 | **Revised:** 18 November 2025 | **Accepted:** 2 March 2026

Keywords: annealing | citric acid crosslinking | common buckwheat | heat-moisture treatment | modified starch | phosphorylation

ABSTRACT

The present study investigated the impact of different physical and chemical modifications on starch extracted from the Pakistani cultivar of common buckwheat (*Fagopyrum esculentum* Moench). The physical modifications included annealing (ABS), which was performed at 50°C for 24 h, and heat-moisture treatment (HBS) was done at 110°C for 16 h. The chemical modifications involved citric acid (CA) crosslinking (non-conventional) and phosphorous oxychloride crosslinking (conventional). CA was added at a level of 10% (CBS_{10}) and 30% (CBS_{30}), whereas phosphorous oxychloride ($POCl_3$) was used at a concentration of 0.05% ($PBS_{0.05}$) and 0.1% ($PBS_{0.1}$), respectively. Native buckwheat starch (NBS) was found to have an A-type polymorphic structure with polygonal granules in the range of 3.18–14.55 μm. The pores with a diameter ranging from 217 to 324 nm were also present on the surface of starch granules. Rheological analysis revealed that all starches were elastic in nature, with phase angles ranging from 3.06° to 9.15°, with the highest being exhibited by the HBS. The percent crystallinity measured through X-ray diffraction was observed in the order of $PBS_{0.1} > HBS > PBS_{0.05} > ABS > CBS_{10} > NBS > CBS_{30}$, suggesting an increase in crystallinity after physical and chemical modifications, except for CBS_{30}. Moreover, all modifications were observed to reduce the digestibility of buckwheat starch. The resistant starch (RS) content observed the following order: $PBS_{0.1} > PBS_{0.05} > CBS_{30} > ABS > CBS_{10} > HBS > NBS$.

1 | Introduction

Buckwheat (BW) exists in the family *Polygonaceae* making it different from cereals which belong to the family *Poaceae*. Despite belonging to a different family, BW possesses some features similar to cereals due to which these are classified as pseudocereals (Sofi et al. 2023). The inherent ecological adaptability of BW allows its cultivation even in marginal areas with rocky and poorly tilled soils where other conventional crops may fail to grow. The global cultivation of BW for the year 2023 was reported to be 2.20 million tonnes with Russia, China, Ukraine, United States of America and Kazakhstan being the top five producers of this commodity (Faostat 2023). Different species of BW are grown worldwide, however common BW (*Fagopyrum esculentum* Moench) and tartary BW (*Fagopyrum tataricum* (L.) Gaertn) are only utilized as food resources. Flour from BW is gaining huge interest from consumers due to its nutraceutical properties along with the gluten-free nature thereby acting as a potentially great ingredient in preventing celiac disease (Zamaratskaia et al. 2024). The chemical composition of BW grains mainly consists of polysaccharides (starch: 59%–70% and dietary fiber: 8.4%–23%), proteins (8.5%–18.8%), lipids (1.5%–4.0%), and ash (1.5%–3.7%) whereas, vitamins and minerals share a minor portion (Ahmed et al. 2014; Lițoiu et al. 2025). The granule size of BW starch is about 1–14 μm (Gao et al. 2025; Li et al. 2014; Qian et al. 1998; Zhu 2016) which is smaller in comparison to corn and potato starches. Amylopectin constitutes the major

https://doi.org/10.1111/jfpe.70428

proportion of buckwheat starch (BWS) which is approximately 75% whereas amylose is only 25%. As the major portion of the starch fraction is shared by long chains of amylopectin, the BWS shares distinct structural characteristics. Starch is a renowned additive used in a variety of processed foods owing to its thickening, gelling, and stabilizing role. The applicability of starch could be improved through different modification techniques such as treatment with chemicals or through green technologies to alter the specific functional characteristics for subsequent utilization in different food formulations. Physical or green modifications pertain to starch treatments that are done in a manner that ensures the starch safety for incorporation into food formulations, as they contain no chemical residues compared to chemically modified starches (Campelo et al. 2020; Guida et al. 2021). Annealing is a form of hydrothermal physical modification, where starch is subjected to heat treatment. For a controlled period varying from 30 min to 48 h, starch is heated below its gelatinization temperature but above the glass transition temperature in excess water (> 60%). This treatment only uses heat energy and water thus, it is considered an eco-friendly modification. Similarly, heat-moisture treatment (HMT) involves heating starch granules above their gelatinization temperature (84°C–140°C) in presence of very low moisture content (10%–35%) so that the starch granules do not get gelatinized during the heating period that varies from 1 to 16 h.

The citric acid (CA) modification involves treatment of starch molecules with CA in presence of water. This is also a green modification as it uses a very safe chemical, that is, CA for modification which is currently in GRAS list of Codex. The CA molecule consists of three carboxylic acid groups and when heated forms CA anhydride. The anhydride form then results in the formation of mono-, di- and triesters as a result of the ester bonding of the anhydride with the hydroxyl groups of starch molecules. The developed starch citrates serve as catalyst for this esterification, and subsequent heating of the starch citrates results in crosslinking reaction. On the other hand, the phosphorus oxychloride ($POCL_3$) modification of starch deals with the treatment of starch granules with multifunctional $POCL_3$ under alkaline conditions. The $POCL_3$ is used as a crosslinking agent leading to the formation of distarch phosphates and is one of the oldest conventional chemical modification techniques.

The present research explored the Pakistani common BW variety which grows in the northern areas such as Gilgit and Baltistan of Pakistan for starch extraction. Consequently, the focus of this research was to evaluate the impact of different physical (annealing and heat moisture treatment) and chemical (CA and phosphorus oxychloride) modifications on functional properties of isolated BWS which in future could serve as a substitute for corn starch as the former has very less challenging agronomic needs compared to the latter. Also, in the current era where the world is facing a shortage of corn grains due to the Ukraine-Russia war (Ukraine being the 4th largest exporter of maize), there is a dire need to hunt alternative starch sources which could suffice the global starch requirements. Therefore, BWS was studied in terms of techno-functional properties so as to predict its usage in commercial food systems. Also, the exploration of digestibility as affected by physical and chemical treatments could help to design low calorie foods for people on calorie deficit diets.

2 | Materials and Methods

2.1 | Procurement of Materials

The dehulled common BW grains were acquired from Gilgit-Baltistan, Pakistan. Reagents of analytical grade were used in the study. CA (anhydrous) was procured from Daejung Chemicals and Metals Co. Ltd. (Siheung, Korea), whereas phosphorus oxychloride was sourced from Sigma Aldrich (Sigma Aldrich GmbH, Sternheim, Germany).

2.2 | Starch Isolation

Starch was extracted from native BW using the technique of Sindhu et al. (2019). The proximate composition was calculated by AACC (2000) and was found to be 99.35% carbohydrate, 0.29% protein (nitrogen content × 6.25), 0.02% ash, and 0.33% fat whereas crude fiber was absent. The amylose content in starch was 18.0% as determined through the method of Landers et al. (1991).

2.3 | Starch Modification

2.3.1 | Annealing

Annealing of NBS was done as per the procedure of Shih et al. (2007) with minor adjustments. Briefly, the NBS was mixed along with distilled water in a ratio of (1:4) w/w to form a slurry. The slurry was then equilibrated overnight at 4°C. Following that, the slurry was incubated for 24 h at 50°C in a shaking water bath. After incubation, the temperature of the slurry was reduced to room temperature. Finally, the starch sample was dried in a hot air oven maintained at 40°C for 12 h and designated as ABS.

2.3.2 | Heat-Moisture Treatment

The NBS was physically modified via HMT as per the methodology of Liu et al. (2015) by using starch with 35% moisture level kept at a temperature of 110°C for 16 h. The heat-moisture treated starch was labeled as HBS.

2.3.3 | Citric Acid Modification

CA modification of starch was performed by adopting the procedure carried out by Butt et al. (2019b) using 10% and 30% (w/v) CA solution and labeled as CBS_{10} and CBS_{30}, respectively.

2.3.4 | Phosphorous Oxychloride Modification

The crosslinking of starch was done by adopting the procedure of Kaur et al. (2006). The phosphorous oxychloride ($POCL_3$) was used at 0.05% and 0.1% levels based on starch weight (db) and was labeled as $PBS_{0.05}$ and $PBS_{0.1}$, respectively.

2.4 | Degree of Substitution of Citric Acid Modified and Phosphorous Oxychloride Cross Linked Starches

The degree of substitution (DS) was calculated by the method followed by Liu et al. (2014) for starch citrates and by the method of Chatakanonda et al. (2000) for phosphorous oxychloride cross-linked starches.

2.5 | Morphological Characteristics

The native and modified BWS were examined at 4000× and 12,000× magnifications by using a scanning electron microscope (JSM, 6380A, Jeol, Japan) (Li et al. 2014).

2.6 | X-Ray Diffraction

The NBS and modified BWS were examined for their percent crystallinity and X-ray diffraction (XRD) pattern through an X-ray diffractometer (Philips/PANalytical, PW 3040, Netherlands) (Shaikh et al. 2019).

2.7 | Swelling Power and Solubility

The swelling power and solubility of NBS and modified BWS were determined using the technique described by Liu et al. (2016).

2.8 | Paste Clarity

The percent transmittance of starch samples was measured at 650 nm on 0 day and after one and 7 days of cold storage using UV–VIS spectrophotometer (model: V670, JASCO Corporation, Tokyo, Japan) in accordance with the method adopted by Mehboob et al. (2021).

2.9 | Rheological Properties

Rheological properties of native and modified BW starches were studied on Discovery Hybrid Rheometer DHR-1 (TA instruments, New Castle, DE, USA). First, a 10% w/w solution was gelatinized in boiling water bath for 15 min. The solution after cooling was poured over peltier pre-set at 25°C. Parallel plate geometry with 40 mm diameter was used as an upper geometry for amplitude, frequency and in-shear structural recovery measurements. However, for temperature sweep measurements, a 10% w/w (dry basis) starch solution was directly placed over a peltier plate in ungelatinized suspension form using cone-plate with 60 mm diameter and cone angle of 2° as an upper geometry and a geometry gap of 300 μm.

2.9.1 | Amplitude and Frequency Sweep Measurements

At a constant frequency of 1 Hz, amplitude sweep measurements were performed on native and modified BWS at 25°C, separately within a strain range of 0.01%–100%. The values of percent critical strain, storage (G') and loss moduli (G'') and phase angle were determined using TRIOS (V.4.1.031739) software provided by TA Instruments. A frequency sweep trial was conducted between 1.0 rad/s to 100.0 rad/s at the same temperature in the linear visco-elastic region (LVR).

2.9.2 | In-Shear Structural Recovery Measurements

The in-shear structural recovery measurements for NBS and modified BWS were determined by using the method of Pajak et al. (2012) with slight modifications. The measurements were performed at 25°C in three stages and are as follows: (first stage) steady shear rate at 1 s^{-1} for 180 s (second stage), steady shear rate at 50 s^{-1} for 180 s, and then (third stage) steady shear rate at 1 s^{-1} for 420 s. The shear structural recovery value was determined by adopting the procedure used by Butt et al. (2019a).

2.9.3 | Temperature Sweep Measurements

With a few minor modifications, the method of Mehfooz et al. (2021) was utilized to examine the temperature sweep profiles of NBS and modified BW starches. The starch suspension (10%, w/w) was put onto the Peltier plate, which was then covered with an evaporation hood. To further inhibit moisture loss, silicon oil was used to cover the side edges of the sample before enveloping it with a moisture hood. The starch slurry was initially raised from a temperature of 35°C–95°C at a rate of 5°C/min, followed by a temperature decrease from 95°C to 35°C at the same rate. Trios software (TA Instruments, DE, USA) was used to evaluate the following parameters: pasting temperature (T_f), highest viscosity (MV), time required for achieving MV (TT_{MV}), temperature attained at MV (T_{MV}), viscosity recorded at the end of the heating cycle ($V_{95°C}$), viscosity recorded at 35°C during the cooling cycle ($V_{35°C}$).

2.10 | Determination of Readily Digestible Starch (RDS), Slowly Digestible Starch (SDS), and Resistant Starch (RS)

The in vitro digestibility of NBS and modified BWS was determined by following the procedure of Liu et al. (2014) and for the preparation of enzyme solution, the protocol described by Juansang et al. (2012) was followed.

2.11 | Statistical Analysis

IBM Statistical Package for Social Science (SPSS) version 17.0 was used to evaluate the data statistically at a 95% confidence interval. The experimental data was examined using one-way ANOVA followed by implementation of Duncan's Multiple Range post hoc test. For two samples, significant differences between the mean values were examined by applying the paired sample *t*-test.

TABLE 1 | Impact of different modifications on degree of substitution, substituent functional groups, swelling power and solubility of buckwheat starch[a].

Sample	DS (%)	FGS (%)	SP (g/g)	Solubility (g/g)
NBS	NA	NA	12.6 ± 0.6^{a}	0.747 ± 0.018^{a}
ABS	NA	NA	11.4 ± 0.7^{b}	0.804 ± 0.011^{a}
HBS	NA	NA	6.9 ± 0.1^{c}	0.601 ± 0.444^{a}
CBS$_{10}$	0.1126 ± 0.004^{A}	10.855 ± 0.330^{A}	15.3 ± 0.3^{d}	0.106 ± 0.002^{b}
CBS$_{30}$	0.1477 ± 0.006^{B}	13.772 ± 0.495^{B}	13.1 ± 0.1^{a}	0.129 ± 0.021^{b}
PBS$_{0.05}$	0.00034 ± 0.000^{a}	0.006 ± 0.000^{b}	5.4 ± 0.2^{f}	0.055 ± 0.007^{b}
PBS$_{0.1}$	0.00062 ± 0.000^{b}	0.013 ± 0.000^{a}	5.5 ± 0.2^{f}	0.096 ± 0.003^{b}

Note: Mean values with similar superscript (upper case letters) in a single column are insignificantly different at $p < 0.05$ between CBS$_{10}$ and CBS$_{30}$ whereas, same superscript (lower case letters) in a column represent insignificant difference at $p < 0.05$ between PBS$_{0.05}$ and PBS$_{0.1}$ samples.

Abbreviations: CBS$_{10}$, buckwheat starch treated with 10% (w/v) anhydrous citric acid solution; CBS$_{30}$, buckwheat starch treated with 30% (w/v) anhydrous citric acid solution; DS, degree of substitution; FGS, functional groups substituted; NA; not applicable; PBS$_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride based on starch weight (db); PBS$_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride based on starch weight (db); SP, swelling power.

3 | Results and Discussion

3.1 | Degree of Substitution (DS)

Table 1 displays the DS and functional groups substituted (FGS) values for chemically modified BWS. With the increase in levels of CA used for modification, the values for DS increased concomitantly. The DS for CBS$_{10}$ was found to be 0.1126%, which increased to 0.1477% for CBS$_{30}$. Similarly, the DS when BWS was crosslinked with 0.05% $POCl_3$ was found to be 0.00034% which increased to 0.00062% as the concentration was raised to 0.1% for phosphorous oxychloride during the modification. Yoneya et al. (2003) observed a similar increase in DS after crosslinking potato starch with $POCL_3$. The % FGS in PBS$_{0.05}$ and PBS$_{0.1}$ were measured in terms of phosphorus content as it is the requirement of FAO/Codex Alimentarius. For CA modification, the FGS were measured in terms of % citrate groups. The % CA groups after reacting BWS with (10% and 30%) w/v CA solutions were found to be 10.855% and 13.772%, respectively. Whereas, when BWS was cross-linked using multifunctional phosphorous oxychloride at 0.05% and 0.1% levels, the FGS were observed to be 0.00642% and 0.01265%, respectively. According to the JECFA (2021) monograph, phosphorus content should not be more than 0.5% for potato and wheat, and not more than 0.4% for other starches after modifications. Thus, the BWS modified with 0.1% and 0.05% phosphorous oxychloride were observed to be far below the limit set by JECFA (2021). As far as starch citrates are concerned, there is no limit set by the JECFA monograph on modified starches in terms of DS or functional groups as CA is a safe chemical and is in GRAS (generally recognized as safe) list of FAO. Also, HMT and annealing modifications are not entitled to be verified through safety assessment procedures as these modifications exclude use of any chemicals and thus carry the title of clean labeled starches.

3.2 | Morphological Properties

The morphological characteristics of NBS and modified BWS were evaluated to study the impact of different modifications (Figures 1 and 2). It could be observed in Figure 1 that granules of BWS were majorly irregular and polygonal in terms of shape. However, some small-sized granules in contrast to medium and large-sized granules were found to be spherical. Similar morphological characteristics were also reported by Dar et al. (2018) and Li et al. (2014) for oat, BWS and maize starches. Based on the size (measured as the largest axis of starch granule), the starch granules of NBS and modified BWS were divided into small, medium and large-sized granules. However, for both native and modified starches, the population of medium-sized granules was much higher compared to small and large BWS granules. No significant impact of modifications was observed on the granular size of starches and the small, medium and large-sized granules ranged between 3.18–5.45 μm, 5.91–8.64 μm and 9.09–14.55 μm, respectively. These results are in line with the finding of Suri et al. (2025) who reported the diameter of different common BWS as 1.84–14.60 μm. Dents and lumpiness could also be observed in both native and modified starch. However, Figure 1 demonstrated that the physically modified HBS starch experienced the harshest impact of modification, as evident by surface disruption and erosion, indicating that the granules' surfaces have undergone partial gelatinization. This could be considered as an attribute of the high temperature (greater than gelatinization temperature) used during HMT. The non-homogenous water distribution might have caused some gelatinization over starch granules where the water level was sufficient to cause swelling. Importantly, it was found that the BWS granules' surfaces had pores with diameters ranging from 21 to 324 nm, as illustrated in Figure 2 for both native and modified BWS. However, modifications either physical or chemical brought an insignificant impact on the size of the pores. Pores, which have also been noted for BWS by Wu et al. (2021), Górecki et al. (2018), and Sujka and Jamroz (2007), are nanoscale holes that may be seen on the surface of starch granules. The BW is a pseudocereal but similar pores were also observed for some cereal starches like corn, sorghum and rice with size ranging from 100 to 289 nm (Ali and Hasnain 2014; Sujka and Jamroz 2010).

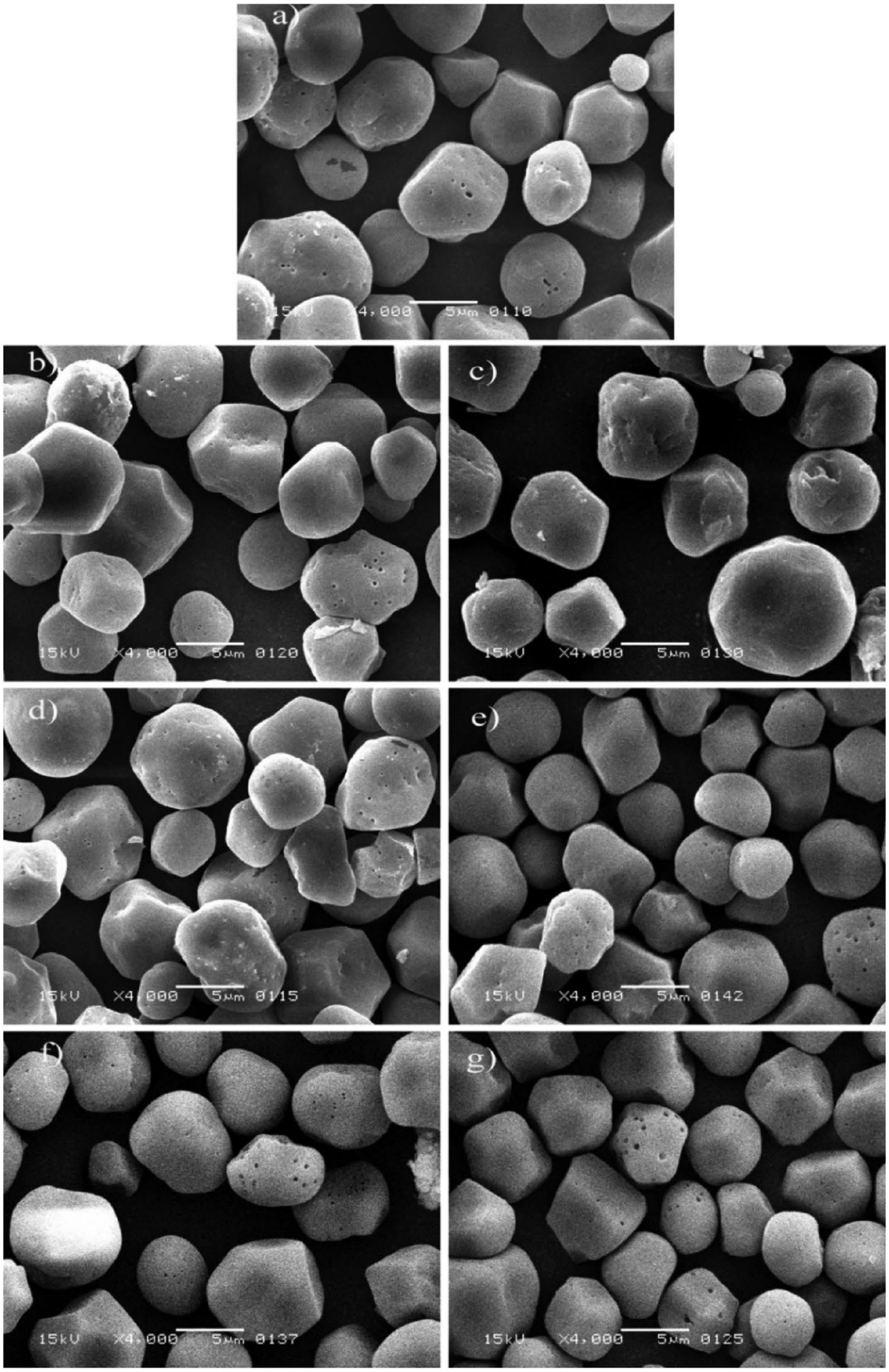

FIGURE 1 | Impact of different modifications on morphological characteristics of buckwheat starch at 4000× magnification. (a) Native buckwheat starch, (b) annealed buckwheat starch, (c) heat-moisture treated buckwheat starch, (d) buckwheat starch treated with 10% (w/v) citric acid solution, (e) buckwheat starch treated with 30% (w/v) citric acid solution, (f) buckwheat starch treated with 0.05% phosphorous oxychloride based on starch weight (db), and (g) buckwheat starch treated with 0.1% phosphorous oxychloride based on starch weight (db).

3.3 | X-Ray Diffraction Analysis

The Table 2 shows the relative crystallinity and characteristics of diffraction peaks of native and modified BW starch. The crystalline pattern of NBS was A-type, with diffraction peaks at $2\theta = 14.79°$, 17.18°, and 22.71°. Tao et al. (2025) also discovered similar diffraction peaks at 2θ for common BWS. The starch obtained from Chinese BW cultivars also displayed an A-type crystalline pattern (Liu et al. 2015), similar to Pakistani BWS. Interestingly, all starches retained their A-type crystalline structure after modifications, except for those modified with HMT, as the latter showed a pronounced peak at 13°. The crystalline pattern for HBS was found to be a V-type polymorph. A similar shift in the type of starch polymorph for rice starches after HMT modification was also noted by Shih et al. (2007). The formation of amylose-lipid complexes could

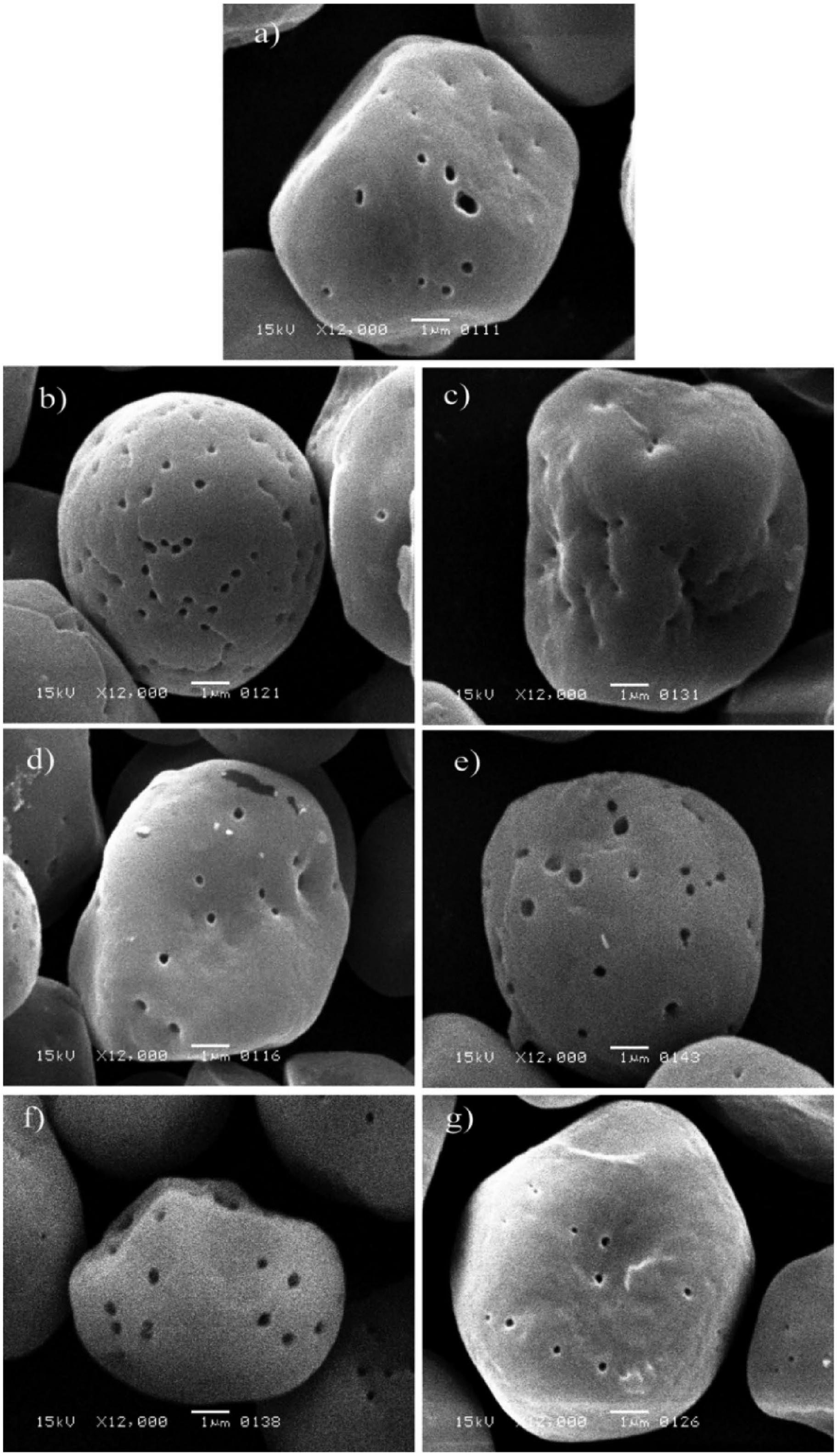

FIGURE 2 | Impact of different modifications on morphological characteristics of buckwheat starch at 12,000× magnification. (a) Native buckwheat starch, (b) annealed buckwheat starch, (c) heat-moisture treated buckwheat starch, (d) buckwheat starch treated with 10% (w/v) citric acid solution, (e) buckwheat starch treated with 30% (w/v) citric acid solution, (f) buckwheat starch treated with 0.05% phosphorous oxychloride based on starch weight (db), and (g) buckwheat starch treated with 0.1% phosphorous oxychloride based on starch weight (db).

explain the V-type pattern observed in HBS. Furthermore, inside the amylose helix, there is a hydrophobic fatty acid chain that aids in the further entanglement between starch molecules and increases the RS content (Shah et al. 2016). The NBS had a crystallinity of 31.81%, which increased after physical treatments (annealing and heat-moisture). The relative

TABLE 2 | Impact of different modifications on relative crystallinity and characteristic peaks of buckwheat starch[a].

Sample	Xc (%)	Characteristic peaks (2θ) (°)
NBS	31.81	14.79, 17.18, 22.71
ABS	36.37	14.96, 16.18, 18.26, 22.94
HBS	40.01	13.34, 22.94, 20.94, 22.71
CBS_{10}	36.25	15.01, 16.99, 23.09
CBS_{30}	28.13	14.99, 17.16, 22.79
$PBS_{0.05}$	39.93	14.51, 17.19, 20.24, 23.01
$PBS_{0.1}$	41.36	14.86, 17.24, 20.03, 22.76

Abbreviations: ABS, annealed buckwheat starch; CBS_{10}, buckwheat starch treated with 10% (w/v) citric acid solution; CBS_{30}, buckwheat starch treated with 30% (w/v) citric acid solution; HBS, heat-moisture treated buckwheat starch; NBS, native buckwheat starch; $PBS_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); $PBS_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db).
[a]Xc = percent crystallinity.

crystallinity of NBS increased by 14% after the annealing treatment but showed a higher increment of about 26% after the HMT. The increase in % crystallinity in ABS and HBS suggested improvement of crystalline patterns owing to the re-orientation of double-helical chains. The higher degree of crystallinity in HBS compared to ABS could be associated with a higher number of crystalline regions and more crystallites due to better organization produced through HMT. A similar trend and increase in relative crystallinity after annealing and HMT with a 35% moisture level were also observed by Liu et al. (2015) for BWS. The degree of crystallinity after 10% and 30% CA treatment was observed to be 36.25% and 28.13%, respectively. CA modification resulted in the formation of both monoesters and di-esters besides partial hydrolysis due to the presence of acid at high temperatures. Interestingly, CBS_{10} showed a higher % crystallinity compared to NBS whereas on modification with 30% CA anhydrous the % crystallinity was found to be even less than that of NBS. This decline could be due to a very high level of monoesters in starch with bulky citrate groups which destroyed the organization within the granule. Also, the higher degree of hydrolysis might be the cause of the lower % crystallinity in CBS_{30} compared to NBS. A similar trend of decline in crystallinity was also observed by Wang et al. (2009) after CA modification of waxy maize starch. The degree of crystallinity after cross-linking with $POCL_3$ at different concentrations (0.05% and 0.1%) increased by 25% and 30%, respectively. The increase in percent crystallinity of $PBS_{0.05}$ and $PBS_{0.1}$ was due to the formation of distarch phosphate crosslinks in the amorphous region of the granules. The cross-linking of otherwise separately existing starch chains through di-esterification or di-starch phosphate links improves the organizational structure within the starch granule leading to higher crystallinity values. A similar increase in relative crystallinity was also observed by Karmvir et al. (2018) for white sorghum starch when cross-linked with phosphate groups. Moreover, the % crystallinity increased with the increase in concentrations of $POCL_3$ which was expected as a higher level of $POCL_3$ addition resulted in the formation of more crosslinks, as evident by phosphorus content values in Table 1 where $PBS_{0.1}$ demonstrated higher phosphorus content in contrast to $PBS_{0.05}$. Overall, % crystallinity observed the order $PBS_{0.1} > HBS > PBS_{0.05} > ABS > CBS_{10} \approx CBS_{30} > NBS$. Thus, it could be concluded that HMT, a green modification, can increase crystallinity almost to the same level as that of di-starch phosphate crosslinks without any employment of harsh chemicals.

3.4 | Swelling Power and Solubility

Table 1 displays the swelling power (SP) and solubility of NBS and modified BWS. Except for CBS_{10}, which demonstrated a significant rise, all the treatments resulted in a decrease in the SP of BWS. However, when treated with 30% CA, there was an insignificant increase in SP of CBS_{30} compared to NBS. After being treated with 10% CA, the swelling power of BWS was significantly enhanced. This was caused by the addition of higher molecular weight citrate groups, which boosted the penetration of water within the starch molecule. However, with the treatment of starch with a 30% solution of CA anhydrous, SP reduced compared to CBS_{10}, which shows that more cross-links or di-starch citrates might have formed instead of monoesters leading to the reduction in the SP of starch. The loss in SP of BWS following HMT is known to be a moisture-dependent factor. Also, molecular rearrangement and formation of highly ordered new crystallites manifested by better amylose-amylopectin interactions during modification tend to restrict the hydration process. Furthermore, this decrease might be linked to the creation of stiff structures composed of organized double-helical amylopectin side chains, which was also evident as HMT showed significantly higher % crystallinity compared to NBS (Table 2). Whereas, the SP for starches cross-linked with different concentrations of $POCL_3$ were the least among all physically and chemically modified BWS and may also be associated with their concomitantly higher percent crystallinity values (Table 2). The cross-linked phosphate groups reinforce the hydrogen bonds holding the granules together and eventually caused restricted swelling. A similar reduction in SP for sweet potato starch was observed by Syeda et al. (2025) when cross-linked with $POCL_3$. The solubility of modified BWS was insignificantly different after both physical modifications compared to NBS. However, with chemical modifications, both CA anhydrous and phosphorous oxychloride resulted in significantly reduced solubility as both are cross-linking/esterifying agents. However, the impact of higher concentrations of modifying reagents was not observed on solubility as CBS_{10} was insignificantly different from CBS_{30} in terms of solubility. Similarly, $PBS_{0.05}$ and $PBS_{0.1}$ solubilities were not significantly different from each other at $p < 0.05$. However, it is obvious from the results that phosphorus oxychloride had a more pronounced decline in solubility compared to CA, suggesting that $POCL_3$ formed a higher number of cross-links (distarch phosphates), which ultimately reduced the solubilization of starch chains to a greater extent when compared to distarch citrates. $POCL_3$ only forms diesters whereas CA forms both monoesters and diesters at different stages (Kapelko-Zeberska et al. 2016). The decline in solubility after CA modification and the addition of $POCL_3$ was also observed by Kim and Yoo (2010) and Martins et al. (2018) for sweet potato, rice, and potato starches.

TABLE 3 | Impact of different modifications on percent transmittance (%T) of buckwheat starch[a].

Samples	Transmittance (%T)		
	Day 0	Day 1	Day 7
NBS	1.709 ± 0.464^{aA}	1.577 ± 0.025^{aB}	1.037 ± 0.000^{aC}
ABS	1.075 ± 0.019^{bA}	0.763 ± 0.017^{bB}	0.452 ± 0.013^{bC}
HBS	0.879 ± 0.070^{cA}	0.540 ± 0.003^{cB}	0.176 ± 0.008^{cC}
CBS_{10}	0.929 ± 0.002^{cA}	0.906 ± 0.008^{dA}	0.761 ± 0.022^{dB}
CBS_{30}	1.545 ± 0.009^{dA}	1.447 ± 0.023^{eB}	1.170 ± 0.020^{eC}
$PBS_{0.05}$	0.019 ± 0.002^{e}	ND	ND
$PBS_{0.1}$	0.026 ± 0.006^{e}	ND	ND

Note: Mean values with similar superscript (upper case letters) in a single row are insignificantly different at $p < 0.05$, whereas same superscript (lower case letters) in a single column are insignificantly different at $p < 0.05$.

Abbreviations: ABS, annealed buckwheat starch; CBS_{10}, buckwheat starch treated with 10% (w/v) citric acid solution; CBS_{30}, buckwheat starch treated with 30% (w/v) citric acid solution; HBS, heat-moisture treated buckwheat starch; NBS, native buckwheat starch; ND, not detected; $PBS_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); $PBS_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db).

3.5 | Paste Clarity

Both physical and chemical modifications significantly decreased the paste clarity of NBS which was observed to be (1.709%) (Table 3). On the zero day, among the physical modifications, the paste clarity of starch after HMT was the lowest, that is, 0.879%. Whereas, among chemical modifications, BWS treated with 0.1% phosphorous oxychloride showed the least paste clarity of 0.026%. The decrease in paste clarity after annealing and HMT could be due to the rearrangement and close packing of granule arrays causing a decline in amylose leaching (Falade et al. 2019). However, heat-moisture treated BWS showed a more pronounced decline in paste clarity compared to ABS. In HMT, native BWS was exposed to a temperature higher than gelatinization temperature (i.e., 110°C), after moisture equilibration to 35%. Exposure to high temperature under limited moisture conditions lead to the destruction of glycosidic bonds in amylopectin producing short chains. After cooling, these short chains re-associated to form a network, resulting in cloudiness and hence higher opacity values (lower transmittance) was observed for HBS (Gul et al. 2014). The decline in the paste clarity was also observed after the action of CA treatment which is because of the insertion of bulky citrate groups on the starch molecules. The branched structure of starch is partially hydrolyzed into the linear structure by CA which therefore hindered the pathway of light and induced opacity (Ghanbarzadeh et al. 2011; Zehra et al. 2020). The opacity however significantly increased in CBS_{30} compared to CBS_{10} which was due to the increased number of citrate groups inserted into the starch molecule (Table 1). Zehra et al. (2020) showed a similar reduction in paste clarity after CA treatment of corn and sorghum starches. However, the reduced paste clarity of starch cross-linked with phosphorus oxychloride could be due to the fact that starch granules escape disintegration and may stay intact during the gelatinization process. This decline in % transmittance could also be owed to the reduced SP of $PBS_{0.05}$ and $PBS_{0.1}$ as shown in Table 1 which further hindered the pathway of monochromatic light as swelled granules with higher volume facilitate the light transmittance. Thus, the higher number of dense granules in phosphorylated BWS per unit volume refracted more light, resulting in lower paste clarity. Moreover, the effect of the cold storage period was also studied on the paste clarity of BWS solution for 7 days. The significant decrease in paste clarity of native and modified BWS during the cold storage period might be an attribute of the retrogradation of amylose and debranched amylopectin in starch gels resulting in the formation of crystals that lead to decreased paste clarity (Martínez et al. 2019). However, the clarity of $PBS_{0.05}$ and $PBS_{0.1}$ drastically reduced only after one day of storage and became completely opaque for visible light at the wavelength of 650 nm. Both physical treatments, that is, HMT and annealing reduced SP as could be observed in Table 1. This shows that molecular rearrangement buries the hydrophilic sites in starch granules resulting in an overall decline in granule interaction with media. However, granule-granule interaction is promoted between starch chains leading to an overall decline in (%T) after 7 days of storage. Whereas, the reduced retrogradation rate after treatment with CA might be due to the substitution of hydroxyl groups in starch with the bulky citrate groups (monoesters). These ester groups prevented close re-associations of starch chains during storage due to steric hindrance and eventually, a reduced retrogradation rate was observed.

3.6 | Rheological Properties

3.6.1 | Amplitude Sweep Measurements

The phase angle values observed for native and modified BW were in the range of 3.06°–9.15°, indicating the elastic behavior of starches as all values were less than 45° (Table 4). The values for critical strain and phase angle for NBS were observed as 3.98% and 4.24°, respectively. The insignificant difference in phase angle was observed after annealing treatment. However, the values for critical strain significantly increased to 9.95% from 3.98%, which suggests that the resistance of starch granules against deformation increased after annealing due to an increase in rigidity of the starch granules owing to improvement in crystalline structure leading to broader LVR. Whereas, a decline was observed in % critical strain (1.11%) and an increase in phase angle (9.15°) values for HBS. The HMT is known to destroy the amylopectin crystallites which lowered the stability

TABLE 4 | Impact of different modifications on percent critical strain, phase angle and structural recovery of buckwheat starch[a].

Sample	Critical strain (%)	Phase angle (°)	Structural recovery (%)
NBS	3.98 ± 0.002^{c}	4.24 ± 0.177^{ab}	75.11 ± 1.20^{a}
ABS	9.95 ± 0.686^{d}	3.94 ± 0.770^{ab}	84.15 ± 1.04^{b}
HBS	1.11 ± 0.065^{a}	9.15 ± 0.303^{d}	47.45 ± 1.50^{c}
CBS_{10}	10.06 ± 0.015^{e}	4.79 ± 0.357^{bc}	95.08 ± 0.88^{d}
CBS_{30}	9.98 ± 0.058^{e}	6.07 ± 1.089^{c}	95.32 ± 2.14^{d}
$PBS_{0.05}$	3.98 ± 0.011^{c}	4.27 ± 0.465^{ab}	41.52 ± 1.58^{e}
$PBS_{0.1}$	2.50 ± 0.231^{b}	3.06 ± 0.175^{a}	29.28 ± 0.18^{f}

Note: Mean values with similar superscript (lowercase letters) in a single column are insignificantly different at $p < 0.05$.
Abbreviations: ABS, annealed buckwheat starch; CBS_{10}, buckwheat starch treated with 10% (w/v) citric acid solution; CBS_{30}, buckwheat starch treated with 30% (w/v) citric acid solution; HBS, heat-moisture treated buckwheat starch; NBS, native buckwheat starch; $PBS_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); $PBS_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db).

during mechanical stress thus reducing the values of % strain. A decline in % critical strain was also observed by Molavi and Razavi (2018) for corn starch. Moreover, HBS with restricted swelling power results in a very weaker gel strength leading to higher phase angle values but reduced LVR region. The citrates produced from BWS showed a broader LVR compared to NBS. However, an increased DS with the addition of a higher amount of CA did not affect amplitude sweep results. This increase in % critical strain might be an attribute of mono-starch and di-starch citrates which resulted in better tolerance against applied strain values. CBS_{30} also showed a higher phase angle value compared to NBS. Similar results were also observed by Zehra et al. (2020) for CA treated corn and sorghum starches. The values for critical strain were insignificantly different in $PBS_{0.05}$ whereas the value was significantly reduced in $PBS_{0.1}$ (2.5%). Thus, less viscous behavior and a shorter LVR region of $PBS_{0.1}$ was due to an increase in elastic character as evident by lower phase angle value and substantial decline in the loss modulus compared to $PBS_{0.05}$.

3.6.2 | Frequency Sweep Measurements

Figure 3 shows the change in storage modulus and loss modulus as a function of angular frequency for native and modified BWS. The storage modulus was found to be higher than the loss modulus and no cross-over point occurred. Thus, all samples behaved more like solids and the polymers both native and modified were essentially elastic ($G' > G''$) at all frequencies. The phase angle values for native and modified BWS at an oscillatory frequency of 1, 25.1, and 100 rad/s are reported in Table 5. The phase angle value for NBS at 1 rad/s was observed to be 3.26° which increased with increasing angular frequency. It was observed that all treatments, with the exception of HBS at 1 rad/s and 25.1 rad/s, were seen to lower the phase angle values compared to NBS. Thus, HBS was observed to have the highest phase angle value among all. The increased phase angle value is an attribute of a decline in storage modulus after the HMT which can be an attribute of the combination of different factors such as increased deformability of starch granules or a reduction in the continuous phase elasticity, which may be related to the reduced ability of continuous phase amylose to form gels. Yousefi and Razavi (2015) also observed a decline in storage modulus for pearl millet starch after HMT. Also, HBS in amplitude sweep measurements showed the lowest % critical strain which again points to the fact that it had the least resistance against deformation and lacked elastic behavior and thus dissipated more energy. Phase angle values irrespective of physical and chemical modifications were insignificantly different compared to NBS for shorter time scales (higher frequency) suggesting similar viscoelastic behavior of starch gels at higher shear rates. Whereas, ABS was observed to have lower phase angle values of 1.175° and 3.04° at the angular frequency of 1 and 25.1 rad/s, respectively. The lower values of ABS compared to NBS suggested that ABS had a more pronounced gel strength. Annealing leads to the strengthening of bonds as modifications take place under ample moisture content below its gelatinization temperature leading to more elastic natural gels with lower phase angle values. Osundahunsi et al. (2011) showed a similar decrease in loss factor following annealing of cassava starch. Similarly, the phase angle values for CBS_{10} and CBS_{30} were also observed to be significantly lower compared to NBS. Thus, as compared to NBS, the drop in phase angle values was driven by a rise in the storage modulus of starch gels, revealing the presence of more structural and elastic gels. However, the decline among starch treated with different levels of CA was insignificantly different from each other. Moreover, the esterification and di-esterification of starch upon treatment with CA also led to the formation of elastic gels. Zehra et al. (2020) found comparable results with sorghum and maize starch when chemically modified with CA. The value for the phase angle of starch treated with phosphorus oxychloride significantly decreased compared to NBS. However, the decline in phase angle was insignificantly different at different levels of $POCL_3$ treatment. The decline in phase angle for $PBS_{0.05}$ and $PBS_{0.1}$ suggested the increased gel characteristics compared to native.

3.6.3 | In-Shear Structural Recovery Measurements

The structural recovery values for both native and modified BWS are shown in Table 4. The NBS was observed to have a structural recovery of 75.11%, while only annealing and CA-modified starches (CBS_{10} and CBS_{30}) reflected higher structural recoveries than native. The HBS, $PBS_{0.05}$, and $PBS_{0.1}$ were found to have lower structural recoveries. The BWS modified with annealing treatment significantly improved the capability of starch to return to its original structure. This significant increase is attributed to the increased polymeric network which led to a higher association between amylose chains with each other and also with the short-chained branches of amylopectin which subsequently increased the elasticity of starches and percent recovery was increased. In contrast, the structural recovery of NBS decreased after HMT (47.45%). As a result of the formation of rigid structures composed of highly ordered double-helical amylopectin side chains, the molecular density increases and the starch becomes more structurally resistant after heat- moisture treatment (Zavareze and Dias 2011). Interestingly, the starches treated with CA were observed to have the highest value of in-shear structural recoveries suggesting elastic structure of citrate gels as these were stabilized by mono-ester

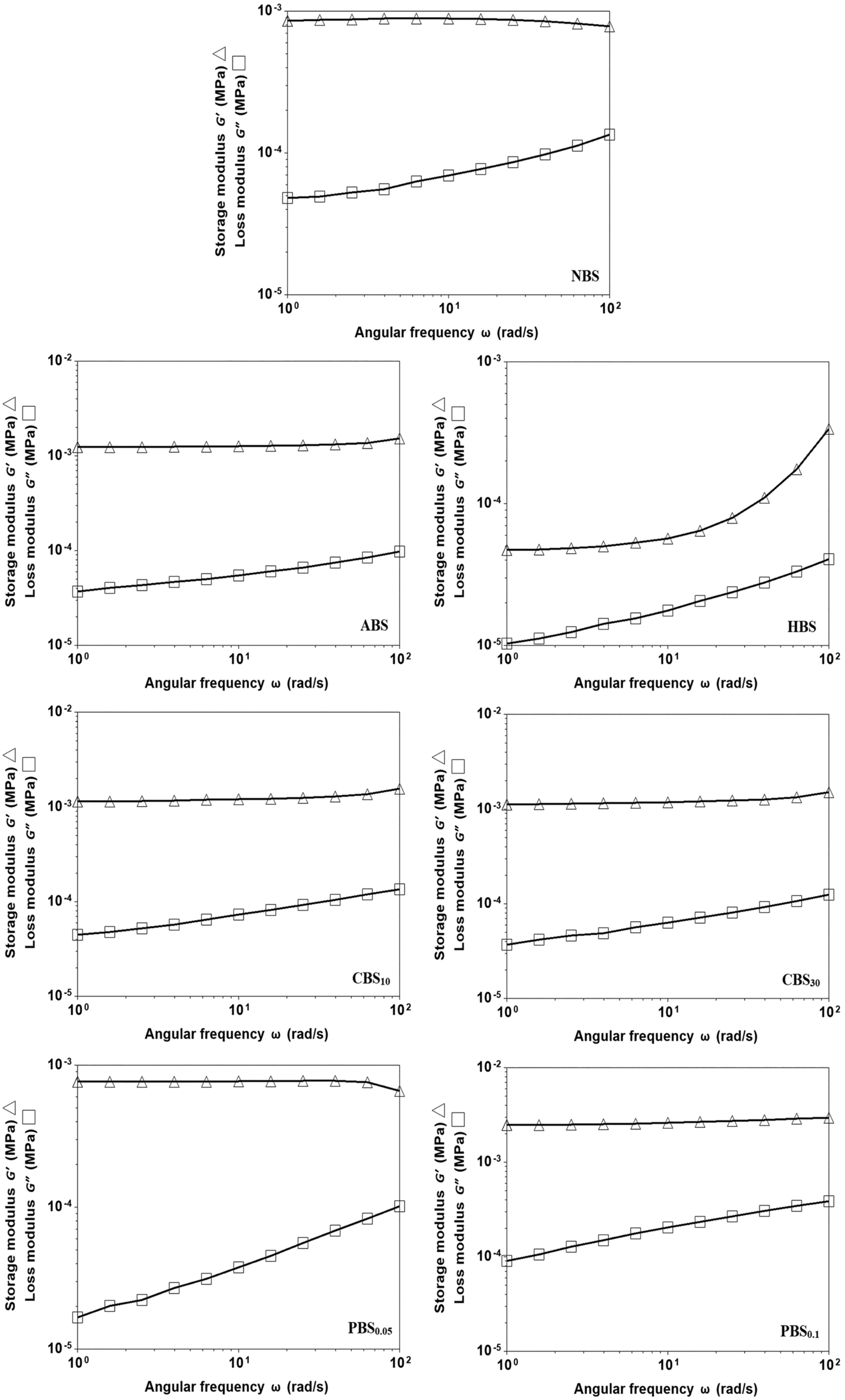

FIGURE 3 | Impact of different modifications on storage and loss moduli of buckwheat starch. ABS, annealed buckwheat starch; CBS$_{10}$, buckwheat starch treated with 10% (w/v) citric acid solution; CBS$_{30}$, buckwheat starch treated with 30% (w/v) citric acid solution; HBS, heat-moisture treated buckwheat starch; NBS, native buckwheat starch; PBS$_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); PBS$_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db).

phosphate groups. Whereas, the addition of crosslinks in $PBS_{0.05}$ and $PBS_{0.1}$ were observed to decrease the structural recoveries for BWS and % recovery was directly related to the phosphorous oxychloride added for the treatment of BWS. Phosphorous oxychloride being a multi-functional reagent crosslinks the starch chains through the addition of di-starch phosphates, that is, two starch chains get covalently bonded by the phosphate group. The addition of this crosslink restricts the molecular mobility of starch chains which could be the major cause of the decline in %recovery of the starch. Such cross-linked starches may take a longer time to recover and are usually hydroxypropylated to increase the structural recovery in a shorter span of time after intense shear treatment.

3.6.4 | Temperature Sweep Measurements

The pasting temperature (T_f) was found to be 66.1°C for NBS (Table 6). The T_f was insignificantly different in ABS, CBS_{10}, and CBS_{30} while significantly increased in HBS, $PBS_{0.05}$ and $PBS_{0.1}$. The significant increase from 66.1°C to 68.5°C after HMT reflected the strengthening of bonds during modification above glass transition temperature in BWS. Moreover, the increase in T_f could also be attributed to higher crystallinity after HMTs from 31.81% in NBS to 40.01% (Table 2) which in turn restricted swelling and thus increased the temperature of viscosity rise. However, there was a drastic increase in T_f to 88.1°C and 86.7°C after phosphorous oxychloride treatments. This increase in T_f is considered an attribute of the crosslink bonds which increased the strength of starch granules and reinforced the already present hydrogen bonding in the granules. Thus, the cross-linked starch formed is considered to be more heat resistant compared to native. Except starches cross-linked with phosphorous oxychloride, all modified starches showed significantly higher MV compared to NBS. The maximum viscosity for NBS (45 Pa s) was significantly reduced to 20 Pa s and 30 Pa s after treatment with 0.05% and 0.1% phosphorous oxychloride based on starch weight (dry basis), respectively. The decline in peak viscosity of $PBS_{0.05}$ and $PBS_{0.1}$ could be related to the formation of di-starch phosphate linkages which reduced the overall mobility of the molecules and also lowered the number of hydrophilic sites accessible for interaction with water leading to lower viscosity compared to NBS that is why cross-linked starches are further modified to form ethers or esters to make them viscosifying or thickening agents with improved shear and thermal stability. The reduction in peak viscosity was also evident by the reduction in the swelling power of $PBS_{0.05}$ and $PBS_{0.1}$ (Table 1) which also suggest that the crosslink bonds inhibited the swelling without breaking the starch granules (Chung et al. 2004; Deetae et al. 2008). However, in the case of both physical modifications, that is, annealing and HMT, MV increased compared to native starches even though both have shown lower swelling power with respect to native starch (Table 1). The MV of HBS with SP less than ABS had even shown higher MV. HMT of starch under low moisture conditions and at a temperature which is greater than gelatinization temperature promotes association among starch chains by destroying the amorphous region and also disrupts the crystalline region near the surface (Gunaratne and Hoover 2002). This rearrangement both in the crystalline and amorphous region caused a decline in swelling

TABLE 5 | Impact of different modifications on phase angle of buckwheat starch recorded at different frequencies[a].

	Phase angle (°)		
Samples	**1 rad/s**	**25.1 rad/s**	**100 rad/s**
NBS	3.26 ± 0.07^{c}	5.31 ± 0.01^{d}	8.13 ± 3.31^{a}
ABS	1.75 ± 0.00^{ab}	3.04 ± 0.26^{a}	7.02 ± 4.70^{a}
HBS	11.80 ± 0.73^{d}	16.29 ± 0.52^{e}	7.22 ± 0.52^{a}
CBS_{10}	2.27 ± 0.03^{b}	4.60 ± 0.37^{c}	6.95 ± 2.85^{a}
CBS_{30}	1.91 ± 0.04^{ab}	3.70 ± 0.77^{b}	5.39 ± 0.95^{a}
$PBS_{0.05}$	1.36 ± 0.16^{a}	4.08 ± 0.33^{bc}	11.70 ± 4.13^{a}
$PBS_{0.1}$	2.02 ± 0.12^{ab}	5.48 ± 0.16^{d}	7.44 ± 0.03^{a}

Note: Mean values with similar superscript (lowercase letters) in a single column are insignificantly different at $p < 0.05$.
Abbreviations: ABS, annealed buckwheat starch; CBS_{10}, buckwheat starch treated with 10% (w/v) citric acid solution; CBS_{30}, buckwheat starch treated with 30% (w/v) citric acid solution; HBS, heat-moisture treated buckwheat starch; NBS, native buckwheat starch; $PBS_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); $PBS_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db).

TABLE 6 | Impact of different modifications on pasting properties of buckwheat starch[a].

Sample	T_f (°C)	MV (Pa s)	TT_{MV} (min)	T_{MV} (°C)	$V_{95°C}$ (Pa s)	$V_{35°C}$ (Pa s)
NBS	66.1 ± 0.2^{a}	45.0 ± 7.1^{a}	12.8 ± 0.1^{a}	73.3 ± 0.1^{a}	16.2 ± 1.0^{a}	50.0 ± 0.0^{a}
ABS	67.2 ± 0.1^{ab}	90.0 ± 0.0^{b}	14.5 ± 0.3^{b}	78.3 ± 0.7^{b}	26.0 ± 0.9^{bc}	65.0 ± 7.1^{b}
HBS	68.5 ± 0.2^{b}	200.0 ± 0.0^{c}	18.1 ± 0.0^{c}	89.3 ± 0.3^{c}	100.0 ± 0.0^{d}	300.0 ± 0.0^{d}
CBS_{10}	65.8 ± 0.2^{a}	100.0 ± 0.0^{d}	16.6 ± 0.0^{d}	84.7 ± 0.1^{d}	50.0 ± 0.0^{e}	65.1 ± 7.1^{b}
CBS_{30}	65.5 ± 1.2^{a}	100.0 ± 0.0^{d}	16.7 ± 0.2^{d}	85.1 ± 0.7^{d}	45.0 ± 7.1^{e}	70.3 ± 0.0^{b}
$PBS_{0.05}$	88.1 ± 1.6^{c}	20.0 ± 0.0^{e}	20.4 ± 0.1^{e}	94.1 ± 0.2^{e}	20.0 ± 0.0^{ab}	04.0 ± 1.41^{e}
$PBS_{0.1}$	86.7 ± 9.8^{c}	30.0 ± 0.0^{f}	20.2 ± 0.1^{e}	95.1 ± 0.0^{e}	30.0 ± 0.0^{c}	15.0 ± 3.38^{f}

Note: Mean values with similar superscript (lowercase letters) in a single column are insignificantly different at $p < 0.05$.
Abbreviations: ABS, annealed buckwheat starch; CBS_{10}, buckwheat starch treated with 10% (w/v) anhydrous citric acid solution; CBS_{30}, buckwheat starch treated with 30% (w/v) anhydrous citric acid solution; HBS, heat-moisture treated buckwheat starch; MV, maximum viscosity; NBS, native buckwheat starch; $PBS_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); $PBS_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db); T_f, temperature where first rise in viscosity was recorded; T_{mv}, temperature of maximum viscosity; TT_{MV}, time taken to reach maximum viscosity; $V_{35°C}$, viscosity recorded at 35°C; $V_{95°C}$, viscosity recorded at 95°C.

power and rendered thermal stability to the granules which is obvious as solubility was also reduced after HMT. These thermally stable/rigid granules thus promote more granule-granule interaction and thus possessed higher MV. Whereas, annealing in contrast to HMT occurred at non-restricted moisture levels and at a temperature less than the gelatinization temperature of starch and promotes perfection in the crystalline region of starch through reorganization of amylopectin double helices and also promotes interaction between starch chains. The crystallinity observed in ABS was less than HBS (Table 2) which suggests that the order of perfection was higher in HBS and therefore ABS had lower thermal stability or granular rigidity leading to lower MV due to lower granular–granular interaction. Furthermore, chemical crosslinks as formed through phosphorylation were observed to have a higher impact on the granular swelling and therefore led to lower MV in the case of PBS starch. Whereas, the increase in MV after CA modification was due to the insertion of hydrophilic bulky citrate groups which bonded more water and allowed the development of higher viscosities. When treated with CA, Babu et al. (2015) also observed an improved MV for sweet potato starch. The time taken for native and modified BWS to achieve their maximum viscosities was significantly increased after all modifications and was referred to as TT_{MV}. The NBS was observed to reach MV in the minimum time of 12.8 min. The increase in TT_{MV} could be due to the increase in temperature for achieving the maximum viscosity referred to as T_{MV}. The increase in T_{MV} and TT_{MV} after both physical modifications; ABS and HBS was due to improvement in the organizational structure of starch granules after these modifications, which eventually led to an increase in the % crystallinity (Table 2). Thus, these perfected more crystalline starch granules required higher temperatures and more time to achieve maximum viscosity (Simsek et al. 2012). Furthermore, the significant difference between both physical modifications might be due to the differences in their % crystallinities. Thus, the HBS shares more % crystallinity compared to ABS, therefore, this might be the reason for the higher TT_{MV} of the former compared to ABS. There was a significant increase in T_{MV} and TT_{MV} in CBS_{10} and CBS_{30}, however, the effect was insignificant in terms of the level of the CA used for modification. The increase in T_{MV} and TT_{MV} after CA treatment is associated with the formation of the di-starch citrates which reinforces the starch chains leading to more time and higher temperature to achieve the peak viscosity. Similarly, the increase in time and temperature required to reach maximum viscosity for $PBS_{0.05}$ and $PBS_{0.1}$ could be considered an attribute of the di-starch phosphate linkages which restricted swelling and required more time and temperature to attain peak viscosity. Di-starch phosphate linkages in comparison to di-starch citrates are more efficient in restricting swelling power as phosphorylated starches consumed the longest time and demonstrated the highest temperature to reach maximum viscosity. Thus, phosphorylation can confer more thermal stability to starch granules. Hot paste viscosity was recorded at 95°C and referred to as $V_{95°C}$ was significantly increased after annealing (26.0 Pa s) and HMT (100 Pa s). The significant increase of $V_{95°C}$ after the physical modifications might be due to the formation of a tightly packed array of swollen, deformable granules and leached-out amylose. This contributed to the increase in the viscosity of paste during heating along with the increased rigidity of granules due to insufficient gelatinization. Thus, the rigidity of granules caused an increase in the viscosity due to more resistance against shearing (Adebowalea et al. 2005; Jacobs et al. 1995). Similarly, the hot paste viscosity was also observed to increase after CA and phosphorus oxychloride treatments. The rise in $V_{95°C}$ was due to the insertion of mono and di-starch citrates in CA-modified starches. Cold paste viscosity is the viscosity of the starch molecules after cooling. The tendency to gel upon cooling was assessed in terms of cold paste viscosity. Moreover, when a hot paste of starch is allowed to cool, the increase in the viscosity is said to be due to the re-association of the starch molecules (Hagenimana et al. 2006). The cold paste viscosity of native and modified BWS was measured at 35°C after gelatinization and referred as $V_{35°C}$. The cold paste viscosity significantly increased after all physical and chemical modifications except phosphorus oxychloride treated BWS where $V_{35°C}$ was significantly decreased. The decline in $V_{35°C}$ observed for $PBS_{0.05}$ and $PBS_{0.1}$ could be associated with restricted swelling power as could be seen in Table 1 which in turn resisted the gelation tendency upon cooling due to less pronounced interactions with water. The significant increase in $V_{35°C}$ after annealing and HMT could be owed to the increased ability of starch granules to enhance their elastic component as a result of a strengthened polymeric network, thus the increased ability of starch granules for the reassociation of amylose back with each other or with the outside branches of amylopectin upon cooling can also be considered a factor for the improved $V_{35°C}$. This result indicated that of the two physical modifications, HMT had a higher gelation tendency. In addition, the higher value of $V_{35°C}$ for HBS compared to NBS may be due to the more properly arranged and aligned starch molecular chains, which may led to the stronger structural rigidity of HBS compared to ABS on cooling. Due to di-starch citrate cross-links, which resulted in the formation of intermolecular bridges and also due to the addition of covalent bonds within the starch granules, CBS_{10} and CBS_{30} vary substantially from NBS in terms of $V_{35°C}$ and showed higher values because of higher interaction with water on cooling which resulted in a better gel structure.

3.7 | In Vitro Digestibility

The digestibility properties of native and modified BWS are presented in Table 7. The native BWS showed the RDS of 51.05%, SDS of 32.24%, and RS content of 16.71%. In the literature, the RS content of different BW cultivars was observed to be in the range of 7%–37% (Bhavsar et al. 2013; Qin et al. 2010; Skrabanja and Kreft 1998; Wijngaard and Arendt 2006). The RS observed in NBS from Pakistani-grown BW kernels was also found to be in the same range. Both physical and chemical modifications significantly increased the RS of NBS in the range of 16.71%–58.95%. The significant increase in RS and SDS content of native BWS after annealing treatment is correlated with a decline in the RDS of BWS. This increase in RS and SDS could be due to the structural changes mainly brought up during the annealing process where the starch was treated with excess water but above the glass transition temperature which increased the molecular reorganization and alignment between starch chains leading to a higher degree of crystallinity making it more resistant to enzymes (Table 2). An increase in SDS and RS was also observed by Marboh and Mahanta (2021) for the sohphlang tuber starch after annealing. However, after HMT, there was also a significant increase in RS content with a significant decline in SDS

TABLE 7 | Impact of different modifications on in vitro digestibility of buckwheat starch^{a}.

Sample	RDS (%)	SDS (%)	RS (%)
NBS	51.05 ± 1.21^{a}	32.24 ± 1.29^{a}	16.71 ± 0.08^{a}
ABS	25.23 ± 0.15^{b}	38.94 ± 0.29^{b}	35.84 ± 0.44^{b}
HBS	50.95 ± 2.05^{a}	24.26 ± 1.24^{c}	24.79 ± 0.82^{c}
CBS$_{10}$	45.04 ± 0.02^{c}	25.72 ± 1.45^{cd}	30.24 ± 0.05^{d}
CBS$_{30}$	32.66 ± 0.07^{d}	26.54 ± 0.31^{d}	40.80 ± 0.38^{e}
PBS$_{0.05}$	13.47 ± 0.29^{e}	42.65 ± 0.36^{e}	43.88 ± 0.06^{f}
PBS$_{0.1}$	19.22 ± 0.25^{f}	21.84 ± 0.32^{f}	58.95 ± 0.06^{g}

Note: Mean values with similar superscript (lowercase letters) in a single column are insignificantly different at $p < 0.05$.
Abbreviations: ABS, annealed buckwheat starch; CBS$_{10}$, buckwheat starch treated with 10% (w/v) anhydrous citric acid solution; CBS$_{30}$, buckwheat starch treated with 30% (w/v) anhydrous citric acid solution; HBS, heat-moisture treated buckwheat starch; NBS, native buckwheat starch; PBS$_{0.05}$, buckwheat starch treated with 0.05% phosphorous oxychloride (db); PBS$_{0.1}$, buckwheat starch treated with 0.1% phosphorous oxychloride (db); RDS, rapidly digestible starch; RS, resistant starch; SDS, slowly rapidly digestible starch.

while RDS was insignificantly different from native starch. The significant decrease in SDS after HMT might be because of the disruption of double-helical structures along with the reorientation of the crystallites. Thus, the decrease in SDS eventually increased the RS content of HBS which could be considered as an effect of increased interaction of the starch chains but the RS produced through HMT was still lower than the RS produced through annealing treatment. This might be because of the high temperatures used during HMTs which could have led to partial gelatinization of starch leading to lower SDS compared to native and lower RS compared to annealing where modification is done below gelatinization temperature. A similar decline in SDS and increased RS was also observed by Chung et al. (2009) for corn, pea, and lentil starches when subjected to HMT. The RS content for CBS$_{10}$ and CBS$_{30}$ were observed to be 30.24% and 40.80%, respectively which represent that there was an increase of 80.97% and 144.17% RS content compared to NBS followed by 10% and 30% CA treatments, respectively. The increase in RS and SDS content of NBS after CA treatment could be attributed to the low molecular weight chains produced upon hydrolysis of acid which produced resistance against enzymatic digestions through the formation of double helices and compartmentalization of amylose-amylose, amylose-amylopectin and amylopectin–amylopectin chains during the CA modification along with heat Chung et al. (2009). Moreover, when CA is heated, it dehydrates and forms an anhydride. The anhydride produced is esterified to produce starch citrates, which further crosslinks upon heating to form a diester. The cross-linking formed due to diester formation creates hindrance against the action of digestive enzymes and as a result, the RS and SDS increase. The RS content in CBS$_{30}$ was observed to be higher compared to CBS$_{10}$. This increase might be due to the increased number of low molecular weight chains attached to the starch, forming a double helix under the influence of HMT. The presence of more di-starch esters due to bulky citrate groups also resulted in reduced digestibility of CBS$_{30}$ compared to CBS$_{10}$. A similar increase in RS was also observed by Shaikh et al. (2019) for corn and sorghum starches after CA modification.

The most pronounced effect on resistant starch was observed after cross-linking with POCL$_3$. The RS for PBS$_{0.05}$ and PBS$_{0.1}$ was observed to be 43.88% and 58.95%, respectively which was found to be the highest RS produced among all modifications employed on BWS. The increase in RS content after phosphorylation was due to the formation of strong cross-links that led to the prevention of amylase from entering the inside of starch through different channels and pores. Moreover, the reduction in swelling power of PBS$_{0.05}$ and PBS$_{0.1}$ as described in Table 1 could also be a possible cause of increased RS content. However, RDS and RS significantly increased along with a decline in SDS with the increase in the concentration of POCL$_3$ from 0.05% to 0.1%. The significant increase in RS after increase in the concentration of POCL$_3$ was due to the increased number of di-starch phosphates (crosslinks) and a higher degree of crystallinity (Table 2) which restricted enzymatic digestion. The increase in RDS and decrease in SDS of PBS$_{0.1}$ compared to PBS$_{0.05}$ was due to a higher degree of chemical substituents which may destroy the internal starch structure to some extent and thus allowed easier infiltration of enzyme in the amorphous region of PBS$_{0.1}$ leading to higher RDS and lower SDS.

4 | Conclusion

It could be concluded that the BWS modified either by physical or chemical treatments depicted significantly altered % crystallinity, techno-functionality and reduced digestibility. This opens a vast gateway for the utilization of BWS in wide applications in various foodstuffs. Di-starch phosphate BWS may find applications in high shear applications as these starches did not show any change in their V$_{95°C}$ with respect to maximum viscosity suggesting their highest shear tolerance. While, CA modified and annealed starches can be used as viscosifying agents because of their significantly higher final viscosity like mayonnaise, ketchup and spreads. On the other hand, heat-moisture treated starch behaved as a gelling agent as it showed the highest final viscosity compared to all other BWS. In applications where very quick recoveries are required, CA modified starches can play an important role as CBS were found to have the highest in-shear structural recoveries. The most pronounced increased in resistant starch content was observed after crosslinking with POCL$_3$. In future, the modified BWS with higher resistant starches could be used in development of low calorie products to target diabetic and obese population.

Author Contributions

Salman Haider: investigation, methodology, formal analysis, writing – original draft. **Tahira Mohsin Ali:** conceptualization, methodology, resources, supervision, writing – review and editing, visualization, project administration. **Marium Shaikh:** resources, writing – original draft, writing – review and editing, visualization, data curation. **Ghulam Mustafa:** investigation, software, data curation. **Angelo Maria Giuffrè:** software; visualization; supervision; writing – review and editing; project administration.

Acknowledgments

Open access publishing facilitated by Universita degli Studi Mediterranea di Reggio Calabria, as part of the Wiley - CRUI-CARE agreement.

Funding

The authors have nothing to report.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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