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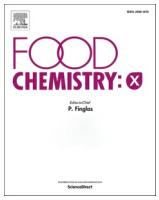

Construction of sodium alginate/trehalose/wheat starch ternary complex and its effects on storage stability of frozen dough system

Tongchao Su, Wenkai Du, Jie Zeng, Haiyan Gao, Benguo Liu *

School of Food Science, Henan Institute of Science and Technology, Xinxiang 453003, China

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ABSTRACT

In order to improve the quality of frozen dough, a calcium alginate-coated sodium alginate/trehalose/wheat starch ternary complex was designed in this paper. The ternary complex was added to dough, and the dough quality were measured after 0–30 d of frozen storage. The XRD and FT-IR results showed the ternary complex was mainly starchy crystal. The TGA curves showed the starting (To), peak (Tp) and termination temperature (Tc) were increased. The interaction between sodium alginate and trehalose enhanced the thermal performance of ternary complex. As the ternary complex addition to dough increased, the maximum ice crystal formation zone of the frozen dough passed faster, resulting in more uniform and smaller ice crystals. The dough with 0.8% addition contained more bound water and had better hardness, springiness and cohesiveness. In conclusion, the study provides a novel insight and understanding for the development of ternary complex as food additives in frozen food industry.

1. Introduction

As a kind of semi-finished product, frozen dough can maintain the performance of dough and prolong the preservation period of dough through frozen storage, and it is widely used in the process of food chain processing. In recent years, frozen dough technology has brought people a lot of convenience, but also encountered some problems after its rapid development (Conte, 2019). Although frozen dough products could have a long storage time and were conducive to storage and transportation, there were some problems compared with fresh dough products, such as reduced taste, small size, poor texture and performance (Liu et al., 2020). So appropriate food additives could be added to enhance the the yeast activities and improve the dough quality characteristics such as freeze-thaw stability, gluten network structure and bread texture (Chen et al., 2022; Tao et al., 2018). Trehalose was considered as one of the most commonly used additives, which not only had properties similar to antifreeze, but also more natural and safe, and it's widely used in the field of food industry (Li et al., 2021).

Trehalose had the function of protecting biological macromolecules. It was a non-reducing disaccharide formed by the combination of two molecules of glucose through the glucoside bond (Dhaene et al., 2020; Walmagh et al., 2015). It was an emergency metabolite synthesized under some extreme environmental conditions such as high temperature, freezing, drying and radiation (Assoni et al., 2021; Ohtake & Wang, 2011). It played a protective role on organisms and biological macromolecules and could protect yeast cells from various pressures (Pastinen et al., 2017), and further improves the activity and gas production of dough yeast during frozen storage (Stefanello et al., 2018). It's found that the ice crystals formed when water freezes in the presence of trehalose were effective in minimizing damage to the flesh of fish. The ice crystal forms presented by sucrose solution and trehalose solution were observe dunder a microscope, and it's found that the ice crystal edges of sucrose solution were sharp and easier to puncture muscle cells, while the crystal form of trehalose solution was relatively round, which was smaller in size and less likely to puncture cells (Sei et al., 2002).

Calcium alginate was reported to be a material that could encapsulate probiotics, enzymes and drugs (Blemur et al., 2015; Hassan et al., 2020). Sodium alginate with the molecular formula $(C_6H_7NaO_6)_x$, was a linear *co*-polymer composed of the G and M unit, which represented α-L-guluronic acid and β-D-mannronic acid, respectively and they were connected by the β-1,4-glycosidic bond (Ta et al., 2021). The G-unit reacted more readily with calcium ions, whereas the M-unit could not discriminate between calcium ions and other metal ions, and then bound to any metal ion, so it was possible to use this property to encapsulate samples in beads formed by sodium alginate and calcium ions. Cui et al. found that the peak gelatinization temperature could be significantly

* Corresponding author.
E-mail address: liubenguo@hist.edu.cn (B. Liu).

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increased when potato starch particles were wrapped in calcium alginate beads. Compared with encapsulated starch particles, the contents of slow-digestible starch and resistant starch were significantly increased to 27.5% *vs* 18.3%, respectively (Cui et al., 2022).

In this paper, a binary complex containing trehalose and starch were formed with Ca^{2+} and sodium alginate, named as modified trehalose. Then, in order to obtain the ternary complex containing calcium alginate of different thickness, the binary complex were soaked in sodium alginate of different concentrations, and then studied the microstructure, hardness, springiness and thermostability of the binary and ternary complex (CA-TL-WS) (CA: Calcium alginate, TL: trehalose, WS: Wheat starch). The constructed CA-TL-WS were added to the frozen dough to study its anti-freezing properties. The influence of different CA-TL-WS concentrations on the quality characteristics of frozen dough were investigated, and the theoretical research on influence of CA-TL-WS on the anti-freezing changes quality of dough during frozen storage was enriched. Moreover, it provided a theoretical basis for studying the effects of CA-TL-WS on the quality change of dough during frozen storage, and also extended the application prospect of ternary complex as food additives in food preservation.

2. Materials and methods

2.1. Materials

Calcium chloride, white granulated sugar, trehalose and sodium alginate were purchased from Tianjin Guangfu Development Co., Ltd.; Wheat flour was obtained.

from Jinlongyu Flour Group Co., Ltd.; distilled water.

2.2. Construction of sodium alginate/trehalose/wheat starch ternary complex

The ternary complex was prepared by two-step method. Firstly, 0.5 g sodium alginate was completely dissolved in distilled water at 1% *w/v* concentration. Secondly, mixed the sodium alginate: wheat starch: trehalose in a mass ratio of 1:20:3. Stirred well with a magnetic mixer (ZD-85, Changzhou Guohua Electric Appliance Co., Ltd.) at 25 °C for 15 min, then transferred to a syringe. Then, dropped the above mixture of of sodium alginate/trehalose/wheat starch into 2% w/v calcium chloride solution at the rate of 3 mL/min while stirring at 25 °C, and the fresh starch beads were obtained after stiring for 1 h. The obtained CA-TL-WS beads were named as modified TL. In order to form ternary complex, the obtained CA-TL-WS beads were placed in sodium alginate solutions of different concentrations (0.125–0.5% *w/v*) and stirred at 200 rpm at 25 °C for 3 min. Let stand in the 2% (*w/v*) calcium chloride solution for 1 h. The prepared beads and CA-TL-WS ternary complex were washed several times with distilled water. Finally, dried at 45 °C for 24 h, then crushed with a high speed universal crusher (FE-100, Beijing Yongguang Medical Instrument factory.) and passed through a 100-mesh sieve. The CA-TL-WS ternary complex obtained by immersion in sodium alginate solutions at different concentrations of 0.125%, 0.25%, 0.5%(w/v) were named as 0.125 CA-TL-WS ternary complex, 0.25 CA-TL-WS ternary complex and 0.5 CA-TL-WS ternary complex, respectively. For comparison, TL-free starch bead (noted as CA-WS bead), 0.125 CA -WS bead were prepared by the same method, 0.25 CA -WS bead and 0.5 CA -WS bead.

2.3. Technical analysis of the beads and CA-TL-WS ternary complex

2.3.1. Texture properties

Placed the fresh beads or ternary complex on the texture analyzer (TA-XT Plus texture analyzer, StableMicroSystems, UK) and tested for hardness and elasticity using a texture analyzer with a probe P36R, the test speed was 1.0 mm/s and the compression degree was 50% (Lozano-Vazquez et al., 2015).

2.3.2. Microstructure

The beads and ternary complex were freeze-dried for 48 h at 4 Pa at −55 °C. The freeze-dried beads and capsules were sprayed with gold for electron microscope scanning (Quanta 200, FEI Co., Inc., Hillsboro, OR, USA). Magnification was 500.

2.3.3. X-ray diffraction (XRD) analysis

Crushed the dried beads and ternary complex with a high-speed crusher and filtered with a 100-mesh sieve. Then the obtained dry beads and ternary complex powder were evenly dried for 48 h in a dryer containing a saturated sodium chloride solution (relative humidity =76%). X-ray diffraction patterns from 4° to 40° Angle (2θ) were recorded (Bruker D8 Advance A25 X-ray diffractometer Bruker AG). The relative crystallinity was calculated according to the following the formula:

$$X_c = I_c / I_0 \times 100\% \quad (1)$$

In the formula, X_c: crystallinity of the sample, I_c: the integral intensity of all diffraction peaks of the sample, I_0: integral strength of 100% crystalline.

2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of freeze-dried beads and ternary complex was performed on a thermogravimetric analyzer (STA 449 F5, NeTSch Scientific Instrument Trading Co., LTD). Under a nitrogen atmosphere, the flow rate was 50 mL/min, and the heating rate from room temperature to 800 °C was 10 °C/min.

2.3.5. Fourier transform infrared spectroscopy (FT-IR) analysis

The pulverized beads and ternary complexes were determined by using Fourier infrared (TENSOR 27, BRUKER Spectroscopic Instruments, Germany) with 100 mesh screen. A clean potassium bromide blank background spectrum was first established, and spectral scans were awakened on beads and capsule samples with the ration of 1:100 (sample *vs* KBr). The parameters of ATRFTIR spectra were obtained in 32 scans with a spectral resolution of 4 cm^{-1}.

2.3.6. DSC analysis

The beads and capsules were determined by DSC (Q200, TA Ltd.). Wheat starch, pellets and ternary complex were weighed (2.0 mg), added with 4 μL of water, and placed in the crucible for pressure disc sealing for 12 h. Tested with a blank crucible for comparison. The heating rate was 10 °C/min and the temperature was heated from 25 °C to 125 °C (Ashwar et al., 2018).

2.4. Preparation of mixed powder and frozen dough

The flour was mixed well with 0–1.0% CA-TL-WS ternary complex, respectively. Mixed the flour evenly, added 50% water, 1% sugar and 1% yeast, knead it in a pasta machine for 6 min, manually circle until the dough surface was smooth, and fermented in a fermentation box (HYC-TH-80DH, Dongguan Hongjin Testing Instrument Co., Ltd.) at 37 °C for 30 min.

Divided the dough into several 5 g small dough, wrapped them with plastic wrap respectively, and then froze the dough for 2 h in a low temperature incubator at −30 °C. Then the dough was frozen in an incubator at −18 °C. The samples were collected at 0–30 d and thawed for 2 h at room temperature for further analysis. The forming process and frozen dough were analyzed.

2.5. Technical analysis of mixed powder

2.5.1. Silty properties

According to the Cruz-Tirado's method (Cruz-Tirado et al., 2021), added compound powder to the mixing tester (Mixolab mixing tester, Chopin Technology Co., LTD) and bowl, and the total mass of powder

and water was set at 75 g. The estimated water absorption rate and the water content of the compound powder were input, and the amount of compound powder and water was adjusted until C1 was within 1.10 ± 0.05 Nm.

2.5.2. Gelatinization characteristics

The gelatinization property of mixed flour was determined by a rapid viscosity analyzer (TecMaster, Newport scientific instruments LTD., Australia). Put 3.0 g of mixed powder (corrected at 14% wet basis) into an aluminum can and added distilled water. The gel properties of the mixture of modified trehalose and flour were analyzed.

2.6. Technical analysis of frozen dough

2.6.1. Color determination

The dough color was analyzed according to Wang's method. The prepared dough was pressed and cut into slices, and a calibrated precision colorimeter was used to measure the color changes (CR-40 color difference meter, Minolta Corporation, Japan) at three uniform points in the prepared slices, and recorded the L*, a*, and b* values. Before measurement, turned on the colorimeter and warmed up for 5 min (Wang et al., 2022).

2.6.2. Freezing curve determination

Placed the frozen dough into the freezer, then placed the sensor recording the temperature in the dough center and recorded the center temperature of the dough every 2 s. when the temperature dropped to −18 °C, plotted the freezing curve of the dough.

2.6.3. Moisture migration

As described by Meng's method (Meng et al., 2021), the resonance center frequency was tested by FID, and the spin relaxation time (T2) of the samples were measured by the CPMG pulse sequence (NMI20-040 V-I NMR Imaging analyzer, Suzhou Niumai Analytical Instruments Co., Ltd.). After thawing, the frozen dough (5.0 ± 0.01 g) was weighed into a test tube and placed in the center of the permanent magnet field of the radio frequency coil, and the scanning test of CPMG pulse sequence was performed. The parameters of the CPMG test were as follows: main frequency = 20 (MHz), offset frequency = 628,049.19 (Hz), number of sampling points TD = 40,014, number of repetitive scans NS = 4, sampling interval time TW = 2000 ms, half echo time τ = 6.52 μs, temperature = 32 °C. The T2 relaxation time inversion spectra of the samples were obtained using the T2 inversion program. The determination was repeated three times for each sample, and the results were expressed as the mean ± standard deviation.

2.6.4. Textural properties

Refering to Luo's method (Luo et al., 2015), the dough was defrosted and made into a ball dough with a radius of 3 cm. The dough was analyzed with a texture analyzer (P36R probe). Test parameters were as follows: pre-test speed 2 mm/s, test speed 1 mm/s, and post-test speed 1 mm/s, compression ratio 70%, trigger force 5 g, compression interval 5 s.

3. Results and discussion

3.1. Textural properties of the beads and CA-TL-WS ternary complex

As it's shown in Fig. 1, the hardness of the samples with the TL addition showed a decreasing trend compared to those without TL. The hardness of the capsule formed after calcium alginate encapsulation was higher than that of CA-TL-WS and CA-WS. Because of the elevation of

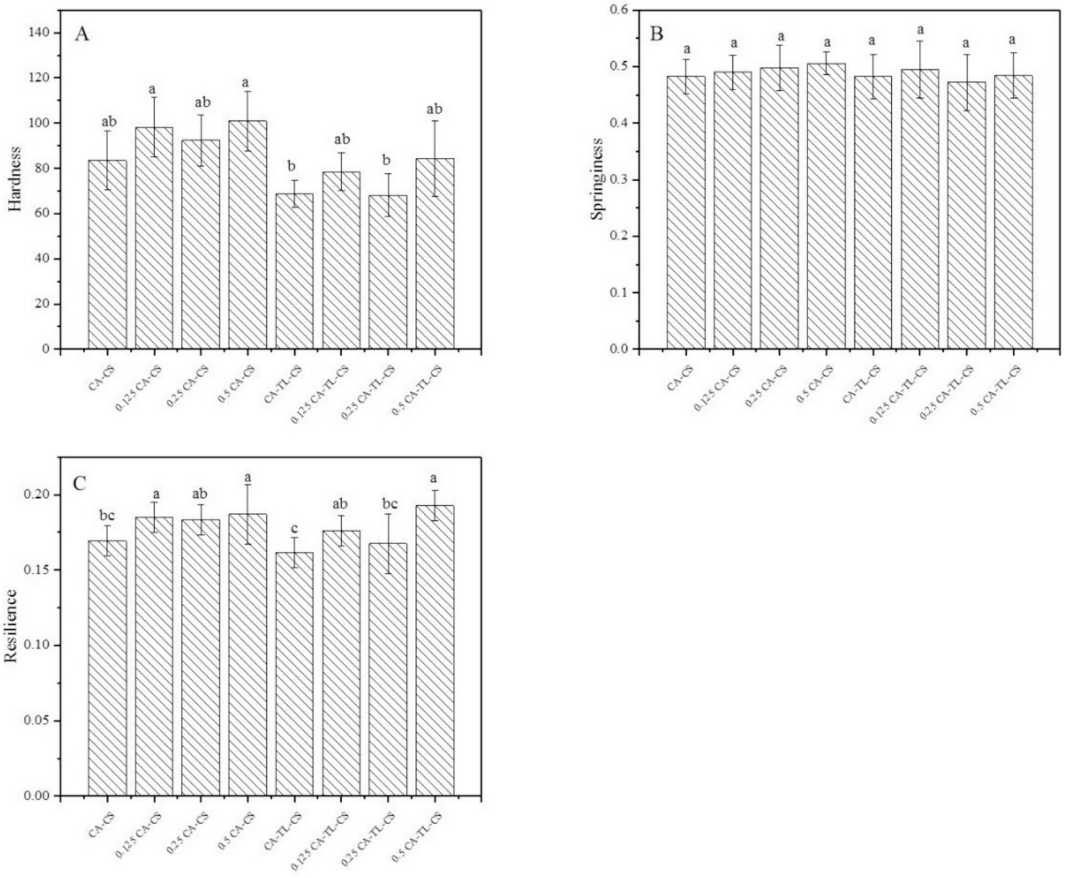

Fig. 1. Texture properties of the beads and CA-TL-WS ternary complex (A: Hardness; B: Springiness; C: Resilience).

sodium alginate concentration in the outer shell, the hardness of CA-WS beads and CA-TL-WS ternary complex increased from 83.50 ± 23.02^{ab}, 68.72 ± 6.06^{b} to 100.96 ± 23.2^{a}, 84.44 ± 16.72^{ab}, respectively. Calcium alginate formed by sodium alginate and Ca^{2+} was the main factor affecting capsule hardness, the higher the sodium alginate concentration, the more calcium alginate shell, the greater the capsule hardness (Xiao et al., 2017). And the hardness of beads and capsules with TL was lower than that of beads and capsules without TL because the hydroxyl groups in the TL molecule were all hydrophilic ethane, so TL could effectively lock water in aqueous solutions. No significant changes in the elasticity of beads and capsules were found. Meanwhile, the recoverability of the capsules coated with sodium alginate solution was significantly higher, and when 0.5% sodium alginate solution was added, the capsules with calcium alginate core-shell structure had a protective effect, and it was easier to restore to the original shape and better resilience after being subjected to pressure.

3.2. Microstructure of the beads and CA-TL-WS ternary complex

Fig. 2 showed the beads and capsules microstructure, it could be seen that the outer layer of the beads and capsules is mainly composed of wheat starch granules. In the CA-WS beads and CA-TL-WS ternary complex, starch granules had been damaged, deformed and the structure were looser, which may be due to the micro-mechanical damage caused by stirring during the preparation process. As the sodium alginate concentration increased, the distribution of starch particles showed a more compact and uniform trend. At the same time, the surface was smooth with no holes, collapses, and rupture, a tighter calcium alginate structure was formed by sodium alginate and calcium ions, which firmly bonded the starch granules together and could protect the starch granules. These results showed that the sodium alginate concentration and calcium ion was positively correlated with the density of calcium alginate network structure, and the higher the concentration, the better the density, which was consistent with other researchers results (Yuan et al., 2018). Besides, the structure of the capsule with TL added was more compact on the surface of the capsule with TL added compared to that without TL added, indicating that TL could act together with sodium alginate to make the starch granules uniformly and stably aligned.

3.3. Characterization of the beads and CA-TL-WS ternary complex

3.3.1. XRD analysis

The XRD profiles and crystallinity of the beads and CA-TL-WS ternary complex were illustrated in Fig. 3A and B. The XRD patterns of beads and ternary complex showed that there were double peaks at 17° and 18°, and the diffraction peaks were obvious at 15° and 23°, respectively, which was a typical starch A-type crystal structure. Compared with wheat starch, the peak positions of beads and capsules did not change significantly, indicating that the structure was dominated by the amylose crystal structure, but some of the diffraction peaks had lower intensities, which might be due to the non-starch components (TL and calcium alginate) affecting the intermolecular interactions among the starch molecules. According to Fig. 3B, it's shown that the crystallinity of the beads and capsules changed significantly, the crystallinity of the blank starch was 22.41%, while the crystallinity of CA-WS and CA-TL-WS was 15.95% and 13.04% ($p<0.05$), which was lower compared with the blank starch, and it indicated that the combined action of sodium alginate and trehalose reduces the degree of starch molecular rearrangement. The recrystallization and degradation of amylopectin were inhibited (Niu et al., 2018). As a small molecule sugar, TL could easily enter into the starch molecular chain, which was the first key basis for TL to participate in the recrystallization of starch. In addition, the polyhydroxyl structure formed by alginate could be combined with the carbonyl groups exposed at the end of the starch molecular chain, and the combination could effectively inhibit the interaction of starch molecules with each other, which could prevent the recrystallization process, and slow down the double-helix structure formation (Hou et al., 2020).

3.3.2. TGA analysis

The TG and DTG curves of the beads and CA-TL-WS ternary complex were shown in Fig. 3C and D. According to the thermogravimetric curves, it can be seen that the degradation of the beads and capsules mainly had two processes. The first stage of mass loss occurred between 30 °C and 150 °C, and this stage was mainly related to water evaporation. As the temperature increased, the rate of mass loss of the CA-WS beads and the CA-TL-WS ternary complex was faster than that of the WS, because the sodium alginate and the TL had good water retention, and the sample had a high relative water content so that the loss of mass

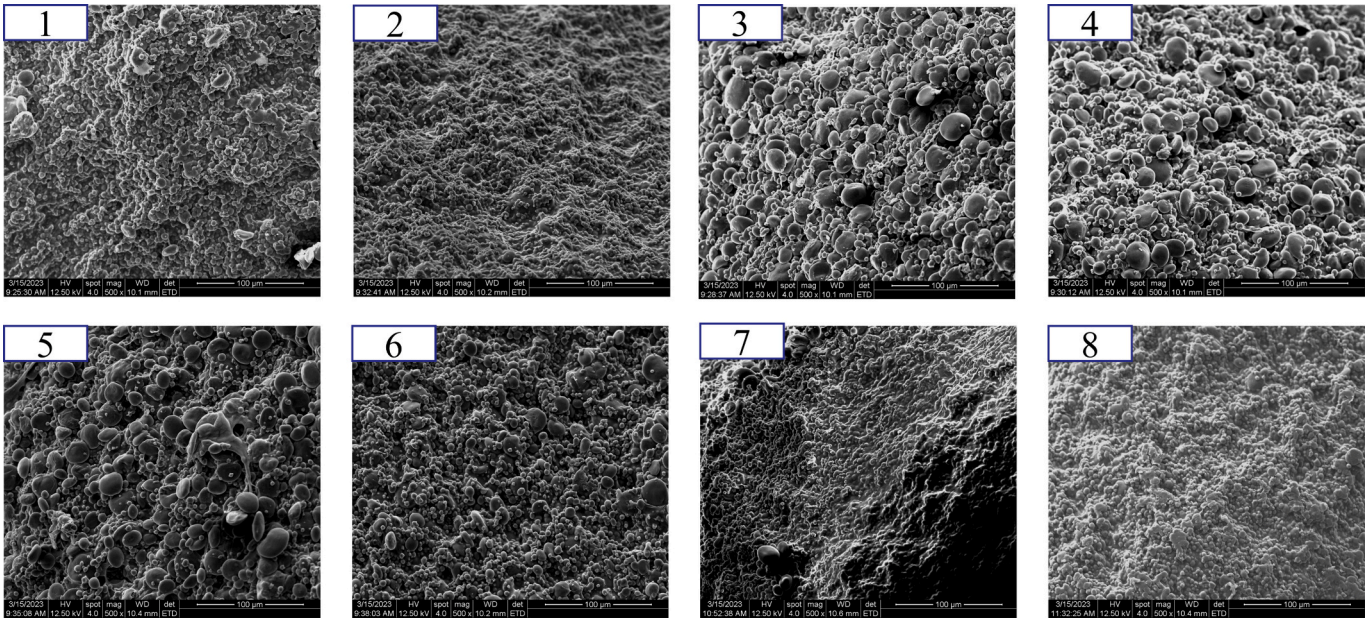

Fig. 2. Microstructure of the beads and CA-TL-WS ternary complex (1 to 4 are CA-WS, 0.125 CA-WS, 0.25 CA-WS, and 0.5 CA-WS, respectively 5 to 8 are CA-WS, 0.125 CA-TL-WS, 0.25 CA-TL-WS, and 0.5 CA-TL-WS, respectively).

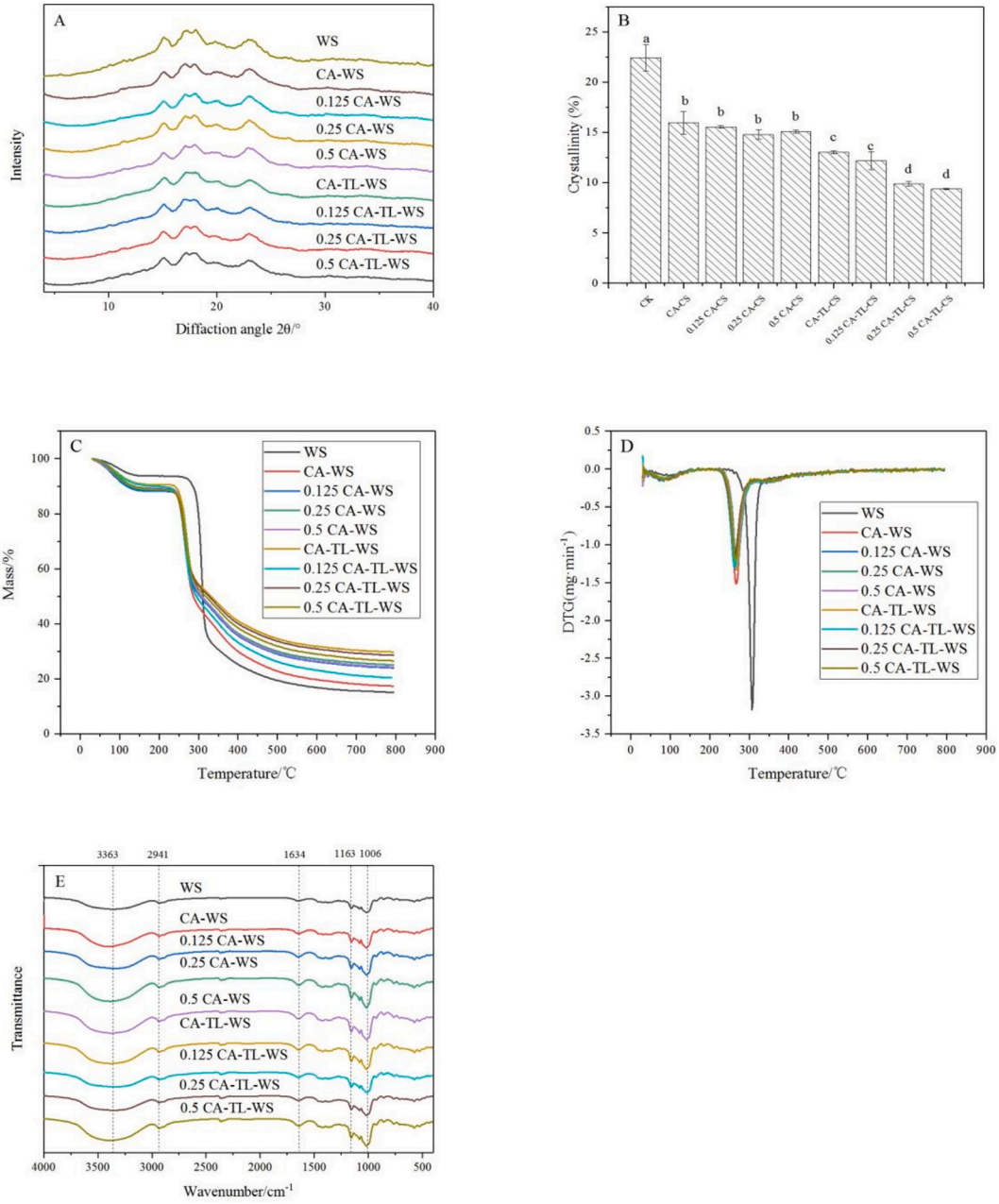

Fig. 3. Technical analysis of the beads and CA-TL-WS ternary complex (A: XRD patterns; B: Crystallinity; C: TG curves; D: DTG curves; E: FT-IR spectra).

was much more. The second stage occurred between 210 °C and 350 °C, at which the weight loss was obvious, the rate of weight loss achieved the peak value, and the DTG curve showed the most apparent peak of mass loss. At this stage, the hydroxyl group of the glucose ring was rapidly dehydrated and decomposed, and the main decomposition products were H_2O, CO, CO_2, *etc.*, among which not only the backbone was broken, but also the chemical bonds (C—O, C-C-H *etc.*) were broken (Pineda-Gómez et al., 2011). This phase of weight loss was mainly due to the decomposition of starch at high temperatures, and the starch structure was destroyed and burned in contact with air. At this stage, the decomposition process of beads and capsules played a leading role, but compared with starch at 210 °C to 350 °C, the rate of loss was lower, which was because of the internal binding of water precipitation volatilization, calcium alginate, sodium alginate, TL, so combustion of residual substances and ash was higher than that of starch. The third stage was between 350 °C and 800 °C, during this period the remaining mass loss was carbonization process. The appearance of the mass loss was due to the complete breakdown of starch decomposition products, and the final mass loss rate of the beads and capsules were higher than the WS, which indicated that the beads and ternary complex ultimately precipitated more ash.

3.3.3. *FT-IR analysis*

The FT-IR spectra (Fig. 3E) showed a wide and stronger absorption peak at about 3363 cm^{-1} (Chen & Huang, 2018), which was due to the -OH group stretching vibration, and the absorption peak at 2941 cm^{-1} was due to the C—H group stretching vibration. In the FT-IR spectrum of CA-TL-WS ternary complex, the peaks may be caused by the hydrogen bond formed between starch particles, sodium alginate and TL, and the phenomenon of hydroxyl region absorption band widening. Compared with the beads, the spectral peak type of the capsules was the same, and no new absorption peak appeared, which indicated that no new chemical reaction was generated. The peak at 1667–1550 cm^{-1} represented the asymmetric stretching vibration of C═O, and the peak representing

stretching vibration of the glucose C-O-C bond was at 1163 and 1006 cm^{-1}. The signal bands between 1200 cm^{-1} were closely related to specific polysaccharide structures and contain pyran ring vibrations, C-OH stretching vibrations, C—C vibrations, and vibrations of glycosidic bonds. The presence of water caused the absorption peak at 1634 cm^{-1}, while the absorption peak of CA-TL-WS ternary complex was stronger than WS, possibly because TL has better stability and water holding capacity.

3.3.4. Thermal properties

When the wheat starch was continuously heated during the scanning of DSC from 25 °C to 150 °C, the breaking of internal hydrogen bonds within the starch granules was induced, and then the hydrogen bonds were formed with water molecules, the granules absorbed water and swelled. The Tp, To, and Tc contents of wheat starch, bead granules, and capsules were shown in **Table S1**. The temperature after gelatinization was named the starting temperature (To), the corresponding maximum temperature during gelatinization was named the peak temperature (Tp), and the corresponding temperature at the basic end of gelatinization was called the termination temperature (Tc). Compared with WS, the contents of To, Tp and Tc in CA-TL-WS ternary complex increased, indicating that the hydrogen bond between sodium alginate and TL molecules was strengthened, which led to dense structures formation, and further impeded the water flow and improved the thermal stability of starch (Li et al., 2019). Compared with the blank control, the Tp of 0.5 CA-WS bead and 0.5 CA-TL-WS ternary complex increased significantly from 65.03 °C to 68.86 °C at a concentration of 0.5% sodium alginate, which indicated that starch and sodium alginate and trehalose formed a strong force due to intermolecular hydrogen bonding, stabilized the molecular structure of starch, and delayed the melting of the starch crystals. With the increase of sodium alginate concentration, Tc of the sample gradually increased. Compared with 0.5% CA-WS bead and 0.5% CA-TL-WS ternary complex, TC increased from 84.02 °C and 80.76 °C to 86.00 °C and 87.00 °C. And the enthalpy of pasting (ΔH)was higher than WS for CA-TL-WS ternary complex and CA-WS beads, which indicated that sodium alginate and TL interacted with the starch molecules to form a more stable structure, and therefore more energy was needed to melt the crystalline zone.

3.4. Influence of CA-TL-WS ternary complex on thermal mechanical properties of the frozen dough

The thermal mechanical properties of frozen dough with CA-TL-WS ternary complex were shown in **Table S2**. Water absorption was a key factor reflecting the characteristics of flour, the aging rate of pasta products could be reduced more effectively with the higher water absorption, the stability time of dough was positively correlated with the toughness of dough, and the formation time of dough can reflect the gluten strength, that is, the longer the time, the better the kneading resistance of dough, the gluten strength (Pineda-Gómez et al., 2011). The degree of protein weakening was closely related to the destructive resistance of dough, the higher the protein weakening degree was, the smaller the gluten strength was (Schmiele et al., 2012). In **Table S2**, it's shown as the CA-TL-WS ternary complex concentration continued to increase, the water absorption, dough formation and stability time all firstly increased and then decreased, but the water absorption had been continuously increasing, and the water absorption (62.03%), formation time (5.01 min) and stabilization time (8.17 min) reached the maximum value when 0.8% CA-TL-WS ternary complex was added, which indicated that the aging rate of the formed dough was reduced, and it had a better processing property, more resistant to kneading, and higher gluten protein strength. It could be because that CA-TL-WS ternary complex could interact with gluten protein and delayed dough formation time, or CA-TL-WS ternary complex could absorb water well, which increased the water absorption rate, affected the formation time of dough and the gluten strength increased. When the content of CA-TL-WS ternary complex was higher, it may affect the cross-linking between gluten proteins and gluten and starch, weaken the formation of gluten network structure, reduce its firmness, so the stability decreased (Peng et al., 2017).

3.5. Effects of CA-TL-WS ternary complex on gelatinization characteristics of the frozen dough

The gelatinization characteristics of flour with CA-TL-WS ternary complex were shown in **Table S3**. Pasteurization was a key factor in flour quality, which showed great significance on flour processing. The breakdown reflected the thermal stability of the samples, which was inversely proportional to the stability, and the regrowth value reflected the change of viscosity of the sample after gelatinization in the process of cooling, and was related to the degree of aging of the samples (Dangi et al., 2019). Compared to the blank control, the peak viscosity of frozen dough with 1% addition increased from 1647.20 cP to 1811.40 cP, the minimum viscosity, from 1215.80 cP to 1338.60 cP, and the final viscosity, from 2234.75 cP to 2441.60 cP in **Table S3**, which may be due to the interaction of CA-TL-WS ternary complex with gluten protein. The final viscosity increased from 2234.75 cP to 2441.60 cP, probably because the CA-TL-WS ternary complex interacted with the gluten protein and increased the pasting viscosity of the samples, or it could be that the CA-TL-WS ternary complex competed with the wheat flour in absorbing water, which led to an overall increase in the viscosity system. The attenuation value of flour firstly showed a tendency to decrease and then increased with the additive amount increased, and the attenuation value minimized to 428 cP at 0.8% addition, which indicated that the addition with an appropriate amount could improve the starch granules stability in the dough, and the dough did not decompose easily and had better shear force resistance. At the addition amount of 0.2% addition, the regain value of the samples decreased significantly, and the results indicated that the moderate addition of CA-TL-WS ternary complex could make the molecules of straight-chain starch reordered and arranged, and inhibit the recrystallization of straight-chain starch during the cooling process.

3.6. Influence of CA-TL-WS ternary complex on color changed of the frozen dough

In Fig. 4, L* values represent brightness, a* values represent red to green from positive to negative, and b* values represent yellow to blue from positive to negative (Lamsal & Faubion, 2009). With the increase addition of CA-TL-WS ternary complex to dough, the L* value increased and the b* value decreased. Compared to the blank control, the L* value

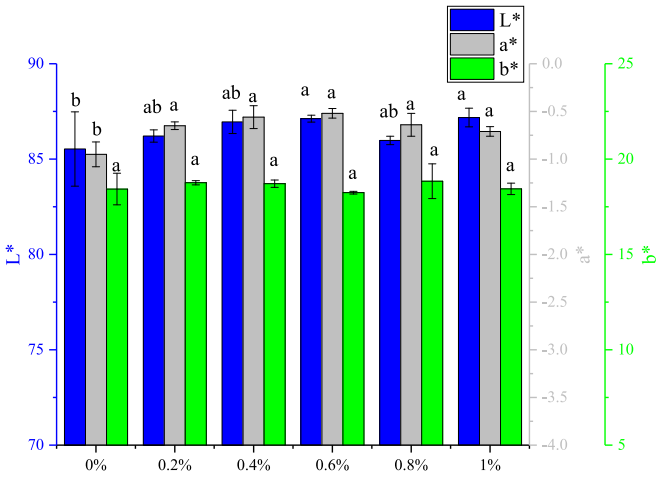

Fig. 4. Influence of CA-TL-WS ternary complex on color changed of the frozen dough.

of the dough with 1% addition increased from 85.53 to 87.18, which indicated that the addition could increase the whiteness of the dough, because the CA-TL-WS ternary complex composed of starch, TL and sodium alginate, and the sample color was whiter, which could increase the brightness of the dough. The a* values of all the dough with the addition of CA-TL-WS ternary complex were greater than the samples with pure wheat dough, indicating that the addition increased the redness of the dough. As the CA-TL-WS ternary complex addition increased, the b* value of dough became smaller and smaller, indicating that the addition was negatively correlated with the yellowness of dough, and the greater the addition amount, the lower the yellowness and the better the effect.

3.7. Influence of CA-TL-WS ternary complex on characteristics of frozen dough

Freezing curves of frozen dough with different CA-TL-WS ternary complex additions were illustrated in Fig. 5A. The dough freezing curve was usually divided into three stages: in the first stage, the initial temperature dropped to 0 °C, at this time and the outside temperature difference was large, so the temperature drop was faster, the curve was steeper; in the second stage, the temperature reached the freezing point of the dough, most of the water froze into ice and gradually forms ice crystals, at this time, a lot of heat was released, so the temperature dropped slowly and the curve was relatively flat. It can be seen that with the increase amount of CA-TL-WS ternary complex addition, the time for the dough to pass through the maximum ice crystal generation zone became faster, and it reached the minimum time with the 1% addition. The third stage of the freezing curve decreased more slowly, when most of the water in the dough had been frozen and the heat released partly makes the ice colder and partly kept the remaining water frozen, so the curve was smoother. In Fig. 5A, it's proved as the CA-TL-WS ternary complex addition increased, the freezing speed of dough was accelerated, the time required to reach −18 °C was shorter, and the time required to pass through the maximum ice crystal formation zone (0–5 °C) was also shorter, and the generated ice crystals were more uniform and fine, so that the gluten protein structure was maintained with higher integrity (Meziani et al., 2012). The results showed that the CA-TL-WS ternary complex could make the ice crystals generated in the dough smaller and more uniform during the freezing process, causing less mechanical damage to the dough, the dough network structure was better protected from damage, and the quality of the dough was easier to be maintained.

Fig. 5B-D showed the influences of different CA-TL-WS ternary complex additions on the hardness, springiness, and cohesion of frozen dough with different freezing times, respectively. Hardness as the main index of texture, the greater the hardness, the harder the dough (Li et al., 2021). The springiness of the dough was related to the number of pores inside, and cohesion was the energy applied to chew the food (Sanz et al., 2009). Sufficient protein aggregates were needed to form gluten scaffolds during dough making, but over-polymerization could cause the dough to miss the optimal level. As the frozen storage time increased, the hardness of the dough became larger, and the springiness and cohesion reduced, indicating that freezing deteriorated the dough textural

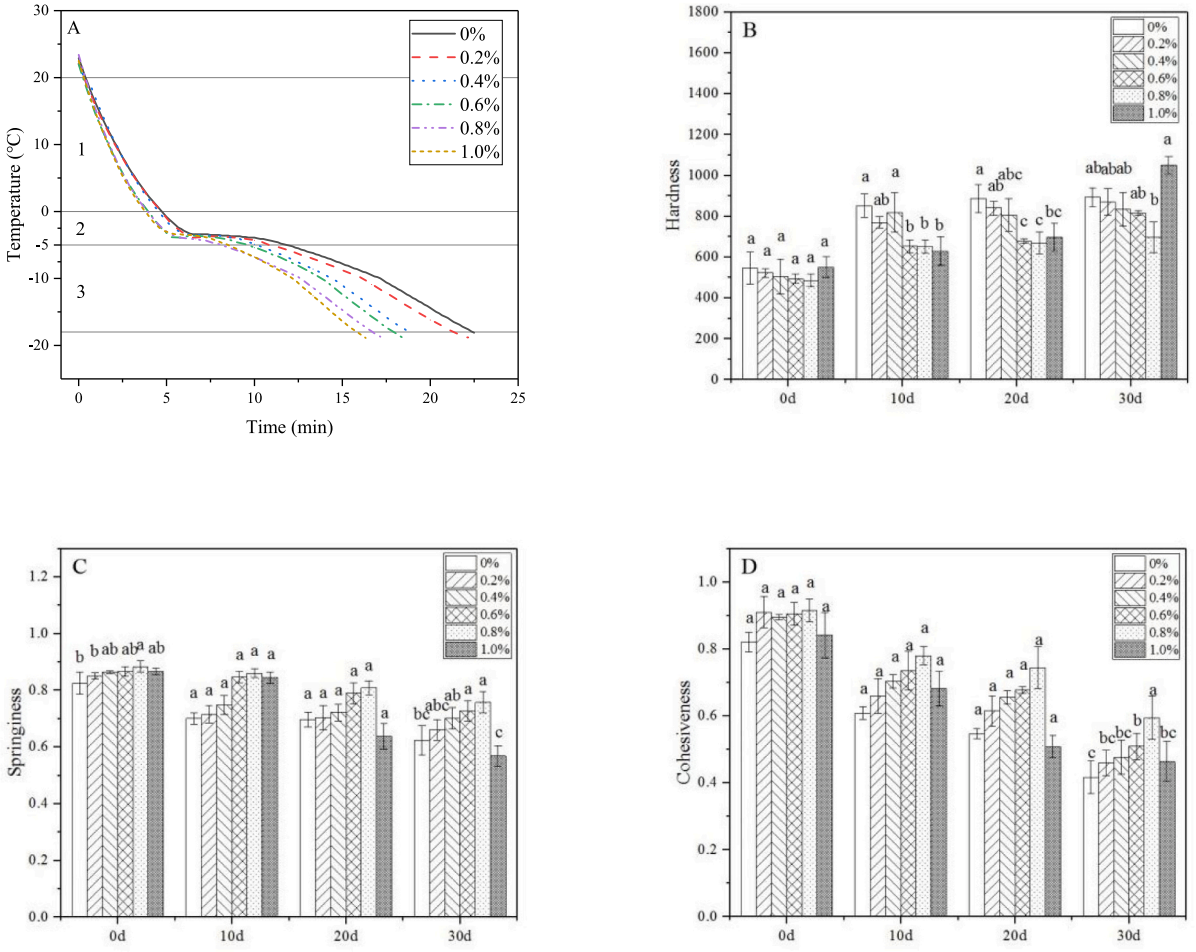

Fig. 5. Influence of CA-TL-WS ternary complex on characteristics of frozen dough (A: Freezing curves; B: Hardness; C: Springness; D: Cohesiveness).

properties, and with the addition of appropriate amount, the hardness reduced, and the springiness and cohesion increased compared with that of blank group, which indicated that the water-holding property of the dough was better after the addition of CA-TL-WS ternary complex, and it became softer. At the addition of 0.8%, the dough hardness reached the minimum value and springiness reached the maximum value. The results reveled that the addition of CA-TL-WS ternary complex formed a strong cross-linked network structure with gluten protein, changed the gluten structure in dough, and made the dough texture more soft and elastic. As the addition increased again, the textural properties of the dough decreased, probably because the excess CA-TL-WS ternary complex competed for water with gluten protein, which led to the decrease of dough springiness. As the addition amount increased, the cohesion of dough firstly increased and then decreased, which indicated that at the addition of 0.8%, the large internal bonding force required for dough formation, dough resistance to damage and tight bonding, so that it can be better to maintain the intact form and more resilient.

3.8. Effects of CA-TL-WS ternary complex on water distribution and migration of the frozen dough

Table 1 represented the effects of CA-TL-WS ternary complex on the water distribution and migration in frozen dough system, where T_{21} was bound water, which was the main form of water present, and T_{22} was the free water content (Kim & Cornillon, 2001). The relative percentage of water content of each component was expressed by A_{21}, A_{22}, which was the ratio of each peak area to total peak area. In Table 1, the peak area of A_{21} of the dough was about 98% of the total peak area, and A_{22} was about 1% of the total peak area, which indicated that the water mainly existed in the state of bound water, and only a small portion of the water was free water. At 0d of freezing time, A_{21} was 98.84% and A_{22} was 1.16% in the blank control group, and A_{21} was significantly higher at 99.23% and A_{22} was significantly lower at 0.77% ($P < 0.05$) in the dough with the addition of 0.8% CA-TL-WS ternary complex. With the extension of dough refrigeration time, the bound water gradually decreased, and the free water gradually increased, indicating that in the dough the bound water gradually migrated to the free water with the extension of refrigeration time. Overall, compared with the pure wheat flour, the bound water content of the dough with the CA-TL-WS ternary complex addition was higher, and the free water content was lower than that of indicating that the addition had an inhibitory effect on the diffusion of bound water to free water in the frozen dough. For all the frozen dough samples, at the adding 0.8%, the content of A_{21} in dough reached the maximum and the content of A_{22} reached the minimum, indicating that adding proper amount of CA-TL-WS ternary complex could promote the binding of dough and water molecules.

Table 1
Effects of CA-TL-WS ternary complex on water distribution and migration of the frozen dough.

Frozen storage time (d)	CA-TL-WS addition (%)	T_{21}	T_{22}	A_{21}	A_{22}
0	0	10.26 ± 0.81^{a}	133.05 ± 18.52^{a}	98.84 ± 0.05^{c}	1.16 ± 0.06^{a}
	0.2	10.26 ± 0.81^{a}	147.24 ± 30.17^{a}	99.01 ± 0.22^{bc}	0.99 ± 0.27^{b}
	0.4	10.02 ± 0.81^{a}	140.77 ± 40.92^{a}	99.05 ± 0.23^{b}	0.95 ± 0.21^{b}
	0.6	9.79 ± 0.00^{a}	133.05 ± 18.52^{a}	99.05 ± 0.02^{b}	0.95 ± 0.11^{b}
	0.8	10.72 ± 0.81^{a}	133.05 ± 18.52^{a}	99.23 ± 0.12^{a}	0.77 ± 0.06^{c}
	1	10.02 ± 0.00^{a}	130.48 ± 32.31^{a}	98.84 ± 0.15^{c}	1.16 ± 0.13^{a}
10	0	14.18 ± 0.00^{a}	132.19 ± 0.00^{b}	98.70 ± 0.06^{b}	1.30 ± 0.04^{a}
	0.2	14.18 ± 0.00^{a}	159.58 ± 13.14^{a}	98.77 ± 0.08^{ab}	1.23 ± 0.05^{a}
	0.4	14.18 ± 0.00^{a}	176.46 ± 34.60^{a}	99.04 ± 0.30^{ab}	0.96 ± 0.12^{ab}
	0.6	14.18 ± 0.00^{a}	151.99 ± 0.00^{ab}	99.03 ± 0.01^{a}	0.97 ± 0.24^{ab}
	0.8	14.18 ± 0.00^{a}	174.75 ± 0.00^{ab}	99.15 ± 0.27^{ab}	0.85 ± 0.09^{b}
	1	14.18 ± 1.13^{a}	159.58 ± 13.14^{ab}	98.86 ± 0.14^{b}	1.14 ± 0.01^{ab}
20	0	11.53 ± 0.93^{b}	133.48 ± 26.17^{a}	98.66 ± 0.14^{b}	1.34 ± 0.12^{a}
	0.2	11.26 ± 1.13^{b}	145.39 ± 11.43^{a}	98.99 ± 0.07^{ab}	1.01 ± 0.03^{ab}
	0.4	11.53 ± 0.00^{b}	126.00 ± 36.76^{a}	98.96 ± 0.27^{ab}	1.04 ± 0.02^{ab}
	0.6	10.72 ± 0.00^{b}	133.05 ± 18.52^{a}	98.74 ± 0.21^{b}	1.26 ± 0.12^{a}
	0.8	10.72 ± 0.00^{b}	150.02 ± 37.15^{a}	99.13 ± 0.21^{a}	0.87 ± 0.15^{b}
	1	14.18 ± 1.13^{a}	151.99 ± 0.00^{a}	98.79 ± 0.05^{ab}	1.21 ± 0.06^{ab}
30	0	11.53 ± 0.00^{a}	123.59 ± 12.17^{a}	98.47 ± 0.24^{a}	1.53 ± 0.13^{a}
	0.2	10.72 ± 0.81^{a}	114.98 ± 0.00^{a}	98.38 ± 0.12^{a}	1.62 ± 0.27^{a}
	0.4	10.26 ± 0.00^{a}	133.05 ± 18.52^{a}	98.40 ± 0.09^{a}	1.60 ± 0.14^{a}
	0.6	10.72 ± 0.93^{a}	126.45 ± 9.94^{a}	98.35 ± 0.04^{b}	1.55 ± 0.29^{b}
	0.8	11.26 ± 0.00^{a}	127.31 ± 21.37^{a}	98.82 ± 0.24^{b}	1.18 ± 0.01^{b}
	1.0	10.72 ± 0.00^{a}	132.19 ± 0.00^{a}	98.79 ± 0.12^{b}	1.21 ± 0.18^{b}

The data in the table are expressed as mean ± SD (standard deviation).Different letters in the same column indicate significant difference ($P < 0.05$).

4. Conclusion

The ternary complex mainly composed of sodium alginate, trehalose, wheat starch. TP elevation of the ternary complex was 68.01 °C compared with that of WS, which enhanced the thermal performance. The dough with 0.8% addition had a lower breakdown of 428 cP, which increased the thermal stability of the flour; the formation time (5.01 min) and stabilization time (8.17 min) of the dough were longer; the bound water content was more and it could inhibit the conversion of bound water to free water; the hardness, elasticity, and cohesion properties of the dough were better. The addition of appropriate amount of ternary complex can improve the frozen dough stability and quality, and this study provides technical support and reliable basis for the ternary complex application as an additive in frozen dough.

CRediT authorship contribution statement

Tongchao Su: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Wenkai Du:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Jie Zeng:** Writing – review & editing, Writing – original draft, Visualization, Funding acquisition, Formal analysis. **Haiyan Gao:** Writing – review & editing, Writing – original draft, Software, Methodology, Funding acquisition. **Benguo Liu:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.101641.

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