Preparation and Properties of Whey Protein Packaging Film

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Abstract: A protein packaging film was successfully prepared using whey protein concentrate (WPC) as raw material. Protein concentration, plasticizers concentration and temperature were discussed. Research results show that the increasing of protein concentration lead to decreasing barrier properties of WPC film but improving its mechanical properties. Though barrier properties of WPC film lost to some extent owing to addition of glycerol, its extensibility was greatly improved. When heating temperature is 80℃, the barrier properties and tensile strength of WPC film come to the best. Response surface analyses indicate that WPC film shows the optimal packaging performance when concentration of WPC is 10.2%, heating temperature is 82℃ and concentration of glycerol is 2.7%.

Key words: whey protein; concentrate packaging; film performance optimization

1. Introduction

Since the 1990s, "environment and development" has become the focus of the world's common concern. The green packaging has become the development direction of packaging industry all over the world [1]. Edible film has become the main food industry technology development project in many of the "green packaging" study. There is a trend that edible film will take place of plastic and paper [2]. Edible film, similar to the plastic material, was made of polysaccharides or protein with good strength, elasticity, moisture resistance and antibiotic property. Whey protein has good nutrition and the film forming characteristic. Whey protein are attracting researchers' attention in recent years, because it can form a transparent, soft and elastic, water-insoluble film which with good aromatic substances barrier property ,grease barrier property and oxygen barrier property in low humidity. This paper aims to study WPC film-forming technology and to obtain the appropriate packaging performance.

2. Experimental materials and method

2.1 Experimental materials

Whey protein concentrate powder (WPC80), New Zealand constant natural Co., LTD; Glycerol (analytical pure), ShenYang DongXing reagent factory; Sodium carboxymethylcellulose(analytical pure), Enterprise group chemical reagent Co., LTD; Other common reagent for analytical pure ones.

2.2 Experimental facilities

AR2140Electronic analytical balance, Meitele−Tuoliduo Instrument Co., LTD; HH − 4Digital temperature water-bath, Soochow Experimental products Co., LTD; JJ −4Precise timing electric mixer, Jiangsu province jintan RongHua Equipment manufacture Co., LTD; BTY-B1Permeability tester, Jinan Labthink Packaging equipment Co., LTD; ZLD Electronic tensile tester, ChangChun Mingyue Test equipment Co., LTD.

2.3 Preparation of whey protein film

Some WPC80 power was dissolved by distilled water after weighting. The mixture fluid was stirred evenly with the pH value adjusting to 8.0.After that, it was stirred slowly for 15 min from the bath temperature reach to some extent. During this time, 0.35% tackifier was added to the mixture. Some glycerol was added with good mix after cooling. The film-forming fluid was spread out on PMMA board with flow coating. The film was peeled off from the PMMA board after drying. The sample was balanced for 24h under the environment with 25℃,50% of the relative humidity. Figure 1 is the preparation process of WPC film.

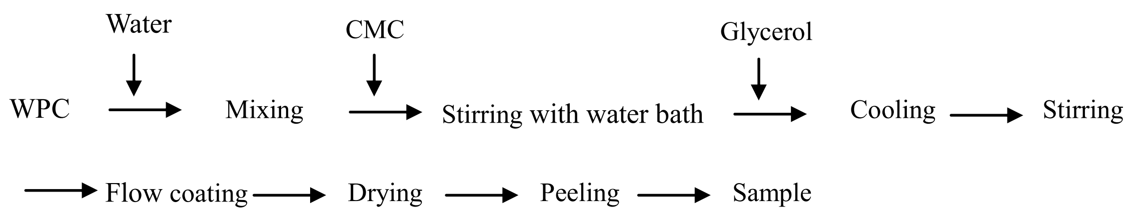

Figure 1.Preparing process of whey protein

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2.4 Packaging performance measurement

As everyone knows, package film not only need mechanical performance but also need good barrier property. Oxygen permeability (OP), water vapor permeability (WVP), tensile strength (TS) and elongation (E) of WPC film was observed in this experiment. ASTM standard method D3985-81 was used to test the OP of WPC film [3]. The WVP of WPC film was tested by ASTM (American Society for Testing and Materials) method [4, 5]. GB13022-91 Plastics-Determination of tensile properties standard method was utilized in measuring the TS and E of WPC film.

2.5 Data statistics and analysis

Data in this paper is three times the average value of a parallel determination. Design Expert software(Version7.0, Stat Ease Inc. MN, USA, 2005) was utilized in experimental design of process optimization. SAS software (SASS8.1, U.S.A SASS corporation) was used in response surface analysis. Significant level is Alpha = 0.05 in analysis.

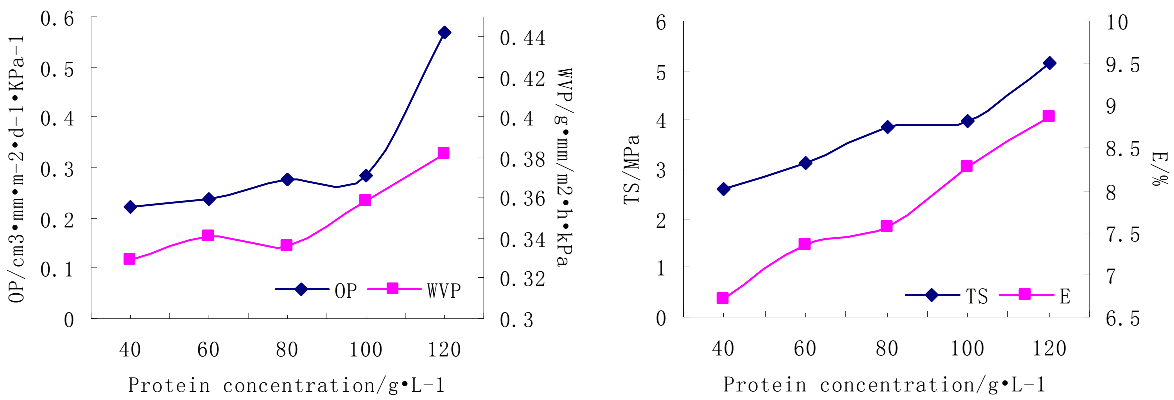
3. Results and discussion

3.1 Effect of protein concentration on main packaging properties of WPC film

OP, WVP, TS and E of WPC film was investigated under the condition of keeping glycerol concentration 30g/L and respectively changing protein concentration 40 g/L,60g/L,80 g/L,100 g/L,120 g/L.

The results showed that film can be formed when protein concentration is low. However, the thickness is too thin to unveil WPC film. When protein concentration is high (>120g/L), film-forming fluid easily change to gelatin which lead to fluid unable to flow completely. As figure2(a) shows, OP of WPC film rise with the increasing of protein concentration especially exceed 100g/L.WVP of WPC film have little difference with protein concentration 40g/L,60g/L and 80g/L, but it increased significantly when protein concentration change form 80g/L to 120g/L. As we know from the calculation formula, both OP and WVP have a positive correlation with film thickness. Film thickness increased significantly with the increasing of protein concentration. This is the main reason why OP and WVP increased with the increasing of protein concentration [6,7].

As figure 2(b) shows, the higher protein concentration the film with bigger TS. The biggest strength can reach 5.1 MPa. The elongation (E) of WPC film increased with the increasing of protein concentration. The elongation (E) of WPC film increased 32.04% when protein concentration vary from 40g/L to120g/L. Protein is the basic material in forming WPC film. So WPC film's mechanical performance is decided directly by the space structure of protein. Heating makes the protein parts degeneration. More hydrophobic bond, disulfide bond, hydrogen bond were exposed to outside when more protein heated. This result benefits to whey protein film's mechanical performance [8]. Therefore, TS and E of WPC film increased with the increasing of protein concentration.



(a) (b)

Figure2. Effect of protein concentration on main packaging properties of WPC film

3.2 Effect of glycerol concentration on main packaging properties of WPC film

Whey protein film is crisp without adding plasticizer. Film is hard to unveil from board. Glycerol is common plasticizer for edible film. WPC film is flexible when some glycerol adds to film-forming system. OP, WVP, TS and E of WPC film was investigated under the condition of keeping protein concentration 100g/L and respectively changing glycerol concentration 20 g/L,25 g/L,30 g/L,35 g/L and 40 g/L .

Figure 3(a) is the effect of glycerol on OP and WVP of WPC film. Effect of glycerol concentration on OP is not significant(P>0.05) when glycerol concentration vary from 20 g/L to 25g/L. WPC film has low OP, that is to say WPC film has good function of resistance of the oxygen. OP of WPC film rise significantly (P<0.05) with the increasing of glycerol concentration which vary form 25 g/L to 40g/L. OP achieve to the maximum when glycerol concentration is 40g/L. On this occasion, WPC film has worst function of resistance of the oxygen. The WVP of WPC film increases with the increasing of glycerol concentration too. The effect is significant especially glycerol concentration vary form 30 g/L to 35g/L. Therefore, barrier property of WPC film decrease when glycerol concentration increase.

Glycerol is a kind of low molecular weight molecule which has good hydrophilicity. Glycerol can get into polymer's molecular chain and reduce the action among molecular chains. At the same time, glycerol also increases the mobility of polymer molecule which contributes to the transport of water molecule. Therefore, WVP will rise when glycerol concentration increase [9,10]. That hydrogen bond form between glycerol and the polypeptide chains of protein will weaken rigid direct action among polypeptide chains. Film system was endowed with elastic and extensibility by adding glycerol which plays a good plasticized role. The action between glycerol and polypeptide chains of protein makes the compactness of film drop. This is probably the main reason why OP of WPC film decrease.

Figure 3(b) is the effect of glycerol on TS and E of WPC film. As the figure shows, the effect of glycerol concentration on TS and E is significant(P<0.05) when glycerol concentration vary from 20 g/L to 40g/L. TS and E of WPC film increase with the adding of glycerol. The action between glycerol and polypeptide chains benefits the rearrangement among molecular chain of protein, thus improving the flexibility of polymer. Protein film system was endowed with good flexibility, elasticity, extendibility and maneuverability [11]. The action between glycerol and protein was weakened by adding glycerol to film-forming system. So the TS of WPC film decrease.

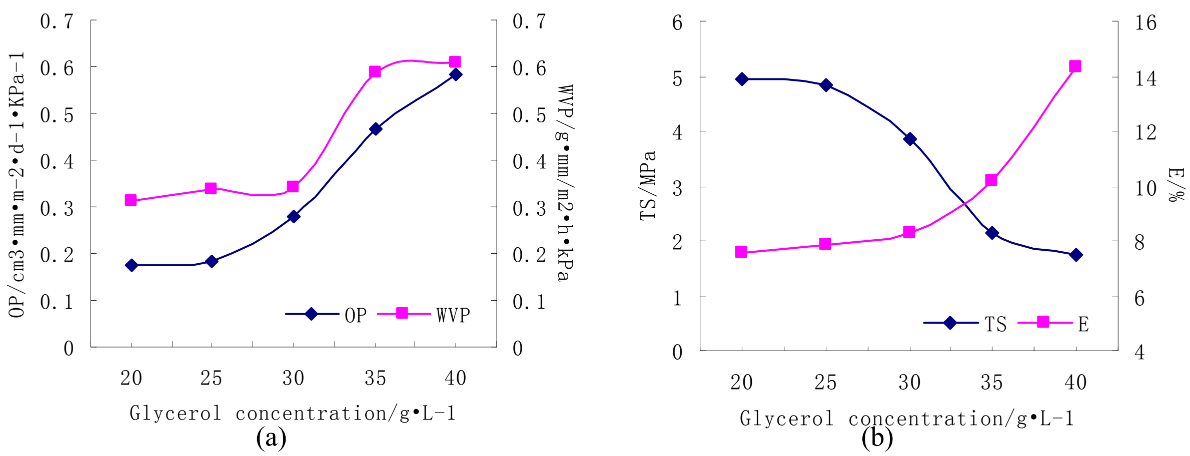


Figure3. Effect of glycerol concentration on main packaging properties of WPC film

3.3. Effect of heating temperature on main packaging properties of WPC film

OP, WVP, TS and E of WPC film was investigated under the condition of keeping protein concentration 100g/L and respectively changing heating temperature 50℃、60℃、70℃、80℃、90℃.

Figure 4(a) is the effect of heating temperature on barrier property of WPC film. The results show that effect of heating temperature on OP and WVP is significant(P<0.05) when heating temperature vary from 60℃ to 90℃. OP and WVP of WPC film decrease at first and increase later with the increasing of heating temperature. OP and WVP come to the lowest when heating temperature is 80℃. That is to say, WPC film has the best barrier property. Because 80℃ may be the denaturation temperature of whey protein. That proper denaturation of the protein occurring at this temperature contributes to form good network structure of WPC film.

As the figure 4(b) shows, effect of heating temperature on TS is significant (P<0.05) when heating temperature varies from 50℃ to 90℃. The trend is increasing at first and decreasing later. Effect of heating temperature on E is significant (P<0.05) when heating temperature varies from 50℃ to 70℃ and 80℃ to 90℃. But the trend is decreasing at first and increasing later.

Heating can modify the three-dimensional structure of protein molecules and expose the functional groups such as carbonyl. Therefore, some amino acid groups and hydrophobic groups on latentchain appear in native conformation of protein. The electrostatic interactions among functional groups take place via the crosslinking of intermolecular hydrogen bond. This is why the intermolecular force is strengthen when protein is heated. The denaturation temperature of whey protein is about 80

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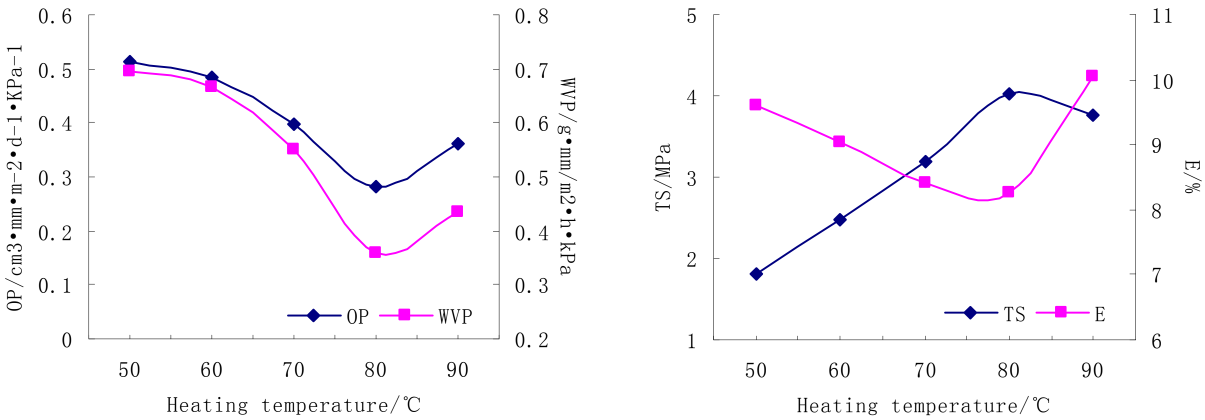
℃. That protein denatures at this temperature best and fit for forming solid network structure of film. Protein denatures excessively if overheated. On the contrary, chain segment of protein unfolds insufficiently if not fully heated and bad network structure of protein will be formed. E of WPC film comes to the lowest when heating temperature is 80℃. It is considered that network structure of protein at 80℃ shows the worst extensibility.



(a) (b)

Figure4. Effect of heating temperature on main packaging properties of WPC film

3.4 Film-forming procedure optimization

Considering its practical applicability and the design of experiment which uses OP, WVP, TS, and E as the main packaging performance, response surface methodology (RSM) was applied in optimizing film-forming procedure.

The main factors affecting whey protein film's properties are protein concentration (A), glycerol concentration (B) and heating temperature (C) which were discussed above. Ascertaining pH value of film-forming system is 8.0; quadratic regressive experiment and analysis were established for A, B, C three factors. The response of OP, WVP, TS, E and combination property is Y1, Y2, Y3, Y4 and Y respectively. Combination property Y is the fitted value of Y1, Y2, Y3, and Y4. OP values from different samples rank from low to high. The lowest OP standing for the best barrier property was endowed with 100 point. The highest OP was endowed with 0 point. Similarly, the point of WVP can be obtained. TS values from different samples rank from high to low. The highest TS was endowed with 100 point and the lowest was endowed with 0 point. Similarly, the point of E can be obtained. In computing combination property of WPC film, weighting coefficient of OP, WVP, TS and E is all 0.25. Box-Behnken design was used. Table 1 shows the factors and Levels for film forming procedure optimization.

15 groups of experiment were performed respectively with three factors and three levels as the setting show in table 1. Regression analysis of Y1, Y2, Y3, Y4, and Y was completed by RSREG of SAS software. The results were shown in table 2.

15 experiments were divided into two categories. One is factorial point which has12 points. Another is zero point which is the central point. Experiment at zero point repeat three times in order to estimate the error. Analysis of variance was performed for secondary model by SAS. The effect of three experimental factors on Y1, Y2, Y3, Y4, and Y was shown as following regression equation.

Y_1=0.18-0.061A+0.075B+0.021C-0.052AB-0.013A C+0.024 B C+0.052 A^2+0.090B^2+0.056C^2

Y_2=0.45+0.089A+0.098B-0.016C-0.026A B - 0.0000975 AC -0.099 BC+0.057A^2+0.12B^2+0.092C^2

Y_3=4.16+0.48A-1.04B+0.56C+0.17AB+0.15AC-0.11BC -0.067A^2-0.11 B^2-0.94 C^2

Y_4= 8.27+0.32 A+1.22 B+0.39C-0.040 AB-0.11A C+0.065 BC+0.16 A^2+0.51 B^2+0.462 C^2

Y=86.59+3.15A-8.09B+4.88C+3.91AB+2.42AC+3.12B C-4.36A^2-10.48 B^2-11.78C^2

Table 3 is the analysis of variance of packaging property regression equation. As the F-test shown in Table 3, the P- value of regression equation of Y is 0.0082(<0.01), which indicates the equation fits well. A comparison measured and predicted also indicates the

Table 1.Factors and Levels for film forming procedure optimization

Level	A(protein concentration g/L)	B(glycerol concentration g/L)	C(temperature℃)
-1	80	25	70
0	100	30	80
1	120	35	90

Table 2.Box-Behnken experimental design and results

Run	A	B	C	OP	WVP	Ts	E	point
1	-1	-1	0	0.246	0.430	4.32	7.46	79.91
2	-1	1	0	0.475	0.590	2.07	10.03	60.67
3	1	-1	0	0.276	0.701	5.56	7.92	75.00
4	1	1	0	0.297	0.757	3.98	10.33	71.40
5	0	-1	-1	0.206	0.470	3.84	8.14	74.68
6	0	-1	1	0.274	0.554	4.61	7.93	74.93
7	0	1	-1	0.332	0.952	1.83	10.42	47.50
8	0	1	1	0.497	0.640	2.15	10.47	60.21
9	-1	0	-1	0.379	0.493	2.29	7.51	61.50
10	1	0	-1	0.233	0.649	2.34	8.63	66.35
11	-1	0	1	0.371	0.561	3.67	9.35	69.71
12	1	0	1	0.174	0.678	4.32	10.04	84.24
13	0	0	0	0.179	0.45	4.18	8.27	86.72
14	0	0	0	0.181	0.44	4.15	8.26	86.84
15	0	0	0	0.183	0.448	4.16	8.27	86.21

Table 3.Analysis of variance of Packaging Property regression equatiion

sources of variation	Df	Sum of squares	F -value	P- value	significant
Total regression	9	1889.09	11.08	0.0082	**[a]
First terms	3	794.21	14.67	0.0386	*[b]
Quadratic terms	3	987.84	18.25	0.0379	*
Interaction terms	3	123.44	2.28	0.2110	
Residual	5	90.20			

"a" stands for highly significant ($P<0.01$); "b" stands for significant ($P<0.05$)

Table 4.Variance analysis of factors

Factor	Df	Sum of squares	Mean square	F -value	P- value	significant
A	4	234.20	58.55	3.24	0.1566	
B	4	1029.73	257.43	14.06	0.0083	**[a]
C	4	764.99	191.25	10.60	0.0458	*[b]

"a" stands for highly significant ($P<0.01$); "b" stands for significant ($P<0.05$)

equation fits well. Therefore, regression equation in observed range can predict effectively.

Table 4 is the variance analysis of factors. Factors ranked by their influence are glycerol concentration, heating temperature and protein concentration in turn. Not only was the mechanical performance changed by adding appropriate amount glycerol, but also the barrier property.

Optimum analysis of SAS indicates that optimal level of factors is protein concentration 102g/L, glycerol concentration 27 g/L, and heating temperature 82℃. The results of verification test show that optimal packaging performance is OP0.153 cm3 · mm/m2 · d · kPa, WVP0.427 g· mm/m2· h· kPa, TS4.46Ma, E8.21%. The discrepancy between verification and pridection is 4%(OP), 15%(WVP), 2.5%(TS) , 3%(E).

4. Conclusion

The affect of factors including protein concentration, glycerol concentration and heating temperature for whey protein film's packaging performance was studied. And the film-forming procedure was optimized by RSM. Several conclusions can be reached as follow.

1) The increasing of protein concentration lead to decreasing barrier properties of WPC film but improving its mechanical properties. Though barrier properties of

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WPC film lost to some extent owing to addition of glycerol, its extensibility was greatly improved. When heating temperature is 80℃, the barrier properties and tensile strength of WPC film come to the best.

2) Factors ranked by their influence are glycerol concentration, heating temperature and protein concentration in turn.

3) The optimal results indicate that whey protein film show the best packaging performance (OP 0.153 $cm^3 \cdot mm/m^2 \cdot d \cdot kPa$; WVP0.427 $g \cdot mm/m^2 \cdot h \cdot kPa$; TS4.46Ma;E8.21%), when protein concentration is 102g/L, glycerol concentration is 27 g/L, heating temperature is 82℃.

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