Thermal, Kinetic, and Mechanical Properties of Glycerol-Plasticized Wheat Gluten

Yongkang Pan, Xuehong Wang, Qiaolong Yuan

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

ABSTRACT: Glycerol-plasticized wheat gluten was prepared by mixing in an internal mixer equipped with sigma rotors, and then thermally compression-molded to form a sheet for crosslinking and tensile tests. Referring to rubber vulcanization process, rotorless curemeter was applied to test the vulcanization characteristic parameters of the molded round samples, which could be used to calculate the activation energy and reaction rate of crosslinking occurring in wheat gluten when heated. Vulcanizing curves obtained show that the optimum temperature for processing glycerol-plasticized wheat gluten is 150°C, and that activation energy and reaction rate of crosslinking in wheat gluten plasticized with 20 wt % glycerol reach minimum and maximum values, respectively. In addition, glycerol content, plasticizing time, and temperature have significant effects on the mechanical properties of thermomolded wheat gluten plastics. The factors are closely related to the establishment of a covalent network resulting from the formation and rearrangement of disulfide bridges in wheat gluten. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 797–804, 2011

Key words: glycerol-plasticized wheat gluten; rotorless curemeter; activation energy; reaction rate

INTRODUCTION

In recent years an increasing environmental concern over the use of petrochemicals in the international community has provided a new opportunity for plant proteins to regain a place in the nonfood polymer market. Among proteins, wheat gluten has attracted much attention of material researchers, owing to abundant resources, low cost, and good biodegradability and environmental benign. All wheat gluten materials fully vanished within 50 days when buried.[1] Although Beccari from Italy could extract gluten from flour almost 300 years ago,[2] studies on industrial application of wheat gluten started with the 1980s.

Wheat gluten are amorphous and can be prepared using common thermoplastic processing such as kneading, extrusion, and compress-molding.[3,4] Without plasticizer the proteins are too brittle to handle for typical plastic applications. To improve the processability and reduce the final material brittleness, wheat gluten has been plasticized through the addition of small polar molecules, such as water, glycerol, polyethylene glycols of molecular weight 200, 400, 1500, and 3400, amino compounds (diethanolamine, triethanolamine).[5–7] Glycerol has been used commonly as a plasticizer since it possesses highly polar and better plasticizing effect. It was noted that plasticizer addition increased both elasticity and extensibility, but decreased tensile strength and Young's modulus.[6] Thus, to seek the balance between the process requirements and the desired material stiffness, the optimum plasticizer content plays an important role in the processing.

Mechanical properties of wheat gluten plastics are correlated with the density of the tridimensional network formed through disulfide crosslinks by heat and shear force. Because of extensive aggregation, the Young's modulus and the fracture stress were higher, and the fracture strain were lower at the higher temperatures.[8] However, an increase in processing temperature led to thermal degradation and oxidation of wheat gluten. To develop a commercially useful material, it plays a crucial role in defining an optimal processing temperature.

By controlling the plasticizer content and the thermal treatment conditions, it is possible to modify the processability and mechanical properties of wheat gluten plastics. But whatever the processing conditions, the activation energy (E_a) of gluten-based materials is difficult to calculate. Hélène Angellier-Coussy et al.[9] demonstrated that the specific mechanical energy (SME; kJ g^{-1}) was computed from the

torque curve during mixing. Domenek et al.[10] also showed that the formation of the three-dimensional protein network could be described by a simple mathematical model, and activation energies of gluten unfolding, refolding, and precipitation were calculated with the Arrhenius law to 53.9, 29.5, and 172 kJ mol^{-1}, respectively. In addition, the rate of protein solubility loss decreased as the crosslinking reaction proceeded, which may be attributed to the formation of the three-dimensional network progressively hindering the reaction.[11–13] Transglutaminase-crosslinked wheat gluten was blended with poly (lactic acid) in a Brabender mixer. The activation energy and pre-exponential factor for blend were determined according to Borchardt and Daniels kinetics approach from modulated differential scanning calorimetry (DSC) by heating and cooling cycles to show the level of compatibility between the two polymers. The blends showed increased E_a values with an increase in the amount of crosslinked gluten and a number of cycles.[14] However, no work has been performed to describe in detail how to calculate the activation energy of gluten-based materials.

The purpose of this work is to investigate the effect of plasticizer content, mixing temperature, and time on properties and processability of plasticized wheat gluten. In the experiments, glycerol-plasticized wheat gluten materials were prepared via thermoplastic process consisting of first mixing the components in an internal mixer operated under lower temperature to avoid crosslinking reactions occurring, and second thermoforming the obtained dough at higher temperature, which led to the formation of the three-dimensional macromolecular network. Referring to rubber vulcanization process,[15] rotorless curemeter was first applied to investigate vulcanization characteristic parameters of glycerol-plasticized gluten dough, such as M_H, M_L, t_{10}, and t_{90}, which could be used to calculate the activation energy and reaction rate of crosslinking according to Arrhenius law.

EXPERIMENTAL

Materials

Vital wheat gluten was purchased from Tianguan Group (Henan, China). Its protein content was 86.2% by weight according to Kjeldahl nitrogen determination method. Its moisture content, determined by weighing after heating at 105°C for 24 h, was 5.4% by weight. Anhydrous glycerol was obtained from Lingfeng Chemical Reagent (Shanghai, China) and used as received.

Sample preparation

Wheat gluten was mixed with glycerol using an internal mixer (Haake, model Rheomix R600,

Germany) equipped with sigma rotors running at 60 rpm for 5 min to obtain the glycerol-plasticized wheat gluten dough. Wheat gluten was premixed with glycerol manually, and then added into the mixing chamber which was filled with a constant total mass of 50 g. Mixing was conducted under different plasticizing temperature conditions. Meanwhile, torque and material temperature were continuously recorded. The wheat gluten mixture contained 10, 15, 20, 25, or 30 wt % glycerol as a plasticizer.

Compression molding was performed in a heated press (model XQLB−350 × 350, China) with a pressure of 10 MPa. Ten grams of the mixed dough was deposited in a round mold ($\phi 50 \times 3$ mm^2) and compression-molded at 60°C for 3 min. The obtained round sample with a thickness of 3.0 ± 0.1 mm was performed for crosslinking testing on rotorless curemeter. Fifty grams of the mixed dough was placed in a squared mold (145 × 145 × 2 mm^3) and compression-molded at 150°C for 5 min. The obtained squared sheet with a thickness of 2.0 ± 0.1 mm was cut into dumbbell-shaped specimens for tensile testing.
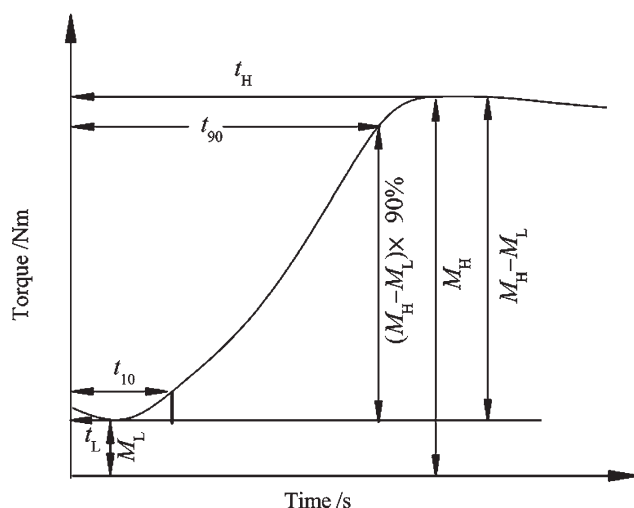
Crosslinking tests

Crosslinking tests of obtained round samples were conducted on a rotorless curemeter (model MDR-2000, China) with oscillation frequency of 1.7 Hz and swing angle of ±0.5°. The samples were vulcanized under 130, 140, 150, 160, and 170°C. Meanwhile, torque of crosslinking process was continuously recorded as a function of time throughout the experiment.

Raman spectroscopy

Raman Spectrum was performed on a Raman spectroscopy (model inVia + Reflex, British). The samples were scanned by the laser with 785 nm wavelength in the range of 400–1800 cm^{-1}.

Mechanical properties

Tensile tests were performed on a universal testing machine (Zwick, model ProLine Z010, Germany) supplied with an automatic extensometer. The dumbbell-shaped specimens of 75 mm overall length and 4 mm width for the elongating part (5A type, standard ISO 527-2, 1993) were stored at 25°C and 60% relative humidity for 1 week. The extensometer grips were set to a standard length of 20 mm, and the crosshead speed was set at 50 mm min^{-1} for all examined samples. Force and deformation measurements were recorded electronically and the resulting stress-strain tensile curves were recorded.

Figure 1 Schematic diagram of rubber vulcanization process.

Calculation of the average rate and activation energy of crosslinking reaction

Schematic diagram of rubber vulcanization process is shown in Figure 1. Characteristic parameters of crosslinking, such as t_{10}, t_{90}, M_H, and M_L, were observed. The maximum torque M_H and minimum torque M_L reflect the modulus and the plasticity of wheat gluten under vulcanizing temperature respectively, whereas t_{10} and t_{90} are defined as scorch time and optimum cure time, when corresponding torque reaches $(M_H - M_L) \times 10\% + M_L$ and $(M_H - M_L) \times 90\% + M_L$, respectively.

Shear modulus M is in direct proportion to crosslinking density ρ according to the basic principle of rotorless curemeter. Therefore, M can be expressed as follows:

$$M = \rho \cdot RT \tag{1}$$

where R is a gas constant, J (mol K)$^{-1}$ and T is an absolute temperature, K.

The chemical reaction between sulfydryls of gluten proteins upon mixing was studied by Morel et al.[16] in detail. Schematic illustration of sulfydryl/disulfide interchange of proteins is demonstrated in Figure 2. Gluten proteins can undergo aggregation reaction through sulfydryl/disulfide bonding interchange to form disulfide bonds upon heating, which leads to an increase in crosslinking density of macromolecular network. Therefore, $\nu(t)$, the rate of crosslinking reaction at time t can be defined as follows:

$$\nu(t) = \frac{d\rho}{dt} = \frac{1}{\lambda} \cdot \frac{dM}{dt} \tag{2}$$

To calculate accurately the rate of crosslinking reaction of wheat gluten, $\overline{\nu}$, the average rate of crosslinking reaction can be described by integral expression as follows:

$$\nu = \frac{\int_{t_{10}}^{t_{90}} \nu(t) dt}{t_{90} - t_{10}} = \frac{1}{\lambda} \cdot \frac{\int_{t_{10}}^{t_{90}} \left(\frac{dM}{dt}\right) dt}{t_{90} - t_{10}} \tag{3}$$

Thus, the average rate of crosslinking reaction with the unknown parameter λ is presented based on the principle of rotorless curemeter. In the interest of being convenient to evaluate the average rate of crosslinking reaction, the unknown parameter λ is on the assumption that is equal to 1.

Heating and shearing treatment can facilitate intramolecular or intermolecular sulfydryl/disulfide interchanges among gluten proteins. On the assumption that reverse reaction can be neglected during heating, it is possible to calculate the rate constant of crosslinking reaction. Thus, the crosslinking reaction process can be expressed as follows:

$$\text{Protein} - \text{SH} + \text{SH} - \text{Protein}$$
$$\rightarrow \text{Protein} - \text{S} - \text{S} - \text{Protein}$$
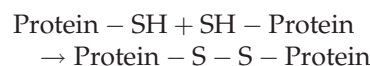
Based on the above self-terminating reaction during crosslinking process of gluten protein, it is
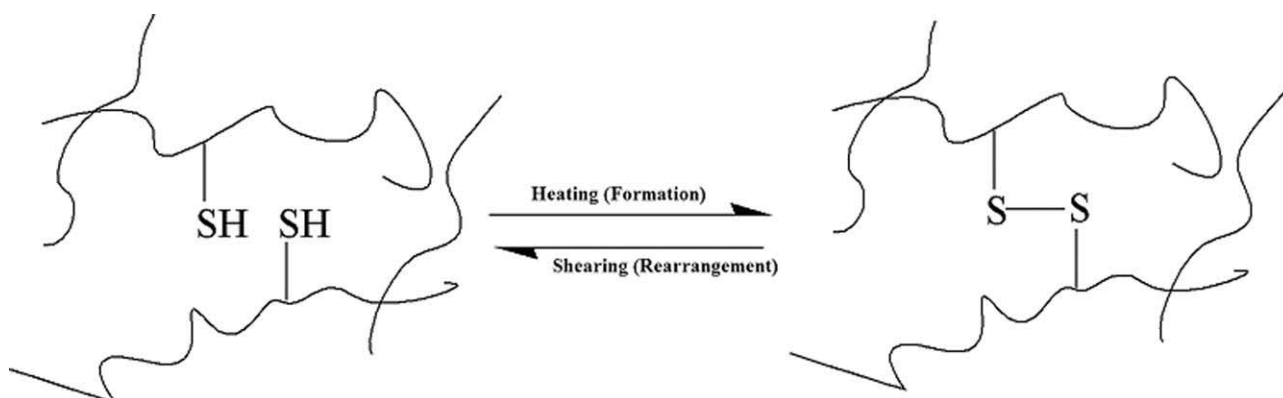
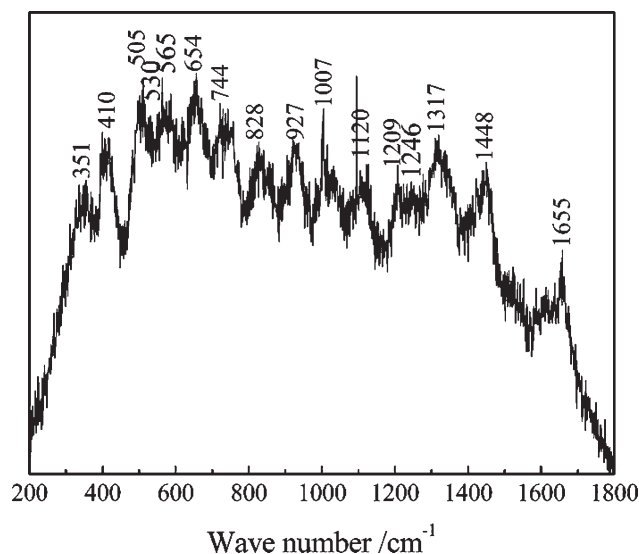**Figure 2** Schematic illustration of sulfydryl/disulfide interchanges.

Figure 3 Raman spectrum of vital wheat gluten.

evident that the rate of crosslinking is in direct proportion to the square of sulfydryl concentration. Therefore, the rate of crosslinking reaction can be described as follows:

$$v(t) = -\frac{d[SH]}{dt} = -\frac{dC}{dt} = k \cdot C^2 \qquad (4)$$

where C is the concentration of sulfydryl and k is the rate constant of crosslinking reaction.

Thus, the rate constant of crosslinking reaction can be expressed by the following equation:

$$k = \left(\frac{1}{C_{10}} - \frac{1}{C_{90}}\right) \cdot \frac{1}{t_{90} - t_{10}} = \mu \cdot \frac{1}{t_{90} - t_{10}} \qquad (5)$$

where C_{10} and C_{90} is the concentration of sulfydryl at the time of t_{10} and t_{90} respectively, μ is used to instead of the known concentration of sulfydryl.

According to Arenhenius law, the rate constant of crosslinking reaction can also be expressed by the following equation:

$$k = Ae^{-\frac{E}{RT}} \qquad (6)$$

where A is the frequency factor and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). E, which is presented in joules per mole, is activation energy, and T, which is presented in Kelvin, is vulcanizing temperature.

Combining eqs. (5) and (6), it is possible to determine the relationship between t_{90} and t_{10} and T, which can be expressed by the following equation:

$$\ln(t_{90} - t_{10}) = \ln\left(\frac{\mu}{A}\right) - \frac{E}{RT} \qquad (7)$$

Through the plotting of ln $(t_{90} - t_{10})$ as a function of $1/T$, a linear curve can be obtained. Therefore, activation energy can be calculated from the slope of the linear curve.

RESULTS AND DISCUSSION

Raman analysis of wheat gluten

Raman spectrum is sensitive to strong symmetric group. The Raman spectrum of vital wheat gluten is shown in Figure 3. The characteristic peaks of disulfide bonds are at 505, 530 cm^{-1}.[10] Owing to less content of sulfydryl bonds in wheat gluten, it does not appear the corresponding characteristic peaks on the Raman spectra. By comparison, the four samples which were mixing within t_0 (vital wheat gluten), t_L, t_{50}, and t_{90} (see Fig. 1) were opted to investigate the variation of disulfide bonds in wheat gluten. Provided the intensity of disulfide bonds in the vital wheat gluten is assumed as zero, and the other relative intensity of disulfide bonds in the different wheat gluten are shown in Table I. The results show that the intensity of disulfide bonds enhances with increase of the mixing time. More the disulfide bonds occur, more the crosslinking networks form in the wheat gluten during mixing. This reflects that the chemical reaction between sulfydryls of protein arises in the wheat gluten during processing.

Preparation of glycerol-plasticized wheat gluten

Typical changes in torque and temperature versus mixing time for wheat gluten containing glycerol of 20% by weight are shown in Figure 4. The plasticizing curves could be divided into three portions, at which the corresponding torque was defined as initial, maximal, and balance stage, respectively. During the mixing process, the torque rises rapidly from zero to a maximal value, then decreases gradually and stabilizes finally. The initial torque increase is associated with the consistency transition from the gluten powder/glycerol dispersion to viscoelastic material. In addition, the material temperature

TABLE I
Relative Intensity of Disulfide Bonds of Wheat Gluten Upon Mixing Within Various Time

Samples mixed in various time	Relative intensity at different wavenumber cm^{-1}	
	505	530
t_0	0	0
t_L	556	352
t_{50}	2529	2134
t_{90}	6989	7119
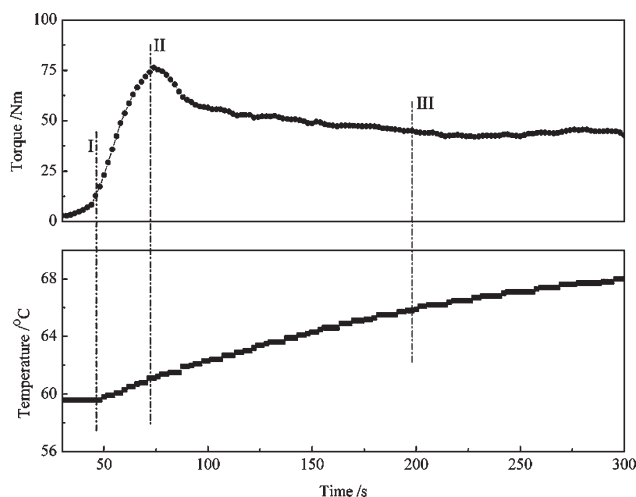
Figure 4 Plasticizing curve of wheat gluten containing glycerol of 20 wt %.

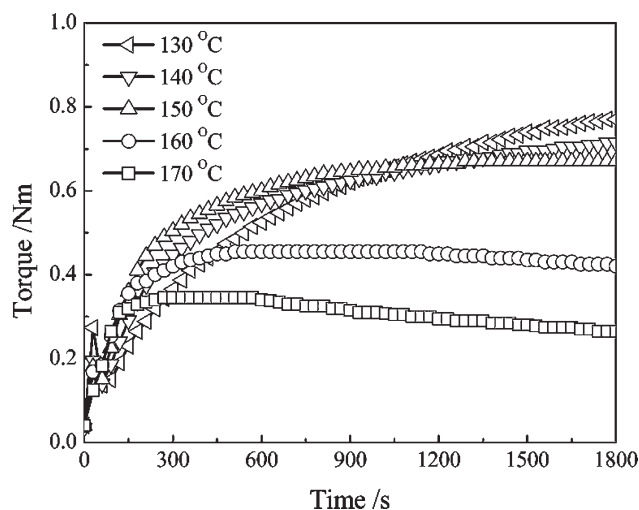**Figure 5** Effect of vulcanizing temperature on crosslinking curves of wheat gluten containing glycerol of 20 wt %.

increases gradually from 60 to 67°C, despite the thermostatic control of the mixing chamber and adopting sigma rotors of low shear force. Torque and temperature evolutions during mixing glycerol-plasticized wheat gluten are presented in Table II. It is obvious that initial, maximal and balance torque, as well as balance temperature of the mixtures, decrease with increasing glycerol content. In addition, the mixing temperature of wheat gluten containing glycerol of 30 wt % is close to the setting value of 60°C, indicating that redundant glycerol leads to excessive softening of the mixture. Therefore, the optimum plasticizer content is thus a compromise between the process requirements and the desired material stiffness.

Effect of vulcanizing temperature

Figure 5 shows the typical changes in torque versus vulcanizing time and temperature for wheat gluten containing glycerol of 20 wt %. An increase in vulcanizing temperature leads to a continuous decrease

of both M_H and M_L, and shortening of the plateau vulcanization step. In the case of 150°C, the torque gradually rises to a plateau value, and then slightly declines. The increase of initial torque is associated with crosslinking reaction between sulfydryls of wheat gluten, which was initiated by heat transfer to the material. Whereas the slight decline of plateau torque is attributed to oxidation and degradation of wheat gluten under higher temperatures. The effect of vulcanizing temperature on the average rate of crosslinking reaction is demonstrated in Figure 6. The change reveals that $\bar{v}$ increases with elevating vulcanization temperature, reflecting faster crosslinking between sulfydryls of protein. According to vulcanizing curves and $\bar{v}$, the optimum temperature for compression-molding of plasticized wheat gluten is set at 150°C.

TABLE II
Effect of Glycerol Content on Plasticizing Curves of Wheat Gluten

Parameters at different stage		Content of glycerol/wt %				
		10	15	20	25	30
I	Time/s	183	79	46	41	25
	Torque/Nm	18.2	15.9	13.7	12.2	8.9
	Temperature/°C	60.3	60.3	59.8	59.9	60.1
II	Time/s	234	124	75	70	60
	Torque/Nm	83.5	74.8	73.9	70.3	53.8
	Temperature/°C	61.7	61.6	61.2	60.3	60.2
III	Time/s	300	298	249	184	177
	Torque/Nm	69.7	53.6	42.6	43.6	3.8
	Temperature/°C	66.6	69.8	67.0	64.5	60.3
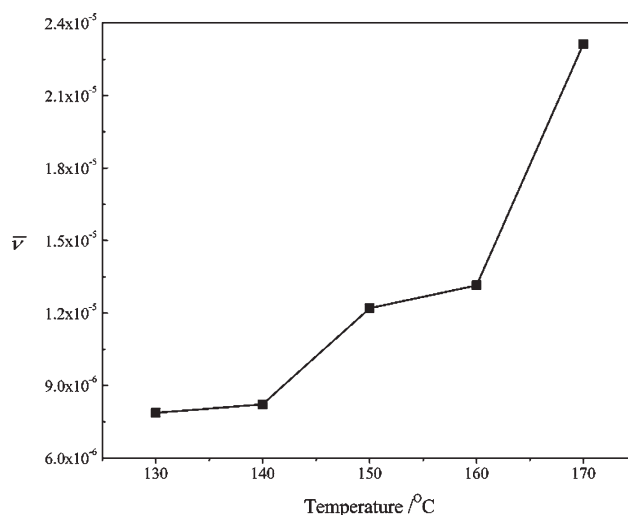
Figure 6 Effect of vulcanizing temperature on $\bar{v}$ of wheat gluten containing 20 wt % glycerol.
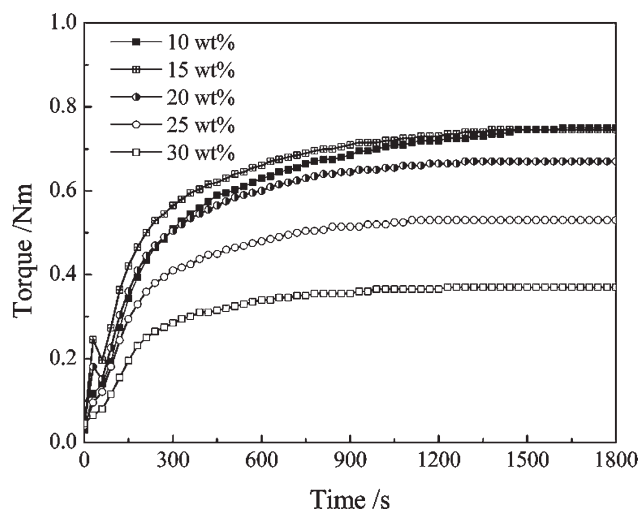
Figure 7 Effect of glycerol content on crosslinking curves of plasticized wheat gluten at 150°C.

Effect of glycerol content

Effect of glycerol content on crosslinking curves of plasticized wheat gluten is shown in Figure 7. Because of the plasticizing effect of glycerol, M_H, M_L, and t_{90} of the plasticized wheat gluten decrease with increasing glycerol content. Effect of glycerol content on $\bar{v}$ of the plasticized wheat gluten is presented in Table III. It is distinct that the $\bar{v}$ of wheat gluten containing glycerol of 20 wt % reaches the maximal value. The phenomenon is attributed to the hydrogen bonding interactions between wheat gluten and glycerol instead of the interactions among the gluten polypeptide chains. The more interactions occurring between sulfydryl/disulfide interchange the higher rate of crosslinking arising during thermal molding. However, the excessive addition of glycerol in wheat gluten increases the mobility of protein chains and isolates the sulfydryl/disulfide interchanges. Accordingly, the average rate of the plasticized wheat gluten is reduced. The equibiaxial extensional deformation of glycerol plasticized wheat gluten also revealed that increasing volume fraction of glycerol in wheat gluten led to increase of average relaxation time of wheat proteins.[17]

Activation energy of glycerol-plasticized wheat gluten

Activation energy of glycerol-plasticized wheat gluten had been investigated in the temperature range of 130–170°C, and computed in terms of eq. (7) and shown in Table IV. The results show that the activation energies of the molded wheat gluten sheets plasticized with a low amount of glycerol are lower than that molded wheat gluten sheet without plasticization. However, the activation energy of the plasticized wheat gluten is more than that of the

vital wheat gluten when the addition of the plasticizer up to 30 wt %. The calculated activation energy of plasticized wheat gluten is 97.7 kJ mol^{-1}. The obtained values of activation energy are essentially the same as those previously reported.[10] The calculated activation energy is consisted of two parts, one occurring at gluten unfolding with a low amount of glycerol, and the other at gluten refolding with the addition of 30 wt % glycerol. Heat-induced variations in gluten proteins are unfolded on heating up to 75°C,[18] and facilitates sulfydryl/disulfide interchanges between exposed groups. Simultaneously, the exposition of hydrophobic protein zones may occur. The addition of the glycerol in wheat gluten increases the mobility of gluten protein chains, and induces more unfolding conformation forming in the wheat gluten. In consequence, the possibility of the sulfydryl/disulfide interchanges and hydrophobic interactions augment. On the other hand, the energy barrier for gluten chain unfolding is higher than that for the chain refolding in thermodynamics. Provided the addition of the glycerol is too many in the plasticized wheat gluten, the gluten chain refolding occurs since the mobility of the protein chains is facile. The refolding conformation of the gluten protein makes the sulfydryl/disulfide interchanges and hydrophobic interactions difficult. The activation energy of the vulcanization arising in the wheat gluten plasticized by glycerol of 30% by weight increases instead. This phenomenon also implies the occurrence of the chain refolding in the gluten. Therefore, activation energy of glycerol-plasticized wheat gluten is strongly influenced by glycerol content.

Mechanical properties of glycerol-plasticized wheat gluten

Effect of glycerol content on mechanical properties of wheat gluten is presented in Figure 8. With increase of the addition of glycerol, the elongation at break of the plasticized wheat gluten sheets increase, but the tensile strength of the sheets decrease. In addition, the increase of elongation at break of the plasticized wheat gluten sheets occur evidently when the glycerol content in the sheets is above

TABLE III
Effect of Glycerol Content on Cross-Linking Reaction Rate of Plasticized Wheat Gluten

Glycerol content/wt %	M_H/Nm	M_L/Nm	t_{90}/s	t_{10}/s	$\bar{v}$/mol s^{-1}
10	0.75	0.14	900	90	1.76E-07
15	0.75	0.20	750	90	1.90E-07
20	0.67	0.16	690	90	1.93E-07
25	0.53	0.12	630	90	1.71E-07
30	0.37	0.08	630	90	1.22E-07

TABLE IV
Activation Energy of Glycerol-Plasticized Wheat Gluten in Vulcanization
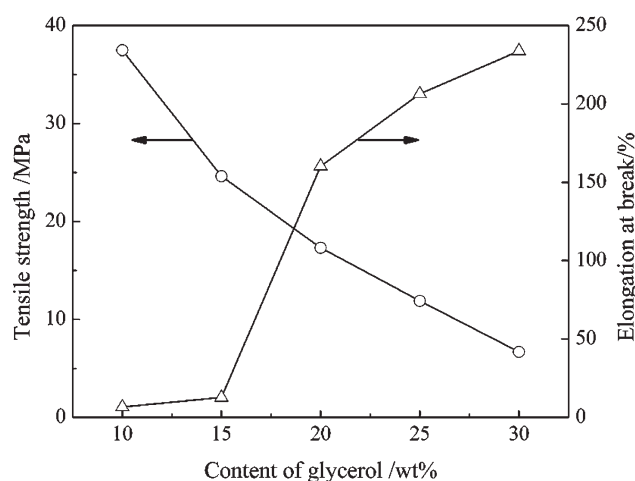
Glycerol content in the plasticized wheat gluten/wt %	$\ln(t_{90} - t_{10})$ at different vulcanizing temperature/s^{-1}					E/kJ mol^{-1}
	130°C	140°C	150°C	160°C	170°C	
0	−0.457	−0.959	−1.954	−2.996	−	124.6
10	−0.418	−0.525	−1.492	−2.223	−2.996	101.4
15	−0.405	−0.780	−1.696	−2.390	−3.178	106.0
20	−1.099	−1.261	−1.843	−2.708	−3.689	97.7
25	−0.470	−0.981	−1.843	−2.708	−3.401	112.5
30	−0.087	−0.959	−1.897	−3.401	−4.094	155.2

15 wt %. The plasticizing effect of glycerol in wheat gluten is similar to the recent reports.[6,19] This phenomenon reflects that the plasticizing effect of glycerol reduces the interactions within protein molecules and increases the flexibility, extensibility, and processability of wheat gluten. The conformation of the plasticized gluten chains vary from folding to unfolding and refolding with increasing glycerol content. With addition of 20 wt % glycerol, the plasticized wheat gluten is of appropriate tensile strength and elongation at break. The results listed in Table III show that the crosslinking rate of the plasticized wheat gluten achieves the maximum when the glycerol content of the gluten is 20 wt %. However, the tensile strength of the plasticized wheat gluten is not the maximal value. This reflects that the effect of disulfide bonds on the mechanical properties of the plasticized gluten is not a key factor in comparison with hydrophobic interactions and hydrogen bonds.

In the interest of understanding effect of temperature on the plasticization of wheat gluten, the plasticization of wheat gluten containing glycerol of 20 wt % was performed at four temperatures: 50, 70, 90, and 110°C, respectively. Effect of plasticizing temperature on mechanical properties of the glycerol-plasticized wheat gluten sheets is given in Table V. The results show that the tensile strengths of the plasticized wheat gluten sheets increase with enhancing the plasticizing temperature and that the elongation at break decreases with increase of the temperature. Extraordinarily, the elongation at break abruptly declines when the plasticizing temperature go up to 110°C. The alteration suggests that the temperature-induced biochemical changes occur during thermomixing. Rising temperature causes wheat gluten proteins unfolding which results in the exposition of hydrophobic groups and cysteine residues and facilitates sulfydryl/disulfide interchange reaction among exposed groups to form the gluten network.[10,18] Water-plasticized wheat gluten can aggregate in the mixing process if the temperature is higher than 60°C, and the gluten proteins undergo crosslinking reactions in the temperature range 70–160°C.[20] The variation of elongation at break against mixing temperature shown in Table V indicates that the aggregation of the glycerol-plasticized wheat gluten can arise when the mixing temperature is higher than 70°C. The change of tensile strength with temperature reveals that the heat-activated reactions can take place if the mixing temperature reaches at 70°C. Therefore, the plasticizing temperature of wheat gluten can be chosen at 60°C to avoid the formation and rearrangement of disulfide bridges.

The aforementioned investigations show that with plasticizing at 60°C, the activation energy and crosslinking reaction rate of the wheat gluten containing

Figure 8 Effect of glycerol content on the mechanical properties of glycerol-plasticized wheat gluten sheets.

TABLE V
Effect of Plasticizing Temperature on Mechanical Properties of the Plasticized Wheat Gluten

Plasticizing temperature/°C	Mechanical properties	
	Tensile strength/MPa	Elongation at break/%
50	19.2	133.9
70	23.0	131.5
90	25.4	112.3
110	28.4	13.7
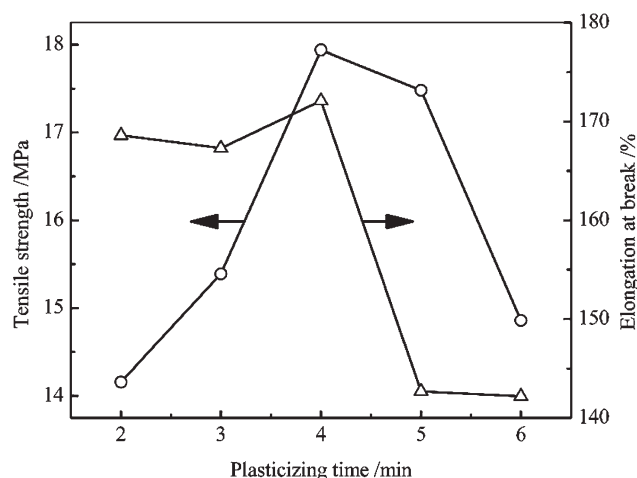
Figure 9 Effect of plasticizing time on mechanical properties of plasticized wheat gluten.

glycerol of 20 wt % in vulcanization attain minimal and maximal value, respectively. In addition, the effect of plasticizing time on mechanical properties of glycerol-plasticized wheat gluten at plasticizing temperature of 60°C is shown in Figure 9. The significant increases of mechanical properties of the plasticized wheat gluten are noted only when the plasticizing time is 4 min. The phenomena suggest that an increase in plasticizing time might enable complete plasticization, as well as intense aggregation of protein by heat and shear force in the process of mixing. However, the tensile properties of the plasticized wheat gluten sheets decline if plasticizing period lasts more time. The reductions of tensile properties of the plasticized wheat gluten sheets reflect that the interactions among the protein chains decline. The deterioration of the properties of the wheat gluten sheets is attributed to the refolding of wheat gluten protein chains. At temperature of 60°C, the effect of standing shear on the plasticized wheat gluten can enhance the mobility of the protein chains, and that the lower energy barrier for refolding leads to the decreases of sulfydryl/disulfide interchanges, hydrophobic interactions and hydrogen bonds in the plasticized wheat gluten sheets.

CONCLUSIONS

Glycerol-plasticized wheat gluten materials were successfully prepared by a thermoplastic process consisting of a plasticization process in an internal mixer equipped with sigma rotors at lower temperature followed by a thermal compression-molding at higher temperature. Rotorless curemeter was firstly

applied to investigate vulcanization process of glycerol-plasticizing wheat gluten. The activation energy and average rate of crosslinking in molding wheat gluten with 20 wt % glycerol are 97.7 kJ mol^{-1} and 1.93E-07 mol s^{-1}, respectively. It means that method of rotorless curemeter can provide an important basis for study on vulcanization process of wheat gluten. In addition, glycerol content, plasticizing time and temperature have significant effects on the mechanical properties of thermal compression-molded wheat gluten sheets. The tensile strengths of the plasticized wheat gluten sheets increased with enhancing the plasticizing temperature, but decreased with increase of the addition of glycerol. And that the elongation at break decreased with increase of the addition of glycerol and the temperature. The significant increases of mechanical properties of the 20 wt % glycerol-plasticized wheat gluten is noted only when the plasticizing time is 4 min and the plasticizing temperature of wheat gluten is chosen at 60°C.

References

1. Domenek, S.; Feuilloley, P.; Gratraud, J.; Morel, M.-H.; Guilbert, S. Chemosphere 2004, 54, 551.
2. Day, L.; Augustin, M. A.; Batey, I. L.; Wrigley, C. W. Trends Food Sci Technol 2006, 17, 82.
3. Sun, S.; Song, Y.; Zheng, Q. Food Hydrocolloids 2008, 22, 1006.
4. Zhang, J.; Mungara, P.; Jane, J. Polymer 2001, 42, 2569.
5. Georget, D. M. R.; Belton, P. S. Biomacromolecules 2006, 7, 469.
6. Song, Y.; Zheng, Q. Bioresour Technol 2008, 99, 7665.
7. Irissin-Mangata, J.; Bauduin, G.; Boutevin, B.; Gontard, N. Eur Polym Mater 2001, 37, 1533.
8. Cuq, B.; Boutrot, F.; Redl, A.; Lullien-Pellerin, V. J Agric Food Chem 2000, 48, 2954.
9. Angellier-Coussy, H.; Torres-Giner, S.; Morel, M.-H.; Gontard, N.; Gastaldi, E. J Appl Polym Sci 2008, 107, 487.
10. Domenek, S.; Morel, M.-H.; Bonicel, J.; Guilbert, S. J Agric Food Chem 2002, 50, 5947.
11. Domenek, S.; Morel, M.-H.; Redl, A.; Guilbert, S. Macromol Symp 2003, 197, 181.
12. Pommet, M.; Redl, A.; Morel, M.-H.; Domenek, S.; Guilbert, S. Macromol Symp 2003, 197, 207.
13. Domenek, S.; Morel, M.-H.; Redl, A.; Guilbert, S. Macromol Symp 2003, 200, 137.
14. Mohamed, A.; Xu, J. J Appl Polym Sci 2007, 106, 214.
15. Dick, J. P.; Pawlowski, H. Polym Test 1995, 14, 45.
16. Morel, M.-H.; Redl, A.; Guilbert, S. Biomacromolecules 2002, 3, 488.
17. Song, Y.; Wang, Z.; Zheng, Q. Food Hydrocolloids 2008, 22, 414.
18. Schofield, J. D.; Bottomley, R. C.; Timms, M. F.; Booth, M. R. J Cereal Sci 1983, 1, 241.
19. Song, Y.; Zheng, Q. Food Hydrocolloids 2008, 22, 674.
20. Kokini, J. L.; Cocero, A. M.; Madeka, H.; de Graaf, E. Trends Food Sci Technol 1994, 5, 281.