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Measurement of Viscoelastic Properties of Heat Denatured Gluten Network

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열변성 글루텐의 점탄성 측정에 관한 연구

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Abstract

A method for the measurement of viscoelastic properties of heat denatured gluten network was developed in order to evaluate the noodle making quality of wheat flour. The stress relaxation of elongated heat denatured gluten network could be expressed by 6-element generallized Maxwell model. The tensile force of heat denatured gluten network increased by the heating time. The elastcity and viscosity of the first exponential term which covers 70-74% of the total relaxation increased as cooking time was extended up to 1q min. The addition of gluten network strengthening agent, potassium bromate, at 1000ppm level reduced the elasticity and viscosity, while weakening agent, L-cystein, increased them. The relaxation time decreased after 11 min of cooking in both cases. The elasticity and viscosity of heat denatured gluten were affected differently by the concentration of added urea.

Key words: gluten, heat denatured gluten, viscoelastic properties

Introduction

The rheological properties of gluten have been studied widely by many investigators. Tkachuk and Hlynka[1] studied the effect of D_2O addition on the extensograph and farinograph of wheat dough, and Inda[2] investigated the effects of D_2O and urea addition on the tensile property of gluten in order to evaluate the influence of hydrogen bonds in the gluten network. Jankiewicz and Pomeranz[3]reported that the dough strength of farinograph decreased drastically when 3M-urea was added to the dough.

The effects of oxidizing and reducing agents on the gluten network strength were also studied[4-6]. It is generally understood that the oxidizing agents, such as $KBrO_3$, KIO_3, and L-ascorbic acid, exert a gluten network strengthening effect, while the reducing agents, such as L-cystein and glutathion, have weakening effect on dough strength. These investigations have been mainly concerned with the properties of vital gluten, which has great influence on the dough rheology and loaf volume formation before baking.

In case of noodle, the dough rheology and loaf formation is not so important as baking. The characteristic noodle texture is formed during the boiling of noodle strand. The heat denaturation and structure setting of gluten network in noodle dough sheet during cooking may play important role for the formation of cooked noodle texture.

In the present study, a method for the measurement of the rheological properties of heat

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denatured gluten was developed with stress relaxation principle. A specially designed spcimen moulding cell was made and specimen preparation procedure was established. The effects of the addition of urea, ascorbic acid, potassium bromate and L-cystein on the rheological property of heat denatured gluten network were compared.

Materials and methods

Specimen preparation

A flour, made from 1985/86 Australian Standard White was used. Gluten was prepared by AACC hand-washing method [7] and dried on an hot-air drier at 35℃. It was ground in a coffee grinder, and particles in the size of 0.149-0.177mm, passing through ASTM No. 80 screen but remaining on No. 100 screen, were selected for the specimen preparation. The test specimen was prepared as follows.

1. 1.7g of gluten powder was put in the moulding cell and tapped slightly in order to eliminate air pocket.
2. 2ml of water was evenly added to the powder with micropipette.
3. The moulding cell was covered with lid and wrapped with polyethylene film, and then wrapped again with aluminium foil, in order to prevent the penetration of water into moulding cell.
4. It was fixed with clamp and placed in boiling water.
5. After heating for a certain time in boiling water, it was moved to 25℃ water and cooled for 2min.
6. The heat denatured gluten specimen was taken out from the moulding cell and applied to the tensile test holder for the measurement.

Design of specimen moulding cell

Fig. 1 shows the detail design of specimen moulder for the tensile test of gluten network. In order to prevent attachment of wet gluten specimen to the surrounding wall, the inner wall of moulding cell was made with teflon. The outer supporting plates were made from aluminum.

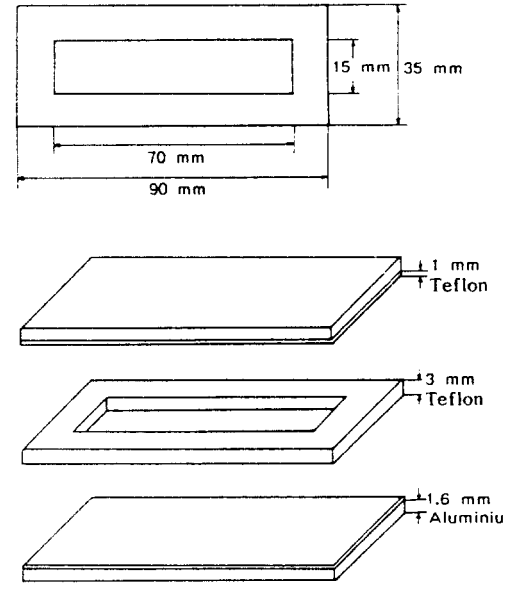

Fig. 1. Detail design of specimen moulder for the tensile test of gluten network.

Stress relaxation test

Rheometer (Sun Instrument Co., Japan, Model M-1107) was used for the stress relaxation after tensile deformation . Fig. 2 shows the schematic diagram of tensile test conditions. The stress relaxation curve was obtained and analyzed by successive residual method [8].

Addition of dough improvers

In order to evaluate the effect of oxidizing and reducing agents to the stress relaxation of heat

denatured gluten network, 1000ppm of $KBrO_3$, ascorbic acid, L-cystein and 1M, 3M and 5M of urea, respectively, were added to gluten powder before heat denaturation.

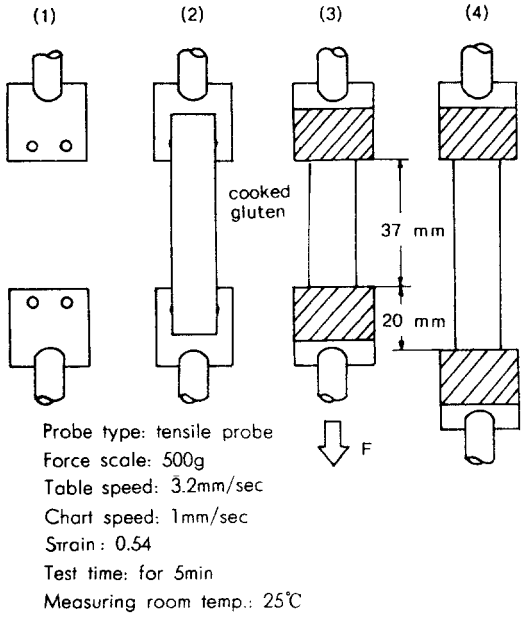

Fig. 2. Application of specimen to the sample holder of Rheometer and tensile test conditions.

Results

Mathematical analysis of stress relaxation curve of heat denatured glutens

Stress relaxation test is made by measuring the force dissipated by time in a sample deformed at a constant strain. For the mathematical analysis of stress relaxation a generalized Maxwell model is often used.

$$\sigma(t)=\varepsilon_0(Ed_1e^{-t/T_1}+Ed_2e^{-t/T_2}+\cdots+Ed_n e^{-t/T_n}+E_e)$$

where

$\sigma(t)$: stress at time t

ε_0 : strain at $t=0$

$Ed_1, Ed_2, \cdots E_e$: elastic modulus

$T_1, T_2 \cdots T_n$: relaxation time

Fig. 3. shows a typical stress relaxation curve of cooked gluten network boiled in water for 7min. The table speed for tensile force application was 3.2mm/sec and the force decay by time was measured at a constand strain of 0.54. From the straight line of original curve (Top line in Fig. 3 the intercept slope were estimated. The stress (dyne/cm²) was calculated from the intercept 117.69g, gravitational acceleration 980cm/s² and the cut area of gluten specimen of 0.45cm².

$$\text{Intercept}_1=\frac{117.69g\times 980cm/s^2}{0.45cm^2}=256302.7 dyne/cm^2$$

The first relaxation time were

$$T_1=-(\frac{1}{\text{slope}})=-(-\frac{1}{0.00027425})$$

$$=3546.3 sec$$

and the first exponential term of stress decay was

$$\sigma_1=256302.7\, e^{-t/3546.3}$$

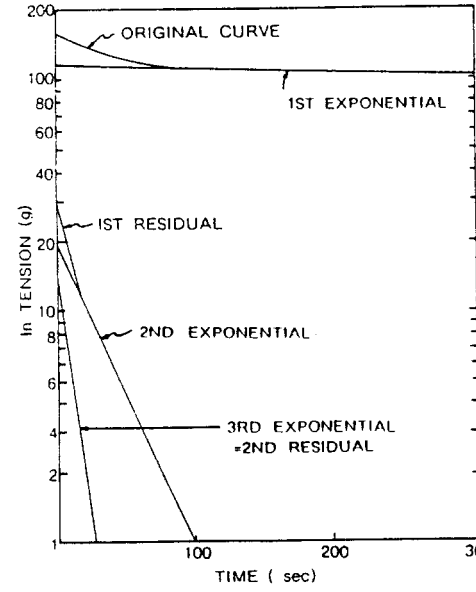

Fig. 3. Analysis of stress relaxation of gluten network by the method of successive residuals.

The first residual curve was obtained by the difference between original curve and first exponential straight line, as shown in the middle of Fig 3. The second exponential straight line of first residual curve was drawn and the intercept to the force coordinate was 19.29g. Therefore, the stress, 2nd relaxation time and 2nd term stress decay were as follows.

$$\text{Intercpt}_2=\frac{19.29\text{g}\times 980\text{cm/s}^2}{0.45\text{cm}^2}=42009.3\text{dyne/cm}^2$$

$$T_2=-(-\frac{1}{0.0282})=35.5\text{sec}$$

$$\sigma_2=42009.3\,e^{-t/35.5}$$

The first residual curve was not considered to be complete straight line. Therefore, a second residual curve was drawn from the difference between first residual curve and 2nd exponential straight line. From the third straight exponential straight line, the intercept$_3$, 3rd relaxation time and 3rd exponential term of stress decay were calculated.

$$\text{Intercept}_3=\frac{15.78\text{g}\times 980\text{cm/s}^2}{0.45\text{cm}^2}=34365.3\text{dyne/cm}^2$$

$$T_3=-(-\frac{1}{0.211})=4.7\text{sec}$$

$$\sigma_3=34365.3\,e^{-t/4.7}$$

As the third exponential straight line appeared to fit completely to the 2nd residual curve, the relaxation curve of the heat denatured gluten network could be expressed mathematically with the generalized Maxwell model as follows.

$$\sigma(t)=256302.7\,e^{-t/3646.3}+42009.3\,e^{-t/35.3}+34365.3\,e^{-t/4.7}$$

Effect of loading speed on the stress relaxation of heat denatured gluten

Table 1 shows the changes in tensile force and the estimated intercepts and slopes of successive residual exponential terms of heat denatured gluten by the table speed of tensile test. The tensile force did not changed significantly by the changes in table speed from 0.64 to 3.20 mm/sec. The first intercept estimated 80% of tensile force, and 90% of tensile force was covered by the first and second intercepts. In all cased, the tensile force was completely estimated by the intercepts estimated from the first to the third exponential terms. This fact indicates that the viscoelastic property of heat denatured gluten network can be explained by the generalized Maxwell models arranged in parallel. Table 2 shows the relaxation parameters calculate from the data shown in Table 1.

The relaxation time of first exponential term tended to incerase as the table speed increased.

Table. 1. Tensile force and estimated tensile force and slopes of cooked gluten network

Table speed		1st Exponential				2nd Exponential				3rd Exponential			
(mm/sec)	F	A_1	$B_1(\times10^{-4})$	r_1	%	A_2	B_2	r_2	%	A_3	B_3	r_3	%
3.20	136.6	97.70	-2.1601	.992	71.52	18.3702	-0.0285	.998	84.97	17.6518	-0.233	.996	97.89
1.60	147.2	115.81	-2.6527	.987	78.68	15.2330	-0.0270	.999	89.02	11.8145	-0.162	.999	97.04
1.07	144.2	112.78	-2.6708	.986	78.21	18.8577	-0.0287	.999	91.29	9.1555	-0.195	.995	97.64
0.80	147.2	118.62	-2.7495	.990	80.58	17.1744	-0.0282	.999	92.25	10.1929	-0.192	.998	99.17
0.64	140.8	117.07	-2.5680	.988	83.15	14.1690	-0.0261	.998	93.21	9.7885	-0.193	.978	100.02

F: Tensile force (g)
A: Estimated tensile force of each exponential term. (g)
B: Slope of each exponential term.
r: Correlation coefficient of each exponential term.
%: A/Tensile force ×100

Table 2. Changes in relaxation time, elasticity and viscosity of cooked gluten network by table speed

Table speed	1st exponential			2nd exponential			3nd exponential		
(mm/sec)	T_1	E_1	$\eta_1(\times10^9)$	T_2	E_2	$\eta_2(\times10^6)$	T_3	E_3	$\eta_3(\times10^6)$
3.20	4629.6	394019.7	1.82415	35.1	74085.6	2.600406	4.3	71188.4	0.306110
1.60	3770.7	467061.6	1.76114	37.0	16433.6	2.273041	6.2	47647.0	0.295411
1.07	3744.2	454826.5	1.70296	35.5	93374.3	3.314789	5.1	36923.5	0.188310
0.80	3637.0	478389.6	1.73990	35.5	69263.1	2.458839	5.2	41107.2	0.213757
0.64	3894.1	472150.4	1.83860	38.3	57142.5	2.188558	5.2	39476.3	0.205277

T: Relaxation time of each exponential term (sec)
E: Elasticity of each exponential term (dyne/cm²)
η: Viscosity of each exponential term (Poise)

The first term elasticity tended to decrease by the increasing table speed, while viscosity varied inconsistently with the loading speed.

Effect of heating time of gluten on the stress relaxation

Fig 4 shows the stress relaxation curve of gluten cooked for various period of heating time. The tensile force increased as the cooking time increased from 3min to 19min. Table 3 shows the tensile force, and the rheological parameters of cooked gluten network. The elasticity and viscosity increased as the cooking time increased. The relaxation time increased with cooking time up to 15min and then slightly decreased with further cooking to 19min.

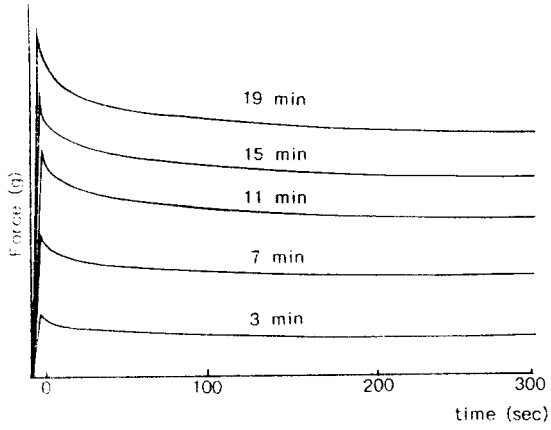

Fig. 4. Typical stress relaxation curve of gluten cooked for various periods of time.

Table 3. Changes in relaxation time, elasticity and viscosity of cooked gluten network by cooking time

Cooking time	1st Exponential			2nd Exponential			3rd Exponential		
	T_1	E_1	$\eta_1(\times10^9)$	T_2	E_2	$\eta_2(\times10^6)$	T_3	E_3	$\eta_3(\times10^6)$
3	2954.9	119440.4	0.352934	37.3	24720.2	0.922064	6.6	12837.6	0.084728
7	3646.3	474644.7	1.730690	35.5	77795.5	2.761742	4.7	63634.3	0.299081
11	4083.0	713854.9	2.914660	34.5	108674.4	3.749268	7.0	89320.4	0.625243
15	4323.0	842678.7	3.642890	35.7	124988.4	4.462087	5.8	124986.0	0.724919
19	3895.1	1008231.4	3.927160	35.8	152541.8	5.460996	5.2	149440.5	0.777090

T: Relaxation time of each exponential term (sec)
E: Elasticity of each exponential term (dyne/cm²)
η: Viscosity of each exponential term (Poise)

Effect of the addition of oxidizing and reducing agents

Fig. 5 shows the changes in the tensile force of gluten network added with oxidizing and reducing agents. Contrast to the case of vital gluten, the oxidizing agent, potassium bromate, which was known to have gluten network strengthening effect, decreased the tensile force of heat denatured gluten. Whereas, the reducing agent, L-cystein, which was known to have gluten network weakening effect, increased the tensile force of heat denatured gluten. Ascorbic acid did not change much the tensile force of heat denatured gluten.

This findings can be interpreted as follows. In case of vital gluten, the nework structure will be strengthened by the action of oxidizing agents which accelerates the formation of disulfide bond in the protein network. When gluten network is heated, the denaturation or unfolding, and aggregation will be taken place. Ferry suggested that when the denaturation rate was higher than aggregation rate, the protein gel would have higher elasticity and firmness[9]. The added oxidizing agents will increase the aggrgation rate through the s-s bond before heat denaturation, but retard unfolding of protein network.

In case of L-cystein addition, the cleavage of s-s bond before heat denaturation will enhance undfolding and subsequent thermal aggregation resulting in more wide spread gelation

This fact was reflected to the elasticity and viscosity of the heat denatured gluten network. As shown in Fig 6 and 7, potassium bromate reduced the elasticity and viscosity of heat denatured gluten network drastically, while L-cystein enhance them. Asocrbic acid did not exert such dramatic effects as shown by potassdium bromate. In case of viscosity, as sharp reduction in the rate of viscosity increment by cooking time was observed over 11 min of cooking. This phenomenon was refected by the reduc-

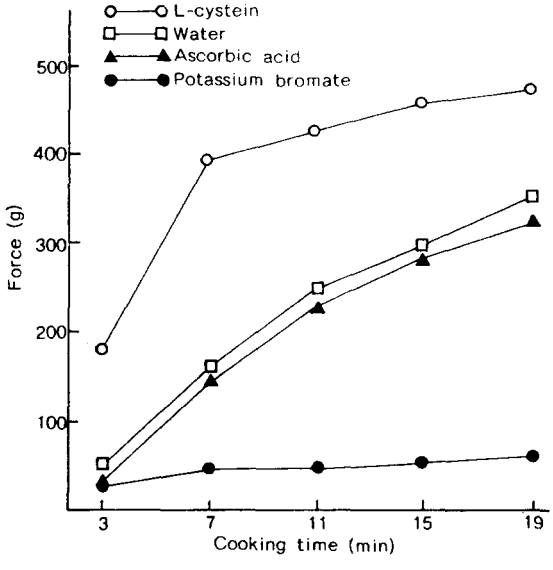

Fig. 5. Changes in tensile force of heat denatured gluten network by the addition of oxidizing and reducing agents.

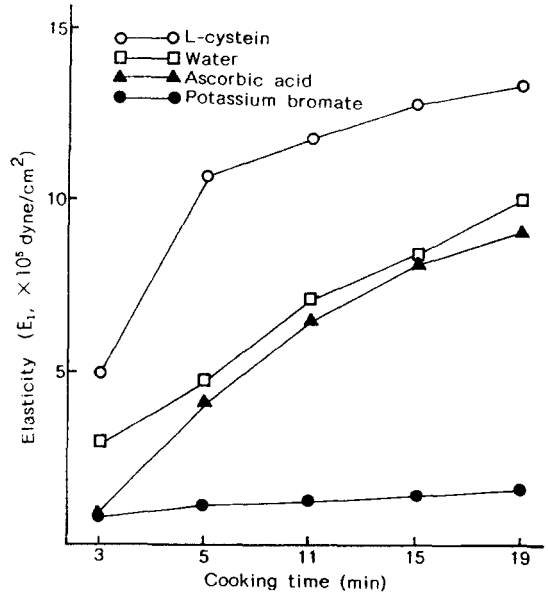

Fig. 6. Changes in elasticity(E_1) of heat denatured gluten network by the addition of oxidizing and reducing agents.

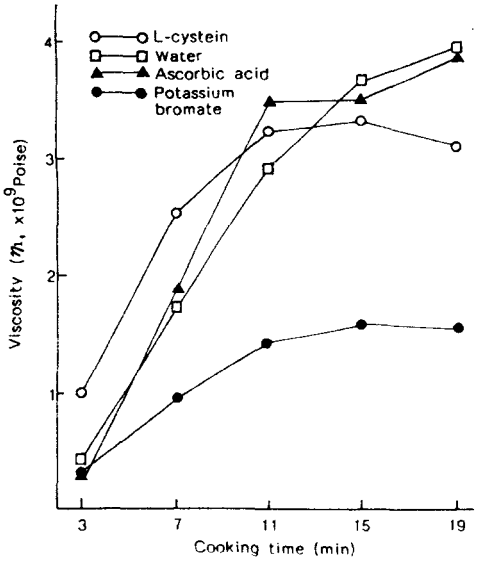

Fig. 7. Changes in viscosity(η) of heat denatured gluten network by the addition of oxidizing and reducing agents.

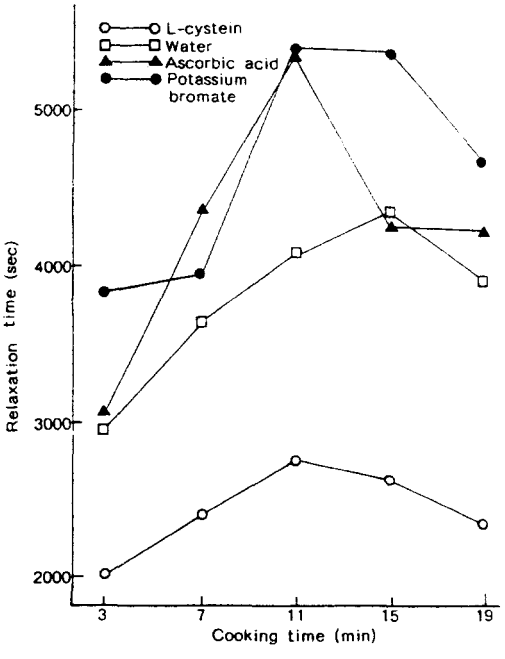

Fig. 8. Changes in relaxation time(T_2) of heat denatured gluten network by the addition of oxidizing and reducing agents.

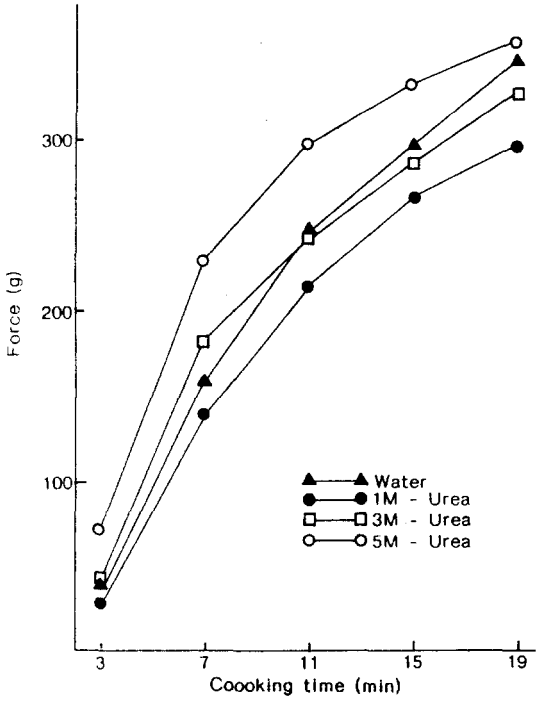

Fig. 9. Changes in tensile force of gluten network by the addition of urea.

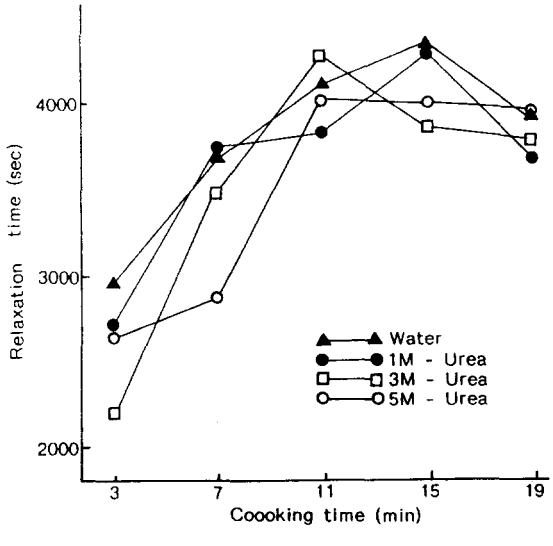

Fig. 10. Changes in relaxation time(T_1) of gluten network by the addition of urea.

tion of relaxation time at over 11min of cooking, as shown in Fig 8. The relaxation time increased by the addition of potassium bromate and ascorbic acid, but decreased by the addition of L-cystein.

Effect of addition of urea

In case of vital gluten, the addition of urea reduces the tensile force of gluten network due to the breakdown of hydrogen bonds in the protein network. Addition of urea prior to heat denaturation of gluten decreased the tensile force of heat denatured gluten network at the lower concentration (1M urea) but increased at the higher concentration (5M urea). The elasticity and viscosity of heat denatured gluten were affected differently by the concentration of added urea; 1M urea increased those viscoelastic parameters. The rate of viscosity increment by cooking time diminished at over 11 min of cooking, and this was reflected by the reduction of relaxation time over 11min of cooking(Fig. 10).

Discussion

The stress relaxation test of heat denatured gluten network was shown to be a sensitive method to evaluate the gluten quality of noodle flour. The results obtained in this experiment was, at a glance, quite opposite to our expectation. The addition of gluten network strengthening agents, such as potassium bromate and ascorbic acid, reduced the tensile force and elasticity, but the addition of gluten network weakening agent, L-cystein, increased the tensile force and elasticity of heat denatured gluten. This fact is explained by the Ferry's protein gelation mechanism. On the other hand, the concentration of added agents, which was 1000ppm was far excess of the amount normally added to bread dough making. This effect will also be studied more carefully in the future. The heat denatured gluten network enlongated to a strain of 0.54 exhibited slight deviation from linear-viscolasticity. However, Maxwell model was applied for the mathematical evaluation with the assumption that the error is in the range of tolerance.

요 약

밀가루의 제면특성을 평가하는 방법을 수립하기 위하여 열변성 글루텐의 점탄성 측정 방법을 연구하였다. 열변성 글루텐의 인장력 완화시험에서 얻어진 완화곡선은 6개의 점탄성 요소를 포함하는 일반화 맥스웰 모델로 표현될 수 있었다. 열변성 글루텐의 인장력은 열처리 시간이 경과할수록 증가하였으며 전체 완화분의 70-74%를 차지하는 제1차 지수항에서의 탄성과 점성은 열처리 시간 19분 동안 계속 증가하였다. 글루텐의 강화제로 알려져 있는 $KBrO_3$를 1000ppm 수준으로 첨가할 경우 탄성과 점성은 감소하였으나 글루텐 약화제인 L-시스텐은 이들을 증가시켰다. 두 경우 모두 완화 시간은 가열 11분 후부터 감소하였다. 이들 파라미터들은 또한 尿素의 첨가농도에 따라 상이하게 변화되었다.

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