

Rheological Properties of Soyprotein Dope

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Abstract

The dynamic rheological properties of the dope and the hydrated dispersion of the soyprotein, as a starting material of soyprotein fiber, were studied to investigate their viscoelastic properties. The increase of protein concentration in the both cases of the dope and the dispersion resulted in the establishment of intermolecular reaction of the protein. With the addition of alkali solution to the dispersion, the dope shows the characteristics of very lightly cross-linked high molecular weight polymer. In contrast, the dispersion shows the properties of an amorphous polymer. The effects of chemical modification of the dispersion on the dynamic properties were also investigated.

Key words: rheological property, soyprotein, dope

Introduction

Generally, the concentrated dispersions for high molecular weight polymers show the important food viscoelastic properties. Since the structure of a sample is destroyed through the conventional methods of rheological testing, it is very difficult to understand the exact intrinsic properties of the sample itself by those conventional methods such as static rheology. Recently, a new method which made it possible to grasp the exact properties of sample itself without destroying the structure of the sample was proposed as a dynamic rheology; the structure of oscillated sample by giving sinusoidal strain shows important viscoelastic properties of the sample.

In the field of food science and engineering, the papers which involved a study of the viscoelastic properties with a dynamic test have rarely been published. Cumming and Tung^(1,2) studied the dynamic shear properties of commercial vital wheat gluten and the modification effect of rehydrated commercial wheat gluten. Zanger⁽³⁾ studied the viscoelasticity of gluten dough to determine bakeability by rheometrical technique using very small size sample. Taneya *et al.*⁽⁴⁾ studied dynamic viscoelasticity of cheese. By comparing the relaxation time distribution of processed cheese with that of natural cheese, they conclu-

ded such that the network structure of casein in processed cheese is weaker than in natural cheese.

In this sense, using a dynamic rheology, we studied the viscoelastic properties of the soyprotein dope to have fundamental knowledges to prepare soyprotein fibers.

Materials and Methods

Materials

The soyprotein isolate, commercially available as Promine-D, which is used to prepare the hydrated soyprotein dispersion (HSD) and dope (D) was purchased from Central Soya Co. (U.S.A.). All the other chemicals used were obtained from commercial sources and were of analytical grades.

Preparation of soyprotein dispersion

Promine-D was mixed with distilled water by Waring blender at room temperature and hydrated at 4°C for 24 hr in refrigerator and equilibrated at 20°C for 2 hr on a water bath. To see the effect of protein concentration and chemical modification on the properties of HSD, HSDs were prepared as represented in Table 1.

Preparation of dope

The sodium hydroxide solution was slowly added to HSD on a water bath at 20°C and mixed thoroughly with Waring blender. HSD of slightly yellow color gradually changed to dough with darkly brown color and final NaOH concentration was 0.6% (w/v), consi-

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Table 1. Notation of experimental sample

Notation	Description	Remark
HSD HSP-5	5% protein concentration	Standard
HSD-9	9% protein concentration	
HSD-12	12% protein concentration	
HSD-15	15% protein concentration	
HSD-18	18% protein concentration	
HSD-15-A	HSD-15 in 0.1 N HCl	
HSD-15-G	1% glutaraldehyde treated HSD-15	
HSD-15-Ca	HSD-15 + 20 mM CaCl ₂	
HSD-15-H	HSD-15 + heated at 85°C, 30 min	
D D-12	12% protein concentration	Standard
D-15	15% protein concentration	
D-18	18% protein concentration	
D-15-3	HSD-15 in 0.3% NaOH	
D-15-9	HSD-15 in 0.9% NaOH	

dered as the standard to dope series. To examine the effect of protein concentration and denaturation by the NaOH solution, dopes were prepared as presented in Table 1.

Rheological measurement

The measurements of dynamic rheological properties of the samples were accomplished at Rheometrics Co. (U.S.A.) with the viscoelastic tester. The range of applied maximum strain amplitudes was adjusted to 20-50%, taken a consideration not to destroy the structure of sample, and oscillatory frequency were varied from 0.10 to 100 rad/sec at 20°C. The type of apparatus equipped strain was disk and plate.

Statistical procedure

Three rheological parameters were determined for the various samples. These were the dynamic shear storage (G'), loss moduli (G'') and dynamic viscosity (η'). Dynamic shear loss tangent ($\tan\phi$) and loss compliance (J'') were calculated by the following equations (5); $\tan\phi = G''/G'$ and $J'' = G''/(G'^2 + G''^2)$. Table 2 shows a list of symbols used in calculation and their definition for dynamic shear studies. The simple and multiple linear regression analyses and line comparisons were performed on the rheological data obtained, if necessary.

Results and Discussion

In all the HSD and D samples, the relationship of dynamic viscosity and oscillatory frequency in the

Table 2. List of symbols employed for dynamic shear studies of soyprotein

Symbol	Description
G'	Dynamic shear storage modulus (dyne/cm ²)
G''	Dynamic shear loss modulus (dyne/cm ²)
η'	Dynamic viscosity (poise)
J'	Dynamic shear storage compliance (cm ² /dyne)
J''	Dynamic shear loss compliance (cm ² /dyne)
$\tan\phi$	Dynamic shear loss tangent
ω	Oscillatory frequency (sec ⁻¹)
C_p	Protein content of specimen (% w/v)
C_n	Sodium hydroxide content of specimen (% w/v)

Table 3. Simple linear regression coefficient of dynamic viscosity against oscillatory frequency in logarithmic scale*

Sample	Slope	Regression coefficient
HSD-5	-0.274	-0.891
HSD-9	-0.517	-0.893
HSD-12	-0.689	-0.959
HSD-15	-0.808	-0.999
HSD-18	-0.728	-0.997
HSD-15-G	-0.964	-1.000
HSD-15-Ca	-0.801	-0.996
D-12	-0.781	-0.998
D-15	-0.800	-0.997
D-18	-0.824	-0.999
D-15-3	-0.829	-0.998
D-15-9	-0.841	-0.999

*Oscillatory frequency 0.1-100 rad/sec

form of $\log \eta'$ vs. $\log \omega$, is highly correlated. The simple linear regression analyses of the sample are summarized and presented in Table 3.

In regions where G'' is flat, η' is inversely proportional to frequency, whereas when G'' rises steeply, η' flatten out. These phenomena explain the deviation from the straight line of $\log \omega$, especially in the cases of HSD-5 and HSD-9. Fig. 1 confirmed this relationship. The plateau regions, where G' or G'' are flat, suggested "entanglement" network in polymer and existed over the intermediate range of frequency.

Effect of protein concentration

The loss tangent ($\tan\phi$) is a measure of the relative distribution of viscous (G'') and elastic (G') components. Since decreasing $\tan\phi$ means development of three dimensional structure, it will be considered that

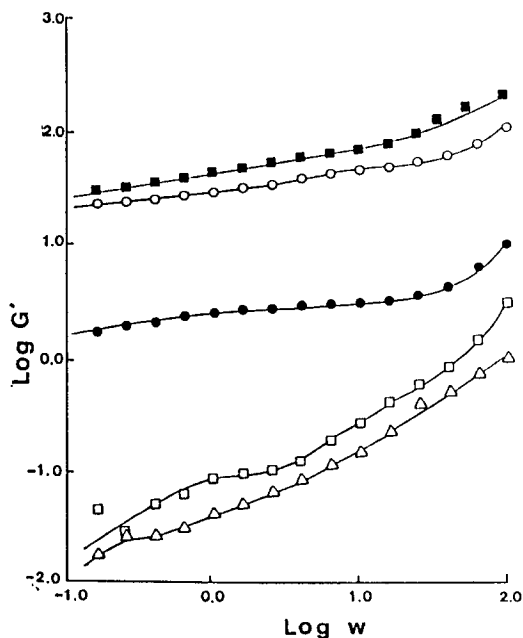


Fig. 1. Effect of oscillatory frequency on dynamic shear storage modulus in HSD at various protein concentrations

△-△; HSD-5, □-□; HSD-9, ●-●; HSD-12, ○-○; HSD-15, ■-■; HSD-18

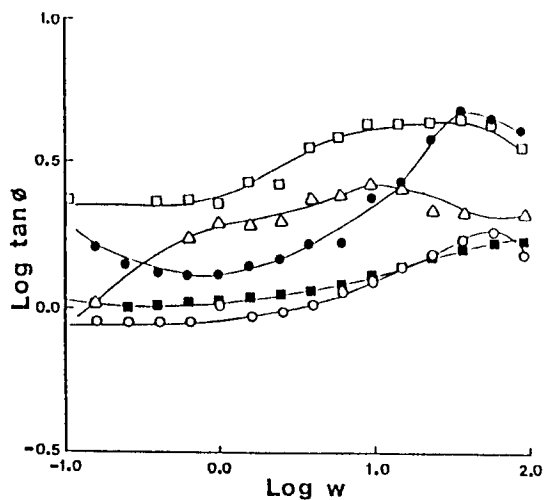


Fig. 2. Effect of oscillatory frequency on loss tangent in HSD at various protein concentrations

△-△; HSD-5, □-□; HSD-9, ●-●; HSD-12, ○-○; HSD-15, ■-■; HSD-18

the structures of HSD increased with the concentrations of protein. Fig. 2 shows that a structure of HSD-15 is most developed, except the high frequency region where a structure of HSD-18 is the mostly deve-

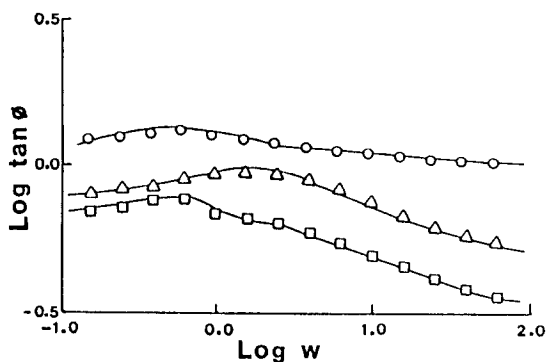


Fig. 3. Effect of oscillation frequency on loss tangent in dope at various protein concentrations

○-○; D-12, △-△; D-15, □-□; D-18

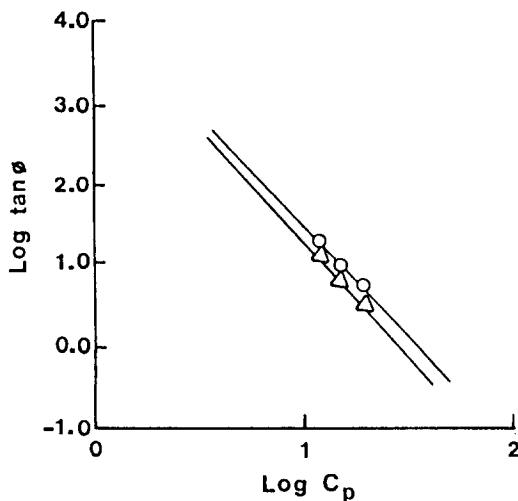


Fig. 4. Effect of protein concentrations on loss tangent in dope

○-○; Oscillatory frequency at 1 rad/sec, △-△; Oscillatory frequency at 10 rad/sec

loped. The profile of $\tan\phi$ in HSD-12 showed typical profile of a high molecular weight amorphous polymer.

In contrast to HSD, $\tan\phi$ of dope (D), which was alkali treated HSD, went through a pronounced maximum for all cases of dope, as shown in Fig. 3. As the same strain amplitude, the maximum shifted to the high frequency zone, when $\tan\phi$ at the high frequency zone increased with the concentration of protein. The more increases the concentration of protein, the more is entangled between the protein molecules (Fig. 4). In general, at the very low and very high frequencies $\tan\phi$ will be constant for the cross-linked polymer. At the intermediate region, $\tan\phi$ will

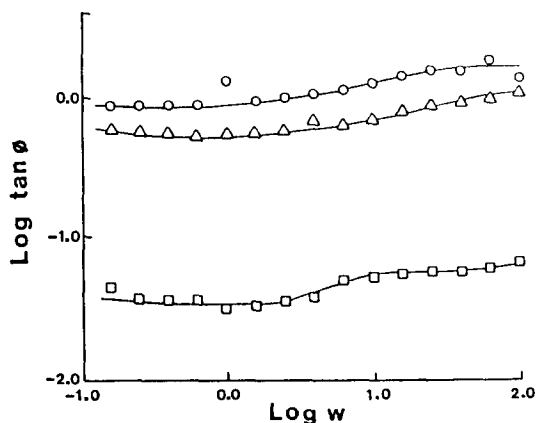


Fig. 5. Effect of oscillatory frequency on loss tangent in HSD at various chemical treatments

○—○; HSD-15-Ca (20 mM CaCl_2), \triangle — \triangle ; HSD-15, \square — \square ; HSD-15-G (1% glutaraldehyde)

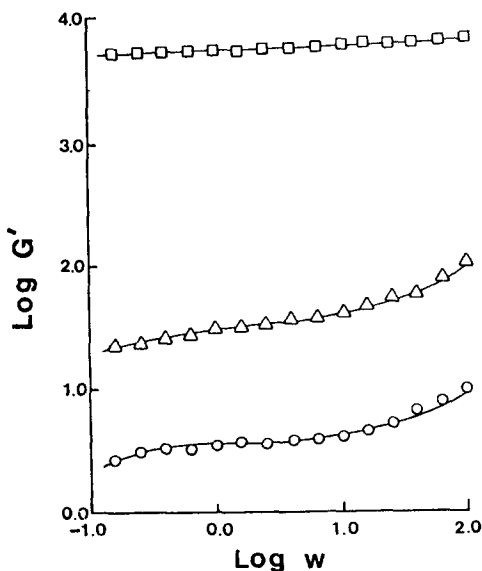


Fig. 6. Effect of oscillatory frequency on dynamic shear storage modulus in HSD at various chemical treatments

○—○; HSD-15-Ca (20 mM CaCl_2), \triangle — \triangle ; HSD-15, \square — \square ; HSD-15-G (1% glutaraldehyde)

increase, but then, decrease. Consequently, the peak of the $\tan\delta$, as shown in Fig. 3, will be appeared⁽⁵⁾.

The notion of coupling at widely separated points led to the concept of adherence of the polymer molecules at specific loci in case of the high molecular weight polymer system. Such a locus is a temporary cross-link. The effects of entanglement coupling appear universally; examples include nonpolar poly-

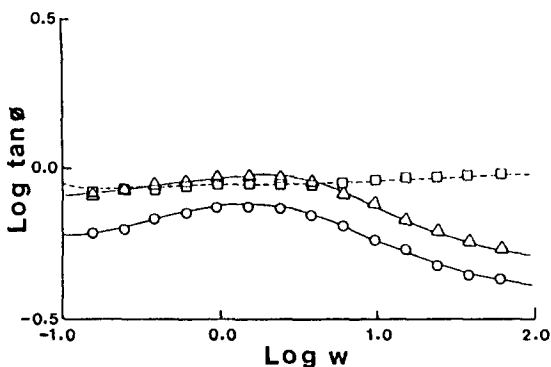


Fig. 7. Effect of oscillatory frequency on loss tangent in the dope at various NaOH concentrations

○—○; D-15-9, \triangle — \triangle ; D-15, \square — \square ; D-15-3

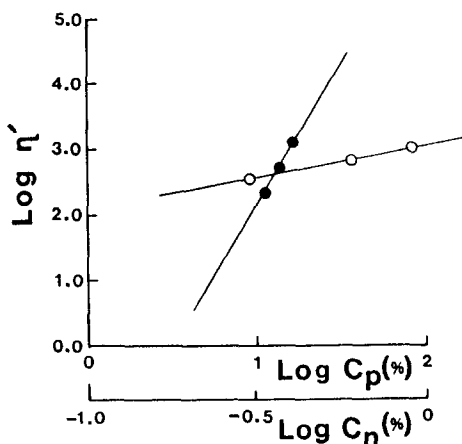


Fig. 8. Effect of protein and alkali concentrations on dynamic viscosity

○—○; Alkali concentration (%), ●—●; Protein concentration (%)

mers where the intermolecular attractive forces are small and there is no suspicion of structural heterogeneity. It seems, therefore, that the coupling must be topological rather than due to intermolecular forces, thus justifying the term "entanglement". A concept which retains the idea of a specific locus is an entanglement where two chains are tightly kinked around each other by bending back on themselves in short-range contour. However, molecules which are relatively stiff and extended such as cellulose derivatives⁽⁷⁾, deoxyribonucleic acid⁽⁸⁾ or a helical polyamino acid⁽⁹⁾ exhibit the effects of entanglement coupling even more prominently than does highly flexible polymer. The presence of bulky side groups does not markedly inhibit the entanglement coupling⁽¹⁰⁾. This

phenomena occurred in HSD and dope of soyprotein.

Effect of chemical modification

Loss tangent for HSD-15-G was extremely low value about 4.1×10^{-2} . This indicates that elastic property is dominant. In other words, three dimensional network of HSD-15-G may be more highly developed than HSD-15, as shown in Fig. 5. It seems to be probable that the G' profile of HSD-15-G shows the characteristics of glass-like polymer (Fig. 6). Surprisingly, $\tan\phi$ of HSD-15-Ca was lower value than that of HSD-15. This indicates that the elastic properties of HSD-15-Ca is superior to those of HSD-15. While, the other rheological parameters of HSD-15-Ca were smaller than those of HSD-15. (Only G' profile as shown in Fig. 6). It appears that the axial ration of the protein particles may be changed by addition of calcium ion causing flocculation of protein. This consideration may be proved by the observation of scanning electron microscopical microstructure for HSD-15-Ca which will be published elsewhere.

Effect of alkali concentration

The effect of time on the dynamic viscosity (η') in the dope was not significant. Within 10 min, η' approaches the steady-states (data not shown). In the both cases of D-15 and D-15-9, the $\tan\phi$ profile of the dope shows a pronounced maximum corresponding to maximum of $J''(\omega)$. In the case of D-15-3, $\tan\phi$ increased with frequency, gradually without the maximum of $\tan\phi$. It is considered that the proteins were not fully denatured by NaOH or the preparation time of D-15-3 was insufficient. The relationship of the concentration of NaOH (C_n) between η' was hi-

ghly correlated, but the increasing extent of η' with C_n was smaller than that of the concentration of protein (Fig. 7 and 8).

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알칼리를 처리한 콩단백질 용액의 물성

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계산과 구조적으로 유사한 대두단백 섬유는 dope를 방사하여 얻은 것으로, 대두단백의 dispersion이나 dope의 성질에 의존한다. 대두단백섬유의 출발물질인 대두단백의 dispersion과 dope의 동적 물성을 측정함으로써 그들의 점탄성을 조사하였다. 단백질 농도가 증가할때 dispersion이나 dope 모두 단백질간의 상호반응이 일어났다. Dispersion에 알칼리 용액을 넣은 dope는 고분자 중합물질에 상호연결된 특성을 나타내었다. 반면에 dispersion에서는 무정형 중합물질의 특성이 나타났다. Dispersion에 대한 화학변형이 동적물성에 미치는 영향도 관찰하였다.