

## Rheological Approaches to Classify the Mixed Gel Network of $\kappa$ -Carrageenan/Agar

Seung Ju Lee\*, Young Ho Kim, and Jae-Kwan Hwang<sup>1</sup>

Department of Food Science and Technology, Dongguk University, Seoul 100-715, Korea

<sup>1</sup>Department of Biotechnology, Yonsei University, Seoul 120-749, Korea

**Abstract** The type of mixed gel network of  $\kappa$ -carrageenan/agar was determined by applying rheological principles. Apparent Young's modulus of the mixed gels was mathematically analyzed with (a) simply adding the moduli of two component gels, (b) phase-separated type's upper and lower bound models, (c) interpenetrating type's logarithmic model. The experimental data fitted the estimates from the operation (a). Whereas, as for the models (b), the experimental values in the agar-rich region fitted the estimates of the upper bound model, but in the  $\kappa$ -carrageenan-rich region slightly deviated from those of the lower bound model. It reflected an evidence of a phase-separated type, although it was not typical, that there must be data good-fit in the agar-rich and  $\kappa$ -carrageenan-rich regions with the upper and lower bound models, respectively. Experimental values disagreed with estimates of the model (c). Gel time was analyzed to evince the phase-separated type. As agar concentrations increased at a fixed amount of  $\kappa$ -carrageenan, gel time gradually decreased and then sharply increased and decreased again. The pattern of such change in gel time also represented a typical behavior of phase-separated type's mixed gels.

**Keywords:** phase-separated mixed gel,  $\kappa$ -carrageenan/agar, rheology, phase inversion

### Introduction

Mixed gels are composites, and used to modify or improve each component gel's properties. Mixed gels classified in their physical structures and chemical compositions according to combinations of component gels (1). Researches on mixed gels have been tried in a number of combinations of various component gels. In the meantime, it had been suggested that mixed gel of  $\kappa$ -carrageenan/agar might be possible to belong to phase-separated network type (2). But any related papers have not been published yet. In this research, classification of network type of carrageenan/agar mixed gel has been attempted with rheological analysis.

Mixed gels are generally composites with two components, and categorized into two types, depending on gelling function of each component. Type I gel contains one material with gelling ability and the other without gelling ability, and type II gel two materials with gelling ability. The type II gel is divided more to three kinds of interpenetrating, phase-separated, and coupled network (3). Interpenetrating type is just in blended state that component gels interact only through mutual entanglements. It is difficult to be formed in unlike biopolymers with mutual incompatibility (4, 5). Phase-separated type is the most general one that each component gel is either continuous or dispersed phase, and a number of studies have been made (6-8). Coupled type is in the state that two materials are mixed and bound with ionic and covalent bonds (9-11).

Rheological models with modulus ( $M$ ) and volume ratio ( $\phi$ ) had been applied to studies in classification of mixed gel types (2).

$$M^n = M_1^n \cdot \phi_1 + M_2^n \cdot \phi_2 \quad (1)$$

$$M = M_1 \cdot \phi_1 + M_2 \cdot \phi_2 \quad (2)$$

$$M^{-1} = M_1^{-1} \cdot \phi_1 + M_2^{-1} \cdot \phi_2 \quad (3)$$

$$\log M = \phi_1 \cdot \log M_1 + \phi_2 \cdot \log M_2 \quad (4)$$

Equation (1) is the general mixture rule of rheological properties of mixed gels, which is converted into Eq. (2) and (3) with  $n$  values of 1 and -1, respectively. Equation (2), upper bound model of phase-separated mixed gels, indicates that overall strength of the mixed gels is dominated to a great extent by strong component, for two components are connected in parallel in terms of rheological phenomenological model. Whereas Eq. (3), lower bound model, reflects that weak component controls overall strength due to two components' connection in series. Logarithmic mixture rule of Eq. (4), which is a special case of the general mixture rule, is for interlocking or interpenetrating networks in which two networks are random and the resultant gel isotropic. It also holds for a range of compositions where both phases are partly continuous and modulus changes very rapidly with composition in phase inversion that occurs for phase-separated types.

The most common type of gels, the phase-separated, could be analyzed with gel time (12, 13). Phase inversion, in which a continuous phase is converted to a dispersed phase, was observed when gel time changed drastically as concentration of the dispersed phase increased. Dynamic modulus, optical rotation, phase diagram, NMR and DSC characteristics, microstructure, etc. could also be a successful means to study the mixed gels of tree different types (12, 14, 15).

In this study, classification of  $\kappa$ -carrageenan/agar mixed gels was tried by simulating mixed gel's modulus with rheological equations and modeling with phenomenological rheological springs in a parallel or series position.

\*Corresponding author: Tel: 82-2-2260-3372; Fax: 82-2-2260-3372

E-mail: Lseungju@dongguk.edu

Received May 24, 2005; accepted January 2, 2007

**Materials and Methods**

**Materials**  $\kappa$ -Carrageenan (with added 3% w/w, KCl, MSC Inc., Korea) and agar (first grade, MSC Inc., Korea) were used. The mixtures were prepared by mixing at the ratios of  $\kappa$ -carrageenan to agar of 100:0, 80:20, 60:40, 40:20, 20:80, and 0:100, respectively.

**Apparent Young's modulus** The samples were prepared as single component gels and mixed gels. For single gels, each of  $\kappa$ -carrageenan and agar was dispersed with 100 mL distilled water at the concentrations of 0.4, 0.8, 1.2, 1.6, and 2.0%(w/w) in 100 mL beaker. For mixed gels, solid concentration of the mixtures was fixed at 2.0%. The solution was heated at 95°C for 40 min with a magnetic stirrer. Then it was cooled at 25°C for 3 hr, and formed to a gel. The beaker including sample was placed on the platform of texture analyzer (TA-XT2; Stable Micro Systems Ltd., Surrey, UK) and subjected to compression test with a flat-ended cylindrical probe (diameter 27 mm). Plot of force vs. deformation gave a slope of curve. The slope of curve was assumed as an apparent Young's modulus (force/length) which is different from a general Young's modulus (stress/strain). In a preliminary test, apparent Young's moduli of most samples remained constant until the compression speeds reached 1 mm/sec, then the moduli changed irregularly with increase in the speeds. Finally, 1 mm/sec was employed as test speed. The tests were repeated ten times on each sample.

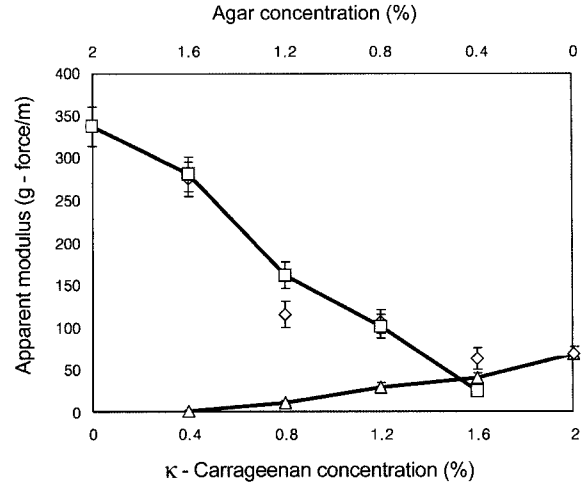
**Gel time**  $\kappa$ -Carrageenan 0.5%(w/w) and agar 0, 0.2, 0.3, 0.5, 1.0, and 1.5% were dispersed with 10 mL distilled water in 15 mL cylindrical vials (diameter 23 mm). A fixed weight (10 g) of solution was put in a series of vials. The solution was heated on a magnetic stirrer at 95°C for 40 min. The samples were quenched from 90°C to 5, 10, and 20°C, respectively, and maintained to within 0.1°C in a thermostated water bath. The vials were then inverted sequentially and the time required to form a gel strong enough to remain held was measured (12).

**Results and Discussion**

**Modulus** Apparent Young's modulus of single and mixed gels with the same amount of solid contents is shown in Fig. 1. The mixed gel modulus at the region of excess agar approaches that of the stronger single gel, agar, whereas the modulus at the excess  $\kappa$ -carrageenan seemed to be sum of those of two component gels. Equation (2) was modified into Eq. (5) by substituting the products ( $M \cdot \phi$ ) of single gel modulus of 2%(w/w) solid concentration and volume ratios with single gel modulus ( $G$ ) of the same solid concentration as the corresponding component in mixed gels.

$$M = G_1 + G_2 \tag{5}$$

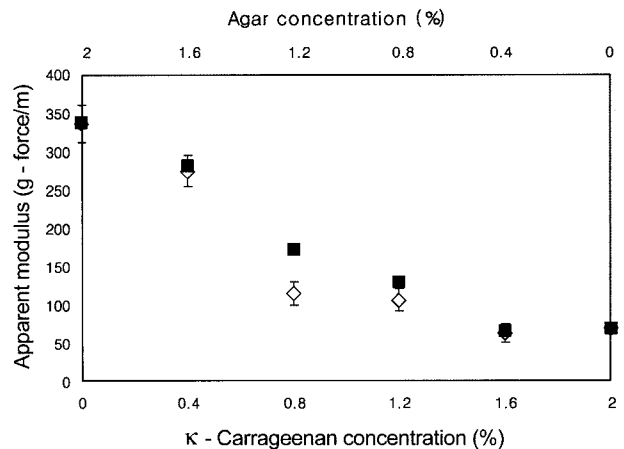
Figure 2 shows the experimental data of the modulus fit the calculated values, but there are a little differences in the mid range of the  $\kappa$ -carrageenan/agar ratios. It indicates that the mixed gels with excess amount of either of components have a structure where two gels are connected



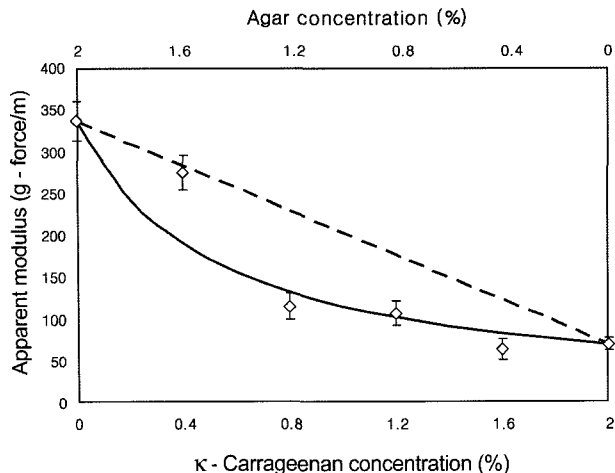
**Fig. 1. Apparent Young's modulus of single and mixed gels of  $\kappa$ -carrageenan/agar with varying concentrations.**  $\square$ , agar;  $\triangle$ ,  $\kappa$ -carrageenan;  $\diamond$ , mixed gel. Bars indicate standard deviations.

in parallel. In the mid ratios of two components, on the other hand, the modulus of the mixed gels was smaller than the sum of those of each component, of which characteristics are closer to in-series connected gels. The mixed gels connected in series have no continuous phase but two dispersed phases (2).

Mathematical analysis was tried with applications of Eq. (2) and (3) to calculate modulus of mixed gels according to concentrations of each component. Volumetric ratios in the equations were regarded as the same as mass ratios, though mass ratios would be correctly converted to volume ratios by considering densities. It was assumed that densities of each component are the same, because a mathematical modelling generally accompany simplification of any relevant conditions. Furthermore, to measure densities of each component in the mixture is practically almost impossible. In the phase-separated type, mixed gel strength with more strong component is close to the sum



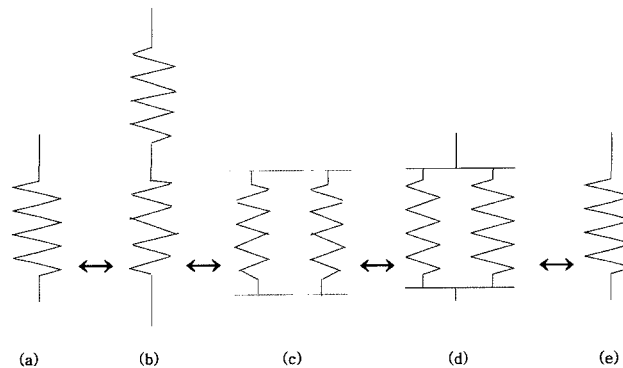
**Fig. 2. Comparison in apparent Young's modulus of  $\kappa$ -carrageenan/agar mixed gels between the estimates from the modified upper bound model of Eq. (5) and experimental values.**  $\blacksquare$ , estimates;  $\diamond$ , experimental values.



**Fig. 3.** Comparison in apparent Young's modulus of  $\kappa$ -carrageenan/agar mixed gels between the estimates from the upper and lower bound models of Eq. (2) ( $M = 336 \cdot (1-\phi) + 69 \cdot \phi$ ; where  $M$ , modulus;  $\phi$ ,  $\kappa$ -carrageenan conc. (%) divided by 2) and Eq. (3) ( $1/M = (1-\phi)/336 + \phi/69$ ), and experimental values. --, upper bound; —, lower bound;  $\diamond$ , experimental values.

of two component strength, and gel strength with more weak component is governed by that of the weak component (2). So, the mixed gels rich in strong component belong to upper bound model Eq. (2), weak component-rich gels to lower bound model Eq. (3), and mixed gels with mid levels of each component to between the lower and upper bound models. Figure 3 represents the curves from calculation of modulus with Eq. (2) and (3) for phase-separated type with two components connected in parallel and series, respectively. In the range of low  $\kappa$ -carrageenan/agar ratios, the calculated values of the upper bound model fit the experimental, whereas in the other range they were higher than the experimental. The upper bound model describes the gel network in parallel connection (1). Meanwhile, the experimental data in the range of high and mid  $\kappa$ -carrageenan/agar ratios approximated the estimates of the lower bound model. The lower bound model represents a network structure in serial connection of two components. Finally, such shift in modulus across the upper and lower bound models is a phase inversion, indicating a gel network conversion. This pattern of curves had been found in the typical phase-separated network mixed gels (3).

**Structural diagram** In comparison between Fig. 2 and 3, a modified upper bound model, Eq. (5), showed better fitness than the upper and lower bound models for phase-separated type. In order to validate this discrepancy, phase inversion mechanism was analyzed with rheological phenomenological models as shown in Fig. 4 and 5. Figure 4 illustrates typical phase inversion process that the configuration shifts from spring elements connected in series to parallel as strong component in mixed gel increases. Contrarily, Fig. 5 was proposed in this study as a new mechanism. There is a difference between the existing and proposed mechanisms for phase inversion. In the former mechanism, the modulus of the weak gel-rich

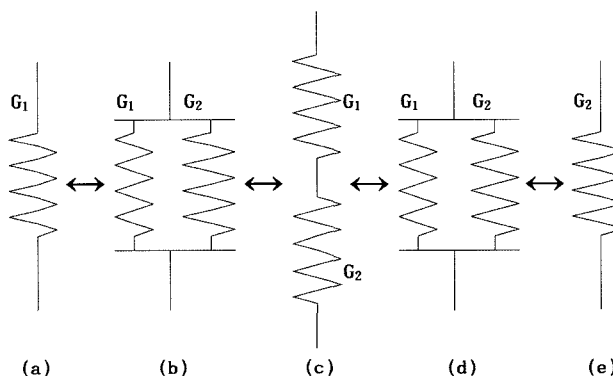


**Fig. 4.** Structural diagram of the phase inversion processes with spring elements connected in parallel or series. (a), Single gel of weaker component; (b), mixed gel; (c), transient region of phase inversion; (d), mixed gel; (e), single gel of stronger component.

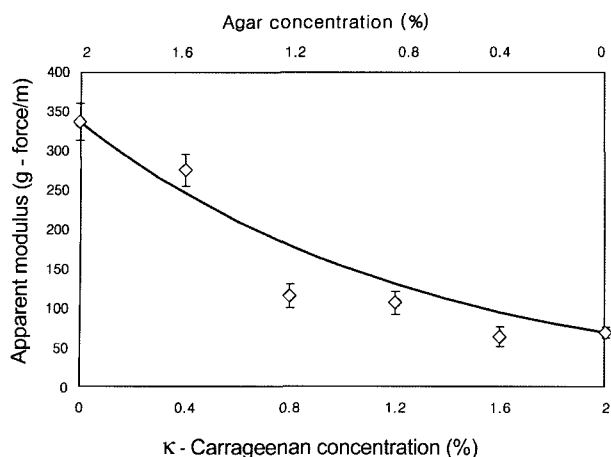
mixed gels was estimated in different way from the strong gel-rich ones, but in the same way in the latter mechanism. The proposed mechanism is based on the assumption given in Eq. (5) that two components in the mixed gels are connected in parallel in the whole range of mixed ratios except for the phase inversion point. The proposed mechanism, of course, might not be true to the different kinds of mixed gel. There is, however, common fact that both Eq. (5) and Eq. (2) & (3) stem from the phase inversion which occur only in the phase-separated type, and the proposed mechanism may be worth a modification of the existing one.

Figure 6 shows comparison in modulus between estimates from Eq. (4) of interpenetrating type and experimental data. The curve of the estimates roughly fitted the experimental data. From a rheological point of view, so, it was concluded that the  $\kappa$ -carrageenan/agar was a little far from interpenetrating type of mixed gels.

**Gel time** Gel times at 5, 10, and 20°C are shown in Fig. 7. Gel time decreased with increase in agar concentrations, and there was a sudden rise around 1.0% agar, followed by a rapid fall at 1.5% agar. Decrease in the amount of the



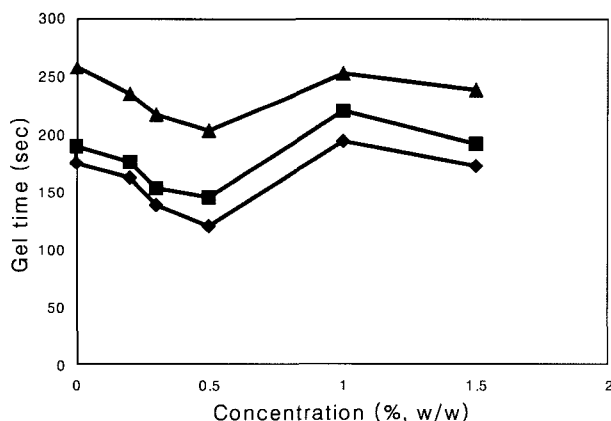
**Fig. 5.** Newly proposed structural diagram of the phase inversion processes with spring elements connected in parallel or series. (a), Single gel of weaker component; (b), mixed gel; (c), transient region of phase inversion; (d), mixed gel; (e), single gel of stronger component.



**Fig. 6.** Comparison in apparent Young's modulus of  $\kappa$ -carrageenan/agar mixed gels between the estimates from the logarithmic model of Eq. (4) ( $\log M = (1-\phi)\cdot\log 336 + \phi\cdot\log 69$ ; where  $M$ , modulus;  $\phi$ ,  $\kappa$ -carrageenan conc. (%) divided by 2) and experimental values. —, estimates;  $\diamond$ , experimental values.

continuous phase,  $\kappa$ -carrageenan, reduced the time required to make self-supporting gel, and at a phase inversion point, the continuous phase changes from  $\kappa$ -carrageenan to agar, resulting in sudden change in gel time. Such phase inversion had been reported for gelatin/dextran (16), gelatin/maltodextrin (DE 10-13) (17), gelatin/matodextrin (12), etc. The discontinuity in gel time, phase inversion, is basically due to thermodynamic incompatibility between two component gels (18).

Finally, it was concluded that the  $\kappa$ -carrageenan/agar mixed gel is classified as a phase-separated type. A modified mechanism of phase inversion was proposed to describe the change in modulus of mixed gels with different ratios of two components. Rheological phenomenological models in series or parallel position were applied in the proposed mechanism, and the estimates from the models agreed with the experimental data. Besides, sudden change in gel time with concentrations of agar corresponded



**Fig. 7.** Variation in gel time with increasing concentration of agar in mixed solutions with 0.5% (w/w)  $\kappa$ -carrageenan at 5, 10, and 20°C, respectively. ▲, 20°C; ■, 10°C; ◆, 5°C.

to phase inversion and therefore confirmed that the mixed gel is classified as a phase-separated type.

## Acknowledgments

This work was supported by the National Research Lab program through the Functional Biopolymer Lab at Yonsei University (2000-N-NL-01-C-299).

## References

- Nielsen LE, Landel RF. Mechanical Properties of Polymers and Composites. Marcel Dekker, Inc., New York, NY, USA. pp. 392-397, 502-503 (1994)
- Brown CRT, Foster TJ, Norton IT, Underdown J. Influence of shear on the microstructure of mixed biopolymer systems. pp. 65-83 In: Biopolymer Mixtures. Harding SE, Hill SE, Mitchell JR (eds). Nottingham University Press, Nottingham, UK (1995)
- Morris VJ. Multicomponent gels. pp. 87-99. In: Gums and Stabilizer for the Food Industry, 3<sup>rd</sup> ed. Phillips GO, Wedlock DJ, Williams PA (eds). Elsevier, London, UK (1986)
- Amici E, Clark AH, Normand V, Johnson NB. Interpenetrating network formation in agarose-sodium gellan gel composites. Carbohydr. Polym. 46: 383-391 (2001)
- Rogovina LZ. Approaches to multicomponent systems of biopolymers. Food Hydrocolloid 12: 325-331 (1998)
- Haug IJ, Draget KI, Smidsrod O. Physical behavior of fish gelatin- $\kappa$ -carrageenan mixtures. Carbohydr. Polym. 56: 11-19 (2004)
- Haug IJ, Williams MAK, Lundin L, Smidsrod O, Draget KI. Molecular interactions in, and rheological properties of, a mixed biopolymer system undergoing order/disorder transitions. Food Hydrocolloid 17: 439-444 (2003)
- Ould Eleya MM, Turgeon SL. Rheology of  $\kappa$ -carrageenan and -lactoglobulin mixed gels. Food Hydrocolloid 14: 29-40 (2000)
- Turgeon SL, Beaulieu M. Improvement and modification of whey protein gel texture using polysaccharides. Food Hydrocolloid 15: 583-591 (2001)
- Stainsby G. Proteinaceous gelling systems and their complexes with polysaccharides. Food Chem. 6: 3-14 (1980)
- Kavanagh GM, Clark AH, Gosal WS, Ross-Murphy SB. Heat-induced gelation of beta-lactoglobulin/alpha-lactalbumin blends at pH 3 and pH 7. Macromolecules 33: 7029-7037 (2000)
- Kasapis S, Morris ER. Phase equilibria and gelation in gelatin/maltodextrin systems-Part II. Polymer incompatibility in solution. Carbohydr. Polym. 21: 249-259 (1993)
- Kasapis S, Morris ER. Phase equilibria and gelation in gelatin/maltodextrin systems-Part III. Phase separation in mixed gels. Carbohydr. Polym. 21: 261-268 (1993)
- Donald AM, Durrani CM, Jones RAL, Rennie AR, Tromp RH. Physical methods to study phase separation in protein-polysaccharide mixtures. pp. 99-116 In: Biopolymer Mixtures. Harding SE, Hill SE, Mitchell JR (eds). Nottingham University Press, Nottingham, UK (1995)
- Williams MAK, Keenan RD, Halstead TK. The use of NMR in characterizing biopolymer mixtures. pp. 117-142 In: Biopolymer Mixtures. Harding SE, Hill SE, Mitchell JR (eds). Nottingham University Press, Nottingham, UK (1995)
- Tolstoguzov VB. Functional properties of protein-polysaccharide mixtures. pp. 385-415. In: Functional Properties of Food Macromolecules. Mitchell JR, Ledward DA (eds). Elsevier, London, UK (1986)
- Marrs WM. Gelatin/carbohydrate interactions and their effect on the structure and texture of confectionery gels. Prog. Food Nutr. Sci. 6: 259-268 (1982)
- Kasapis S. Phase separation in hydrocolloid gels. pp. 193-224. In: Biopolymer Mixtures. Harding SE, Hill SE, Mitchell JR (eds). Nottingham University Press, Nottingham, UK (1995)