

## Syneresis and Texture Stability of Hydrogel Complexes Containing Konjac Flour over Multiple Freeze-thaw Cycles

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**Abstract:** Hydrogel complexes formed by a 1% mixture of konjac flour and secondary gums ( $\kappa$ -carrageenan or xanthan) at different ratios between 70:30 and 30:70 were investigated for syneresis and texture stability under multiple freeze-thaw cycles. Increasing of freeze-thaw cycles caused the syneresis generated by all konjac/ $\kappa$ -carrageenan gels significantly increased ( $p < 0.05$ ) while their peak force values decreased ( $p < 0.05$ ). As compared with the gels freshly prepared, significant differences ( $p < 0.05$ ) in syneresis and peak force values were found in all konjac/ $\kappa$ -carrageenan gels after the first freeze-thaw cycle, in exception of the konjac/ $\kappa$ -carrageenan (50:50) gel that showed the most stable gel texture until the end of the second cycle. Konjac/xanthan gels ranged from 70:30 to 50:50 demonstrated increasing syneresis but decreasing peak force values with increasing freeze-thaw cycles. Whilst, no syneresis were found ( $p > 0.05$ ) in the gels formed by konjac/xanthan blends at 40:60 and 30:70, which also maintained their gel texture over the fourth freeze-thaw cycle.

[Akesowan A. **Syneresis and Texture Stability of Hydrogel Complexes Containing Konjac Flour over Multiple Freeze-thaw Cycles.** *Life Sci J* 2012;9(3):1363-1367] (ISSN:1097-8135). <http://www.lifesciencesite.com>. 197

**Keywords:** Konjac flour, freeze-thaw stability, hydrogel, syneresis, texture characteristic

### 1. Introduction

In the food production, hydrocolloids or gums have special importance and wide variety of applications. They are contributed to the thickening and stabilizing effects, texture modification, control of moisture and water mobility and improvement of overall product quality (Sae-kang and Suphantharika, 2006; Šubarić et al., 2011). It is therefore to apply in many food products such as bakery, meat, confectionery, jam and jelly. The storage condition and gel stability are considered as key factors affecting food product quality and perception. Frozen food products, which their characteristics are sensitive to the temperature fluctuation, are of considered as a challenge for food manufacturers. Ice crystals within the food matrix which formed during freezing cause physical stress and damage to food; consequently, loss of moisture and changes in textural characteristics often occur upon thawing, resulting in reduction of product quality and consumer acceptance (Williams et al., 2009).

Konjac flour, prepared from the tuber of *Amorphophallus konjac*, is a high molecular weight polysaccharide consisting of mannose and glucose in a ratio of 3:2 with  $\beta$ 1, 4-linkage. It has a strong water-binding ability and forms a gel by deacetylation in mild alkali solution or combining with other secondary gums (e.g. carrageenan, gellan and xanthan) (Thomas, 1997; Takigami, 2000). This unique gelling mechanism could be used to increase

retention or absorption of moisture and other ingredients of which products it is applied. The consistency of konjac hydrogel complexes that provides texture stability will enhance the quality of frozen food products (Chin et al., 2009). In addition, for low-fat meat processing, konjac gel can be used as a fat analogue that is an alternative for animal fat replacement (Akesowan, 2008; Jiménez-Colmenero et al., 2012). The stability of konjac gel would be the informative data required to develop or improve the quality of food products, especially gel-based products when they are stored at specific conditions such as chilled, frozen and freeze-thaw storages.

To better understand the characteristics of konjac hydrogel complexes under multiple freeze-thaw cycles, this work was aimed to investigate the syneresis and texture stability of the gels formed by a 1% mixture of konjac and secondary gums ( $\kappa$ -carrageenan or xanthan) varying from 70:30 to 30:70 under discrete temperature fluctuation. Four freeze-thaw cycles were studied to imitate the product distribution from the processing plant to retail until to consumer.

### 2. Material and Methods

#### Materials

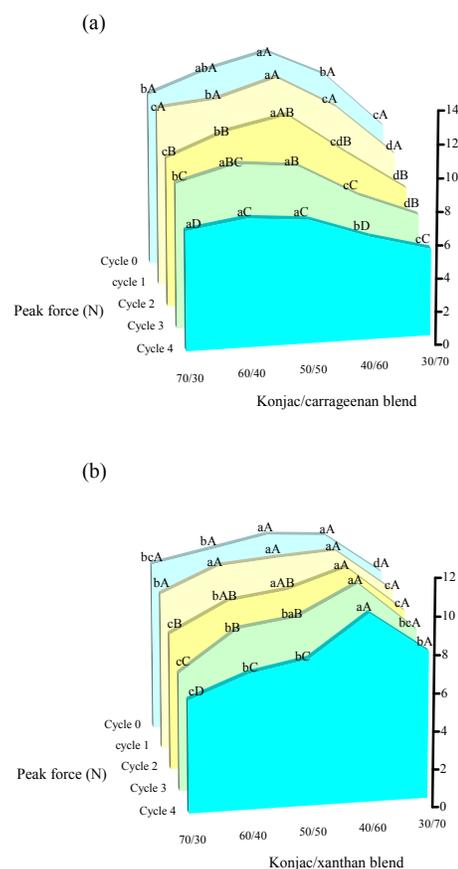
Hydrocolloids used were konjac flour (Chengdu Newstar Chengming Bio-Tech Co., Ltd, China),  $\kappa$ -carrageenan (MSC5744, MSC Ltd., USA)



were optimal for syneresis resistance. It was evident that the various ratios between konjac and  $\kappa$ -carrageenan from 70:30 to 30:70 significantly ( $p < 0.05$ ) influenced on syneresis of the mixed gum gels in different manners depending on the proportion of  $\kappa$ -carrageenan combined in the blend and a number of freeze-thaw cycles. When the  $\kappa$ -carrageenan proportion was higher than that of konjac, the more “excess” proportion of  $\kappa$ -carrageenan chains can form double helix structure and crystalline junction zones alone, causing thermoreversible and brittle gels upon cooling. In general, much syneresis is one of disadvantage characteristics of the  $\kappa$ -carrageenan gel (Whistler and BeMiller, 1993); consequently, partial part of separated water would be come from carrageenan gels. This is the reason why higher proportion of  $\kappa$ -carrageenan than konjac flour in a blend produced a hydrogel with more syneresis. In this work, the lowest syneresis was observed in the 1% konjac/ $\kappa$ -carrageenan (50:50) gel until the third freeze-thaw cycle was over. Although abundant hydroxyl groups in konjac facilitated the formation of hydrogen bonding with  $\kappa$ -carrageenan and led to good miscibility (Shen et al., 2009), the three-dimensional networks of mixed gums are limited by interactive sites of both polymers. Under this condition, the networks will imbibe water due to the osmotic driving forces of the network chains and also the additional water is assumed to fill the space between the network chains and/or the center of larger pores, macropores or voids. If much more konjac proportion in a blend such as the konjac/ $\kappa$ -carrageenan blends at 60:40 and 70:30, the excess konjac molecules can undergo self association and hinder the interactions of the gums, resulting in incomplete strong cohesive gels that produced more syneresis. The ability of the hydrogel complexes to hold water is dependent on the conformation of konjac flour and  $\kappa$ -carrageenan in the system, which relates to gel formation via intramolecular and intermolecular hydrogen bonding (Takigami, 2000).

The strong initial water-holding capacity of konjac/ $\kappa$ -carrageenan gel was occurred after processing because the heating (up to 90°C) involving in the hydrogel formation promoted the chemical interaction between konjac flour and  $\kappa$ -carrageenan. After the first freeze-thaw cycle, apparent syneresis averaging 1.45, 3.41 and 3.65% were detected in the konjac hydrogel complexes formed with  $\kappa$ -carrageenan in ratio of 50:50, 60:40 and 70:30, respectively (Figure 1a). When the freeze-thaw cycle was repeated twice, the formation of ice crystals within the gel texture was occurred again, causing physical stress to the gels and upon thawing

the melting of these ice crystals led to moisture loss. The loss of water after freeze-thaw cycles reflects the instability of the intra- and intermolecular bonding, which may be due to prolong mechanical treatment weakening a gel network of konjac hydrogel complexes formed with  $\kappa$ -carrageenan. The finding implies that the optimum level of konjac addition can improve water holding capacity and reduce the degree of syneresis of  $\kappa$ -carrageenan in a mixed gum gel. However, non-significantly ( $p > 0.05$ ) highest syneresis were determined in all konjac hydrogel complexes with any combinations which kept until completing the fourth cycle.



**Figure 2.** Texture stability of hydrogel complexes under multiple freeze-thaw cycles: (a) konjac/carrageenan blend and (b) konjac/xanthan blend.

The results of texture stability of konjac/ $\kappa$ -carrageenan gels at different levels from 70:30 to 30:70, represented by the peak force are shown in Figure 2a. After gel preparation or zero freeze-thaw cycle, the lowest peak force was observed in the hydrogel prepared with a konjac/ $\kappa$ -carrageenan

(30:70) blend; moreover, peak force was increased with decreasing  $\kappa$ -carrageenan proportion from 70 to 50% in the gum combination. The highest peak force values were significantly found ( $p < 0.05$ ) in hydrogel complexes prepared with konjac/ $\kappa$ -carrageenan blends at 50:50 and 60:40; nevertheless, the gel at 70:30 tended to decrease in peak force. This finding implies a relationship between a konjac/ $\kappa$ -carrageenan ratio and the gel texture, namely the higher proportion of  $\kappa$ -carrageenan than konjac produced a hydrogel with more brittle texture, which was easier to break down. Whilst, at much more konjac proportion used, the greater influence by high konjac chains might have hindered the interaction between konjac and  $\kappa$ -carrageenan, consequently producing a soft and tender gel with decreasing peak force.

At the end of the first freeze-thaw cycle, all konjac/ $\kappa$ -carrageenan gels significantly decreased ( $p < 0.05$ ) in peak force values, in exception of the konjac/ $\kappa$ -carrageenan (50:50) gel which maintained the peak force ( $p < 0.05$ ) until the end of the second cycle. The decrease in peak force with increasing freeze-thaw cycles suggests the inability of the gel system to withstand temperature fluctuation. This is possibly due to water expands when freezing to form ice crystals, consequently gel network in hydrogel complexes are ruptured, resulting in decreasing of gel strength. As the fourth cycle was over, the gel structure would be extremely damaged. Similar result was confirmed by Williams et al. (2009) who showed that the gel strength of curdlan (galactomannan)/ $\kappa$ -carrageenan was continuously declined after each freeze-thaw cycle and completely destroyed at the end of the fifth freeze-thaw cycle.

#### Freeze-thaw stability of the konjac/xanthan gel

Unlike the konjac/ $\kappa$ -carrageenan gel, the use of xanthan as a secondary gum for konjac gel forming resulted in an elastic gel with good syneresis resistance; however, this effect varied with the proportion of xanthan in a mixed gum combination. In case of 1% konjac hydrogel complexes formed with xanthan, konjac/xanthan blend at 70:30 and 60:40 showed significant ( $p < 0.05$ ) increases in syneresis with increasing freeze-thaw process (Figure 1b). The increased syneresis suggests the increment of molecular association between konjac and xanthan, resulting in the release of water from the gel structure. On the contrary, the gels produced by konjac/xanthan blend at 40:60 and 30:70 demonstrated no syneresis (separated water) throughout 4 freeze-thaw cycles, while the syneresis was detected in a konjac/xanthan (50:50) gel after the fourth freeze-thaw cycle. No syneresis means that a

hydrogel complex has strong and stable water-holding capacity, which is important for food application. The result also showed that hydrogel complexes containing a lower proportion of xanthan than konjac demonstrated a higher syneresis. Xanthan gum is an anionic linear hydrocolloid with a (1 $\rightarrow$ 4) linked  $\beta$ -D-glucose backbone and has a large side unit on every other glucose unit at location C-3 (Sworn, 2000; Williams et al., 2009). The highly substituted nature of this gum allows for excellent hydration and hydrogen bonding activity with any polysaccharides (Argin-Soysal et al., 2009). Consequently, each gum concentration contained in a mixed gum blend is responsible for a hydrogel characteristic.

As compared with the result of konjac/ $\kappa$ -carrageenan gel, the higher syneresis was observed for the konjac/ $\kappa$ -carrageenan gel than konjac/xanthan gel, could be partly due to the soft texture of the konjac/xanthan gel which provided less resistance to the deformation caused by centrifugation (Sae-kang and Suphantharika, 2006). It is well recognized that the extent of syneresis measured by the centrifugation method is dependent upon rigidity and elasticity as well as extent of phase separation (Yuan and Thompson, 1998). It is therefore a reason why a higher proportion of xanthan incorporated in the konjac hydrogel complexes resulted in the zero syneresis or such strong synergistic effects between konjac and xanthan via some other specific interactions, besides Van der Waals forces (Liang et al., 2011).

The results for texture stability of konjac/xanthan gels shown in Figure 2b reveal that peak force values of hydrogels formed by a combination of konjac and xanthan at 30:70 and 40:60, respectively were consistent over the fourth freeze-thaw cycle. This suggests that these two gels were stable than other treatments. The decreases in peak force values of konjac/xanthan gels at ratio of 50:50, 60:40 and 70:30, respectively were dependent on increasing freeze-thaw cycles. It can be seen that, when a lower proportion of xanthan than konjac was applied, the texture of konjac/xanthan gel at 50:50 and 60:40 were significantly stable after the end of the second freeze-thaw cycle; nevertheless, the konjac/xanthan (70:30) gel tended to lose its gel texture faster than did other mixed gum gels. This was in consonance with the observation recorded for syneresis results in which this gel showed the highest syneresis.

#### Conclusion:

The variation in the proportion of konjac and secondary gums affected freeze-thaw stability and texture characteristics of hydrogel complexes. The

konjac/carrageenan (50:50) gels was observed for the best stability up to 2 freeze-thaw cycles whereas the gels containing konjac and xanthan ranged from 30:70 to 40:60 showed their stability throughout 4 freeze-thaw cycles. The storage stability of konjac/secondary gum gels as affected by sucrose and sodium chloride under chilling and/or freezing conditions is proposed to the further investigation.

#### Acknowledgements:

The author would like to thank the University of the Thai Chamber of Commerce for the financial support.

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7/16/2012