

## **Pectin-based superabsorbent hydrogels crosslinked by some chemicals: synthesis and characterization**

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### **Summary**

Synthesis of superabsorbent hydrogels from pectin was investigated using three kinds of crosslinkers,  $\text{CaCl}_2$ , ethylene glycol diglycidyl ether (EGE), and glutaraldehyde (GA). Among them, GA was the most suitable to attain high absorbency, reaching ca. 500 g/g in pure water. On the contrary, hydrogels crosslinked by  $\text{CaCl}_2$  and EGE absorbed much less water, their maximum absorbency was around 200 g/g and 40 g/g, respectively. Absorbency in 0.9% NaCl solution of hydrogel crosslinked by GA was as low as 15 g/g, which indicates absorbency of hydrogels in the present study is sensitive to salt concentration. Biodegradability of pectin-based hydrogels in activated sludge at 25°C for 18 days was 60-65%.

### **Introduction**

Superabsorbent hydrogels are loosely crosslinked water-soluble polymers, which can absorb large amount of water, saline solution, or physiological fluids [1,2]. Most of commercially available superabsorbent hydrogels are crosslinked sodium polyacrylates, and they have no biodegradability. Since the major applications of superabsorbent hydrogels are in disposable goods, their use may result in environmental pollution. Therefore, research on biodegradable superabsorbent hydrogels based on poly(amino acids) [3-7] and carboxymethylcellulose [8-10] as a substitute for synthetic polymers has been reported.

While concern is increasing in the environmental problem today, various naturally occurring polymers should be utilized instead of synthetic ones. Among them, pectin is one of candidates because it exists in fruits abundantly. Commercial pectin is obtained as an extract either from citrus peel or from apple pomace, which are by-products of juice manufacturing [11]. Since pectin is naturally occurring polysaccharide and has carboxylic group, it is expected that it can be used as a substitute for acrylic acid polymers, without environmental problems. Though pectin is well known as gelling agent in food industry, only a few studies on the pectin-based superabsorbent hydrogels are reported so far [12,13].

In the present study, synthesis of pectin-based superabsorbent hydrogels has been carried out by use of three kinds of crosslinker, and their absorption properties have been investigated. Further, biodegradability of the hydrogels was evaluated to confirm the influence of crosslinking.

## Experimental

### *Materials*

Pectin (from citrus fruits, galacturonic acid content 93.5%, methoxy content 9.4%, Sigma-Aldrich),  $\text{CaCl}_2$  (anhydrous), ethylene glycol diglycidyl ether (EGE), and glutaraldehyde (25% aqueous solution, GA) were commercially available and used without purification. Cellulose (powder, 20 $\mu\text{m}$ , Aldrich) for standard material of biodegradability test was purchased and used as received.

### *Preparation of hydrogels crosslinked by $\text{CaCl}_2$*

Pectin (0.5 g, 2.8 mmol for galacturonic unit) was added to water (3.0 g) and stirred to obtain a colorless semi-transparent solution. To this solution, aqueous solution of  $\text{CaCl}_2$  (conc. 1%) was added dropwise under vigorous stirring. The feed amounts of  $\text{CaCl}_2$  were 1, 5, 10 and 20 mol% for galacturonic unit of pectin. The mixture was stored at room temperature for 24 h, and aqueous solution of NaOH (conc. 10%, 1.1 g, equimolar for galacturonic unit of pectin) was added to this mixture. Then 10 mL of methanol was added to precipitate the product. After stored overnight, the precipitate was filtered and dried under reduced pressure. The white solid was finely cut with mixer and screened through a 16-mesh sieve to give off-white granule product.

### *Preparation of hydrogels crosslinked by EGE*

Pectin (0.5 g) was added to water (3.0 g) and stirred. To this solution, EGE (neat; 10, 20, 40, and 100 mol% for galacturonic unit of pectin) and pyridine (equimolar of epoxy group of EGE) was added and vigorously stirred. The mixture was heated at 50°C for 24 h, and after cooling to room temperature, aqueous solution of NaOH (conc. 10%, 1.1 g) was added to this mixture. Then 10 mL of methanol was added to the mixture. After stored overnight, the precipitate was filtered and dried under reduced pressure. The white solid was finely cut with mixer and screened through a 16-mesh sieve to give off-white granule product.

### *Preparation of hydrogels crosslinked by GA*

Pectin (0.5 g) was added to water (3.0 g) and stirred. To this solution, GA (25% aqueous solution; 10, 20, 40, and 100 mol% for galacturonic unit of pectin) and 2 drops of HCl (0.35% aqueous solution) was added, and vigorously stirred to homogenize it. The mixture was heated at 50°C for 24 h, and aqueous NaOH solution (conc. 10%, 1.1 g) was added to this mixture. Then 10 mL of methanol was added to the mixture. After stored overnight, the precipitate was filtered and dried under reduced pressure. The white solid was finely cut with mixer and screened through a 16-mesh sieve to give off-white granule product.

### *Measurements*

Intrinsic viscosity ( $[\eta]$ ) of pectin in 0.5% NaCl solution at 30°C was measured by using Ubbelode-type viscometer.

Water absorbency of the product was measured by the tea-bag method with the reference to Japanese Industrial Standard, JIS K 7223. Nylon tea-bag whose length and width were 200 mm and 100 mm, respectively, was prepared by heat sealing, and

the superabsorbent sample (0.2 g) was charged in it. The tea-bag was immersed in deionized water at 25°C. After 3 h immersion, the tea-bag was picked up from the water, and excess water was drained for 5 min. The weight of tea-bag and hydrogel was then measured ( $W_t$ ), and absorbency was calculated according to the following equation;

$$\text{Absorbency} = (W_t - W_b - W_p) / W_p \quad (1)$$

where  $W_b$  is the weight of blank tea-bag after water treatment, and  $W_p$  is the weight of dry superabsorbent sample. Again, the tea-bag was dipped for 21 h, and picked up for 5 min to evaluate absorbency (total treatment time: 24 h). Absorbency after 48 h, 72 h, and 96 h was estimated in the same way. Further, absorbency in aqueous NaCl solution (concentration: 0.9 wt%) was evaluated similarly.

Biodegradability of the product hydrogel was estimated according to the method with the reference to JIS K 6950 in which the sample was placed in activated sludge at 25°C. The activated sludge was kindly supplied from Tatara-gawa sewage-treatment plant (Fukuoka, Japan), and used as received. The biodegradability was evaluated by monitoring the biological oxygen demand (BOD) using an OM3001 coulometer of Ohkura Electric Co.Ltd., Japan.

## Results and discussion

### *Preparation of superabsorbent hydrogels*

To estimate the molecular weight of pectin in the present study, viscosity measurement in 0.5% NaCl solution at 30°C was carried out. The  $[\eta]$  value was 380 mL/g, which indicates the high molecular weight of pectin. This result supports the idea that pectin is a suitable starting material of superabsorbent hydrogels, because high molecular weight of the polymer composing hydrogels is one of the indispensable factors to attain high water absorbency [1,2].

Various kinds of crosslinking reagents (isocyanates, epoxides, amines, acid unhydrides, etc) are known to date. Most of them, however, are soluble only in organic solvents. Moreover, many of them are sensitive to moisture and difficult to handle in aqueous condition. On the other hand, pectin is only soluble in water. Thus crosslinker suitable for pectin is limited. In the present study, three kinds of crosslinker ( $\text{CaCl}_2$ , EGE, GA) were employed because they are both soluble and stable in water. Among them, it is well known that divalent cations such as  $\text{Ca}^{2+}$  can induce gelation of pectin [11].

When  $\text{CaCl}_2$  is introduced into a solution of pectin, gel formed immediately. The structure of crosslinking is explained by so-called "egg-box" model [11], based upon the linkage conformations of the galacturonic residues.

As is other epoxy compounds, the epoxide group of EGE will react with carboxyl group to form ester group. In the present study, apparent gel formation was not observed, which indicates the formation of crosslinking is rather restricted.

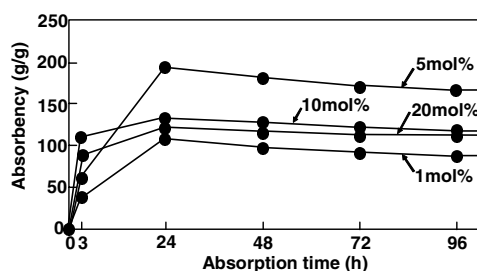
In the case of GA, apparent gel formation was observed during the crosslinking process, which indicates the reaction of GA proceeded more preferably than that of EGE.

Overall yields of the crosslinked product were 92-88% for those crosslinked by  $\text{CaCl}_2$ , 88-70% for those crosslinked by EGE, and 94-82% for those crosslinked by GA, respectively. In general, the more the feed amount of the crosslinker was, the lower

the yield was. These results indicate all the crosslinker in feed did not react, and the amount of unreacted crosslinker increased as the feed amount of crosslinker increased. Among them, yields of those crosslinked by EGE were lower than those crosslinked by  $\text{CaCl}_2$  or GA, which indicates the crosslinking reaction of EGE proceeded less efficiently than those of others.

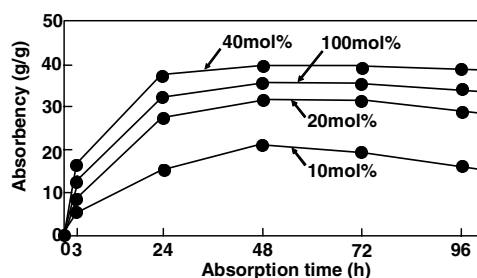
#### Water absorbency

Figure 1 shows time dependence of absorbency in pure water of hydrogels derived from pectin by changing the  $\text{CaCl}_2$  feed amount. Absorbency increased in early period of time and slightly decreased after 24 h treatment. As the feed amount of  $\text{CaCl}_2$  increased from 1 mol% to 5 mol%, absorbency also increased. On the other hand, as the feed amount of  $\text{CaCl}_2$  increased from 5 mol% to 20 mol%, absorbency inversely decreased. Consequently, 5 mol% was the optimal feed amount to attain high absorbency, reaching ca. 200 g/g after 24 h treatment.



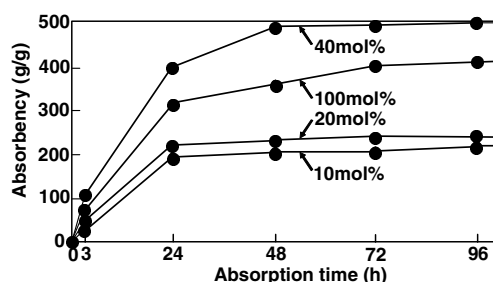
**Figure 1.** Absorbency of pectin-based hydrogels crosslinked by  $\text{CaCl}_2$ .

In the case of EGE as a crosslinker, feed amount of 40 mol% induced the highest water absorbency among those examined, but absorbency was totally low (maximum ca. 40 g/g), as shown in Figure 2.



**Figure 2.** Absorbency of pectin-based hydrogels crosslinked by EGE.

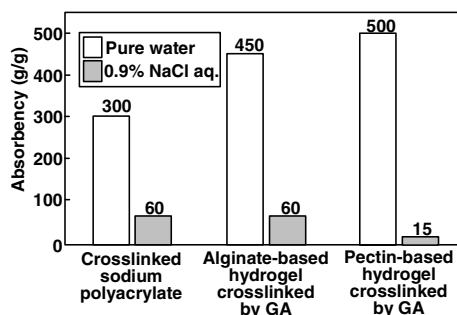
When GA was employed as a crosslinker, water absorbency increased steadily, irrespective of GA feed amount (Figure 3). The value of water absorbency was by far higher than those crosslinked by  $\text{CaCl}_2$  and EGE. The highest value was 500 g/g, which was obtained when the GA feed amount was 40 mol%. No decrease of absorbency was observed during the absorbency test, which is in contrast to the case of  $\text{CaCl}_2$  and EGE. This indicates that the crosslinking of GA is stable in water.



**Figure 3.** Absorbency of pectin-based hydrogels crosslinked by GA.

The differences of absorbency of hydrogels crosslinked by three chemicals are discussed in view of structure of their crosslinking points. First, the structure of crosslinking point of hydrogels crosslinked by  $\text{CaCl}_2$  is explained by egg-box model, as mentioned above. Strictly speaking, however, this is not crosslinking “point” but “region” along the main chain, which might restrict the chain expansion and high water absorption. This might be the reason why hydrogels crosslinked by  $\text{CaCl}_2$  absorbed somewhat less water than those crosslinked by GA, which will form crosslinking “point” successfully. On the other hand, crosslinking by EGE proceeded less efficiently than those by  $\text{CaCl}_2$  or GA, judging from the appearance during the crosslinking reaction (no gelation) and lower yields of products. Further, the residual amount of hydrogels crosslinked by EGE inside the tea-bag after absorbency test was less than 40% of the feed. This indicates more than half of the products flew out during the test because of the insufficient crosslinking, which might lead to low water absorbency. Consequently, it has been proved that GA was the most suitable crosslinker among those examined to attain high water absorbency. Similar tendency was observed when absorbency of alginate-based hydrogels crosslinked by  $\text{CaCl}_2$ , EGE, and GA was evaluated [14].

Figure 4 shows the comparison with absorbency of various hydrogels. Crosslinked sodium polyacrylate swelled quite rapidly. Its absorbency saturated after 1 h, and its maximum absorbency was 300 g/g in pure water, and 60 g/g in 0.9% NaCl solution, respectively [14]. Alginate-based hydrogel swelled slowly and exhibited the similar maximum absorbency value to that of crosslinked sodium polyacrylate [14]. On the other hand, pectin-based hydrogel in the present study absorbed more pure water but less 0.9% NaCl solution, i.e., the decrease of absorbency by the salt was more remarkable than other hydrogels, as shown in Figure 4.



**Figure 4.** Comparison with absorbency of various hydrogels.

It is well known that one of the main driving forces of water absorbency of superabsorbent hydrogels is osmotic pressure which generates from the difference of ionic concentration between inside the gel and outside [1,2]. Sodium polyacrylate and sodium alginate contain one sodium carboxylate group per repeating unit, so their ionic concentrations inside the gel are supposed to be high, which also means they are less susceptible to salt concentration of the outer medium. On the other hand, more than half of carboxylic acid group of pectin in the present study is esterified by methyl group, so the ionic concentration inside the gel is lower than those of sodium polyacrylate and alginate. This may be the reason why the pectin-based hydrogel was sensitive to salt concentration.

### Biodegradability

Figure 5 shows biodegradability of various materials measured by continuous BOD method. Cellulose was used as the standard material to check the biodegradation activity of the activated sludge. The activated sludge degraded ca. 75% of cellulose and ca. 85% of unmodified pectin for 18 days. On the other hand, 60-65% of pectin-based hydrogels were degraded by this activated sludge, irrespective of kinds of crosslinkers. Thus it was found that the chemical crosslinking suppressed the biodegradation speed of pectin to some extent, but crosslinked pectins kept biodegradable character as shown in Figure 5. Crosslinking structure seems to remain during the evaluation and restrict the biodegradation. Further study on relationship between structure of hydrogels including crosslinking point and biodegradability is still on progress.

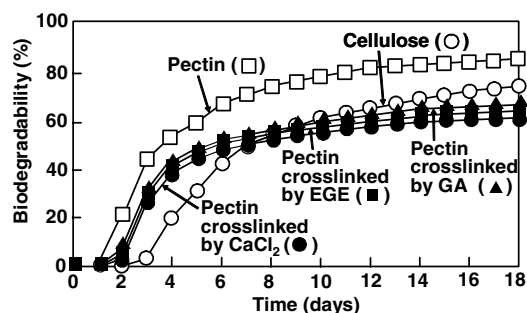


Figure 5. Biodegradability of various materials measured at 25°C.

### Conclusion

We have investigated the preparation of superabsorbent hydrogels from pectin by use of three kinds of crosslinkers. Among them, hydrogel crosslinked by GA absorbed high amount of pure water. Absorbency was sensitive to the salt concentration of medium. Therefore, hydrogels in the present study have a potential as salt sensors. Further, they are environmentally friendly material because they exhibited biodegradability.

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