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# Application of Polyvinyl Alcohol (PVA)/Carboxymethyl Cellulose (CMC) Hydrogel Produced by Conventional Crosslinking or by Freezing and Thawing

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Hydrogels for this study were prepared from a mixture of PVA and CMC using three different techniques, i.e., freezing and thawing, electron-beam irradiation or combined freezing and thawing and electron beam irradiation. A comparative study between the three techniques was carried out in terms of gel fraction (%) and swelling (%). It was found that the physical properties of the hydrogel were improved when the combination of freezing and thawing and irradiation were used rather than just freezing and thawing, or irradiation only. The effects of temperature and soil fertilizers on swelling (%) were examined to evaluate the usefulness of the hydrogel as a super absorbent in the soil. It was found that the swelling ratio increased as the composition of CMC increased in the blend. Hence, the blend having the composition 80/20 (CMC/PVA) was used as a super absorbent in the soil for agriculture. Moreover, the water retention increased in the soil containing this hydrogel. Thus, this type of hydrogel can be used to increase water retention in desert regions.

**Keywords:** hydrogel; freezing and thawing; PVA; CMC; superabsorbent hydrogel

## 1 Introduction

Hydrogels are defined as a two component system. One of the components is a hydrophilic polymer, insoluble in water because of the three dimensional network, and the second one is water. These hydrogels may swell in water up to an equilibrium state and retain their original shape (1–3).

Actually, hydrogels have been prepared by chemical methods for a long time. However, in recent years, irradiation techniques to produce hydrogels are being used increasingly around the world. This technology is convenient because the physical properties can be manipulated easily by irradiation (4, 5).

A development or new technique for obtaining hydrogels is the repeated freezing and thawing processes. Analysis of previous work in the development of freezing and thawing processes is presented, focusing on the implications of such materials for a variety of applications. The future directions involving the further development of freeze/thawed PVA hydrogels are addressed (6).

PVA must be crosslinked in order to be useful for a wide variety of applications, specifically in the area of agriculture. Moreover, the crystalline nature of PVA has been of specific interest particularly for physically, crosslinked hydrogels prepared by repeated cycles of freezing and thawing (7).

On the other hand, Na-CMC as an amylose with many hydroxy and carboxylic groups can absorb water and moisture, so the resulting hydrogel has many excellent properties, such as high water content, good biodegradation and a wide source for a low cost material (8).

Due to the simple preparation and low cost, the hydrogel prepared by PVA/CMC polymer has good application in water retention for agriculture (9).

In this work, attempts were made to prepare a hydrogel from a mixture of PVA/CMC by freezing and thawing, electron-beam irradiation, and a combination of freezing and thawing and electron-beam irradiation. The physical properties such as gel fraction and SW (%) were examined to evaluate its usefulness as superabsorbents.

## 2 Experimental

### 2.1 Materials

PVA, Laboratory grade, used in this study was in the form of a powder, having an average molecular weight of 125,000,

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obtained from the Laboratory Rasayan. The sodium salt of CMC (pure polymer) in the form of granules was supplied by El-Nasr Pharmaceutical Chemical-Prolabo, Egypt.

## 2.2 Preparation of Hydrogel

PVA was dissolved in hot water at 95°C, while CMC was dissolved in cold water. PVA and CMC solutions were mixed with different ratios by a mechanical stirrer at room temperature to give a PVA/CMC solution. Hydrogels from a mixture of these polymers were made by freezing and thawing, exposure to electron-beam irradiation or both freezing and thawing and electron-beam irradiation. The irradiation process was carried out by using the electron beam accelerator of 1.5 MeV and 25 kW made by High Voltage Engineering, USA, at the National Center for Radiation Research and Technology, Cairo, Egypt. The required dose was obtained by adjusting the electron beam energy parameters and conveyor speed (2.7 m/min.). The doses being used were (20, 30, and 50 kGy).

Freezing and thawing was repeated up to three cycles to crosslink PVA/CMC solution physically. Each cycle of freezing and thawing involved lowering the temperature to ~30°C, and left standing at this temperature for 1 h, then raising the temperature to room temperature. In this technique, aqueous solutions of PVA and its blend between 2.5 and 15% (wt%) were frozen at -20°C and lowered back to room temperature, resulting in the formation of crystallites. The formation of these crystallites was found to be related to the concentration of the polymer in solution, freezing and thawing time. Overall, the crystallinity was found to increase with increasing freezing time. During the thawing process, the size of the crystallites initially increased and then decreased. This was attributed to the breakdown of the crystalline structure. The degree of crystallinity was found to increase with increasing the PVA solution concentration.

## 2.3 Determination of Gel Fraction (%) (GF%)

A known weight ( $W_1$ ) of the irradiated samples were extracted by water in a Soxhlet apparatus for 24 h. then dried to a constant weight in vacuum ( $W_2$ ). The soluble fraction (SF%) was determined according to the following equation:

$$SF\% = W_1 - W_2 / W_1 \times 100 \quad (1)$$

Thus, GF (%) was calculated as follows:

$$GF\% = (1 - SF) \times 100 \quad (2)$$

## 2.4 Swelling Percentage of CMC/AAm Hydrogel (SW%)

A known dry weight of the insoluble part of the hydrogel ( $W_1$ ) after calculation of the gel fraction (%) was immersed in distilled water, as well as in salt fertilizers at room

temperature for 24 h. The swollen part of the hydrogel was weighed ( $W_2$ ).

The dependence of SW% on temperature, was followed by immersing the insoluble part of the hydrogel in water at different temperature 30, 40, 50°C. The SW% is determined by:

$$SW\% = W_2 - W_1 / W_1 \times 100 \quad (3)$$

## 2.5 Water Retention Measurement

Referring to the literature (10), 100 g of dry soil granules were mixed well with 2.0 g of hydrogel and 200 g of distilled water was added in to it in a 250 ml beaker. The beaker was put in the lab under room temperature and weighed every 5 days. After a period of 30 days, the observation was terminated. At the same time, the controlled experiment, namely without any hydrogel, was also carried out. The evaporation percentage (EP) of the water was calculated using the following equation:

$$EP\% = m_0 - m_i / 200 \times 100\% \quad (4)$$

Where,  $m_0$  was the initial weight of the beaker containing the hydrogel,  $m_i$  was the weight of the beaker without the hydrogel.

## 3 Results and Discussion

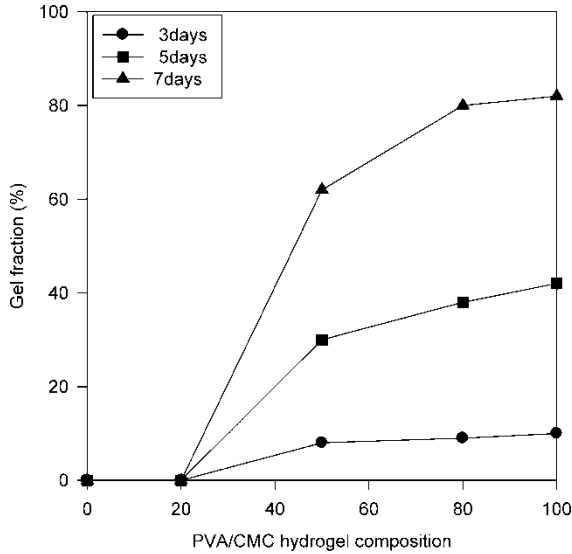
PVA and CMC polymers have been considered to be of specific interest for preparing hydrogels through difunctional crosslinking agents by the use of electron-beam or gamma irradiation. In this study, further development of hydrogels by freezing and thawing were studied.

An attempt was made to obtain hydrogels from PVA/CMC by repeated freezing and thawing cycles, irradiation and repeated freezing and thawing with irradiation.

A series of preliminary experiments were carried out with the objective of studying GF% and SW% of the prepared hydrogel.

### 3.1 Gel Fraction (GF%)

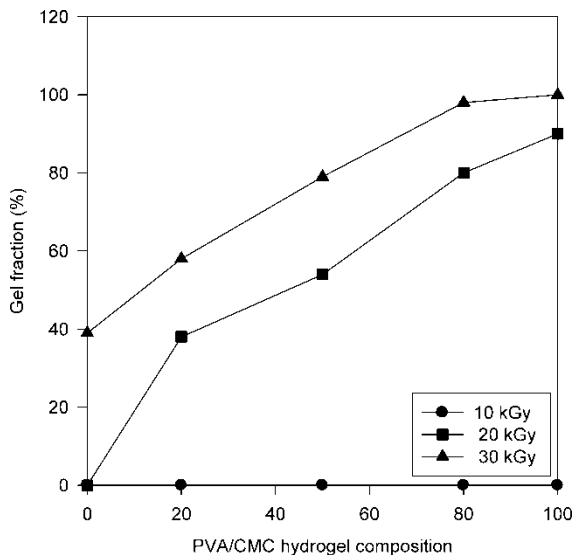
The dependence of GF% of PVA/CMC hydrogel as a function of blend composition after repeated cycles of freezing and thawing are studied. The results obtained are shown in Figure 1. From these results, it was observed that the gel fraction increases with increasing the time of freezing and thawing for all the blend compositions under investigation. This was explained by the fact that an aqueous solution of PVA and CMC can undergo gelation when submitted to a series of freezing and thawing cycles. In the freezing-thawing processes, water crystallization results in creating interstitial domains of high polymer concentrations (11).



**Fig. 1.** Effect of repeated freezing and thawing without irradiation on gel fraction (%) of PVA/CMA at different blend compositions.

Moreover, GF% increased as PVA amount in the blend increased. It is well known that the procedure of freezing and thawing for PVA results in the formation of crystallites that serve as physical crosslinks to render the material insoluble in water (12).

The GF% of PVA/CMC hydrogel, as a function of blend composition at different irradiation dose, was studied. The results obtained are shown in Figure 2. From these results, it was found that there is an increase in the gel fraction with irradiation dose at all blend composition. An important remark is that the formation of hydrogel begins from 20 kGy, which is in accordance with previous work (11). At a dose lower than 20 kGy there is no gel formation for all



**Fig. 2.** Effect of irradiation dose on gell fraction (%) of PVA/CMA at different hydrogel compositions.

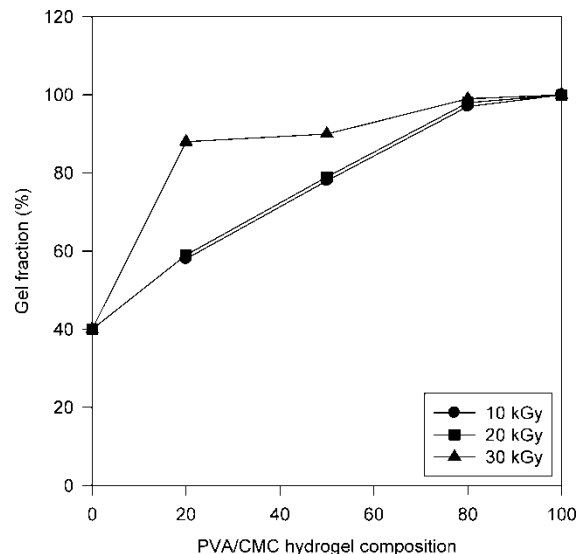
blend composition. For example, the GF% is equal to 75% and 92%, and at 50% and 80% PVA at the same dose. While at 80% PVA, the GF% was equal to 79% and 96% at 20 and 30 kGy, respectively. This was explained by the nature of each polymer, PVA is a crosslinked polymer (13), while CMC is a degradable one (14).

In the case of irradiation, GF% shows a value higher than that in freezing and thawing due to the fact that the cross-linking network can be formed between PVA and CMC molecules when the irradiation process is used. The gel results from the coupling of polymer radicals that were directly and indirectly produced from PVA or CMC by gamma rays. The indirect formation of polymer radicals is mainly due to the  $H^\bullet$  and  $OH^\bullet$  arising from water molecules, both of which attract the hydrogen atoms to form hydrogels (15).

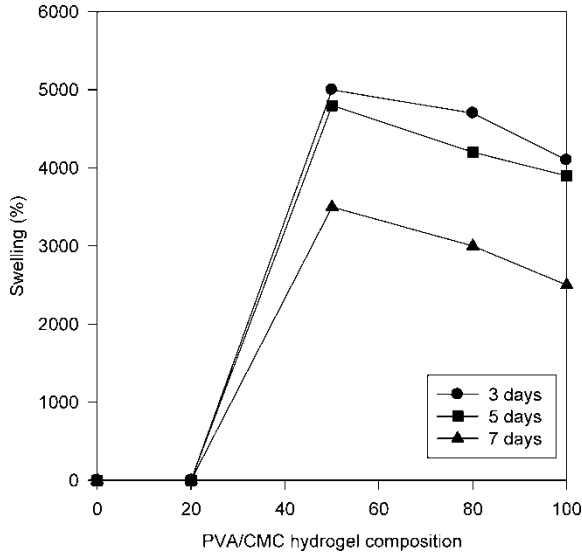
The dependence of GF% on the blend composition after 3 cycles of freezing and thawing then irradiated to different doses were studied. The results obtained are shown in Figure 3. From this figure it was found that the maximum gel fraction is obtained at 30 kGy and three cycles of freezing and thawing. Also, it was found that the GF% increases with increasing irradiation dose at all blend composition under investigation.

Furthermore, it was also found that GF% increases with increasing PVA content at dose rates equal to 10 kGy and 20 kGy, whereas at 30 kGy the increase of PVA did not affect GF%.

The results obtained from the study of the GF% under three different experimental conditions show that freezing and thawing only causes some crosslinking which renders the hydrogel insoluble in water, but swells whereas GF% increases upon irradiation only. The higher GF% was obtained in cases of both freezing and thawing and irradiation.



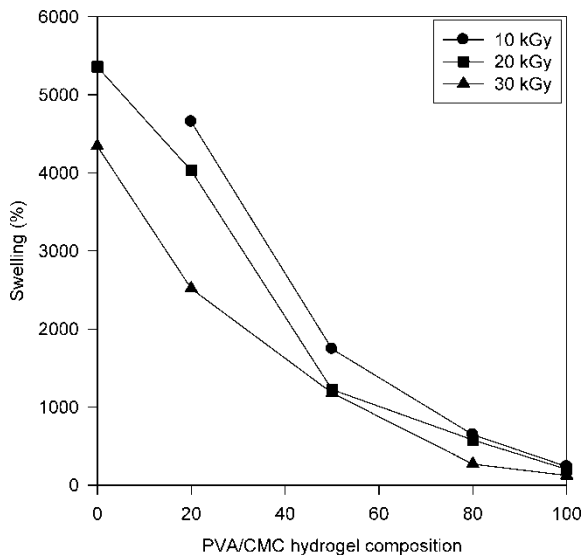
**Fig. 3.** Effect of freezing and thawing for 3 days, then irradiation at different irradiation dose of PVC/CMC hydrogel at different compositions.



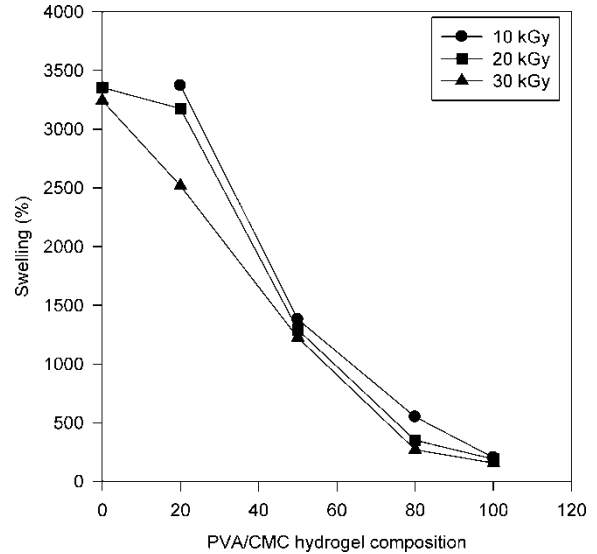
**Fig. 4.** Effect of various hydrogel composition PVA/CMC on the SW% at repeated freezing and thawing without irradiation.

**3.2 Swelling Behavior % (SW%)**

The swelling behavior in water of the hydrogel prepared by three different techniques was discussed. The results obtained are shown in Figures 4, 5, and 6. From these results, it was found that the SW% was inversely proportional to the GF%. SW% of the hydrogel obtained from only freezing and thawing, as shown in Figure 4, was higher than that obtained by irradiation or the two-step methods of freezing and thawing and irradiation as shown in Figures 5 and 6, respectively, but the hydrogel formed by freezing and thawing only is not easy to handle. On applying the two other mechanisms, there is a high value of swelling and, at the same time, good handling of the



**Fig. 5.** Effect of hydrogel compositions PVA/CMC on the SW% at different irradiation dose without freezing and thawing.



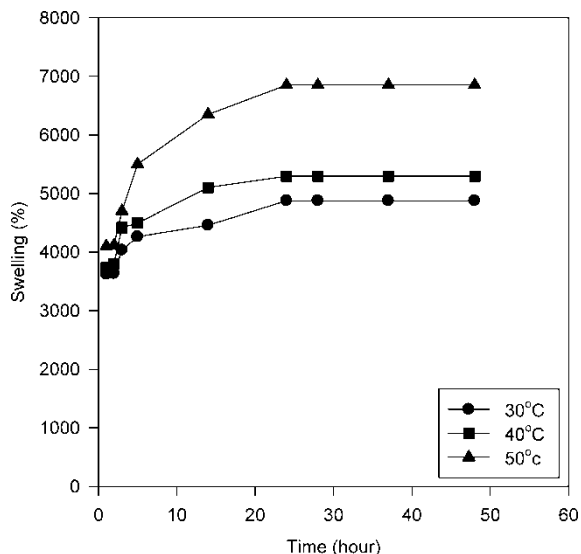
**Fig. 6.** Effect of various blend composition PVA/CMC on the SW% at different irradiation dose after freezing and thawing for three cycles.

hydrogel. Also, the SW% increased as the PVA content in the blend decreased. This was due to the very fast absorption of water due to the high surface hydrophilicity and capillarity of CMC.

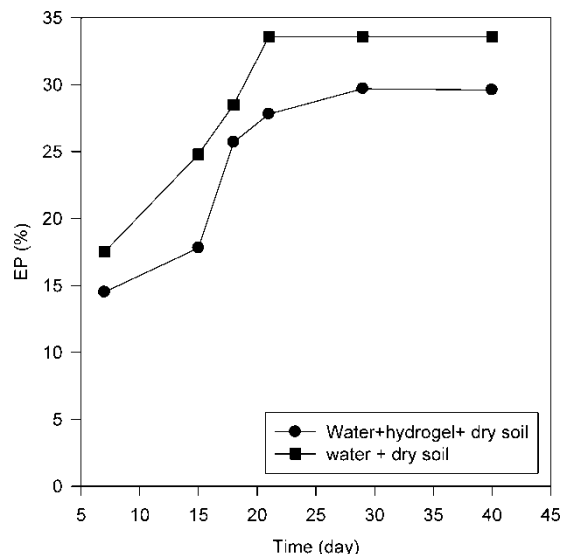
The difference between the three processes used for the preparation of hydrogels in terms of GF% and SW%, may be summarized as follows:

1. Gel formation was strongly affected by freezing and thawing, especially at low periods of times. For example, after one time of freezing and thawing, it was found that the GF% is equal to 10%, 15%, and 19% for 50/50, 80/20, 100% PVA, respectively. On the other hand, at low irradiation dose, namely 10 kGy, the blend with all its composition show complete solubility. This means that this dose is not sufficient for the crosslinking processes. From this result, it can be concluded that using freezing and thawing was more effective in low time than irradiation at low doses.
2. The GF% and SW% is influenced by blend composition in the case of irradiation than freezing and thawing only. This phenomenon can be explained by the fact that a crosslinking network structure between PVA and CMC can be formed in the case of irradiation.
3. The GF% of hydrogels was higher when two steps of freezing and thawing and irradiation were used than just freezing and thawing or irradiation. At the same time, the hydrogel possesses good physical properties.

From the results obtained from GF% and SW%, it was assumed that the blend having the composition 80% CMC/20% PVA is the optimum concentration of the blend which possesses an appropriate value of GF% equal to ~100% and also suitable SW% equal to 2500.



**Fig. 7.** Effect of temperature on swelling (%) of the PVA/CMC hydrogel at different immersion times.



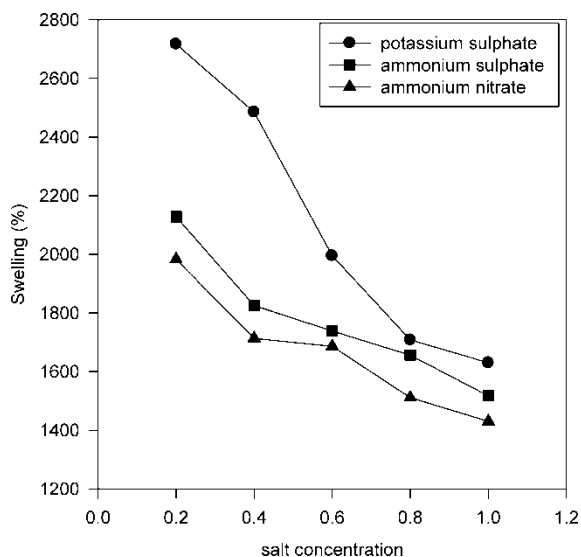
**Fig. 9.** Water retention curve of PVA/CMsC hydrogel.

The response of the prepared hydrogel against environmental conditions was investigated for suitability as super absorbents in the desert regions.

Hence, the dependence of swelling on temperature and different salts used as fertilizers was measured. The results obtained are shown in Figures 7 and 8, respectively. From Figure 7, it was found that all hydrogels exhibit a marked increase in the SW% at all temperature ranges at any time of swelling. The SW% was found to level off after 24 h, which represents the equilibrium swelling. The increase in SW% with immersion time and temperature is due to the very fast absorption of water due to the surface hydrophilicity nature of PVA, which is the measure constituent of the

hydrogel. The leveling off was explained by the stepwise slowdown of the absorption to constant values typical of diffusion mechanisms (16).

The effect of different salts solution used in the soil as fertilizers such as ammonium nitrate, ammonium sulphate and potassium sulphate on the SW% was studied. The results obtained are shown in Figure 8. From these results, it was found that SW% in different salt decreased by increasing salt concentration. At 0.4%, which represents the maximum concentration of salts (fertilizer) actually used in agriculture through drop irrigation system. The SW% is equal to 2500, 1850, 1750 for potassium sulphate, ammonium sulphate and ammonium nitrate, respectively. These values are suitable for using these hydrogels as super absorbance in the soil.



**Fig. 8.** Effect of salt concentrations of different salt fertilizers on the swelling (%).

### 3.3 Water Retention of Hydrogels

Water retention of the hydrogels was evaluated. The results obtained are shown in Figure 9. From these results, it could be observed that the water evaporation rate decreased after the addition of the hydrogel to the soil. This was due to the high superabsorbency property of the hydrogel. Therefore, if this hydrogel was used on farmlands, it would be like a sub-miniature reservoir to retain and supply moisture to crops. In this way, it would enhance efficiency of water utilization, prolong irrigation cycles and reduce irrigation frequency (17).

## 4 Conclusions

In this work, attempts were made to prepare biodegradable hydrogels used for superabsorbent which consist of PVA and CMC. The hydrogels were made by freezing and thawing, gamma ray irradiation, or a two-step method of freezing and thawing and gamma-ray irradiation. The

GF%, SW% were higher when two steps of freezing and thawing and irradiation were used than only freezing and thawing. SW% was increased by temperature. SW% decreased with increasing the concentration of salts fertilizers in soil. The swelling in potassium nitrate is the highest in the swelling ratio from fertilizers. Hydrogels possesses higher water retention in soil. Moreover, the prepared blend possesses high biodegradability in the soil, due to non toxicity and good biocompatibility. It is suggested that CMC based hydrogels may also have wide applications in biomedical materials and agriculture.

## 5 References

1. Rosiak, J.M., Ulanski, P. and Rzeznicki, A. (1995) *Nucl. Instrum. Methods Phys. Res.*, **B 105**, 335.
2. Ch'nh, H.S., Park, H., Kelly, P. and Rabinson, J.R. (1985) *J. Pharm Sci.*, **74(4)**, 399.
3. Yoshii, F., Zhnshan, Y., Isobe, K., Shinozaki, K. and Makuuchi, K. (1999) *Radiat Physchem.*, **55**, 133.
4. Rosiak, J.M., Ulanski, P., Pajewski, L.A., Yoshii, F. and Makuuchi, K. (1995) *Radiat. Phys. Chem.*, **46**, 161.
5. Singh, D.K. and Ray, A.R. (1997) *J. Appl. Polym. Sci.*, **66**, 869.
6. Christie, M.H. and Nikolaos, A.P. (2000) *Advances in Polymer Science*, **153**, 37.
7. Willcox, P.J., Howie, D.W., Schmidt-Rohr, K., Hoagland, D.A., Gido, S.P., Pudjijanto, S., Kleiner, L.W. and Venkatraman, S. (199) *J. Polym. Sci. Polym. Phys. Ed.*, **37**, 343.
8. Wach, R.A., Mitomo, H., Yoshii, F. and Kumo, T. (2001) *J. Appl. Polym. Sci.*, **81**, 3000.
9. Nie, H., Liu, M., Zhan, F. and Guo, M. (2004) *Carbohydrate Polymers*, **58**, 185.
10. Zhang, L.D., Li, Z.B. and Ren, Z.K. (1995) *Fine Chem.*, **12**, 65.
11. Hernandez, R., Lopez, D., Mijangos, C. and Guenet, J.M. (2002) *Polymer*, **43**, 5661.
12. Hassan, C.M., Ward, J.H. and Peppas, N.A. (2000) *Polymer*, **31**, 6729.
13. Hegazy, A., El-Sayed, El-Salmawi, K.A. and El-Naggar, A.A. (2004) *J. Appl. Poly. Sci.*, **94**, 1649.
14. Liu, P., Zhai, M. and Wu, J. International Symposium on Radiation Technology in Emergent Industry Application (IAEA), 2000.
15. Wang, B., Kodama, M., Mukatake, S. and Kokufuta, E. (1998) *Polym. Gels Networks*, **6**, 71.
16. NHO, C.Y. and Park, R.K. (2002) *J. Appl. Polym. Sci.*, **85**, 1787.
17. Zhan, F., Liu, M. and Wu, L.M. (2004) *J. Appl. Polym. Sci.*, **92**, 3417.