Synthetic Absorbent for Dyestuffs Based on Gamma Crosslinked Poly(vinyl alcohol) (PVA)

Sayeda M. Ibrahim

Department of Radiation Chemistry, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

ABSTRACT: This work reports on the characterization and uses of gamma radiation-crosslinked poly(vinyl alcohol) (PVA) films as absorbents for different classes of dyestuffs normally released from textile factors. Dyestuffs were selected from different producers. These dyestuffs were Remacryl Blue (basic dye), Remazol Golden Orange (reactive dye), Solar Orange (direct dye), and Sandolan (acid dye). The percentage dye sorption by PVA was determined by spectroscopic analysis and color-strength measurements of the PVA films after absorbing the different dyestuffs. The results showed that the concentration of dimethylbisacrylamide as a crosslinking agent has a great effect on the gel fraction and percentage swelling in water of the PVA polymer. In general, crosslinked PVA showed a low tendency to absorb the different dyestuffs under investigation at room temperature. This tendency was shown to increase with an increasing temperature of the dye solution from room temperature to 70°C. Meanwhile, the highest percentage of dye sorption was found in the case of the basic dye and the lowest one in the case of the reactive dye depending on the active groups on the dyes. Moreover, the percentage dye sorption by PVA was slightly higher in the acid medium rather than in the alkaline one. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 349–354, 2003

Key words: radiation; crosslinking

INTRODUCTION

Development is needed in the technology of wastewater treatment after the industrial expansion which caused many problems of pollution. Among these problems are those caused by dyewastes from the textile industry. Most dyes used in the textile industry from wastewater are not easily degraded by ordinary treatment processes.[1] This is because most dyestuffs contain, in their chemical structure, at least three fused benzene rings. There have been many attempts to use high-energy radiation to decompose aromatic compounds and dyestuffs.[2] Although these methods appear to be promising, particularly in the field of gas treatment, the degradation process does not affect the main structure but results in other products that may be more toxic than the original ones.

Various adsorbents have been used for the removal of acid and basic dyes from aqueous solutions.[3] Also, the removal of some basic dyes by a poly(vinyl alcohol)/acrylic acid hydrogel[4] was studied. The results showed that this hydrogel possessed good removal affinity for the basic dye Methylene Blue and suggested that such hydrogels are acceptable for practical uses. Moreover, a poly(vinyl alcohol)/poly(carboxymethyl cellulose) (PVA/CMC) blend graft copolymer with styrene was used as a sorbent for acid, basic, reactive, and direct dyes wastes normally released from textile factories.[5] In this regard, the factors that may affect the sorption process such as the time, temperature, weight of the blend graft copolymer, and volume of the dye waste were investigated.

PVA is a well-known material and a good film-forming highly hydrophilic polymer with easy availability. Investigations have been done on its use in the field of separation processes.[6,7] However, such a polymer suffers from poor water resistance and low mechanical strength in an aqueous solution. Therefore, it has to be turned into a complete insoluble stable material with good mechanical properties. A number of investigations have been reported in the literature to modify PVA by crosslinking it with different reagents such as aldehyde,[8] dicarboxylic acid,[9] heat, H_3BO_3,[10] and radiation.[11,12] Thus, this study was aimed at preparing a crosslinked PVA polymer, induced by gamma radiation, suitable for absorbing dyestuffs from wastewater.

EXPERIMENTAL

Materials

The PVA polymer (laboratory grade) used in this study was in the form of a powder, had an average molecular weight (M_w) of 125,000, and was obtained from Laboratory Rasayan (India). *N,N*-Methylenebisacrylamide (MBAM) from Aldrich (Milwaukee, WI) was used as a crosslinking agent. Four dyestuffs be-

longing to different classes were used throughout this work. These dyes were Remacryl Blue (basic dye), Sandolan E-3GSL (acid dye), Remazol Golden Orange (reactive dye), and Solar Orange (direct dye). The basic and reactive dyes were kindly supplied by Hochest (Germany), while the acid and direct dyes were supplied by Sandoz (Switzerland).

Preparation of crosslinked PVA

Films of the PVA polymer were prepared by the casting-solution technique. A known weight of PVA powder was dissolved in a known volume of distilled water at 95°C and different ratios of the crosslinking agent were added to the solution of PVA before casting. The cast films were dried under ambient conditions for 24 h and then exposed to various doses of gamma radiation. Irradiation to the required doses was carried out in a Co-60 gamma source at the National Center for Radiation Research and Technology, Cairo, Egypt. The PVA films were exposed to gamma irradiation in air at a dose of 2.75 kGy/h.

Determination of gel fraction

Samples of gamma-irradiated PVA films were accurately weighed and then extracted with water using a Soxhlet apparatus. Heating was continued and regulated so that siphoning would take place at a rate of 20–30 times per hour for 24 h. After extraction, the samples were dried to a constant weight in a vacuum at about 50°C. The soluble fraction (SF) was determined according to the following equation:

$$SF = (W_0 - W_1)/W_0$$

where W_0 and W_1 are the initial and the final weights, respectively. Thus, the gel fraction (GF) was calculated as follows:

$$GF = 1 - SF$$

Determination of the percentage swelling

A known weight of the insoluble part after extraction (W_1) was further soaked in H_2O and left for 24 h at room temperature. The swollen sample with the solvent at equilibrium was weighed (W_2). The percentage swelling was determined as follows:

$$Swelling\ (\%) = [(W_2 - W_1)/W_1] \times 100$$

Determination of dye uptake

The determination of the dye uptake of the different dyestuffs and the industrial dye waste by crosslinked

PVA was carried out by a general procedure based on spectrophotometric analysis. In this regard, standard curves were first constructed, representing a relation between different known concentrations from each dye and the corresponding light absorption.[5] The light absorption of the basic, acid, direct, and reactive dyes was measured at wave lengths of 660, 515, 470, and 384 nm, respectively. The different expressions governing these relations were calculated to be as follows:

Light absorbance = 0.223 × basic dye concentration (mg/L)

Light absorbance = 0.026 × acid dye concentration (mg/L)

Light absorbance = 0.028 × reactive dye concentration (mg/L)

Light absorbance = 0.046 × direct dye concentration (mg/L)

In this procedure, a certain concentration from each dye under investigation (20 mg/L) was first dissolved in certain volume of a boiled water solution. A constant weight of crosslinked PVA (0.5 g) was then immersed in the different dye solutions for various lengths of time and, after that, the light absorbance of the residual dye solution was measured. The dye uptake by the PVA films was determined according to the following equation:

$$Dye\ uptake = (C_1 - C_2)/m\ (mg\ dye/g\ PVA)$$

where C_1 and C_2 are the dye concentrations of the solutions before and after immersing PVA films, respectively, and m is the weight of PVA polymer. The light-absorbance measurements were performed using a UV/vis spectrophotometer (UV2 series) made by Unicam, England.

Color-difference measurements

A microcolorimeter unit made by Dr. Lange (Germany) was used for the color measurements. The L^*, a^*, and b^* system used is based on the CIE Colour Triangle (Commission International de I'Eclairage Units X, Y, and Z). In this system, the L^* value represents the dark–white axis, a^* represents the green–red axis, and b^* represents the blue–yellow axis. The L^*, a^*, and b^* values of the PVA films before dye sorption were measured and taken as a reference. The color-difference (ΔE^*) intensity on the PVA samples after sorption was determined as follows:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

RESULTS AND DISCUSSION

Gel fraction and swelling behavior

Figure 1 shows the effect of the irradiation dose on the gel fraction of PVA crosslinked in the presence of

different concentrations of the crosslinking agent MBAM. It should be mentioned that the crosslinking of PVA under the effect of gamma radiation only was so weak that we could not measure the gel fraction. This trend was observed even by using high doses. It can be seen that the concentration of MBAM is a very effective factor regarding the crosslinking of PVA, so that an increase of 0.05% of MBAM caused a significant increase in the gel fraction. This behavior was observed at all irradiation doses. It seems that 0.15% of MBAM is not enough to achieve a complete gel formation of PVA because the gel fraction was shown to increase with an increasing irradiation dose. However, a 0.9 gel fraction was obtained by using 0.2% of MBAM at a dose of 70 kGy. By increasing the irradiation dose beyond this value, no noticeable increase in the gel fraction of PVA was seen. Meanwhile, the gelation dose of PVA by using MBAM can be observed to be about 30 kGy.

The swelling behavior is a very important factor for the applicability of synthetic absorbents in the field of the removal of pollutants from wastewater. Figure 2 shows the effect of the irradiation dose on the percentage swelling of PVA crosslinked by gamma radiation in the absence and in the presence of different concentrations of MBAM. At any irradiation dose, the percentage swelling of PVA was found to decrease with an increasing concentration of MBAM. However, a high concentration of MBAM seems to greatly reduce the percentage swelling of PVA, particularly at low doses. Meanwhile, the crosslinking of PVA with gamma radiation and without MBAM displayed the highest percentage swelling, which reflects the importance of MBAM regarding crosslinking. The different
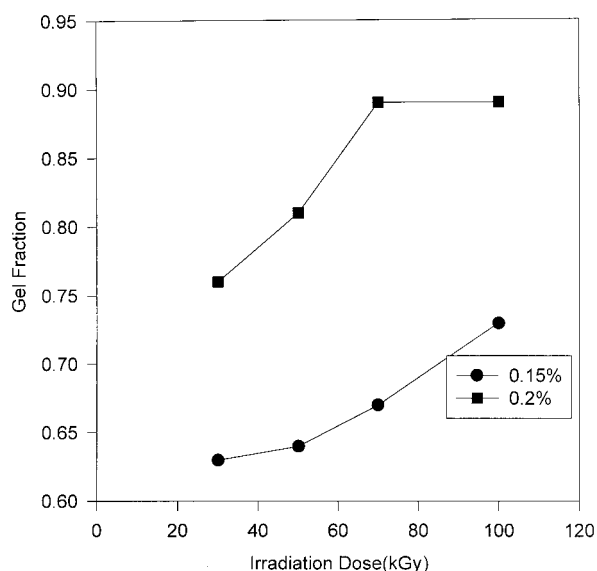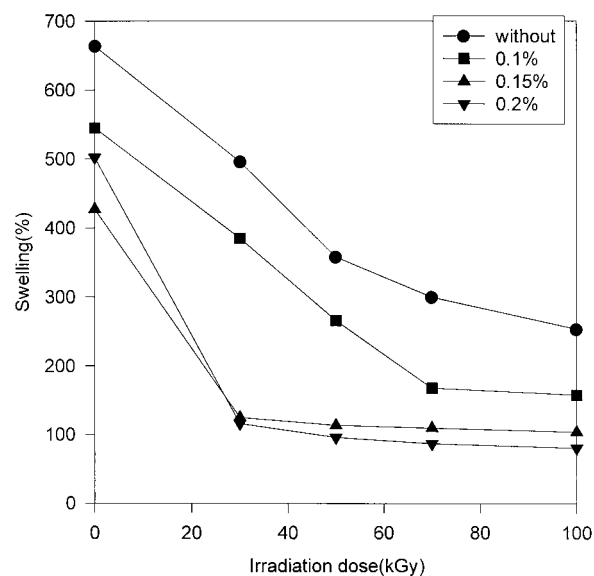

Figure 2 Effect of irradiation dose on the percentage swelling of PVA in water crosslinked in the presence of different concentrations of the crosslinking agent MBAM.

values of the percentage swelling of PVA and PVA containing different concentrations of MBAM before gamma irradiation may be attributed to the occurrence of partial crosslinking. This may occur during the film processing of PVA in the presence of MBAM under the effect of heating. This is because PVA is not soluble at room temperature and needs higher temperatures.

Dye uptake by crosslinked PVA

There are various types of dyes belonging to different classes depending on the kind of fiber to be dyed. For example, the reactive and direct dyes are specific for cotton cellulose fibers, while the acid and basic dyes are used for dyeing protein fibers such as wool and silk. Also, the disperse dyes are now widely used for dyeing synthetic fibers and cotton blends with polyester. In general, the choice of the dyestuff is based on the function groups on both the fiber and the dyestuffs. All these dyes are usually used in textile factories.

In the present work, a solution containing a constant concentration of 20 mg/L of each dye under investigation was prepared. The dye sorption of the different dyes by the crosslinked PVA, as a function of the immersion time and temperature, was investigated as shown in Figures 3–6. It can be seen that the dye sorption–time trend by crosslinked PVA differs from one dye to another. In all cases, the dye sorption was found to increase with an increasing time of immersion and also with increasing temperature. The affinity
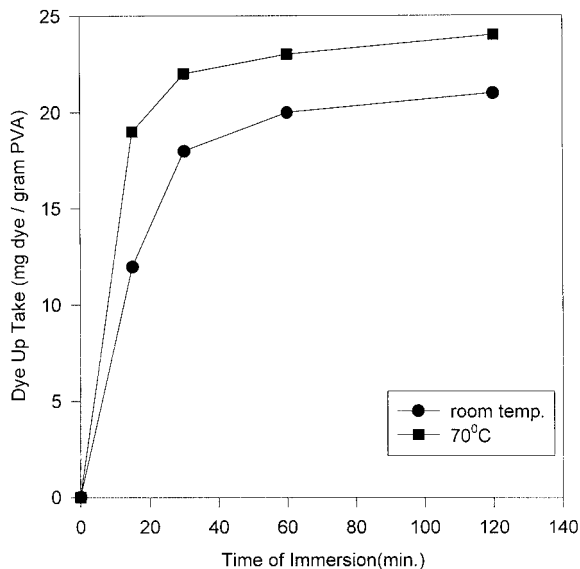

Figure 1 Effect of irradiation dose on the gel fraction of PVA crosslinked in the presence of different concentrations of the crosslinking agent MBAM.

Figure 3 Sorption of the basic dye Sandocryl Blue by crosslinked PVA at room temperature and 70°C as a function of immersion time. Crosslinking conditions: irradiation dose, 70 kGy; MBAM concentration, 0.2 wt %.
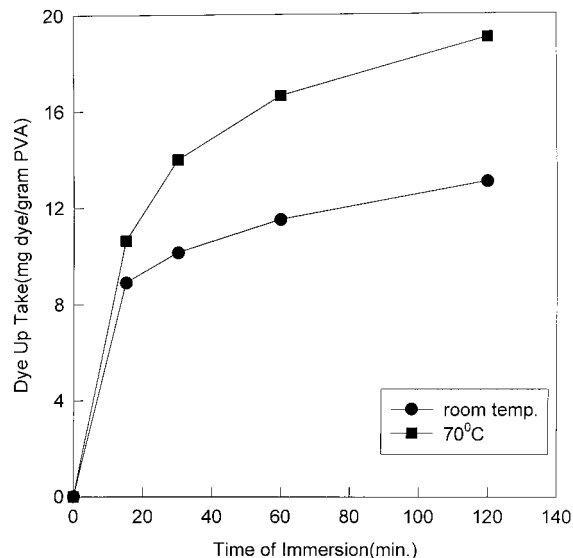
of crosslinked PVA for the different dyes can be arranged as follows:

Basic dye > direct dye > acid dye > reactive dye

The affinity of PVA for the different dye stuffs is essentially dependent on the hydrophilic group present in the polymer (hydroxyl group OH—). Also, the sorption process will eventually go through chemical bonding between the active groups on the differ-

Figure 5 Sorption of the direct dye Solar Orange by crosslinked PVA at room temperature and 70°C as a function of immersion time. Crosslinking conditions are the same as in Figure 3.

ent dyes and the hydroxyl group of the PVA polymer through physical absorption. The chemical interaction between the different dyes and crosslinked PVA was tested by soaking the dyed films with the basic, direct, and reactive dyestuffs at room temperature and at 700°C in acid solutions. It was found that all the dyes were released from the PVA films dyed at room temperature, which implies that the sorption is a physical absorption and not a chemical interaction. On the other hand, when the PVA films dyed at 700°C were subjected to the same dye-release experiment, the
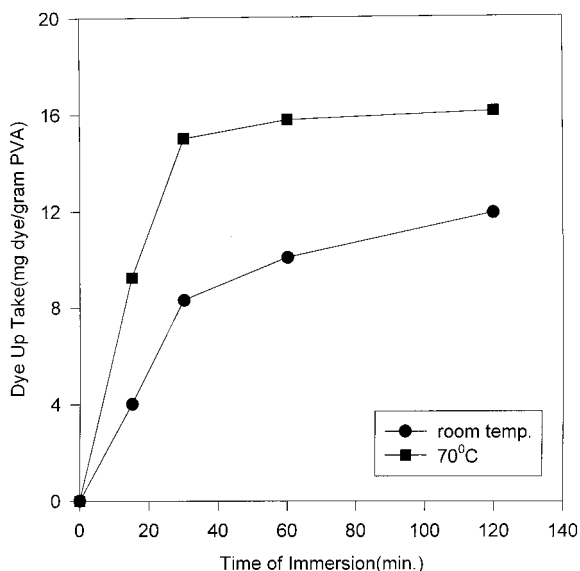

Figure 4 Sorption of the acid dye Sandolan E-3GSL by crosslinked PVA at room temperature and 700°C as a function of immersion time. Crosslinking conditions are the same as in Figure 3.
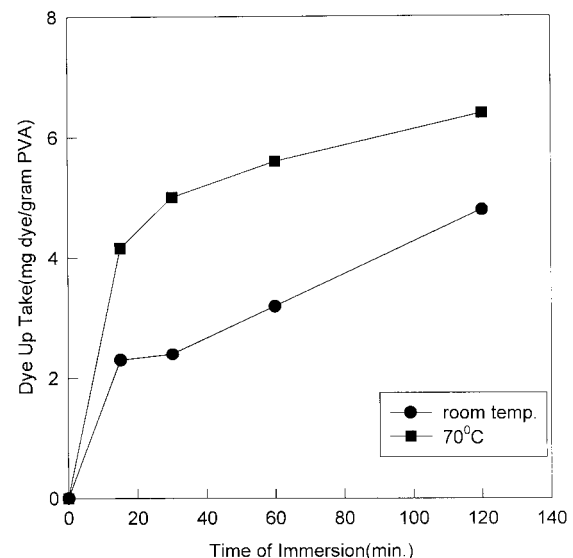

Figure 6 Sorption of the reactive dye Remazol Golden Orange by crosslinked PVA at room temperature and 70°C as a function of immersion time. Crosslinking conditions are the same as in Figure 3.

TABLE I
Color-strength Measurements of Crosslinked PVA after Absorbing the Basic Dye Sandocryl Blue at Room Temperature and Different Temperatures

Temperature	Color-strength parameter			Color difference (ΔE^*)
	L^*	a^*	b^*	
Before aborption	87.1	4	−8.8	—
Room temperature	64.8	−40.6	−36.6	57.1
50°C	54.5	−36.9	35.3	58.6
70°C	57.6	−38.5	−36.4	62.1, 63.2

Crosslinking conditions are the same as in Figure 3.

TABLE III
Color-strength Measurements of Crosslinked PVA after Absorbing the Direct Dye Solar Orange at Room Temperature and Different Temperatures

Temperature	Color-strength parameter			Color difference (ΔE^*)
	L^*	a^*	b^*	
Before absorption	87.1	4.0	−8.8	—
Room temperature	70.0	33.0	26.4	48.6
50°C	65.3	37.4	34.9	59.2
70°C	56.3	39.7	38.9	67.0

Crosslinking conditions are the same as in Figure 3.

films were not affected by the acid solutions. These findings indicate that the sorption of the different dyes by crosslinked PVA at 70°C goes through a chemical bonding similar to the dyeing of fibers. When crosslinked PVA films dyed with the acid dyestuff at room temperature and 70°C were soaked in an alkali solution, the dye was desorbed in both cases. However, the dye release from crosslinked PVA dyed at room temperature was much higher than from that dyed at 70°C. Thus, the sorption of the acid dye by crosslinked PVA either at room temperature or at 70°C goes through a physical absorption.

The chemical interaction between the direct and reactive dyes and crosslinked PVA may be explained on the same basis of the dyeing of cellulosic fibers. In this regard, the dyeing process goes through the OH groups to form a salt linkage with the direct dye and a covalent bond with the reactive dye.

Tables I–IV show the different color interceptions and the color difference (ΔE^*) of the crosslinked PVA after it had been immersed in the dye solution for different dyestuffs for different immersion times. It should be noted that the color difference (ΔE^*) was measured after the sorption process had been completed or the sorption reaches equilbrium. In this case, ΔE^* is proportional to the percentage dye sorption. Also, the great force measuring the color strength of the PVA films after absorbing the different dyestuffs was compared with the data of percentage dye sorption by spectroscopic analysis. In general, it is obvious

that the L^* values of the dyed PVA films decrease with an increasing temperature of the dye solution from room temperature to 700°C with respect to those of the undyed films, regardless of the class of dyestuff. On the other hand, the color difference (ΔE^*) was found to gradually increase with an increasing temperature depending on the class of dyestuff,

The dye uptake of the basic dye by PVA films at room temperature and 500°C was measured analytically to be 20.8 and 23.2 mg dye/g PVA, respectively (Fig. 6), while those measured by the color difference (ΔE^*) at the same temperatures were found to be 22.8 and 23.2 mg dye/g PVA, respectively (Table I). For the acid dye, the dye uptake by PVA at room temperature and 500°C was found to be 11.2 and 16 compared to 11.2 and 12.3 mg dye/g PVA by the color-difference measurements. These findings indicate that there is a good agreement between the data of the dye uptake and the color-difference values.

Effect of pH strength

Piccini et al.[13] reported that dyestuffs are greatly influenced by the pH strength. Figure 7 shows the effect of pH on the dye uptake of the different dyestuffs. For the different dyestuffs under investigation, the dye uptake was found to be enhanced in the acidic medium and was slightly enhanced in the acidic medium and tended to decrease in higher pH values (basic medium).

TABLE II
Color-strength Measurements of Crosslinked PVA after Absorbing the Acid Dye Sandolan E-3GSL at Room Temperature and Different Temperatures

Temperature	Color-strength parameter			Color difference (ΔE^*)
	L^*	a^*	b^*	
Before absorption	87.1	4	−8.8	—
Room temperature	74	25.5	−12.5	57.0
50°C	67.4	26.7	−14.8	30.8
70°C	57.2	37.1	−17.5	45.6

Crosslinking conditions are the same as in Figure 3.

TABLE IV
Color-strength Measurement of Crosslinked PVA after Absorbing the Reactive Dye Remazol Golden Orange at Room Temperature and Different Temperatures

Temperature	Color-strength parameters			Color difference (ΔE^*)
	L^*	a^*	b^*	
Before absorption	87.1	4	−8.8	—
Room temperature	81.2	5.4	−3.3	8.6
50°C	81.5	5.8	−2.7	8.6
70°C	74.2	10.0	3.35	19.0

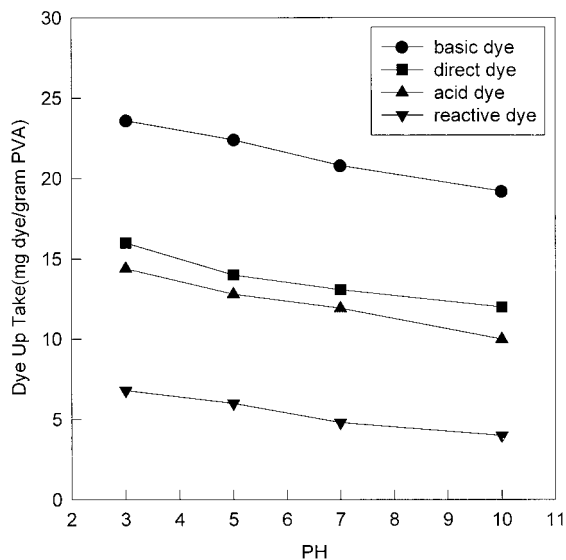Crosslinking conditions are the same as in Figure 3.

Figure 7   Effect of pH on the sorption of different dyestuffs by crosslinked PVA. Crosslinking conditions are the same as in Figure 3.

CONCLUSIONS

The prepared crosslinked PVA showed a low tendency to absorb the different dyestuffs under investigation at room temperature. This tendency was shown to increase with an increasing temperature of the dye solution to 70°C. Such crosslinked PVA has a high affinity toward the basic dye and the lowest affinity was for the reactive dye. Moreover, the sorption of the dye by crosslinked PVA was slightly higher in the acid medium rather than in the alkaline one. The results showed that the sorption of dyestuffs at room temperature is a physical absorption, while at 700°C, it goes through chemical bonding.

References

1. Suzuki, N. et al. Int J Appl Rad Isotop 1975, 26, 726.
2. Karadag, E. et al. Water Air Soil Pollut 1998, 106, 369.
3. Burczak, F. T.; Ikada, Y. Proc Jpn Acad Ser B 1991, 75(5), 83.
4. Hegazy, S. A.; Abdel-Aal, S. E.; Abdel-Rehim, H. A.; Khalifa, N. A.; El-Hosseiny, E. M. In Conference of Nuclear Sciences and Applications, Cairo, Egypt, Feb. 6–10, 2000.
5. El-Salmawi, K. M.; Abu Zaid, M. M.; Ibraheim, S. M.; El-Naggar, A. M.; Zahran, A. H. J Appl Polym Sci 2001, 82, 136.
6. Shantora, V.; Huang, R. Y. M. J Appl Polym Sci 1981, 26, 3223.
7. Koyama, K. et al. J Appl Polym Sci 1982, 27, 2845.
8. Peter, S.; Stefan, R. In Proceedings of the International Symposium of Fresh Water from the Sea; Delyannis, E., Ed.; Athens, 1980; Vol. 2, p 197.
9. Peter, S.; Hense, N.; Stefan, R. Desalination 1976, 16, 161.
10. Katz, M. G.; Wydeven, T. J Appl Polym Sci 1981, 26, 2935.
11. Abd El-Rehim, H. A.; El-Sayed Hegazy, A. M. A. J Appl Polym Sci 1999, 74, 806.
12. Piccinini, N.; Ferrero, F. In International Atomic Energy Agency Symposium, Vienna, 1975; p 249.