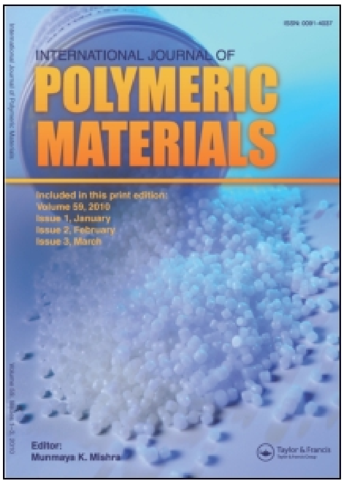

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EFFECT OF CHEMICAL CROSSLINKING ON SWELLING PARAMETERS OF MODIFIED POLY(VINYL ALCOHOL) HYDROGEL

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Graft copolymerization of maleic anhydride (MA) onto partially and fully hydrolyzed poly(vinyl alcohol), PVA, was carried out in presence and in absence of an initiator. The structural features of these grafts were confirmed by ^{1}HNMR analysis. ^{1}HNMR analysis was also used to determine the percentage of grafting. These grafts were crosslinked using different concentrations of either 1,1,1-trimethylolpropane trimethacrylate (TPT) or methylene bisacrylamide (MBA) as Hexa- or tetra-functional crosslinker, respectively. The crosslinkers concentrations ranged from 1% to 30% (wt.%) based on the total weight of grafts. The final water content, volume fraction of the polymer and swelling capacity were determined for all grafts. The effect of MBA and TPT crosslinkers structure on swelling properties of both partially and fully hydrolyzed PVA grafts were also determined.

Keywords: poly(vinylalcohol), modification, hydrogel, chemical crosslinking, swelling parameters

INTRODUCTION

Because of the industrial importance of poly(vinyl alcohol), PVA, it has been the subject of an extensive technical and scientifical literature. Due to the high number of alcohol groups, PVA is one of the most polar and hydrophilic synthetic polymers, it also forms hydrogel [1]. The gel has attracted much attention as a material for artificial muscle or a gel actuator [2]. As pure PVA hydrogels are insensitive to pH changes,

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several recent studies have been reported, where Poly(Acrylic Acid) (PAA) has been mixed with PVA to produce pH-sensitive gels [3, 4–6]. The ionic component of PAA is typically entangled between the semicrystalline PVA chains and forms hydrogen bonds [7–9].

The PVA chains are physically cross-linked by repeatedly freezing and thawing of PVA solutions [3, 7, 10–12]. Also, it was prepared by irradiation methods and reinforced by heat treatment techniques at moderate to high temperatures [13, 14]. In several reports, the physical gel was treated with Glutaraldehyde (GA) in order to introduce covalent cross-links in the network structure [11, 12]. However, because of the high hydrophilicity of PVA, it is usually turned into a completely insoluble material by grafting copolymerization with a hydrophobic monomer [15].

The present investigation aims to prepare PVA hydrogels using chemical cross-linkers. In this respect modified PVA, having different ratios of maleic anhydride (MA) side chains were cross-linked with different concentrations of either hexa- or tetra-functional chemical cross-linking agents. The influence of PVA composition as well as the functionality and concentration of the cross-linking agent, on the swelling parameters of the produced hydrogels are considered.

EXPERIMENTAL

Materials

Two types of poly(vinyl alcohol) (PVA), partially and fully hydrolyzed, were obtained from Aldrich Chemical Co. Inc. (UK). The degree of polymerization for the two types is $D_p = 1750$ and the degree of hydrolysis for the partially and fully hydrolyzed PVA is 88% and 98%, respectively. The PVA samples were purified by repeated solubilization in water and precipitation with methanol. Maleic anhydride (MA) and dimethyl sulfoxide (DMSO) of reagent grade were purchased from Aldrich Chemical Co. Inc. (UK). Hexa-functional cross-linker 1,1,1-trimethylolpropane trimethacrylate (TPT) and tetra-functional cross-linker methylene bisacrylamide (MBA), were also purchased from Aldrich Chemical Co. Inc. (UK) and were used without further purification. Potassium persulfate (KPS) of reagent grade used as initiator was purchased from Kanto Chemical Co. Solvents such as chloroform, methanol and acetone were used as supplied. The water employed for swelling measurements was bidistilled and deionized.

Procedure

Preparation of PVA-MA Grafts

All graft copolymerization of MA onto partially and fully hydrolyzed PVA were carried out in four-necked flask fitted with a mechanical stirrer, thermometer, condenser and nitrogen inlet. As an example, the general experimental procedure is as follow [15]: PVA 5 g and MA 5 g were dissolved in 95 g DMSO and stirred in an atmosphere of nitrogen. The reaction temperature was adjusted as needed (such as 60°C), then 0.5 g of KPS was added as an initiator (if needed) for 5 h. The reaction was stopped at the predetermined reaction time by adding small amount of hydroquinone. The reaction mixture was concentrated to about 20% of its original volume at 60°C under a reduced pressure and was then added to chloroform to precipitate the polymer.

The products precipitated from chloroform were a mixture of grafted copolymer, unreacted PVA and homopolymer of MA. They were separated and purified as reported by Chiang and Hu [15]. The grafted copolymers can be directly dissolved in acetone to eliminate the chloroform separation procedure. The PVA-MA grafts with high grafting percentage could be dissolved in distilled water as well as in methanol, where that of low grafting percentage could be dissolved only in water. Eight different grafts based on both partially and fully hydrolyzed PVA were prepared. The reactants composition and the reaction conditions are listed in Table 1.

The prepared PVA-MA grafts in presence or in absence of the initiator (KPS), were analyzed using Bruker 270-Hz ^{1}HNMR spectrometer type AC 250-F using deutrated DMSO as a solvent at ambient temperature and TMS as an internal standard.

TABLE 1 Sample Compositions and Percentage of Grafting

Sample	Full hydr. PVA g	Partially hydr. PVA g	DMSO g	MA g	KPS g	Temp. °C	% grafting %
PVA-F_{36}	5	–	100	6	–	100	36.3
PVA-F_{10}	5	–	100	2	0.3	60	10.2
PVA-F_{36}	10	–	200	10	0.1	60	36.2
PVA-F_{51}	5	–	200	10	0.3	60	51.4
PVA-P_{40}	–	5	100	6	–	100	40
PVA-P_{25}	–	5	200	2	0.3	60	25
PVA-P_{45}	–	10	200	10	0.1	60	45
PVA-P_{75}	–	5	200	10	0.3	60	75

Preparation of Crosslinked PVA with Heating

Eight grams of 10% aqueous solution of purified PVA grafts were cast in a tubes whose diameter was 0.8 cm. and allowed to dry at 30°C in a vacuum to constant weight before the rods was removed from the tubes. Then the rods were treated in an oven at 150°C for 10 h.

Preparation of Chemically Crosslinked PVA

Both partially and fully hydrolyzed modified crosslinked PVA-MA grafts were prepared *via* solution polymerization technique using water as solvent in the presence of appropriate amount of the KPS initiator and different weight percentages of MBA or TPT crosslinker. The overall concentrations of TBT or MBA crosslinkers were varied from 1% to 30% [wt.%]. The polymerization techniques were reported in our previous papers [16–18]. The designations of the resultant xerogels for the partially and fully hydrolyzed PVA grafts crosslinked with TPT and MBA will be denoted as PVA-$P_{(x)}$-$CL_{(y)}$ and PVA-$F_{(x)}$-$CL_{(y)}$ where (x) and (y) are the percentage of grafting and crosslinker (CL) respectively.

Sol Fraction

The crosslinked polymer rods were post-cured at 105°C in an air oven for 24 h to ensure complete curing. These rods were cut to thin disks and dried in vacuum at 35°C to a constant weight. The dried xerogels discs were transferred into an extraction thimble and were subjected to Soxhlet extraction with deionized water to determine sol fraction, SF [16].

The sol fraction (SF) is expressed as the fractional loss in weight of xerogel, *i.e.*,

$$\%\mathbf{SF} = \frac{W_O - W}{W_O} \times \mathbf{100} \tag{1}$$

where $\mathbf{W_o}$ and W are the weights of the disc before and after extraction respectively.

Swelling Behavior

The swelling parameters: swelling capacities (q), equilibrium water content (EWC) and volume fraction (Φ_p) of the polymeric hydrogel, were determined as reported in previous papers [17]

- The EWC of the gels were calculated from Eq. (2)

$$\mathbf{EWC} = \frac{wt.\ of\ gel - wt.\ of\ xerogel}{wt.\ of\ gel} \times \mathbf{100} \tag{2}$$

- The swelling capacity of the disks ($\mathbf{q}$) was calculated from Eq. (3)

$$\mathbf{q} = \frac{d^2 b}{d_O^2\ b_O} \tag{3}$$

Where $\boldsymbol{b_O}$ and $\boldsymbol{b}$ are the thickness, $\boldsymbol{d_O}$ and $\boldsymbol{d}$ are the diameter of the disk before and after swelling, respectively.

- The volume fraction (Φ_p) of the polymeric hydrogel was obtained from the measured diameters $\mathbf{d_O}$ and $\mathbf{d}$ for the disk, where

$$(\Phi_p) = \{\mathbf{dd_O}\}^3$$

RESULTS AND DISCUSSION

Chemical Structure of the Grafts

The structure of the PVA-MA grafts is confirmed by ^{1}HNMR spectroscopy. The ^{1}HNMR spectrum of a grafted fully hydrolyzed PVA copolymer with MA, PVA-F_{50}, is selected and represented in Figure 1a to illustrate the structure of the grafts. On the other hand, the ^{1}HNMR spectra for different percentages of grafted partially hydrolyzed PVA copolymer with MA (PVA-P-MA%) were used to deduce the percentage of MA grafted onto PVA-P and are shown in Figure 1b–d. For PVA-P-MA%, the hydroxyl proton has a chemical shift at (~2.75 ppm), while the backbone methylene and the proton of –CH attached to hydroxyl group have chemical shifts at (0.8 ppm) and (1.75 ppm) respectively. These types of chemical shifts are observed in the spectra of all grafts. The difference between PVA-F-MA% and PVA-P-MA% grafts is focused in the appearance of a signal at (3.75 ppm) assigned for the backbone –CH attached to the acetate group of PVA-P-MA grafts.

In some recent published articles [19–21], ^{1}HNMR analysis has been used for determining the chemical composition of grafts or block copolymers through integration of the characteristic signals. Accordingly, the same procedure was applied through this work for determining the grafting percentage of the synthesized grafts. In this

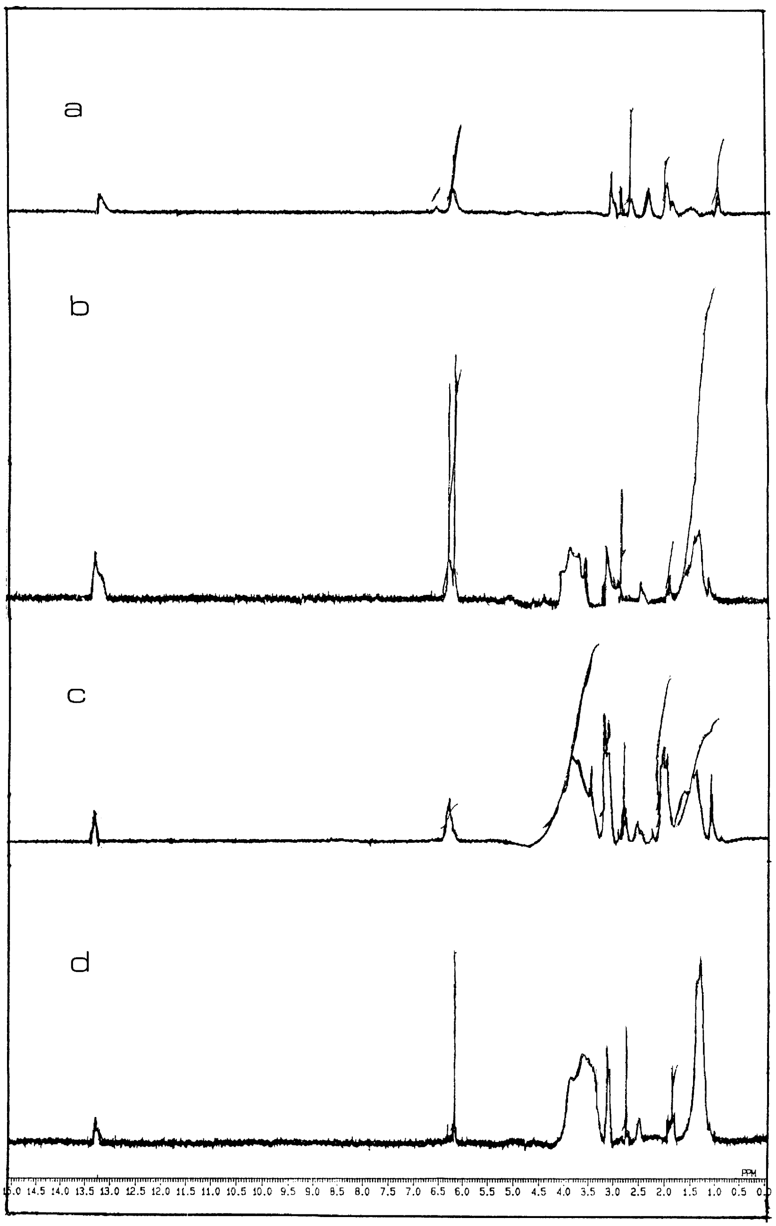

FIGURE 1 ^{1}HNMR spectrum of (a) PVA-F_{50} (b) PVA-P_{25} (c) PVA-P_{45} and (d) PVA-P_{75}.

respect, the composition analysis is based on comparing the integration of mainly two signals, at 2.75 ppm (assigned to ungrafted –OH protons of PVA) and 13.3 ppm (assigned to –COOH protons of MA). The ratio of the integrals of the specified signals was utilized successfully for determining the percentage of grafting. The integrations of (–CH=CH–) protons of MA observed at 6.65 ppm were also used to judge the accuracy of such determination. Sample compositions and calculated percentage of grafting using ^{1}HNMR peak integrations were listed in (Table 1). The values of the percentage of grafting estimated *via* ^{1}HNMR spectra for the fully hydrolyzed PVA grafted with MA were in harmony with that obtained by Chiag and Hu [15] . Also, the values listed for the percentage of grafting Table 1 indicate that the percentage of MA in PVA grafts increases with increased degree of hydrolysis of PVA. This can be attributed to the increase in polarity. The decreased degree of hydrolysis of PVA, results in enhanced probability for the reaction of PVA with MA.

Crosslinking of PVA-MA Grafts

The crosslinked PVA prepared by heat treatment is glassy at room temperature. Also, it does not dissolve in water but forms a swollen hydrogel. The physical states of crosslinked modified PVA-MA were dictated by the percentage of the chemical crosslinker MBA or TPT. Crosslinked PVA with tetra-or hexa-functional crosslinker are elastomeric when 1–2.5% MBA or TPT were used, extending to leathery when MBA or TPT content is increased from 5–10%. Glassy xerogels are obtained for MBA or TPT content above 10% by weight. This difference in the physical appearance may be attributed to different cross-link densities in grafts. Also the xerogels obtained from PVA-MA with KPS initiator are more rigid than that prepared without initiator. This may be due to a higher level of unsaturated double bonds of MA introduced as grafts in presence of KPS initiator, than when no initiator is added [15].

Sol Fraction

When the gel is synthesized a certain fraction of the reactants will fail to be incorporated into the network, such material is known as the sol fraction (SF). In this respect, the xerogels were subjected to Soxhlet extraction to remove the soluble fraction (as described in the experimental section). The SF values of the prepared partially and fully hydrolyzed PVA crosslinked with either MBA or TPT were measured and represented in Figures 2 and 3. The data show that the sol

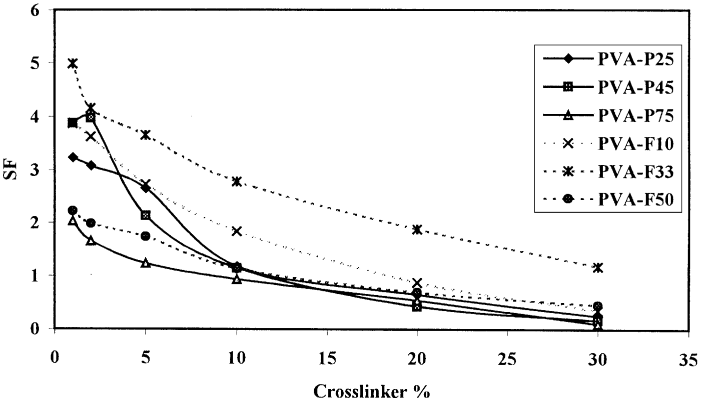

FIGURE 2 Sol fraction of partially hydrolyzed grafted PVA with different percentages of MBA.

fractions generally decrease with increasing the MBA or TPT crosslinker content. Also, it can be seen that the sol fractions upon using MBA are always less than those obtained when TPT is used for both types of hydrolysed PVA. This means that the functionality of the crosslinker affects the degree of crosslinking and SF. This finding reveals that MBA is more reactive than TPT towards PVA-MA grafts. On the other hand, SF values for crosslinked grafted PVA-P are higher than those for crosslinked grafted PVA-F upon using either crosslinkers, Figures 2 and 3. Accordingly, this finding may lead us to the speculation that, the reactivity of MBA or TPT crosslinker towards

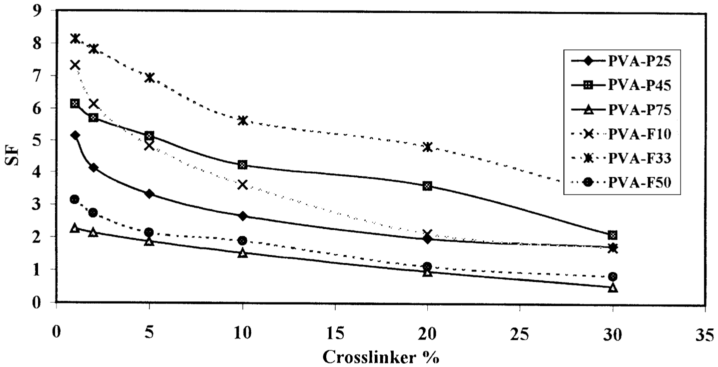

FIGURE 3 Sol fraction of partially hydrolyzed grafted PVA with different percentages of TPT.

TABLE 2 SF and Swelling Parameters of Grafted Partially Hydrolyzed PVA (without initiator) Chemically Crosslinked with MBA or TPT

Sample	Crosslinker %	EWC	SF	q	$\varphi_p \times 10^3$
PVA-P_{40}-MBA	1	98.69	4.14	76.3	8
	2	98.57	3.77	70.1	9
	5	98.48	3.13	65.6	10
	10	98.17	2.43	54.7	13
	20	97.74	1.53	44.3	14
	30	97.30	0.99	37.1	18
PVA-P_{40} TPT	1	96.51	7.77	27.1	22
	2	95.51	6.98	22.3	28
	5	94.65	6.13	18.7	33
	10	92.65	5.17	13.6	39
	20	91.15	4.62	11.3	44
	30	89.81	3.02	9.81	18

PVA is affected by its degree of hydrolysis. This means that PVA-F is more reactive towards the crosslinking agent than PVA-P. This finding is in harmony with previous findings [23, 24] at which the SF was related to the relative reactivity of the mixture components. The SF values estimated for both PVA-P-MA% and PVA-F-MA% xerogels prepared without. initiator were measured and listed in Tables 2 and 3.

TABLE 3 SF and Swelling Parameters of Grafted Fully Hydrolyzed PVA (without initiator) Chemically Crosslinked with MBA or TPT

Sample	Crosslinker %	EWC	SF	q	$\varphi_p \times 10^3$
PVA-F_{36}-MBA	1	98.71	4.11	77.4	9
	2	98.61	3.13	72.1	12
	5	98.51	2.23	67.1	15
	10	98.28	1.56	58.3	18
	20	97.99	0.63	49.7	22
	30	97.49	0.25	39.8	29
PVA-F_{36}-TPT	1	97.47	6.78	38.5	18
	2	96.35	5.32	27.4	28
	5	95.67	4.98	23.1	35
	10	95.05	3.82	20.2	41
	20	94.41	2.65	17.9	53
	30	92.53	1.93	13.4	59

The highest SF values for these xerogels indicate the formation of less efficient networks.

The heat treatment of PVA without crosslinker give xerogels with zero SF. This may be attributed to the variation in the degree of crosslinking of such xerogels. The crosslinks may be formed through esterification or anhybride formation between carboxy1 and hydroxyl groups in PVA-MA grafts besides the intercrosslinking due to the presence of the unsaturation double bonds of MA [25].

Swelling Parameters

The swelling parameters (EWC, q and Φ_p) were determined for the prepared crosslinked PVA-MA grafts after removing the soluble fractions. A plot of the swelling capacities (q) for all prepared PVA hydrogels *versus* the percentage of crosslinker (both MBA and TPT), are represented in Figures 3 and 4.

The swelling parameters, EWC and q for PVA hydrogels crosslinked by heat treatment were determined and listed in Table 4. The hydration curves, EWC *versus* swelling time were determined and representative curves for PVA-P_{40}-MBA crosslinked with different percentages of MBA were illustrated in Figure 6. This figure shows that the overall swelling attains its maximum EWC at times from 3 h to 10 h based on the percentage of MBA crosslinking agent. This behavior was observed for all other systems. The shape of these curves reveals that a very high initial rate of swelling is evident by the

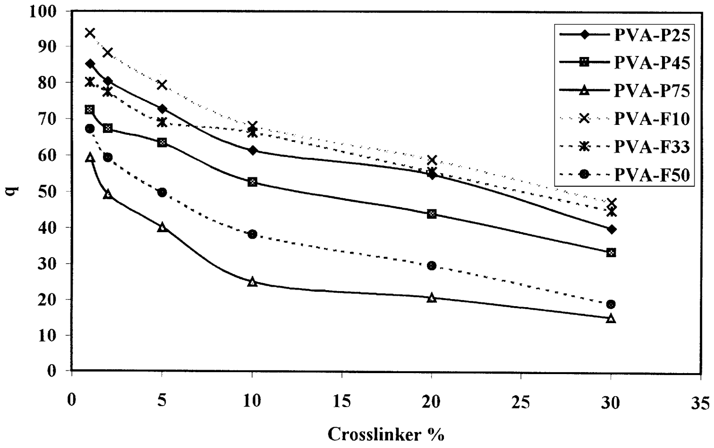

FIGURE 4 Swelling capacities of partially and fully hydrolyzed grafted PVA with different percentages of MBA.

TABLE 4 SF and Swelling Parameters of Heat-treated PVA-MA Grafts

	Partially hydrolyzed PVA				Fully hydrolyzed PVA		
% of grafting	EWC	q	φ_p	% of grafting	EWC	q	φ_p
25	98.33	60.0	0.0166	10	98.49	66.4	0.0156
40	95.51	22.3	0.0448	33	96.43	28.0	0.0357
45	83.33	6.0	0.166	36	87.50	8.0	0.1250
75	75.00	4.0	0.250	50	83.33	6.0	0.1666

attainment of maximum EWC within the first 3 h, and indeed most of the water is absorbed within 30 min. The attainment of a plateau which represents constant value of EWC indicates no water soluble materials were leached out during swelling and confirms the aptness of the technique used for removing the soluble fractions [17].

Comparing the swelling parameters for hydrogels crosslinked by heat treatment with those crosslinked by using MBA or TPT crosslinkers, it was observed that the water content of PVA-MA discs after heat treatment was less than in those prepared by chemical crosslinking. This may be attributed to the high crosslink density which arises from intercrosslinking or reaction between carboxyl and hydroxyl groups in the heat treated PVA. This behavior will affect the concentration of the ionic carboxyl groups of the heat-treated PVA, which in turn decreases the swelling capacities. On the other hand, the water content of PVA-MA discs after heat treatment, decreases when KPS initiator was used in the modification process except in case of PVA-P_{25} and PVA-F_{10}. This may be due to two main reactions introduced in the presence of KPS initiator: esterification with –OH group and grafting copolymerization at PVA main chain [26] and thus show higher crosslink densities than others.

Several works [3, 7, 11] were reported for preparing PVA hydrogels either by heating or freezing–thawing techniques. Hickey and Peppas [3] proved that the swelling capacity of composite membranes of PVA-poly(acrylic acid) (PAA) prepared by freezing and thawing, increases with the PAA content. Here, the higher swelling capacities for crosslinked PVA-MA grafts with TPT or MBA than that prepared by heat treatment, may be due to the ionization of the carboxylic groups of MA moieties and also due to the formation of crosslinked networks.

From the stand point of ultimate end use, special interest is centered on hydrogels of high water content. The data of swelling

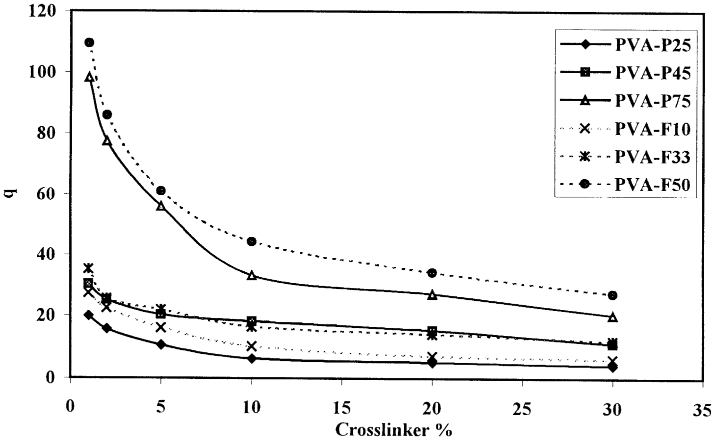

FIGURE 5 Swelling capacities of partially and fully hydrolyzed grafted PVA with different percentages of TPT.

measurements show that the EWC and q for crosslinked PVA grafts were completely different when MBA was replaced by TPT. It is observed that upon using MBA as a crosslinker for both types of hydrolyzed PVA Figure 4, the swelling capacities (q) increase with decreasing the percentage of MA grafted onto PVA. This may be

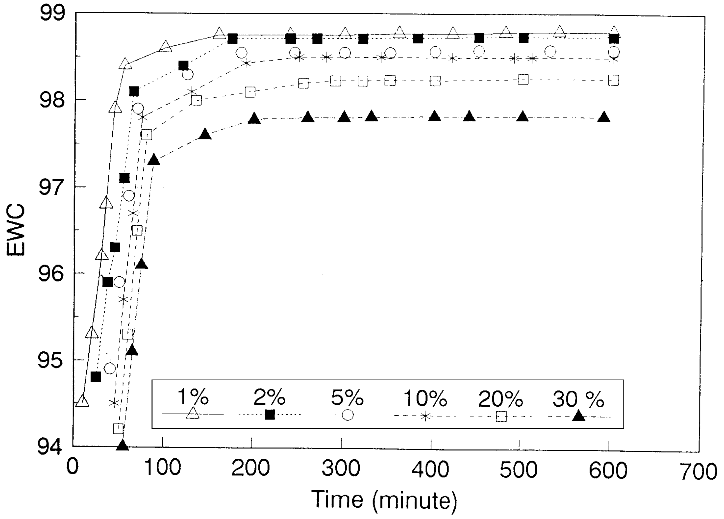

FIGURE 6 Hydration curves for PVA-P_{40} crosslinked with various concentrations of MBA.

attributed to the effect of chemical composition hydrophilicity, chemical structure of the polymer, crosslink densities and in the majority of cases, functionality of the crosslinkers [27]. In contrast, the swelling properties of crosslinked PVA-MA with TPT hydrogels Figure 5 are directly proportional to the degree of unsaturation. In this respect, both PVA-P_{75}-TPT and PVA-F_{50}−TPT (Figure 5) show superior swelling characteristics over other compositions. This may be due to the presence of linear dangling chains or network chains having one end attached at the crosslink point and the other unattached to the network [28]. Such dangling chains contribute to the swelling of the polymer [28]. This leads to the idea that the third double bond in TPT affords an opportunity of forming many dangling chains which in turn accounts for the extra swelling of the discs. Where the ability for the formation of dangling chains, which increases with increasing the degree of unsaturation (% MA on PVA), reflects the high swelling capacities of these polymers. This situation is, of course, not present in case of MBA crosslinker.

The effect of crosslinker concentration on the swelling behavior of crosslinked PVA with either MBA or TPT 15 the same in both cases. It can be seen that the swelling capacity of the prepared hydrogels decreases with increasing crosslinker concentrations. This can be explained by the restiction in expansion of the network structures with increasing the cross-link density.

CONCLUSIONS

The following conclusions may be drawn from the above mentioned results:

- The percentage of grafting of MA onto PVA can be calculated by ^{1}HNMR analysis. The percentage of MA grafted increases by decreasing the degree of hydrolysis of PVA.
- The chemically prepared crosslinked PVA with MBA or TPT are characterized by high EWC when swollen in water.
- The swelling capacity data shows that the extraction regime used for removing the soluble fractions is an efficient technique.
- The higher water content upon using MBA as crosslinker, increases with decreasing the percentage of MA grafted onto PVA and the degree of hydrolysis.
- The higher swelling capacity upon using TPT as crosslinker instead of MBA increases with increasing MA side chain content due to dangling chain formation.

- For the swollen modified PVA hydrogels, the water content is inversely proportional to the reactivity of the crosslinker towards PVA.

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