RADIATION GRAFTING OF HIDROPHILIC MONOMERS ONTO POLYVINYL ALCOHOL SUBSTRATE

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BADAN TENAGA ATOM NASIONAL

PUSAT APLIKASI ISOTOP DAN RADIASI

JL. CINERE PASAR JUMAT, KOTAK POS 2, KEBAYORAN LAMA, JAKARTA SELATAN

RADIATION GRAFTING OF HYDROPHILIC MONOMERS ONTO POLY(VINYL ALCOHOL) SUBSTRATE#

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ABSTRACT

RADIATION GRAFTING OF HYDROPHILIC MONOMERS ONTO POLY(VINYL ALCOHOL) SUBSTRATE. The effort of grafting several hydrophilic monomers onto poly(vinyl alcohol) has been done. Hydrophilic monomers used are N-vinylpirrolidone (N-VP), Hydroxyethyl methacrylate (HEMA), and Polyethylene Glycol # 600 Dimethacrylate (14 G). By using an autoclave, 15 weight % of PVA aqueous solution was prepared. The solution to be cooled at 70°C and then 10 phr of monomer liquid was added. Irradiation was carried out by using gamma rays from a Cobalt-60 source. Before irradiation, hydrophilic monomers and PVA substrate mixture was treated with various methods. After Irradiation, mechanical properties, water absorption, and heat resistance of hydrogels were studied. It was found that mechanical properties as well as heat resistance of hydrophilic monomers grafted PVA hydrogels do not improve if it is compared to ungrafted PVA hydrogels.

These results indicate that the methods for the preparations of grafted PVA should be modified to obtain a better properties.

ABSTRAK

RADIASI GRAFTING MONOMER HIDROFILIK PADA SUBSTRAT POLI(VINIL ALKOHOL). Telah dilakukan upaya menggrafting beberapa monomer hidrofilik pada substrat poli(vinil alkohol). Monomer hidrofilik dimaksud adalah N-vinilpirolidon (N-VP), hidroksietil metakrilat (HEMA), dan etilen glikol # 600 dimetakrilat (14 G). Larutan poli(vinil alkohol) 15 % b/v dalam air dibuat dengan bantuan pemanasan dalam autoclav.

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Larutan didinginkan hingga suhu 70°C, lalu ditambahkan

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monomer dengan konsentrasi 10 phr.Iradiasi dilakukan dengan menggunakan sinar gamma dari sumber Kobalt-60. Sebelum diiradiasi, campuran monomer dan substrat diolah dengan berbagai metoda. Setelah iradiasi, dilakukan pengamatan terhadap sifat mekanik, absorpsi air dan daya tahan panas dari hidrogel yang dihasilkan. Didapatkan bahwa sifat mekanik maupun daya tahan panas hidrogel PVA yang digrafting dengan monomer tidak lebih baik jika dibandingkan dengan PVA hidrogel tanpa grafting. Hasil yang diperoleh ini menunjukkan bahwa perlu dilakukan modifikasi lebih lanjut pada pembuatan grafting PVA untuk mendapatkan sifat-sifat hidrogel yang lebih baik.

INTRODUCTION

Poly(vinyl alcohol) henceforth also referred to as PVA is one of synthetic polymers that widely used in pharmacy and medical. This hydrogel has been studied extensively along time ago , but

as biomaterial, study on it still several years ago. The application of PVA hydrogel as biomaterial included contac lens, artificial kidney, skin replacement, immobilize enzyme, and vitrous body (1,2,3). N.A. PEPPAS (4) presented that application of PVA as contact lens is not more succes than PHEMA, because of high water content and poor optic properties.

Recently methods were developed to prepare hydrogels, especially PVA hydrogel. The methods are based on the freezing PVA aqueous solution. Phase separation to water rich and PVA rich phase take place when PVA sulotion is frozen. The frozen solution is gradually warmed to defreeze. During warming, the mobility of PVA Segments increase and partially crystallize to form microcrystals which act as physical crosslinking in the hydrogels (4,5). The disadvantage of hydrogel prepared by freezing method is the heat resistance of hydrogel is not enough to sterilize with hot water.

Ionizing radiation is another method to prepare PVA hydrogel. Irradiation of aqueous PVA solution with gamma rays from a Cobalt-60 source lead to the hydrogel formation. By this method grafting and/ or crosslinking formed may improve heat resistance as well as mechanical properties.

EXPERIMENTAL

1. Materials.

PVA which has average degree of polymerization 1700 and degree of saponification 98-99 mol % , N-VP, HEMA, and 14 G were used directly without further purification.

2. Procedure.

By using an autoclave, 15 wt % of PVA aqueous solution was prepared. The solution to be cooled at 70°C and then 10 phr of monomer liquid was added. PVA hydrogel films were then prepared from the mixture by several methods as follows:

I. The mixture was poured into a double glasses plate , and kept it at room temperature for 24 hours.

II. The mixture was poured into single glass plate and kept it at roomt temperature for 5 days.

III.The mixture was poured into a double glasses plate, put in freezer at -40° C for 16 hours and followed by puting it in refrigerator at 5° C for 7 hours and finally kept at room temperature.

IV. The film that was obtained from the treatment III, then heated in oven at 60° C to obtain xerogel.

The PVA hydrogel film that was obtained from each treatment above was placed in a polyethylene (PE) bag and before sealed, nitrogen gas was allowed. Irradiation was carried out by using gamma rays from a Cobalt-60 source at room temperature. The dose rate of gamma irradiation field was measured with Fricke dosimeter. The schematically preparation of hydrogel film presented on Figure 1.

After irradiation, degree of swelling, mechanical properties, and

head resistance of films were observed.

Degree of Swelling

PVA hydrogel film was immersed in water up to water saturated achieved and then it was weighed (Ws). The film was then dried in oven at 60° C until a constant weight achieved (Wd).

$$DS = \frac{Ws - Wd}{Wd} \quad \ldots\ldots\ldots\ldots\ 1$$

Mechanical properties

Mechanical properties such as tensile strength and elongation at break were determined according to ASTM (6). The sample was

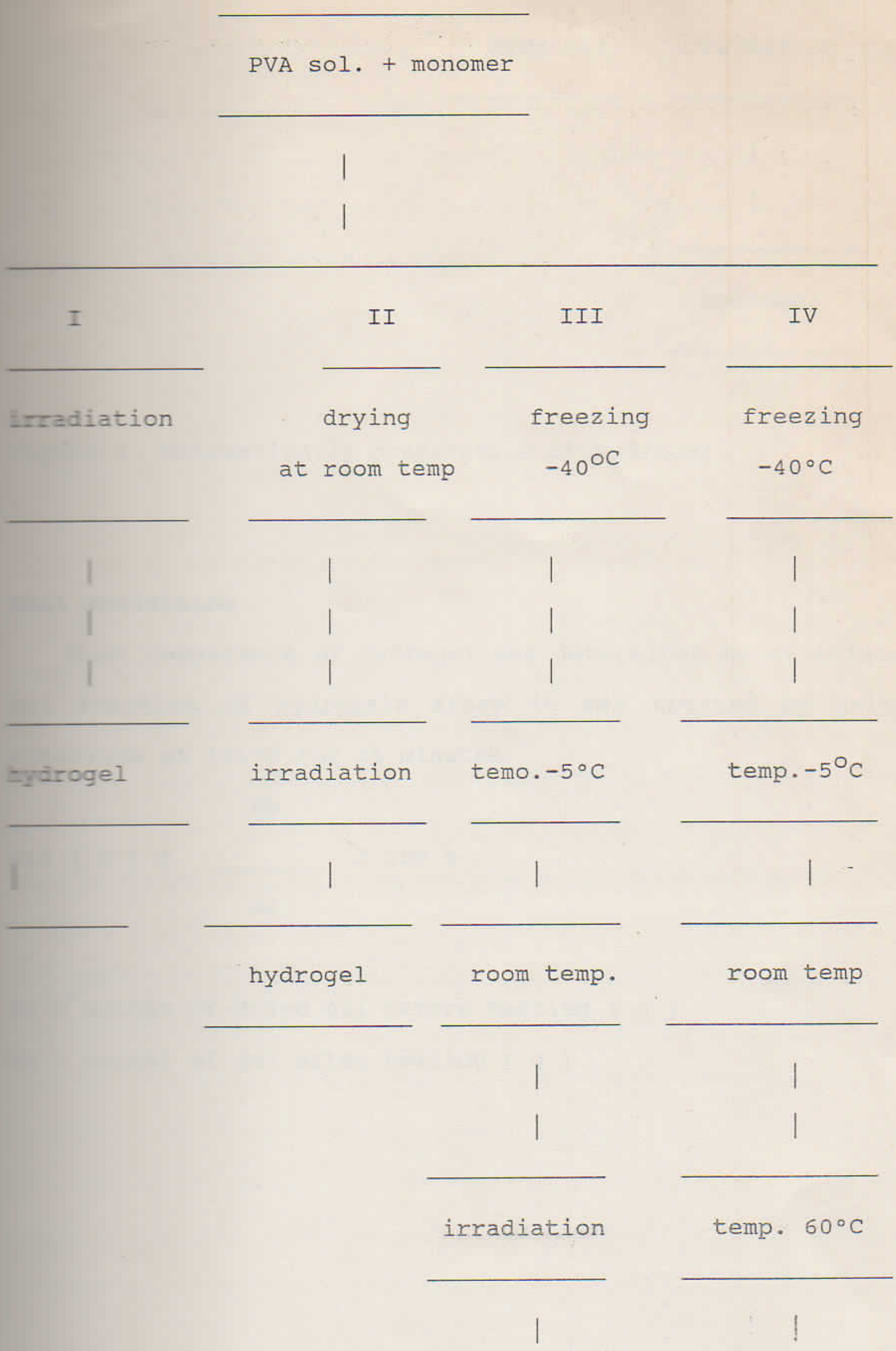
immersed in water until the maximum swelling (about 48 hours) achieved. Cut it into dumbble shape previously measured by using Instron Universal Testing Instrument model 1122.

$$TS = \frac{\text{load (kg)}}{\text{width (cm) X thickness (cm)}} \quad \ldots\ldots\ldots\ldots 2$$

$$EB = \frac{L1 - Lo}{Lo} \times 100\ \% \quad \ldots\ldots\ldots 3$$

Lo = gage length of sample (cm)

L1 = length of sample at break down (cm


PVA sol. + monomer
I
II
III
IV
irradiation
drying
at room temp
freezing
-40oC
freezing
-40°C
hydrogel
irradiation
temo.-5°C
temp.-5oC
hydrogel
room temp.
room temp
irradiation
temp. 60°C

hydrogel → irradistion → hydrogel

Figure 1. Schematically preparation of hydrogel.

Heat resistance

Heat resistance of hydrogel was determined by calculate gel fraction of hydrogels after it was treated by using autoclave at 121°C for 15 minutes.

$$\text{Gel}\ (\%) = \frac{Wb}{Wa} \times 100\ \%$$

Wa = weight of dried gel before heating (g)

Wb = weight of gel after heating (g)

Water content

Hydrogel water content is determined as follows: The gels produced by irradiation was cuted in a certain size. It was then immersed in water up to maximum swelling (Wm), and dried it at 70°C until constant weight (Wd).

$$Wc\ (\%) = \frac{Wm - Wd}{Wm} \times 100\ \%$$

RESULTS AND DISCUSSION

1. Degree of swelling

The ability of hydrogel to absorp water is one of the important aspects in the case of the applications of hydrogel as biomaterials. Degree of swelling of PVA film significantly affected by the tecniques that was applied to prepare the film, kind of monomer and by irradiation dose, as can be seen on figure 2. From the four methods that have been used in this experiment, method I indicate the highest degree of swelling and further more followed by method III, method II and method IV. But the film produced by the method I is full with air bubble on the surface of film. This probably caused by the formation of several gases such as H2, CO, CH4, and CO2 during irradiation (7). By freezing the solution in temperature at -40°C in certain period of time before irradiation, the air bubble can be removed. Addition of monomer lead to decrease the swelling of gel as indicated on figure 3. Similar effect also seem by heating film before irradiation. It was also found that degree of swelling reduce along with the increases of irradiation dose. The decrease of swelling due to the increasing of crosslinking density of hydrogels.

2. Mechanical peoperties

Mechanical properties such as elongation and tensile strength were shown on figure 4 and 5. By using the method I, either elongation or tensile were not observed because the film is full with air buble so make it very poor in mechanics. Drying can improve tensile strength. In any case, the mechanical properties of PVA hydrogel films that was prepared by grafting was found to be inferior as they compared to that film without grafting (control).

3. Heat resistance

Heat resistance of PVA films have been tested by heating the films in an autoclave at 121°C for 15 minutes. The gels at before and after heating was weighed, then the gel fraction was calculated. It was found that there was no remained gel in the samples prepared by method II and IV. This indicate that the chemical crosslinking may not be occured during the two methods. The heat resistance of PVA hydrogel was found 93 to 99 % when it was prepared by treatment I, whereas 45 to 90 % when that was prepared by method IV. The result was presented on tabel 1.

Water content of gel after immersing it in water presented on Tabel 2. It was found that 90 to 99 % water content of gel produced when it prepared by methods I and III whereas 60 to 90 % water content produced by methods II and IV.

CONCLUSION

Several kind of hydrophilic monomers such as NVP, HEMA, and 14 G have been attempted to be grafted onto PVA substrate. It was found that the grafting does not capable to improve mechanical properties as well as heat stability.

Further experiment should be done in more details to obtain a high heat resistance of PVA hydrogel film.

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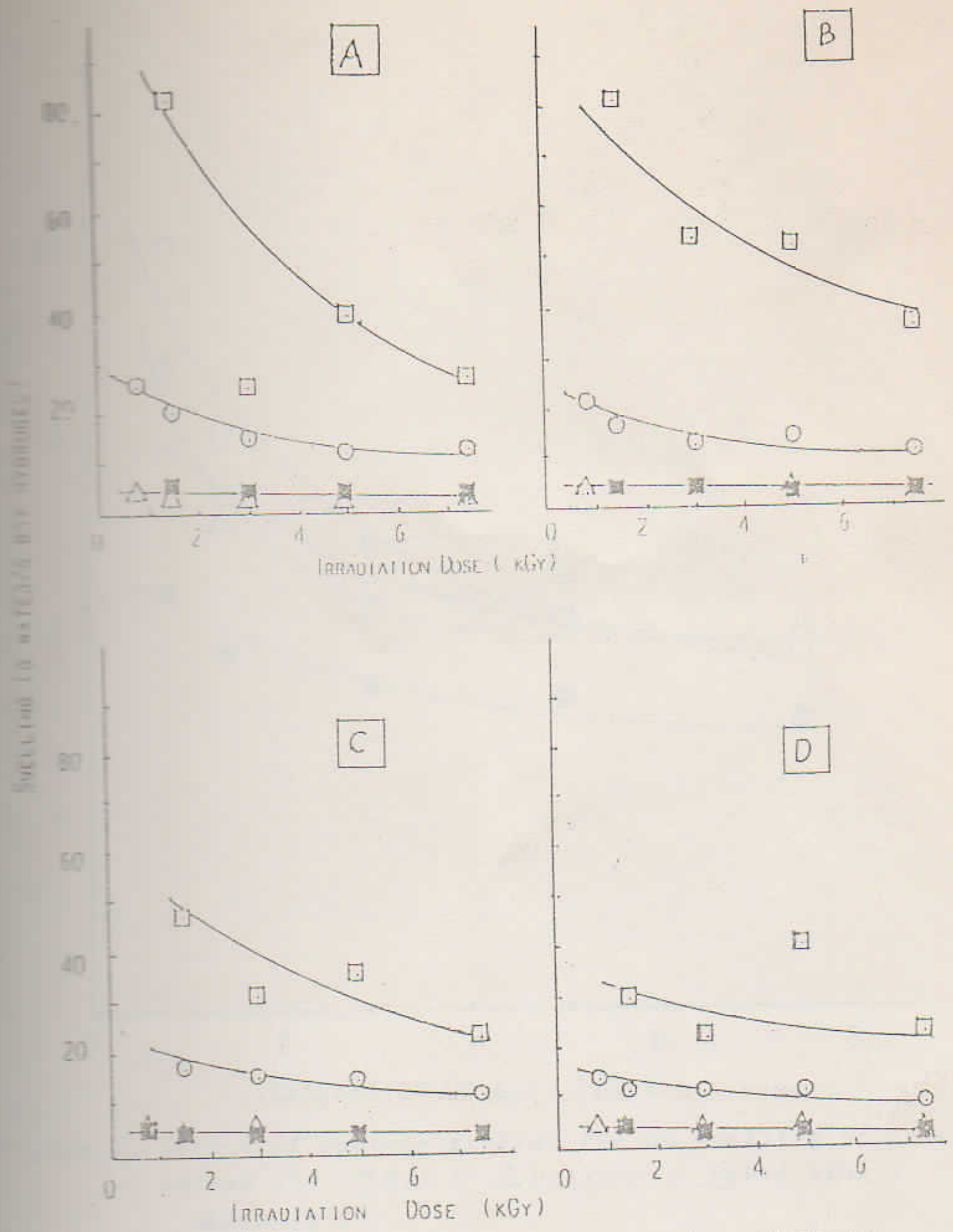
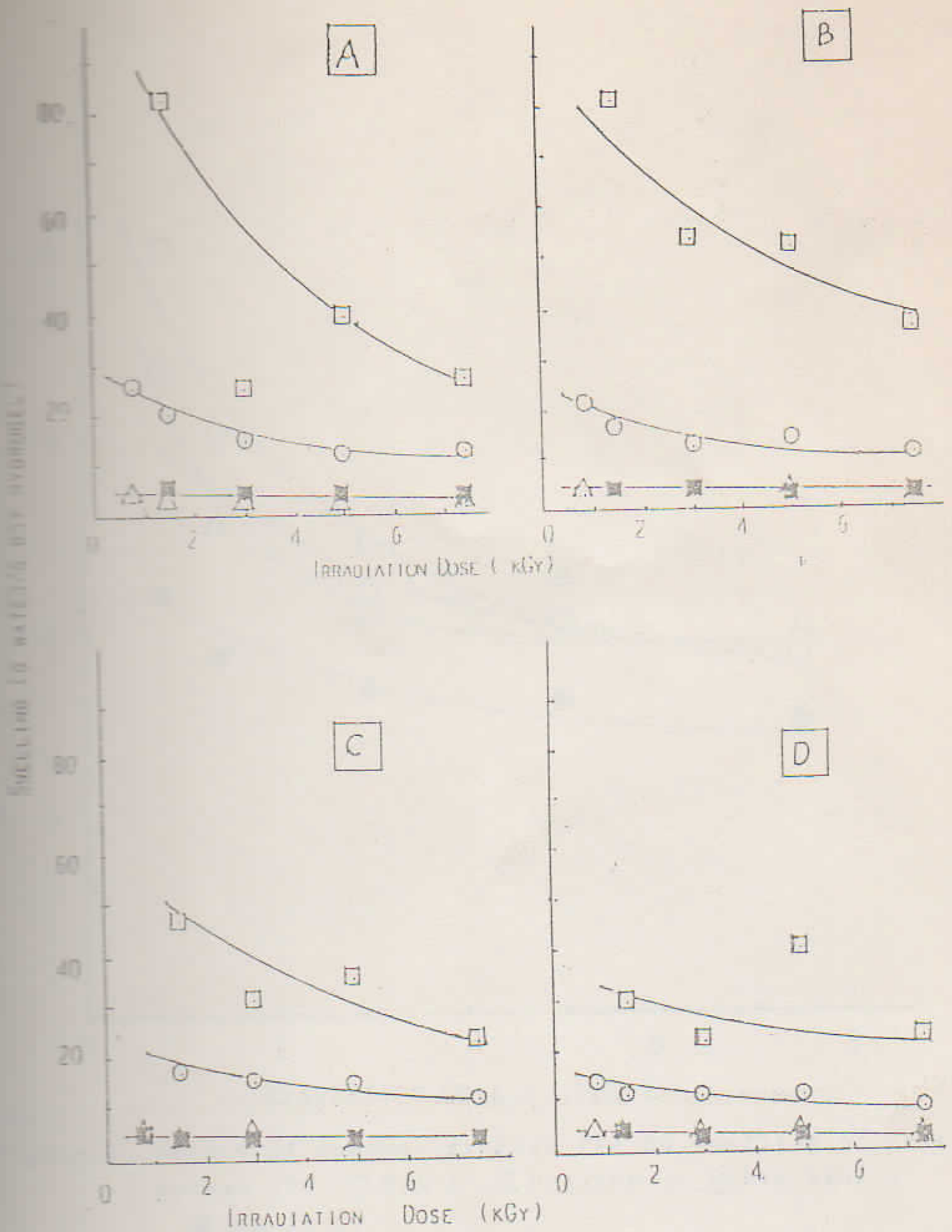


Figure 2. Swelling of gels in different irradiation methods and doses. A = PVA ; B = PVA-NVP ; C = PVA-HEMA ; D = PVA-14 G. □ = method I ; ▣ = method II ; ○ = method III ; △ = method IV.



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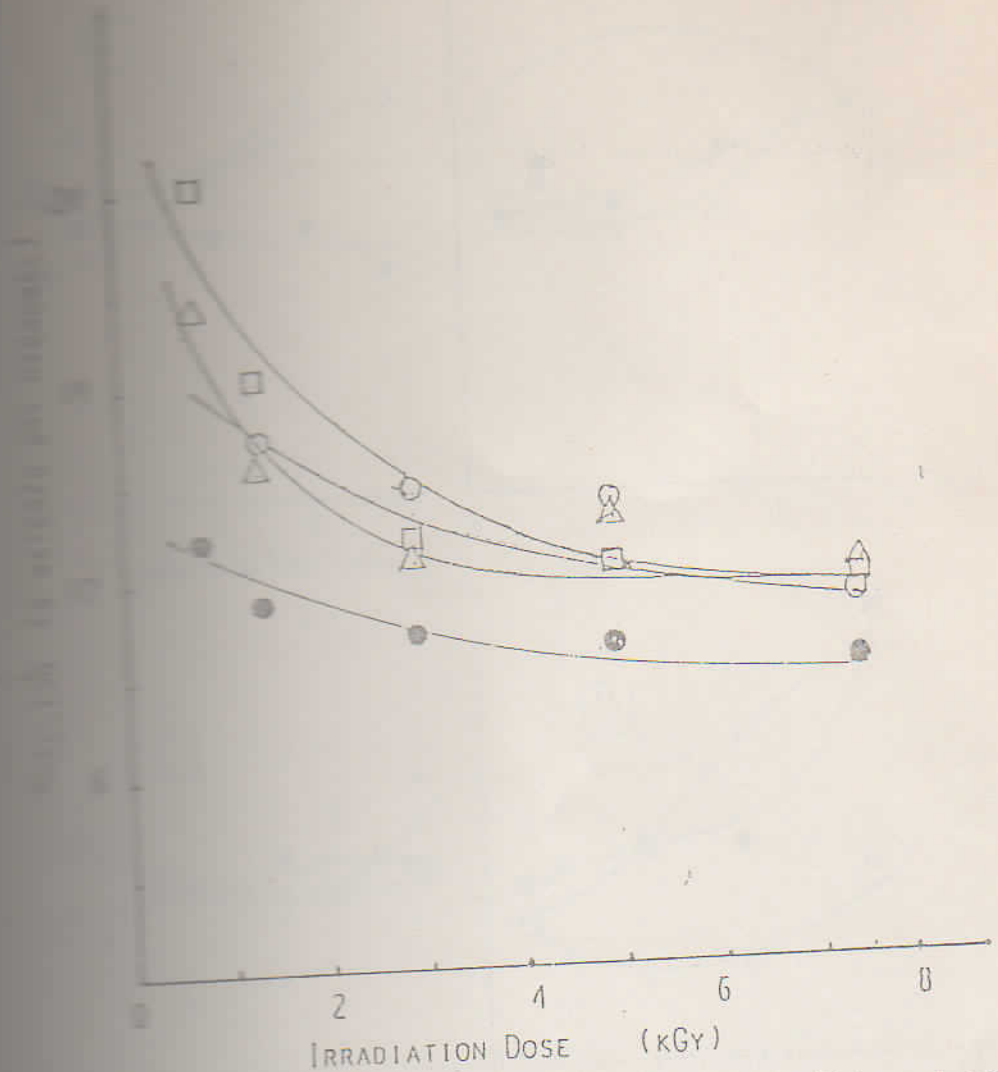

Figure 3. Effect of monomer-grafted PVA on swelling of gels by method IV. □ PVA ; △ PVA-NVP ; ○ PVA-HEMA ; ● PVA-14 G.

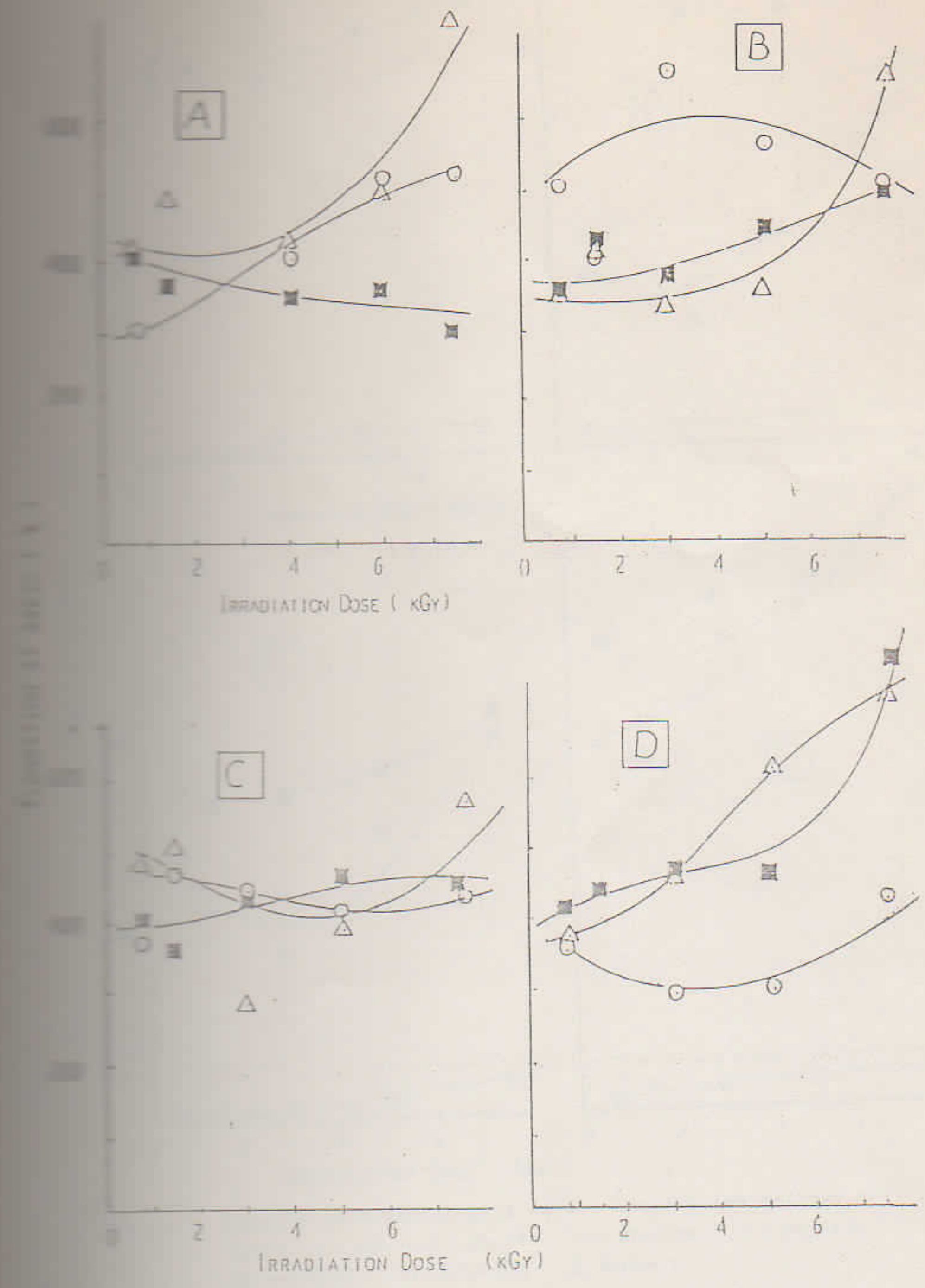

Figure [illegible]. Elongation at break of gels versus irradiation methods and doses. A = PVA ; B = PVA-NVP ; C= PVA-HEMA ; D= PVA-14 G.
■ Method II ; ○ method III ; △ method IV.

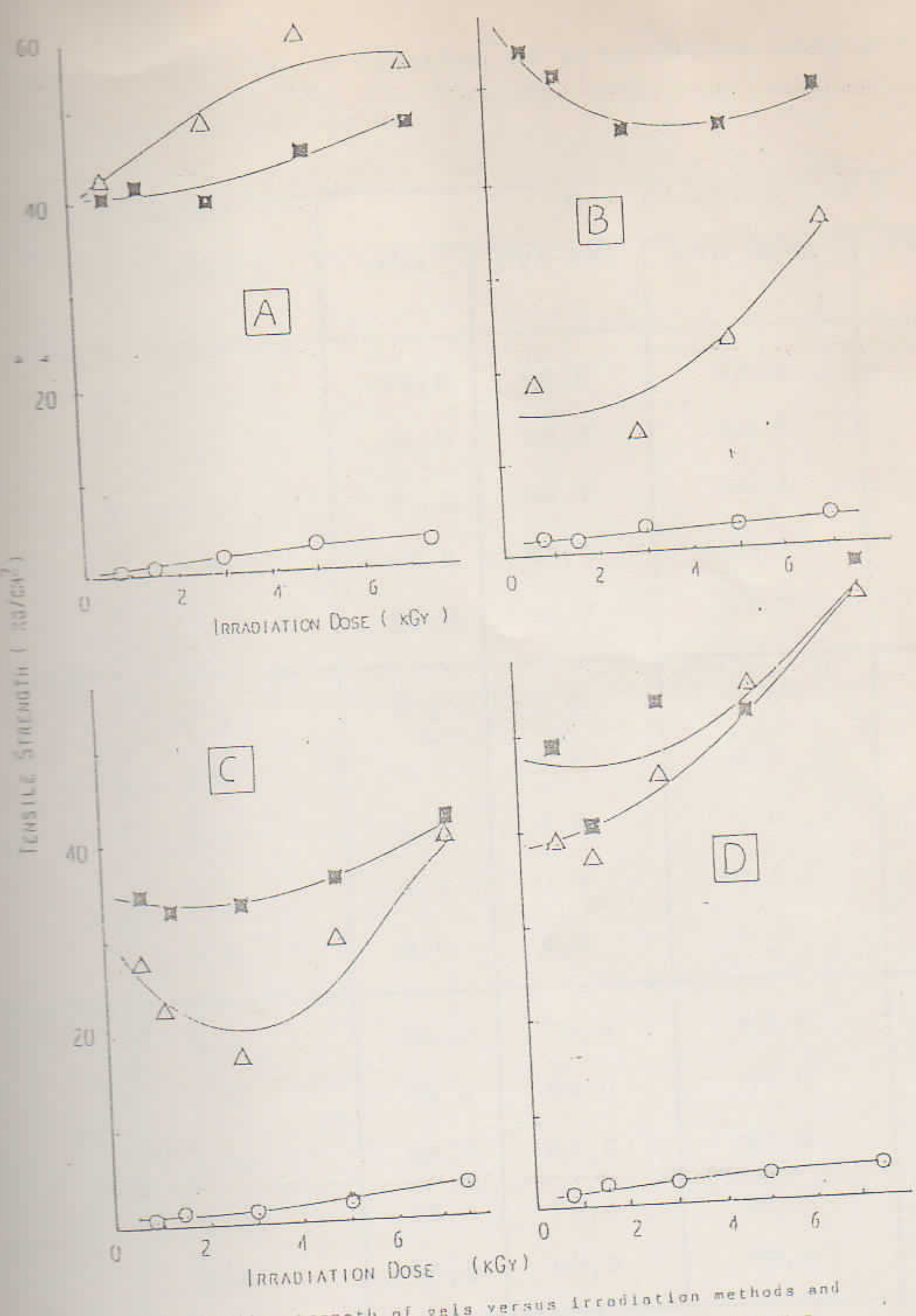

Figure 5. Tensile strength of gels versus irradiation methods and doses. A = PVA ; B = PVA-NVP ; C = PVA-HEMA ; D = PVA-14 G. ▣ method II : ○ method III : △ method IV.

Tabel 1. Gel fraction as a function of preparation method of film and irradiation doses.

preparation methods of film	dose (MRad)	Gel fraction (%)			
		PVA	PVA-NVP	PVA-HEMA	PVA-14G
I	0,8	95,0	94,0	93,8	94,1
	1,5	96,5	96,2	93,8	93,8
	3,0	96,8	96,7	98,6	98,2
	5,0	96,8	98,5	96,7	97,6
	7,5	99,0	98,7	98,7	99,0
II	0,8	0.0	0.0	0.0	0.0
	1,5	0.0	0.0	0.0	0.0
	3,0	0.0	0.0	0.0	0.0
	5,0	0.0	0.0	0.0	0.0
	7,5	0.0	0.0	0.0	0.0
III	0,8	46,2	70,0	43,4	52,4
	1,5	58,4	80,0	51,0	68,5
	3,0	68,7	84,0	91,9	79,2
	5,0	86,8	70,2	67,5	60,0
	7,5	85,9	80,0	75,0	86,0
IV	0,8	0.0	0.0	0.0	0.0
	1,5	0.0	0.0	0.0	0.0
	3,0	0.0	0.0	0.0	0.0
	5,0	0.0	0.0	0.0	0.0
	7,5	0.0	0.0	0.0	0.0