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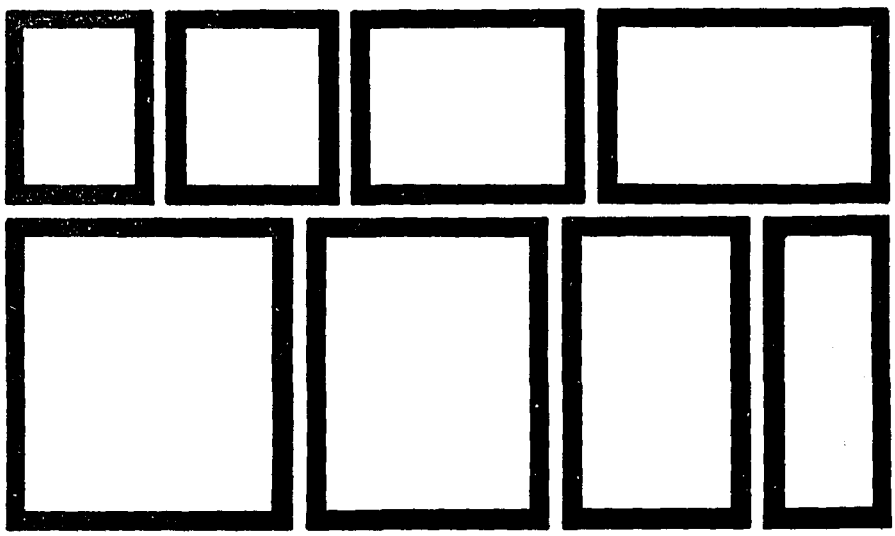
FORMULATION OF EB-CURABLE EPOXY RESIN : SOME IMPORTANT PARAMETERS



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MALAYSIA

FORMULATION OF EB-CURABLE EPOXY RESINS; SOME IMPORTANT PARAMETERS

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ABSTRACT

The works on the electron-beam curing of surface coatings using epoxy acrylic-based resins were discussed. The works covered among other things the effect of molecular weights of the resins on the physical properties of coatings and their physical and chemical characterizations. The emphasis was given to formulating the resins applicable to surface coatings. Curings were done on a low-energy electron beam accelerator operating at 250 kV. A number of parameters deemed important to formulation, such as the molecular weights of the oligomers and monomers, monomer ratios, and HEA additions were explored. It was found that one could modify the physical properties of the coatings by changing or adjusting those parameters.

INTRODUCTION

In recent years, radiation-induced polymerization as a means of curing of coatings has attracted a great deal of attention. Although a variety of radiation sources have been investigated, but the attention has been focused on the use of electron beam.[1,2,3] This is due to its several advantages over the conventional catalytic curing process and/or any other radiation methods. The major advantages are brought about by the energy saving, the use of solvent-free mixtures, high quality products, room temperature process, compact

processing equipment with resultant space saving and instantaneous start-up and shut-down capability. However, since the chemical principles of this curing method are somewhat different from the conventional ones from mechanistic point of view, special new formulations of the coating mixtures have to be found. Therefore it is the objective of this work to determine the basic formulations for newly-developed acrylate-based resins applicable to the surface coatings by studying the effects of their molecular weights, monomer types and functionality, and establishing guidelines for a formulation of EB-curable coatings with optimum physical properties.

The works in this report would describe commercial EB-curable resins with several different molecular weights. These resins possess three structural features that should make them of special interest to radiation curing applications:

1. the terminal acrylic group is expected to provide high reactivity towards polymerization,
2. the epoxy backbone is expected to provide the chemical resistance, the toughness, and the adhesion characteristics associated with epoxy structures and
3. the benzene ring in the backbone is expected to provide hard coating originated from its bulkiness.

Within this resulting reaction formula, various properties of coatings can be built into the structure by using various types of monomers, varying their formulations etc.

MATERIALS AND PROCEDURES

The resins of three different molecular weights used were supplied by Sanwa Chemical Ind. Co., Ltd. They came in solvent contents of between 40 to 70% depending on their molecular weights. Therefore, they were first dried in a reduced-pressure oven for several days. Then the dried resins were dissolved, whenever applicable in mono- and/or poly-functional monomers supplied by Shin-Nakamura Chemical Co., Ltd. - used as received - as their new solvents to certain varying percentages.

The prepared formulations were later coated on to tin-plated steel plates of 10 cm by 20 cm dimensions. An Area-Beam 300 electron accelerator from the Nissin-High Voltage Co., Ltd. was used. The irradiation conditions used are listed below:

Accelerating voltage : 250 kV

Beam current : 10 mA

Conveyor speed : 11.2 m/min

Dose per pass : 2.6 Mrad

Oxygen concentration: ca. 10 ppm

Physical properties (i.e. tensile strength and % elongation) were measured on Instron Universal Testing machine model 4301 and the specimens were prepared in accordance with ASTM D-882. Pencil hardness was measured according to the JIS. K 5401. Measurements of gel percentage were taken by extracting cured films in a soxhlet extractor for 16 hours using acetone as a solvent. The extracted samples were then air dried for 30 min. before drying in a vacuum drier for 6 hours at 50°C. Contact angle was taken on Kyowa Contact Angle meter at 26°C. Torsional braid analysis was done on Rhesca's machine model RD 1100RD. The molecular weight distributions of the resins were taken on Toyo Soda's HPGPC using polystyrene as standard. The solvent used was tetrahydrofuran and the concentration of the samples was about 0.5 weight percent.

RESULTS AND DISCUSSION

Effect of monomers

For this study a number of formulations were prepared using monomers with different number of repeating units. The monomers used were mainly derivatives of ethylene glycol dimethacrylate, that is, difunctional monomer. These monomers acted as solvent for resin PK12AK which possessed molecular weight of 36000.

Fig. 1 shows the gel fraction of a formulation after irradiating with a certain amount of dose. From this figure

it appears that the lower the number of repeating unit of a monomer, the more sensitive the formulation becomes. Majority of the cure are completed at doses lower than 20 Mrad. As the material cures, the growing polymer inhibits the mobility necessary for further reaction. The final gel fraction obtained, doesn't show much difference from one monomer to the others used. But the pencil hardness (P.H.) is able to show big difference for various monomers as shown in Table 1. With the smallest monomer, 1G (i.e. one repeating unit) the coating obtained was rather hard and brittle. Fig. 2 shows that the coatings prepared with monomer 1G imparts the strongest tensile strength (T.S.) up to 600 kg/cm^2 in comparison to the ones prepared with the monomers with higher numbers of repeating units. The figure appears that as the dose increases, the properties improve until at 23 Mrad. At higher doses, the coatings have received too much radiation thus the tensile strength are falling off. On the other hand, for the longer monomers (i.e. with higher numbers of repeating unit) they show some kind of radiation resistance property as indicated in Fig. 2 – a formulation with monomer 4G (4 repeating units). The effect of radiation curing on this formulation was further monitored by measuring the glass transition temperature, Tg of its cured film for each amount of dose given, using torsional braid analyser (TBA) as shown

in Fig. 3. For this formulation, it appears that there are no changes in Tg values as the dose increases, in agreement with the observation made for this formulation previously (Fig. 2 i.e. the curve levels off after a certain dose). From Fig. 4 it shows that formulation with monomer 4G imparts the highest Tg. Perhaps, it is due to the compatibility between the monomer and the resin used.

Effect of molecular weights

For the effect of molecular weights of the resins, the results are tabulated in the Fig. 5, and Tables 2 and 3. From Fig. 5 and Table 2, it can be concluded that resins of smaller molecular weights (smaller number of repeating unit) are more sensitive to irradiation i.e. require smaller dose to cure. This kind of resins when cured results in higher tensile strength but the setback is, it is less flexible, believed to be due to the fact that resins with smaller number of repeating unit give higher network density of crosslinking.[4]

For the resins 140 AK and 141 AK, their molecular weights are rather close i.e. 6100 and 7800 respectively, therefore, it is expected that their resultant cured-form physical properties do not differ too much from each other. On the other hand, with much higher molecular weight resin, PK12AK the differences in these properties becomes more apparent. Differences in molecular weight do not affect pencil hardness

very much. From Table 2, it appears that with resin PK12AK - about 5 to 6 times higher in molecular weight than the other two - its pencil hardness improves by 1 degree only i.e. from F to HB.

Effect of monomer ratios

The data for the effect of monomer ratios are tabulated in Fig. 6 and 7, and Table 4. For this purpose, the resin of the smallest molecular weight i.e. 6100 was chosen with a hope that this resin would be the most sensitive towards radiation. And monomer 4G was selected because in previous findings, it showed more "promising" results. Consequently, any changes were expected to be more easily detected. From Fig. 6, it shows that this resin is more sensitive towards radiation compared to the one described previously. Gel fraction of more than 90% are attainable with the dose of 8 Mrad. Within the studied ratios of 1:1, 1:2 and 1:2.7, there appears to be no obvious trends observed.

Figure 6 also indicates that the more viscous the formulations the more sensitive they become towards radiation. A setback is that with higher resin ratios, the degree of crosslinking decreases, due to a premature polymerization of monomer with itself.[4] Furthermore, when the monomer ratio was reduced, the resin became increasingly difficult to dissolve - the ratio of 1:2.7 was found to be

optimum. Variations in monomer ratio do not give any changes with regard to the pencil hardness as shown by the data in Table 4. As to the other physical property i.e. tensile strength there appears to be no "special" trend observed as shown in Fig. 7.

Effect of HEA additions

The purpose of adding HEA (Ethylene glycol monoacrylate) - hydrophilic in nature - into the formulations was to increase the degree of compatibility between the monomer and the resin studied. Measurements were made by measuring the receding contact angle between a drop of distilled water (2μl) and a cured film. Since the tendency for a drop of liquid to spread over a plane solid surface increases as the contact angle decreases, the contact angle provides a useful inverse measure of wettability.[5] Formulations of higher wettability have a tendency to be more compatible with a substrate. From Fig. 8, it shows that an addition of HEA results in reduction of % gel. This phenomenon is attributable to the fact that HEA is of monofunctional class which in this case was found to be very difficult to cure.

From Fig. 9, it can be seen that the degrees of contact angles decrease as the films cure. They are dependent on the concentration of HEA added.

Therefore, the concentration of HEA added has to be optimized because it can affect the performance of a coating as clearly

shown in Tables 5 and 6.

TBA studies can provide information on the compatibility of a formulation and its Tg.[6,7] As far as TBA measurements were concerned, the addition of HEA did not improve the compatibility very much. From curve D of Fig. 10, it can be seen that there appears to be two separate peaks at lower and higher temperatures originating from, we believe, a chain network and a whole network, respectively.

CONCLUSIONS

The effects of several parameters in the formulations of epoxy acrylic-based resins for radiation curing of coatings were discussed.

EB-cured properties of their coatings seem to be dependent on several parameters like their molecular weight, repeating unit, and monomer ratio. Within these parameters studied, it seems that molecular size i.e. molecular weights of the resins and the monomers show more significant effects in determining the properties of the coatings.

Depending on the ingredient of the formulations, the resins can be cured at relatively low dose i.e. 5-7 Mrad, and can be formulated to suit various end-use requirements.

ACKNOWLEDGEMENTS

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Table 1 The effect of the number of monomer repeating unit on the pencil hardness.

Composition: PK 12 AK: monomer = 1:2.7 (wt)

1G : ethylene glycol dimethacrylate (n=1)

4G : polyethylene glycol dimethacrylate (n=4)

9G : polyethylene glycol dimethacrylate (n=9)

Repeating unit	Pencil Hardness				
	Dose (Mrad)				
	7.8	13.0	18.1	23.3	28.5
1G	-	-	F	3H	5H(B)
4G	B	F	H	H	H
9G	-	(E)	(E)	(E)	(E)

(B) = Brittle (E) = Elastic

Table 2 The effect of oligomer molecular weights on the pencil hardness.

Composition: resin : 4G = 1:2.7 (wt)

$\bar{M}_N$	Resin	Pencil Hardness			
		Dose (Mrad)			
		7.8	13.0	18.1	23.3
6100	140 AK	F	F	F	F
7800	141 AK	HB	F	F	F
36000	PK 12 AK	B	F	H	H

Table 3 The effect of oligomer molecular weights on tensile strength (kg/cm^2) and elongation at break, E.B. (%).

Composition : Resin : 4G = 1:27 (wt.)

Dose (Mrad)	Tensile strength/E.B.		
	Formulation		
	140 AK + 4G	141 AK + 4G	PK 12 AK + 4G
7.8	600.2/6.4	572.8/4.0	-
10.4	620.2/5.4	623.1/5.1	43.2/15.4
13.0	636.3/3.8	611.1/5.6	405.9/6.8
18.1	639.9/5.3	608.5/5.6	516.0/5.7
23.3	636.9/5.9	620.1/4.8	527.0/6.2

Table 4 The effect of monomer ratios on the pencil hardness.

Formulation : 140 AK + 4G

140 AK : 4G Ratio (wt.)	Pencil Hardness				
	Dose (Mrad)				
	5.2	7.8	13.0	18.1	23.3
1 : 1	F	F	F	F	F
1 : 2	2B	F	F	F	F
1 : 2.7	-	F	F	F	F

Table 5 The effect of HEA additions on the pencil hardness.

Composition : PK 12 AK : (4G + HEA) = 1:2.7 (wt.)

% HEA in 4G	Pencil Hardness			
	Dose (Mrad)			
	13.0	18.1	23.3	28.5
10	F	H	H	H
20	F	F	F	F
30	HB	HB	HB	HB
50	B	HB	HB	HB
4G only	F	H	H	H

Table 6 The effect of HEA additions on tensile strength.

Composition : PK 12 AK : (4G + HEA) = 1:2.7 (wt.)

Dose (Mrad)	Tensile strength (kg/cm^2)				
4G:HEA ratio	9:1	8:2	7:3	1:1	4G only
13.0	476.5	431.5	453.0	245.6	405.9
18.1	519.0	494.0	478.9	288.8	516.0
23.3	455.5	495.8	516.6	270.5	527.0
28.5	461.6	495.5	434.3	291.7	546.4

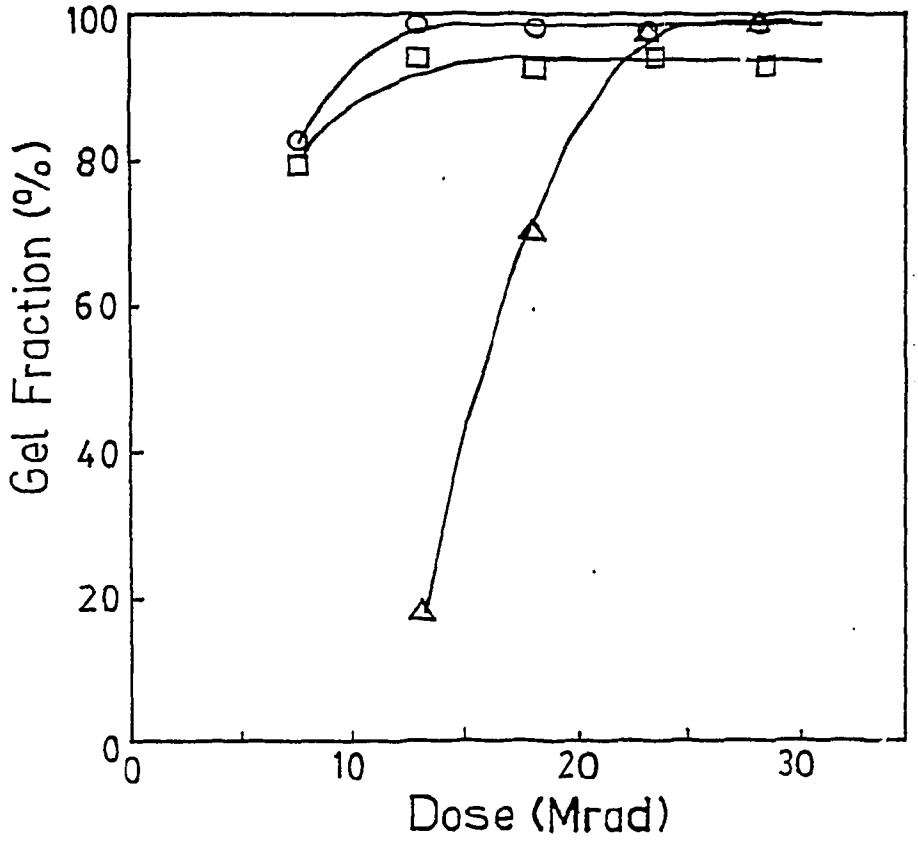

Fig. 1 The effect of the number of monomer repeating unit on gel fraction.

Repeating unit of monomer: △ 1G, ○ 4G, □ 9G

1G: ethylene glycol dimethacrylate (n=1)

4G: polyethylene glycol dimethacrylate (n=4)

9G: polyethylene glycol dimethacrylate (n=9)

Composition: PK12AK:monomer = 1:2.7 (wt.)

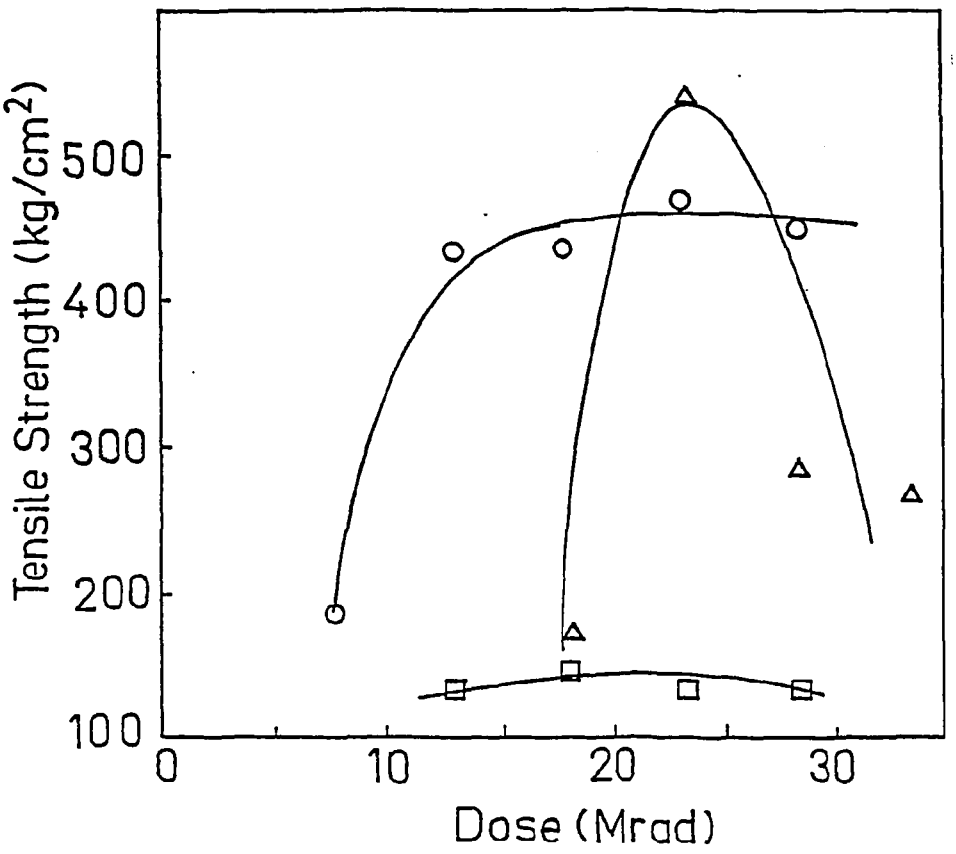

Fig.2 The effect of the number of monomer repeating unit on tensile strength.
Repeating unit of monomer: △ 1G, ○ 4G, □ 9G
Composition: PK12AK:monomer = 1:2.7 (wt.)

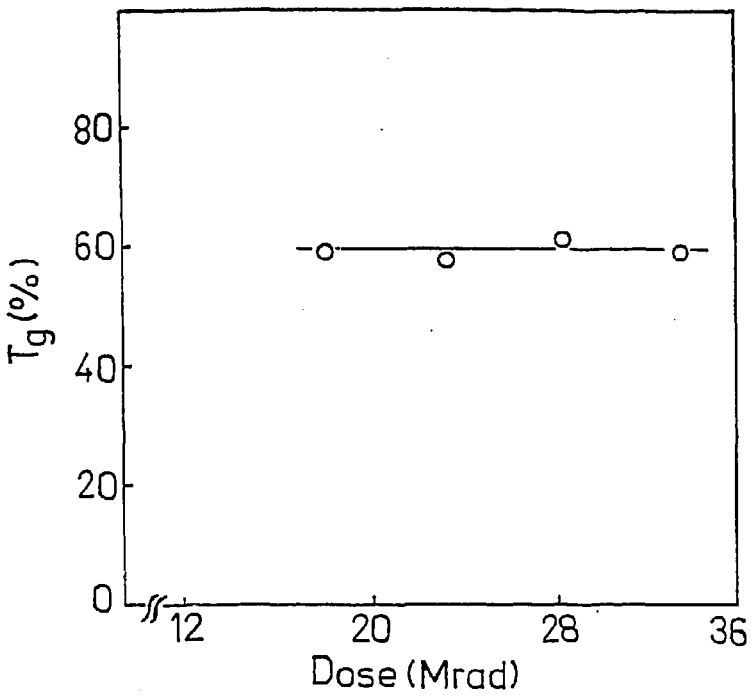

Fig. 3 The glass transition temperature of a cured film.
Composition: PK12AK:4G = 1:2.7 (wt.)

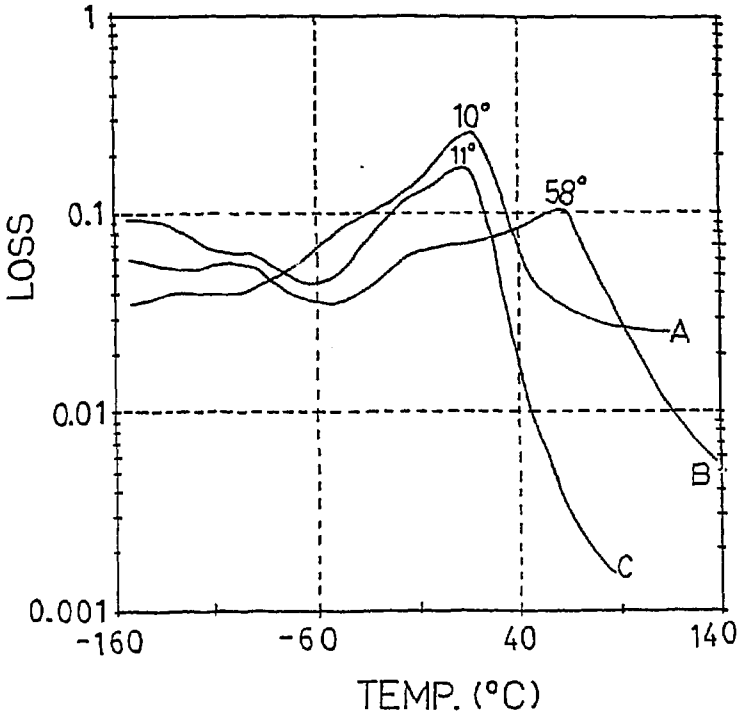

Fig. 4 The effect of the number of monomer repeating unit on Tg.

TBA curves:

A: PK12AK:1G = 1:2.7 (wt.)

B: PK12AK:4G = 1:2.7

C: PK12AK:9G = 1:2.7

Dose: 23.3 Mrad

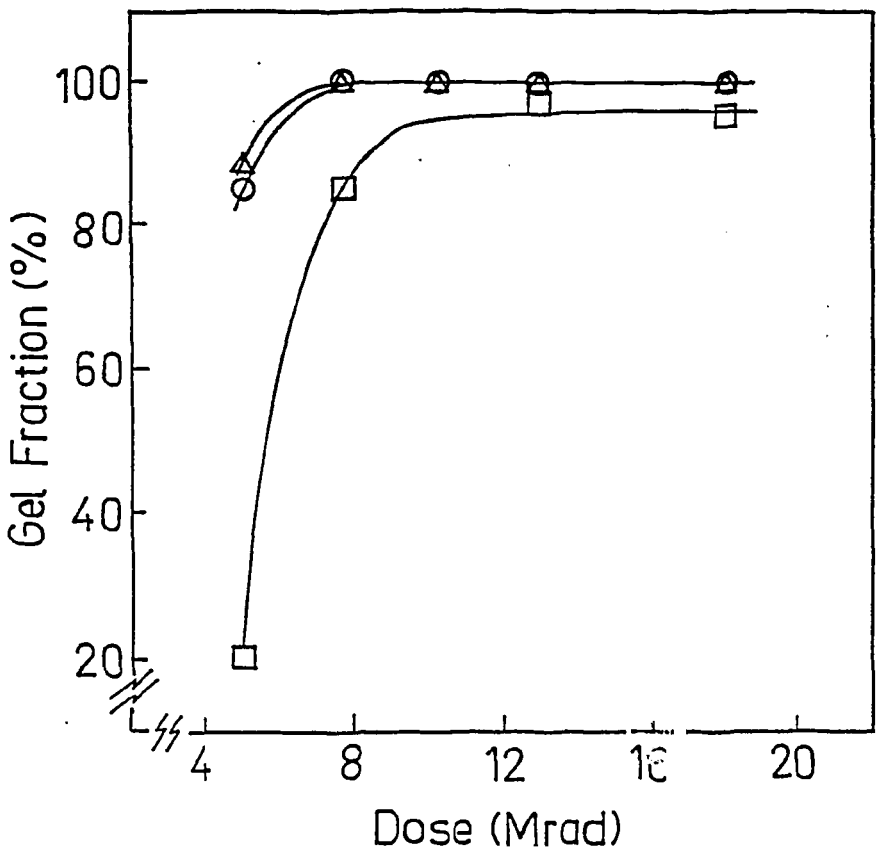

Fig. 5 The effect of oligomer molecular weights on gel fraction.

$\bar{M}_N$:

140AK = 6100; 141AK = 7800; PK12AK = 36000

○ 140AK:4G = 1:2.7 (wt.)

△ 141AK:4G = 1:2.7

□ PK12AK:4G = 1:2.7

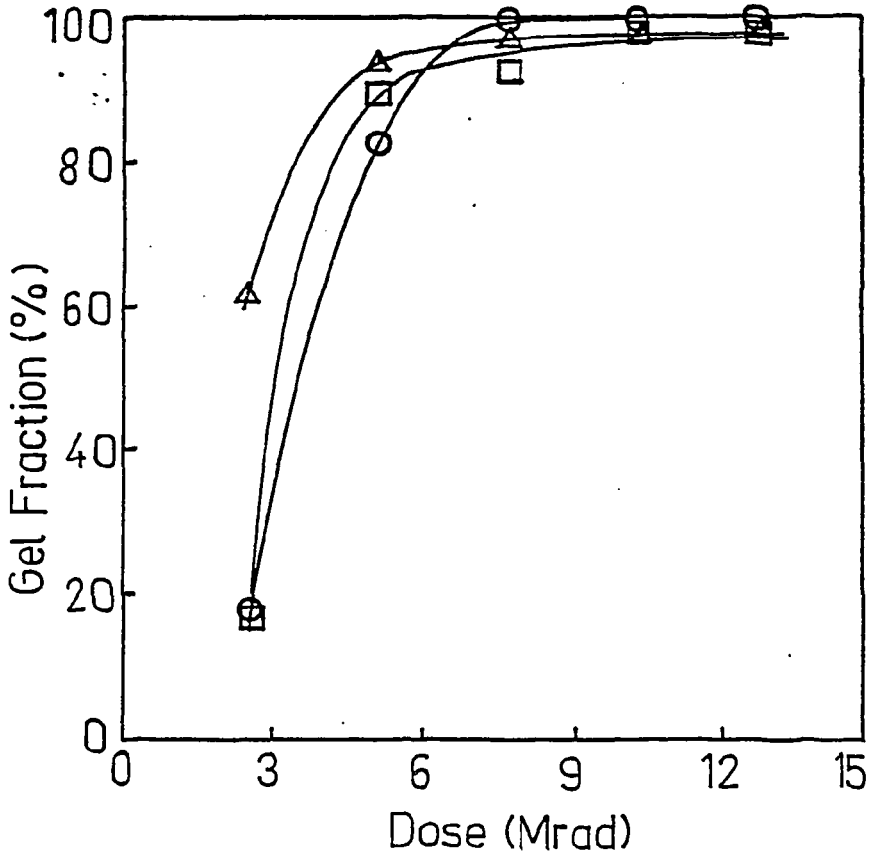

Fig. 6 The effect of monomer ratios on gel fraction.

△ 140AK:4G = 1:1 (wt.)

□ 140AK:4G = 1:2

○ 140AK:4G = 1:2.7

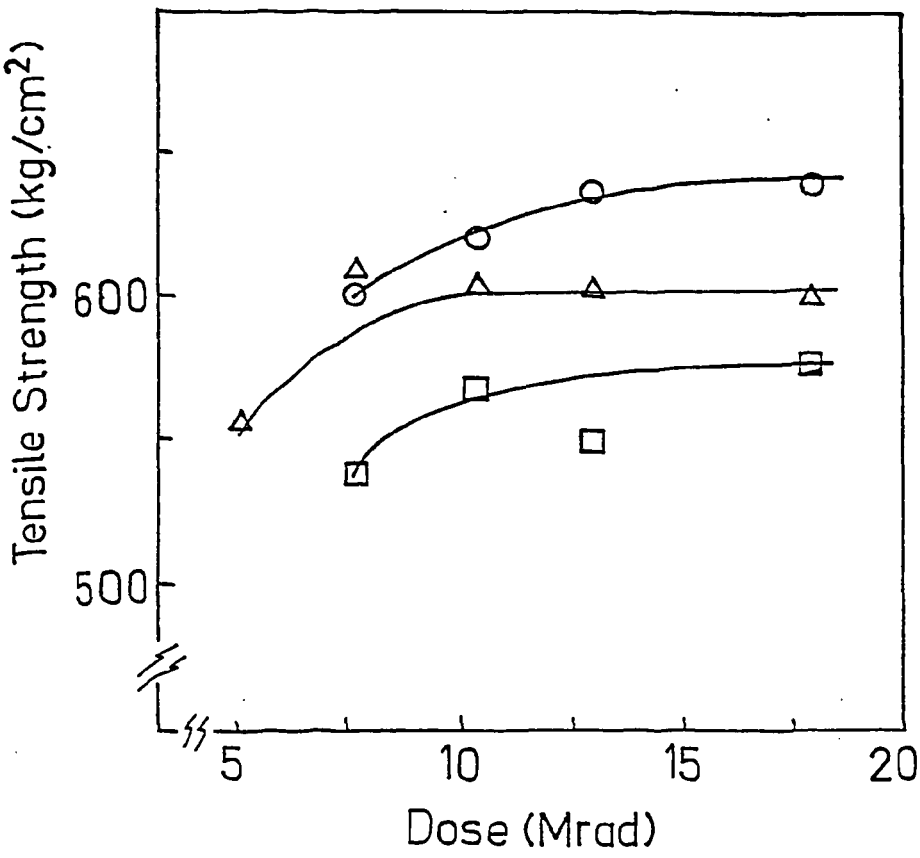

Fig. 7 The effect of monomer ratios on tensile strength.

△ 140AK:4G = 1:1 (wt.)

□ 140AK:4G = 1:2

○ 140AK:4G = 1:2.7

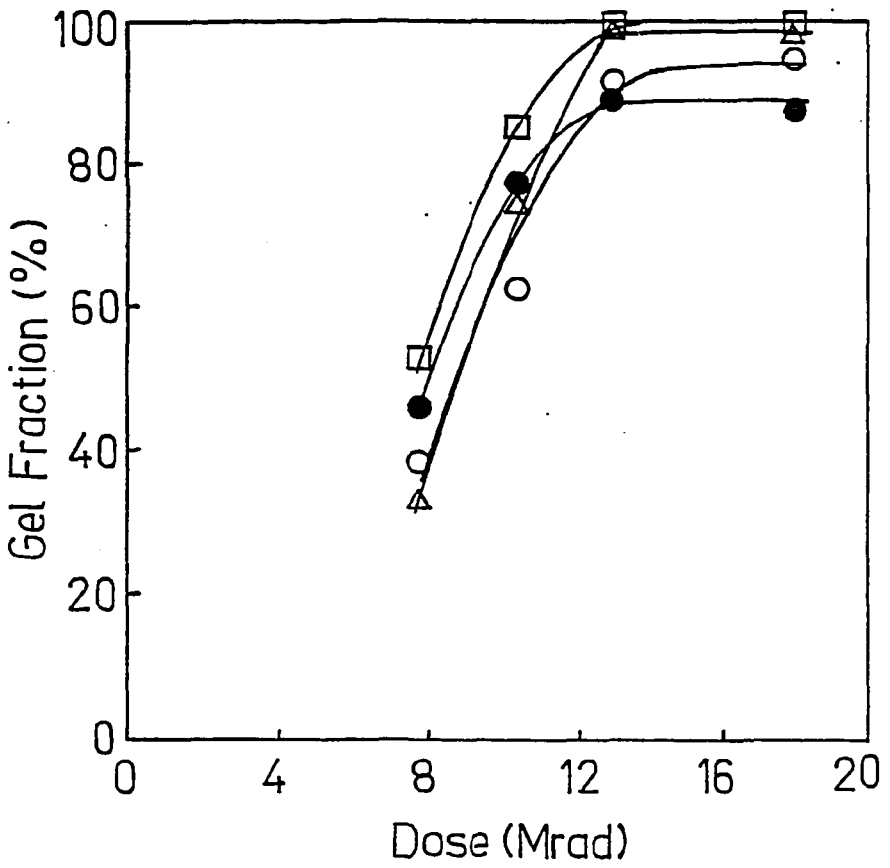

Fig. 8 The effect of HEA additions on gel fraction.
Composition: PK12AK:(4G + HEA) = 1:2.7 (wt.)
where □ 4G:HEA = 9:1
△ 4G:HEA = 8:2
○ 4G:HEA = 7:3
● 4G:HEA = 1:1

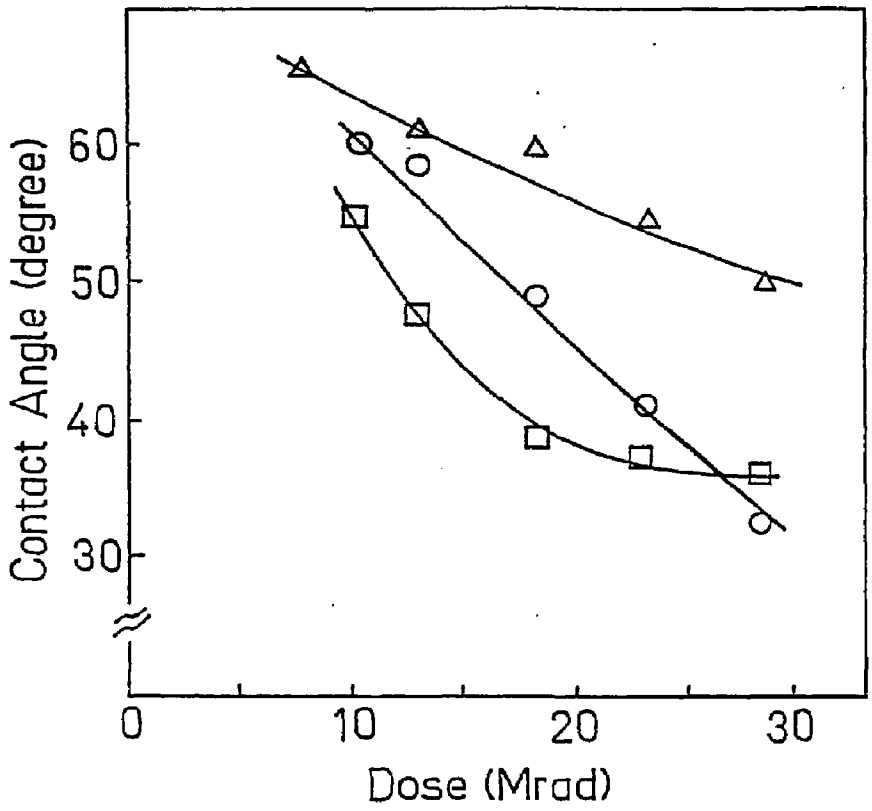

Fig. 9 The effect of HEA additions on contact angle.

Composition: PK12AK:(4G + HEA) = 1:2.7 (wt.)

where □ 4G:HEA = 1:1

○ 4G:HEA = 7:3

△ 4G:HEA = 1:0

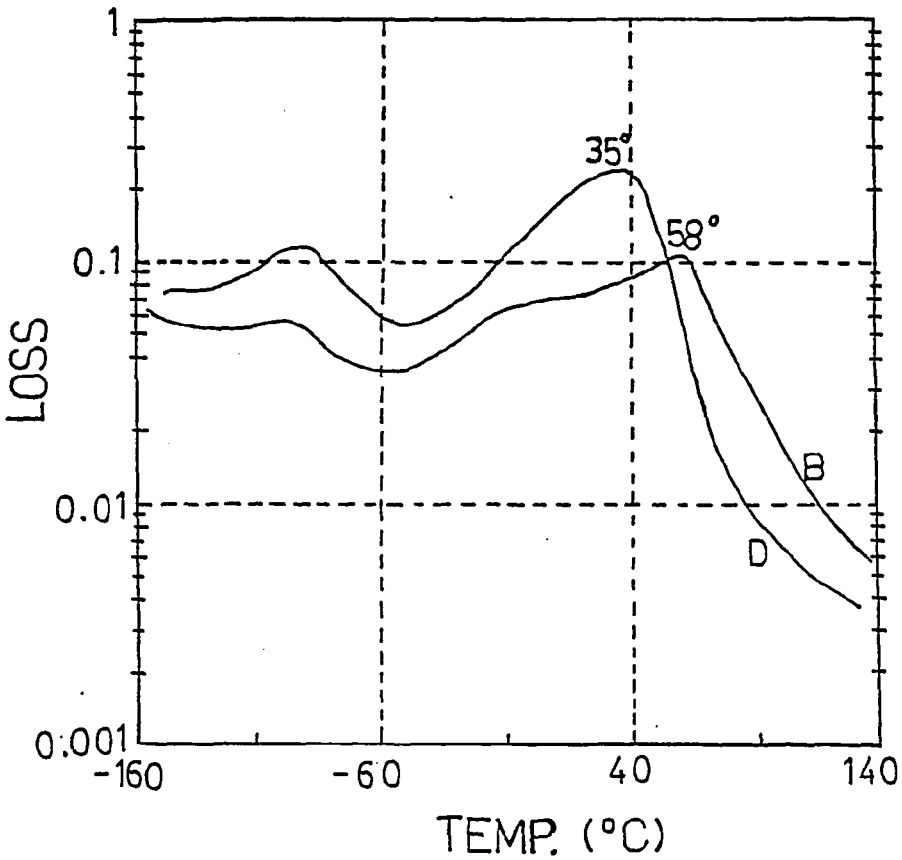

Fig. 10 The glass transition temperatures of cured films.

T3A curves:

B: PK12AK:4G = 1:2.7 (wt.)

D: PK12AK:(4G + HEA) = 1:2.7

where 4G:HEA = 1:1

Dose: 23.3 Mrad