

A STUDY ON RADIATION CROSSLINKING OF POLYDIMETHYLSILOXANE (PDMS) RUBBER LATEX*

Yi-cai Zhu^a, Xiao-hong Zhang^{a, b}, Jin-liang Qiao^b and Gen-shuan Wei^{a**}

^a Department of Applied Chemistry, College of Chemistry, Peking University, Beijing 100871, China

^b SINOPEC, Beijing Research Institute of Chemical Industry, Beijing 100013, China

Abstract Polydimethylsiloxane (PDMS) rubber latex with two sorts of sensitizers, trimethylol propane tri-methacrylate (TMPTMA) and diethylene glycol di-acrylate (DEGDA), was irradiated with γ -rays and electron beams in various conditions. The radiation crosslinking reaction of PDMS occurs in the inner phase of the latex and is relatively isolated from the water phase. Therefore the oxygen and the radicals produced by the radiolysis reaction of water almost have no effect on the crosslinking reaction of polymer. The experimental data correspond with the Charlesby-Pinner relationship in the main. The gelation doses, degree of crosslinking and degradation as well as G values of crosslinking were calculated. From them, the sensitization coefficients were derived to offer a quantitative measurement of the enhancing effect of sensitizer on the radiation crosslinking.

Keywords Radiation crosslinking, Polydimethylsiloxane (PDMS), Latex, Sensitizer, Charlesby-Pinner equation

INTRODUCTION

Silicon rubber belongs to an important class of special-purpose synthetic rubbers that are partly inorganic and partly organic. PDMS, the representative of silicon rubber, is one of the polymers with the most flexible chain. Its backbone does not allow double bonds to be formed, and it has some unique configurational properties^[1] due to the difference in bond angles Si—O—Si and O—Si—O. So PDMS has been widely chosen for the studies of radiation crosslinking.

The radiation crosslinking of PDMS in bulk phase has been extensively studied by a number of workers. Early reports^[2, 3] verified that a crosslinking reaction occurred while PDMS was exposed to high-energy radiation. And the crosslinking mechanism has also been studied^[4]. But thus far no systematic study of the radiation chemistry of the PDMS latex system has been reported, while the latex possesses several advantages in industrial applications. In the latex system, radiolysis of water occurs in the water phase and radiation crosslinking of PDMS occurs simultaneously in inner phase. Thus the radiation chemistry involved in the processing of the latex system is very complex. Our present study has been taken up with the following two objectives: (1) to investigate the factors affecting the radiation crosslinking of PDMS latex; (2) to understand the crosslinking mechanism in the latex system.

In this work two kinds of polyfunctional monomers are used as sensitizers. The possible factors, such as absorbed dose rate, irradiation atmosphere, *etc.*, are studied. Both γ -ray and electron beam (EB) are used. The degree of crosslinking was monitored by measuring the variation of the gel fraction with the absorbed dose.

The method mentioned in this work has been applied in the industrial manufacture of vulcanized silicon

* Contract grant sponsors: Major State Basic Research Projects of China (G1999064800)

** Corresponding author: Gen-shuan Wei (魏根栓), E-mail: gswei@pku.edu.cn

Received November 13, 2002; Revised March 7, 2003; Accepted March 13, 2003

rubber particles of nanometer size^[5, 6]. Compared to the comparable products of the Dow-Corning company and the G.E. company, which are produced with by chemistry crosslinking techniques, the radiation vulcanized silicon rubber particles have some advantages because of their small particle sizes and good controllability of the crosslinking density of the rubber.

EXPERIMENTAL

Materials and Reagents

One kind of commercially available PDMS rubber latex was used. The basic data of this PDMS latex are listed below. The M_n and M_w data were determined by GPC techniques.

$$M_n = 1.55 \times 10^5, M_w = 1.20 \times 10^5, M_w = 1.91 \times 10^5, \text{Dry rubber content} = 30.0\%$$

Two kinds of polyfunctional acrylic monomers were used as sensitizers: trimethylol propane trimethacrylate (TMPTMA) and diethylene glycol di-acrylate(DEGDA). Toluene (AR Grade) was selected for the gel fraction measurement of PDMS rubber films.

Experiment

Sample preparation

Prior to irradiation, PDMS latex was mixed with one or several sorts of sensitizers or other addition agents and stirred for 1 h to disperse the addition agents well. The contents of the addition agents were shown as wt% of the agents relative to the dry rubber in the latex. The samples to be irradiated with γ -rays were obtained by transferring the mixed latex into test tubes and then sealing them. Whenever necessary, these samples were saturated with N_2 , O_2 or N_2O before the tubes were sealed. The other samples, which would be irradiated with EB, were obtained by encapsulating the mixed latex in PE bags.

Irradiation

The prepared samples were irradiated under different absorbed doses with γ -rays at a certain dose rate, as determined by a Fricke dosimeter, or with EB at a constant dose rate known to be 6 kGy/min. The irradiation was carried out at room temperature.

Sol/gel analysis

Rubber films were obtained via casting on a glass plate and dried overnight in vacuum at 50–60°C. Dry films were cut into small pieces, wrapped with lens paper and copper gauze, and extracted with toluene in refluxing extraction apparatus. Antioxidant 1010 was added to prevent degradation induced by heat treatment. The insoluble residue was dried to a constant weight in vacuum at 50–60°C. The extraction time was chosen for 24 h according to the variation of the measured gel fraction with extracting time.

RESULTS AND DISCUSSION

Absorbed Dose and Dose Rate

As expected, the radiation crosslinking behavior of PDMS is similar to that of most other elastomers of radiation-crosslinking type. The gel fraction of irradiated PDMS increase with increasing absorbed dose up to approximately 100 kGy and then tends to a constant value for higher doses. Due to the contribution of degradation also induced by irradiation, the ultimate gel fraction is about 80%. The mathematical relationship between gel fraction and absorbed dose will be discussed below.

It was also expected that absorbed dose rate has little effect on radiation crosslinking of PDMS latex. This has been demonstrated by the results of post-irradiation examination of the samples which were irradiated with γ -rays to the same absorbed dose at different dose rate.

Atmosphere

The radiation crosslinking of PDMS is known as a reaction predominantly of a free radical mechanism^[4]. Oxygen may play the role of radical scavenger in this kind of reaction and thus induce oxidation and degradation. Therefore the presence of oxygen will seriously impede the radiation crosslinking reaction of PDMS, and this net

effect of oxygen on the radiation crosslinking of PDMS in bulk phase is actually observed^[7]. However, the experimental data of the radiation crosslinking of PDMS latex carried out in air, N₂ and O₂ (shown in Fig.1) indicate that oxygen has little effect to the radiation crosslinking of PDMS latex. This phenomenon may be ascribed to the latex system. In the latex system, oxygen, which mainly exists in the water phase, has the priority to react with the free radicals produced by the radiolysis of water. And the crosslinking reaction of PDMS occurred in the inner phase is relatively isolated from oxygen by the surfactant molecule layers. Therefore the crosslinking reaction can proceed independently in the latex system.

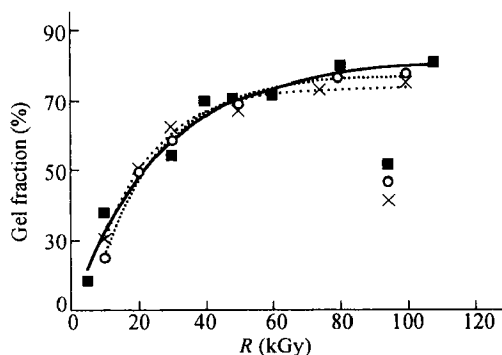


Fig. 1 Crosslinking (gel fraction versus absorbed dose R) of PDMS latex by γ -ray irradiation in different atmosphere
Irradiation conditions: 1% TMPTMA, in air, N₂ and O₂

Since the radiation atmosphere plays an insignificant role in the radiation crosslinking of PDMS latex, irradiation in air, which is much more convenient to carry out, is obviously the best choice for not only experimental but also industrial application.

Polyfunctional Monomers

Two kinds of polyfunctional acrylic monomers (TMPTMA and DEGDA), which were proved to be effective sensitizers for the radiation crosslinking of some rubbers^[8-11], were selected and various concentrations of them were used in the experiments, whose results are presented in Fig. 2 and 3.

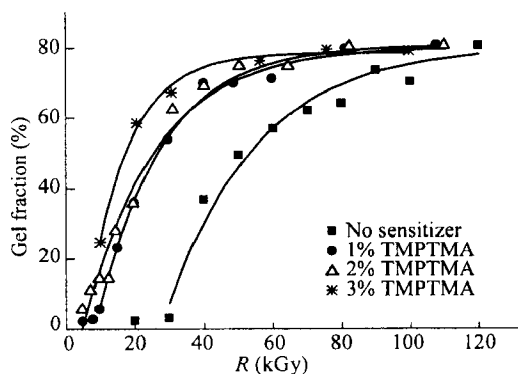


Fig. 2 Crosslinking (gel fraction versus absorbed dose R) of PDMS latex with different content of TMPTMA
Irradiation conditions: γ -ray, in air

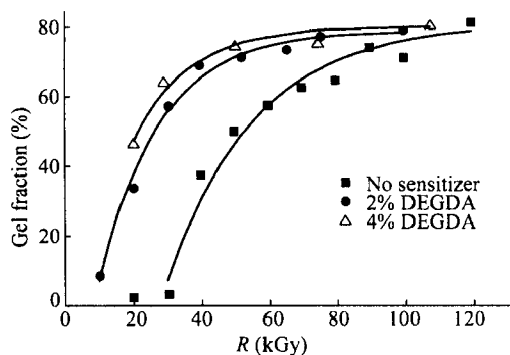


Fig. 3 Crosslinking (gel fraction versus absorbed dose R) of PDMS latex with different content of TMPTMA
Irradiation conditions: γ -ray, in air

The required dose for formation of initial gel (listed in Table 1) is greatly decreased with addition of the sensitizers. And with the increase of the concentration of sensitizers, the gelation dose is decreasing, although the

decrease is slower and slower. For example, the addition of the first 1% TMPTMA can reduce the gelation dose from about 30 kGy to 12.5 kGy, but another 1% TMPTMA only induce an additional decrease of 2.5 kGy.

Table 1. List of the gelation doses of the radiation crosslinking reaction of PDMS latex

Sensitizer	No	1% TMPTMA	2% TMPTMA	3% TMPTMA	2% DEGDA	4% DEGDA
R_{gel} (kGy)	30.0	12.5	10.0	7.5	13.0	10.0

Condition: with γ -ray, in air

Although the samples with sensitizers are more easily crosslinked by irradiation, the extreme value, to which the curves tend, of all those samples are nearly at the same level. This implies that the crosslinking construction of PDMS had not been notably changed by the sensitizers. The obtained data indicate that the two kinds of polyfunctional acrylic monomer, TMPTMA and DEGDA, can both be used as radiation crosslinking sensitizer of PDMS latex. The ability of them may be attributed to the formation of free radicals on irradiation, which would take part in enhancing the crosslinking of PDMS chains. On the other hand, no appreciable increase in the gel fraction has been attained for samples having higher content of sensitizer. Therefore 1% is recommended for the best concentration of sensitizer according to the experimental results.

The efficiency of the two kinds of polyfunctional monomers can be compared from the gelation doses listed in Table 1. Obviously, the trifunctional acrylic monomer TMPTMA does better in sensitizing the radiation crosslinking of PDMS latex than DEGDA, which is a difunctional acrylic monomer. The quantitative discussion will be presented later.

Electron Beam (EB) and Co-60 γ -Ray Irradiation

EB is more extensively used than γ -rays in radiation applications for processing of polymers^[12]. Crosslinking of PDMS latex by EB was confirmed to be more effective in comparison with the γ -irradiation (Fig. 4).

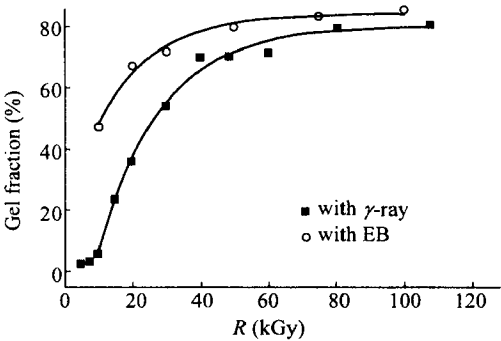


Fig. 4. Crosslinking (gel fraction versus absorbed dose R) of PDMS latex with EB and γ -rays
Irradiation conditions: 1% TMPTMA, in air

This phenomenon can be explained by the temperature effect of the accelerated electrons with high absorbed dose rate. It has been shown earlier^[4, 13] that radiation chemical yields (G value) of the PDMS crosslinking increased essentially with temperature from 1.55 (20°C) to 2.35 (150°C).

Kinetics

The relationship between the sol fraction and absorbed dose would be determined from the gel fraction build-up curves (Figs. 2, 3) by using the Charlesby-Pinner (C-P) equation^[14]:

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 R} \tag{1}$$

where s is the sol fraction, μ_1 is the number average degree of polymerization of PDMS prior to irradiation, R is the absorbed dose, q_0 and p_0 respectively represent the probability of chain crosslinking and degradation induced

by ionizing radiation.

The results of the treatments to the data for the samples with no sensitizers, with 1%, 2%, 3% TMPTMA and with DEGDA are shown in Figs. 5–9, respectively.

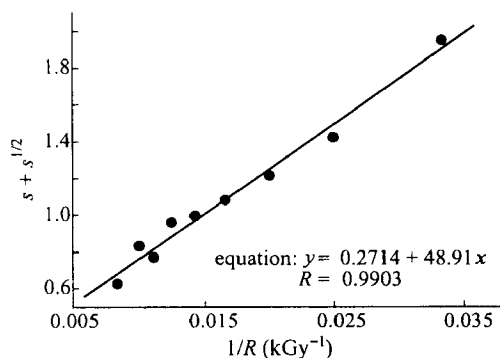


Fig. 5 Linear C-P dependence of PDMS latex without sensitizer

Irradiation conditions: γ -rays, in air

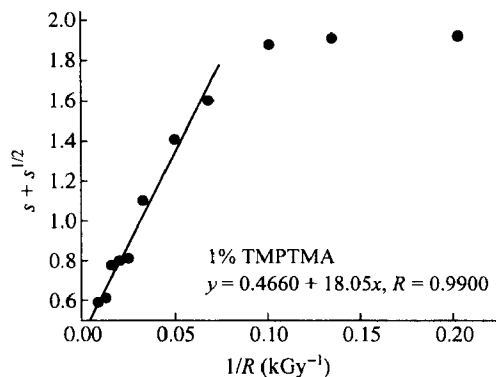


Fig. 6 C-P dependence of PDMS latex with 1% TMPTM

Irradiation conditions: γ -rays, in air

Regarding PDMS with no sensitizers (Fig. 5), the C-P relationship is fundamentally applicable since $s + s^{1/2}$ is, in the main, linearly related to $1/R$. This indicates that the radiolysis of water has little effect on the radiation crosslinking reaction that occurs in the inner phase of latex and, as a result, the crosslinking reaction can proceed independently. However, the experimental data deviates from the C-P equation when the equation is used for the samples with sensitizers. On further consideration of the data shown in Figs. 6–9, we found the linear relationship likely to be valid for high doses (small $1/R$) range but at lower doses (bigger $1/R$) $s + s^{1/2}$ falls off exponentially, within the limits of error. Such behavior has also been observed in the radiation crosslinking of PDMS in bulk phase^[8, 15]. These deviations may be attributed to the distinction in the crosslinking reaction system at different doses. The reaction system in the inner phase varies according to absorbed dose due to the existence of sensitizers. At lower absorbed doses, the crosslinking reactions primarily took place between the PDMS chains and sensitizers because of the high reactivity of sensitizers. As results of these reactions, the PDMS chains were changed to linear or grafted or crosslinked macromolecules with sensitization groups attached. On the other hand, the sensitizers were exhausted with the increase of absorbed dose. This process is equivalent to a radiation graft copolymerization course. Consequently, the crosslinking reactions at higher doses mainly took place among the newly-formed macromolecules and such reactions are believed to conform to the C-P equation. According to the experimental data and this explanation, the C-P equation can also be partly applied in the enhanced radiation crosslinking systems that contain the sensitizers, especially in the higher dose range.

Several coefficients can be derived from the C-P lines shown in Fig. 5. The linear $s + s^{1/2}$ versus $1/R$ dependences were graphically extrapolated to $1/R \rightarrow 0$ to obtain p_0/q_0 ratios and to $s + s^{1/2} \rightarrow 2$ to obtain R_{gel} , theoretical gelation doses. With p_0/q_0 ratios and $1/q_0\mu_1$ values, as determined from the intercepts and the slopes of the lines, the values of p_0 and q_0 could be calculated. And such an equation as follows was applied for the calculation of G values, the radiation-chemical yields:

$$G = 4.83 \times 10^6 q_0 / w = \frac{4.83 \times 10^6}{R_{gel} \overline{M}_w} \quad (2)$$

where W is the molecular weight of the monomeric unit of PDMS, $\overline{M}_w$ is the weight average molecular weight of PDMS. The calculation results are listed in Table 2.

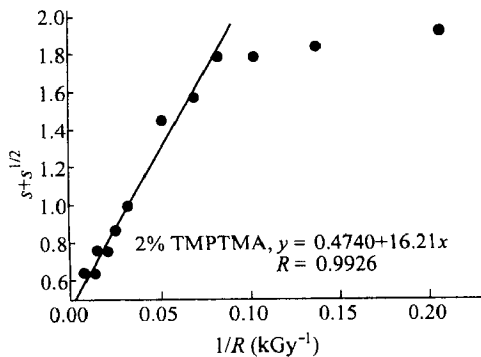


Fig. 7 C-P dependence of PDMS latex with 2% TMPTMA
Irradiation conditions: γ -rays, in air

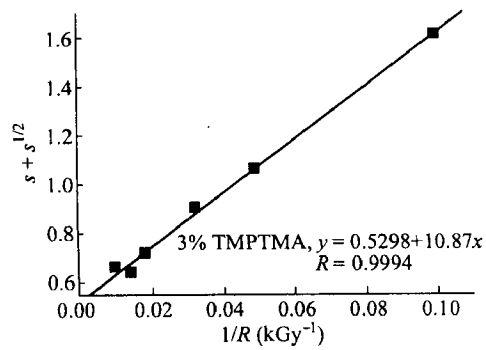


Fig. 8 C-P dependence of PDMS latex with 3% TMPTMA
Irradiation conditions: γ -rays, in air

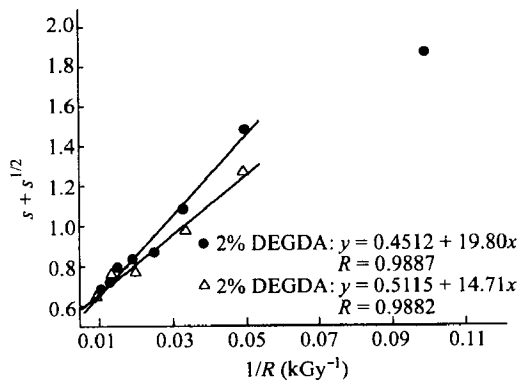


Fig. 9 C-P dependence of PDMS latex with DEGDA
Irradiation conditions: with γ -rays, in air

Table 2. List of the crosslinking coefficients of the radiation crosslinking reaction of PDMS latex with no sensitizer

$1/q_0\mu_1$	p_0/q_0	q_0 (kGy ⁻¹)	p_0 (kGy ⁻¹)	R_{gel} (kGy)	G
48.91	0.271	1.26×10^{-5}	3.42×10^{-6}	28.30	0.90

Condition: with γ -rays, in air

Table 3. List of the gelation doses and the yield of crosslinks of the radiation crosslinking reaction of PDMS latex with presence of sensitizers

Sensitizer	1% TMPTMA	2% TMPTMA	3% TMPTMA	2% DEGDA	4% DEGDA
R_{gel} (kGy)	12.5	10.0	7.5	13.0	10.0
G Value	2.0	2.5	3.3	1.9	2.5

Condition: with γ -rays, in air

Because of the difference between the latex system and the bulk system, the G value listed in Table 2 is not identical with that of the reaction occurring in rubber films, which is about 2.0 at 20°C^[4].

For the systems containing polyfunctional monomers, the yield of crosslinks is dose dependent due to the crosslinking processes mentioned above. Thus, the attempt to analyze the gel-sol data in terms of the C-P relationship is flawed, but the initial yields of crosslinks can still be obtained from the gelation doses by using Eq. (2). The acquired data are listed in Table 3.

These G values listed in Table 3 may be considered to be the total yields of radiation crosslinking. And for the mixture systems of linear polymers and monomers crosslinking reactions of the following two types were considered to be induced by irradiation^[11]: (a) direct crosslinking, the reaction in which the linear polymer chains

directly crosslink each other; (b) indirect crosslinking, the reaction in which the linear polymer chains crosslink through the functional groups of the polyfunctional monomers. If indirect reaction (b) is predominant and the rate constant is bigger than that of direct reaction (a), the polyfunctional monomer has an enhancing effect on the radiation crosslinking of the polymers. The total yields of radiation crosslinking for the system is correspondingly expressed as the combination of the yields of the two kinds of reactions and can be calculated by the following relation:

$$G = X_A G_A + X_B G_B \quad (3)$$

where G_A and G_B are respectively the yields of crosslinking reaction (a) and (b), X_A and X_B are respectively the molecule fraction of crosslinkable units of the polymer ($[-Si(CH_3)_2O-]$ for PDMS) and the functional groups which have an effect on the crosslinking reaction in the mixture system. As for the system in this work, the homopolymerization of the polyfunctional monomers is very limited because of the low concentration of the monomers in the whole system. And on the other hand, the oligomers produced by such homopolymerization also have an enhancing effect to the PDMS crosslinking reaction. Therefore, we can safely assume that all the polyfunctional monomers contribute to the crosslinking. That is to say, X_B is approximately equal to the molecule fraction of all the functional groups of the sensitizer in the mixture system. Then by applying the approximation $X_A + X_B = 1$, Eq. (3) can be changed to:

$$G = (G_B - G_A) X_B + G_A \quad (4)$$

G_A and G_B , which are considered to be constant from the linear $G-X_B$ dependence. X_B can be calculated from the initial content of the sensitizer by using following relation:

$$X_B = \frac{m \cdot n / M_B}{1/w + m \cdot n / M_B} \quad (5)$$

where m , n and M_B are respectively the weight percents, the number of functional groups, and the molecular weight of the sensitizers (TMPTMA: 338, DEGDA: 214), w is the molecular weight of the monomeric unit of PDMS ($[-Si(CH_3)_2O-]$:74).

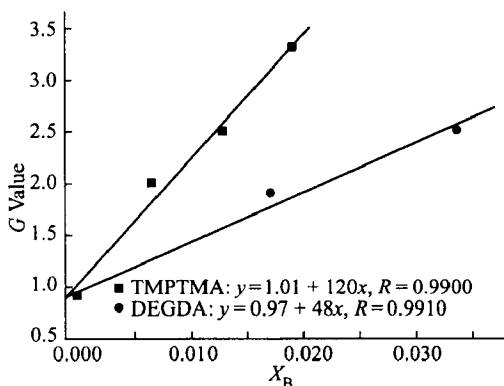


Fig. 10 The linear dependence of $G-X_B$

The results of the treatment mentioned above, as plotted in Fig. 10, indicate that the experimental results conform to Eq. (4) quite well.

G_A and G_B values of TMPTMA and DEGDA are respectively calculated from the linear dependences shown in Fig. 10 and listed in Table 4.

According to Table 4, the G_B value of either TMPTMA or DEGDA is far bigger than G_A . The sensitization coefficient C value (G_B/G_A ratio), as defined to express the enhancing effect of a sensitizer on the radiation

crosslinking of a polymer, is quantitative proof of the ability of sensitizer. It is obvious that TMPTMA, whose C value is about 120, is more effective in the radiation crosslinking of PDMS than DEGDA, whose C value is about 50. Another difunctional acrylate monomer, EGDMA, was reported^[11] to have a C value of 50, which is close to that of DEGDA.

Table 4. List of G_A and G_B values of TMPTMA

Sensitizer	$G_B - G_A$	G_A	G_B	$C = G_B/G_A$
TMPTMA	120	1.01	121	119.8
DEGDA	48		49	48.5

CONCLUSION

Radiation induced crosslinking of PDMS latex in the presence of sensitizers (TMPTMA and DEGDA) occurs effectively in present experiments. In spite of the complication of the environment in the latex system, the oxygen in the water phase and the radicals produced by the radiolysis reaction of water are effectively kept apart from the crosslinking reaction in the inner phase of the latex by the surfactant molecule layers. Therefore the crosslinking reaction is relatively independent and simple. The course of radiation crosslinking shows little dependence on the irradiation conditions studied, which consist of radiation atmosphere (N_2 , O_2 and air), absorbed dose rate and the type of ionizing radiation. Accordingly, within the range studied the most effective and convenient irradiation is just the one carried out in air, without any coagents but sensitizers and irradiated with EB.

The sensitizers TMPTMA and DEGDA can promote the crosslinking reaction so that a lower absorbed dose is required. However, a low concentration of sensitizer is enough because a high content shows little more effectiveness than a low content. Within the two kinds of polyfunctional acrylic monomers investigated, TMPTMA is more effective than DEGDA. The sensitization coefficient value C , which is 120 for TMPTMA and 49 for DEGDA, is presented as a measure of the sensitization ability of the two sensitizers.

REFERENCES

- 1 Zhang, L.X., Xia, A.G., Wang, X.H. and Xu, J.M., Chinese J. Polym. Sci., 1999, 17(4): 347
- 2 Charlesby, A., Nature, 1954, 173: 679
- 3 Charlesby, A., Proc. Roy. Soc., 1955, A, 230: 120
- 4 Ormerod, M.G. and Charlesby, A., Polymer, 1963, 4: 459
- 5 Zhang, X.H., Qiao, J.L., Gao, J.M., Liu, Y.Q., Zhang, S.J., Song, Z.H., Li, J.Q. and Zhu, Y.C., 2000, CN Pat., 00109217.0
- 6 Liu, Y.Q., Zhang, X.H., Wei, G.S., Gao, J.M., Huang, F., Zhang, M.L., Guo, M.J. and Qiao, J.L., Chinese J. Polymer Sci., 2002(1), 20: 93
- 7 Hill, D. J.T., Preston, C.M.L., Salisbury, D.J. and Whittaker, A.K., Radiat. Phys. Chem., 2001, 62: 11
- 8 Wang, M.J. and Yin, M., J. Radiat. Res. Radiat. Proc., 1988, 6(2): 34
- 9 Jayasuriya, M.M., Makuuchi, K. and Yoshi, F., Eur. Polym. J., 2001, 37: 93
- 10 Abdel-aziz, M.M., Youssef, H.A., Miligy, A.A., Yoshii, F. and Makuuchi, K., J. Elastomers Plastics, 1996, 28: 288
- 11 Chen, X.F., Tang, A.Q., Zhang, Y. and Zhang, Z., J. Radiat. Res. Radiat. Proc., 1985, 3(3): 1
- 12 Bao, J.W., Li, Y. and Chen, X.B., Chinese J. Polym. Sci., 2001, 19(1): 53
- 13 Miller, A.A., J. Amer. Chem. Soc., 1960, 82: 3519
- 14 Charlesby, A. and Pinner, S.H., Proc. Roy. Soc., 1959, A, 249: 367
- 15 Fang, Y.E., Li, X., Shi, T., Zhang, S., Du, Z., Yu, S. and Feng, S., J. Radiat. Res. Radiat. Proc., 1990, 8(4): 214