

Exothermic Effect in the Process of Electron-Beam Curing of Epoxy Resins

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ABSTRACT: Temperature measurements have been performed in the process of electron-beam curing of EB-I and EB-II epoxy resin systems. The influence of initiator content, resin type, and dose rate on the temperature of the systems was studied. Transverse and longitudinal temperatures of samples in the glass vessel were also analyzed. The nature of temperature curves varied with the different epoxy resin systems in the steel mold, but did not change with different contents of the initiator. At the same time, the heat had no effect on the gel fraction of epoxy resin systems. The temperature curve was greatly affected by the dose rate, and its peak value, peak width, and plateau value also increased with it. The transverse temperature of EB-II glass vessel samples increased as the radiation dose increased and, in the

same sample, the temperature reduced as the distance between the radiation center and the test point increased. The longitudinal temperature of EB-I and EB-II resin systems in a glass vessel decreased as the radiation depth increased. As the radiation dose increased, the temperature of the EB-I resin system increased simultaneously, while that of the EB-II resin system initially increased and then kept constant when the dose reached a certain value. The temperatures of these two resin systems decreased rapidly when the radiation process stopped. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2217–2222, 2004

Key words: epoxy resin; electron beam curing; crosslinking; temperature; exothermic effect

INTRODUCTION

High-energy electron beam curing of advanced composites is a novel alternative to conventional thermal processing. It involves the application of radiant energy, rather than thermal energy, to induce crosslinking of the polymer matrix and has a number of advantages over thermal curing. Aerospatiale developed EB curing of composites in France in the late 1970s, and in Canada it was developed by AECL (Atomic Energy of Canada Limited). CRADA (Cooperative Research and Development Agreement) began a research program on a wide range of development of EB curing for aerospace and automotive application in the USA in 1994. Considerable progress in this field has been made.^{1–5}

Epoxy resins have taken a major role in the composites industry because of their excellent adhesion, strength, low shrinkage, corrosion protection, processing versatility, and many other properties. Crivello has disclosed that epoxy resins are EB curable in the presence of certain cationic photoinitiators (diaryliodonium and triarylsulfonium salts) in the air.⁶ This development makes it possible to use the large class of common and low-cost epoxy resins to produce com-

posite structures with excellent properties without the need for slow, high-temperature, high-pressure curing cycles or the associated expensive fabrication tools.^{7–9}

Although EB curing of epoxy resin has many advantages, considerable development work will be required before this technology can become accepted in commercial processes. So far, the majority of research programs have focused on development of resin systems, optimizing the formulation of curable matrix, and improving some properties of the system. Not many fundamental investigations of EB curing have been reported.^{10–14} The initiation mechanisms of EB curing and thermal curing processes are different and, during the EB curing process, an exothermic effect is inevitable due to the crosslinking reaction and the absorption of high-energy electrons. So it is important to understand the temperature change and its influence on the properties of EB cured samples. This article describes our recent investigations on the thermal effects during an EB curing process. Temperature change, temperature change regulation, and the influence of temperature on gel fraction were analyzed in the following experiments.

EXPERIMENTAL

Materials

Epoxy resin EB-I ($M_n = 400$, $E = 0.51$), which is a bisphenol A epoxy resin from Resins Institute of

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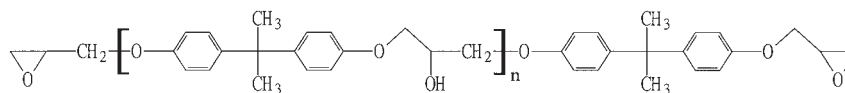


Figure 1 The chemical structure of bisphenol A epoxy resin.

Wuxi, Jiangsu Province, China, and EB-II ($M_n = 500$, $E = 0.61$), which is a phenolic aldehyde epoxy resin from Synthetic Resins Institute, Shanghai, were investigated in these experiments. Their chemical structures can be seen in Figures 1 and 2. The syntheses of the photoinitiator, diphenyliodonium hexafluorophosphate (DPIPF₆), were carried out as described in the indicated literature reference.¹⁵ Other chemical reagents were commercial products. All chemical reagents were purified prior to use.

Radiation equipment

All samples were radiated using a BF-5 electron beam accelerator, manufactured by Tsinghua University and Beijing Normal University, at a Beijing radiation center. The experimental parameters were as follows. Power: 0.7kW; electron beam energy: 5MeV; normal radiation dosage rate: 100Gy/s; magnitude of electron beam: 2×10^{-4} A. The distance between accelerator and sample was 48cm.

Measurements and apparatus

A steel mold, which has an excellent coefficient of heat conductivity, and a glass vessel, which has a poor coefficient of heat conductivity, were used in the experiments. The steel mold was radiated in the air with 50 mm \times 10 mm \times 2 mm cavities, as shown in Figure 3. The glass vessel was shielded with a 10mm aluminum plate and was also radiated in the air with dimensions of 30 mm \times 20 mm \times 40 mm, as shown in Figure 4. For research on EB penetration in the resin in a controllable direction, a taper hole with diameter of 9 mm at the top and 5mm at the bottom was opened in the aluminum plate in the EB incidence direction. The temperature of the resin was monitored during EB curing using thermocouples placed at the center of the steel mold and at specific places on the glass vessel. The gel content of the cured sample was mea-

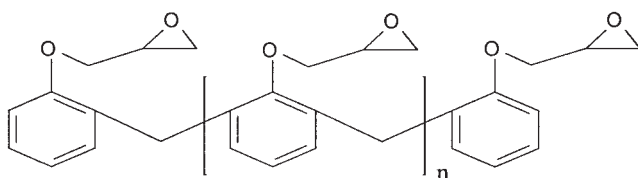


Figure 2 The chemical structure of phenolic aldehyde epoxy resin.

sured by the Soxhlet extraction method. The solvent used in extraction was toluene, and the duration of extraction was 24 h. Differential scanning calorimetry (DSC) was made with a DSC-7 calorimeter from Perkin-Elmer at a heating rate of 10°C/min from room temperature to 400°C under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The epoxy resin systems used in these experiments could undergo thermal cure during the EB curing process by the absorption of high-energy electrons and the heat release of radiation crosslinking reaction. The quantity of heat would be related to resin type, initiator concentration, dosage rate, and radiation mode, and these factors were studied in experiments. The total radiation dosage of the steel mold samples was 50kGy, and that for the glass vessel was 300kGy.

Influence of initiator concentration on temperature of steel mold samples

Temperatures measured during the EB curing with different initiator concentrations in the steel mold samples are shown in Figure 5, and the gel fractions of these samples are given in Table I.

It is obvious, in Figure 5, that when the system was pure resin, the temperature curve rose steadily all through the EB curing, but when there was initiator present, the curves were different. The temperature curves of resin systems with different initiator concentrations were similar: the temperature increased sharply with the increase of dose, and approached a plateau value after reaching a peak. Although the resin systems (without initiator) could not have the heat liberation induced by the radiation crosslinking reaction, they can absorb the energy of electron beams to raise temperature: during the radiation curing process, the high-energy electron beam can transfer en-

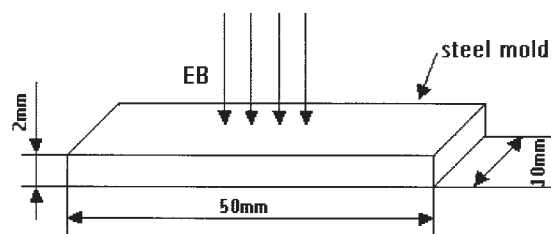


Figure 3 The sketch map of the steel mold.

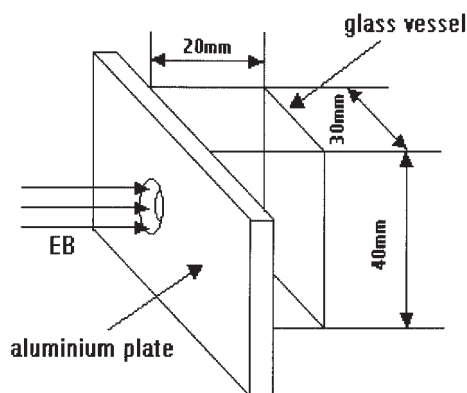


Figure 4 The sketch map of the glass vessel.

ergy to molecules of the resin systems, causing ionization or excitation. Ionization and excitation states are unstable; they can emit part of the absorbed energy in the form of heat, and so the temperature of resin systems rises. Resin systems that have initiator present will experience the crosslinking reaction (an exothermic reaction) simultaneously; therefore, the temperature can also increase. In the initial stage of radiation, the heat release of the crosslinking reaction will increase sharply because of the rapid increase of active center concentration with the accumulation of dose. Consequently, if there is no heat exchange between the resin system and the environment, the temperature will increase to a high value rapidly, and the larger the initiator concentration is, the higher the value is. In the mid and final stage of reaction, the heat capacity of the resin system will increase as a result of the increase of the crosslink density. In addition, the increasing crosslink density at the high radiation dose must reduce the number of curable functional groups in the network due to a crosslinking saturation effect, so the probability of further crosslinking reaction re-

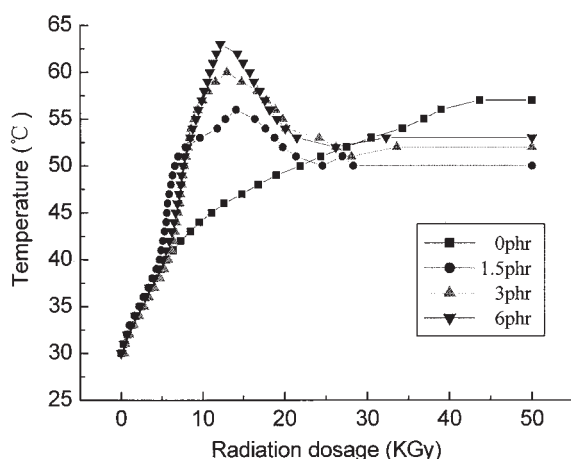


Figure 5 Temperature curve of different initiator concentration of EB-I steel mold samples.

TABLE I
The Gel Fraction of Different EB- I Resin Systems

Dosage of initiator (phr)	Gel fraction (%)
1.5	76.9
3	84.2
6	85.6

duces considerably. Consequently, heat exchange balance between resin systems and the environment is achieved. Overall, the temperature of systems without initiator will increase at all times, but the temperature of systems with initiator will finally reach a plateau value.

These resin systems were also found to be thermally curable, as expected since the photoinitiators used in these formulations have been shown to act as both photo- and thermal initiators for cationic polymerization. The DSC curves of EB-I systems with different contents of initiators were measured experimentally, as shown in Figure 6. It can be found that the onset temperature for thermal curing of these resin systems would be about 200°C. The maximum temperature measured during EB curing was 63°C, far less than 200°C. This indicates that simultaneous thermal curing during EB curing of these systems is impossible. It also can be found in Table I that the gel fraction of these three samples differed considerably, while the temperature of these three samples during EB curing had little variation. Hence, the conclusion that the heat has no direct effect on gel fraction can be induced.

Two exothermal peaks, identified as α and β , can be found in Figure 6. With the increase of initiator concentration, the location of α changed a little but the exotherm increased; meanwhile, β appreciated to α gradually. Reasons for this are possibly related to two reactions occurring during the epoxy resin curing pro-

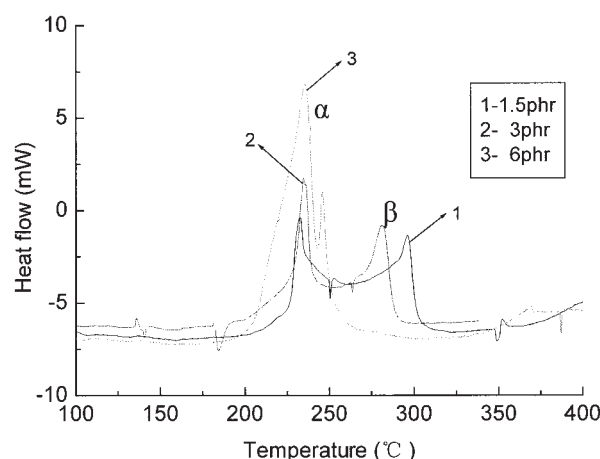


Figure 6 Exotherms measured in a DSC test for resin with increasing initiator concentration.

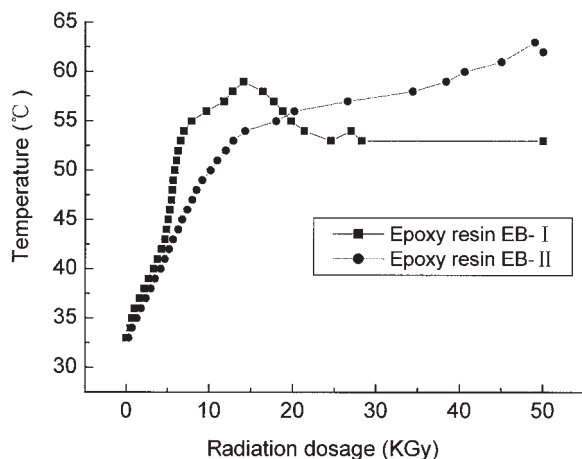


Figure 7 Temperature curve of different resin types of steel mold samples.

cess: one is an addition reaction of the epoxy group initiated by DPIP₆ (referred to as α reaction), contributing to the α exothermal peak; the other is a crosslinking reaction of epoxy groups initiated by alcoholate ion (referred to as β reaction), contributing to the β exothermal peak. With the increase of initiator concentration, a greater degree of α reaction will happen at the same time, so the exotherm will increase. The heat released by α reaction can accelerate β reaction; as a result, β approaches α with the increase of exotherm.

Influence of resin type on temperature of steel mold samples

Figure 7 shows the temperature curves of EB-I and EB-II steel mold resin systems with 1.5 phr content of initiator. It can be observed that the temperature of the EB-II resin system was increasing during the whole radiation process, while that of the EB-I resin system increased quickly in the initial radiation stage and finally approached a plateau value. There are more epoxy groups in the molecular structure of EB-II than that of EB-I; therefore, under the same radiation dose, the EB-II resin system will have more crosslinking reactions than EB-I. In this present research, the total dose was 50kGy, and the curing reaction of the EB-II resin system maintained vigorous during the entire time of radiation, so that the temperature increased all the time. Comparatively, the EB-I resin system achieved heat balance with the environment after some dose of radiation, making the temperature finally plateau.

Influence of dose rate on temperature of steel mold samples

Figure 8 shows the temperature curves of EB-I steel mold systems with 1.5 phr initiator concentration un-

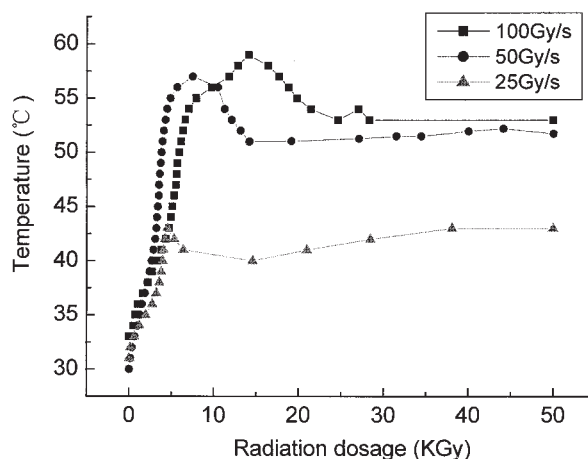


Figure 8 Temperature curve of EB-I steel mold samples with different dose rates.

der different dose rates. These three curves had the same trend: increasing quickly and, after reaching a peak, falling back and approaching an equilibrium temperature. However, the peak temperature, peak width, and equilibrium temperature increased with dose rate from 25Gy/s to 100Gy/s. With increase of the dose rate, more high energy electrons entering the resin system in unit time will lead to more intensive crosslinking reaction and give out more heat, making the peak temperature higher. At the same time, more heat release can also delay the transfer of heat from the system to its surroundings, so that the peak width broadens at a higher dose rate. At a low dose rate, because the crosslinking reaction is less vigorous, the system transfers heat to the surroundings more easily, so the equilibrium temperature for it is lower than that of the system radiated with a higher dose rate.

Table II shows the gel fraction of EB-I resin systems with 1.5phr initiator concentration at different dose rates. It is obvious that the dose rate has no influence on the gel fraction when the total radiation dose is the same, but it has a great influence on the temperature of these resin systems, demonstrating that the temperature of the resin systems also has no relation to gel fraction.

Influence of resin type on temperature of glass vessel samples

Temperatures at different points in the various epoxy resin systems containing 1.5phr initiator in the glass

TABLE II
The Gel Fraction of EB- I Resin Systems with 1.5phr Initiator Concentration Under Different Dose Rates

Radiation dose (KGy)	Dose rate (Gy/s)	Gel fraction (%)
50	25	77.1
50	50	77.3
50	100	76.9

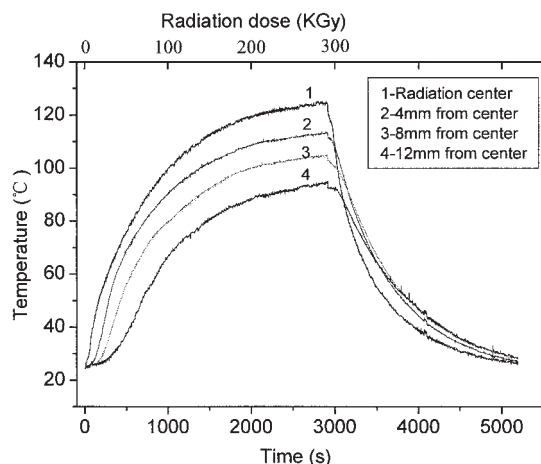


Figure 9 Temperature gradient of the longitudinal direction of the EB-I resin system.

vessel during radiation were also measured. Temperature profiles at four points, 0mm, 4mm, 8mm, and 12mm, referred to as the distance from the center of the taper hole's bottom (referred to as the radiation center) to the test point in the EB incidence direction (referred to as the longitudinal direction), and at three points, 0mm, 4mm, and 8mm, referred to as the distance from the radiation center to the test point in the direction plumbed in the incidence direction (referred to as the transverse direction) were measured until 300kGy radiation. After the radiation stopped, the temperatures of the systems were also measured. The results are shown in Figures 9, 10 and 11.

It can be found, in Figures 9 and 10, that the temperature of different points increased with increase of the radiation dose, but the relative temperature value reduced gradually from the radiation center to the inside of the resin system. According to the theory of ion implantation,¹⁶ the concentration of incident elec-

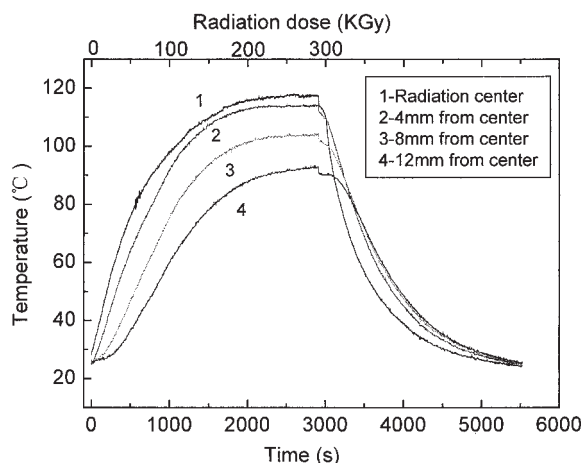


Figure 10 Temperature gradient of the longitudinal direction of the EB-II resin system.

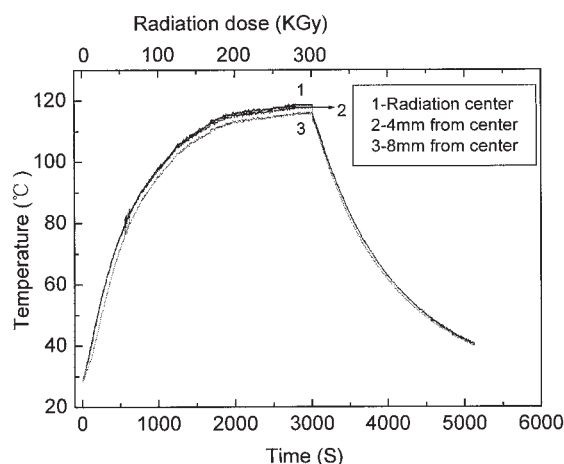


Figure 11 Temperature gradient of the transverse direction of the EB-II resin system.

trons is proportional to the radiation dose and reaches a maximum at the point that is at some extent from the radiation surface: the farther it is apart from the radiation surface, the smaller is the concentration of incident electrons. And the smaller the electron concentration is, the less the energy is absorbed, also the smaller is the release of heat. In addition, there is no gap between the glass vessel and the shielded aluminum plate. The aluminum plate could generate a great deal of heat after absorbing the high-energy electrons, and will transfer the heat to the radiation surface, so the temperature at the radiation surface is the highest. All these will influence the temperature of the resin system, engendering the temperature reduction from surface to interior.

From Figures 9 and 10, the temperature of every point in the EB-I resin system increased gradually until the completion of the radiation process. The temperature of the EB-II resin system also increased during the early and middle period of the radiation process, but then remained constant through the final period of radiation. The reason is that the density of epoxy groups in the EB-II system is larger than that in the EB-I system; hence, the probability of the groups encountering active centers is higher, and the curing reaction is more vigorous. This will lead to a higher temperature in a shorter time due to the large heat release in the system. Also, it will reach a higher degree of crosslinking at a lower radiation dose, so, with the increase of the radiation dose, the quantity of crosslinking reaction with unit dose will decrease. Meanwhile, the heat capacity of the system increases as the curing degree increases. All the factors mentioned above result in the temperature of the system reaching a stable value at the end.

After the radiation process stopped, the temperature of every point decreased rapidly. In the process of radiation, there is a balance between the absorbed

energy, reaction heat release, and thermal transition from the system to the surroundings, and so the temperature reaches a stable value. When the radiation stops, the system does not absorb energy any more and the reaction heat decreases greatly, so the balance is broken and the temperature decreases rapidly.

It is shown in Figure 11 that, with the increase of radiation dose, the transverse temperature, at every point in the EB-II glass vessel sample, increased. The temperature changed from a high value to a low value farther from the radiation center. After the radiation stopped, the trend of decrease in temperature at each point was the same, and the temperature values differed little during the whole radiation process. This is because, when the electron beam enters the resin system across the small hole, the fast electron will interact with the combined electrons and atomic nuclei, resulting in a strong scatter effect. There will be a decrease of energy during the course of scattering, inducing a decrease of secondary electrons as the beam progresses. Therefore, active centers, initiated by the secondary electrons, will decrease along the transverse direction, making the transverse temperature of the system descend slowly. In addition, with the influence of the shielded aluminum plate, which will transfer significant heat to the surface of sample, the temperature values differ little.

CONCLUSION

Results of this study clearly demonstrate that, in the steel mold resin system, the temperature has no direct relation to the gel fraction, and the temperature curves of different types of resin systems will be different. With the increase of initiator concentration, the temperature of the EB-I resin system increases sharply in the initial stage of radiation and finally approaches a plateau value after reaching a peak. Dose rate has a great influence on the temperature of the EB-I resin system: with the increase of the dose rate, the peak

temperature, peak width, and equilibrium temperature increase. In the case of the glass vessel samples, with the increase of radiation dose, temperature at different points in the longitudinal direction of the EB-I resin system will increase during the entire radiation process, while that of the EB-II resin system will finally reach a plateau value. The temperature will reduce gradually from the radiation center to the sample interior. This phenomenon will also be found in the transverse direction.

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References

1. Sui, G.; Zhong, W. H.; Zhang, Z. G. *J Mater Sci Technol* 2000, 16, 627.
2. Strong, A. B.; Black, S. R.; Olcott, D. D. *International SAMPE Symposium* 1991, 36, 173.
3. Janke, C. J.; Lomax, R. D.; Robitaille, S.; Duggan, S.; Serranzana, R. C.; Lopata, V. J. *International SAMPE Symposium* 2001, 46, 2048.
4. Deffort, B.; Drazal, L. T. *International SAMPE Symposium* 2001, 46, 2550.
5. Sui, G.; Zhang, Z. G.; Chen, C. Q.; Zhong, W. H. *Mater Chem Phys* 2003, 78, 349.
6. Crivello, J. V. *Nucl Instr Meth* 1999, B151, 8.
7. Christensson, M. *Mater Technol* 1999, 14, 51.
8. Raghavan, J.; Baillie, M. R. *Polym Compo* 2000, 21, 619.
9. Sui, G.; Zhang, Z. G.; Liang, Z. Y.; Chen, C. Q. *Mater Sci Eng* 2003, 342, 28.
10. Lopata, V. J.; Saunders, C. B.; Singh, A.; Janke, C. J.; Wrenn, G. E.; Havens, S. J. *Radiat Phys Chem* 1999, 56, 405.
11. Lopata, V. J. *Mater Technol* 1999, 14, 63.
12. Singh, A.; Saunders, C. B.; Barnard, J. W.; Lopata, V. J.; Kremers, W.; McDougall, T. E.; Chung, M.; Tateishi, M. *Radiat Phys Chem* 1996, 48, 153.
13. Beziers, D.; Perilleux, P.; Grenie, Y. *Radiat Phys Chem* 1996, 48, 171.
14. Glauser, T.; Johansson, M.; Hult, A. *Polymer* 1999, 40, 5297.
15. Beringer, F. M.; Drexler, M.; Gindler, E. M.; Lumpkin, C. C. *J Am Chem Soc* 1953, 75, 2705.
16. Wang, Y. H.; Hu, Z. Q. *Basis of Ion Implantation and Analysis*; Aviation Industry Press: Beijing, 1992.