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Analyses on curing process of electron beam radiation in epoxy resins

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Abstract

Epoxy resins have already been applied in electron beam (EB) curable composites structures extensively. The effects of different initiators and diluents on Shell Epon 828 radiation reaction were discussed in the paper, and the same radiation reaction systems were also explored using a heat treatment. The experimental results indicated cationic photoinitiator can initiate EB radiation curing of epoxy resin and traditionally heat-cured systems are not always suitable for the EB curing. The use of diluents would reduce the curing degree of resin and reactive diluents have less effect. The cationic ring-opening polymerization process including the decomposition of diaryliodonium salts under EB radiation at the initial stage and production of protonic acid that can initiate polyreaction was validated in the experiments. The characteristic of cured field and penetration process of EB in Shell Epon 828 system was also studied, and the whole cured area was found to be consisting of many lamellar structures.

Keywords: Epoxy resin; Electron beam curing; Radiation dosage; Cationic mechanism; Microstructure

1. Introduction

Electron beam (EB) curing of composites is a processing method that uses high-energy electrons from an accelerator to initiate polymerization and cross-linking of a matrix resin. It is the French company Aerospeticle that began to conduct the research work in the area of EB curable thermoset composites in the late 1970s. EB curing of composites offers many advantages compared to conventional thermal curing, such as reduced cure time, low temperature cure, greater design flexibility, and unlimited materials shelf life. As an innovative curing technology conforming to the developing trend of low cost and nuisance-free, the use of EB in the processing of composites structures has been receiving extensive attention in recent years [1–5]. Many researchers in United States, Canada, Japan and some countries in Europe threw themselves into researches and developments in this field and have been acquiring plentiful research findings. Saunders and Singh have made a lot of research works on the properties of the EB cured epoxy acrylate composites, the effect of the EB on the fiber and its sizing [6–8]. Béziers has been working on the EB curing of filament wound epoxy acrylates and bismaleimide resins composites since the 1970s [9]. The curing of vinyl monomers such as acrylates under high energy EB radiation normally proceeds via a free radical mechanism that is sensitive to oxygen inhibition and the cured resin cannot meet requirement of advanced composites due to high shrinkage, high moisture absorption and inferior mechanical properties. For developing alternative resin with suitable properties for composites application, Crivello et al. studied the cationic curing of epoxy resin by using appropriate onium salts as initiators [10,11]. As one of the polymer matrix widely used in composites, epoxy resin systems have a lot of excellent properties and processing characteristics. Most variety of epoxy resins has been confirmed to possess radiation reactivity and have already become chief resin matrix used in EB curable composites [12–15]. So far, many appropriate material systems and processes have been developed depending on great efforts of research personnel.

While not many works about fundamental investigation of EB curing has been reported, the majority of studies and programs focus on development of resin systems, optimization formula of curable composites and improvement in one property. The understanding of how EB curing takes place and its dependence on materials parameters is limited [16–19]. It is important to offer statistically design data according to desired goal and accelerate the development and maturity of EB process technology. So the basic curing process of radiated system and influence of EB-radiated system parameters on process should be studied carefully.

Although Hult [20], Ledwith [21] and Crivello [13] had proposed abbreviated mechanism of EB-induced cationic polymerization in the presence of onium salts

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photoinitiators, there is lack of dependable analysis and validation for the basic reaction process. In this paper, the radiation curing process of the Shell Epon 828 epoxy sample is studied.

2. Experimental

2.1. Materials

Shell Epon 828 epoxy resin and *N-tert*-butyl-α-phenylnitrone (PBN) as a spin trapping reagent used in this study were purchased from the institute of chemistry of Chinese Academy of Sciences (CAS). The syntheses of the photoinitiator, diphenyliodonium hexafluorophosphate ($DPIPF_6$), were carried out as described in the indicated literature references [22]. Other chemical reagents were commercial products. All chemical reagents were purified prior to use.

2.2. Radiation equipment

All samples were radiated using BF-5 electron beam accelerator at Beijing Radiation Center. The experimental parameters were as follows: power, 0.7 kW; electron beam energy, 5 MeV; radiation dosage rate, $100\,\mathrm{Gy\,s^{-1}}$; magnitude of electron beam, $2 \times 10^{-4}\,\mu\mathrm{A}$.

2.3. Measurements and apparatus

The resin mixture was poured into the aluminium molding with 50 mm × 10 mm × 2 mm in size and radiated in the air. The gel content of cured sample was measured by the Soxhlet extraction method. Differential scanning calorimetry (DSC) was made with DSC-7 calorimeter from Perkin-Elmer at a scanning rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ from room temperature to 400 °C under a nitrogen atmosphere. The IR absorption spectra of samples were conducted with Pekin-Elmer 2000 FTIR spectrometer. The TRIO-2000 mass spectrograph from VG Ltd. of UK was used for testing the mass spectrum of radiated system. The UV absorption spectra of samples were conducted with Shimadza UV at 160 °C. The concentration of $DPIPF_6$ in samples was $4 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ and the concentration of sodium 4-nitrophenoxide as hydrogen ion indicator in samples was $2.65 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$. The electron spin resonance (ESR) spectra of samples were recorded at room temperature in Bruker 300P spectrometer with 100 kHz field modulation operating at 9.77 GHz. The employed microwave power level was 10 mW, with a time constant of 640 ms and a scan range of 40 G. The concentration of PBN as spin trapping reagent was $0.1\,\mathrm{mol\,l^{-1}}$. For research on EB penetration in resin, the container filled with radiated resin system was shielded with 10 mm aluminum plate. A taper hole with diameter of 9 mm at the top and 5 mm at the bottom was opened in aluminum plate in EB incidence direction. The JSM-5800 scanning electron microscope (SEM) from JEOL Ltd. was used to observe the surface of cured field lastly and the cross-section.

3. Results and discussion

3.1. Effect of initiator

EB curing is one of the forms in the radiation curing. $DPIPF_6$ as a cationic photoinitiator and benzoin as a free radical photoinitiator were filled in epoxy resin respectively in the radiation experiment. For comparisons, the epoxy resin mixed with 2,2′-azo-bis-iso-butyronitrile (AIBN) and boron trifluoride ethylamine (BTE), respectively were also radiated with EB. AIBN and BTE are the conventional thermal curing agents, the former is a free radical initiator used in the thermal curing technology and the latter is a cationic thermal initiator.

Above-mentioned initiators ($DPIPF_6$, benzoin, AIBN and BTE) (3 wt.%) were uniformly mixed with epoxy resin, and then all the formulae were radiated in the air. These formulae manifested different features in the radiation process, the color of all samples deepened. The more the absorbed radiation dosage was, the deeper the colors of these samples were. The sample mixed with $DPIPF_6$ had been cured at a radiation dosage of 25 kGy, but the other formulae were not cured up to 300 kGy. The gel fraction of the sample containing $DPIPF_6$ improved from 71.5% at 25 kGy to 87.5% at 300 kGy with increased radiation dosage. Thermal curing experiments were also conducted for above epoxy resin systems. After being heated at 150 °C for 2 h, 200 °C for 2 h and 250 °C for 2 h, the samples containing BTE and $DPIPF_6$ were cured. These experimental results indicated that the $DPIPF_6$ is an initiator of epoxy resin with a high efficiency in EB curing process. Traditionally thermosetting materials are not always suitable for the EB curing; the chief reason is that the different energy form and mode of transfer between the thermal curing and radiation curing bring about diversity in their physics and chemical processes.

Though the epoxy resin sample containing $DPIPF_6$ can be cured in the thermal curing experiment, we can see the thermal initiating temperature of $DPIPF_6$ is above 200 °C from DSC curve of thermal curing reaction (Fig. 1). Because the small exotherm in the EB curing course is not large enough to induce the thermal initiating reaction of $DPIPF_6$, the effect of thermal initiation can be eliminated.

3.2. Effect of diluents

The resin viscosity is an important variable for composites manufacturing, affecting the flow-out properties and the resin wetting characteristics in the composites process. Since viscosity of EB curable resin is usually high, the diluents, mostly being reactive diluents, are used to decrease viscosity of curable system, or to enhance the radiation sensitivity of the systems.

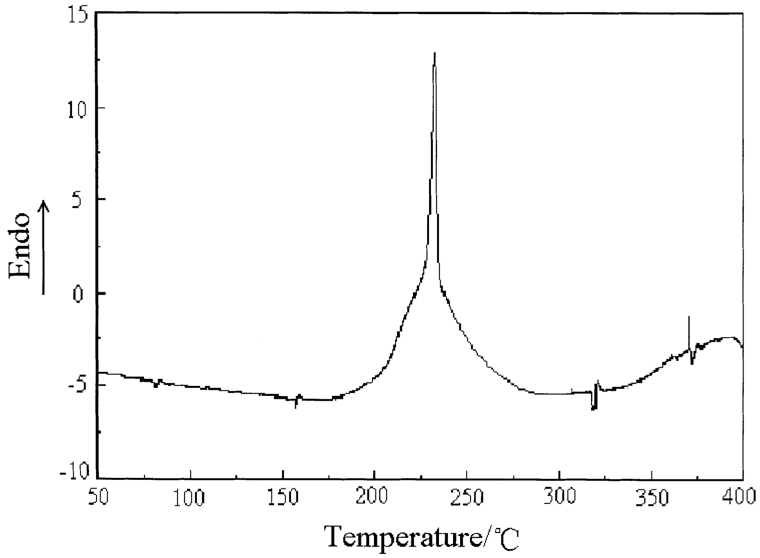


Fig. 1. The DSC curve of Shell Epon 828 epoxy resin mixture containing 3 wt.% DPIPF$_6$.

Five kinds of diluents were used in the experiments: allyl glycidyl ether, dichloromethane, trichloromethane, tetrachloromethane and triethylamine. The first one is a reactive diluent; the rests are non-reactive diluents. The dosage of diluents was 20 wt.%, and the radiation dosage was 250 kGy. The experimental data in contrast to systems containing no diluents was shown in Table 1. From Table 1, we can see that the gel fraction of sample mixed with reactive diluents whose molecules can participate in forming the cross-linked network is the highest, but is lower than that of sample containing no diluents. The resin system containing triethylamine is not cured during the radiation process. The reason may be that triethylamine, which is electron-donating solvent, can inhibit the radiation curing reaction in the cationic mechanism, but the reaction can take place after an induction period. The gel fractions of samples increase along with the mass percent of hydrogen in the electrophilicity solvent including dichloromethane, trichloromethane and tetrachloromethane. This is because the hydrogen in the electrophilicity solvents can facilitate the forming of cationic active center, and accelerate the curing of epoxy resin. From these experimental phenomena, we can also conclude that the curing of epoxy resin proceeds via cationic mechanism under the EB radiation.

Table 1
The effect of diluents on the gel fraction of 828 epoxy resin systems

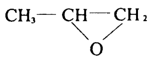
Diluents	Gel fraction (%)
–	88
Allyl glycidyl ether	85
Dichloromethane	83
Trichloromethane	82
Tetrachloromethane	80
Triethylamine	Not cured in the radiation process

The dosage of diluents is 20 wt.%, and the radiation dosage is 250 kGy.

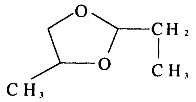
3.3. *Deduction of radiation reaction process of epoxy resin*

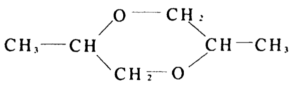
Radiation reaction mechanism of epoxy resin was studied by using epoxy propane as model compound of single epoxy functional group. The radiated system consisted of epoxy propane and 1.5 wt.% DPIPF$_6$. The radiation dosage was 5 kGy. The infrared spectrum of sample before and after EB radiation was shown in Fig. 2. From Fig. 2, the obvious change of radiated sample in infrared spectrum include: C–H stretching vibration peak (2800–3000 cm^{-1}) does not appear owing to particular structure of epoxy propane before being radiated, but strong absorption peak appears here after being radiated; intensity of epoxy group absorption peak (836 cm^{-1}) declines after being radiated; asymmetric stretching vibration peak of aliphatic ethers (1100 cm^{-1}) does not appear before being radiated and a strong absorption peak appear here after being radiated. In view of the above facts, epoxy group of epoxy propane had been opened and the polymerization had taken place during the radiation process resulting in forming of aliphatic ether bond and appearance of C–H stretching vibration peak. Moreover, the appearance of the new absorbance peak (3500 cm^{-1}) after being radiated manifest the forming of –OH on account of ring-opening of epoxy group.

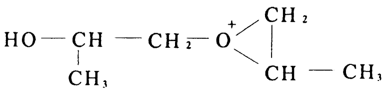
The above radiated epoxy propane system was separated and identified by the combination of gas chromatography and mass spectrometry(GC–MS). The analysis result of GC is shown in Fig. 3 and mass spectrograms are omitted here. According to infrared spectrum and MS of separated component, the radiation products were confirmed to include the following ingredients:

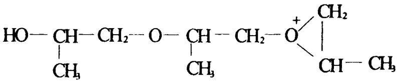

(m/z=58)

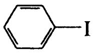

(m/z=78)


(m/z=116)


(m/z=116)


(m/z=117)


(m/z=175)


(m/z=204)

Through the analysis of radiated system, the products in polymerization process such as dimer, trimer of epoxy propane can be seen definitely. Besides, the photolysis products of DPIPF$_6$ such as benzene and iodobenzene can also be seen.

For detecting the existence of free radicals in the radiation reaction, PBN as spin trapping agent was added in above system. The ESR spectrum was tested immediately after 5 kGy radiation. The obtained ESR spectrum (Fig. 4) exhibits that there were several free radical transients indeed produced in the radiation process. These detected signals in ESR spectra correspond to the well-known 6-line pattern described for the nitroso radical resulting from the combination of PBN and radiation-induced radical. These 6-line spectra can be separated into three groups and the relative intensities and symmetry of the spectral line in each group is different. So, these ESR spectra can be assigned to several kinds of radical transients.

According to Crivello [11], and Olah [23] onium salts with non-nucleophilic complex anions can produce protonic acid in photolysis. We made use of sodium 4-nitrophenoxide as hydrogen ion indicator [24], which was added into acetonitrile solution of DPIPF$_6$. As a hydrogen ion indicator, chemical equilibrium of sodium 4-nitrophenoxide can be expressed as: $A^- + H^+ \rightarrow HA$, and $[HA]/[A^-][H^+] = K$, where K is a equilibrium constant. Sodium 4-nitrophenoxide has two absorption peaks in its UV absorption spectrometry, it is believed that absorption peak at 420 nm is assigned to alkali form structure (A^-), and absorption peak at 305 nm is assigned to acid form structure (HA). The UV absorption spectrometry of radiated acetonitrile solution of DPIPF$_6$ is shown in Fig. 5. From Fig. 5, the intensities of peaks at 420 nm descend with the increasing radiation dosage while the intensities of peaks at 305 nm increase. Increased values of absorption intensity at 305 nm for acetonitrile solution of DPIPF$_6$ with and without Shell Epon 828 epoxy resins are illustrated in Fig. 6. It can be found that the increased extent of absorption intensity for solution containing epoxy resins is less than that of the solution containing no epoxy resins under the same radiation dosage. Apparently, the acid

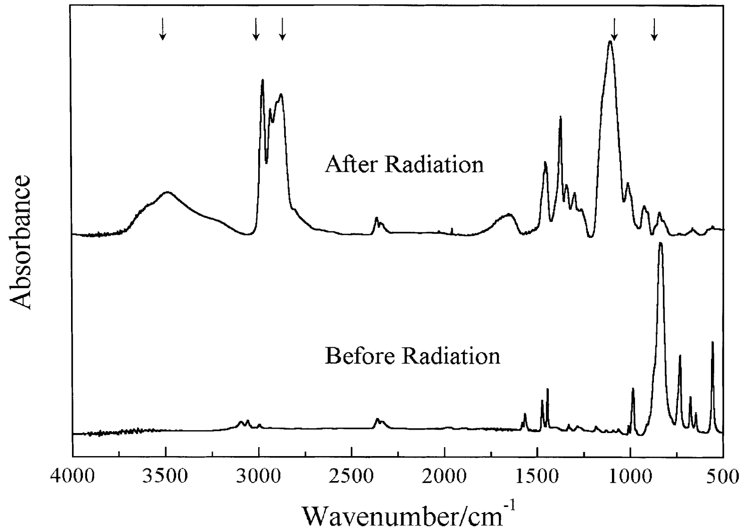


Fig. 2. Infrared spectrum of epoxy propane mixture containing 1.5 wt.% DPIPF$_6$ before and after 5 kGy radiation.

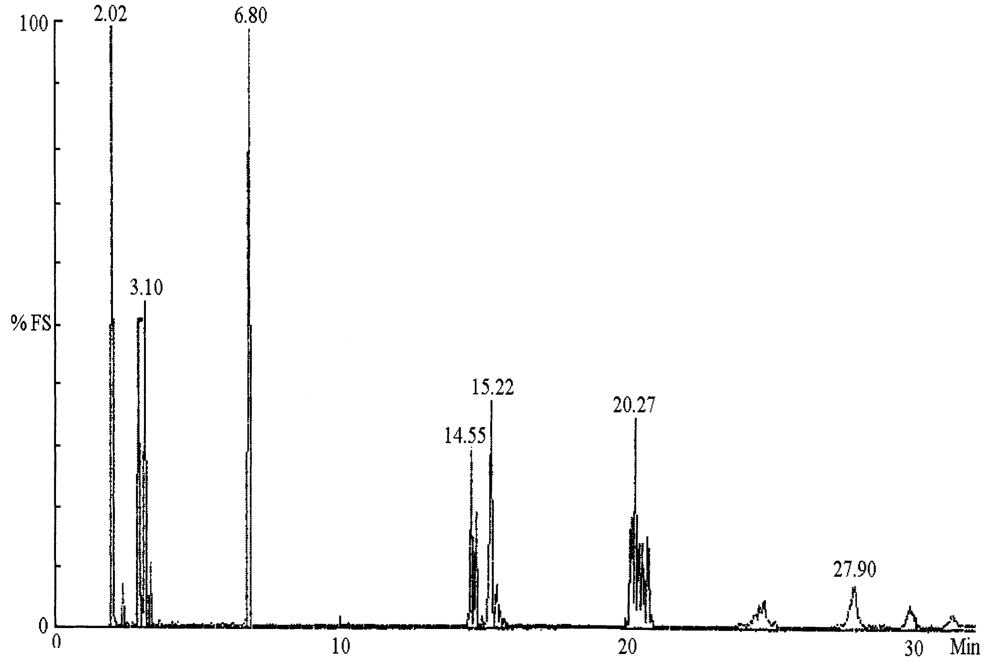


Fig. 3. Gas chromatogram of epoxy propane mixture containing 1.5 wt.% DPIPF$_6$ after EB radiation.

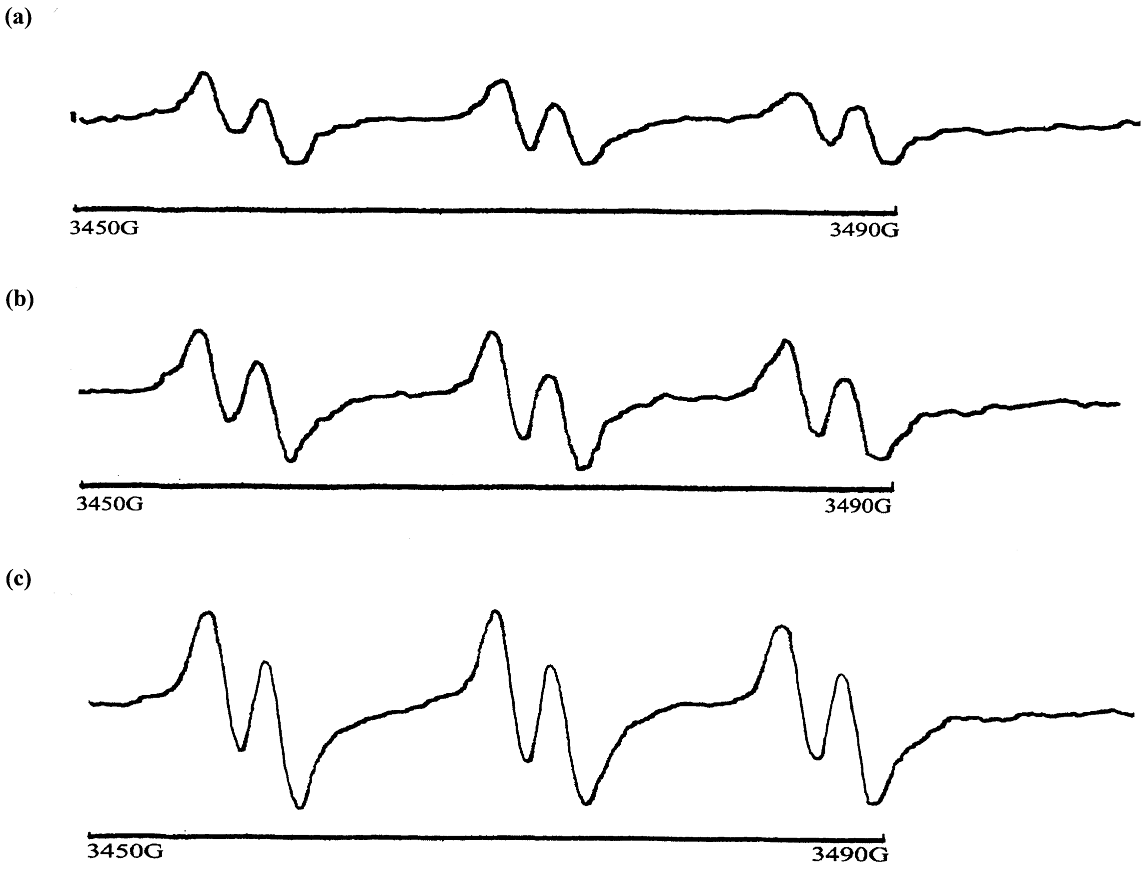


Fig. 4. Electron spin resonance (ESR) graphs of epoxy propane mixture containing 1.5 wt.% DPIPF$_6$ after EB radiation (PBN as spin trapping agent) (a) $f = 9.773556$ GHz; (b) $f = 9.773254$ GHz; (c) $f = 9.773113$ GHz.

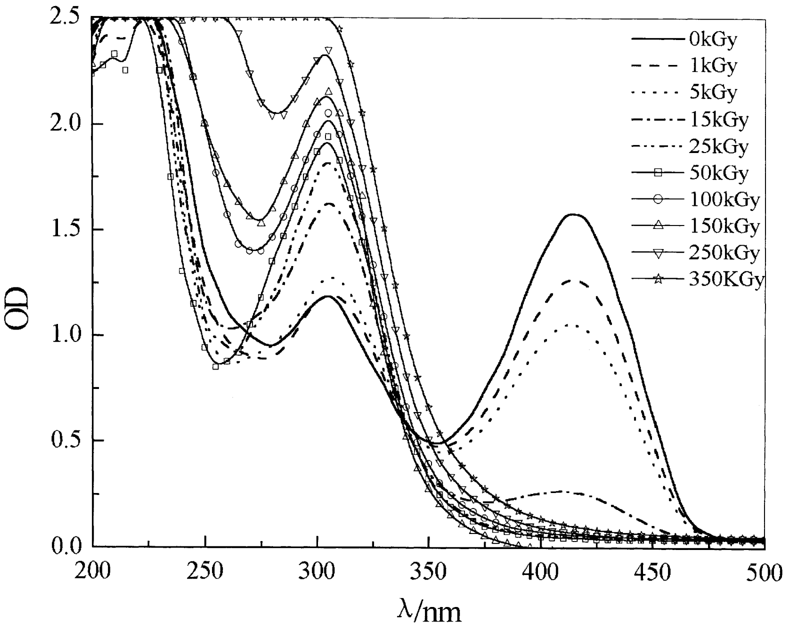
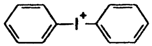


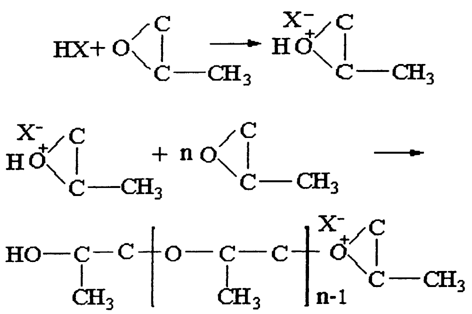
Fig. 5. UV absorption spectrum of the radiated acetonitrile solution of $DPIPF_6$.

is produced and takes part in curing reaction in EB radiation process of epoxy resins.

From above analysis, it can be concluded that polyreaction of epoxy propane system proceeds in terms of cationic mechanism. Above all, $DPIPF_6$ is decomposed under EB radiation and the protonic acid is produced. The protonic acid initiates ring-opening polymerization of epoxy propane. Owing to cationic polyreaction of epoxy propane possess characteristic of step polymerization and the reaction is in initial stages, so the molecular weight of products are relatively low. The detailed reaction process is proposed as follows($Ar_2I^+X^-$ denotes  PF_6^-, and RH denotes monomers, diluents and impurities containing hydrogen.):

$$Ar_2I^+X^- \xrightarrow{EB} ArI^{+\cdot}X^- + Ar\cdot$$

$$ArI^{+\cdot}X \xrightarrow{RH} ArI + HX + R\cdot$$



If the epoxy monomers with polyfunctional group exist in the radiated system, space cross-linked network would be formed according to above mechanism and the curing of materials is achieved.

In the radiation experiment of epoxy resin, when ethanol or para-benzoquinone was added into reaction system, the radiation dosage needed for curing was increased. This is because ethanol can act as proton acceptor and react with cationic active center in the radiation process. While the para-benzoquinone was used as a “radical scavenger”, it can capture the radical-cationic transients produced in EB radiation process to affect the formation of cationic active center. Only the ethanol or para-benzoquinone in reaction system is exhausted, can the curing reaction take place. The

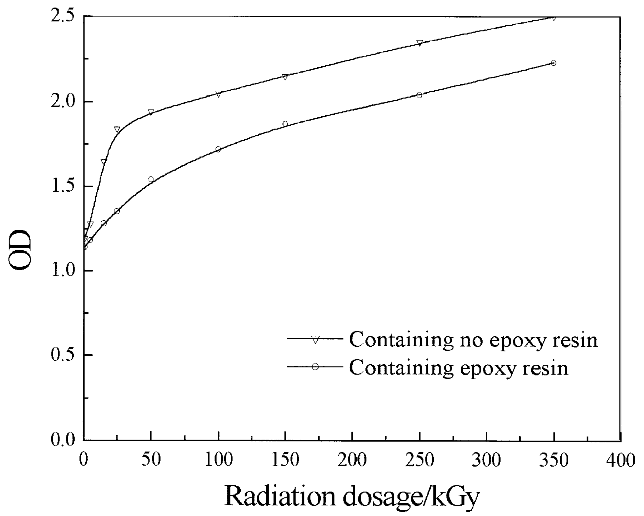


Fig. 6. Absorption intensity vs. radiation dosage at 305 nm in UV spectrum of the radiated acetonitrile solution of $DPIPF_6$.

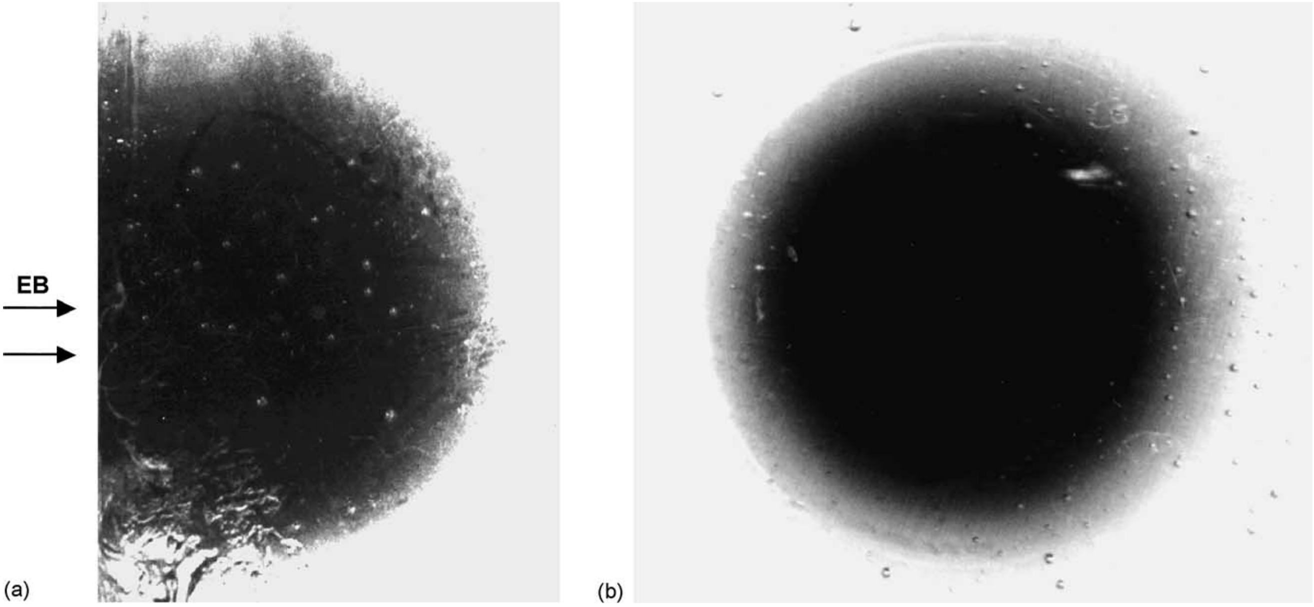


Fig. 7. The appearance of the EB radiated resin (a) front elevation; (b) side elevation.

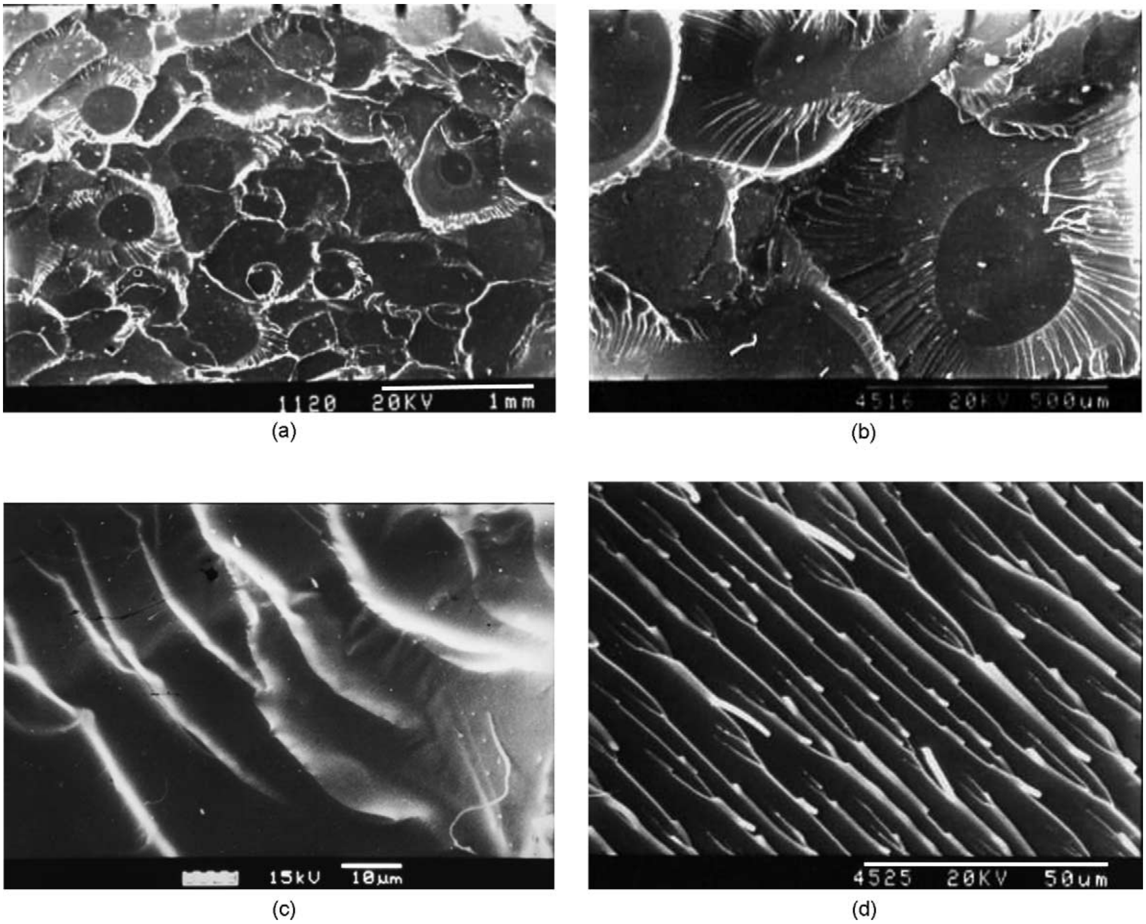


Fig. 8. SEM micrographs of radiation-cured surface of epoxy matrix (a) lamellar structures in the surface of cured resin; (b) the partially enlarged micrograph of (a); (c) the enlarged micrograph for border of lamellar structure; (d) the cross-sectional microstructure parallel with the direction of EB radiation.

elimination of cationic and radical inhibitor is important in the radiation curing of epoxy resins. Moreover, it was found that both vacuum and air have little effect on radiation curing reaction of epoxy resin. Therefore, oxygen diffusion through the resin is severely limited during the radiation process, the active transients in radiated systems was not allowed to react with the oxygen.

3.4. *Observation and analysis of radiation cured field of epoxy resin*

Since the weight of electron is very small, the direction of motion of electron can be easily changed in ionization, radiation and scattering. The route of electron in radiated system is rather tortuous, and the depth of penetration is shorter than actual route of electron. Study on forming and dimension of cured field is important to the determination of radiation parameters and technology.

In experiment, the cured resin extended around the ingoing hole with increasing radiation dosage, and formed a hemispheroidal-like cured field. The dimensions of the cured field are enlarging with the increasing of radiation dosage, but the enlarging extent is decreasing. The color of cured field is gradually light along with depth, as shown in Fig. 7. Around the cured field, some semitransparent and small grains that is indiscerptible in solvent are found, which is a small quantity of gel formed at initial stage of radiation curing reaction of resin. These phenomena show that intense scattering takes place when EB penetrates epoxy resin system, and the energy transfers between high-energy electron and radiated system within certain field around ingoing hole. While the diffusion of protonic acid derives from radiation decompose of $DPIPF_6$ take place and initiate curing reaction in certain area.

The radiated epoxy resin sample was taken out from container and the surface of cured field was washed clean. The SEM was used to observe the surface of cured field and the results were shown in Fig. 8. The obvious developing sheet structure was found in Fig. 8(a), and each sheet structure is made up of tiny lamellar structures actually as shown in Fig. 8(b) and (c). The sheet structure can also be seen evidently from Fig. 8(d), which demonstrates the cross-sectional microstructure parallel with the direction of EB radiation. These facts indicate that EB curing reaction spread forward layer upon layer around active center when EB radiates epoxy resin. Whole cured area is consisting of many lamellar structures. Investigations on formation and influencing factor of structure in cured field are currently under way and the results will be reported in the future publication.

4. Conclusions

Shell Epon 828 was studied in experiment. The EB curing reaction mechanism of epoxy resin was analyzed and validated in this paper. Cationic photo-initiator can initiate EB radiation curing of epoxy resin, and traditional thermal cure system is unsuited for EB curing. For thermal stability of diaryliodonium salts, thermal initiation effect in EB curing process can be negligible. The use of diluents would reduce the curing degree of resin and reactive diluents have less effect, but electron-donating solvent can inhibit from radiation curing of epoxy resin. The IR, ESR,GC-MS were combined to study radiation reaction mechanism of epoxy resin by using epoxy propane as model compound. The cationic ring-opening polymerization process including diaryliodonium salts decomposition under EB radiation in the first instance and production of protonic acid that can initiate polyreaction was deduced. By analyzing on radiation curing area of epoxy resin, it can be seen that the curing reactions take place around incident EB with increasing radiation dosage owing to intense scatter of EB and the diffusion of protonic acid in epoxy resin system. The results of observing the cured areas indicate that EB-cured resin extend outwards layer upon layer around active center when EB radiates epoxy resin. Whole cured area is consisting of many lamellar structures.

Acknowledgements

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