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# RESEARCH ON ELECTRON BEAM CURING OF BISPHENOL A EPOXY RESINS

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**Abstract:** The electron beam (EB) curing process of Shell Epon 828 was studied in this paper. The effect of different initiators and diluents on radiation reaction was investigated, and radiation reaction systems were also researched using heating treatment. The experimental results indicated cationic photo initiator can initiate EB radiation curing of epoxy resin, and traditional thermal cure system is unsuitable for EB curing. Due to the temperature of thermal decomposition of diphenylliodonium salts is above 200℃ and the exotherm of EB curing reaction is usually very small, the thermal initiation effect can be eliminated in EB curing reaction course. The use of diluent would reduce the gel fraction of resin and the electron-donating solvent can inhibit from radiation curing of epoxy resin. The EB curing reaction mechanism of epoxy resin was studied in the experiment. The IR, ESR, GC-MS were combined to study radiation reaction mechanism of epoxy resin by using epoxy propane as model compound of single epoxy functional group. The 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. The effect of radiation dosage on gel fraction of resin, glass transition temperature (Tg) and dynamic modulus was also analyzed in the paper. The resin gel fraction is increased with the rising radiation dosage till 250 kGy, but the increasing extend become very small after the radiation dosage reaches 100kGy. With the rising radiation dosage, the change of dynamic modulus of epoxy resin at 30℃ is not obvious, but the Tg values and dynamic modulus at 120℃ of resin is increased remarkably. So the heat-resisting performance of resin can be improved by absorbing more radiation dosage within critical value.

**KEYWORDS:** Radiation Curing, Epoxy Resins, Electron Beam, Cationic Mechanism, Gel Fraction, Glass transition temperature

## INTRODUCTION

The requirement for the high performance fiber-reinforced polymer matrix composites is growing at a high rate per year. New and innovative manufacture technology must be

developed to meet the increasing need. As a innovative curing technology conforming to developing trend of low cost and nuisance free, EB curing of composite involves using electrons radiation to initiate polymerization and crosslinking reaction in a suitable matrix resin in place of the traditional thermal curing. Many advantages have been realized for EB processing over conventional thermal curing. EB curing of composites has been paid a great attention and a great deal of progress has been made in recent years. The EB curing technology has been used in manufacturing composite parts by various fabrication processes including hand lay up, tow placement, filament winding, resin transfer molding and vacuum assisted resin transfer molding.[1-3]The basis and application researches for this technology are active and indispensable at present.

Epoxy resins that have a lot of excellent properties and different molecular structures are widely used as matrix in composites. Most variety of epoxy resin has been confirmed to possess radiation reactivity and have already become main resin matrix used in EB curable composites.[4,5] In this paper, the radiation curing process of the Shell Epon 828 sample and effect of radiation dosage are researched.

## EXPERIMENTAL

### Materials

Shell Epon 828 and N-tert-Butyl-α-phenylnitrone (PBN) as spin trapping agent used in experiment was purchased from the institute of chemistry of Chinese Academy of Sciences (CAS). The syntheses of the photo initiator, diphenyliodonium hexafluorophosphate ($DPIPF_6$) was carried out as described in the indicated literature references[6]. Other chemical reagents were commercial products. All chemical reagents are purified prior to use.

### Radiation equipment

All samples were irradiated using BF-5 electron beam accelerator at Beijing radiation center. The experimental parameters were as follows. Power: 0.7kW; electron beam energy: 5MeV; radiation dosage rate: 100Gy/sec; magnitude of electron beam: $2\times10^{-4}$μA.

### Testing measurement and apparatus

The IR absorption spectra of samples were determined with Pekin-Elmer 2000 FTIR spectrometer in the institute of chemistry of CAS. ESR spectra of samples were recorded at room temperature in Bruker 300P spectrometer with 100kHz field modulation operating at 9.77GHz. The employed microwave power level was 10mW, with a time constant of 640ms and a scan range of 20G. The thickness of PBN as spin trapping agent was 0.1mol/L. The TRIO-2000 mass spectrograph in the institute of photograph chemistry of CAS was used for testing of mass spectrum. Dynamic Mechanic Analysis (DMA) was performed at a heating rate of 5℃/min with dynamic mechanic thermal analyzer (DMTA-IV; Rheology Co.). The glass transition temperatures (Tg) of irradiated sample was identified by the maximum of the tan δ curves. Differential Scanning Calorimetry (DSC) was made at a scanning rate of 10℃ /min from room temperature to 400℃ under a nitrogen atmosphere using a DSC-7 Perkin-Elmer calorimeter.

Irradiated epoxy resin systems were poured into mould with 50mm long, 10mm wide, 2mm

deep. The gel fraction of irradiated resin was determined by the Soxhlet extraction method.

## RESULTS AND DISCUSSION

### Effect of initiator

In radiation experiment, $DPIPF_6$ as cationic photoinitiator and benzoin as free radical photoinitiator were filled in epoxy resin respectively. For compared to conventional thermal curing systems, the epoxy resin mixed with 2,2'-azo-bis-iso-butyronitrile (AIBN) and boron trifluoride ethylamine respectively were also irradiated with EB, the former is free radical initiator used in thermal curing technology and the latter is cationic thermal initiator.

3wt% above-mentioned initiator was mixed with epoxy resin uniformly, and then all formulae were irradiated in the air. These formulae manifested different feature in radiation process, but the color of all samples deepened. The more the absorbed radiation dosage was, the deeper the colors of these samples were. The sample containing $DPIPF_6$ had been already cured at radiation dosage of 25kGy, but other formulae were not cured up to 300kGy. These experimental results show that $DPIPF_6$ is high efficiency initiator to epoxy resin in EB curing, and epoxy resin system containing benzoin is not sensitive to EB radiation. So the EB radiation curing of epoxy resin proceed in cationic mechanism.

Thermal curing experiments were also made for above several epoxy resin systems. After heated at 150℃ for 2hours, 200℃for 2 hours and 250℃ for 2 hours, the samples containing boron trifluoride ethylamine and $DPIPF_6$ were cured. It indicates that traditional thermal curable systems are not always suitable for EB curing because that different energy form and mode of transfer in thermal and radiation curing bring about diversity in their physics and chemical process.

Though the epoxy resin sample containing $DPIPF_6$ can be cured in thermal curing experiment, but from DSC curve of thermal curing reaction, we can see the reaction temperature is above 200℃ (Figure 1). Because exotherm of EB curing reaction is usually very small, it cannot induce decomposition of $DPIPF_6$, so thermal initiation effect can be eliminated in EB curing reaction course.

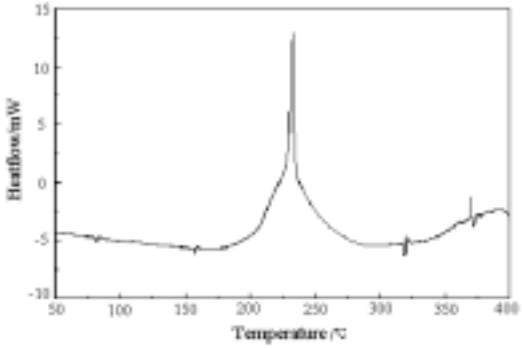



Fig.1 The DSC curve of Shell Epon 828 mixture containing 3wt% $DPIPF_6$

### Effect of diluent

Since viscosity of EB curable resin is high, the diluents, mostly being reactive diluents, are used to decrease viscosity of curable system, even enhance the system radiation sensitivity. Allyl glycidyl ether, trichloromethane and triethylamine were used as diluents in experiment. The former is reactive diluent, the latter two are non-reactive diluents. The usage of diluents is 20wt%, and the radiation dosage is 250kGy. The experimental data contrast to systems not

containing diluents was seen in Table 1. From Table 1, we can see the gel fraction of sample filled with reactive diluents whose molecular can participate in forming the crosslinked network is the highest in resin systems containing diluents, but is lower than sample not containing diluents. The resin system containing triethylamine is not cured during the radiation process. The reason is maybe that triethylamine, which is electron-donating solvent, can inhibit from radiation curing reaction proceeding in cationic mechanism, but the reaction can take place after induction period. From above experimental phenomena, we can also conclude that the curing of epoxy resin proceeding in cationic mechanism under the EB radiation.

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

| Diluents Species | Gel fraction（%） |
|---|---|
| — | 88 |
| Trichloromethane | 82 |
| Allyl glycidyl ether | 85 |
| Triethylamine | Not cured and darken in radiation process, but curing after a time. |

**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 irradiated system consisted of epoxy propane and 1.5wt% $DPIPF_6$ and the radiation dosage was 5kGy. The infrared spectrum of sample before and after EB radiation was shown in Figure 2. From the Figure 2, we can see that obvious change of irradiated 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 radiation, but strong absorption peak appear here after radiation; epoxy group absorption peak (836$cm^{-1}$) is strong before radiation and the intensity of peak is weak after radiation; asymmetric stretching vibration peak of aliphatic ethers (1100$cm^{-1}$) does not appear before radiation and a strong absorption peak appear here after radiation. In view of the above facts, epoxy group of epoxy propane had been opened and the polymerization reaction had taken place during 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 radiation manifest the forming of –OH on account of ring opening of epoxy group.

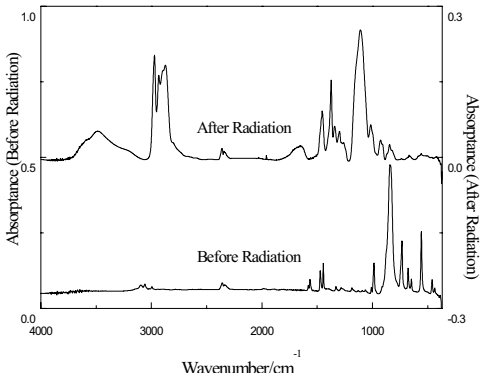
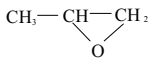
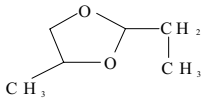



Fig.2 Infrared spectra of epoxy propane mixture containing 1.5wt% diaryliodonium salts before and after radiation

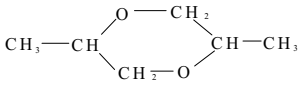
The above irradiated epoxy propane system was separated and identified by the combination of gas chromatograph and mass spectrum (GC-MS). According as MS figures of separated component and infrared spectrum, the radiation products were confirmed to include following ingredient:

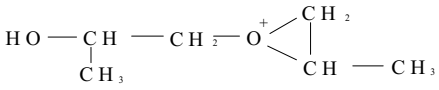

（m/z=58）

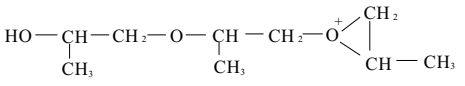

（m/z=78）


（m/z=116）


（m/z=204）


（m/z=116）


（m/z=117）

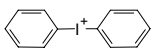

（m/z=175）

Through the analysis of irradiated system, the products in polymerization process such as dimmer, trimer of epoxy propane can be seen definitely. Besides, the photolysis products of $DPIPF_6$ such as benzene and iodobenzene can also be seen.

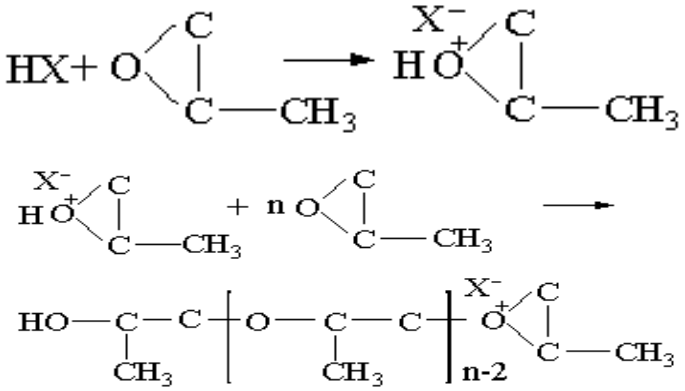
For detecting if the free radicals exist in radiation reaction, PBN as spin trapping agent was added in above system. The ESR spectrum was tested just after 5kGy radiation. The obtained ESR spectrum (Figure 3) exhibit that free radical is produced in radiation process. From the ESR spectrum, we can get: g=2.01；$A_1$=14.35G；$A_2$=2.91G. Intensity ratio of two peaks result from second-order splitting is 1:1, and maybe derives from coupling effect of proton in phenyl, so the obtained free radical was aromatic free radical.


Fig.3 ESR graph of epoxy propane mixture containing 1.5wt% diaryliodonium salts after EB radiation

(f=9.773254)

According to Crivello et al., [7,8] onium salts with non-nucleophilic complex anions can produce protonic acid in photolysis. Therefore the polyreaction process of epoxy propane system in term of cationic mechanism can be concluded. Above all, $DPIPF_6$ is decomposed under EB radiation and the protonic acid is produced. The protonic acid initiates ringopening polymerization of epoxy propane. Owing to cationic polyreaction of epoxy propane possess character of step polymerization and the reaction is in initial stages, so the molecular weight of products are relatively small. The detailed reaction process is as follows（$Ar_2I^+X^-$ denotes  ）：

$$Ar_2I^+X^- \xrightarrow{e\text{-}beam} \left[\begin{array}{l} ArI^+\cdot X^- + Ar\cdot \\ ArI + Ar^+ X^- \end{array}\right] \xrightarrow{\text{monomer or impurity}} HX + ArI + Ar\cdot$$



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

**Influence of radiation dosage**

The Figure 4 shows the change of gel fraction of resin with the radiation dosage. It can be seen that the gel fraction of resin is increasing with the rising of radiation dosage, but the increased extent become very small after the radiation dosage reach 150kGy. On the basis of Charlesby's radiation theory,[9,10] the relation between crosslinking number ( $q_0$ ) and degradation number ( $p_0$ ) and solubility of irradiated sample (*S*) can be expressed in following equation with the assumption that molecular weight of sample is random:

$$S + \sqrt{S} = P_0 / q_0 + \frac{1}{q_0 u_1 R} \qquad (2)$$

Where *S* is the weight fraction of the soluble polymer, *S*=1-g, where g is the gel fraction, $u_1$ is the average degree of polymerization, and *R* is the radiation dosage. The value of $S + \sqrt{S}$ is plotted as function of *1/R* in the Figure 5. Because practical situation is not same as hypothesis entirely, the linear regressions are taken from the experimental data. The intercept of regression line gives $p_0 / q_0$ =0.417, and $q_0$ =0.024/kGy can be worked out by the slope. This result shows that the crosslinking reaction is predominant in EB-irradiated epoxy resin system, but degradation reaction exists simultaneously. Therefore in radiation initial stage, the resin crosslinked network is incompact, and action space of macromolecular with active species is enough, so that the crosslinking reaction probability is much. Furthermore, the thickness of photo initiator in radiation initial stage is high, crosslinking reaction is dominant. Therefore, gel fraction of the resin increase very fast in low dosage radiation stage. With the rising of radiation dosage, crosslinking density of resin system is increased, mobility of macromolecular is weakened and the crosslinking reaction probability is decreasing. Besides, the number of crosslinkable functional group in network is decreased. So unit radiation dosage brings about less crosslinking reaction to take place. At the same time, the radiation degradation reaction is relative independence and the formed crosslinking network is affected mostly by degradation reaction when EB radiation dosage keeps on rising.

As a result, the increased extent of the resin gel fraction becomes small with the rising of radiation dosage.

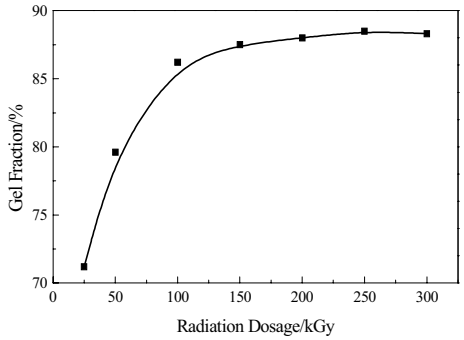



Fig. 4 The curing degree of Shell Epon 828 vs. radiation dosage

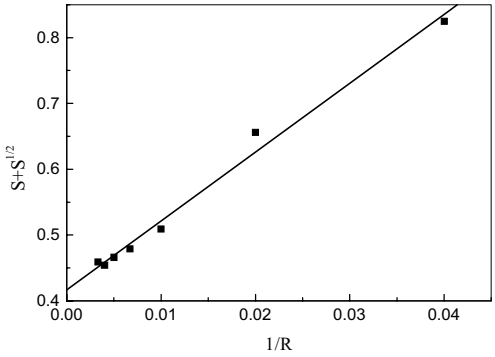



Fig.5 1/R vs. $S+\sqrt{S}$ of Shell Epon 828 in radiation process

Dynamic modulus and Tg of cured epoxy resin systems had been determined in experiment, and the data in Table Ⅱ show that Tg increase with the rising of radiation dosage owing to the increased gel fraction of resin. It also can be seen that dynamic modulus at 30℃ has not obvious change and the dynamic modulus at 120℃ increase with the rising of radiation dosage. This is because the crosslinking reaction take place mostly in amorphous region of resin, so that the change of dynamic modulus of epoxy resin at 30℃ is not obvious and the dynamic modulus at 120℃ is increased remarkably. So the heat-resisting performance of resin can be improved if the radiation dosage rises within critical value.

Table Ⅱ Effect of radiation dosage on epoxy resin system

| Dosage of photo initiator (phr) | Radiation dosage (kGy) | Tg (℃) | E′ at 30℃ (Pa) | E′ at 120℃(Pa) |
|---|---|---|---|---|
| 3 | 50 | 133 | $3.15\times10^{9}$ | $9.02\times10^{8}$ |
| 3 | 150 | 164 | $3.25\times10^{9}$ | $1.75\times10^{9}$ |
| 3 | 250 | 177 | $3.31\times10^{9}$ | $2.06\times10^{9}$ |
| 3 | 300 | 183 | $3.26\times10^{9}$ | $2.08\times10^{9}$ |

## SUMMARY AND CONCLUSIONS

EB radiation Reaction Process of Shell Epon 828 was studied in experiment. Cationic photoinitiator can initiate EB radiation curing of epoxy resin, and traditional thermal cure system is unsuited for EB curing. The use of diluent would reduce the curing degree of resin

and reactive diluent has less effect, but electron donating solvent can inhibit from radiation curing of epoxy resin. The radiation reaction mechanism of epoxy resin was studied by using epoxy propane as model compound of single epoxy functional group. The cation ringopening polymerization process including diaryliodonium salts decomposition under EB radiation in the first instance and production of protonic acid that can initiate polyreaction is deduced. The gel fraction of resin is increased with the rising of radiation dosage, but the increasing extent became very small after the radiation dosage reached 100kGy. the dynamic modulus at 120℃ and Tg of irradiated samples increase with the rising of radiation dosage owing to the increased gel fraction of resin.

## ACKNOWLEDGMENTS

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