

# A study of the photoactivities and thermomechanical properties of epoxy resins using novel [cyclopentadien-Fe-arene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> photoinitiators

Tao Wang<sup>a,\*</sup>, Li J. Ma<sup>a</sup>, Ping Y. Wan<sup>a</sup>, Jin P. Liu<sup>b</sup>, Fang Wang<sup>c</sup>

<sup>a</sup> College of Science, Beijing University of Chemical Technology, 144#, Beijing 100029, China

<sup>b</sup> Institute of Frontier Medical Science, Jilin University, Changchun 130021, China

<sup>c</sup> School of Basic Medical Science, Jilin University, Changchun 130021, China

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## Abstract

The cationic photopolymerization of epoxy resins, initiated by novel cyclopentadien-Fe-arene hexafluorophosphate ([cyclopentadien-Fe-arene]<sup>+</sup>PF<sub>6</sub><sup>-</sup>), has been investigated. The influence of different photoinitiators and the presence of different epoxy monomers on the rate of photopolymerization and on the thermomechanical properties of the UV-cured film obtained had been studied. Using [cyclopentadien-Fe-biphenyl]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFB) as photoinitiator, the photoactivity increased obviously when cycloaliphatic epoxy monomer 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221) was added in epoxy resin (E44), but the film obtained is micro-heterogeneous. However, in spite of the lower activity, the film from glycidylether 1,2,3-(2,3-epoxypropyl)-glycidylether (EPON-812) + E44 is homogeneous. The film obtained from di(2,3-epoxypropyl)3,4-epoxy-1,2-cyclohexanedioate (TDE-85) + E44 possesses the highest glass transition temperature *T<sub>g</sub>*. Photoinitiators can influence the properties of the resulting epoxy resins, including the rigidity, crosslink density, *T<sub>g</sub>* and homogeneity. The resulting epoxy resin initiated by [cyclopentadien-Fe-toluene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFT) with lower photoactivity got the highest crosslink density. Initiated by [cyclopentadien-Fe-diphenylether]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFD) and [cyclopentadien-Fe-anisole]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFA) with greater solubility, the compatibility of epoxy ERL-4221 and E44 can be improved.

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**Keywords:** Cationic photopolymerization; [Cyclopentadien-Fe-arene]<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Epoxy resins; Thermomechanical property; Photoactivity

## 1. Introduction

The photoinitiated polymerization or UV curing of monomers and oligomers has experienced rapid growth in the areas of inks, coatings, and adhesives [1]. Although most of the early commercial success involved photoinitiated free radical polymerization, the corresponding cationic ring-opening epoxy polymerizations are finding increased use in many specialized applications [2,3]. This is due to the low toxicity of the monomers, the insensitivity of the polymerization to the presence of oxygen, and the good adhesion and mechanical properties of the cured products.

Sulfonium and iodonium salts, as cationic photoinitiators are well known. However, for the principal absorption bands in the short-wavelength (220–310 nm) region of the UV spectrum, they cannot match a number of important

light sources (including high-pressure Hg lamp) [4,5]. Ferrocenium salts is a radically different class of cationic photoinitiators [6,7]. The iron-based Lewis acid generated by photolysis is the key species during the epoxy ring-opening polymerization. With the absorption above 300 nm, ferrocenium salts are more efficient than other cationic photoinitiators when used with high-pressure Hg lamp as light source. Now, except [cyclopentadien-Fe-cymene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (I-261) produced by Ciba-Geigy Corporation, research on this kind of photoinitiators had been seldom reported. In our laboratory, a series of ferrocenium salts with different ligands have been synthesized and studied. In this work, using four cyclopentadien-Fe-arene hexafluorophosphate ([cyclopentadien-Fe-arene]<sup>+</sup>PF<sub>6</sub><sup>-</sup>) salts as photoinitiators, the photoactivities and thermomechanical properties of the UV-cured epoxy films were investigated.

To improve the UV-cured speed and the mechanical properties of epoxy resin (E44), and to increase the solubility of photoinitiators, three active epoxy monomers were used. The influence of different epoxy monomers on the properties

\* Corresponding author. Tel.: +86-10-64445350; fax: +86-10-64434898.

E-mail address: [wangtwj2000@163.com](mailto:wangtwj2000@163.com) (T. Wang).

of the UV-cured epoxy films were studied by dynamic mechanical thermal analysis (DMTA).

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Epoxy monomers and oligomer

3,4-Epoxy cyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221), di(2,3-epoxypropyl)3,4-epoxy-1,2-cyclohexanedioate (TDE-85), epoxy resin and 1,2,3-(2,3-epoxypropyl)-glycidylether (EPON-812) were dried over calcium hydride and then purified by fractional distillation.

#### 2.1.2. Photoinitiators

[Cyclopentadien-Fe-toluene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFT), [cyclopentadien-Fe-anisole]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFA), [cyclopentadien-Fe-diphenylether]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFD), [cyclopentadien-Fe-biphenyl]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CFB) were synthesized in our laboratory.

### 2.2. Preparation of [cyclopentadien-Fe-biphenyl]PF<sub>6</sub>

[Cyclopentadien-Fe-arene]PF<sub>6</sub> salts were prepared through the ligand exchange reaction between one ring of ferrocene and arenes according to the method of Nesmeyanor et al. [8]. The process of preparation of [cyclopentadien-Fe-biphenyl]<sup>+</sup>PF<sub>6</sub><sup>-</sup> is given below. The synthesis and character of other iron arene complexes are described in other paper [9]. The data of absorption spectra of [cyclopentadien-Fe-arene]PF<sub>6</sub> in dichloromethane are shown in Table 1.

Under nitrogen, 5.58 g (0.03 mole) ferrocene, 11.7 g (0.09 mole) anhydrous aluminum chloride, 1.35 g (0.05 mole) aluminum powder, 50.0 ml cyclohexane, and 4.7 g (0.03 mole) biphenyl were added to the flask (250 ml). The reaction mixture is then heated under reflux, with rapid stirring, for 12 h. Then the reaction flask was cooled to room temperature and placed in an ice bath, and the reaction mixture was slowly hydrolyzed with 50 ml of ice-water. The aqueous layer was separated after washing with 30 ml cyclohexane. The aqueous solution was filtered into a concentrated aqueous solution of NaPF<sub>6</sub>, then was extracted by CH<sub>2</sub>Cl<sub>2</sub>. The solution of CH<sub>2</sub>Cl<sub>2</sub> was concentrated by distillation and added amount of cyclohexane, and thereby a yellow colored solid was isolated. The solid were recrystallized from a warm acetone–water solution. They were then

dried for at least 24 h in vacuum over P<sub>2</sub>O<sub>5</sub>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 6.59–8.09 (m, 10H), δ 5.13 (s, 5H). Elemental analysis—calc. for C<sub>17</sub>H<sub>15</sub>Fe PF<sub>6</sub>: C, 48.57%; H, 3.57%; found: C, 48.50%; H, 3.46%.

### 2.3. Photolysis

Photolysis was conducted using 700 W high-pressure arc lamp with the intensity of UV radiation at 365 nm of about 2.7 mW cm<sup>-2</sup> at a distance of 15 cm from the sample tube. Surrounding the lamp is a quartz well through which cooling water is pumped. The entire apparatus was placed in a thermostated water bath which controls the temperature at 30 °C within ±0.2 °C.

By irradiating a 2 × 10<sup>-4</sup> M solution in CH<sub>2</sub>Cl<sub>2</sub> in a sample tube (i.d. 1.75 ± 0.01 cm), the photolysis of [cyclopentadien-Fe-arene]PF<sub>6</sub> was monitored by measuring the absorbance decrease in the initiator absorption band at about 240 nm. The photolysis conversion was calculated according to the reported method [10,11].

$$\text{Conversion} = \left( \frac{A_0 - A_x}{A_0 - A_\infty} \right)$$

where  $A_0$  is the absorbance before irradiation,  $A_x$  the absorbance when irradiating,  $A_\infty$  the absorbance after entire photolysis.

The quantum yields of photolysis were calculated using the following equation:

$$\varphi = \frac{[\text{product}] \times V \times 6.023 \times 10^{23} \times E}{I \times S \times t}$$

where  $E = hc/\lambda$ ,  $S = \pi R^2$ , [product] is the concentration of the photolyzed product,  $V$  the volume of the photolysis sample (l),  $E$  the energy of each photon (J),  $I$  the light intensity at 365 nm (mW cm<sup>-2</sup>), and  $t$  the irradiation time (s).

There is less than 0.1% of the incident light which is transmitted through the sample, so no correction factor was applied to compensate for difference in the absorbance between the actinometer and the sample solutions. For each photoinitiator salt, 3–5 quantum yield determinations were made and were averaged to give the reported value.

### 2.4. Curing procedure

Photopolymerizations were carried out using the same apparatus described for the photolysis study. Five percent

Table 1  
Data of absorption spectra of [cyclopentadien-Fe-arene]PF<sub>6</sub> in dichloromethane

[Cyclopentadien-Fe-arene]PF <sub>6</sub>	λ (nm) (ε(1 mol <sup>-1</sup> cm <sup>-1</sup> ))
[Cyclopentadien-Fe-toluene]PF <sub>6</sub>	239 (1.24 × 10 <sup>4</sup> ), 375 (75), 455 (59)
[Cyclopentadien-Fe-anisole]PF <sub>6</sub>	242 (1.47 × 10 <sup>4</sup> ), 396 (136), 466 (72)
[Cyclopentadien-Fe-diphenylether]PF <sub>6</sub>	243 (1.94 × 10 <sup>4</sup> ), 394 (140), 462 (75)
[Cyclopentadien-Fe-biphenyl]PF <sub>6</sub>	253 (1.89 × 10 <sup>4</sup> ), 300 (1.22 × 10 <sup>3</sup> ), 389 (277), 442 (138)

photoinitiator (w/w) was dissolved in epoxy monomers, then were added to epoxy E44 and stirred completely. The formulated mixture was cast on a PP film. The thickness was controlled by the matrix 2 mm thick. The PP film with formulated mixture was put on a thermal plate reactor to control the temperature during exposure. Then the mixture was irradiated. After curing, the cured product was peeled off the PP film.

### 2.5. Gel yield measurements

Curing procedure is same with the above description. The formulated mixture was cast on a glass plate. After irradiation, the glass plate with the mixture was weighed ( $W_1$ ) and then was put into anhydrous alcohol for about 30 min to remove the uncured compositions. Taken from ethanol, the glass plate with cured resin was dried in an oven at 80 °C and then weighed ( $W_2$ ). The gel yield was calculated according to the following formula:

$$\text{Gel yield} = \left( \frac{W_2 - W_0}{W_1 - W_0} \right)$$

where  $W_0$  is the weight of the glass plate (g).

was recorded from 0 to 300 °C with a rate of 5 °C/min. The glass transition temperature  $T_g$  is determined from the top point of  $\tan \delta$  curve.

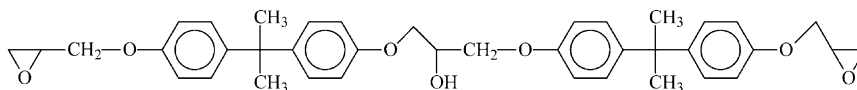
## 3. Results and discussion

### 3.1. Influence of epoxy monomers on the photoactivities and properties

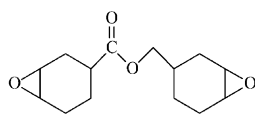
#### 3.1.1. Photoactivity comparison

It has been found that [cyclopentadien-Fe-arene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> salts can initiate the photopolymerization of many kinds of epoxy monomers and oligomers effectively, including diglycidyl ether of bisphenol-A (E44) which is commonly used to form polyethers and epoxy networks [12]. To increase the solubility of [cyclopentadien-Fe-arene]<sup>+</sup>PF<sub>6</sub><sup>-</sup> salts in epoxy resins, three epoxy monomers were used, respectively. They are glycidylether EPON-812, cycloaliphatic epoxides ERL-4221, and TDE-85. The influence of the epoxy monomers on the photoactivities and the mechanical properties of epoxy resin was discussed. The structure of epoxide is as follows:

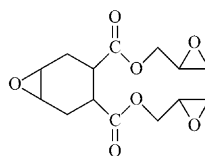
E44:



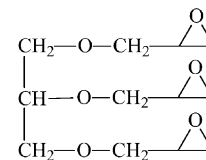
ERL4221:



TDE85:



EPON812:



The curve from the relation of gel yield and irradiating time is called the characteristic curve of the compositions.

### 2.6. Analyses

The UV absorption spectra of the samples in the function of irradiating time were recorded at room temperature with Shimadzu UV-260 spectrometers. Transmittance tests were carried out on UV-752 spectrometers (Shanghai). <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum was recorded on DMX300 (300 MHz), CD<sub>3</sub>COCD<sub>3</sub> as solvent. Elemental analysis was recorded on Flash EA1112.

Dynamic mechanical analyses were performed with a Rheometric Scientific, US, DMTA-V Instrument, at the frequency of 1 Hz in the tensile configuration. The temperature

The UV curing of epoxy mixtures (monomer/E44 = 1/1, w/w) irradiated by 5% [cyclopentadien-Fe-biphenyl]PF<sub>6</sub> are compared in Fig. 1. As shown in Fig. 1, the reaction rate of the iron catalyzed curing depends on the structure of the epoxides. On adding ERL-4221 in E44, its photoactivity increased, obviously. The photoactivity of EPON-812 + E44 is the lowest.

The reason is related to the photoinitiated mechanism of ferrocenium salts, which are very different from other kinds of cationic photoinitiators (Scheme 1). Ferrocenium salts undergo photolysis to generate an iron-based Lewis acid with the loss of the arene ligand [13]. Coordination of this latter species with an epoxy monomer is followed by ring-opening polymerization. Because this mechanism involves epoxy bond with the unsaturated iron center, the steric effect is an important factor to influence the photoactivities.

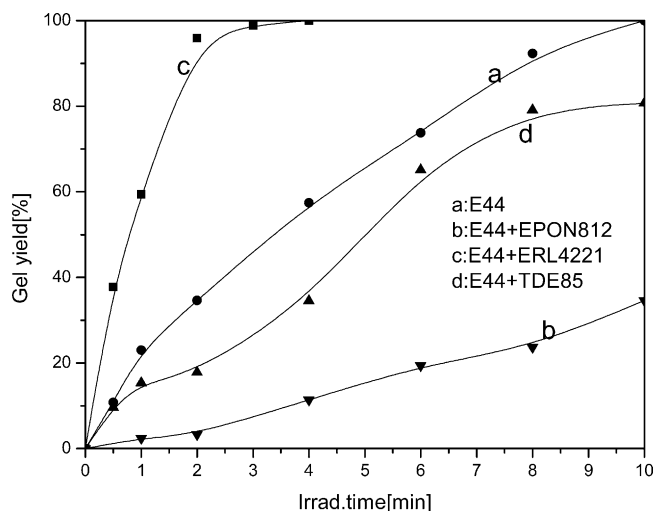


Fig. 1. Characteristic curves of different epoxy compounds with 5% [cyclopentadienyl-Fe-biphenyl] $\text{PF}_6$  as photoinitiator.

Cycloaliphatic epoxides, ERI-4221 and TDE-85 with less steric effect are more reactive than the glycidylether, EPON-812.

### 3.1.2. Thermomechanical properties measurements

Dynamic mechanical analyses of the cured samples were carried out in order to test the mechanical properties of these UV-cured films and to obtain more information of the extent of curing and the morphology of the networks formed. The results of the evolution of  $\tan \delta$  and  $E'$  of the different epoxy resin are presented in Fig. 2(A) and (B) and Fig. 3. The drop in the storage modulus, and the corresponding maximum in the loss factor curves are due to the transitions associated with the increase in internal freedom [14].

It has been argued that the crosslink heterogeneity is directly reflected in the breadth of the glass transition [15].

Table 2

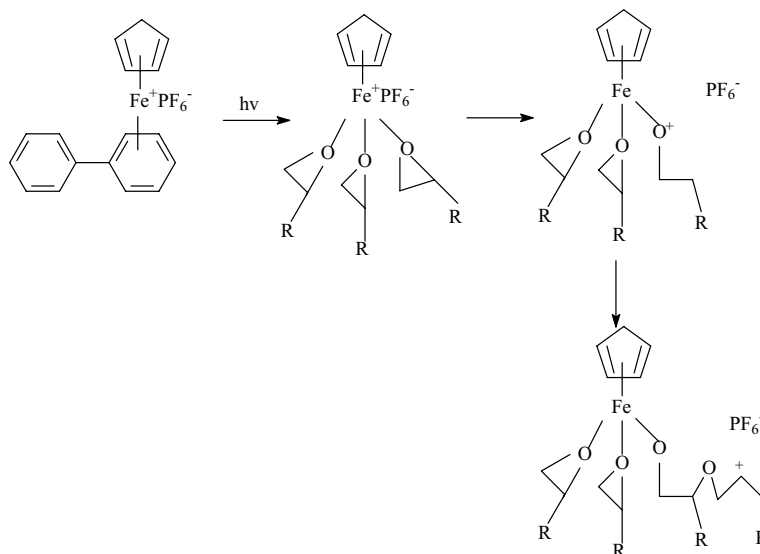
DMTA data of the cured samples of epoxy resin photoinitiated by 5% [cyclopentadienyl-Fe-biphenyl] $\text{PF}_6$  with the different epoxy monomers

Monomer/E44 (1/1, w/w)	$T_g$ ( $^{\circ}\text{C}$ )	$\tan \delta_{\max}$	$E'$ (average) (Pa)
E44	111.86	0.5103	$1.416 \times 10^9$
EPON-812/E44	71.42	0.4173	$1.016 \times 10^9$
ERL-4221/E44	140.66	0.4349	$2.077 \times 10^9$
TDE-85/E44	150.65	0.2345	$1.684 \times 10^9$
ERL-4221	148.15	0.4673	$1.538 \times 10^9$

Compared with the pure epoxy resin E44 (a), the  $\tan \delta$  curve of the ERL-4221+E44 (c) resin is very broad and shows two peaks. However, the  $\tan \delta$  curves of the EPON-812 + E44 (b) resin and the TDE-85 + E44 (d) resin are single peaks. The thin peak indicates that the system is homogeneous; the broad peak can be interpreted by assuming a micro-heterogeneous structure of the network formed or a reverse crosslinking phenomenon happening during the experiment.

Fig. 3 shows the thermomechanical property of the UV-cured film from epoxy monomer ERL-4221. We can see that the two peaks in the  $\tan \delta$  curve of the ERL-4221 + E44 (c) resin attribute to ERL-4221 resin and E44 resin, respectively. This indicates that the resin is heterogeneous, in spite of the highest photopolymerization activity.

From Fig. 2A and Table 2, we can also see that adding ERL-4221 and TDE-85 to epoxy resin E44 can make the  $T_g$  of the UV-cured film higher. Adding EPON-812 to epoxy resin E44 can make the  $T_g$  of the UV-cured film lower. The  $\tan \delta$  peak at higher temperature can be attributed to the formation of a hard domain, while the polymer matrix maintains a more flexible structure showing a lower  $T_g$  value. The effect is due to the hard structure of cycloaliphatic epoxides ERL-4221 and TDE-85.



Scheme 1. Typical ring-opening reaction of an epoxide by an iron-arene complex.

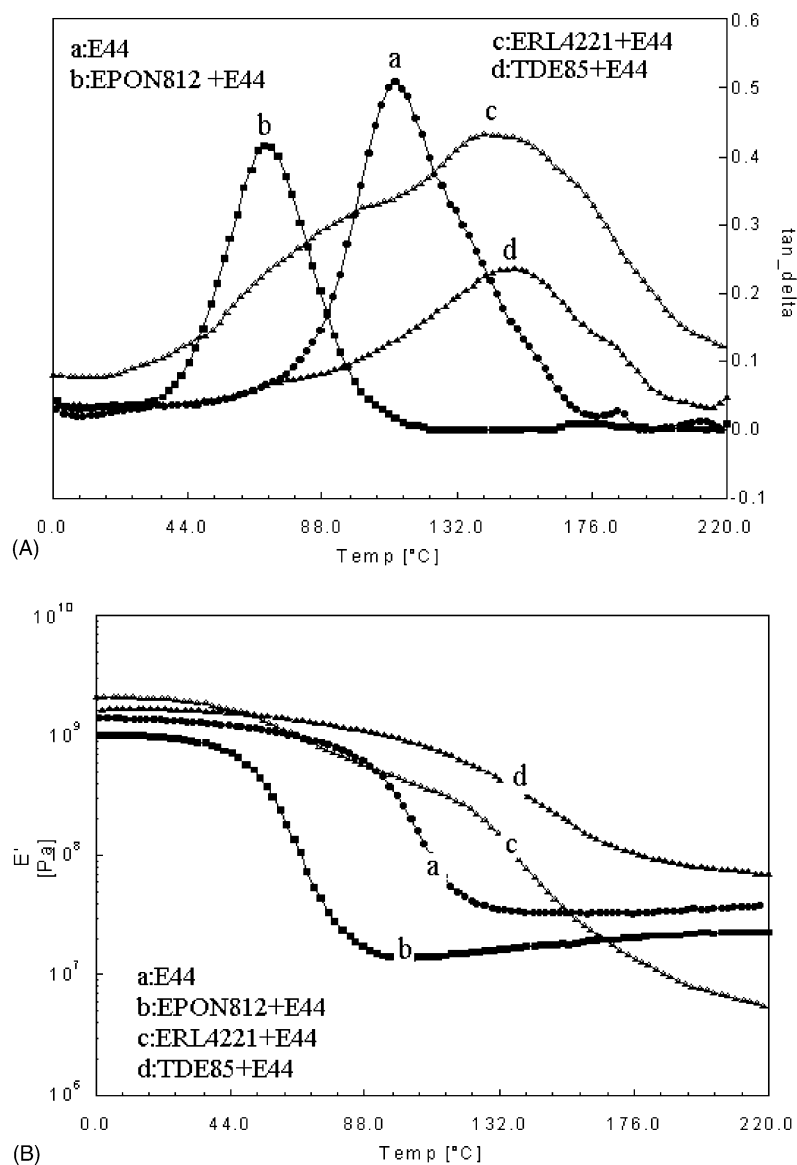


Fig. 2. (A) Evolution of  $\tan \delta$  on the different epoxy resin systems initiated by 5% [cyclopentadien-Fe-biphenyl]PF<sub>6</sub>; (B) evolution of  $E'$  on the different epoxy resin systems initiated by 5% [cyclopentadien-Fe-biphenyl]PF<sub>6</sub>. Epoxy resin system: (a) E44; (b) EPON-812 + E44 (1:1); (c) ERL-4221 + E44 (1:1); and (d) TDE-85 + E44 (1:1).

The temperature dependence of the glass-state moduli of these samples is shown in Fig. 2(B). The modulus varies linearly with temperature in the first range and then the slope changes over the transition interval. According to rubber elasticity theory [16], the crosslink density is proportionate to the storage modulus at  $T_g + 40^\circ\text{C}$ . From Fig. 2(B), we can conclude that the film of TDE-85 + E44 achieves the highest curing degree and the film of EPON-812 + E44 the lowest.

To evaluate the transparency of the resulting epoxy resin, the percentage transmittance of the sample were tested in the wavelength range 300–800 nm. From Fig. 4, it can be seen that the percentage transmittance of epoxy resin reduces in the region from 500 to 800 nm, while it rises in

region from 300 to 500 nm. However, the variation is little compared with what caused by the change of thickness.

### 3.2. Influence of different [cyclopentadien-Fe-arene]PF<sub>6</sub> on the properties

It is known that initiators have a large influence on the processability, mechanical properties, adhesion, long termed stability and reactivity in different chemical–physical environments. To study the effect of photoinitiator on the properties of the UV-cured film and to declare the relationship between the homogeneities and the photoactivities, four ferrocenium salts with different arene complex were

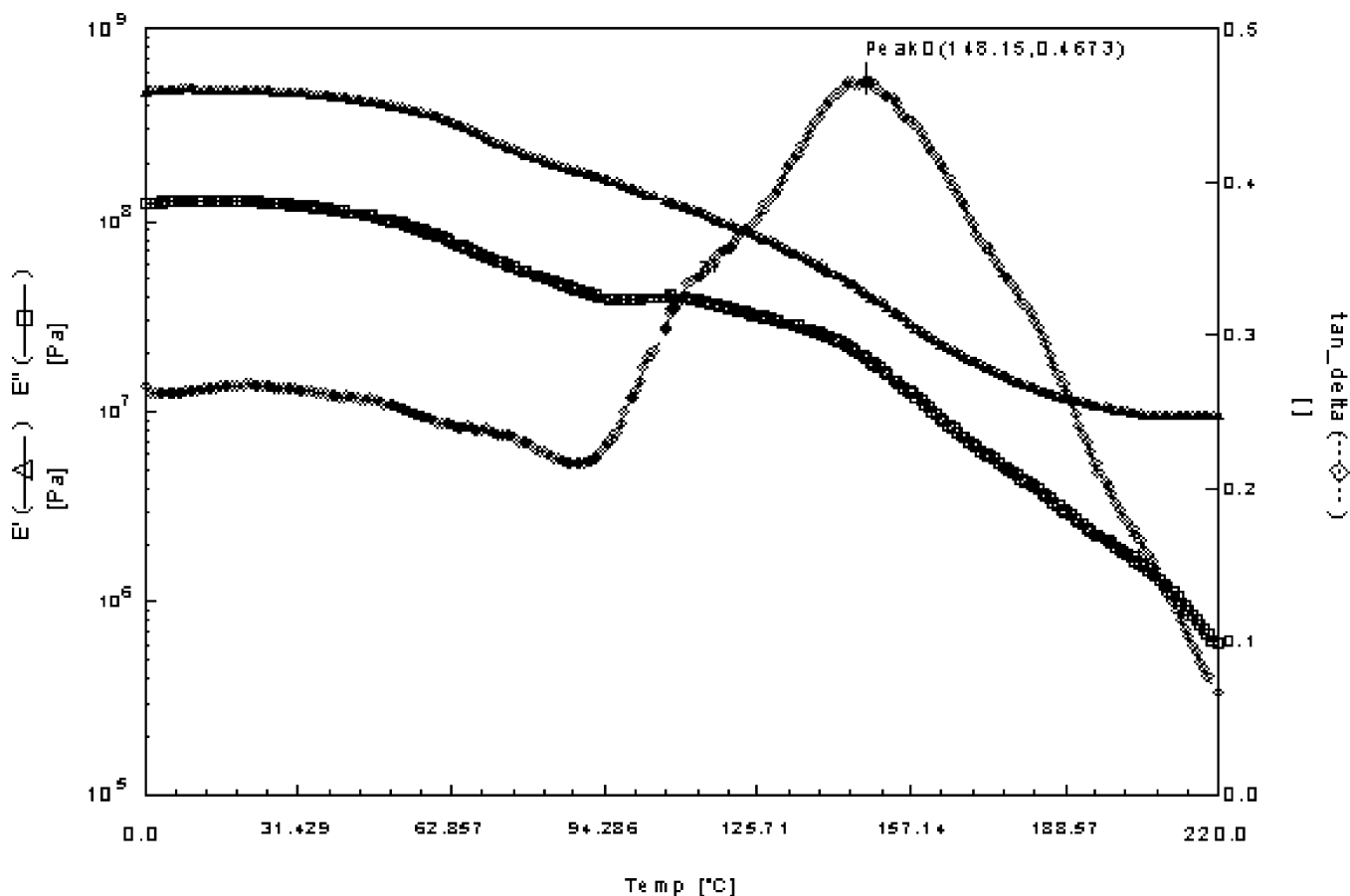


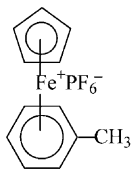
Fig. 3. The thermomechanical property of the UV-cured film from epoxy monomer ERL-4221 initiated by 5% [cyclopentadien-Fe-biphenyl]PF<sub>6</sub>.

discussed. The variations of the dynamic mechanical properties from different photoinitiators are obvious. This effect can be attributed to the photoactivity of the photoinitiator and the solubility. The structure of photoinitiator is as follows:

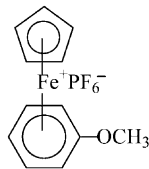
### 3.2.1. Photolysis and photoactivity comparison of ferrocenium salts

It has been recognized that [cyclopentadien-Fe-arene]PF<sub>6</sub> salts generate an iron-based Lewis acid with photoinitiated activity by photolysis. So the photodecomposition rate is

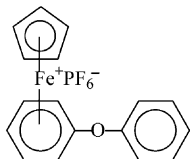
[cyclopentadien-Fe-toluene]<sup>+</sup>PF<sub>6</sub><sup>-</sup>(CFT):



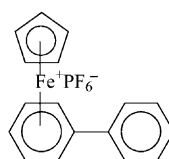
[cyclopentadien-Fe-anisole]<sup>+</sup>PF<sub>6</sub><sup>-</sup>(CFA):



[cyclopentadien-Fe-diphenylether]<sup>+</sup>PF<sub>6</sub><sup>-</sup>(CFD):



[cyclopentadien-Fe-biphenyl]<sup>+</sup>PF<sub>6</sub><sup>-</sup>(CFB):



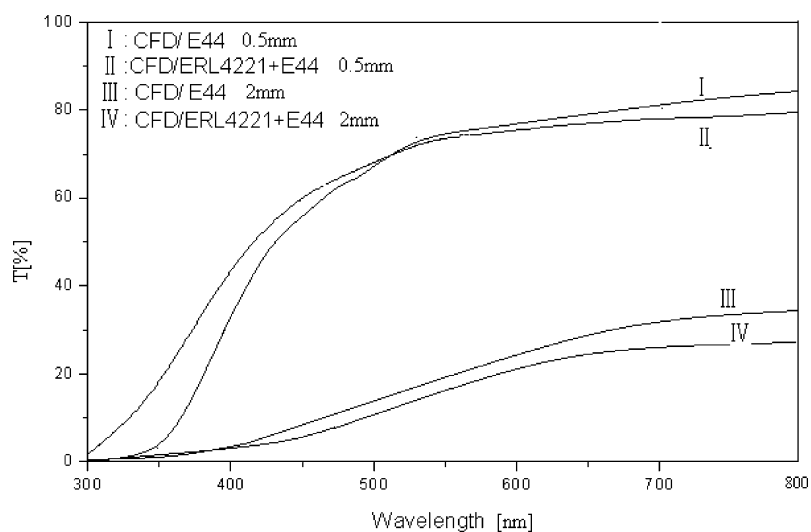


Fig. 4. The percentage of transmission of the epoxy resin E44 (I, III) and epoxy resin E44 + ERL-4221 (1:1) (II, IV) at two different thickness. I and II are 0.5 mm thick; III and IV are 2 mm thick.

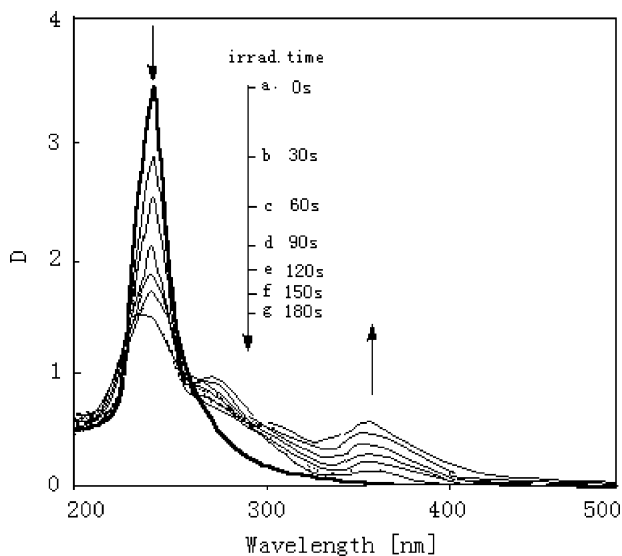


Fig. 5. The effect of irradiation time on the absorption spectrum of [cyclopentadien-Fe-anisole] $\text{PF}_6$  in dichloromethane; concentration is  $2 \times 10^{-4}$  M; light intensity is  $2.7 \text{ mW cm}^{-2}$ .

important to the photoreactivity of initiator. According to the method established in the previous papers [11], the photolysis rate of these four ferrocenium salts was studied by irradiating a  $2 \times 10^{-4}$  M solution in  $\text{CH}_2\text{Cl}_2$ , using 700 W high-pressure arc lamp with the UV radiation at 365 nm.

Table 3

The time of entire photolysis and the quantum yields of four initiators disappearance from UV spectrum

Photoinitiator	Time of entire photolysis (s)	Quantum yields ( $\phi$ )
CFB	60	0.26
CFA	100	0.15
CFD	120	0.12
CFT	180	0.09

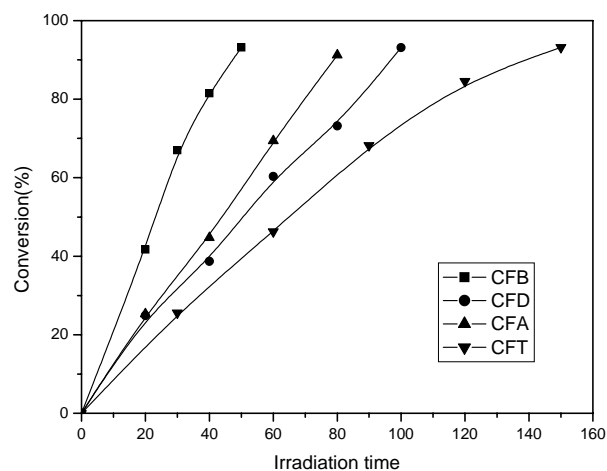


Fig. 6. The dependence of the photolysis conversion of four ferrocenium salts on the irradiation time.

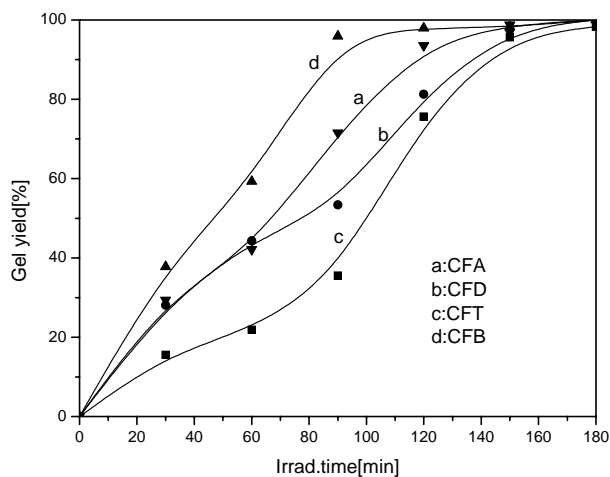


Fig. 7. Characteristic curves of epoxy compounds ERL-4221 + E44 (1:1) photoinitiated by 5% different photoinitiators.

Quantum yields of photolysis and the conversion were determined by UV spectroscopy following the decrease in the initiator absorption band (about at 240 nm) with the irradiation time.

The absorption variations of four ferrocinium salts on irradiation time are similar. As an example, Fig. 5. shows the dependence of the absorption spectrum of [cyclopentadien-Fe-anisole]PF<sub>6</sub> on the irradiation time. Fig. 6. shows the dependence of the photolysis conversion of four ferrocinium salts on the irradiation time. As the curves indicate, photodecompositions of these initiators are quite rapid with approximately 100% reaction occurring within 3 min.

Table 3 lists the time of entire photolysis and the quantum yields of four initiators disappearance. As can be seen from

Fig. 4 and Table 3, the order of photolysis rate is CFB > CFA > CFD > CFT.

To further declare the photoactivity of initiator in epoxy system, gel yields of four ferrocinium salts/ERL-4221 + E44 systems are compared in Fig. 7. From Figs. 6 and 7, it can be seen that the photolysis rate is consistent with the photoinitiating activity. The photolysis rate of [cyclopentadien-Fe-biphenyl]PF<sub>6</sub> is quickest and the activity is the highest.

A statement may be made with regard to these data of quantum yield. Measurement of time of entire photolysis using the method employed in these experiments is subject to an estimated error. Hence, the quantum yield values reported here should also be understood to contain a certain amount of error. Nevertheless, the determinations contained in Table 3

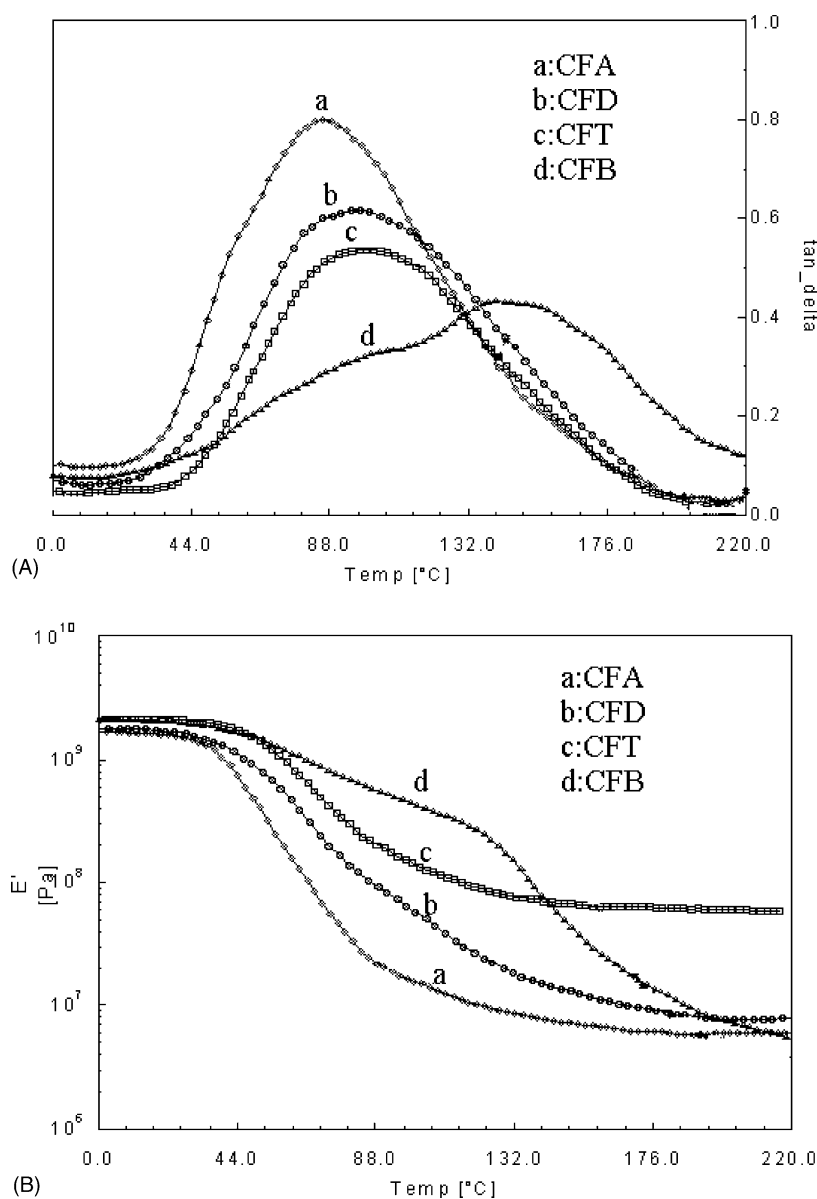


Fig. 8. (A) Evolution of  $\tan \delta$  on ERL-4221 + E44 epoxy resin initiated by 5% different photoinitiators; (B) evolution of  $E'$  on ERL-4221 + E44 epoxy resin initiated by 5% different photoinitiators. Photoinitiators: (a) CFA; (b) CFD; (c) CFT; and (d) CFB.



were made by averaging 3–5 separate values. In all cases, the data were found to exhibit only slight variations in their values and to be highly reproducible.

### 3.2.2. Solubility of photoinitiator in epoxides

In our studies, it was found that ferrocinium salts with the arene complexes attached by different groups have different solubility. The alkyl groups and alkoxy groups attached to phenyl rings of the photoinitiators greatly enhance their solubility, especially in polar solvents and epoxides. Table 4 lists the solubility of these four ferrocinium salts in epoxy ERL-4221 and E44. From the table, it can be seen that the solubility of CFB is worst and that of CFA is the best. Because the amount of photoinitiator often used is within 5%, CFA, CFD, and CFT can be considered to be soluble in epoxy ERL-4221 and E44.

### 3.2.3. Comparison of properties

The dynamic mechanical properties of the UV-cured films of ERL-4221 + E44 photoinitiated by 5% five different photoinitiators are measured. Fig. 8(A) and (B) shows the DMTA spectra of five UV-cured films of epoxy resin. They are CFA/(ERL-4221 + E44), CFT/(ERL-4221 + E44), CFB/(ERL-4221 + E44), CFD/(ERL-4221 + E44). Their  $T_g$  and average storage moduli are listed in Table 5.

As shown in Fig. 8(B), the storage modulus at 50 °C is CFB/(ERL-4221 + E44)  $\approx$  CFT/(ERL-4221 + E44) > CFD/(ERL-4221 + E44) > CFA/(ERL-4221 + E44) indicating that using different photoinitiators can change the rigidity of the resulting epoxy resin. The crosslink density is proportionate to the storage moduli at  $T_g + 40$  °C, thus the order of crosslink density for the resulting epoxy resins initiated by different initiators is CFT/(ERL-4221 + E44) > CFD/(ERL-4221 + E44) > CFA/(ERL-4221 + E44)  $\approx$  CFB/(ERL-4221 + E44). That is consistent with the photopolymerization rate of the epoxy system.

As shown in Fig. 8(A), initiated by higher photoactive CFB, the  $\tan \delta$  curve is very broad and shows two peaks. However, initiated by lower photoactivity CFT, the  $T_g$  value decreases and the systems tend to be homogeneous. From the above discussion, CFT, CFA, and CFD have a greater solubility. That make the systems initiated by these initiators have better homogeneities and lower  $T_g$  values. The transmittance of these UV-cured films at 300–700 nm wavelength was detected by UV-Vis spectroscopy (Fig. 9). The transmittance of films from CFB/(ERL-4221 + E44) is lower which has resulted from the phase-separation.

Table 5

DMTA data of the cured samples from epoxy resin ERL-4221 + E44 photoinitiated by 5% different photoinitiators

Photoinitiator	$T_g$ (°C)	$\tan \delta_{\max}$	$E'$ (average) (Pa)
[Cyclopentadien-Fe-anisole]PF <sub>6</sub>	85.71	0.8042	$1.666 \times 10^9$
[Cyclopentadien-Fe-diphenylether]PF <sub>6</sub>	97.32	0.6173	$1.764 \times 10^9$
[Cyclopentadien-Fe-toluene]PF <sub>6</sub>	102.43	0.5389	$2.202 \times 10^9$
[Cyclopentadien-Fe-biphenyl]PF <sub>6</sub>	140.66	0.4349	$2.077 \times 10^9$

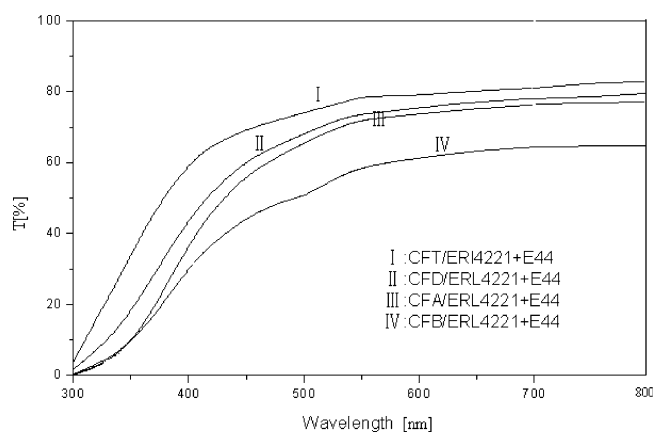


Fig. 9. The transmittance of these UV-cured films from different photoinitiators at 300–700 nm wavelength.

tance of films from CFB/(ERL-4221 + E44) is lower which has resulted from the phase-separation.

It can be concluded that photoinitiators can influence the properties of the resulting epoxy resin, including the rigidity, crosslink density,  $T_g$ , and homogeneity.

## 4. Conclusions

When high-pressure Hg lamp is used as light source, ferrocinium salts can initiate the photopolymerization of epoxy monomers and resins.

In this study, the effect of three epoxy monomers and four photoinitiators on the photoactivities and dynamic mechanical properties of the UV-cured epoxy films has been studied. Using [cyclopentadien-Fe-arene]PF<sub>6</sub><sup>-</sup> as photoinitiator, cycloaliphatic epoxy monomers are more active than the glycidylether. Using initiators and epoxy monomers with higher photoactivities, the system is micro-heterogeneous. Lower activities and better solubilities of the initiators and epoxy monomers can increase the homogeneities of the system. The mixture of E44 with cycloaliphatic epoxides ERI-4221 and TDE-85 possess higher glass transition temperature  $T_g$  than that of E44 with glycidylether EPON-812.

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Table 4

The solubility of the photoinitiators in epoxy ERL-4221 and E44 at 30 °C ( $\pm 1$ )

Photoinitiator	ERL-4221 solubility(g/g)	E44 solubility (g/g)
CFA	>0.3(s)	>0.3(s)
CFD	0.216	0.183
CFT	0.143	0.128
CFB	0.004(i)	0.001(i)

(s): soluble; (i): insoluble.

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