

Thermogravimetric and Fourier-Transform Infrared Analyses on the Cure Behavior of Polycardanol Containing Epoxy Groups Cured by Electron Beam

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ABSTRACT: In this study, the curing behavior of polycardanol containing epoxy groups (diepoxidized polycardanol) was exploited in terms of thermal stability and the cure reaction conversion by means of thermogravimetric analysis and Fourier-transform infrared spectroscopy, respectively. The effect of photo-initiator type and concentration and electron beam absorption dose in the presence of cationic photo-initiators (triarylsulfonium hexafluorophosphate (P-type) and triarylsulfonium hexafluoroantimonate (Sb-type)) on the cure behavior of diepoxidized cardanol (DEC) resin was investigated. The thermal stability of DEC with Sb-type photo-initiator was higher than that with P-type one, being increased with increasing the concentration and electron beam absorption dose. The conversion of cure reaction was gradually increased with increasing the dose, showing the maximum at 800 kGy. The results revealed that Sb-type photo-initiator, the concentration of 2 or 3 wt %, and electron beam absorption dose of about 800 kGy may be preferable for initiating epoxy ring opening in the DEC molecules as well as for efficiently curing the DEC resin by electron beam irradiation. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41599.

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INTRODUCTION

With increasing environmental concerns, environmentally-friendly polymer materials derived from naturally renewable resources, particularly from plants have recently attracted great attention to academia and industries.^{1–4}

Cardanol can be obtained by thermal treatment of cashew nut shell liquid (CNSL) extracted from cashew tree via a series of separation processes, as seen in Figure 1.⁵ It is a phenol derivative mainly composed of the *meta* substitute of a C15 unsaturated hydrocarbon chain with one to three double bonds.^{2,6} CNSL is a naturally abundant, low cost and biomass-based renewable material. Cardanol resin is viscous and thermally curable and it has no volatile organic compounds (VOC). Therefore, it has some potential as glossy formaldehyde-free coatings, finishes, and adhesives.⁷ Studies on the curing behavior of polycardanol^{5–7} and on the application as feasible matrix resin of biocomposites with natural fibers^{3,8,9} have been reported.

Cardanol with two epoxy groups in the molecular chain, simply referred to as diepoxidized cardanol (DEC) hereinafter, is a CNSL-based cardanol derivative, which can be synthesized by

enzymatic polymerization routes and it is also thermally curable.² The unsaturated double bonds in the chain of cardanol molecules were substituted with two epoxy groups in the DEC molecule. One epoxy group is in the chain end and the other one is in the middle of the alkyl chain of the molecule, as shown in Figure 2. It has been reported that epoxy-containing DEC resin can normally be cured by the manner to be used for epoxy curing, for instance, by ultraviolet irradiation¹⁰ and also by thermal treatment.²

In general, thermally cured epoxy exhibits good mechanical and thermal properties whereas it needs a longer period of processing time, high processing cost and high cure temperature in many advanced applications and a relatively large amount of curing agents.¹¹ Electron beam curing can be performed by irradiating high energy electrons from an accelerator to initiate polymerization and cross-linking of a resin.¹² There are many advantages of electron beam curing over conventional thermal curing of epoxy or epoxy-related resins such as short curing time, ambient curing temperature, environmentally friendly, dry and fast process, unlimited materials shelf-life, material design flexibility, and labor safety.^{13–16} In addition, thermal curing of epoxy normally uses a relatively large amount of organic curing

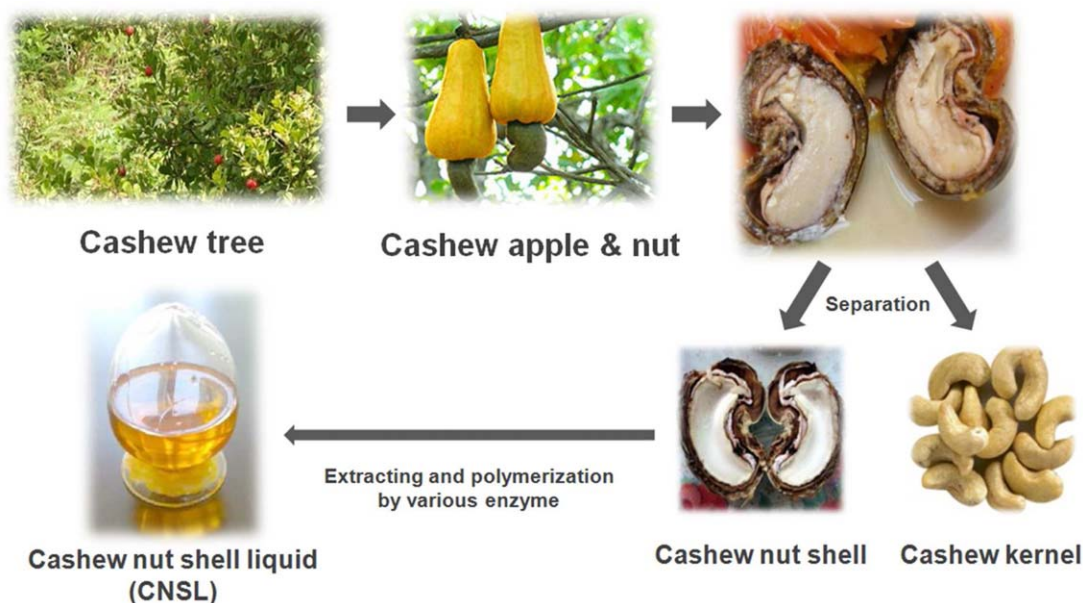


Figure 1. Extracting procedure of CNSL from cashew tree by enzymatic polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

agent whereas electron beam curing of epoxy uses a small amount of photo-initiator. It has been known that curing of epoxy resins by electron beam can be successfully processed in the presence of cationic photo-initiators.^{17–20} The general mechanism of epoxy curing has been described in elsewhere.^{11,14} Electron beam technology in curing epoxy resins and epoxy group-containing resins has been adopted for many years.^{12,21–26} However, studies on the curing behavior on diepoxidized polycardanol have been scarcely reported yet.

Consequently, the objectives of this work is, for the first time, to investigate the thermal and curing behaviors of diepoxidized polycardanol cured according to the electron beam irradiation levels exposed to the DEC resin by means of thermogravimetric analysis (TGA) and Fourier-transform infrared (FT-IR) spectroscopy. The changes of the thermal stability, characteristic absorption peak height, and the conversion of cure reaction as a function of electron beam absorption dose were discussed.

EXPERIMENTAL

Materials

DEC used for electron beam curing in this work, which was synthesized via enzymatic polymerization from the CNSL, was sup-

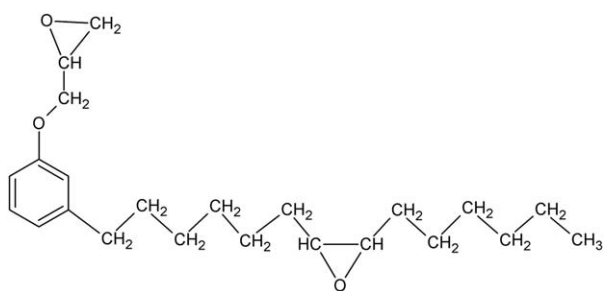


Figure 2. Chemical structure of cardanol containing two epoxy groups, simply referred to as DEC.

plied from the Korea Research Institute of Chemical Technology, Daejeon, Korea. The DEC in liquid state, which is also thermally curable, has a light brown color before cured. The molecular weight of DEC is 450 mol/g and the viscosity is 130~150 cp.

Two different types of photo-initiator onium salts were used for electron beam curing of DEC. The one was triarylsulfonium hexafluorophosphate (phosphate-type photo-initiator, simply designated as P-type photo-initiator) and the other was triarylsulfonium hexafluoroantimonate (antimonate-type photo-initiator, simply designated as Sb-type photo-initiator). In the figure legend, P1, P2, and P3 or Sb1, Sb2, and Sb3 designate 1, 2, and 3 wt % of P-type or Sb-type photo-initiator containing in the DEC resin, respectively. Both photo-initiators were purchased from Sigma Aldrich Co. The densities of P-type and Sb-type photo-initiators were 1.32 and 1.41 g/mL at room temperature, respectively. Their chemical structures are shown in Figure 3.

Electron Beam Curing Process

Electron beam curing process of DEC was performed at 2.5 MeV and 8.1 mA at ambient temperature in air using an electron beam

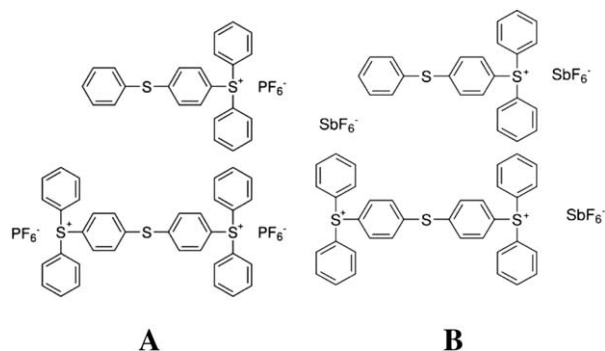


Figure 3. Chemical structures of photo-initiators (A: triarylsulfonium hexafluorophosphate; phosphate-type, B: triarylsulfonium hexafluoroantimonate; antimonite-type).

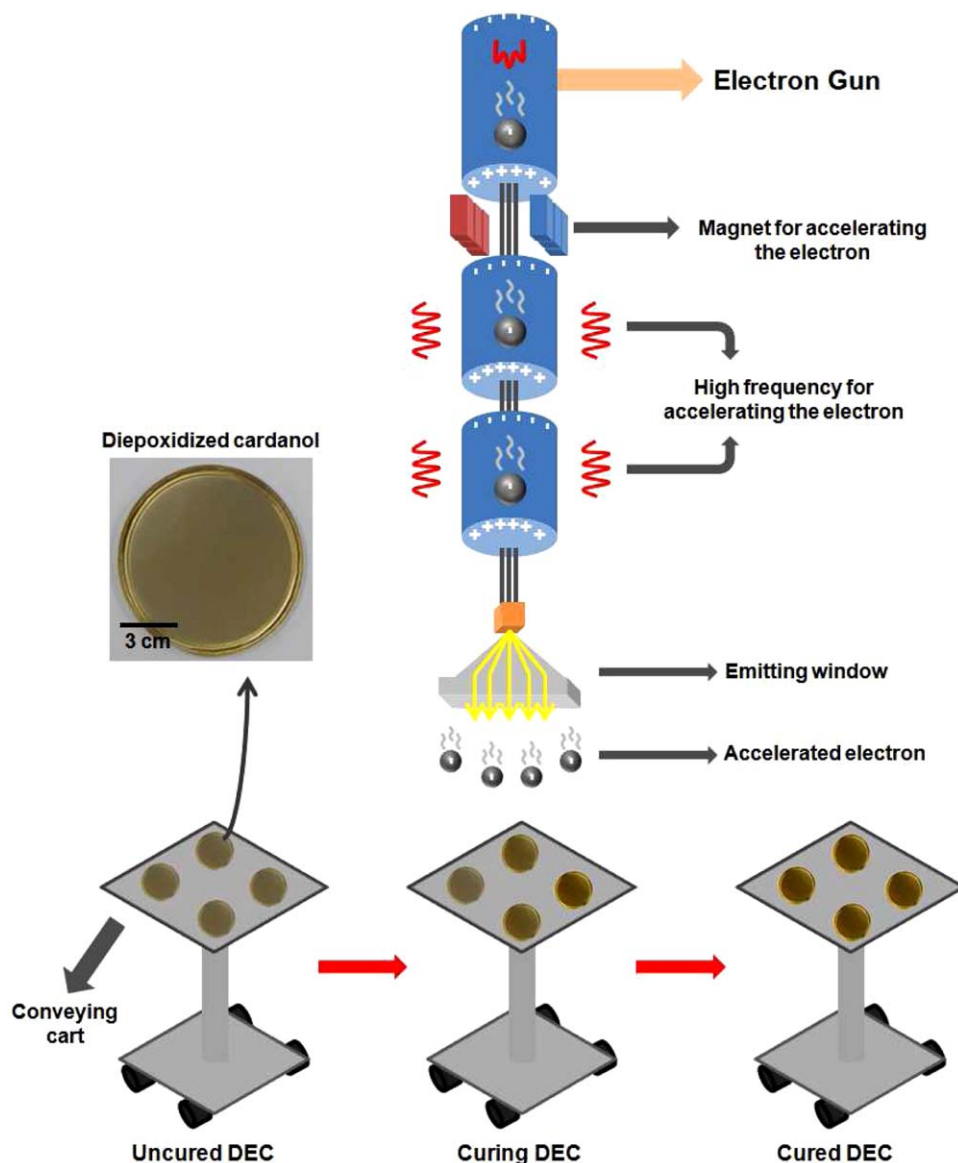


Figure 4. Illustration of electron beam curing processing of DEC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

apparatus (ELV-8, EB Tech, Korea). The process was carried out by the irradiation of samples placed on a conveying cart passing through the irradiation window in the channel with a constant conveying rate, as illustrated in Figure 4. The DEC samples of about 15 mL were placed in aluminum dishes of 92 mm in diameter on top of a conveying cart. The conveying speed was 10 m/min throughout the irradiation process. The dose rate was 33.3 kGy per second (10 kGy/scan). The electron beam absorption doses used were 0, 10, 50, 100, 200, 300, 400, 600, and 800 kGy. Each dose was controlled by counting the rotation number of a conveying cart passing through the channel equipped with electron beam irradiation facility in the middle of the channel. A dosimetry system by international standards ISO/ASTM 51649 method²⁷ and ISO/ASTM 51650 method²⁸ using cellulose triacetate (CTA) film was used. The uncertainty of the electron beam absorption dose to the samples was less than $\pm 0.5\%$. The total

length of electron beam emitting window was 1200 mm and the central zone of 800 mm was used for irradiation. The uniformity of electron beam absorption dose was less than $\pm 0.1\%$. The thickness of each sample was 2–2.5 mm in average, irradiated at a dose rate ranging 33.1–33.5 kGy/s. The dose rate was about 33.1 kGy/s at the top surface and about 33.5 kGy/s at the bottom surface of the sample. The thickness was not significantly changed before and after the irradiation at each electron beam absorption dose given.

Characterization

Thermogravimetric analysis (TGA Q500, TA Instruments) was used to investigate the thermal stability of DEC samples un-irradiated and irradiated at various electron beam absorption doses. A can-type alumina sample pan with the depth of 10 mm was used. The initial weight of each sample was about 15 mg.

Triarylsulfonium hexafluorophosphate (P-type)

Triarylsulfonium hexafluoroantimonate (Sb-type)

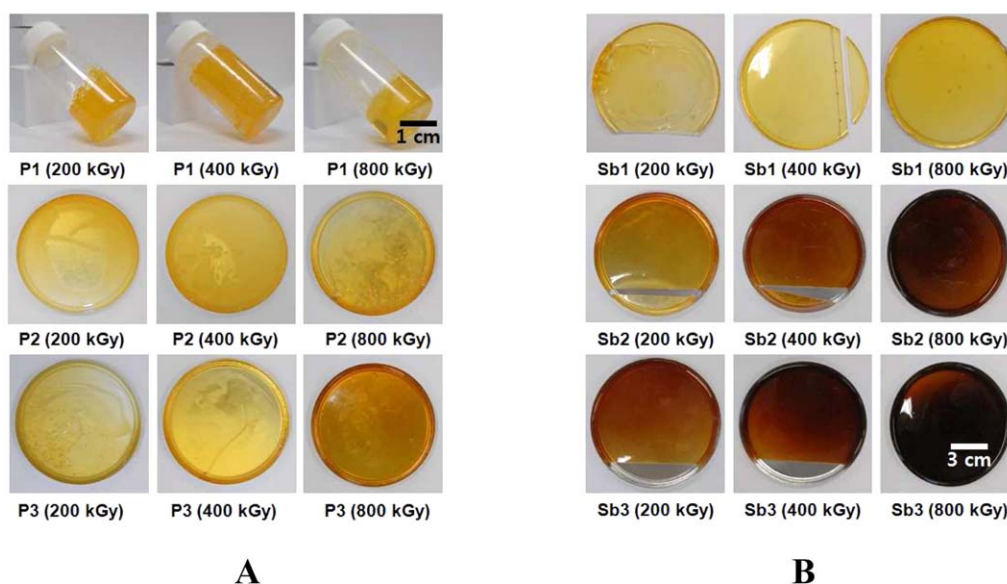


Figure 5. Appearance of DEC samples with P-type (A) and Sb-type (B) photo-initiators cured at various electron beam absorption doses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

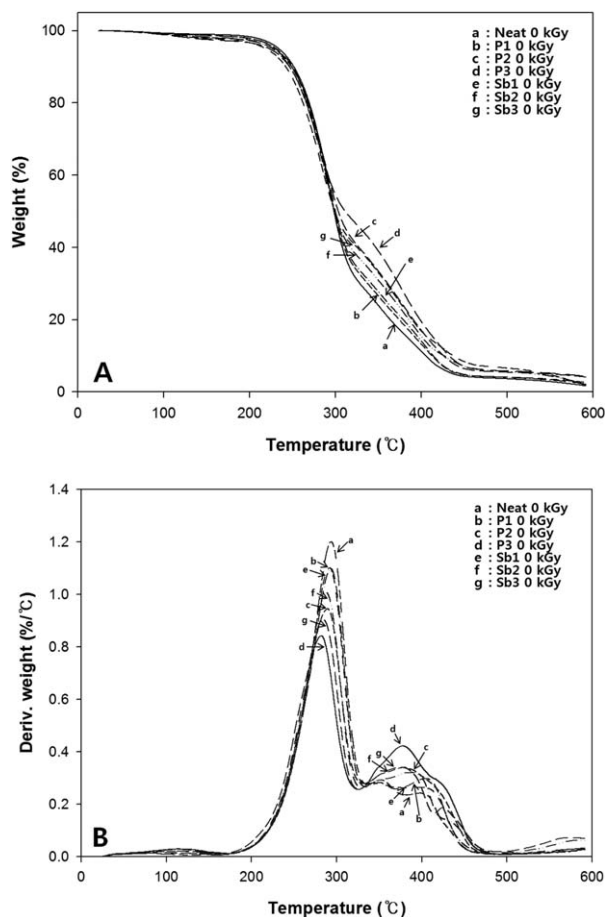


Figure 6. TGA (A) and DTG (B) curves for un-irradiated DEC resins with different types and concentrations of photo-initiators.

Each measurement was carried out from 20 to 600°C purging a nitrogen gas at a flow rate of 40 mL/min. The heating rate was 20°C/min. Derivative thermogravimetric (DTG) analysis was also performed to inspect more closely the thermal behavior as a function of temperature.

FT-IR spectroscopy (Nicolet 6700 FT-IR Spectrometer, Thermo Fisher Scientific) was performed to analyze the change of the absorption band of each DEC samples un-irradiated and irradiated at various electron beam absorption doses. The KBr pellet-type samples were used. According to the absorption band change, the change of functional groups in the DEC was examined and also the change of residual epoxy groups in the DEC molecules was studied by relatively comparing the change of the peak height of characteristic absorption band resulting from epoxy group, depending on the electron beam absorption dose. Based on the result, the percent conversion of cure reaction of DEC as a function of electron beam absorption dose was analyzed.

RESULTS AND DISCUSSION

Figure 5 displays the color change occurring in the DEC samples when each sample was exposed to various electron beam absorption doses. Figure 5(A,B) are for the samples containing P-type and Sb-type photo-initiators at 1, 2, and 3 wt % concentrations, respectively. With the P-type photo-initiator at 1 wt %, the DEC samples exposed up to 800 kGy remained liquid state in a vial, as seen in the top three photos. At 2 and 3 wt % of P-type photo-initiator, the DEC samples in a round-shape aluminum dish were getting cured and yellowish gradually with increasing the electron beam absorption dose. It was likely that the surfaces were relatively coarse, compared with the views of cured DEC samples shown in the Figure 5(B). On the other hand, in the case of Sb-type photo-initiator, the DEC samples were sufficiently cured even at 1 wt % concentration. With increasing the dose

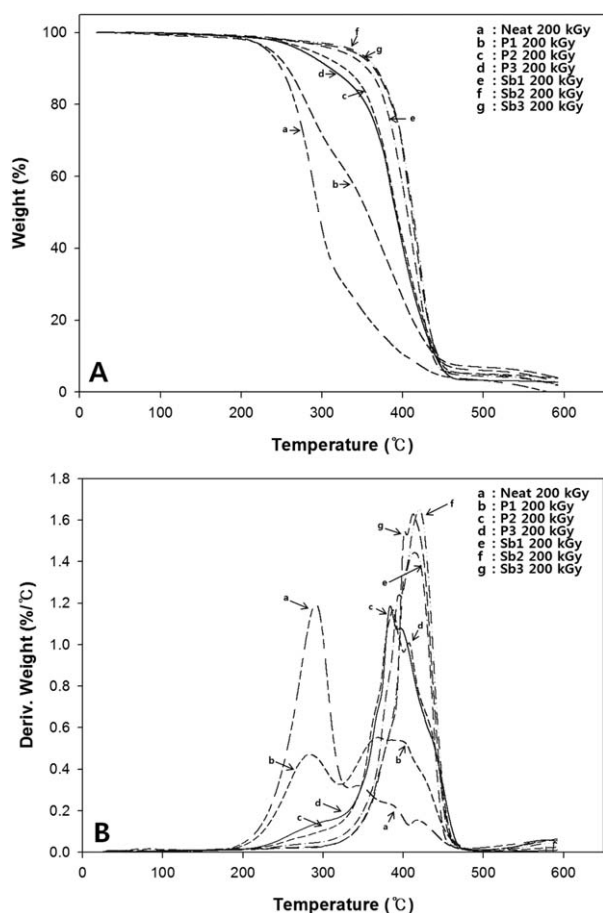


Figure 7. TGA (A) and DTG (B) curves of electron beam-irradiated DEC resins at 200 kGy with different types and concentrations of photo-initiator.

and also with increasing the concentration of Sb-type photo-initiator, the sample color was getting darker. With the Sb3, the color was changed to dark brown. One reason for the change of the sample color can be explained by that in an epoxide group-containing compound cured by photo-initiator the color becomes darker with increasing the concentration of photo-initiator used due to the increased rate and extent of polymerization.²⁹ Another possible reason is that some oxidation may be possibly occurred during the electron beam processing done in an aerial environment at ambient temperature, causing the color change. It seemed that the surfaces of the cured DEC samples were smooth and uniform. As a result, it was considered that the electron beam irradiation ranging from 33.1 to 33.5 kGy/s and the electron beam current of 8.1 mA were appropriate for curing process of the DEC resin.

Effect of Electron Beam Curing on the Thermal Stability

Figure 6 shows TGA and DTG curves measured with un-irradiated DEC resins with different types and concentrations of photo-initiators. About 2 wt % weight loss from the initial weight was occurred at about 190°C for all the un-irradiated samples. There was the secondary weight loss between 200°C and 330°C, indicating similar thermal behavior. As seen in the DTG curves of Figure 6(B), the peak temperature of neat DEC,

which reflects the fastest weight loss temperature, was found at 295°C and it was about 3~10°C higher than that of DEC samples containing P-type or Sb-type photo-initiator. As shown in Figure 6(A), the weight loss depended on the type and concentration of photo-initiator used, displaying the tertiary weight loss, in particular above 300°C. Neat DEC without photo-initiator exhibited the lowest thermal stability at above 300°C, whereas P3 sample indicated the highest thermal stability in the range of 300–430°C. It can be said that the thermal stability of DEC samples at above 300°C was more or less increased with increasing the photo-initiator concentration. It may be expected that possible chemical reaction can be progressed to some extent in DEC resin during the mixing of DEC with photo-initiator or by thermal scanning during TGA measurement.

Figure 7 compares TGA (A) and DTG (B) curves measured with neat DEC and DEC samples irradiated at 200 kGy. The weight loss against temperature strongly depended on the type and concentration of photo-initiator. It was obvious that the thermal stability of DEC with Sb-type photo-initiator was higher than that with P-type. With the Sb-type photo-initiator (curves e, f and g), the thermal stability was increased with increasing the concentration from 1 to 3 wt % whereas with the P-type the stability above about 250°C was slightly higher with P2 (curve c) than with P3 (curve d). Neat DEC (curve a) exhibited the lowest

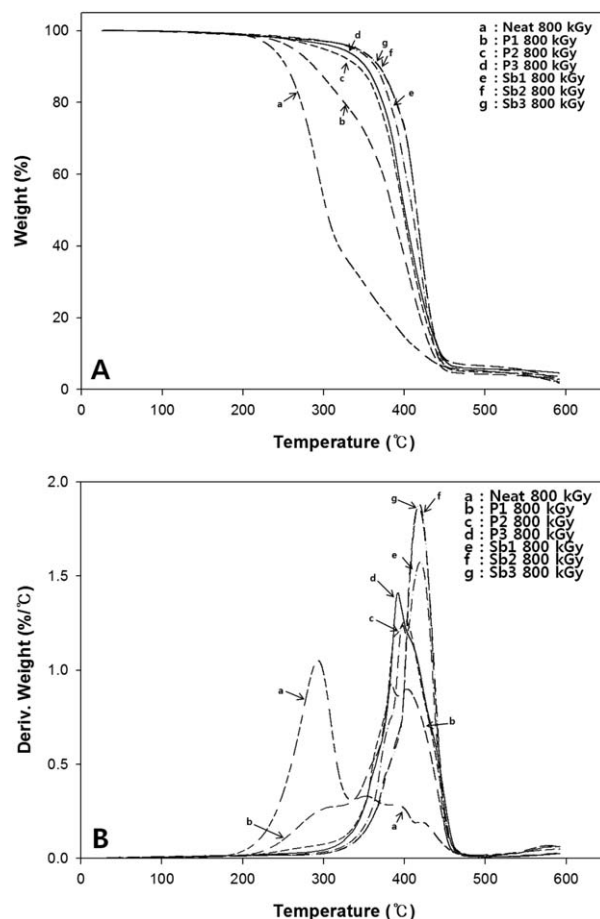


Figure 8. TGA (A) and DTG (B) curves of electron beam-irradiated DEC resins at 800 kGy with different types and concentrations of photo-initiator.

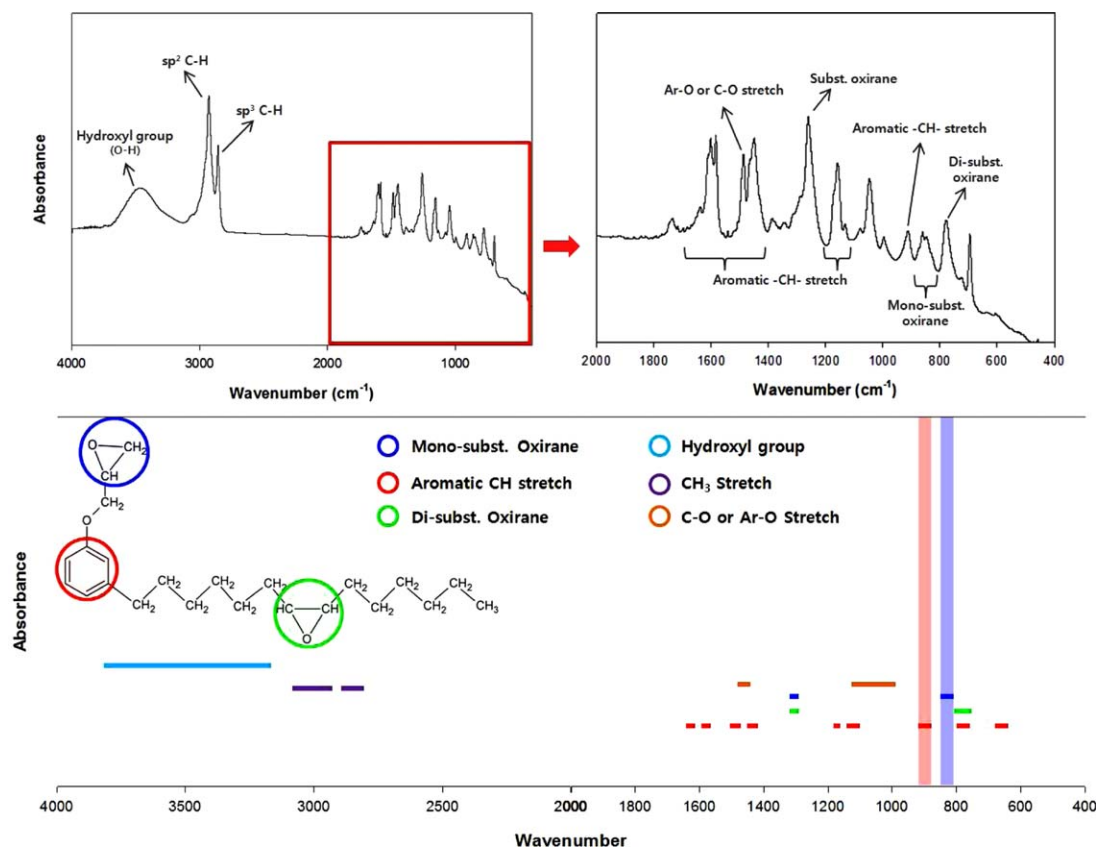


Figure 9. FT-IR spectrum of neat DEC sample and the assignment of major characteristic absorption peaks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermal stability whereas the Sb3 DEC sample exhibited the highest (curve g). DTG curves informed that neat DEC exhibited the lowest weight loss temperature with a fast weight loss rate. The curve for P1 200 kGy (curve b) showed two distinguishable peaks, which were not found in the rest of the samples. It is noted that the primary peak with the maximum at 290°C is due to the removal of uncured DEC resin even after the irradiation and the secondary peak with the maximum at about 380–400°C was due to the degradation of partially cured resin by the irradiation at 200 kGy. It was found that there was a small shoulder at around 300°C (curve d) with the P3 200 kGy sample. It indicates that part of the DEC with P-type photo-initiator of 3 wt % remained uncured after electron beam curing at 200 kGy. The curves e, f, and g similarly exhibited the primary weight loss change at about 410°C, at which is the highest temperature among the samples, indicating no shoulder near 300°C.

It may be insisted that according to the thermal stability behavior, electron beam irradiation at 200 kGy with P-type photo-initiator of 1 wt % (curve b) was too weak to cure the neat DEC. Also, 200 kGy with P-type photo-initiator (curves c and d) was not intense enough to sufficiently cure the DEC. In the case of Sb-type photo-initiator, the concentration of 1 wt % was slight low to sufficiently cure the DEC resin at 200 kGy whereas 2 or 3 wt % was high enough to cure the resin at 200 kGy.

Figure 8 exhibits TGA (A) and DTG (B) curves measured with neat DEC and the DEC samples irradiated at 800 kGy. Once

each curve in Figure 8 compares with the curves shown in Figure 7 at the corresponding photo-initiator type and concentration, it was found that the weight loss change as a function of temperature was significantly influenced by the electron beam absorption dose. It was clear at a glance that the thermal stability of DEC samples cured at 800 kGy was higher than that at 200 kGy. As similarly observed in Figure 7, at 800 kGy the thermal stability of DEC with Sb-type photo-initiator was higher than that with P-type one. The thermal stability of the cured DEC sample with Sb2 and Sb3 was slightly higher than that with Sb1. Among the P-type photo-initiator, above about 250°C the thermal stability of the cured DEC with P3 (curve d) was higher than that with P2 (curve c). It can be interpreted that the uncured portion of DEC with P3 at 200 kGy, as was found in the curve d of Figure 7, was further cured by the irradiation at 800 kGy. There was no shoulder found with the P3 sample. The sample P1 (curve b) exhibited the lowest thermal stability among the P-type samples. It can be said that 1 wt % of P-type photo-initiator was lacking in curing the resin even at such a high electron beam of 800 kGy. As expected, neat DEC irradiated at 800 kGy showed the lowest thermal stability because no photo-initiator was used. Combining the TGA results, it was concluded that Sb-type photo-initiator was comparably more efficient than P-type one to cure the DEC resin by electron beam technology and use of Sb-type photo-initiator of 2 or 3 wt % would be appropriate for curing the DEC resin.

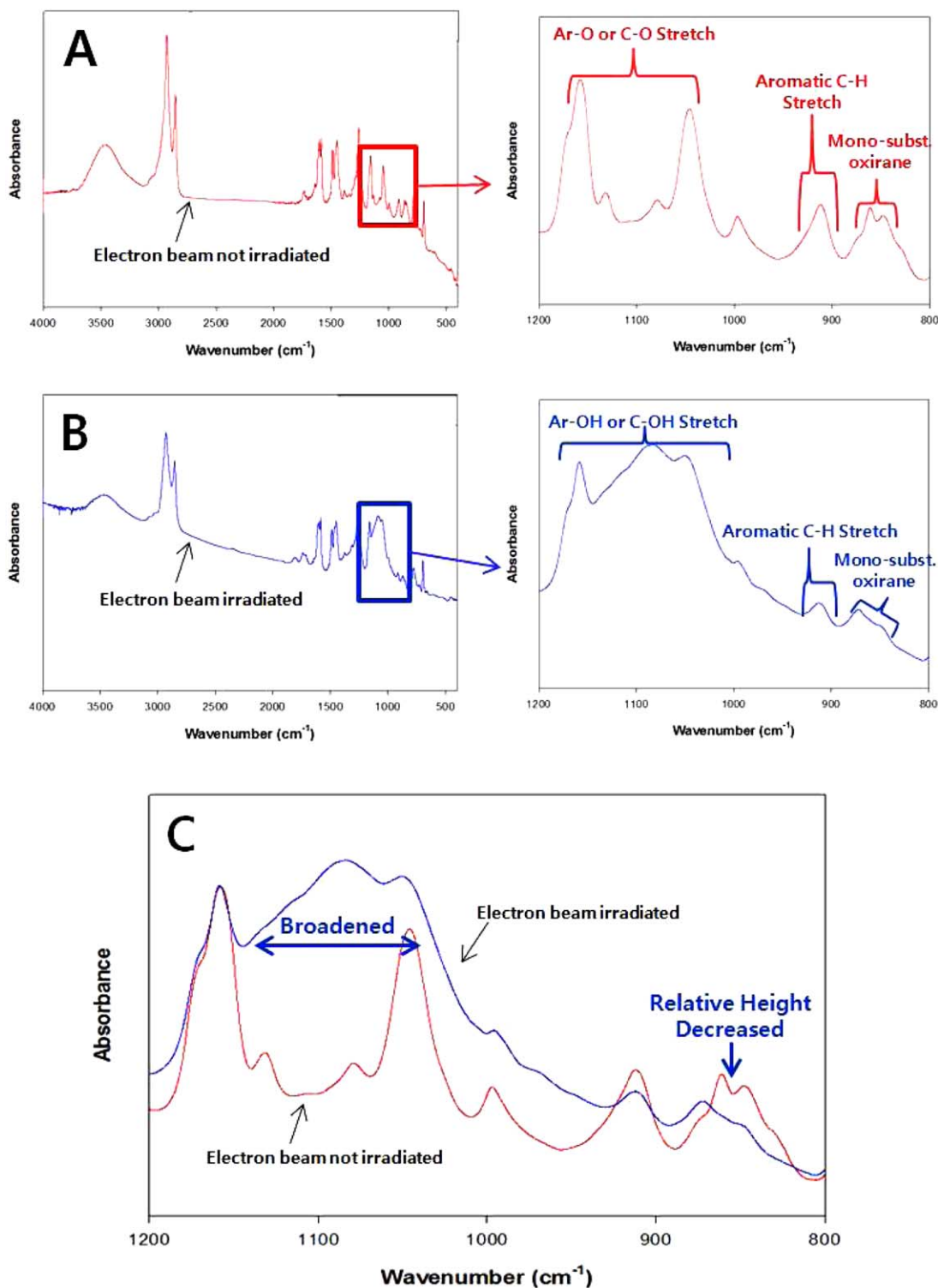


Figure 10. Absorption peaks observed from neat DEC (A) without irradiation, Sb₃ DEC sample (B) irradiated at 800 kGy, and the combined spectra (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Electron Beam Curing on the Infrared Absorption Spectrum

Figure 9 displays an FT-IR absorption spectrum of neat DEC and assigns major characteristic absorption peaks resulted from the chemical groups in the DEC molecules. The spectrum between 2000 and 400 cm^{-1} was expanded for clear assignment

of the peaks in the top right of Figure 9. Although there is no hydroxyl group in the DEC molecule, a broad OH stretching peak is observed in the range of 3700 to 3100 cm^{-1} . There are two possible reasons for the appearance of OH absorption peak. One reason is due to the remaining hydroxyl groups, which may not be completely substituted to epoxide group during the

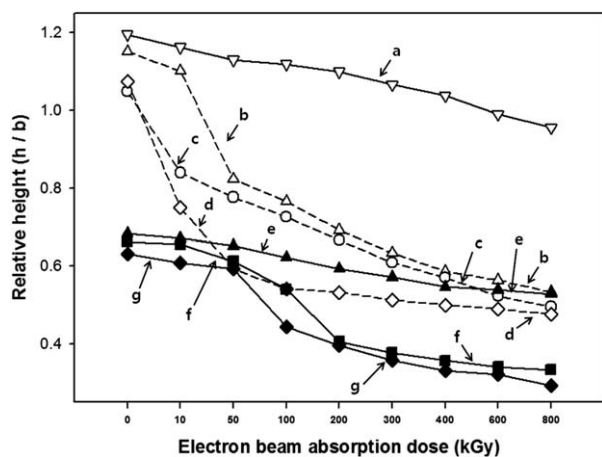


Figure 11. Variations of the relative height of the absorption peaks for electron beam-cured DEC as a function of electron beam absorption dose (a: neat DEC, b: P-type 1 wt %, c: P-type 2 wt %, d: P-type 3 wt %, e: Sb-type 1 wt %, f: Sb-type 2 wt %, g: Sb-type 3 wt %).

DEC preparation, and the other reason is due to the remaining cardol component in the DEC molecule.

Two —CH stretching peaks found strongly below 3000 cm^{-1} were due to sp^3 hybridization and a shoulder appeared just over 3000 cm^{-1} was due to sp^2 hybridization of =CH in the aromatic ring. The split peaks between 1700 and 1400 cm^{-1} and between 1200 and 1150 cm^{-1} were typically due to CH stretching vibration of the aromatic group in the molecular chain. The triple peaks resulted from out-of-plane bending of *meta*-substitution in the aromatic ring were found at in the range of 900 to 690 cm^{-1} , being overlapped with the peaks from oxirane (epoxy) groups. The peaks at 850 and 770 cm^{-1} were due to *mono*-substituted and *di*-substituted oxirane groups, respectively. A single peak at about 1255 cm^{-1} was observed to be due to the substituted oxirane group in the DEC molecule. Also, the absorption peaks from the C—O stretching by oxygen attached with the aromatic and aliphatic carbon atoms were also found at about 1485 and 1140 cm^{-1} .

Figure 10 represents the absorption peaks observed from neat DEC sample (A) without irradiation and the Sb3 DEC sample (B) irradiated at 800 kGy , respectively. The spectra A and B were expanded in the range of 1200 to 800 cm^{-1} , as shown in the right. This is to more closely inspect the spectral changes due aromatic and aliphatic C—O, aromatic C—H, and substituted oxirane groups, which were occurred before and after the electron beam curing. The combined spectra of uncured and electron beam-cured DEC samples are shown in Figure 10(C) for comparison. It was noted that the relative height of characteristic *mono*-substituted oxirane peak in the range of 900 – 850 cm^{-1} for uncured DEC sample was somewhat decreased after electron beam curing. According to eq. (1),³⁰ the relative peak height (h/b), which depends on participation of the *mono*-substituted oxirane groups to the cure reaction, was determined.

$$\begin{aligned} \text{Relative peak height} &= \text{Oxirane peak height} / \text{Base peak height} \\ &= h/b \end{aligned} \quad (1)$$

Here, h indicates the peak height at 850 cm^{-1} resulting from the *mono*-substituted oxirane groups remaining in the cured

sample and b indicates the base peak height at 920 cm^{-1} resulting from the aromatic C—H stretching. The relative peak height was decreased gradually with increasing electron beam absorption dose, depending on the type and concentration of photo-initiator used, as can be seen in Figure 11. The relative peak height of neat DEC was lowered from 1.20 to 0.95 with the absorption dose. This indicates that although no photo-initiator was involved in the DEC, epoxy ring opening may be occurred in the presence of electron beam irradiation applied and the ring opening can be populated with increasing the electron beam absorption dose. In the case of P-type photo-initiator, the relative peak height was down to 0.55 – 0.46 (curves b, c, and d) whereas the peak height was down to about 0.3 (curves f and g) with Sb-type photo-initiator. It reflects that the Sb-type photo-initiator was more efficient than the P-type one not only for initiating the epoxy ring opening in the DEC molecules but also for curing the DEC resin by electron beam irradiation. Accordingly, the conversion of cure reaction was calculated from the relative peak height changes by using the eq. (2).³⁰

$$\text{Conversion of cure reaction (\%)} = [1 - (h_1/b_1)/(h_0/b_0)] \times 100 \quad (2)$$

where b_0 is the base peak height before curing, b_1 is the base peak height after curing, h_0 is the oxirane peak height before curing, and h_1 is oxirane peak height after curing. The result is given in Figure 12. Based on the relative peak height, which is relevant with the epoxy groups remaining in the DEC sample after the irradiation, the conversion of cure reaction was increased with increasing the electron beam absorption dose. As can be seen, the conversion was increased to about 20% with the irradiation even at 10 kGy and further increased to about 37% at 800 kGy . Although the curing was partially proceeded owing to some ring opening in the presence of electron beam irradiation without photo-initiator, the sample state remained liquid. In the case of P-type photo-initiator of 1 or $2\text{ wt } \%$, the conversion of the DEC sample was increased gradually with increasing the dose and exhibited 55 – 60% at 800 kGy ,

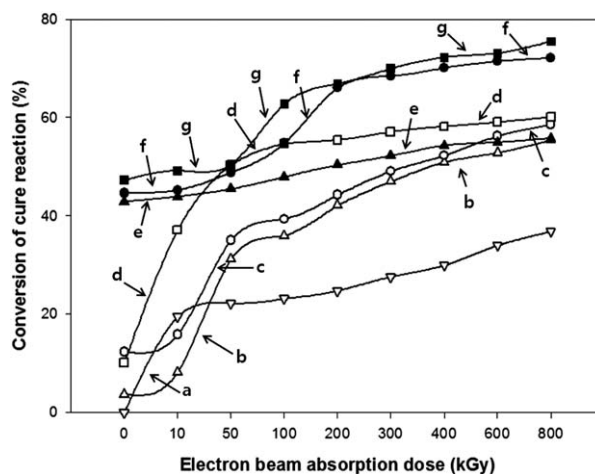


Figure 12. Variations of the conversion of cure reaction for electron beam-cured DEC as a function of electron beam absorption dose (a: neat DEC, b: P-type 1 wt %, c: P-type 2 wt %, d: P-type 3 wt %, e: Sb-type 1 wt %, f: Sb-type 2 wt %, g: Sb-type 3 wt %).

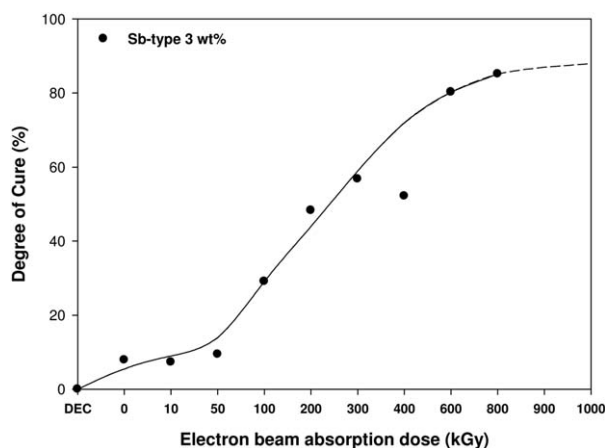


Figure 13. Degree of cure as a function of electron beam absorption dose for electron beam-cured DEC with antimonate-type photo-initiator of 3 wt %.

indicating insufficiently cured state. The conversion of the sample with the P-type at 3 wt % was enhanced noticeably at 50 kGy, reaching 51%. This turns out that electron beam curing of DEC resin can be processed more rapidly with the increased amount of photo-initiator involved.

With the Sb-type photo-initiator of 1 wt %, the cure reaction was took place slowly, in comparison with the P-type photo-initiator of 2–3 wt %, resulting in slightly less percent conversion. It was noticeable that the cure reaction was proceeded, indicating the conversion of about 63% at 100 kGy with the Sb-type photo-initiator of 3 wt % and at 200 kGy with the Sb-type of 2 wt %. With increasing the dose, the percent conversion was gradually increased reaching about 75% at 800 kGy. It was noticed that at 0 kGy with the Sb-type photo-initiator, the initial conversion was high to about 42–46%. This may be due to high cure reactivity of Sb-type photo-initiator. It is explained by that DEC sample may be partially cured by heat (at 70°C for 40 min) given at the sample preparation stage of mixing DEC resin with Sb-type photo-initiator, prior to electron beam irradiation.³⁰

Figure 13 shows a plot of the degree of cure as a function of electron beam absorption dose. The degree of cure (%) was determined from the change of the peak area in the range of 1200–1000 cm^{-1} due to aromatic C–H stretching and C–O and Ar–O stretching vibrations with varying the electron beam absorption dose. The peak area in the range of 1200–1000 cm^{-1} was compared to the peak area in the range of 950–900 cm^{-1} due to aromatic C–H stretching, where no significant spectral change and overlapping with other peaks were found. The absorption peak area of neat DEC in the same spectral range was obtained for comparison. The degree of cure for the DEC cured with antimonate-type photo-initiator of 3 wt % was gradually increased with increasing the absorption dose, showing an S-curve shape. The maximum degree of cure reached about 85% at 800 kGy. Beyond 800 kGy, it is expected that the degree of cure would be slightly increased and then remain constant.

CONCLUSIONS

The weight loss and decomposition of uncured DEC resin were more or less affected by the type and concentration of

photo-initiator, particularly in the range of 300–430°C, exhibiting the lowest thermal stability in neat DEC. The thermal stability of DEC with Sb-type photo-initiator was higher than that with P-type one, being increased with increasing the concentration and electron beam absorption dose. With Sb-type photo-initiator of 3 wt % the DEC resin exhibited the highest stability. TGA studies indicated that Sb-type photo-initiator was more efficient than P-type one for electron beam curing of diepoxidized polycardanol and use of Sb-type photo-initiator of 2 or 3 wt % was appropriate for curing the polycardanol.

The relative peak height, which is relevant with the epoxy groups remaining in the DEC sample after the irradiation, was decreased gradually with increasing the electron beam absorption dose, depending on the type and concentration of photo-initiator. Based on the relative peak changes, the conversion of DEC cure reaction by electron beam was gradually increased with increasing the electron beam absorption dose and the maximum degree of cure obtained with the DEC cured with antimonite-type photo-initiator of 3 wt % was found to be about 85% at 800 kGy. FT-IR studies also indicated that antimonate-type photo-initiator was more efficient than phosphate-type one not only for initiating epoxy ring opening in the DEC molecules but also for curing the diepoxidized polycardanol by electron beam irradiation.

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