Cationic Photopolymerization of 3- Benzyloxymethyl -3-ethyl-oxetane

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ABSTRACT

The cationic photpolymerization of 3-benzyloxymethyl-3-ethyl-oxetane (TR-TCM104) initiated by triphenylsulphonium hexafluoroantimonate (TR-PAG20002) under UV light was conducted. The kinetics was investigated by RT-FTIR and the mechanical and thermal properties of poly(TR-TCM104) were examined by DMA and TGA. To adjust the properties of the polymer, different initiator concentrations, co-monomers were applied. The result showed that the conversion of TR-TCM104 was improved significantly from 17% to almost 90% by adding a certain amount of 3,4-epoxycyclohexane carboxylate or diglycidylether of bisphenol A epoxy resin, while no effects was observed by adding 1,4 - butanediol diglycidyl ether. Moreover, the glass transition temperature, decomposition temperature and Young`s modulus of poly(TR-TCM104) were improved by adding different amount of diglycidylether of bisphenol A epoxy resin. Oxetane conversion and Oxrine conversion at same curing condition has been compared.   The physical properties of different cured formulations have been studied.

KEYWORDS: Oxetane, Cationic photopolymerization, Diglycidylether of bisphenol A epoxy resin, Copolymerization, Kinetics.

INTRODUCTION

Over the years, cationic photopolymerization has received great interest as its highlighted advantages over the free radical photopolymerization.[1,2] The practical monomers,[3-5] susceptible to cationic photopolymerization are less toxic and irritant than other (meth)acrylates[6] which are widely used in free radical photopolymerization, are mainly epoxides, vinyl ethers and propenyl ethers.[7] According to Crivello,[8] the epoxy monomers used in cationic photopolymerization could be divided into three classes. Class I, like cyclohexene oxide has no stable intermediate protonated species (secondary oxonium ions) or tertiary oxonium intermediates, they can polymerize rapidly and exothermically on UV irradiation. Class II, alkyl glycidyl ethers as a representative, they were characterized by an extended induction period because of the stable secondary oxonium ion intermediates. Once initiated, these induction periods are followed by rapid, exothermic autoaccelerated polymerization. Class III, typical monomers

like aryl glycidyl ethers, which possess oxygen atoms that are less effective in stabilizing the intermediates and without an obvious induction period but undergo slow, retarded photoinitiated cationic polymerization.

Oxetanes as one kind of strained, reactive heterocyclic compounds that undergo cationic ring-opening polymerization were noticed. Their high ring strain energy(107 KJ/mol), is very similar to that of cycloaliphatic epoxides（114 KJ/mol),[9] and the basicity (Pk$_a$=2.0) of the heterocyclic oxygen in oxetanes is higher than that (Pk$_a$=3.7)in epoxides.[10,11] Moreover, oxetanes could be synthesized by inexpensive, environmentally friendly starting materials[12] and have low orders of acute and chronic toxicity and non-mutagenic. Researches about oxetane-based monomers for cationic polymerization have been reported. Yang et al[13] fabricated cycloaliphatic epoxy oligo-siloxane (CAEO)/oxetane organic/inorganic hybrid materials which showed a high crosslinking density and flexibility and could be applied to various applications, including optics and display fields. Feser[14] reported that oxetane-functionalized organic semiconductors have been used for fabricating multilayer OLEDs from solution and for lithographic patterning. Ghosh et al[15] established oxetane-substituted chitosan-polyurethane (OXE-CHI-PUR) crosslinked networks that is capable of self-repairing. Lelière et al[16] prepared a photo-patternable electrochromic materials from oxetane precursors. However, it was found that these pure oxetane monomers undergo apparently sluggish reactions and the conversion was very low which makes them generally unsuitable for high-speed automated applications. Earlier work by Wu[17] suggested that the rate-determining step for BCOM (3,3-bis(chloromethyl)oxetane) is the ring-opening of the tertiary oxonium ion. In the polymerization of BCMO, monomer was slowly depleted, until after 100 hr the polymerization mixture consisted of 8.2% monomer, 75.4% polymer, and 16.4% tertiary oxonium ion. Spectral Assignments indicated that 40% of the monomer was consumed within the first 5 min. The initial ring opening and formation of tertiary oxonium ions is so fast. After the free acid is consumed, the subsequent ring opening is much slower, and almost 6 hr were necessary for 60% of monomer to be consumed.

According to the mechanism commonly accepted of the ring-opening polymerization, the presence of a long-lived tertiary oxonium ion intermediate generated by the reaction of the initially formed secondary oxonium ion intermediate with the cyclic ether monomer limited the initiating rate (Scheme. 1).[18] It is assumed that, for this oxetane monomer, the tertiary oxonium ion intermediate is very stable and has very long living time, much more energy is needed to overcome the $Ea3$ of step 4. Once triggered, the polymerization rate of the oxetane monomers is very rapid and exothermic. The "kick-starting" ring-opening mechanism was also proposed in some of the seminal studies of Crivello.[12,19-21] To solve this problem, Crivello[18] put forward three general methods for shortening the induction period (1) carrying out the photopolymerization at higher temperature, (2) copolymerizing with more reactive epoxide monomers, and (3) using free-radical photoinitiators as synergists. Under this instruction, Crivello[22] studied and found out that by combining with acrylate monomers into hybrid photopolymer systems, 3, 3-disubstituted oxetane monomers can be markedly accelerated. Crivello and Sangermano[23,24] prepared the silicon-containing UV curable oxetane monomers and investigated the effects of molecular structures on the curing kinetics and surface properties. The results from photo-DSC showed that the maximum photopolymerization rate decreased while the oxetane conversion increased with the content of reactive polysiloxane increasing. Until now, most of the investigations focused on copolymerization especially with the commercially available cycloaliphatic di-epoxide, 3, 4-epoxycyclohexylmethyl 3, 4-epoxycyclohexanecarboxylate[25] and acrylate monomers into hybrid photopolymer.

In this work, the method to increase the conversion and the rate of photopolymerization of oxetane monomer (TR-TCM104) was investigated through copolymerizing with less expensive and generally

employed commercial available Diglycidylether of Bisphenol A Eoxy resin (DGEBA), and the thermal and mechancal properties of copolymers were examined as well.
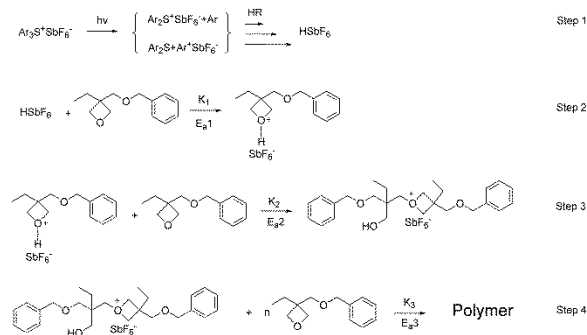

SCHEME 1 The photoinitiated cationic ring-opening mechanism of TR-TCM104.

EXPERIMENTAL

Materials

Diglycidylether of Bisphenol A Eoxy (DGEBA) was obtained from Jiangsu Sanmu Group Corporation, (Wuxi, China). 3-benzyloxymethyl-3-ethyl-oxetane (TR-TCM104) and triphenylsulphonium hexafluoroantimonate (TR-PAG20002) were both given by Changzhou Tronly New Electronic Materials Co., Ltd. (Changzhou, China). 1, 4-butane dioldiglycidyl ether (BDDGE) was purchased from SY NASIA (Suzhou) Co., Ltd. 3,4-epoxycyclohexane carboxylic acid, methyl ester (EPCM) was purchased from Secco work (Beijing) chemical technology co., LTD. All other agents were purchased from Sinopharm Group Chemical Reagent Co. Ltd. (Beijing, China) and used as received. The chemical structures of the regents were shown in Scheme 2.
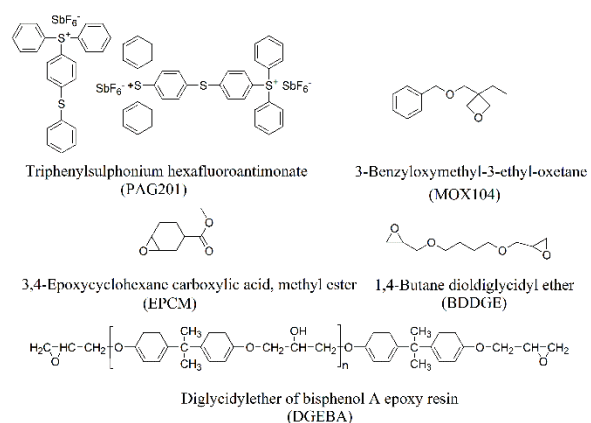
SCHEME 2 Structures of monomer and photoinitiator.

The kinetics of photopolymerization

The mixtures of monomer and photoinitiator were applied between two KBr crystals and irradiated by a UV spot light source (EFOS Lite, 100 W miniature arc lamp with 320–500 nm filter and 5 mm crystal optical fiber, Canada) at room temperature. The light intensity was determined by a UV-light Radiometer (Beijing Normal University, China).

A real-time IR (RT-IR) spectrometer (Nicolet 5700) equipped with a MCT/A KBr detector-beam splitter combination was used to monitor the photopolymerization kinetics. The spectrometer was operated in the absorbance mode, the polymerization kinetics was determined by the RT-IR spectrometer working in the rapid mode with an average 3 scans s^{-1} collection rate (4 cm^{-1}) and calculated by the decrease of the area of epoxide group absorption peak around 980cm^{-1} (oxetane)[26] or 915cm^{-1} (oxirane). The conversion of oxetane (C_4%) and oxirane (C_3%) were calculated by eq(1) and eq(2), respectively:

$$C_4\% = \left[1 - \frac{(A_{960-1006})_t}{(A_{960-1006})_0}\right]\ldots\ldots eq(1)$$

$$C_3\% = \left[1 - \frac{(A_{894-927})_t}{(A_{894-927})_0}\right]\ldots\ldots eq(2)$$

Where $(A_{960-1006})_0$ and $(A_{960-1006})_t$ were the absorption peak of the oxetane before and after photopolymerization at time t, respectively. $(A_{894-927})_0$ and $(A_{894-927})_t$ were for oxirane.

The polymerization rate (Rp) could be calculated from the slope of the initial linear portion of the Conversion–Irradiation time curves as follows:

$$R_p = [M]_0 \frac{d(C\%)}{dt}$$

Where $[M]_0$ is the initial concentration of epoxy group (mol^{-1}).

Thermal stability

The thermal gravimetric analysis of polymer was performed by using a TA Q500 (TA, USA) apparatus. Scans were carried out in nitrogen atmosphere. About 5 mg of sample was heated from ambient to 650 °C at a heating rate of 20 °C min^{-1}.

DMA analysis

Dynamic mechanical analysis of polymer films was obtained with a DMA242C (Netzsh, Germany) instrument at a frequency of 1 Hz in tensile configuration: the scan was carried out from -50 to 200 °C with a heating rate of 5 °C min^{-1}.

RESULTS AND DISCUSSION

Effects of photoinitiator concentration

As we know, photoinitiator[27,28] is a key component in the UV cured formulation because the active species generated from photoinitiator has a great influence on the parameters of polymerization and the properties of cured sample, such as the conversion of monomer, the polymerization rate, the thermal stability and so on. From Figure 1, it could be easily seen that both the polymerization rate and the monomer conversion were increased by increasing the TR-PAG20002 concentration. However, there was a slight change of monomer conversion (less than 20%) when the concentration of TR-PAG20002 was lower than 3wt% because of the impurities and moisture in the system could quench the cationic active center. While with the increasing content of photoinitiator, the quenching effect would be lessen. Although it was noted that approximately 60% monomer conversion was achieved when 5wt% TR-PAG20002 was applied, high concentration of initiator would cause side effects like high cost, yellowing, light screen effect in the bottom of polymerization layer. On the basis of the kinetic results,

the formulation contained 3wt% TR-PAG20002 was chosen to be used in the further investigation as the conversion (17%) of TR-TCM104 in this formulation was very low, which could let us see easily the change of conversion as other component was added and the side effects could be ignored.
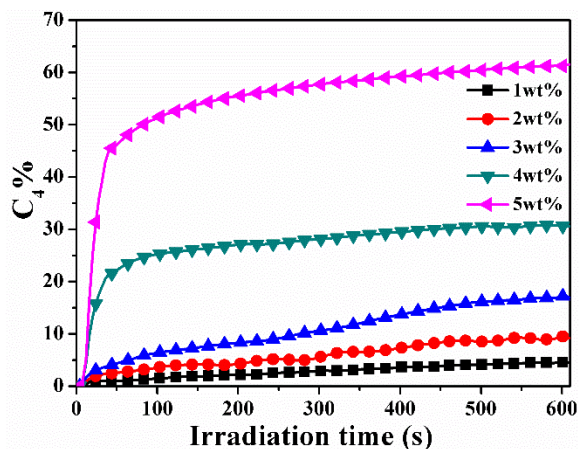

FIGURE 1 Effects of TR-PAG20002 concentration on polymerization of TR-TCM104. (light intensity 30mW/cm^2).

Effect of 1, 4-butanediol diglycidyl ether

According to the mechanism in Scheme 1, the tertiary oxonium ion intermediate is stable and has a long living time by using oxetane as monomer, more energy was needed to overcome the *Ea3* of step 4.

In order to investigate the effect of adding aliphatic epoxy monomers on the curing kinetics of oxetane monomer, different content of BDDGE were mixed with TR-TCM104. The results in Figure 2 showed that the highest monomer conversion of TR-TCM104 is 36% increased about 2 times compared with 17% for TR-TCM104 itself.
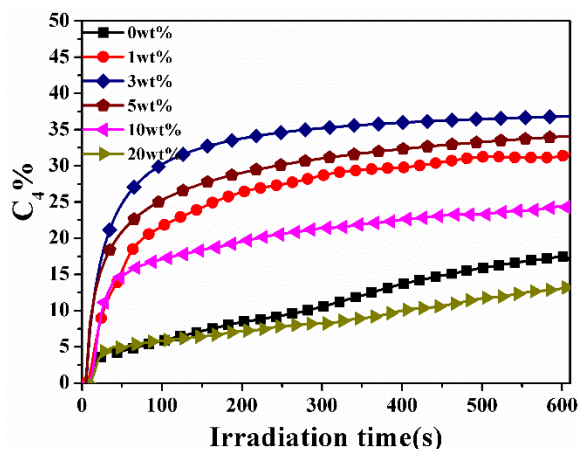

FIGURE 2 Effect of BDDGE on polymerization of TR-TCM104. (light intensity 30mw/cm^2, TR-PAG20002 concentration 3wt%).

1, 4-butanediol diglycidyl ether, neopentyl glycoldiglydicyl ether, benzyl glycidyl ether, and other mono- and multifunctional alkyl glycidyl ethers (Class II monomers) display an extended induction period. Crivello[8] proved that neopentylglycol diglycidyl ether and other alkyl glycidyl ethers possess a

neighboring ether oxygen atom that has a similar basicity and proton affinity to the oxirane oxygen. In addition, this ether oxygen is located such that it can stabilize the secondary oxonium ion species by hydrogen bonding through a tautomeric pseudo-five-membered ring. Calculations showed that these two protonated cyclic structures represent local minimum-energy conformations, implying considerable stabilization. TR-TCM104 as well as BDDGE, both of them have stable oxonium ion intermediates and are difficult to be initiated. So the conversion is not very high.

Effect of Cycloaliphatic epoxy

Cycloaliphatic epoxy such as cyclohexene oxide and cyclopentene oxide were highly reactive monomers (Class I monomer) used in cationic photopolymerization. These monomers exhibit essentially no induction period and very high rate of ring-opening polymerization[3]. As we know, epoxide ring-opening polymerizations was exothermic with molar heat quantity (18–24 kcal mol^{-1})[29] which would increase the temperature of the reaction system. So it was assumed that 3, 4-epoxycyclohexane carboxylic acid, methyl ester (EPCM) might increase the Rp and the final conversion of oxetane. Different content of EPCM was added into TR-TCM104 and the results were shown in Figure 3, which demonstrated that the rate of polymerization and monomer conversion were improved with the increase of EPCM, only 5wt% is enough to promote the ring-opening of oxetane. Over 80% conversion could be reached as 10wt% EPCM was added, it was about 5 times higher than the TR-TCM104 itself.
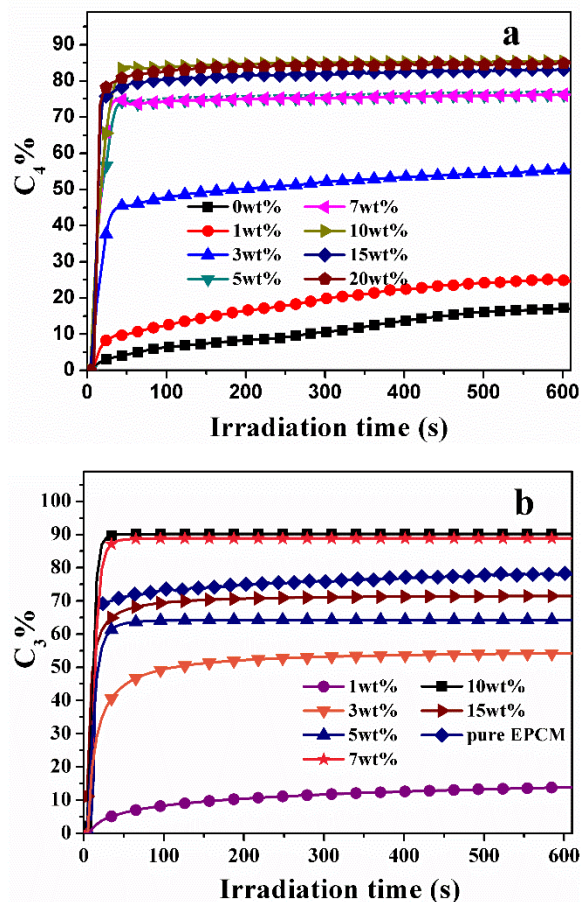

FIGURE 3 Monomer conversion of (a) TR-TCM104 and (b) EPCM in the TR-TCM104/EPCM system. (light intensity 30mw/cm^2, TR-PAG20002 concentration 3wt%).

The similar results were also found in Crivello's study.[12] The "kick-starting" mechanism was proposed that limonene dioxide could produce carbocations species in the presence of strong photogenerated acids, while these active species could rapidly alkylate with unhindered 3, 3-disubstituted oxetanes via S_N1 mechanism to initiate rapid ring-opening polymerization. In this work, the greater reactivity of cyclohexene oxide resulted in the formation of the correspondingly more reactive oxiranium ions, which could rapidly induce the polymerization of the less reactive oxetane monomer. The high speed of ring opening of cyclohexene oxide also generate considerable thermal energy, which could increase the reaction temperature and drive the stable tertiary oxonium ion intermediate of oxetane to be eliminated and polymerization occurred immediately.

Effect of DGEBA

DGEBA, which is one of the low cost commercial epoxide monomers, was always used in thermal polymerization reacted with amines, amides or anhydrides[30,31] or used as building blocks induced by electron beam.[32]

When different content of DGEBA was added into TR-TCM104 formulation, the results were showed in Figure 4. The polymerization rate and conversion of TR-TCM104 and DGEBA was generated by following the IR band at 980 cm^{-1} and 915 cm^{-1}, respectively.
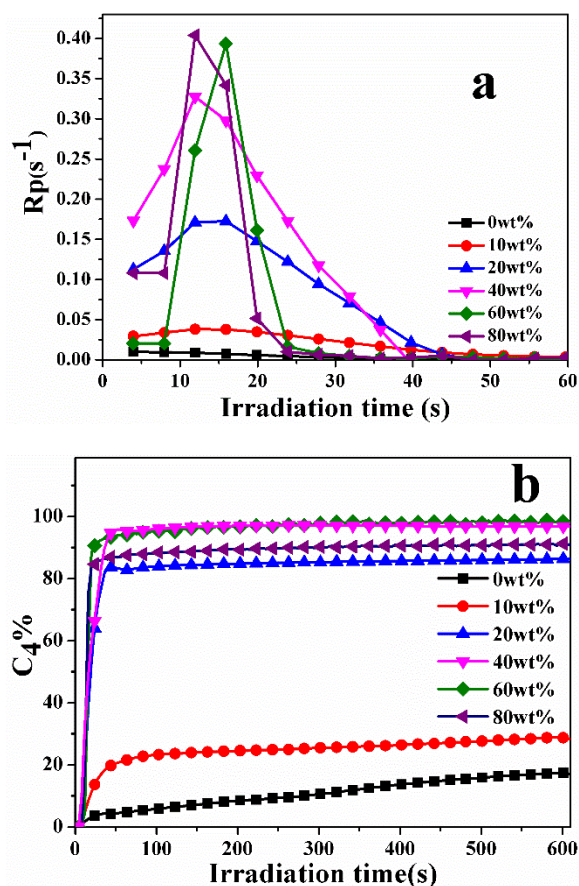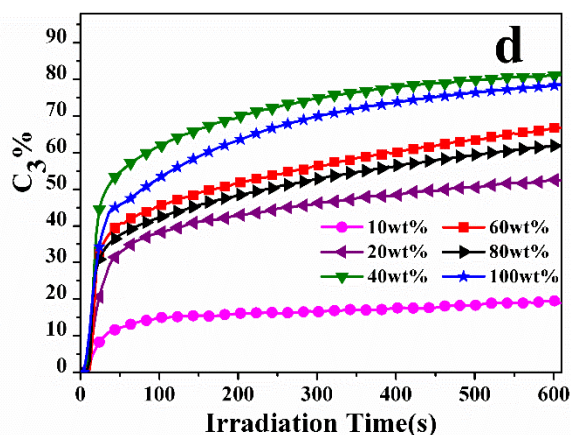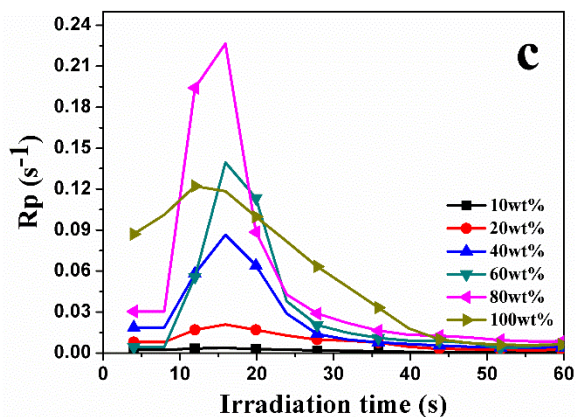
FIGURE 4 The (a, c) Polymerization rate and (b, d) conversion of TR-TCM104 and DGEBA in the TR-TCM104/DGEBA system, respectively.

As shown in Figure 4(b), only 17% conversion of TR-TCM104 was achieved when adding no DGEBA, however, by increasing the content of DGEBA, the conversion of TR-TCM104 increased dramatically over 80% and then kept almost steady at around 95%. The maximum polymerization rate, showed in Figure 4(a), was progressively improved with the adding of DGEBA with almost 20 times higher than the pure TR-TCM104. That is DGEBA, as Class III monomer, underwent slow, retarded polymerization, but without an obvious induction period, which made the free acid and oxonium ion initiate the oxetane continuously. In addition, once the polymerization of DGEBA released enough thermal energy for the tertiary oxonium ion intermediate to overcome E_a3 then step 4 reacted and the polymerization of oxetane was significantly improved. The curves of Rp-Time in Figure 4(a) demonstrated the conjecture, there was slight variation in conversion of DGEBA when the proportion of DGEBA increased from 20wt% to 80wt%, however, the curing time decreased from 45s to 25s.

The polymerization parameter of DGEBA in Figure 4(d) showed that the highest conversion was 80% when the ratio of TR-TCM104 and DGEBA was 60:40, which was comparable with the polymerization of DGEBA itself. However, further increase of DGEBA would decrease the conversion which is ascribed to the increased viscosity caused by the crosslinking and winding of di-functional DGEBA and the "trigger" effect of DGEBA.

Summary table of Oxetane and Oxrine conversion changing at same curing condition:

Table 1. Conversion Change comparison under influence of 10% CPEM or 10% Oxetane

C4 with 10% C3:   **85% from 17%**
C3 with 10% C4:   **90% from 80%**

Table 2. Conversion Change comparison under influence of DGEBA and Oxtane

C4 with 10% C3:   **85% from 17%**
C3 with 10% C4:   **80% from 70%**

From table1 and 2, we can adjust conversion of Oxetane and Oxirne accordingly.

Physical Properties comparison between different formulations:

Raw Materials	LED Formulation		
TCM-201/Oxetane	29%	49%	68%
EPCM / Epoxy	68%	49%	29%
TR-PAG20001	1.95%	1.95%	1.95%
TR-PSS303/P. S.	0.05%	0.05%	0.05%

Physical property tests (20 M/minute)

LED lamp	1Pass	1Pass	1Pass
Pencil H.	4H	4H	4H

Adhesive	5	3	2
Flexibility	1	2	3

Tg / Td and Young's modulus Properties tests

Figure 3 and Figure 4 indicated that by adding EPCM or DGEBA into TR-TCM104 could both increase the conversion of oxetane tremendously. However, concerning the high cost of EPCM, properties tests were only conducted of TR-TCM104/DGEBA. When DGEBA was mixed with TR-TCM104 in different contents in the range from 0wt% to 100wt%, it was found that the sample contained 0wt% or 10wt% DGEBA could not be cured exhaustively which limited their thermal property tests with TGA and DMA. However, with increasing DGEBA contents from 20wt% to 100wt% in the mixed system, the samples be came harder and harder.

DMA

In dynamic mechanical test, copolymer samples were usually under a variable sinusoidal stress. The glass transition temperature (*Tg*) of the TR-TCM104/DGEBA was measured with dynamic mechanical analysis. From Figure 5, it could easily be seen that the Tg was increased by increasing the content of DGEBA in the formulation.
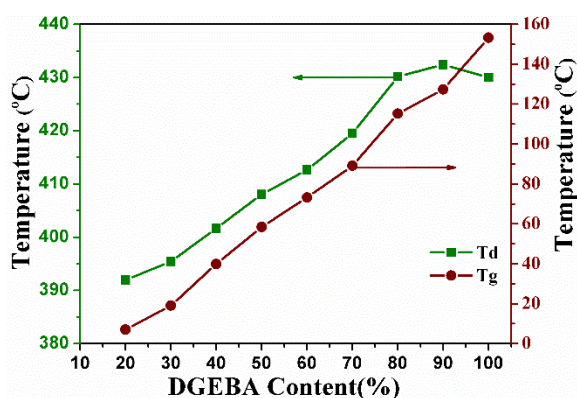

FIGURE 5 Glass transition temperature (Tg) and maxmum decomposition temperature (Td) with different DGEBA content in the TR-TCM104/DGEBA blending system.

The DMA tests indicated two glass transition temperatures with 90wt% DGEBA content or higher, as showed in Figure 6(a) and (b), however, Figure 6(c) and (d) showed a single glass transition temperature when DGEBA content was 80wt% or lower. It was supposed that systems of pure DGEBA or high DGEBA

content existed high viscosity and crosslinking density which limited further curing of the system at room temperature, once heated an apparent thermal post-curing occurred which produced the double *Tg*.

In addition, the Young's modulus varied from 2300 to 3200Mpa while it showed no significant distinction with different blending proportion.
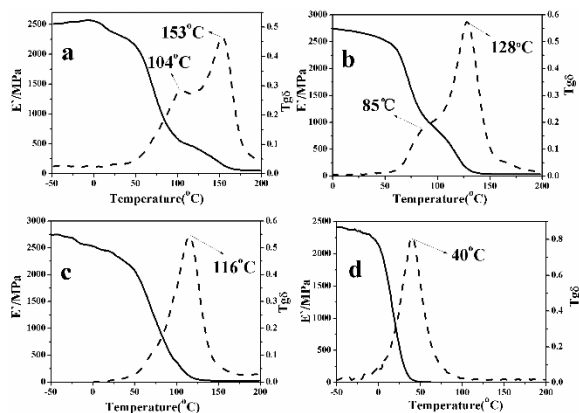

FIGURE 6 Solid lines: Storage modulus (E', MPa), Dashed lines: loss tangent (tanδ, ratio of loss to storage modulus) for different cured samples. (a) pure DGEBA; (b) 90wt% DGEBA + 10wt% TR-TCM104；(c) 80wt% DGEBA + 20wt% TR-TCM104；(d) 40wt% DGEBA + 60wt% TR-TCM104.

TGA

Thermo gravimetric analyses of the polymers were performed in N_2 to study the thermo gravimetric behavior of the cured films. The thermal stability of the copolymers were estimated by the maximum decomposition temperature (Td), showed in Figure 5, was generated by the intersection point of extrapolated initial decomposition temperature and maximum decomposition rate tangent. It can be seen the Td increased from 392 to 430°C with the increasing glass transition temperature of TR-TCM104/DGEBA and corresponding increasing content of DGEBA. Thermal behavior of polymers was controlled by two factors: the molecular structure and crosslinking density of polymers. The TGA tests indicated that cured TR-TCM104/DGEBA was unstable, and the temperatures of maximum weight loss was 430°C, which was mainly ascribed to the existence of DGEBA.

CONCLUSIONS

A cationic ptotopolymerizaton of oxetane (TR-TCM104) was investigated in the presence of TR-PAG20002. To increase the conversion and rate of oxetane ring-opening reaction, different initiator concentrations, varieties of co-monomer were carried out in this study. The kinetics of photopolymerization were monitored by using real time-FTIR.

All the results showed that a significant improvement occurred on the conversion of TR-TCM104 in the presence of 3, 4 - epoxycyclohexane carboxylate or diglycidylether of bisphenol A epoxy resin. By studying the cationic ring-opening ptotopolymerizaton mechanism, we assumed that the synergistic effects of the mixing monomers took place and provided the additional energy to overcome the activation energy of one certain step in the initiating stage.

The thermal and mechanical properties of DGEBA/TR-TCM104 copolymers with different DGEBA content were studied by DMA and TGA analysis. Single Tg of the polymer indicated there is no phase separation occurred which is in accordance with the cross-propagation mechanism.

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