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UV curing kinetics and mechanism of a highly branched polycarbosilane

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The UV curing process in both air and nitrogen atmosphere for the highly branched polycarbosilane system was investigated by differential scanning photo calorimeter. The UV cured products were characterized by Fourier-transform infrared spectrometry (FTIR). By comparison with the FTIR results of the uncured liquid mixture and the cured samples, the possible cross-linking reactions were determined. The kinetics of the curing systems was studied. The rate constant *k* was calculated based on the experimental results. The activation energies in different curing conditions were obtained. According to these results, it was learned that the mechanism for the UV curing in nitrogen was controlled by the photolysis of photoinitiator. Comparably, the UV curing process in air was complicated. It was affected by not only the photolysis of photoinitiator, but also oxygen and tripropane glycol diacrylate.

Keywords: UV curing; kinetics; mechanism; polycarbosilane; activation energy

Introduction

Liquid polycarbosilane with vinyl or allyl end groups can be crosslinked by UV curing. Therefore, technologies such as lithography or stereography could be used to fabricate complex shape devices to fulfill the advantages of polymer precursor derived ceramics.[1,2] In order to obtain better control of the homogeneity of the reactants, a good knowledge of the kinetic behavior of the curable polycarbosilane system is required. An accurate kinetic model for the systems would not only help to predict cure behavior for process design and control, but also could be used to compare the cure behaviors of the different systems.

In recent years, the kinetics of photoinitiated polymerization have attracted much attention.[3–9] Different kinetic models have been built up to describe the UV curing process.[4–8] Generally, the kinetic models are phenomenological models[4,5,7,8] or mechanistic models.[5,8,9] In practice, the phenomenological models are often applied to describe the photoinitiated polymerization process because of its complicated nature. Despite extensive studies on UV curing behaviors, the complex curing mechanism of the materials during the photocuring process is still not completely clear. Therefore, it is necessary to undertake a thorough study of UV curing kinetics of the curable polymer system.

In the previous study,[10] we investigated the effects of different parameters on the UV curing process of a highly branched polycarbosilane (HBPCS) by differential scanning photo calorimeter (DPC) measurements. The results indicated that the ripropane glycol diacrylate (TPGDA) content, photoinitiator concentration, temperature and light intensity had their own optimal values to obtain the maximum ultimate conversion and the reaction rate. In this study, a detail examination of the cured samples was carried out by Flourier-transform infrared (FTIR) spectrometry. The possible curing reactions were determined from these results. A modified autocatalytic model was applied to describe the kinetics of the HBPCS system. The curing mechanisms are discussed based on the curing activation energies.

Experimental Procedure

Liquid polycarbosilane with a highly branched structure, Photocure-1173 (2-hydroxy-2-methyl-phenyl-propane-1-one) and TPGDA were used in this study. The chemical formulae of Photocure-1173 and TPGDA are shown in Fig. 1. The detailed information about these chemicals was described in the previous study.[10]

The UV curing reaction kinetics was studied in the condition of 4 wt% photoinitiator, 10 wt% TPGDA and a light intensity of 38.8 mW/cm^2 by a differential scanning photo calorimeter. The curing temperatures varied from 0 to 75 °C. Heat flow as a function of curing time was recorded in isothermal mode under air or nitrogen atmosphere. The DPC system, the sample preparation, the treatment of the thermogram, and the computation of conversion and reaction rates have also been described.[10]

FT-IR spectra for liquid samples were obtained by placing the liquid on NaCl plates using a Nicolet Avator 360 Spectrometer (Wisconsin, USA). The structures of cross-linked samples were also characterized by FT-IR, using pellets made from a mixture of the solid powders and dried KBr powders.

Results and Discussion

Investigation of UV curing mechanism

The functionalities in the system of HBPCS with 4 wt% photoinitiator were investigated by FTIR (Fig. 2). Compared with the FTIR spectrum of pure HBPCS [Fig. 2(a)], a strong band at around 1675 cm^{-1} is assigned to C=O stretching in the photoinitiator 1173 [Fig. 2(b)]. After the system has been UV cured for 10 min in

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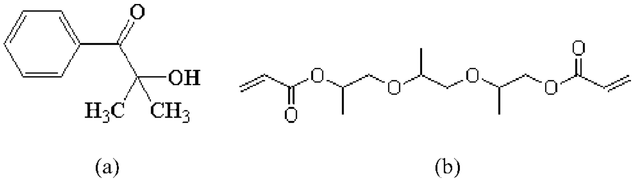


Figure 1. The chemical formula of photocure-1173 (a) and TPGDA (b).

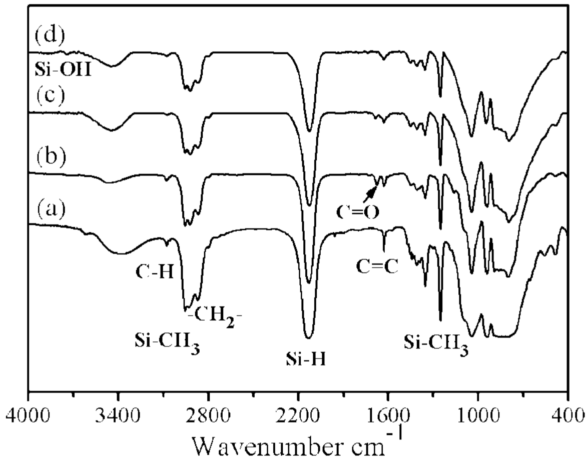
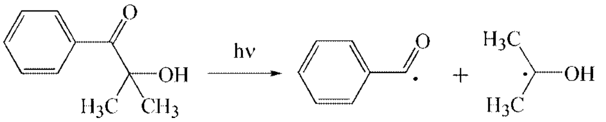


Figure 2. FTIR spectra of (a) HBPCS, (b) PCS–4 wt% 1173 un-cured liquid, (c) PCS–4 wt% 1173 UV cured for 10 min in nitrogen atmosphere and (d) PCS–4 wt% 1173 UV cured for 10 min in air atmosphere.



Scheme 1. Photolysis of 2-hydroxy-2-methyl-phenyl-propane-1-one (1173).

nitrogen atmosphere, C–H stretching in $-CH{=}CH_2$ (3073 cm^{-1}) almost disappears and the intensity of the absorption band is attributed to C=C (1630 cm^{-1}) being reduced [Fig. 2(c)]. This result indicates that the $CH_2{=}CH-$ functionality evolves in the crosslinking reaction. Since the UV curing temperature is much lower than that in thermal curing process,[11,12] the thermal crosslink reactions such as hydrosilylation rarely take place in the UV curing process. The crosslink reactions in the UV curing process are shown as follows:[13]

Under UV irradiation, benzoyl and hydroxgy isopropyl are first dissociated from reactive radicals (Scheme 1). Subsequently, the C=C bond in the HBPCS structure will be initiated by the reactive radicals (Scheme 2). The unsaturated groups initiated by radicals further polymerize to propagate the polymeric chains (Scheme 3), which results in a three-dimensional structure. In some cases, the propagating polymer chains stop growing because two radicals react with each other by coupling, or by disproportionation, or by their combination (Scheme 4).[14]

After HBPCS–4 wt% 1173 system has been cured by UV irradiation in air atmosphere, the C=O stretching band disappears in the FTIR spectrum [Fig. 2(d)]. It is believed that the decarbonylation reaction (Norrish type I) may occur in the curing process (Scheme 5):[15,16]

A small band at around 3700 cm^{-1} is also observed in Fig. 2(d). This band is attributed to the O–H stretching in Si–OH[17,18] that is formed due to the following reaction:[18]

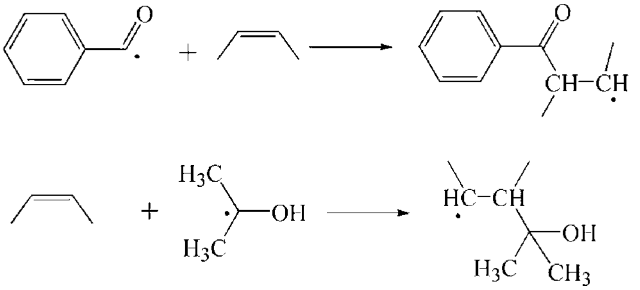
$$2Si{-}H + O_2 \rightarrow 2Si{-}OH \qquad (1)$$

Other possible reactions would also lead to Si–OH. The $SiCH_3$ functionality can be broken under UV raidation to form an $Si^{\cdot}$ center defect, which will interact with OH/H_2O to form Si–OH.[17,19]

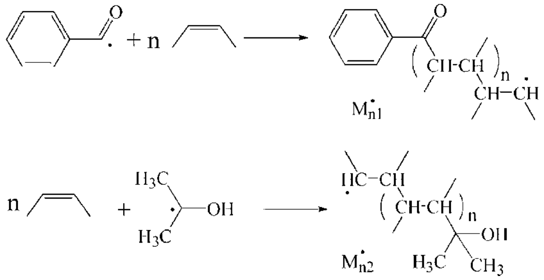
$$SiCH_3 + eV\,\text{ϟ} \rightarrow Si^{\cdot} \qquad (2)$$

$$2Si^{\cdot} + 2H_2O \rightarrow 2SiOH + H_2 \qquad (3)$$

The FTIR results for the system of HBPCS (with 10 wt% TPGDA) without photoinitiator are shown in Fig. 3. Compared with the FTIR spectrum of pure HBPCS [Fig. 3(a)], Fig. 3(b) shows two additional bands that are attributed to TPGDA: one is at around 1731 cm^{-1},



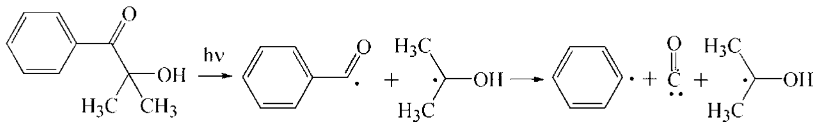
Scheme 2. Initiation of chain.



Scheme 3. Propagation of chain.

$$M^{\cdot}_{n1} + M^{\cdot}_{n2} \longrightarrow M_{n1} + M_{n2} \text{ or } M_{n1+n2}$$

Scheme 4. Termination of chain.



Scheme 5. Norrish type I reaction of photocure-1173.

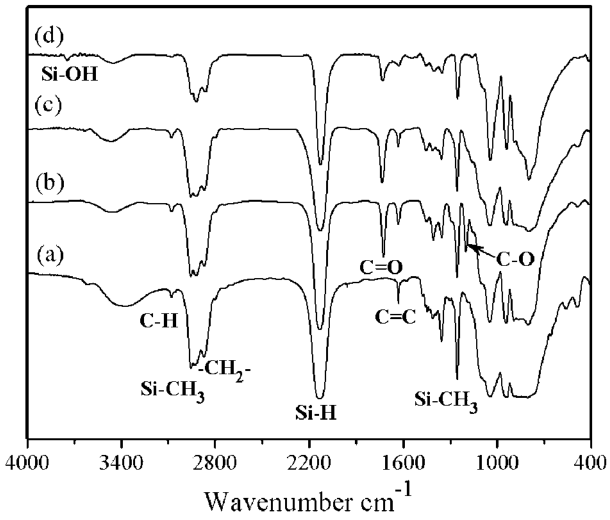


Figure 3. FTIR spectra of (a) HBPCS, (b) HBPCS–10 wt%TPGDA un-cured liquid, (c) HBPCS–10 wt%TPGDA UV cured for 10 min in nitrogen atmosphere and (d) HBPCS–10 wt%TPGDA UV cured for 10 min in air atmosphere.

which is attributed to C═O stretching vibration, and the other is at around 1195 cm^{-1}, which is assigned to C–O stretching vibration. The C–O band disappeared after the HBPCS–10wt%TPGDA system had been UV cured in either nitrogen [Fig. 3(c)] or air [Fig. 3(d)] atmosphere for 10 min. It is indicated that the TPGDA is decomposed under the UV irradiation. Compared with the uncured system [Fig. 3(b)], the intensity of C═C in the sample cured in nitrogen [Fig. 3(c)] changes little, which indicates that the potopolymerization seldom takes place in nitrogen atmosphere without the reactive radicals from photoinitiator. However, the C═C bond of the sample cured in air [Fig. 3(d)] decreases its intensity. It is noted that the stretching vibration band related to C═O (1731 cm^{-1}) of TPGDA also decreases in intensity after curing in air [Fig. 3(d)], which can be attributed to Norrish type I reaction. Such a reaction could give some free radicals, which will initiate the polymerization to some extent, as shown in Scheme 2. This may be the reason for the reduction in C═C intensity of the samples cured in air. A small band (3700 cm^{-1}) due to O–H stretching in Si–OH is also found in Fig. 3(d), which indicates the occurrence of the oxidation reactions in equations (1)–(3).

For the HBPCS system with 4 wt% photoinitiator and 10 wt% TPGDA, the FTIR spectra (Fig. 4) indicate the effects of both photoinitiator and TPGDA. C═O (1731 cm^{-1}) and C–O (1195 cm^{-1}) bands in TPGDA and C═O (1675 cm^{-1}) band in the photoinitiator are all observed in the un-cured liquid system [Fig. 4(b)]. The spectrum of cured sample in nitrogen [Fig. 4(c)] shows a combination effect of TPGDA and photoinitiator 1173. Based on the FTIR results and the above discussion, the UV curing process for HBPCS system with both photoinitiator and TPGDA in nitrogen can be described as follows. Firstly, photolysis of photoinitiator takes place under the UV irradiation while the C–O bands in TPGDA and the double band in the acrylate groups are broken. Secondly, the double bonds in both HBPCS and TPGDA are then initiated by the dissociated radicals from the photoinitiator. Subsequently, polymerization of the reactive species and free radicals takes place to propagate the polymeric chains. During these two processes, TPGDA provides a large number of double bonds and free radicals to accelerate the curing rates. Finally, a three-dimensional polymeric structure is formed by the termination reaction.

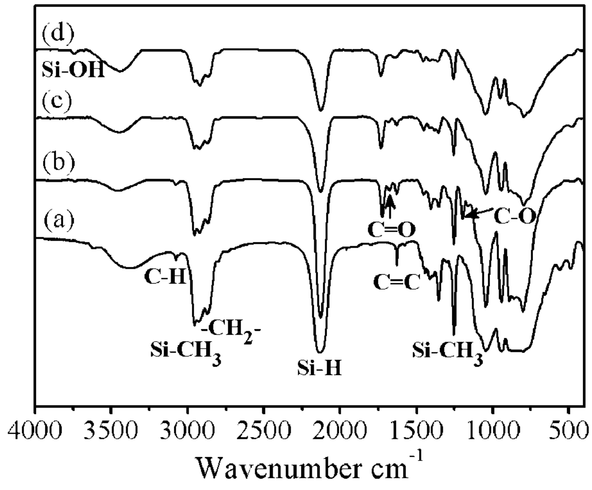


Figure 4. FT-IR spectra of (a) HBPCS, (b) un-cured liquid PCS–4 wt% 1173–10 wt% TPGDA, (c) PCS–4 wt% 1173–10 wt%TPGDA UV cured for 10 min in nitrogen atmosphere and (d) PCS–4 wt% 1173–10 wt%TPGDA UV cured for 10 min in air atmosphere.

As can be seen in the spectrum of cured sample in air [Fig. 4(d)], the band assigned to C═O in photoinitiator 1173 and the band assigned to C–O in TPGDA have both disappeared. Si–OH is also shown in FTIR as a result of the oxidation of Si–H in HBPCS. Considering the curing process for HBPCS system with both photoinitiator and TPGDA in air, the oxygen curing process happens simultaneously besides the process occurring in nitrogen. The oxidation reactions of equations (1)–(3) will take place during the curing process.

Investigation of UV curing kinetics

A typical curve for the reaction rate as a function of curing time is shown in Fig. 5, which indicates the characteristics of an autocatalytic reaction.[8] In this curve (Fig. 5), the reaction rate rapidly reaches its maximum just after curing for a few seconds. The movement of radicals is subsequently restricted and an auto-accelerative gel effect occurs. Accordingly, the cure

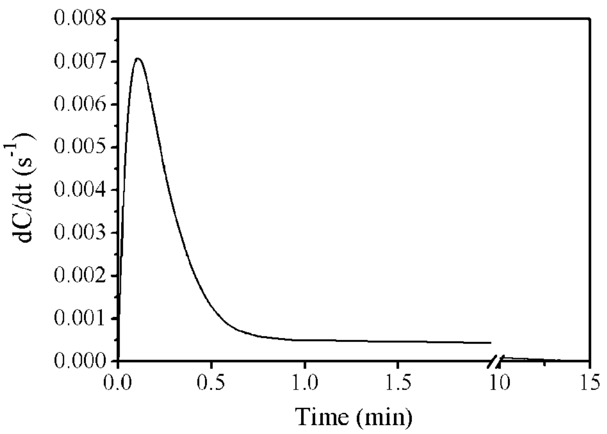


Figure 5. A typical figure of photoinitiated polymerization rate as a function of curing time.

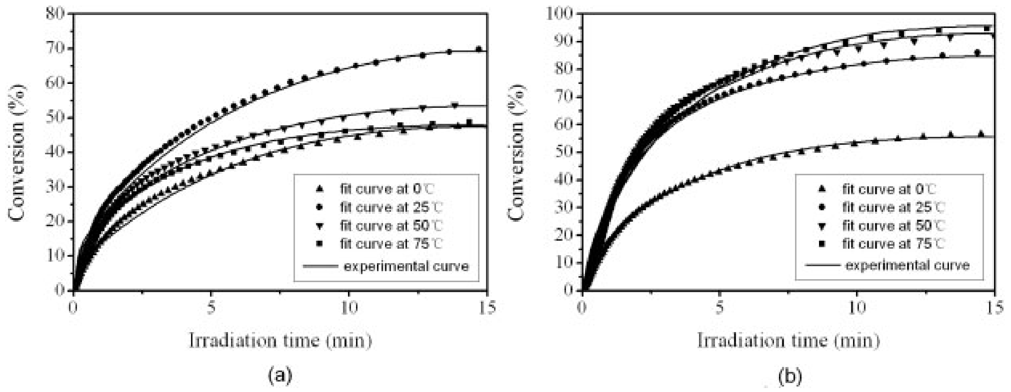


Figure 6. The conversion percentage as a function of curing time in N_2 (a) and in air (b) atmosphere (with 10 wt% TPGDA).

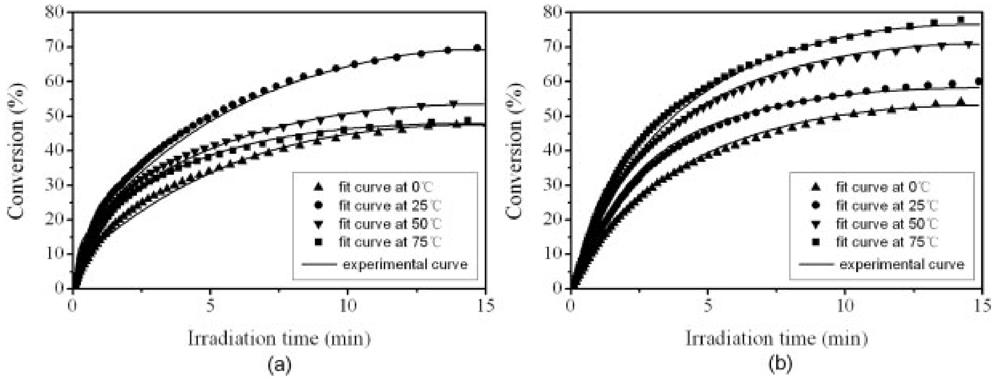


Figure 7. The conversion percentage as a function of curing time in N_2 (a) and in air (b) atmosphere (without TPGDA).

kinetics for polycarbosilanes can be expressed as the formula for the autocatalytic reaction:[8]

$$\frac{\mathrm{d}C}{\mathrm{d}t} = kC^m(1-C)^n \tag{4}$$

where C is the relative conversion, k the rate constant, m the autocatalytic exponent, and n the order of the propagation reaction.

Considering the diffusion effect during the curing process, equation (4) is modified by introducing a diffusion term:[20]

$$f(C) = \frac{1}{1+\exp[a(C-b)]} \tag{5}$$

where a is a constant and b the critical conversion. When $C < b$, $f(C)$ is approximately equal to unity and the effect of diffusion is negligible. The modified equation can be written as:[21]

$$\frac{\mathrm{d}C}{\mathrm{d}t} = kC^m(1-C)^n\frac{1}{1+\exp[a(C-b)]} \tag{6}$$

The kinetic parameters, k, m, n, a and b, can be obtained using a least square regression method to fit the conversion curves (Figs 6 and 7). As can be seen, the regression curves match the experimental data very well in the whole curing temperature range in either nitrogen or air atmosphere. The regression results are listed in Table 1.

The rate constant k obeys the Arrhenius law:

$$k = Ae^{-E/RT} \tag{7}$$

where A is a pre-exponential constant, E the activation energy, R the gas constant, and T the curing temperature. In order to obtain the value of E, equation (7) can be rewritten as follows:

$$\ln k = \ln A - \frac{E}{RT} \tag{8}$$

The obtained ln$k$ as a function of $1/T$ is plotted in Fig. 8. The activation energies for the curing process are calculated from the Fig. 8 and are listed in Table 1. As can be seen, in a nitrogen atmosphere, the curing activation energies for the systems with and without TPGDA are identical. This result indicates that TPGDA does not change the curing mechanism in inert atmosphere, although it accelerates the curing rates. As mentioned above, the UV curing process for the HBPCS system includes the photolysis of photoinitiator, initiation of chain, propagation of chain and termination of chain. Despite the fact that TPGDA increases the concentration of double bonds, the activation energy is still unchanged. Thus, the controlled process for UV curing in inert atmosphere should be the photolysis of the photoinitiator.

Compared with the activation energies for the curing systems in a nitrogen atmosphere, those for curing systems in air atmosphere are rather lower. As mentioned above, the oxygen curing process also takes place besides the UV curing process under UV radiation in air. The curing process should not be controlled by the photolysis of photoinitiator alone; the oxidation process is also involved in

Table 1. UV kinetic parameters of the HBPCS system at different temperatures

TPGDA (wt%)	Atmosphere	Temperature (°C)	*k* (min^{-1})	*m*	*n*	*a*	*b*	*E* ($kJ\ mol^{-1}$)
10	N_2	0	0.0095	0.0631	3.1893	0.01	0.22	12.07
		25	0.0163	0.2644	1.8937	0.02	0.52	
		50	0.0221	0.3770	3.2521	0.11	0.40	
		75	0.0304	0.5339	4.0557	0.12	0.51	
	Air	0	0.0201	0.3721	2.8899	0.02	0.26	2.62
		25	0.0230	0.3020	1.2099	0.10	0.45	
		50	0.0246	0.4331	1.0199	0.01	0.62	
		75	0.0258	0.5042	0.9012	0.01	0.75	
0	N_2	0	0.0057	0.3088	4.4978	0.62	0.06	12.81
		25	0.0111	0.3817	4.3011	0.61	0.09	
		50	0.0159	0.3732	3.8101	0.11	0.15	
		75	0.0191	0.5471	3.5376	0.21	0.35	
	Air	0	0.0099	0.2379	2.318	0.18	0.06	5.59
		25	0.0134	0.3214	2.0178	0.35	0.11	
		50	0.0161	0.3088	1.7081	0.25	0.18	
		75	0.0168	0.2957	1.3878	0.15	0.21	

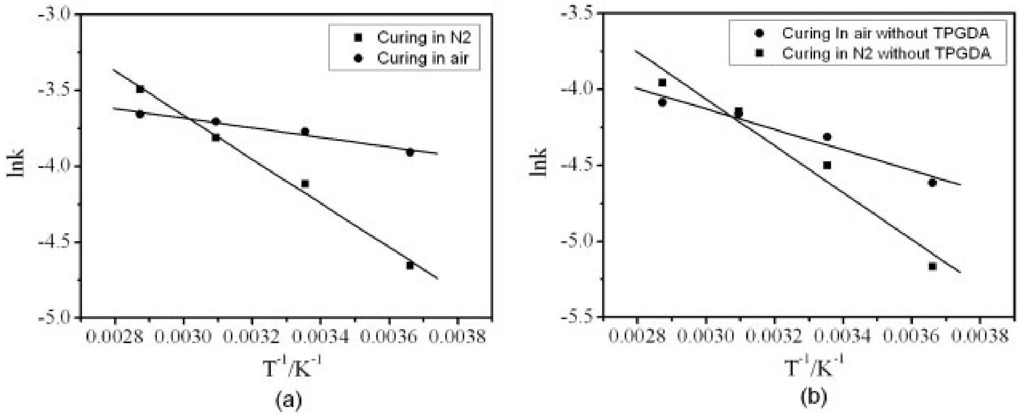


Figure 8. Relationship between ln*k* and T^{-1} for HBPCS curable systems in different reaction atmospheres (a) with 10wt% TPGDA and (b) without TPGDA.

the process. Therefore, the activation energies for the samples UV cured in air should be lower than those in an inert atmosphere. It is also noted that the activation energy for the curing system with TPGDA in air is about half of that for the system without TPGDA in air. As mentioned above, the decomposition of C=O (1731 cm^{-1}) in TPGDA according to the Norrish type I reaction would provide extra free radicals, which would accelerate the curing process. Thus, the existence of TPGDA in the curing system in air atmosphere could stimulate a new curing process, which could further reduce the activation energy for UV curing.

Conclusion

In summary, the UV curing process for the system of HBPCS–Photocure 1173–TPGDA was studied in both air and nitrogen by DPC. FTIR was used to characterize the cured products in different curing conditions. The possible reactions were determined from the FTIR results. The kinetics of the curing system was investigated. The kinetic parameters were calculated based on the relationship between conversion percentage and curing time. The activation energies in different curing conditions were obtained. Based on these results, the mechanisms for the UV curing process of HBPCS–Photocure 1173–TPGDA were determined:

- In nitrogen atmosphere, the UV curing process was controlled by the photolysis of photoinitiator.
- In air atmosphere, the UV curing process was controlled by not only the photolysis of the photoinitiator, but also the oxidation in air and decomposition of TPGDA according to Norrish type I reaction.

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