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UV curing behavior of a highly branched polycarbosilane

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Abstract The UV curing behavior of a highly branched polycarbosilane (HBPCS) was studied by differential scanning photo calorimeter (DPC) measurements. 2-Hydroxy-2-Methyl-Phenyl-Propane-1-one (Photocure-1173) was selected as photoinitiator. In order to accelerate the curing reaction rate of polycarbosilane, acrylic reactive diluent tripropane glycol diacrylate (TPGDA) was also added to the polymer system. The effect of TPGDA content, photoinitiator concentration, temperature, light intensity, and the curing atmosphere was investigated. The results indicated that the TPGDA greatly enhanced the reaction rate of the HBPCS system. The TPGDA content, photoinitiator concentration, temperature, and light intensity had their own optimal values to get the maximum ultimate conversion percentage and the reaction rate. The oxygen atmosphere helped to increase the final conversion percentage though it could retard the reaction rate.

Introduction

The technique to fabricate ceramics from polymer precursors has been attracting considerable interest due to its unique advantages such as fabricating unconventional structures and getting ceramics at relatively low temperatures [1–3]. The ceramics obtained by such a technique have high thermal stability [4], oxidation and corrosion resistance [5–8], and excellent electrical properties [9]. Thereby, they are potentially used as materials for the ceramic microelectromechanical systems (MEMS), which could be applied in aerospace, micro-combustors, heat exchangers, and high-energy micro-optics systems fields [10, 11]. However, suitable methods are required to fabricate the complex structures from polymer precursors in order to fulfill the advantages of the polymer-derived ceramics.

The UV Curing process converts a reactive liquid polymer into a solid one through photo-polymerization and crosslinking reactions induced by UV radiation. Compared with the traditional thermal treatment, this technology has a number of advantages such as ultra-fast curing, ambient temperature operation, and environment-friendly aspect (no emission of volatile organic compounds, low energy consumption) [12, 13]. In the past decades, a great deal of attention has been paid to UV-initiated applications in layer preparation regarding to microlithography [14], MEMS [15], protective coatings [16], printing inks [17], and dental stratification [18], as well as stereolithography [19].

Liquid polycarbosilane precursors with vinyl or allyl end groups can conveniently be crosslinked into unmeltable, preceramic network by UV-curing. Thereby, they are suitable to fabricate the ceramic parts with complex structures and shapes by photo-initiated polymerization process. However, little understanding about the UV curing behavior of polycarbosilane has been reported. In this article, we were trying to illustrate the UV curing behavior of a liquid highly branched polycarbosilane (HBPCS) with allyl groups by using differential scanning photo calorimeter (DPC) measurements. Influences of the parameters, including photoinitiator concentration, light intensity, reaction atmosphere, and temperature on the curing behavior were well studied. In order to increase the inherent low curing speed of polycarbosilane, tripropane glycol diacrylate (TPGDA) was

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introduced into the UV curing systems according to the previous research [20]. Subsequently, influence of the reactive diluent's concentration on the UV curing behavior was also discussed.

Experimental procedure

The liquid HBPCS with allyl groups was synthesized in the Advanced Materials Laboratory at Xiamen University [21, 22]. The chemical formula of the HBPCS was $[SiH_{1.2}(CH_3)_{0.71}(CH_2CH=CH_2)_{0.09}CH_2]_n$. The molecular weight and polydispersity index of this HBPCS were 670 and 2.9, respectively. Photocure-1173 (2-Hydroxy-2-Methyl-Phenyl-Propane-1-one, Jingjiang Hongtai Chemical Engineering Co. Ltd., China) was selected as the photoinitiator. Acrylic reactive diluent TPGDA was purchased from Guangzhou Hongyun Polymer Materials Corporation in China.

For each sample, HBPCS was mixed with different contents of TPGDA and photoinitiator in a beaker. The mixture was stirred at room temperature for 2 h. During this process, the beaker was wrapped by aluminum foil to avoid light.

The UV curing process of the samples was monitored by DPC, which contained a differential scanning calorimeter (MDSC 2910, Waters-TA instrument, USA) and a photo calorimeter accessory (Novacure 2100, EXFO Photonic Solutions). The light source was a 100 W middle-pressure mercury lamp with a wavelength range of 320–500 nm. The measurement procedures were as follows: The UV light intensity was set at a desired value (the actual light intensity exposed on specimen is about 10% of the set value [23]), followed by adjusting the curing atmosphere (N_2 or Air). 1.5 ± 0.5 mg sample was placed in an uncovered aluminum pan, which was then laid on the calorimeter furnace with a distance of 20 mm to the UV source. After 3 min stabilization in the furnace, the sample was then irradiated for 15 min under the UV light. TA Universal Analysis 2000 software was employed to record the data automatically.

The measured heat flow from DPC experiments can be converted to the ultimate conversion percentage and reaction rate [20, 24]. Since the UV-irradiated reaction for HBPCS curable system (HBPCS, photocure-1173, and TPGDA) has only one single reaction and no other enthalpic events will happen, it can be assumed that the measured heat flow is proportional to the conversion rate during the cure process [20]. The convention rate can therefore be defined as follows [24, 25]:

$$R_p = \frac{dC}{dt} = \frac{1}{\Delta H_{\text{total}}}\frac{dH}{dt} \qquad (1)$$

where R_p is the conversion rate, C the degree of conversion, t the curing time, dH/dt the measured heat flow, and ΔH_{total} the theoretical heat for complete conversion. Taking into account the polymerization enthalpy values of double bonds in allyl (84 kJ/mol) and acrylate (77.9 kJ/mol) groups, the theoretical enthalpy ΔH_{total} can be calculated using Eq. 2 [20, 26, 27]:

$$\Delta H_{\text{total}} = \omega_1 f_1 \Delta H_{p1}/M_1 + \omega_2 f_2 \Delta H_{p2}/M_2 \qquad (2)$$

where ω is mass concentration of each compound in the curing system, f the average functionality, ΔH_p polymerization enthalpy, M the average molecular weight. For the HBPCS used in this study, the allyl band content calculated from ^{1}H NMR spectra is 0.0039 mol/g. ΔH_{total} in the curable polymer systems with different TPGDA contents can thus be calculated.

The degree of conversion was calculated from the integrated form of Eq. 1:

$$C_t = \frac{\Delta H_t}{\Delta H_{\text{total}}} \qquad (3)$$

where ΔH_t is the cumulative heat of reaction up to curing time t.

Results and discussion

Influence of TPGDA content

In the HBPCS system, the photoinitiator concentration was fixed at 4 wt% and TPGDA content varied from 0 to 40 wt%. Isothermal DPC measurements were conducted at 25 °C with a light intensity of 38.8 mW/cm^2 in nitrogen and air atmosphere. The reaction rate and the conversion percentage as a function of curing time for the HBPCS curable system in nitrogen and air are shown in Figs. 1 and 2, respectively. The maximum reaction rate and the ultimate conversion percentage as a function of TPGDA content are drawn in Fig. 3. It can be seen from the shapes of Figs. 1 (a) and 2 (a) that there is one exothermic peak during the UV curing process for the samples with TPGDA. However, no obvious exothermic peaks are observed for the samples without TPGDA inside in either nitrogen or air atmosphere. This result indicates that the reactions between radical units produced from photoinitiator and the allyl groups in the HBPCS structure are pretty slow. The addition of TPGDA introduces reactive acrylic groups in the system, which would highly accelerate the reaction rate because of the higher radical polymerization activity of acrylic groups than that of allyl groups [17, 28]. After the acrylic groups in the system are largely consumed, the curing reaction rate slows down rapidly and is close to that for the one without TPGDA.

It can also be found that the more the TPGDA content is, the higher maximum- reaction-rate is (Fig. 3a). It is easily

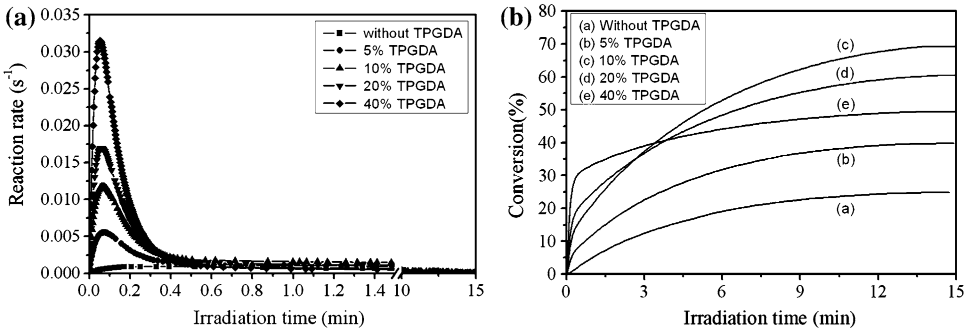

Fig. 1 Reaction rate versus curing time (**a**) and conversion percentage versus curing time (**b**) curves for HBPCS systems with different TPGDA content in nitrogen atmosphere. The curing condition is: light intensity 38.8 mW/cm^2, photoinitiator concentration 4 wt%, and isothermal curing at 25 °C

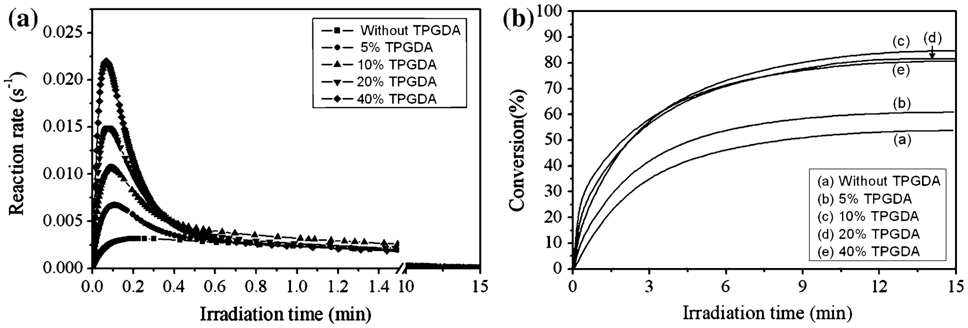

Fig. 2 Reaction rate versus curing time (**a**) and conversion percentage versus curing time (**b**) curves for HBPCS systems with different TPGDA content in air atmosphere. The curing condition is: light intensity 38.8 mW/cm^2, photoinitiator concentration 4 wt%, and isothermal curing at 25 °C

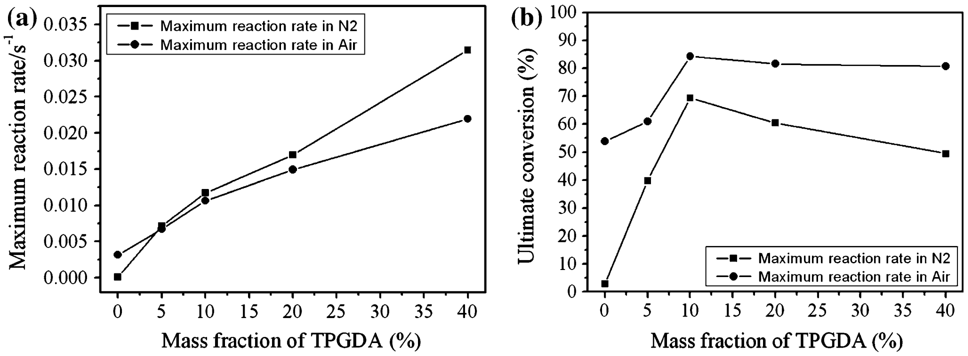

Fig. 3 Influence of TPGDA content on **a** maximum reaction rate and **b** ultimate conversion percentage

understood that more content of high reactive groups leads to higher reactivity. At the first 3 min, the conversion percentages increase with increasing TPGDA content (Figs. 1b and 2b). However, the ultimate conversion percentages decrease when the TPGDA content is higher than 10 wt% (Fig. 3b). High TPGDA content results in the quick formation of a dense cross-linked network under UV irradiation, which will increase the viscosity of the polymer system and then limit the reactions of radicals with double bands. When the TPGDA content is over a certain value, such a limitation exceeds the acceleration effect of TPGDA, resulting in the reduction of the ultimate conversion percentage.

Influence of photoinitiator concentration

The influence of photoinitiator concentration on UV curing behavior of the HBPCS system was carried out at 25 °C with a light intensity of 38.8 mW/cm^2 in nitrogen and air atmosphere. TPGDA content was fixed at 10 wt% and the photoinitiator concentration varied from 0 to 7 wt%. The curves of the reaction rate as a function of curing time (Fig. 4) in either nitrogen or air atmosphere have similar shapes to those abovementioned. In Fig. 4a and b, there is one exothermic peak during the UV curing process for the HBPCS systems with photoinitiator 1173. No obvious exothermic peaks are observed when the systems consist of only HBPCS and 10 wt% TPGDA in either nitrogen or air atmosphere. It is indicated that the allyl groups in HBPCS and acrylic groups in TPGDA are hard to be UV-initiated without the radicals dissociated from photoinitiator. The maximum reaction rate and ultimate conversion percentage reach their maximum values with 4 wt% photo-initiator 1173 in the HBPCS system in both nitrogen and air atmosphere (Fig. 5).

At the beginning of the reaction, if the initial conversion rate is higher than the photoinitiator dissociation rate, the

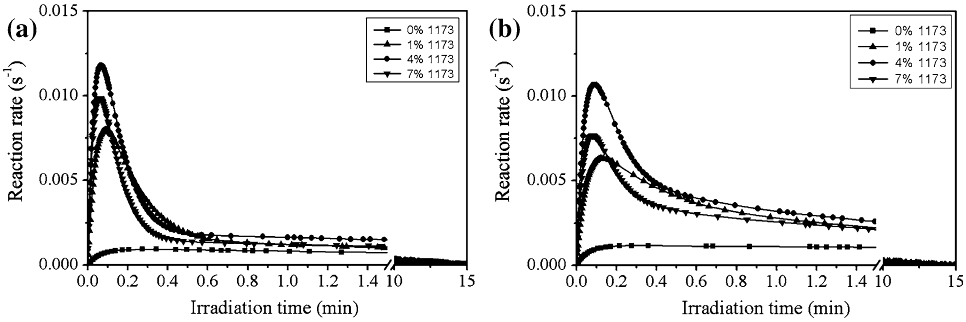

Fig. 4 Reaction rate versus curing time curves for HBPCS systems with different photoinitiator concentration in **a** nitrogen and **b** air atmosphere. The curing condition is: light intensity 38.8 mW/cm^2, TPGDA content 10 wt%, and isothermal curing at 25 °C

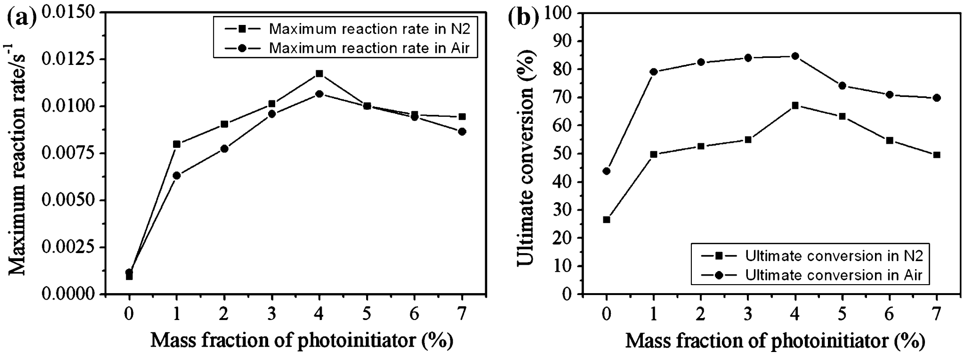

Fig. 5 Influence of photoinitiator concentration on **a** maximum reaction rate and **b** ultimate conversion percentage

steady-state assumption leads to the following equation [24]:

$$R_{p_i} = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = \frac{k_p}{k_t^{0.5}}[M](\Phi\varepsilon[A]_0 I_0)^{0.5} \qquad (4)$$

where R_{pi} is the conversion rate at the beginning of the reaction, Φ the quantum yield, ε the photoinitiator molar extinction coefficient, k_p and k_t the propagation and termination rate constants, *[M]* the molar concentration of double bonds, *$[A]_0$* the initial concentration of photoinitiator, and I_0 the initial light intensity.

Figure 6 shows the conversion rate as a function of $[A]_0^{1/2}$ in both nitrogen and air atmosphere at a conversion percentage of 3%. A linear relationship is obtained when the photoinitiator concentration $[A]_0$ is lower than 4 wt%. When $[A]_0$ is increased, the conversion rate derivates from the linearity.

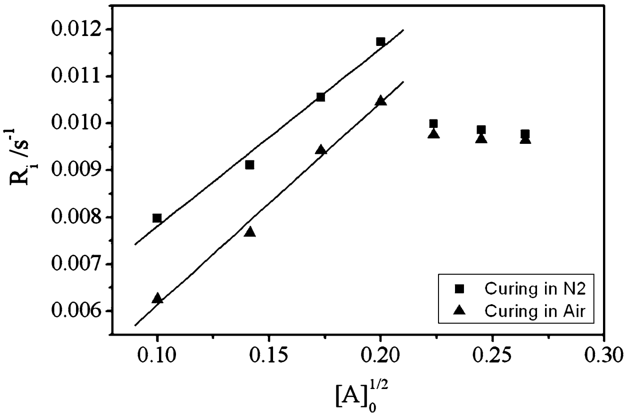

Fig. 6 Conversion rate as a function of $[A]_0^{1/2}$ in both N_2 and air atmosphere at the conversion percentage of 3%

Equation (4) indicates that the increase in $[A]_0$ would lead to increasing the conversion rate. However, it is valid only when the other parameters are constant. According to L. Lecamp [24], in the steady-state assumption, the quantum yield Φ relates not only to the photo-dissociation efficiency of initiator but also to the competition between the following two processes: (1) the reaction of the primary radical A* (decoupling from photoinitiator) with a double bond during the initiation, whose rate is proportional to $[A^*][M]_0$; (2) the coupling reaction of these two primary radicals with a rate proportional to $[A^*]^2$. Accordingly, the increase in [A*] results in the decrease in Φ [24]. Therefore, the increase of $[A]_0$ and the decrease of Φ should be the reason why there is a maximum value for R_{pi} and why the conversion rate derivates from the linearity at high photoinitiator concentrations (Fig. 6).

Influence of light intensity

The influence of UV light intensity on the curing behavior of the HBPCS system was studied at 25 °C in nitrogen and air atmosphere. TPGDA content and photoinitiator concentration were fixed at 10 wt% and 4 wt%, respectively. The light intensity varied from 8.32 to 110.9 mW/cm^2.

The curves of reaction rate and conversion percentage as a function of curing time are similar to those

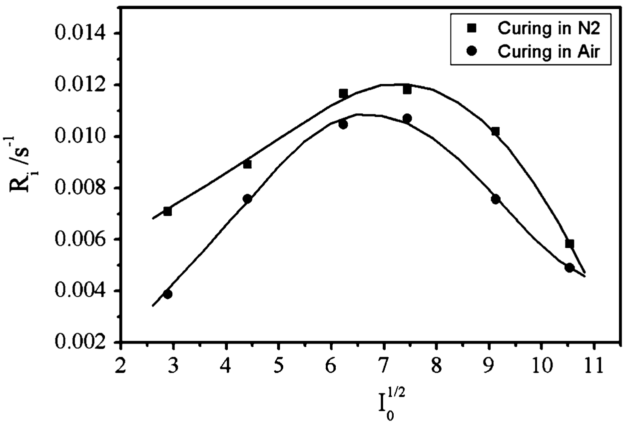

Fig. 7 Reaction rate as a function of $[I]_0^{1/2}$ in both N_2 and air atmosphere at the conversion percentage of 3%

aforementioned. According to equation (4), the initial conversion rate R_{pi} is proportional to the square root of light intensity $[I]_0^{1/2}$, which has been found in many studies [20, 24]. We calculated the initial conversion rate R_{pi} at the conversion percentage of 3%, and plotted them as a function of $[I]_0^{1/2}$ in Fig. 7. It is found that the R_{pi} increases linearly with $[I]_0^{1/2}$ at low light intensities. When the light intensity exceeds a certain value, R_{pi} begins to decrease. At low light intensities, the increase in R_{pi} with the light intensity is attributed to the free volume effect, which is caused by the delay in the volume shrinkage rate [24]. Since the initiation conversion rate is high in photo-initiated polymerization and the volume shrinkage rate is much smaller than the chemical reaction rate, the cross-linking systems can not be in volumic equilibrium. The difference in shrink rate and reaction rate results in a temporary excess of free volume, which enhances the mobility of the residual double-bond and leads to a higher conversion percentage [29]. Thus, the initial conversion rate R_{pi} increases with the light intensity. On the other hand, the high light intensity leads to a high conversion rate, which will result in the increase in viscosity. When the light intensity is over a certain value, the increase in viscosity of polymer due to polymerization can exceed the reverse effect in viscosity due to the free volume change. The increased viscosity can reduce the segmental or translational diffusion of the reactive species. The collision between two radicals thus becomes more and more difficult [24]. Due to the great decrease in the mobility of species, termination rate constant k_t, the propagation rate constant k_p, and $k_p/k_t^{1/2}$ will decrease quickly [30]. According to equation (4), the initial conversion rate R_{pi} should decrease with the increase in the light intensity.

Similarly, the curves of maximum reaction rate as a function of light intensity show a peak value both in nitrogen and air atmosphere (Fig. 8a). This result could also be understood by the above explanation: The excess free volume that is produced at low light intensities promotes the reaction rate. At high light intensities, the competition of the two controversial effects of free volume change and high cross-linking reaction rate results in a peak value for maximum reaction rate.

Influence of temperature

The effect of temperature on the curing behavior of the HBPCS system was carried out in nitrogen and air atmosphere. The TPGDA content and photoinitiator concentration were fixed at 10 wt% and 4 wt%, respectively. The light intensity was set as 38.8 mW/cm^2. The curing temperature varied from 0 to 75 °C.

The curves of reaction rate versus curing time and conversion percentage versus curing time are like the aforementioned ones. The maximum reaction rate as a function of temperature is shown in Fig. 9a. It is found that there is a maximum value in either nitrogen or air atmosphere at the temperature of 25 °C. In the curing system, the mobility of reactive species will be enhanced with raising the temperature, which leads to the increase in the reaction rate. Nevertheless, with increasing the temperature, the gelation of the polymer could easily happen, which results in reducing the mobility and the diffusion of the radical species. The conversion rate is thus decelerated. Similar trend on the relationship between ultimate conversion percentage and temperature in nitrogen atmosphere is also observed (Fig. 9b). This can also be explained by

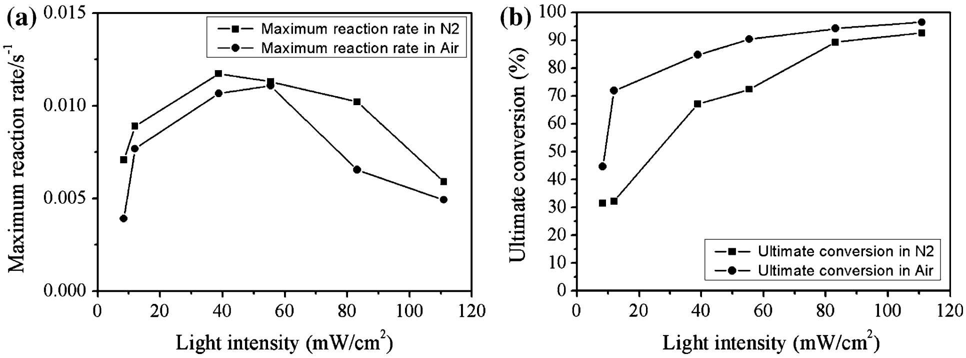

Fig. 8 Influence of light intensity on **a** maximum reaction rate and **b** ultimate conversion percentage

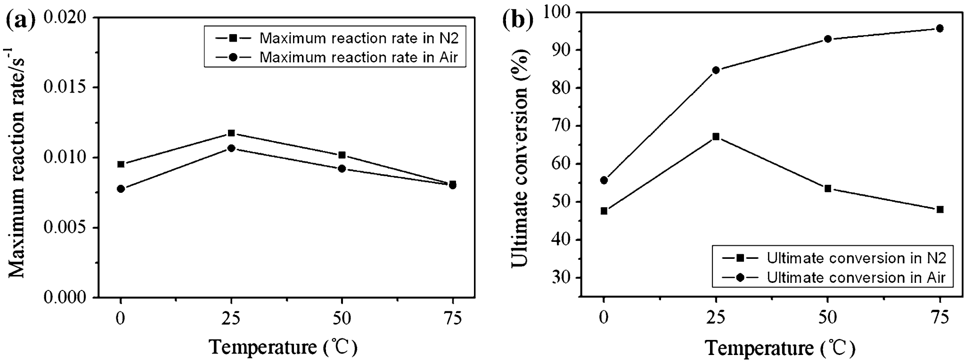

Fig. 9 Influence of temperature on **a** maximum reaction rate and **b** ultimate conversion percentage

the points of view mentioned in the section "Influence of light intensity".

Influence of curing atmosphere

Whatever the other curing parameters varies, the maximum curing rate in nitrogen is higher than that in air atmosphere (Figs. 3a, 5a, 8a, and 9a,), while the ultimate conversion percentage of the HBPCS systems is lower (Figs. 3b, 5b, 8b, and 9b).

The inhibition effect of oxygen can be used to explain this phenomenon [31]. Free-radical photopolymerization is known to be inhibited by molecular oxygen, which can quench the excited triplet state photoinitiator molecules and scavenge the initiator and polymer radicals. Since the radicals formed during the UV curing process are partially consumed by oxygen, the reaction rate will be slower compared with that in nitrogen atmosphere. On the other hand, the oxygen could lead to the polymerization of polycarbosilanes [32]. Therefore, there is a higher final conversion percentage in oxygen atmosphere than in nitrogen atmosphere due to the extra polymerization process.

Conclusion

Differential scanning photo calorimeter was utilized to study the UV curing behavior of a HBPCS. 2-Hydroxy-2-Methyl- Phenyl-Propane-1-one (Photocure-1173) was selected as photoinitiator. Acrylic reactive diluent TPGDA was also added to the polymer system to accelerate the curing reaction rate of polycarbosilane. The effect of TPGDA content, photoinitiator concentration, temperature, light intensity, and the curing atmosphere was well investigated. The results indicate that the parameters such as TPGDA content, photoinitiator concentration, temperature, and light intensity had their own optimal values to obtain the maximum ultimate conversion and the reaction rate. Although oxygen retarded the curing rate, it could increase the final conversion percentage.

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