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ISOTHERMAL CURE CHARACTERIZATION OF DICYCLOPENTADIENE
The glass transition temperature and conversion

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Conversion (α) and the glass transition temperature (T_g) were investigated during the isothermal cure of *endo*-dicyclopentadiene (DCPD) with a Grubbs catalyst for different temperatures using differential scanning calorimetry. Conversion *vs.* ln (time) data at an arbitrary reference temperature were superposed by horizontal shift and the shift factors were used to calculate an Arrhenius activation energy. Glass transition temperature *vs.* conversion data fell on a single curve independent of cure temperature, implying that reaction of the norbornene and cyclopentene ring of DCPD proceeds in a sequential fashion. Implications of the isothermal reaction kinetics for self-healing composites are discussed.

Keywords: *conversion, dicyclopentadiene, DSC, glass transition temperature*

Introduction

Curing of thermosetting materials involves the transformation from low molecular mass liquids to high molecular mass amorphous solids by means of chemical conversion. As cure reaction advances, the glass transition temperature progressively increases and reaches a maximum with a fully crosslinked structure. Understanding the cure process is particularly important in determining optimum conditions (e.g. time, temperature, catalyst loading) in thermosetting materials to obtain desired properties. Wisanrakkit and Gillham [1] have reported that the glass transition temperature (T_g) can be a useful parameter to monitor the cure process. They showed a one-to-one relationship between T_g and chemical conversion (α) for a high-T_g epoxy/amine system. Careful analysis of the variation of T_g and conversion with respect to isothermal cure temperatures and soak times not only provide information on cure kinetics (e.g., activation energy) but also better understanding of the cure systems (e.g., state of cure, reaction mechanism).

An autonomic damage repairing technique in polymer matrix composites has generated significant attention since the methodology for the repair was first reported in the literature [2]. The new repair concept involves recovery of mechanical strength by means of a liquid healing agent (monomer) which autonomically fills and vitrifies between crack planes. The healing agent is first microencapsuled in a polymer shell and then embedded in a host matrix with additional embedded catalyst. Upon damage induced cracking, the healing agent is released into the cracks by capillary action when microcapsules are ruptured by the propagating crack fronts. The embedded catalyst in the matrix subsequently initiates polymerization of the released healing agent, preventing further crack development and bonding the crack faces together, effectively healing the material.

Endo-dicyclopentadiene (*endo*-DCPD) has been used extensively as the healing agent in self-healing composites and the healing efficiencies for these systems triggered by embedded Grubbs' Ru catalyst were evaluated mainly by means of monotonic fracture [3–8] and fatigue tests [9, 10] for a damaged epoxy composite. The ring-opening metathesis polymerization (ROMP) of *endo*-DCPD leads to a highly crosslinked polymer with high modulus and excellent impact resistance. Although thermal and physical properties of the polymerized self-healing agent are key parameters for healing efficiency, only limited work has been reported to date. Cure kinetics of the ROMP for DCPD have been reported using various kinetic models for dynamic scans at different heating rates [5]. Also, *endo*-DCPD and 5-ethylidene-2-norbornene and their blends have been evaluated as potential candidates for effective autonomic healing [11, 12]. In this study, the ROMP kinetics and cure behavior of *endo*-(DCPD) were investigated for samples isothermally cured at different cure temperatures in the presence of Grubbs catalyst. We use the glass transition temperature (T_g) and

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conversion (α) as parameters to monitor the isothermal cure and estimate the performance of DCPD from the subsequent temperature scans immediately after the isothermal treatments. Also discussed is a relationship between T_g and conversion (α), which is independent of cure temperature (T_{cure}). The results obtained in this study could be used as an index for evaluating and improving the mechanical properties of the polymerized healing agent.

Experimental

Endo-Dicyclopentadiene (DCPD with 95% *endo*-isomer, Acros Chemical Co., Belgium) and Grubbs first generation catalyst (bis (tricyclohexylphosphine) benzyllidiene ruthenium(IV) dichloride, Aldrich Chemicals Inc., USA) were used in this study. Chemical formulae of the reactants are represented in Fig. 1.

The catalyst was first dissolved in dichloromethane and rapidly recrystallized using dry nitrogen flow, to obtain the catalyst in smaller and more soluble form, in order to accelerate the dissolution kinetics of the catalyst powder [13]. The monomer and catalyst were blended together by stirring mechanically at room temperature for 10 s in a vial. The catalyst loading was 0.26 mass% (2.67 mg mL^{-1}) in all experiments. The short initial mixing time (with vigorous agitation) was necessary to prevent unwanted premature exothermic reaction during mixing.

All experiments in this study were performed using a DSC (Perkin Elmer Pyris 1, Perkin Elmer Instrument, USA) equipped with a mechanical cooler to measure T_g and the residual exotherm of the reaction after the material had been subjected to isothermal curing for prespecified temperatures (T_{cure}=25 to 120°C) and times (t_{cure}=2 to 480 min). For the experiments, the uncured mixture was dropped into liquid N_2 immediately after mixing in order to prevent further reaction due to the severe exothermic heat that can develop in the bulk form. For each experiment, about 8 mg of frozen sample was removed from the liquid N_2, placed into an aluminum DSC pan, and cured isothermally, followed by a temperature scan. The temperature scan was from –50 to 250°C at a heating rate of 10°C min^{-1} under dry nitrogen atmosphere. The glass transition temperature and the heat of reaction were determined from the inflexion point of the stepwise transition and the area under the exothermic peak on the temperature scan, respectively. From the residual heat of reaction (ΔH_r) for the sample isothermally cured and the total heat of reaction (ΔH_T) for an unreacted sample, the fractional conversion (α) was calculated as

$$\alpha = 1 - \frac{\Delta H_r}{\Delta H_T} \qquad (1)$$

Results and discussion

A series of DSC curves for an uncured sample and for samples cured at 25°C for different times is shown in Fig. 2. For the uncured sample, a big and broad exothermic peak at 75°C, due to the cure reaction, and an endothermic peak at 12.5°C, due to the melting transition, were observed. The heat of reaction from the exotherm was measured to be 393.9 J g^{-1} in this study. The melting point of the uncured DCPD disappeared after 30 min of isothermal cure at 25°C. The glass transition appeared after 60 min of isothermal cure as a stepwise transition on the curve. The T_g increased progressively along with a decrease of the exothermic peak area as cure proceeds. Note that T_g values are marked by arrows in Fig. 2. The sharp endothermic peak at 0°C for the uncured sample and

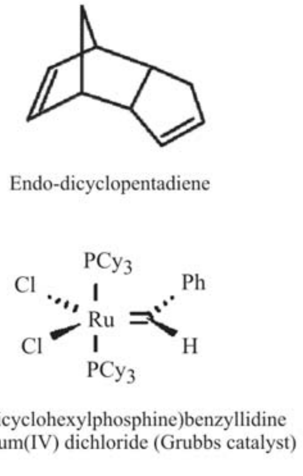

Fig. 1 Chemical reactants used in this study

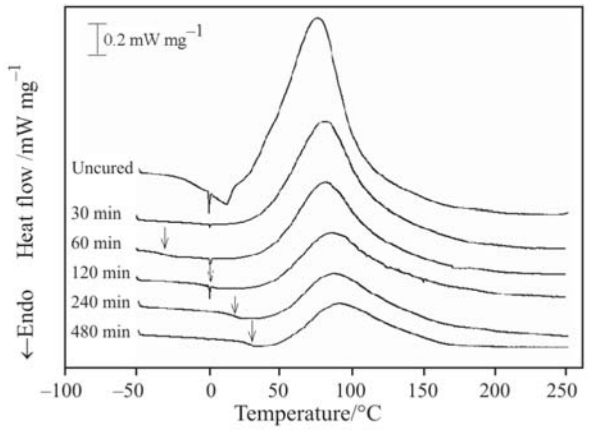

Fig. 2 A series of DSC temperature scans of uncured and cured samples at 25°C for different times

the samples cured isothermally up to 120 min originates from moisture condensation during the flash freezing of the sample in liquid nitrogen immediately after mixing and/or the delivery of the sample from liquid nitrogen to the DSC cell.

The basic parameter governing the state of the material is chemical conversion (α) while T_g is considered to be an important parameter controlling the physical/thermal properties. These two parameters are known to be in a unique one-to-one relationship [1]. Many investigations have been reported on isothermal cure behavior using the two parameters (i.e., T_g and conversion) mostly for epoxy resins [1, 14, 15].

In this study, measurements of T_g and the residual heat of reaction (ΔH_r) were made for isothermally-cured DCPD samples. Conversion (α) was determined from ΔH_r and ΔH_T using Eq. (1).

When ΔH_T was determined from the peak area of an uncured DSC curve, the baseline was determined using an initial point (17.5°C) as the end of melting transition, neglecting the less than 0.5% of cure before the end of the melting region [5].

In Fig. 3, the resulting conversion (a) and T_g (b) for samples isothermally cured at different temperatures and times are plotted *vs.* ln (time). As shown in the figure, conversion and T_g increase with increasing cure temperature and time. For the lowest cure temperature in this experiment (25°C), conversion and T_g gradually raised from 0.20 to 0.67 and –30 to 20°C after 480 min of cure, respectively. However, after curing at the highest temperature of 120°C for 2 min, the material reached a conversion level of 0.98 with a T_g of 120°C. After 480 min at the cure temperature, T_g reached 140°C, which corresponds to the maximum T_g=($T_{g\infty}$) obtained by a dynamic scan to 250°C.

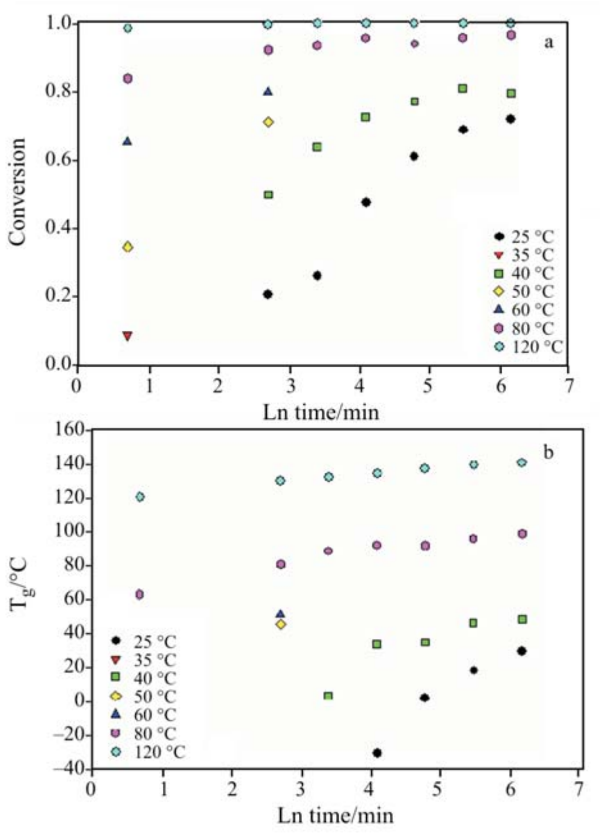

Fig. 3 a – Conversion *vs.* ln (time) and b – T_g *vs.* ln (time)

In order for self-healing to be effective, the liquid healing agent in the microcapsules must be able to flow between the crack planes in the damaged material, and polymerize into a rigid enough adhesive to transfer and carry significant load across the crack interface. It is most desirable that this rigidity be obtained after substantial polymerization for the healing efficiency to be maintained over the often wide range of temperatures to which the healed material may be exposed. Since the rigidity and subsequent adhesive performance of reactive systems depend on the chemical conversion, healing efficiency must be directly related to the degree of cure of the healing agent and therefore the glass transition temperature. As shown in this study, at 25°C, the glass transition of the material was well below RT after 60 min (T_g= –30°C, α=0.47), and it took 480 min for the glass transition to raise near RT (T_g=20°C, α=0.67). This indicates that the polymerization reaction of *endo*-DCPD is so slow that the healed effect may not be retained above RT. However, the reaction proceeded very fast with high T_g and conversion (T_g=120°C, α=0.98 in 2 min of cure) at 120°C. Therefore, heating of the self-healed material is an option to improve the healing efficiency using *endo*-DCPD over the wide temperature range.

Since determination of T_g is more accurate than measurement of ΔH_r, T_g is considered to be a better index to monitor the cure process than conversion for epoxy systems [1]. However, in our ROMP reaction system, there are difficulties in measuring T_g as accurately as for epoxies. First, glass transition temperatures of uncured DCPD samples can not be determined since the monomer is frozen below the melting point (T_m of DCPD=12.5°C). Also complicating the measurements is that as T_g raises with cure time, the glass transition approaches the exothermic cure peak and is disturbed by the residual reaction occurring during the glass transition. Finally, due to limitations of our instrument, T_g values lower than –40°C can not be detected in this experiment. Therefore, a greater number of more accurate data points can be obtained from the heat of reaction. In this study, conversion data was used for further analysis. Conversion *vs.* ln (time) data in Fig. 3a were horizontally shifted to longer times for higher temper-

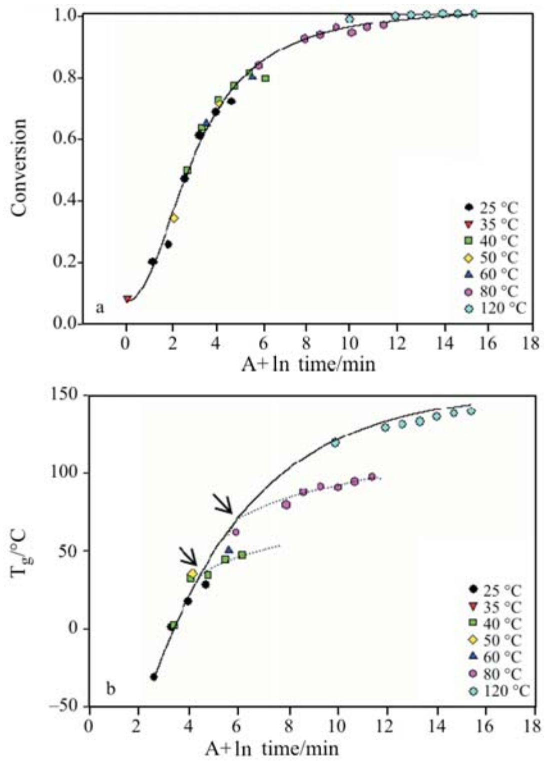

Fig. 4 Superposition of a – conversion and b – T_g *vs.* A+ln (cure time) data to form a master curve at 40°C by shifting each curve

ature data and to shorter times for lower temperature data at a reference temperature (T_r=40°C).

As shown in the figure, the data formed a single master curve after the horizontal shift and the result is shown in Fig. 4a. The same shift factors from the conversion calculations were applied on T_g *vs.* ln (time) data in Fig. 3b and the results are displayed in Fig. 4b. The master curve represents the progression of conversion and T_g when the material is cured at 40°C, if the reaction is only kinetically controlled. The liquid prepolymer reacts in a kinetically-controlled regime until its continuously rising T_g becomes coincident with T_{cure}. Above T_{cure}, reaction is retarded greatly since the system becomes vitrified and diffusion-controlled kinetics govern the reaction. The vitrification points at 40 and 80°C of cure temperature are marked by arrows on the master curve (indicated by solid line) in Fig. 4b. Data points branching off (indicated by dot line) from the master curve shortly after the vitrification points is due to the transition to diffusion controlled kinetics.

For a kinetically controlled reaction mechanism, the temperature dependence of the rate constant is generally given by an Arrhenius relationship:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(\frac{-E_a}{RT_{cure}}\right) f(\alpha) \qquad (2)$$

where E_a is the apparent activation energy for the overall reaction, R is the universal gas constant, $f(\alpha)$ is a function of conversion (α) independent of temperature. Rearranging Eq. (2) and integrating yields,

$$F(\alpha) = \ln\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \ln A + \ln t - \frac{E_a}{RT_{cure}} \qquad (3)$$

At the arbitrary reference temperature (T_r), Eq. (3) becomes

$$F(\alpha) = \ln A + \ln t_r - \frac{E_a}{RT_r} \qquad (4)$$

By subtracting Eq. (3) from Eq. (4), the equation for the shift factors, $A(T)$, is related to the inverse of absolute temperature:

$$A(T) = \ln t_r - \ln t = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_{cure}} - \frac{1}{T_r}\right) \qquad (5)$$

The ln (time) shift factors, $A(T)$, are plotted *vs.* $1/T$ in Fig. 5. The resulting plot is a straight line, the slope of which yields an activation energy for the reaction of 58.0 kJ mol^{-1}. This value shows an excellent agreement with the result from fitting the experimental data using dynamic temperature scan experiments at different heating rates by the n^{th} order

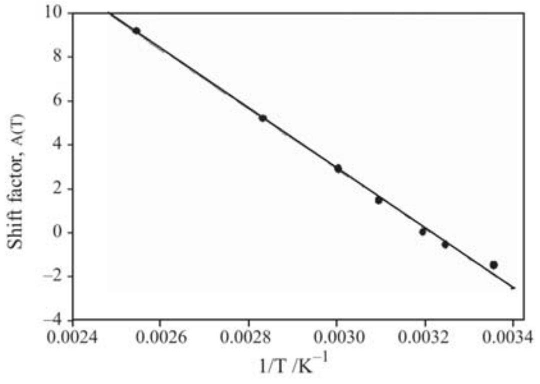

Fig. 5 Shift factor *vs.* $1/T$ to calculate activation energy

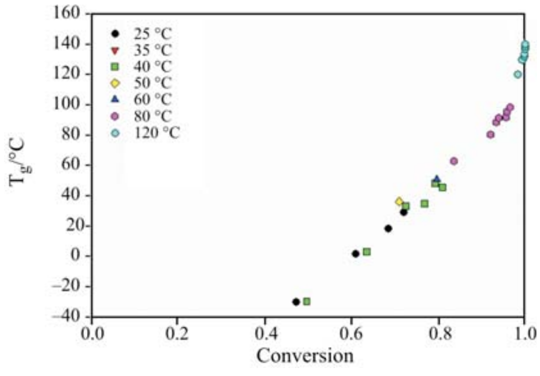

Fig. 6 T_g *vs.* conversion

with autocatalysis cure kinetics model for *endo*-DCPD (58.16 kJ mol^{-1}) [5].

Figure 6 shows all the detectable experimental T_g data as a function of conversion obtained from partially isothermally cured samples at different cure temperatures. It is evident that T_g is a unique function of conversion independent of the cure temperature. This behavior may take place a) if only one chemical reaction is involved or b) if more than one reaction takes place with similar activation energies or c) if two or more reactions with different activation energies occur sequentially [15]. In the case of dicyclopentadiene, there are two sites of functionality available; the double bond of the norbornene ring and that of the cyclopentene ring. It is generally known that ROMP occurs at the highly strained norbornene ring first, followed by the cyclopentene unit, leading to a crosslinked polymer [16]. This unique one-to-one relationship indicates the subsequent reaction of the norbornene and cyclopentene ring. Notice that T_g shows a noticeable increase with a small amount of conversion particularly at the later stage of cure.

Conclusions

Cure process was monitored by measuring T_g and conversion from DSC experiments for *endo*-DCPD isothermally cured in the presence of 0.26 mass% (2.67 mg mL^{-1}) Grubbs catalyst. At RT, conversion and T_g values reached 0.67 and 20°C after 480 min of cure, respectively. At 120°C, T_g as 120°C after just 2 min of cure. *Endo*-DCPD reacting very slowly at RT may not possess the requisite physical/thermal properties to function as an effective self-healing agent, but heating the material improves healing efficiency. The results also showed that Grubbs catalyst worked well for ROMP of *endo*-DCPD at the elevated temperatures. The horizontal shift of conversion *vs*. ln (time) data at an arbitrary reference temperature generated a single curve. Arrhenius activation energy in *endo*-DCPD was calculated to be 58.0 kJ mol^{-1} from the horizontal shift factors. T_g *vs*. conversion data formed a single curve independent of cure temperature, implying that the reaction mechanism of the two functional groups of *endo*-DCPD, the norbornene ring and cyclopentene ring, operates in a sequential fashion.

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