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TTT CURE DIAGRAM FOR AN AMBIENT TEMPERATURE CURING EPOXY-AMINE THERMOSET

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ABSTRACT

The different transitions involved in the curing reaction of a commercial epoxy thermoset called Sikadur®-30 which consists mainly of diglycidyl ether of bisphenol A (DGEBA) and a trimethylhexane diamine was studied to develop a time-temperature-transformation (TTT) isothermal cure diagram for this system. The TTT diagram is expected to enhance the cure cycles for different cure regimes which will allow back calculation of cure time for an isothermal cure temperature. This is not given in the manufacturer's data sheet. Therefore this allows better flexibility in using the epoxy system, which is often needed when assembling civil engineering structures under changing outdoor conditions. The gel times were identified using oscillatory rheological measurements. Vitrification times were determined through differential scanning calorimetry (DSC) studies. Glass transition temperatures of the unreacted system (T_{g0}) and fully reacted system ($T_{g\infty}$) were found to be - 48 °C and 69 °C respectively. For a known isothermal cure temperature, the occurrences of gelation and vitrification against time provides important information in structural applications. Specifically the gelation curve provides maximum pot life at various isothermal cure conditions which enables optimisation of operations and handling of epoxy system at preceding environmental conditions. As the vitrification is the point at which the reaction rate is severely retarded due to the change in reaction mechanism from kinetically controlled to diffusion controlled, this information enables users to understand the capacity of the adhesive as it also implies that the system has reached a glass transition temperature equal to the cure temperature. Therefore the TTT diagram allows optimised operations and handling of an epoxy system on site allowing users the flexibility to adapt to varying environmental conditions or practical constraints.

1 INTRODUCTION

Epoxy thermosets are the most widely used structural adhesive in civil engineering composite applications. This is due to the unique combination of properties of epoxies; including low cure shrinkage, high strength, high adhesion strength, excellent corrosion and chemical resistance. While significant advancements have been made in application of bonded composites in civil engineering over the past few decades [1], fiber reinforced polymers (FRPs) and adhesives used are largely limited to those off-the shelf solutions provided by manufacturers. Aerospace and automotive industries widely use advance adhesive systems designed specifically for the needs of those applications, civil engineering is pinned with limited solutions set by manufacturers with little information available to the end users. Existing research has clearly shown that some of these off-the shelf systems are far from optimal, and by changing the adhesive used, much higher performances could be obtained from bonded joints [2]. In order to exploit the true benefits of FRP applications within civil engineering applications, it would be necessary for structural engineers to carry out optimal designs using targeted material selection. For structural engineers to make such decisions, better understanding of the adhesives available and their properties is necessary. Such an understanding can also lead towards development of new adhesives best suited for different civil engineering applications. This study strives to understand the curing behaviour of a commercial epoxy thermoset namely Sikadur®-30, through investigation of the chemistry and cure kinetics. This will help develop an optimized curing condition for bonded joints with complex geometries considering structural and construction performance criteria. In particular, a TTT diagram is generated for Sikadur®-30. The TTT diagram aims to provide elaborate phase transition information for all cure temperatures.

There have been a large number of TTT diagrams developed for numerous polymers [3]. However the motive of these studies has been to compare two or more systems by slightly varying their chemical composition.

2 EXPERIMENTAL

2.1 Materials

The epoxy resin is a two-component thixotropic commercial adhesive called Sikadur®-30. The epoxide (Part A) has a 10% - 30% concentration of diglycidyl ether of bisphenol A (number average molecular weight <= 700g/mol). The hardener (Part B) is made of 2,2,4(or 2,4,4)-trimethylhexane-1,6-diamine and silicon oxide (Quarts).

2.2 Sample preparation

Two part thermoset epoxy was weighed and mixed in ratio resin to hardener of 3 : 1 as recommended by the manufacturer. Small batches were hand mixed thoroughly until a uniform colour was achieved. All mixed batches were kept at ambient temperature (25 ºC) for 15 minutes before subjecting to any curing regime or testing. This window of time was used to weigh, record the weights and encapsulate samples in Aluminium pans for calorimetric tests or to position between parallel plates for rheological tests which will be described in the following sections.

3 TECHNIQUES

3.1 Differential Scanning Calorimetry

The Differential Scanning Calorimetric studies were done using a TA Instruments DSC Q2000.This was used to determine the glass transition temperatures. Epoxy resin samples were cured under various curing regimes and tested as shown schematically in Figure 1. The analysis was done for T_{cure}(curing temperature) -25ºC, 4ºC, 27ºC, 35ºC, 45ºC and 55ºC. Sample size for Differential Scanning Calorimetry was maintained 4 – 7 mg as suggested from the literature [3]. Dynamic mode heating at 20ºC/min allowed determination of glass transition temperatures of samples as recommended in ASTM D3418 – 15[4]. The samples were cooled down to 30ºC lower than the expected glass transition temperature and were heated up at 20ºC/min to capture the phase transition smoothly on the heat flow curve (to approximately 30ºC higher than the expected glass transition temperature)[4]. The calorimeter had a temperature range of -90 ºC to 400ºC. DSC uses a Refrigerated Cooling System (RCS90) to achieve temperatures below room temperature and was calibrated using Indium as a standard. According to manufacturer specifications, baseline reproducibility with Tzero pan and lid is ±10µW and the equipment possesses a sensitivity of 0.2µW. As shown in Figure 3, the variation of the glass transition temperature against cure time at various isothermal cure temperatures is the experimental foundation of this study. The samples were subjected to isothermal cure conditions in an oven for temperatures higher than ambient temperature. For temperatures lower than ambient temperature, the samples were kept in a freezer. Subsequently the samples were loaded on to the Differential Scanning Calorimeter (DSC) and was tested. Each experiment was repeated twice for accuracy and reproducibility according to ASTM D3418 – 15[4].

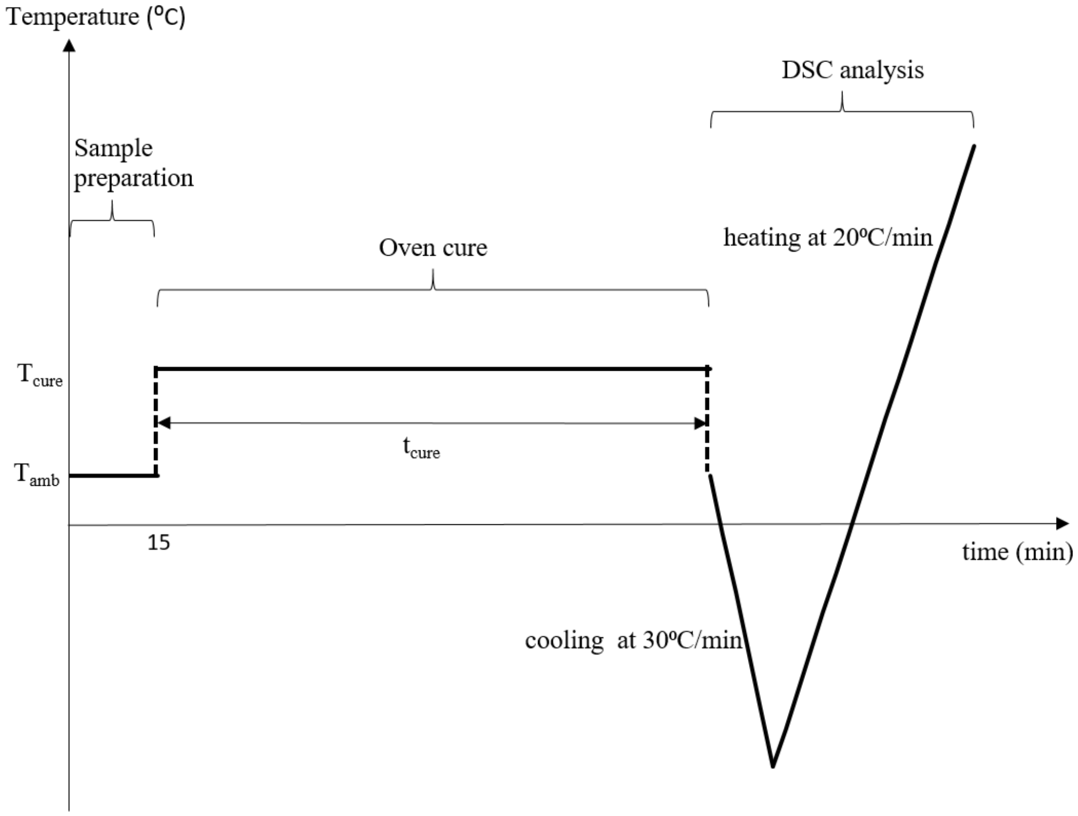

Figure 1: Temperature cycle of Sikadur®-30 sample subjected to curing and consequent DSC analysis.

3.2 Rheology

Discovery Hybrid Rheometer (HR-2) was used to measure the rheological properties of the epoxy. The equipment was operated in oscillatory mode, parallel plate geometry. The operating temperature range of the HR-2 is between -85⁰C and 300⁰C with the support of an air chiller system (ACS-3). The metal plates were grit blasted to roughen the surface and to remove the weak surface layer (e.g., oxide layer) as recommended by existing guidelines [5,6] and was found to be the most effective[7]. Aluminium is an economical soft metal which can be machined easily. However due to its' very high rate of oxidation, the purpose of grit blasting is lost when a weak layer of oxide is formed again. Brass is an alloy which contains approximately 70-76% of Copper, 20-30% Zinc and Aluminium, Iron and Arsenic in minute percentages [8]. Copper stands at a very low reactivity level in the activity series of metals. Due to the ease of machining and low oxidation rate, brass was used to manufacture parallel plate disposable fixtures to carry out the rheological experiments.

4 RESULTS AND DISCUSSION

4.1 Gelation study

Gelation is a critical transition which corresponds to the generation of a giant macromolecular structure that percolates the reaction medium. This phenomenon occurs at a fixed extent of conversion and can happen at different temperatures. This is microscopically characterised by the change from a liquid to a solid [9]. Rheological properties were used to identify the gelation of the system. Gel time was assigned as that corresponding to the crossover point of storage modulus and loss modulus. Figure 2 illustrates the variation of dynamic mechanical properties, the storage and loss moduli with time as the epoxy cures at an isothermal temperature of 55 ⁰C. Initially a prominent viscous behaviour leads to a higher loss modulus. However as the epoxy cures, storage modulus increases as the elastic behaviour significantly influence the response of the system. The gelation time was recorded as 22 minutes at which the crossover of storage modulus and loss modulus occurs. This experiment was repeated at 20 °C, 27 °C, 35 °C, 45 °C, 65 °C and 80 °C isothermal cure conditions and the gel times were recorded as shown in Table 1. All experiments were done at a frequency of 1 Hz, 15% strain and on 25mm diameter brass parallel plates with an adhesive gap of 2mm. The plate fixtures were calibrated for inertia, oscillatory mapping and thermal expansion. The environmental chamber and the fixtures were heated/cooled to the required curing temperature, prior to loading the sample.

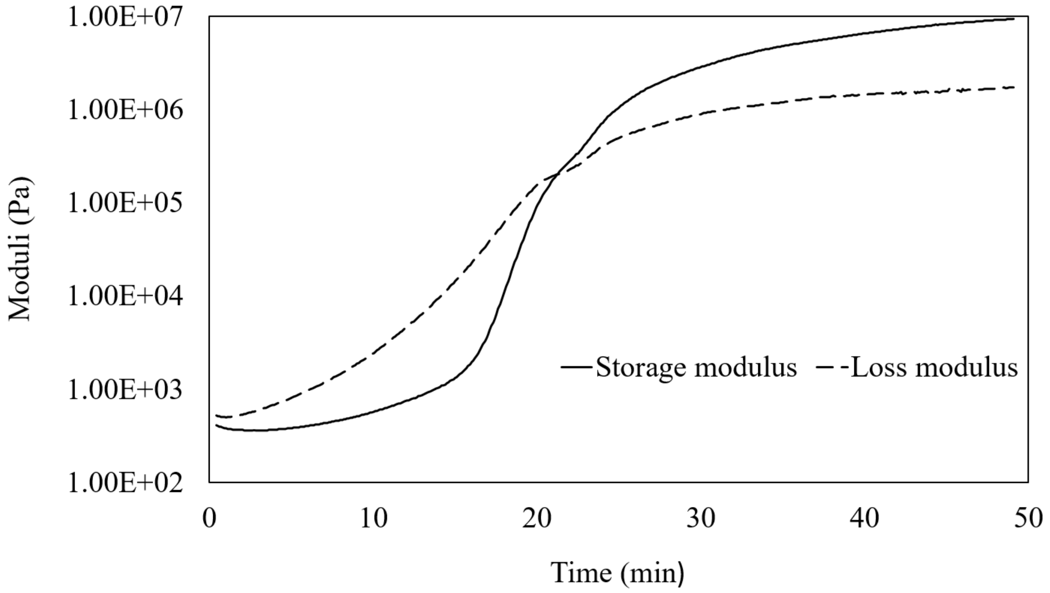

Figure 2: Variation of rheological moduli against time during isothermal cure of Sikadur®-30 at 55 °C

4.2 Vitrification study

Vitrification is defined as the point at which the molecular weight or cross-link density of the curing polymer exceeds that which is thermodynamically stable as a rubber, and the material undergoes a transition from a rubber to a glass, at which point the reaction dramatically slows due to the reduced mobility of the reactants [10]. Figure 3 shows the variation of glass transition temperature (T_g) as a function of cure time for different isothermal cure temperatures. It has been shown that at $T_g = T_{cure}$, the polymerisation kinetics are severely retarded due to the change of phase from rubber to glass [3]. This phenomena is called vitrification. It can occur before or after gelation and is dependent on the cure temperature [9]. DSC dynamic experiments were carried out to identify the T_g of systems. Plots of dH/dt as a function of temperature shows an endothermic step change in heat capacity at the glass transition. However the transition does not occur suddenly at one unique temperature but rather over a range of temperatures. The midpoint of the transition is taken as the T_g [11]. When developing the TTT diagram, the glass transition temperatures of the unreacted system (T_{g0}) and fully cured system ($T_{g\infty}$) carry higher significance. These values are found to be - 48 °C and 69 °C respectively for Sikadur®-30. As Sikadur®-30 is an ambient temperature curing structural adhesive, the chemical reactions start instantly as the two parts are mixed. However to identify the T_{g0}, the reaction had to be retarded until the heat flow is measured by the DSC. As liquid nitrogen is a cryogenic liquid with a -90 °C boiling point, the samples were submerged in liquid nitrogen forcing a phase change (ungelled liquid to ungelled glass) immobilizing the functional groups of the system. Subsequently the DSC tests were performed on the samples to characterise the initial unreacted glass transition temperature (T_{g0}).

Cure Temperature (^{o}C)	Gel time (min)	Vitrification time (min)
-25	-	13630
4	-	1470
20	240	-
27	141	390
35	97	251
45	42	153
55	22	121
65	12	-
80	5	-

Table 1: Times of gelation and vitrification of Sikadur®-30 (vitrification times are averages of three replicates)

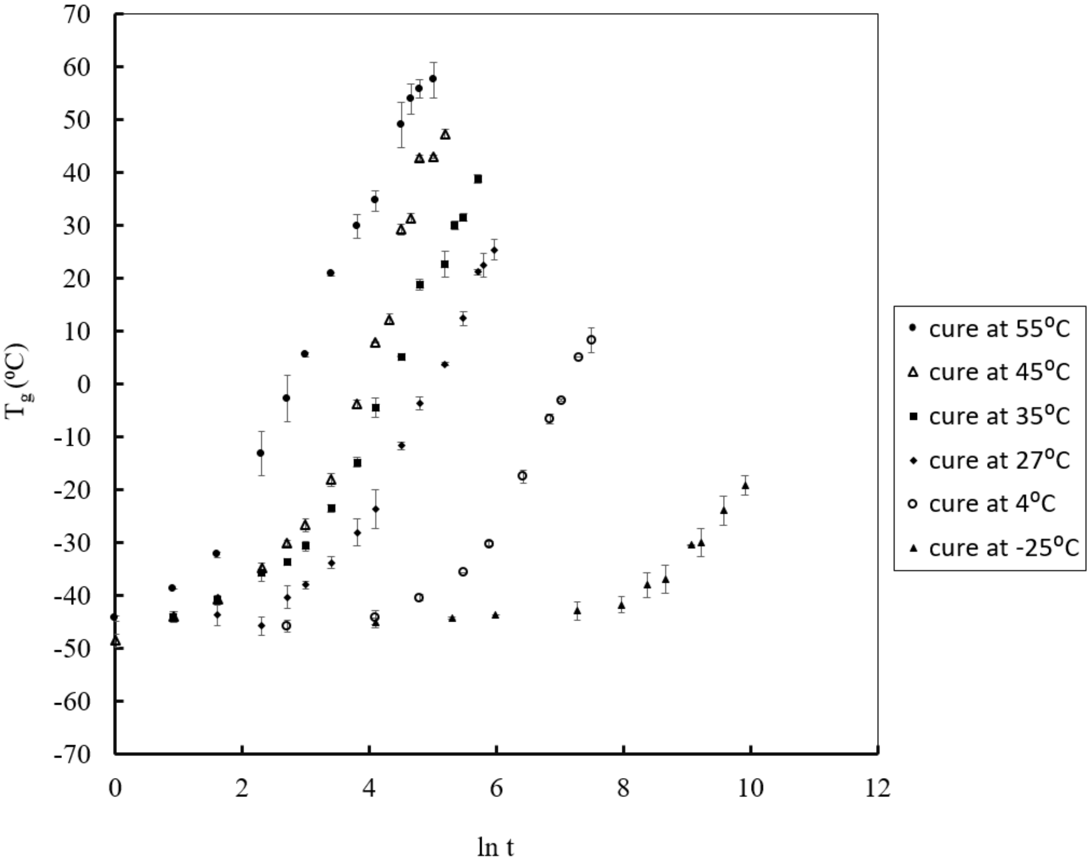

Figure 3: T_g versus ln time (min) for various cure temperatures for Sikadur®-30.Error bars represent ± standard deviation of three replicates

As shown in Figure 4 TTT diagram of Sikadur®-30 was developed using the experimentally determined T_{g0}, $T_{g\infty}$ and gelation and vitrification times in Table 1. The TTT diagram mainly separates the ungelled-liquid, ungelled-glass, gelled-liquid and gelled-glass phases of the epoxy system. The vitrification curve is an S shaped curve which indicates the crossover of the reaction mechanism from kinetically controlled to diffusion controlled.

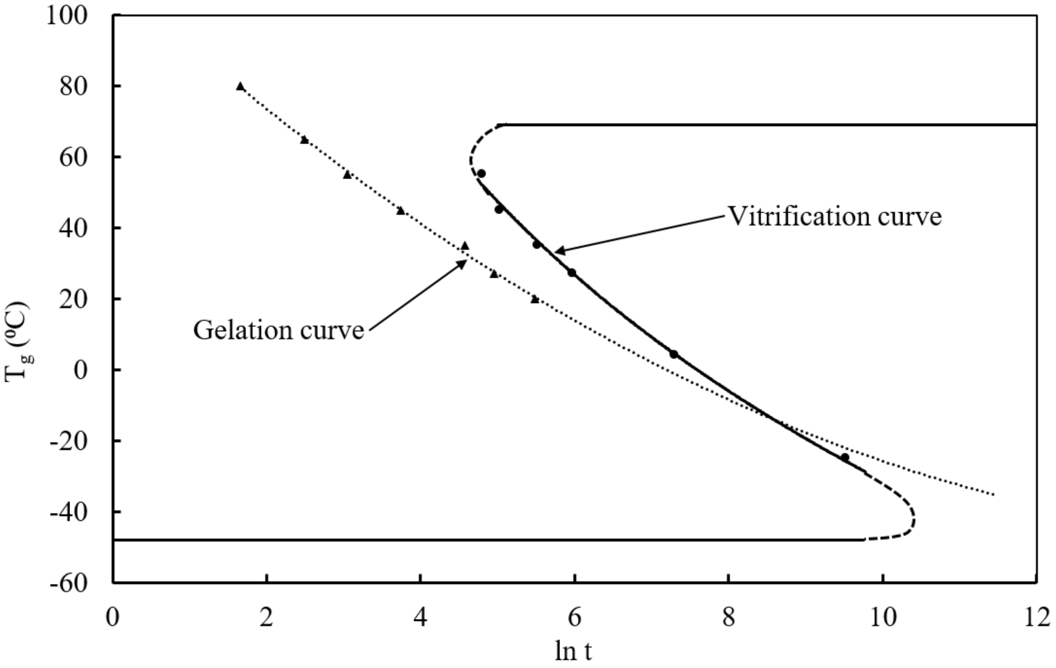

Figure 4: Time-temperature-transformation diagram for Sikadur®-30 (time is measured in minutes)

In structural applications, the usual practice with Sikadur®-30 is ambient temperature curing for 7 days. Additionally the manufacturers provide properties such as compressive strength, shear strength and tensile strength for a few cure conditions. This information prevents users from optimising the properties of structural adhesives. Sikadur®-30 is taken as an example system to demonstrate the possibility of optimising the usage of commercial structural adhesives. Using the TTT diagram, one can acquire information such as phase transitions against cure time for various cure temperatures. This information enables the user to better understand the thermoset cure behaviour.

As these adhesives are used in large structures where the ambient conditions vary throughout the day and vary seasonally, the gelation curve in the TTT diagram gives the time frame the system will remain ungelled. Thus leading to better knowledge of pot life at various temperatures. The Manufacturer's data sheet only provides pot life at 35 °C. On a sunny day a steel structure will easily reach temperatures much higher than 35 °C. Therefore the gelation curve facilitates an insight to optimised operations and handling before gelation at various temperatures.

Vitrification is an important phenomena to understand the rate of reaction. After vitrification the reaction mechanism changes from kinetics to diffusion controlled where the reaction rate is significantly retarded. Another important information is at vitrification, the system reaches a T_g equal to the cure temperature. However further studies must be carried out to determine the variation of degree of cure (α) and T_g and validate the widely used Di-Benedetto equation. This relationship has previously been reported in the literature, where T_g has been used as a measure of conversion. The modified semi-empirical Di-Benedetto equation is as follows [12],

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (1)$$

Where α is the degree of conversion of epoxide. The degree of cure cannot be measured directly, however the T_g of a system can be easily determined through a DSC experiment. Therefore with the availability of a validated Di-Benedetto equation for the system, the degree of cure can be determined.

9 CONCLUSIONS

A TTT diagram was developed for the two-component commercial epoxy system Sikadur®-30 which provides a valuable insight of the phase transitions for all possible cure temperatures for the epoxy system. This specifically addresses the lack of cure condition information provided by manufacturers which hinders the usage of the commercial epoxy system over a wide range of cure temperatures. Characteristic temperatures T_{g0} and $T_{g\infty}$ were determined. This will allow the users better understanding of the glass transition temperature range of the system. The TTT diagram shows the occurrences of phase transition against time at different isothermal cure conditions. Gelation curve provides maximum pot life durations at various isothermal cure conditions which helps optimise operations and handling of epoxy at site for any precedent environmental condition. Vitrification curve separates the different reaction mechanisms providing the users the information about the time the reaction rate is severely retarded. It also gives information of an approximate glass transition temperature for the system which is equal to the cure temperature. Cure durations longer than vitrification time promises a T_g higher than the cure temperature. The TTT diagram helps users optimise operations and handling of an adhesive system giving its users the flexibility to adapt to practical/equipment constraints and varying environmental conditions.

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