

EFFECT OF CURING ON THE GLASS TRANSITION TEMPERATURE OF THE EPOXY/GNP SYSTEM

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Abstract: Epoxy systems are highly valued for their exceptional properties and find widespread use across various applications. A comprehensive understanding of the curing process is essential to achieve the desired material properties, particularly considering the influence of diffusion processes below the glass transition temperature. This study focuses on assessing the impact of graphene nanoplates (GNP) on the curing process by examining the degree of conversion at different glass transition temperatures (T_g). Interestingly, the addition of 1wt.% GNP does not significantly affect the cure and T_g of the epoxy. The observed behavior suggests a two-stage reaction, one occurring prior to gelation and another following. The findings indicate no substantial impact from treatment with GNP on the glass transition temperature (T_g) during the curing process.

Keywords: Epoxy resin, Graphene nanoplatelets, glass transition temperature.

Fundings: FAPERGS Inova Clusters Tecnológicos (Project 22/2551-0000839-9), STINT/CAPES (n. 88881.304743/2018-01) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (n. 408193/2021-2 and 305814/2021-4).

Introduction

Epoxy resins are widely used in coatings, electrical insulation, adhesives, composites, and construction. Therefore, understanding the curing process is crucial to achieve the desired properties in these applications. The curing reaction involves the formation of complex crosslinked networks, which greatly influence the properties of epoxy systems. Factors such as resin and hardener chemistry, stoichiometric ratio, curing conditions, and adding additives and fillers contribute to the nature of these networks [1].

Nanoparticles can impact the viscosity and curing process of resins. This effect is typically attributed to the formation of a percolated network or the presence of oxygenated groups that accelerate the opening of the epoxide ring [1, 2]. For instance, graphene nanoparticles (GNP) and carbon nanotubes (CNT) can enhance the epoxy curing enthalpy. However, the effect on resin viscosity varies depending on their dispersion. For example, mechanical percolation is typically not observed in nanocomposites of GNP with epoxy (0-1 wt.%). On the other hand, systems containing 0-1 wt.% of CNT exhibit percolation at quantities exceeding 0.5 wt.% [3]. Notably, alterations in

viscosity will affect resin curing and consequently impact the final properties of the material, necessitating careful consideration of heat treatments after curing.

Changes in amorphous materials' mechanical and physical properties are inevitable when their molecular mobility undergoes alterations during the glass transition interval. To investigate the change in reaction rate during the vitrification process, the relationship between the glass transition temperature (T_g) and the conversion (α) of the partially cured reaction can be analyzed. This relationship helps determine the occurrence of vitrification during the curing process, where T_g equals the curing temperature (T_{cure}). If T_g is lower than T_{cure} , the reaction of a thermosetting material typically follows chemical kinetics. However, if T_g is higher than T_{cure} , the reaction rate becomes diffusion-controlled due to the rapid reduction in molecular mobility [4].

Considering the influence of graphene nanoparticles (GNP) on the epoxy system's curing process and its significance in designing, analyzing, and optimizing final materials, this study aims to compare the impact of GNP on epoxy resin curing. The study evaluates the performance of these particles in the curing process by measuring the degree of conversion at various glass transition temperatures (T_g).

Experimental

The epoxy resin used in this study is AR260, obtained from e-composites (Brazil), with an average molecular weight of 750 g/mol (measured via GPC using THF and polystyrene standards). The hardener employed is HY951, triethylenetetramine (TETA), purchased from Huntsman. A stoichiometric mixing ratio of 100 parts resin to 13 parts hardeners by weight is utilized, along with adding one part accelerator by weight. The hardener is added to the epoxy resin and mixed for two minutes. All these procedures are carried out at room temperature. The GNP was mixed by mechanical stringing and ultrasonicated (VCX 750 Sonics 20 kHz, 110 W, 60 min.) into the resin and hardener to prevent agglomeration.

DSC Q2000 differential scanning calorimeter was employed for calorimetric measurements. The analysis involved studying pure epoxy samples and epoxy samples containing 1 wt.% GNP. At each temperature, the isothermal analysis was conducted at 60, 80, 100, and 120 °C for various durations (5, 10, 20, 40, and 60 minutes). The sample size used was approximately 10 mg. During the analysis, the system temperature was maintained at the specified isotherm for the respective analysis time and then cooled to -90 °C to determine the glass transition temperature resulting from the curing conditions. Subsequently, the temperature was increased at a rate of 10 °C/min up to 250 °C to measure the residual heat of the reaction. To determine initial glass transition temperature, T_{g0} the samples were cooled to -90 °C and then heated at 10 °C/min. For infinite glass transition temperature, $T_{g\infty}$ determination, the samples underwent a complete curing cycle at 160 °C for one week. Subsequently, DSC measurements were performed at 10 °C/min from room temperature to 250 °C.

Results and Discussion

In the case of pure epoxy, the measured values for T_{g0} and $T_{g\infty}$ were -38.8°C and 103.4°C, respectively. When the epoxy was loaded with 1wt.% GNP, the corresponding values obtained were -37.2°C for T_{g0} and 104.7°C for $T_{g\infty}$. Fig. 1 illustrate the method employed to track the heat flux evolution over time during isothermal experiments, specifically comparing samples with equilibrium at 80°C and an isothermal duration of 5 minutes.

By integrating the heat flux curves and dividing the result by the sample mass, the integrated area in J/g is obtained. Next, the exothermic peaks of the respective sample are combined, and the percentage of reacted material is determined by comparing it with the total area. Finally, the conversion (α) of the reaction is calculated using Eq. 1,

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{total}} \quad (1)$$

where $\Delta H(t)$ represents the enthalpy of the reaction at a specific isothermal time, which is characterized by being fast and exothermic. The term ΔH_{total} refers to the total enthalpy of the reaction.

By determining the conversions of neat epoxy and 1% GNP epoxy reactions, the study examines the vitrification transition during the curing process at temperatures 60, 80, 100, and 120 °C. This transition signifies the irreversible transformation from the epoxy to a glassy gel state, occurring when the system's glass transition temperature (T_g) matches the isothermal curing temperature. Once this transition is reached, the reaction kinetics are altered, impeding further reactions, although a slow diffusion process may persist within the glassy state [5].

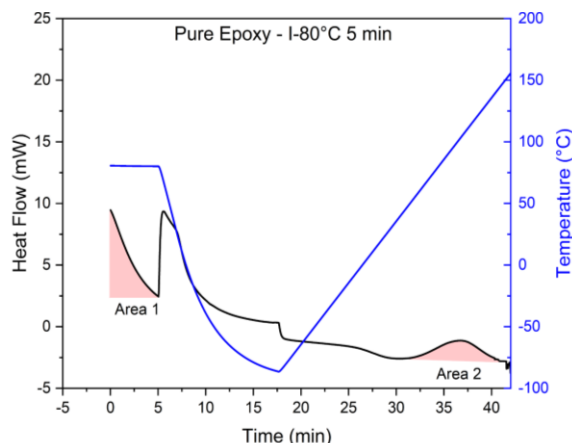


Figure 1 – Isothermal DSC scan of the pure epoxy sample at 80 °C for 5 minutes, followed by a cooling ramp to -90 °C and a heating ramp to 250 °C.

Fig. 2 provides a representative example of conversion curves obtained during a 60-minute timeframe at various isothermal temperatures. The results demonstrate that for both systems, temperatures of 100 and 120°C yield a degree of conversion surpassing 0.8. At temperatures below 100°C, the conversion level reaches approximately 0.6. In both cases, the curves display an initial rapid acceleration followed by a gradual reaction process, suggesting a diffusion-controlled mechanism. This behavior is typically observed when the system is near the glass transition temperature, indicating the influence of molecular mobility on the reaction kinetics [5].

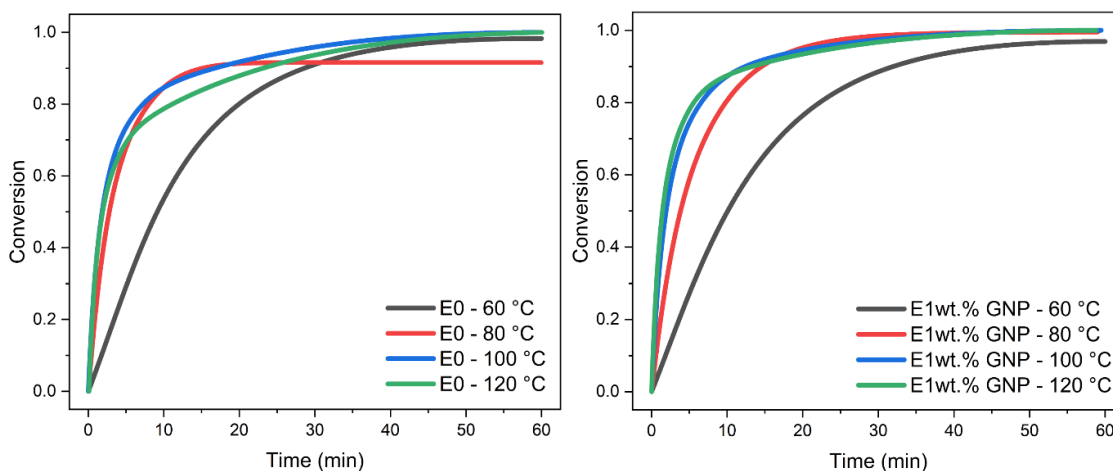


Figure 2 – Reaction conversion of epoxy systems as a function of isothermal cure time at 60, 80, 100 and 120 °C in 60 min., (a) pure epoxy and (b) 1wt.% GNP.

Based on the hypothesis that the molecular structure of a material is interconnected with its chemical conversion and that this molecular structure correlates with the glass transition temperature (T_g), we can deduce a direct association between T_g and the degree of conversion (α). The DiBenedetto equation is commonly employed as the constitutive equation to characterize this relationship within thermoset systems. This equation, expressed as Eq. 2, incorporates a parameter λ , which can be adjusted from 0 to 1 [5].

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (2)$$

The λ parameter of the DiBenedetto equation was adjusted according to Eq. 2, resulting in a value of 0.136 for the pure epoxy system and 0.096 for the epoxy with 1 wt.% GNP, as depicted in Fig. 3. These values align with previous findings in the literature [5]. No significant difference between the analyzed samples can be inferred since both fall within the same 95% prediction interval. This observation is expected because adding GNP does not significantly alter the T_g values. This outcome can be attributed to the absence of mechanical percolation, implying that the resin viscosity remains relatively unaffected, thus avoiding any hindrance in the reaction. Additionally, the presence of oxygenated groups, while increasing the enthalpy, may influence the initial stages of the reaction [1, 2].

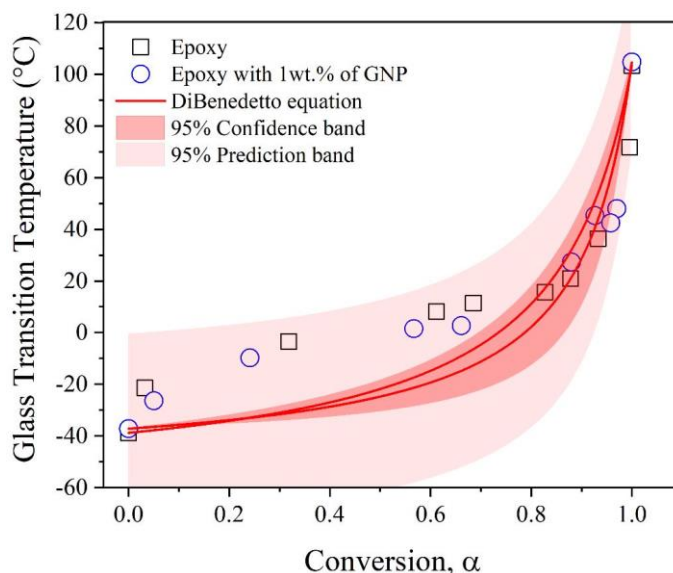


Figure 3 – T_g of epoxy system as a function of the degree of conversion with good correlation from experimental data using Eq. 2, for both systems $R^2 > 0.81$.

Considering the conversion value at the gel point of 0.58, it is evident that T_g points exhibit greater dispersion below this threshold as a function of the degree of conversion [5]. This phenomenon arises from the fact that at low conversion values, T_g is more reliant on the molecular mass of the resin. However, as the degree of conversion increases, T_g rises due to the formation of crosslinks. Consequently, these systems exhibit two distinct stages of T_g increase.

In the first stage ($T_{cure} < T_g$), the rate of T_g increase is rapid. However, as T_g approaches T_{cure} , the rate of growth diminishes significantly. The boundary between these two stages is called the point of vitrification. The rate of the chemical curing process primarily influences the curing reaction before vitrification. As the chemical reaction progresses and crosslink density rises, the discrepancy between the transient T_g value and the curing temperature decreases. The higher crosslink density creates a state that severely hampers the physical movement of molecules. In the second stage, the reaction becomes dominated by diffusion-controlled mechanisms, where the limited mobility of the active groups results in a substantial decrease in the overall rate of crosslinking conversion, often by several

orders of magnitude. This transition towards diffusion-type control is a consequence of the increasing crosslink density, which impedes the overall mobility of molecules and decreases the conversion rate.

Conclusions

The study investigated the impact of 1 wt.% graphene nanoparticles (GNP) on epoxy resin's curing and glass transition. The Dibenedetto equation established a correlation between the degree of conversion and the glass transition temperature of the systems. The findings indicate no substantial changes in the glass transition temperature (T_g) during the curing process.

Acknowledgments

The authors gratefully acknowledge the support received from various funding sources. The Brazilian Agency Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil), Finance Code 001, and project STINT/CAPES (n. 88881.304743/2018-01) are deeply appreciated. The Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil).

References

1. L. S. Cividanes; E. A. N. Simonetti; M. B. Moraes; F. W. Fernandes; G. P. Thim Polym Eng Sci 2014, 54, 2461. <https://doi.org/10.1002/pen.23775>.
2. R. Sheikh; A. Sufyan; K. Antonios; E. Ahmed; G. K. Panagiotis Thermochim Acta 2020, 694, 178785. <https://doi.org/10.1016/j.tca.2020.178785>.
3. J. A. Cruz; L. Paim; R. Joffe; P. Fernberg; S. Amico; O. Bianchi in 6th Brazilian Conference on Composite Materials, Minas Gerais, 2022.
4. M. Urbaniak, Polimery 2017, 62, 5. [dx.doi.org/10.14314/polimery.2017.394](https://doi.org/10.14314/polimery.2017.394).
5. H. Teil; S. A. Page; V. Michaud; J. A. E. Månson J Appl Polym Sci 2004, 93, 1774. <https://doi.org/10.1002/app.20631>.