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# Relaxation phenomena in the glass transition of epoxy/N-phenylaminopropyl – POSS nanocomposites

Vinicius Pistor[a,*], Luiz G. Barbosa[a,c], Bluma G. Soares[b], Raquel S. Mauler[a,*]

[a] Universidade Federal do Rio Grande do Sul – UFRGS/Instituto de Química – IQ/PGCIMAT, Av. Bento Gonçalves, 9500, Porto Alegre – RS 91501-970, Brazil
[b] Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro Ilha do Fundão, Centro de Tecnologia, Bl. J, Rio de Janeiro, Brazil
[c] Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul (IFRS) – Campus Erechim – Rio Grande do Sul, Brazil

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ABSTRACT

The epoxy resin curing process can be characterized by the formation of an inhomogeneous microstructure with cooperative rearranging regions (CRR). In this study, polyhedral oligomeric silsesquioxane (POSS) N-phenylaminopropyl was utilized as a substitute for the curing agent of the epoxy resin. Various parameters were determined via the Williams–Landel–Ferry (WLF) and Vogel–Tammann–Fulcher (VTF) equations to evaluate the relaxation phenomena of the glass transition. The relaxation and retardation spectra were calculated based on the master curves, and the results are discussed with respect to the microstructure observed by transmission electron microscopy and atomic force microscopy. The incorporation of POSS as a curing agent significantly reduced the number of CRR groups, which demonstrates that this system approaches an ideal glass transition. The evidence presented here shows that the addition of POSS improves the inhomogeneity of the three-dimensional network of the epoxy resin.

## 1. Introduction

Thermosetting epoxy resins are widely used because of their good mechanical properties, thermal stability, chemical resistance and ease of processing [1,2]. The curing process of this class of resin can be considered as an inhomogeneous process, and the corresponding surface has a morphology that contains nodular regions characterized by high crosslinking densities [3,4].

Various chemical modifications related to nanotechnology are currently being investigated to improve the properties of epoxy resins. One such modification is the incorporation of polyhedral oligomeric silsesquioxane (POSS) into the resin [5–8]. POSS oligomers are hybrid compounds with a typical size of approximately 1.5 nm that have a core composed of inorganic silicon atoms surrounded by organic groups with the formula $(RSiO_{1.5})_n$ [6]. These organic moieties that bear functional groups can chemically interact with the epoxy matrix and improve the interaction of inorganic particles with the organic matrix. Specifically, the use of POSS that bears amino groups may increase the three-dimensional network percolation and reduce the dynamic fragility of the epoxy.

Dynamic fragility is a characteristic of the glass transition process and is dependant on cooperative relaxation phenomena (which depend on the degrees of molecular freedom [9] of the structural interfaces and other variables). According to Saiter et al. [10], the reorganization of a structural unit is only possible if a number of neighbouring elements are also cooperatively rearranged. This structural reorganization of the neighbouring elements is known as a cooperative rearrangement region (CRR). Adam and Gibbs [11] have defined a CRR as a subsystem that can rearrange by thermal fluctuation into another configuration independent of its environment. In 1948, Kauzman [12] found that supercooled liquid shows an excess of entropy, which deviates from Arrhenius behaviour. This phenomenon is known as an entropic crisis and occurs because the supercooled liquid possesses fluctuations in the potential energy of the hypersurface. The presence of the CRR is associated with the potential energy hypersurface. Therefore, an ideal glass transition is difficult to observe with a minimum of residual entropy. The theoretical temperature for an ideal glass transition was described as Kauzman temperature ($T_k$) [13]. The main factor contributing to the fragility of the epoxy resin is related to the interface between the CRR (characterized by a discontinuity of the three-dimensional network) that is caused by fluctuations in the hypersurface of the potential energy, as mentioned above. Thus, the objective of this work was to investigate the effect of octafunctional (*n*-phenylaminopropyl) POSS on the crosslink density of the epoxy network. For this purpose, the conventional curing agent, triethylene-tetramine (TETA), was progressively substituted with the functionalized POSS.

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[*] Corresponding author.
*E-mail addresses:* pistorv@yahoo.com.br (V. Pistor), raquel.mauler@ufrgs.br (R.S. Mauler).

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## 2. Materials

The following materials were utilized in this study (Fig. 1): the epoxy resin diglycidyl ether of bisphenol-A (DGEBA) (Araldite Gy–251) and the curing agent triethylenetetramine (TETA) (Ren Hy–956) supplied by Hustman Advanced Materials. Polyhedral oligomeric silsesquioxane N-phenylaminopropyl–POSS (AM0281) ($(C_9H_{12}O)_n(SiO_{1.5})_n$; ($n$ = 8, 10 and 12)) was obtained from Hybrid Plastics™.

## 3. Methods

### 3.1. Manufacturing of the nanocomposites

The epoxy resin (DGEBA) was prepared based on the equivalents of reactive groups (g/eq) using triethylenetetramine (TETA) as a curing agent. A molar ratio of 1/1 (g/eq) between the epoxy and amine groups was maintained. To obtain the nanocomposites, a pre-mix between the N-phenylaminopropyl–POSS and the curing agent TETA was performed at 50 °C and 400 rpm for 20 min to ensure the homogeneity of the system. Subsequently, 1, 5 and 10 wt.% of POSS was added to the resin. The incorporation of TETA/POSS in DGEBA was realized by maintaining the ratio of the epoxy and amine groups at 1/1 (g/eq). The curing of the resin was performed at a temperature of 25 ± 3 °C for 24 h. After curing, the samples were post-cured in an oven under vacuum (300 mm Hg) for 24 h at 100 °C.

### 3.2. Gel content (Gc)

The determination of gel content (Gc(%)) was performed using approximately 2 g of sample in a wire cage (120 mesh) suspended in a flask containing 250 mL of ketone at 80 °C. Extraction occurred for 6 h as described in ASTM D 2765-01. After extraction, the samples were dried in a vacuum oven at 100 °C for 24 h. The gel content of the samples was calculated as described in Eq. (1):

$$\mathrm{Gc}(\%) = {}^{m_i}/_{m_s} \times 100 \tag{1}$$

where $m_i$ is the insoluble and $m_s$ is the soluble mass of the sample contained in the cage.

### 3.3. Preparation of samples for TEM and AFM analyses

An RMC Power Tome XL ultramicrotome equipped with a diamond knife was used to cut samples at a thickness of 50 nm with a speed of 0.3 mm/s at room temperature. The sections were collected on copper grids (300 mesh) and analysed by transmission electron microscopy (TEM). The base of the sections was analysed by atomic force microscopy (AFM) in an SPM 5500 AFM equipment from Agilent Technologies in acoustic mode. A conventional silicon tip with resonance frequencies of approximately 300 kHz that can oscillate between 200 kHz and 400 kHz, corresponding to a spring constant of the tip ranging from 20 N/m and 75 N/m, was utilized. The radius at the height of the tip was less than 10 nm. The images were obtained at scanning frequencies of 0.5 Hz, and the relationship between the amplitude of the free set point and the imaging was adjusted to 90% to minimise the effects of the phase contrast on the topographic image. Three scans were performed on every sample with areas of 1 $\mu m^2$–25 $\mu m^2$.

### 3.4. Dynamic-mechanical thermal analysis (DMTA)

The viscoelastic properties were characterized with a Q800 AT DMA instrument in a single-cantilever clamp using rectangular specimens of 35 × 10 × 2 mm. The sweep experiments were carried out at glass transition temperatures in the range of 40–120 °C. The frequency was varied from 100 to 0.1 Hz with 10 points per decade at intervals of 3 °C after temperature equilibration. The isothermal curves were utilized for the application of the Williams–Landel–Ferry (WLF) equation [14]. The parameters calculated in this study are directly related to the WLF and Vogel–Fulcher–Tumman (VTF) equivalence, as previously described [15,16]. The relaxation ($H(\tau)$) and retardation ($L(\tau)$) spectra were determined using nonlinear regularization (NLREG) software [17–21].

### 3.5. Equivalence between Williams–Landel–Ferry (WLF) and Vogel–Tammann–Fulcher (VTF) and polymer fragility

The equivalence of the Williams–Landel–Ferry (WLF) (Eq. (2)) and Vogel–Tammann–Fulcher (VTF) (Eq. (3)) equations was first pointed out by Kovacs [15]. These well-known identities are described by Eqs. (4) and (5) [16]:

$$\log a_T = \log\left[{}^{\tau(T)}/_{\tau\left(T^*\right)}\right] = C_1\left(T - T^*\right)/\left[T - \left(T^* - C_2\right)\right] \tag{2}$$

$$\tau = \tau_0 \exp\left({}^{B}/_{(T - T_0)}\right) \tag{3}$$

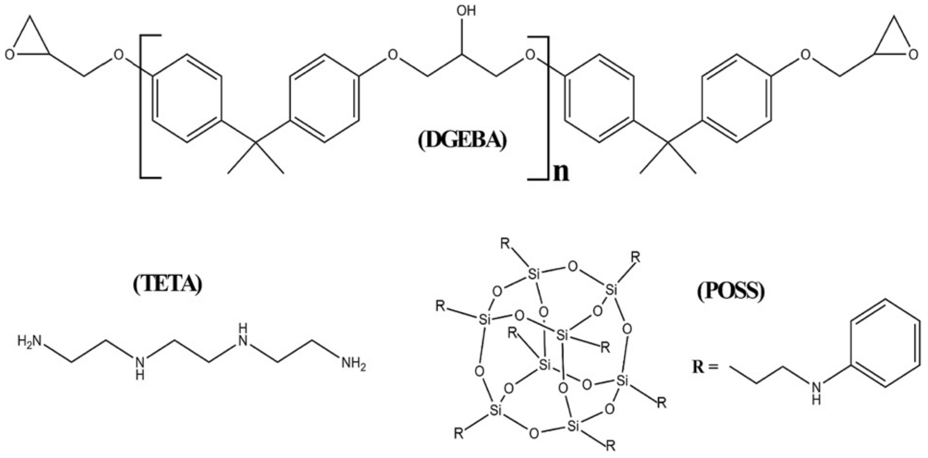

**Fig. 1.** Schematic drawing of chemical structures used in the development of nanocomposites studied in this work.