Materials Science and Engineering A 532 (2012) 339–345

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Dynamic mechanical characterization of epoxy/epoxycyclohexyl–POSS nanocomposites

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ARTICLE INFO

Article history:
Received 14 June 2011
Received in revised form
22 September 2011
Accepted 24 October 2011
Available online 3 November 2011

Keywords:
Nanocomposites
POSS
Angell fragility
Viscoelasticity

ABSTRACT

In this study, an epoxy matrix containing 1, 2 and 5% of a polyhedral oligomeric silsesquioxane (POSS) was analyzed by dynamic mechanical analysis (DMA) in isothermal and non-isothermal runs in order to evaluate the interactions between the epoxy/POSS systems obtained. Non-isothermal DMA curves showed that, upon POSS addiction, the storage modulus in the rubbery region (E_r) and the loss modulus decrease due changes caused in the average crosslink densities in the epoxy/POSS systems. The glass transition temperature (T_g) keep the same trend for all nanocomposites studied and there was higher activation energy (E_a) values with the incorporation of the nanofiller due an enhancement in the cohesive energy density. Through isothermal DMA curves studied, it is noted an increase in the Kauzmann temperature and the fragility concept proposed by Angell upon POSS addiction, suggesting a formation of a kinetically weaker system.

1. Introduction

Organic–inorganic nanocomposite materials have attracted a great deal of attention, due to their potential as candidate materials for replace conventional nanocomposites [1]. The incorporation of the polyhedral oligomeric silsesquioxanes [POSS, or $(R\,SiO_{1.5})_n$, core cage structures where $n = 6, 8, 10, \ldots$ with sizes from 1 to 3-nm in diameter] [1,2] in both linear or crosslinked polymers [3] has some advantages. Some of them are the improvement in the physical properties [4], thermal and oxidation resistance and flammability reduction [1]. Also, organic substituents attached to each cage Si atom can improve compatibility with the polymer matrix. Nevertheless, aggregation and phase separation of POSS into tiny domains commonly occurs [2].

Many studies were developed in relation to POSS application in thermorigid matrices (for example, epoxy resin) aiming evaluates its overall properties [5–12].

The strong/fragile Angell fragility concept has had and continues to have a profound and useful influence on the study of the relaxation behavior of materials that exhibits Arrhenius or VFT temperature dependence. Strong liquids tend to form strong, directed intermolecular bonds, exhibiting Arrhenius behavior over the entire accessible temperature range, whereas fragile liquids tend to form rather weak, undirected intermolecular bonds, exhibiting super-Arrhenius behavior over the lower part of the accessible temperature range and Arrhenius behavior with rather low activation energy in the upper part of the accessible temperature range [13]. This information gives an approach of the kinetic fragility of determinated material with POSS incorporation. This is an important feature, since in the glass transition temperature; there are both relaxation and thermodynamic manifestations [13]. In the former, it is manifested by different levels of departure from Arrhenius kinetics. In the latter, it is manifested by the difference rates (with respect to temperature) at which the excess entropy of the liquid relative to crystal diminishes upon supercooling. It can be estimated the degrees of freedom that are lost/gained at the glass transition temperature [14].

The Angell fragility concept was initially applied in pure liquids and many plastic crystals [14] however it can be extended to reinforced polymers aiming to evaluate the influence of the reinforcement content in the mobility of the matrix.

The aim of this study was to examine the dynamic mechanical properties of this class of POSS–epoxy networks in both isothermal and non-isothermal conditions by dynamic mechanical analysis.

2. Materials

The materials used in this study were: epoxy resin of diglycidyl of bisphenol-A (DGEBA); Araldite Gy – 251, aliphatic amine

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doi:10.1016/j.msea.2011.10.100

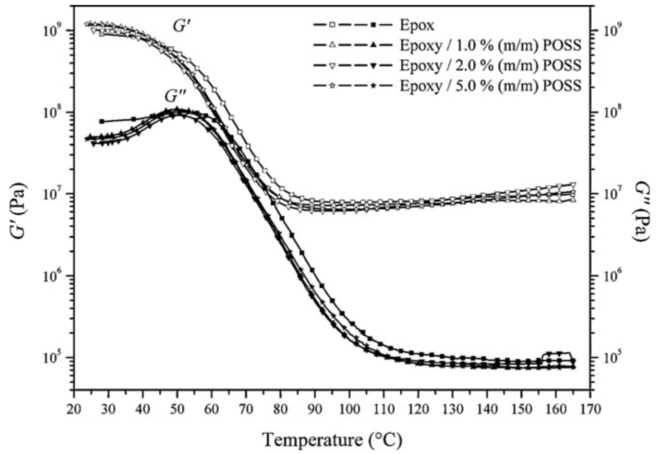

Fig. 1. Storage and loss modulus as a function of temperature for the neat epoxy and the nanocomposites studied.

(triethylenetetramine – TETA); Ren Hy – 956 supplied by Hustman Advanced Materials. It was used the polyhedral oligolsilsesquioxane epoxycyclohexyl–POSS (EP0408) ($(C_8H_{13}O)_n$ $(SiO_{1.5})_n$; $n = 8$, 10, and 12 ($n = 8$)) from Hybrid Plastics^{TM}.

3. Methods

3.1. Sample preparation

It was realized a pre-mixture of the epoxy resin and POSS reinforcement at a pre-set temperature of 50 °C in the following ratios: 1, 2 and 5% (m/m) of epoxycyclohexyl–POSS. The samples were prepared in the proportion 5:1 epoxy/TETA (Eq/Eq) and the nanocomposites were manufactured by manual mixture. After this process, the samples were deposited in a silicon mold (50 mm × 10 mm × 3 mm) and after that, the cure was realized at 30 °C by 24 h. Consequently, the samples were post-cured in a vacuum oven (−300 mm Hg) at 100 °C by 24 h.

3.2. Dynamic mechanical analysis (DMA)

The viscoelastic properties were characterized using an Anton Paar Physica MCR 101 DMTA equipment and rectangular specimens 50 mm × 10 mm × 3 mm. Tests were performed at the frequencies of 1, 3, 10 and 30 Hz aiming to obtain activation energy values (E_a) in the glass transition temperature (T_g) [15]. For non-isothermal runs, the specimens were heated from room temperature (≈23 °C) to 160 °C at a heating rate of 3 °C min^{-1} and the experiment was carried out in torsion mode at strain amplitude of 0.08%. The sweep experiments were carried out in the glass transition temperature (determined by non-isothermal runs) for each sample at 2 °C intervals after temperature equilibration. At each temperature the frequency was changed from 40 to 0.1 Hz.

4. Results and discussions

4.1. Dynamic mechanical analysis (DMA)

4.1.1. Non-isothermal analyses

Fig. 1 shows the storage and loss moduli as a function of temperature for the pure epoxy and the nanocomposites containing 1, 2 and 5% (m/m) of POSS content. For the storage modulus, in the glassy region, no trend can be noted in relation to the different samples, but the lowest value was obtained for the pure epoxy. This is to be expected, since there is no reinforcement in the system and thus no interface for stress transfer. Also, the thermal expansion coefficient of the polymeric matrix is induced to change by POSS incorporation, occasionating different residual stress field. There is no trend in relation to the POSS content in this region.

It is known that for epoxy resins, modulus increases with increasing the crosslinking densities (this effect is mainly observed in the elastomeric modulus) [16]. The inclusion of the POSS reinforcement promotes a decreasing in the crosslinking density of the polymeric matrix by interconnecting between the epoxy chains. By occupying a large volume, the mobility of the resin is assisted. So, the storage modulus maintains practically the same values in comparison to the neat epoxy in the elastomeric region. In the glassy region, the modulus is dependent of the intermolecular forces, the packing of the chains and the interaction between chains rather than on the crosslinking density.

As the temperature increases, the samples pass through a glass transition region reaching the elastomeric region, where more segments in the chain are moving in a cooperative way [17]. Above T_g, network chains have sufficient thermal energy to overtake the potential barriers linked to Van der Waals interactions. They undergo fast conformational changes by cooperative segmental motions, but crosslinking prevents any liquid flow [16,18]. Also, in this region there is a decrease in the storage modulus as the POSS content is incorporated. In theory, incorporation of reinforcement should promote higher modulus values, however, this is not observed. According to Ni et al. [19,20], this is due to changes in the average crosslink density of the epoxy/POSS systems due to the higher molecular weights of the POSS reinforcement. However, a higher molecular weight does not necessarily represent a higher storage modulus, mainly in the elastomeric region. This can be explained by higher chain lengths promoted by the POSS incorporation. Thus, higher flexibility can be obtained in the system even when a rigid component is incorporated.

The network chains and crosslinks can be studied on a macromolecular structural scale (10–100 nm) by the rubber elasticity of macromolecular science. In this domain, a relatively high stiffness can be combined with a high ductility/toughness/impact resistance.

There are three distinct types of networks. The first relates to homogeneous ideal networks, resulting from a single-step polymerization mechanism of a stoichiometric mixture of monomers, reacted to full conversion. The second is the homogeneous nonideal networks, obtained through the same chemical route as the previous type. This system is the result of incomplete curing, nonstoichiometric composition, or the presence of monofunctional monomers. The third type is the inhomogeneous open network, characterized by spatial fluctuations of the crosslink density (nodular/globular morphologies, microgels, etc.) [16].

Within this perspective, using the rubber elasticity model [1,21,22] it is possible to calculate the average crosslink density of the epoxy system when different POSS contents are incorporated into the system. As can be noted in Fig. 1, the storage modulus in the rubbery region increases linearly with temperature according to the theory of ideal rubbers as seen in Eq. (1):

$$E_r = 3\phi \upsilon_e RT \tag{1}$$

where ϕ is the front factor, that takes into account every factor that distinguishes thermosets from ideal rubbers (e.g., the short length of the elastic chains); υ_e is the concentration of elastic chains (mol/cm^3); R is the gas constant; and T is the absolute temperature [1].

The value of ϕ may be obtained from the behavior of the model networks, but the value of $\phi = 1$ may, therefore, be used for a good order-of-magnitude prediction.

Through the rubbery elastic modulus, the concentration of elastic chains could be determined. The density values at 160 °C were estimated from the typical values of the volumetric expansion