



Curing kinetics of epoxy/alkyl phosphonium modified nanoclay composites for high performance applications



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ABSTRACT

Alkyl phosphonium salts are novel and unexplored modifiers for polymer based composites which can improve the clays compatibility and dispersion in the polymer matrix. These salts can enhance the thermal stability of the modified clays, which is an indispensable requirement for thermosetting composites curing and processing occurring at high temperatures. In this work, a raw bentonite was ion exchanged with tributyl(hexadecyl) phosphonium bromide and then a novel epoxy/nanoclay composite was synthesized. The curing kinetics of the nanocomposites was studied. An extensively kinetic study was performed by FT-IR analysis and models accounting for many potential reactions and diffusion restrictions were proposed. A relationship between the H-bonding interactions and the kinetics was found. Also, the effect of the modifier of bentonite was found to affect the reaction yield.

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1. Introduction

Epoxy-based thermosetting polymers are used in a variety of industrial applications, such as in adhesives, coatings, electronics and high performance composite materials, due to their excellent thermal, mechanical and chemical properties [1–3]. Epoxy resins reinforced with nanometer sized layered silicates have received great attention due to the possibility of improving several properties, like stiffness, strength, fire resistance, dimensional stability, shrinkage, among others, even at low filler loadings [4,5]. Untreated nanoclays, like bentonite, are not easily dispersed in most polymers because of their natural hydrophilicity, and thus they are incompatible with organic polymers [6]. For this reason, clays can be chemically modified through ion exchange reactions with organic cations to enhance the interfacial interactions and promote the intercalation of polymers into the interlayer galleries, therefore, facilitating the formation of an exfoliated structure [7].

Many authors have reported the improvement of various properties of epoxy/clay nanocomposites by incorporating alkyl ammonium modified organoclays [8,9]. It has also been studied that loading of the alkyl ammonium exchanged montmorillonite in the epoxy matrix facilitates the curing reaction of epoxy based nanocomposites [10–12]. However, the incorporation of

ammonium modified clays into thermoset matrices is limited because of their poor thermal stability. The same problem has been found for melt compounding and injection molding of thermoplastic polymer nanocomposites at high processing temperatures exceeding 200 °C [13,14]. In contrast, alkyl phosphonium salts enhance the thermal stability of the organoclays [15,16], which is necessary for the curing and processing of the composite materials with high performance applications, for example in windmill blades, petroleum pipelines and automotive pieces. There are few reports on the systematic study of epoxy resins loaded with alkyl phosphonium exchanged organoclays to improve the thermal and mechanical properties [17,18]. Nevertheless, there are no reports regarding the effect of alkyl phosphonium modified clays on the curing reaction or kinetic of epoxy resins.

The first challenge to overcome when preparing an epoxy/nanoclay composite is to disperse (intercalate or exfoliate) the nanoclays. XDR is a suitable and commonly used technique to verify the clay dispersion. The second challenge is to keep the matrix chemical and structural properties, such as curing and crosslinking degrees, to a level which does not negatively affect the mechanical properties, chemical stability and other features intended to get improved with the modification.

Normally, the structure and properties of epoxy/clay nanocomposites depend on the formation of the crosslinked molecular network, which is frequently influenced by the curing mechanism and kinetics of curing of the epoxy resin that involves several chemical reactions [19]. The knowledge of the cure process in the

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epoxy system is crucial to get a better control of the cure reactions and, as result, to optimize the properties of the final product [20]. One of the most widely used techniques for studying the kinetics of the cure reaction of epoxy systems is the thermal analysis by differential scanning calorimetry (DSC), in isothermal or dynamic modes [21]. Modulated differential scanning calorimetry (MDSC) is a newer technique which allows getting more information about a thermal process. In conventional DSC, an isothermal or linear time/temperature program is used. After subtraction of the empty pan curve, correction for heat transport effects and calibration, one gets the curve of the heat flow rate $Q(t)$ into the sample versus temperature. In modulated-temperature DSC, the common temperature program is superimposed with a dynamic temperature change (sinusoidal in most cases). The measured signal is influenced by heat transfer conditions which change both the amplitude and the phase shift. After subtraction of the empty pan measurement under the same conditions and calibration, the heat flow rate into the sample $Q(t)$ can be calculated from the measured signal. The measured heat flow rate is usually separated into the underlying heat flow rate Q_{li} (this is approximately the conventional DSC curve) and the dynamic component Q_{d} . One method employed for the determination of these curves, which is commercially used by MDSC (TA-Instruments), is the procedure published by Reading and co-workers [22–25]. In this method, the reversing component of the heat flow rate, Q_{rev} , is calculated from the dynamic component; whereas, the so-called non-reversing component $Q_{non-rev}$ is the difference between Q_{li} and Q_{rev} [26]. In order to measure the heat of reaction, free from the sensible heat, the non-reversing heat flow is used [27].

Another powerful technique widely used to follow kinetic processes, is the Fourier transform infrared spectroscopy (FTIR). In particular, near infrared spectroscopy (NIR) provides a quantitative technique where glass sample holders can be used, with the advantage of a practical experimental setup to monitor a rather thick reactive sample. Besides, OH signals can be well detected, quantified, and a reasonable differentiation of their chemical associations can be attained [28–29]. Conversion – time curves from FTIR experiments can be used to compare the evolution of reaction with time, and thus to confirm the observations made by MDSC.

A better understanding of the experimental MDSC and FTIR data could be achieved by proposing a kinetic mechanistic model which describes all the reactions taking place in the system. Although the epoxy – amine system has been widely studied, the physical processes which take place during the polymerization complicate the interpretation of the experimental data. Vitrification is a phenomenon which slows the reaction rate due to a loss in the reactive groups' mobility. In an isothermal cure process, vitrification will be always observed if the curing temperature (T_c) is selected in the range between the unreacted systems glass transition temperature (T_{g0}) and the glass transition temperature of the fully cured network ($T_{g\infty}$). This isothermal trajectory leads to a lower final conversion than the unity ($x < 1$), limited by vitrification. A post curing step at $T > T_{g\infty}$ is needed to attain the complete conversion ($x = 1$). An isothermal curing trajectory at $T_c > T_{g\infty}$ leads to complete conversion, but due to high values of reaction heat and polymerization rate, it is usually not possible to keep isothermal conditions. The sample temperature continuously increases as it is impossible to dissipate the reaction heat at the rate at which it is generated [30]. Kinetic mechanistic models have been proposed for curing temperatures above $T_{g\infty}$. These approaches consider that the general reactions which can take place during epoxy – amine polymerization are: epoxy – primary amine, epoxy – secondary amine, etherification and homopolymerization. Etherification only occurs at high temperatures [30,31] and homopolymerization requires the presence of a Lewis base or

acid [32]. Epoxy – amine reactions can proceed catalyzed by OH groups. OH may be initially present in the reactive mixture and they are always formed by the reaction between epoxy and amino groups. Epoxy monomers contain OH in their chains, which can catalyze the polymerization from the beginning of the process, and in the systems here studied, where nanoclays are incorporated to the reactive system, OH are present in the clays platelets. These OH, also initially present in the reactive mixture, may or may not play a role in the curing kinetics. Besides, and despite drying the reactants and clays, traces of water retained in the hydrophilic bentonite may also contribute OH catalytic groups [33,34]. Also the formation of an epoxy – hydroxyl complex was proposed in the literature, which can be in equilibrium [34] or out of equilibrium [35].

In the case of the isothermal curing trajectories below $T_{g\infty}$, not only a chemical limiting factor restricts the conversion, but also a diffusional limiting term must be considered. Accordingly, the overall kinetic rate constant k is expressed in terms of a reaction-limited term (k_{chem}) and a diffusion-limited one (k_{diff}) [36,37]:

$$\frac{1}{k} = \frac{1}{k_{chem}} + \frac{1}{k_{diff}} \quad (1)$$

Chern and Poehlein [38] proposed a very simple equation coming from the free volume theory to estimate the ratio of the diffusion-controlled to reaction limited rate constant:

$$\frac{k_{diff}}{k_{chem}} = \exp[-C(x - x_c)] \quad (2)$$

where C is a constant which depends on the structure, system and curing temperature and x_c is a critical conversion. For values of conversion significantly lower than x_c , diffusion control is negligible. This allows determining the chemical kinetic constant for conversions lower than x_c and then employing this value when fitting the whole conversion curve, adjusting only the diffusional parameters [39].

The critical conversion responds to the conversion from which vitrification becomes efficient. The value of x_c has been reported to be similar to the gel conversion at low temperatures, and higher as temperature increases, approaching $T_{g\infty}$ [39].

There are no many reports which consider models for both regimes, below and above $T_{g\infty}$. In general, researchers select one of the two regimes to make the kinetic analysis [39–42].

In this work, epoxy/organo-modified nanoclay composites were prepared. Pristine and tributyl(hexadecyl) phosphonium exchanged bentonites were used to obtain the composites. The influence of both, bentonite and organo-bentonite, in the epoxy – amine reactions, was studied by means of MDSC and FTIR. A kinetic model was proposed and used together with FTIR data with the aim of understanding the changes occurred in the reaction parameters.

2. Experimental

2.1. Materials

A commercial diglycidyl ether of bisphenol A resin, DGEBA (DER 383, Dow chemicals) having epoxy equivalent about 176–183 g eq⁻¹ and a viscosity of 9000–10,500 mPa.s at 25 °C, and triethylenetetramine (TETA, Novarchem S.A.), the hardener, were employed. The clay in the study was a bentonite supplied by Minarmco S.A. (Argentina). The cation exchange capacity (CEC) of bentonite was found to be 0.939 meq g⁻¹, measured by the methylene blue method [43]. The organic modifier used to exchange the pristine bentonite was tributyl(hexadecyl) phosphonium bromide provided by Sigma Aldrich, EEUU.

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