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Interfacial characterization of epoxy/silica nanocomposites measured by fluorescence

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ABSTRACT

Fluorescence labeling was used as a tool for the interfacial characterization of nanocomposites. The solvatochromic probe dansyl chloride was employed as interfacial reporter in epoxy/silica nanocomposites. Molecular spacers (organosiloxanes and polyetheramines) of different lengths were used to vary the location of the chromophore at the interface. The steady state and time resolved fluorescent responses reflect a rigid polar interface. Fluorescence changes during heating at a constant rate were analyzed for determining the local glass transition (T_g) at the interface region. The fluorescence results were then compared to the T_g obtained from differential scanning calorimetry and the results showed the existence of a gradient interface of a few nanometers thick having different properties than the bulk matrix. The thickness of this interface is small but its altered dynamics due to strong interactions with the nanofiller spreads its influence throughout the whole matrix.

1. Introduction

The properties of polymer nanocomposites are associated with the dispersion and distribution state of the nanoparticles, and their interaction with the matrix. Their nanoscale size provide them with some of their most valued properties: low percolation threshold and high interfacial volume, which provides matrix-nanofiller interactions with different properties than the bulk polymer [1–4]. As a consequence, the overall properties of the combined system are altered compared to those of the traditional composite materials. One of the aspects that is still controversial is the comprehension of the interfacial architecture because of the complex sum of factors that determine its properties: physico-chemical interactions, topological effects and mechanical stresses among others. Specifically, the effects of the strength and the extent of the region of influence of the nanofillers on the polymer matrix are still not clear. There are even conflicting views on the definition of the extent of the interface. It is widely accepted that the properties of the interfacial region spread across the whole matrix affecting to a greater or lesser degree the structural relaxation dynamics of the polymer chains. The effect on the glass transition temperature (T_g) is particularly of great importance, because it gives an idea on how polymer dynamics varies, and in addition, it is a key property for many applications. It is generally assumed that the T_g tends to increase when favorable interactions exist between the nanofiller and the matrix. On the contrary, the presence of unfavorable interactions depresses the T_g. The extent of T_g variation is also closely linked to the dispersion state the nanofiller [5,6] because it defines the distribution and connectivity of the interfacial volume within the whole matrix and, as a consequence, the restriction level of chains mobility.

This behavior has been often analyzed in the literature on nanoconfinement effects on ultra-thin films. A T_g

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depression is usually observed in free-standing ultra-thin films as the thickness of the film decreases [7]. This depression depends on the polymer-substrate interaction in supported thin films [8] and has led some authors to elaborate analogies between nanoconfinement and T_g behavior in nanocomposites [9,10]. This apparent similarity has been used to justify some results in nanocomposites [11] even persisting some reluctance about this analogy [12,13]. In any case, it is generally postulated the existence of a polymeric layer around the nanoparticles whose properties are different from those of the bulk to explain the global behavior of the T_g [13–17]. Filler-matrix or substrate-film attractive interactions reduce the local mobility of the polymeric chains [8,13,16,17], whilst unfavorable interaction enhance the mobility [11]. For nanocomposites, the thickness of this layer is generally estimated between 1 and 10 nm depending on the studied system and on the employed experimental technique [18–22]. An important question that still remains open is to know in which way this polymer layer is able to impact the macroscopic properties of the nanocomposites. There are recent publications about this subject on thermoplastics filled with silica nanoparticles [13,22–25] but there is a lack of literature focused on thermosetting nanocomposites despite the important number of applications of these materials. Thermosetting nanocomposites are in fact complex systems due to the importance of the crosslinking density as it has been underlined by Brinson and coworkers [26]. In these materials the different T_g behavior observed with the nanofiller content or the nanofiller-matrix interaction is often explained by the creation of heterogeneities in the network [27–29]. Anyways it is usual to observe an increase of the T_g values in case of favorable interactions [30,31] and these obviously depend on the curing agent [32] and on the nanofiller concentration [28,33].

Therefore, for a given system and its associated network structure, an important feature of nanocomposites is to know how the specific dynamics of the interface is propagated through the whole matrix. The object of this work is to improve the knowledge about how and to which extent the interfacial structure affects the whole thermosetting matrix. With this purpose, a fluorescent reporter will be placed on one end of several molecular spacers of varying size tethering both the probe and the nanofiller. The fluorescence of molecular probes is in fact an appreciated technique to study polymer materials [34]. It can provide information on a scale smaller than conventional light scattering and comparable to SANS [35]. For sensing molecular dynamics in condensed phases, a fluorescent dye should change its fluorescence signal on changes in the rotational diffusion of its surrounding media. It is well known the sensibility of some flurophores to rigidity, polarity or free volume variations of their close environment. Spectral shifts are caused by a combination of fluorophore-solvent interactions and charge transfer separation in the excited state but there is no single theory which account for all these effects [36,37]. Specifically, the so-called solvatochromic probes have large variations in their emission spectrum depending on the degree of stabilization of the excited state by the environment of the chromophore [38]. Since the pioneering work of Loutfy [39] which related the variation of free volume of a PMMA matrix with the emission of a molecular rotor, fluorescence spectroscopy has been widely used to study thermal transitions in polymers. Torkelson and cowokers have extensively employed this technique to study confinement and relaxation processes in polymer films and nanocomposites [10,40–43]. Other authors have analyzed also thermal transitions in a high variety of polymer matrices [44–47].

The fluorescent marker selected for this work is 5-(dimethylamino)naphthalene-1-sulfonyl chloride (Dansyl chloride, DNS), a well-known solvatochromic probe with charge transfer (CT) character. Intramolecular charge transfer in dansyl comes from the mixing of the $\pi-\pi^*$ transition of the aromatic ring and the lone electron pair of the amine N $(1-\pi^*)$ which acts as a donor [48]. This coupling is more efficient for the $1L_a$ (polar) state, and is the origin of a CT state. The $1L_b$ (non-polar) state has less charge transfer capacity and remains in practice as a $\pi-\pi^*$ transition and it is usually called the locally excited (LE) state. Due to this charge transfer, excitation enhances very much more the dipole moment of the $1L_a$ state. Thus, in polar solvents, the emission comes from a CT state and is usually reflected by a red shift. On the contrary, in hydrophobic or non-polar solvents, the emission is mainly from the LE state. If the energy of both states is similar, the emission would come from both. In fact, DNS has been extensively used for solvent polarity studies, gelation and swelling or solvation dynamics in micellar environments [49–53]. Dansyl has been also employed to monitor microheterogeneity in surfaces [54] and polymer networks [55], curing behavior of thermosets [56,57], and thermal transitions and conformational changes in polymers, hybrid materials and composites [58,59]. In previous works, we used this fluorophore to study phase separation and morphology in blends [60] and the interface in PMMA nanocomposites [47].

In this work we have selected a low curing temperature system (DGEBA/m-xylylenediamine) as a model thermosetting system. As nanofiller we have selected silica nanoparticles that will be surface treated with functionalized silanes (short tethers) and with two Jeffamines (long tethers) of different size. DNS will be placed at the end of the tethers to probe different zones of the interfacial region. In addition, labeling of the hardener will allow characterizing the chromophore response when it is located in the bulk resin in presence of untreated silica nanoparticles. Along with the steady-state fluorescence, fluorescence decays will also be analyzed due to their higher sensitivity to the presence of transient states and relaxation phenomena. Finally, interfacial information will be confronted with macroscopic T_g determined by calorimetry.

2. Experimental section

2.1. Materials

Colloidal suspensions of silica nanoparticles (DMAC-ST, 20% by weight in N,N-dimethylacetamide) were supplied by Nissan Chemical Industries, Ltd. Size distribution of