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A new extra situ sol–gel route to silica/epoxy (DGEBA) nanocomposite. A DTA study of imidazole cure kinetic

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Abstract Silica nanoparticles were obtained through the Stöber method, from mixtures of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTS). The nanoparticles were dispersed in tetrahydrofuran (THF) and coupled to bisphenol A epoxy resin (DGEBA) through surface amino groups. After removing THF non-isothermal cure was performed at different heating rates (2–20°C/min), using imidazole (2–4 wt%) as curing agent. For the sake of comparison bare DGEBA epoxy polymers were also prepared with similar schedule A nanocomposite of well-dispersed silica nanoparticles (5 wt%) in a fully cured epoxy matrix was easily obtained. Lower cure kinetics were observed with silica addition. This was attributed to reduction of the imidazole volume concentration. Cure activation energy was not influenced by silica presence, whereas it changed with the imidazole content. Therefore, experimental results suggested that silica had only an indirect effect (the reduction of the imidazole molar concentration) on the epoxy matrix cure kinetics. Glass transformation temperatures, T_g, as high as 175°C were recorded. The nanocomposite glass transformation temperature depended on the heating rate of the cure process, the imidazole and silica content. T_g changes as high as 40°C were detected as a function of the heating rate. At higher imidazole content no differences in T_g values between bare polymer and the nanocomposite were observed. This suggests that a higher imidazole content assures a better interconnection between the compatibilizing epoxy shell around the nanoparticles and the epoxy matrix. The new proposed methodology is an easy route to engineer both nanocomposites structure and interfacial interactions, thus tailoring their properties.

Keywords Silica-epoxy nanocomposites · Non-isothermal cure kinetic · Nanocomposite structure

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Introduction

Epoxies are well-known low cost materials widely used in adhesives, coatings, electronic encapsulants, medical devices, optical components, and structural composites [1]. Recently organic–inorganic nanocomposite materials received great attention [2]. The intimate mixing of organic and inorganic components leads to a new class of materials combining desirable properties of both of them. In these nanocomposite materials, the inorganic component is, usually, dispersed at a nanoscale level in the organic matrix. The volume fraction of the interaction region increases with the organic–inorganic interface area getting pretty high values as the filler size enters the nano-region. This can lead to huge properties changes that depend on the dispersion state, shape, surface properties, particle size, and particle size distribution.

The sol–gel method offers a valuable route to produce both hybrid and nanocomposite materials [2]. In fact, it actually is a low temperature process to produce ceramic materials with high purity [3]. An outstanding sol–gel route is the Stöber method that is employed to obtain monodisperse silica particles ranging from several micrometers down to a few nanometers in size [4]. It is known that particles size changes with pH, TEOS and water concentrations. Correlations between nanoparticles size and these synthesis parameters have been widely ascertained in the literature [4–8]. Moreover, the obtained silica nanoparticles can be easily functionalized with specific organic groups. Functionalization can be carried out either through reactivity of silanol groups on the surface of silica nanoparticles or using alcoxide precursors bearing organic non-hydrolysable groups [3]. When preparing nanocomposite materials, functionalization is of paramount importance for tuning the interfacial interactions, thus obtaining a good dispersion of the dispersed phase into the matrix. In fact a suitable compatibilizing agent must be employed to obtain a strictly interconnected network thus preventing macroscopic phase separation [2, 9].

Over the past decades, there have been intensive studies to produce polymer nanocomposites showing improved properties such as stiffness, toughness, and tribological behavior. Efforts of scientific community are focused on enhancing the poor compatibility between the organic matrix and inorganic fillers, during the preparation of nanocomposites. Ultrasonic and mechanical methods are sometimes used to disperse the nanoparticles in epoxy resin [10–13]. However, surface chemical compatibilization was required for sol–gel silica nanoparticles [14]. A precursor with an epoxy group has sometimes been used for co-condensation reactions with tetraalchoxysilanes, usually employed in the synthesis of silica nanoparticles [15–17]. Hybrid silane coupling agents are often used to treat the silica filler due to their bifunctional nature, with one end able to react with the silanol groups on silica surface and the other end compatible with the polymer [18, 19]. Recently, a novel approach consisted in chemical functionalization through the reaction between the silanol groups of silica and the oxirane rings of epoxy compounds [14]. Another very interesting route to epoxy/silica hybrid materials involves the hydrolysis and polycondensation of alcoxide precursors in acidic medium. In that case “branched polymers” can be obtained that can form an interpenetrating network (IPN) with epoxy resin [20].

This article shows a new synthesis protocol for diglycidyl ether of bisphenol A (DGEBA)/silica nanocomposite materials. Silica nanoparticles were obtained, in the experimental conditions of the Stöber method, through hydrolysis and polycondensation, in ethanol, of a mixture of two alcoxides: tetraethoxysilane (TEOS) and aminopropyltriethoxysilane (APTS). It is worth pointing out that the studied system consists of silica spherical particles, 200 nm in mean diameter, dispersed into the epoxy matrix. Nanocomposites are, conventionally, defined as multiphase materials where one of the structural units is in a defined size range 1–100 nm. The studied particles are therefore at the border line between nano and micro size, yet they actually suffer the problems of dispersion into a polymer matrix. This is the reason why the term nanocomposite was however used. Using both TEOS and APTS mixtures had the nanoparticles surface covered with aminopropyl groups.

Since DGEBA shows low solubility in ethanol in an alkaline environment, as required by the Stöber method, the nanoparticles were recovered through centrifugation and resuspended into tetrahydrofuran (THF) and then DGEBA was added to the obtained sol. Bisphenol A (DGEBA) epoxy groups were coupled to surface amino groups of nanoparticles.

After removing THF, the sample was non-isothermally cured using imidazole. As it is known imidazole [21] is widely used as epoxy-curing agent for its fast catalytic action and also the fine mechanical properties it produces in the cured resin. Some chemically modified imidazoles are highly effective epoxy-curing agents, producing epoxy resins with superior physical properties (better heat resistance, lower tensile elongation, higher modulus) than amine cured systems. The chosen percentages (2–4%) should assure high cross-linking density [22]. The cure process was studied through thermal analysis. The cure activation energy was evaluated through the Kissinger [23] and the Ozawa equations [24], largely used in the literature [25–28]. Glass transformation temperature (T_g) was evaluated through thermal analysis. All results were compared to those of bare epoxy resins.

Degree of conversion (DC) increases with increasing silica filler loadings [29]. However, silica amount in nanocomposites has no effect on the apparent activation energy of the cure reaction [30]. Cure rates of resin–imidazole–organic montmorillonite systems were lower than neat systems at higher temperature [30].

Experimental section

Materials

Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysylane (APTS), ammonia solution in ethyl alcohol, diglycidyl ether of bisphenol A (DGEBA) epoxy resin, tetrahydrofuran (THF), and imidazole were purchased by Sigma-Aldrich (Milan, Italy).

Synthesis

The nanocomposite synthesis was performed in four stages:

(1) Silica-based nanoparticles bearing surface amino groups were prepared from a mixture of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTS), the latter bearing one not hydrolyzable aminopropyl group. First, a mixture containing 5% mol/mol of APTS was dissolved into 40 ml of ethanol. Then, ammonia and finally water were added. Concentrations in the final solution were: NH_3 0.1 M, H_2O 8.8 M, total alcoxides (TEOS + APTS) 0.15 M. After 2 h, particles were recovered by centrifugation (11,500 rpm) in water.

(2) The nanoparticles were suspended in 30 ml of tetrahydrofuran (THF) solution 1.50×10^{-2} M in diglycidyl ether of bisphenol A (DGEBA) epoxy resin and kept reacting for 3 days at room temperature; this step was intended to promote coupling with epoxy matrix through reaction between amino and epoxy groups.

(3) DGEBA (4.25 mg) was added and THF was removed at 60°C (1 day) and 70°C (1 h). Then, imidazole, in concentration 2 and 4% w/w, was added under stirring at 80°C, temperature at which the resin was fluid enough. The imidazole concentrations are referred to the resin amount in the nanocomposite.

(4) The cure was performed in DSC apparatus at heating rates 2, 5, 10, 20°C/min.

For the sake of comparison bare DGEBA epoxy polymers were prepared by non-isothermal cure with imidazole, added under stirring at 80°C, in weight concentration 2 and 4%.

Materials characterization

Differential thermal analysis (DTA) was performed in a DSC heat flux Netzsch apparatus 404, at heating rates in the range 2–20°C/min, under a nitrogen flux, using alumina as reference. The glass transformation temperature, T_g, of the cured samples was measured on DTA curves recorded at 10°C/min, as the inflection point, i.e., the peak of first derivatives of DTA curves (DDTA curves).

Thermogravimetric analysis (TGA) was performed through a thermogravimetric Apparatus, Netzsch TG209, at a heating rate of 10°C/min under a nitrogen flux.

Fourier transform infrared (FTIR) transmittance spectra of KBr pellets were recorded in the 400–4000 cm^{-1} range using a Nexus 5200 FT-IR spectrometer.

Fracture surfaces (produced with the aid of a knife blade) were observed in scanning electron microscopy (SEM) through Leica Stereoscan 440 microscope.

Dynamic mechanical thermal analysis (DMTA) measurements were carried out using a Triton Technology mod. Tritec 2000 testing machine. Tests were performed in single cantilever bending mode, using a constant frequency of 1 Hz. Samples were heated from room temperature to 230°C at a heating rate of 2°C/min, under a nitrogen flux. The glass transformation temperature, T_g, was taken as the peak temperature of tanδ curve.

Results and discussion

Nanocomposites composition and structure

Figure 1 shows DSC curves of non-isothermal cure of nanocomposites, with imidazole 2%. Thermograms of non-hysothermal cure of bare epoxy resins and of nanocomposites cured with 4% of imidazole are pretty similar, therefore, they were not reported.

All the cure thermograms (see Fig. 1) show a low temperature exo-peak. During epoxies cure, the role of tertiary amines, such as imidazole, is to initiate chain-growth polymerization. It is accepted [23, 31] that the pyridine type nitrogen of imidazole attacks the epoxy functional group forming 1:1 adduct. In a second step, the newly generated pyridine type nitrogen attacks another epoxy group to produce 1:2 adduct. The low temperature peak can just be attributed [25, 32–34] to adducts formation.

FTIR spectra (not reported) confirm the high degree of cure achieved. In fact, the band at 914 cm^{-1}, attributed to the epoxy ring, is no longer present in the spectra of both bare epoxy polymers and nanocomposites cured with 2 and 4% imidazole, after the non-isothermal cure at different heating rates up to 240°C, [35]. Therefore, FTIR results suggest that in all samples the cure went to completion. Moreover, silica characteristic bands, around 470 and 1100 cm^{-1}, appear in FT-IR spectra of SiO_2/DGEBA nanocomposites.

Figure 2 reports the SEM micrographs of the nanocomposite and pure polymer, both cured with 4% imidazole at 2°C/min. Similar results were obtained for samples cured with 2% imidazole. As can be seen the synthesis protocol allowed a good dispersion of SiO_2 nanoparticles into the nanocomposite material. It is worth pointing out that the authors prepared the same nanocomposites also by dispersing

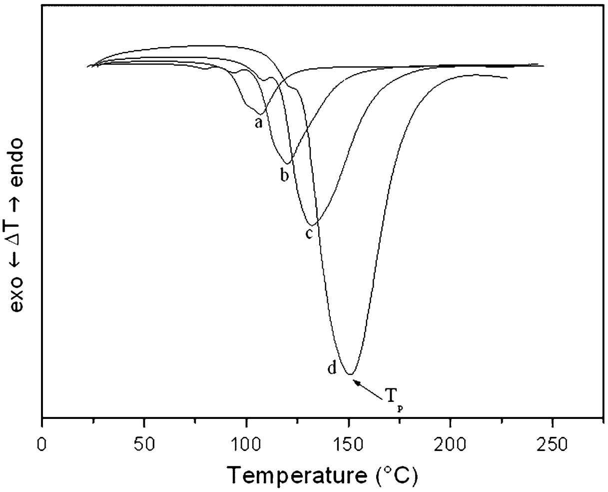

Fig. 1 Cure DTA curves of nanocomposite (2% imidazole): 2°C/min (*a*), 5°C/min (*b*), 10 °C/min (*c*), 20°C/min (*d*)

Stöber silica particles of the same size directly into DGEBA epoxy resin at 80°C altogether with imidazole. The particles appeared aggregated in clusters in the final polymer.

As reported in literature, chemical compatibilization of inorganic filler is required to avoid its segregation and aggregation in the organic matrix [14–20]. The good dispersion shown in Fig. 2 is, therefore, attributed to step 2 in the synthesis route. It is known, in fact, using suitable coupling agent allows to obtain a strictly interconnected network preventing macroscopic phase separation [2, 9]. Amino-propyl groups are not hydrolizable, therefore hydrolysis and poly-condensation of TEOS/APTS mixtures leads to nanoparticles bearing surface amino-propyl groups. Moreover, the reaction of the amino group with epoxy ring is well known; primary amines are, in fact, commonly employed as curing agents of epoxy resins. Therefore, the formation of a "compatibilizing" epoxy shell around silica nanoparticles through reaction of surface amino groups with epoxy monomers, as described in Fig. 3, is expected and can justify the good dispersion of silica nanoparticles into the epoxy matrix.

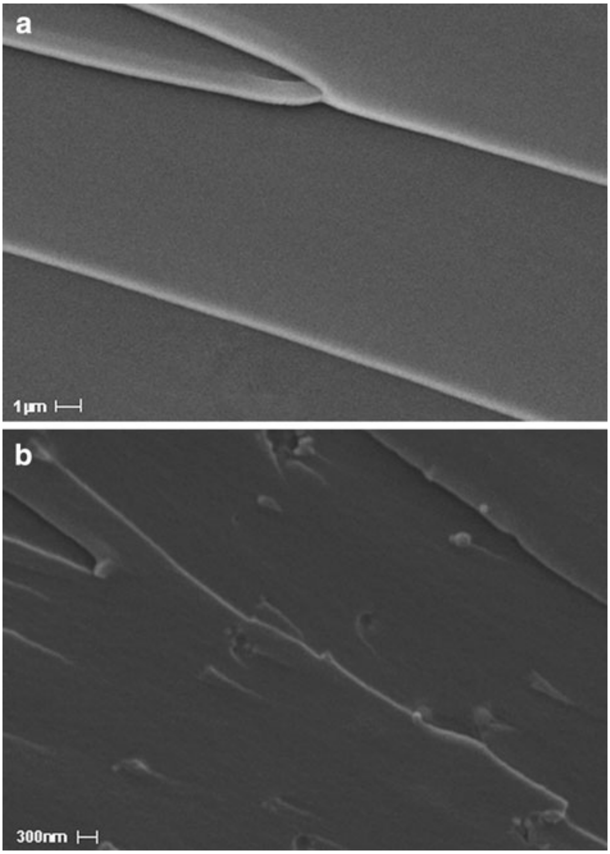

Fig. 2 SEM micrographs of polymer (**a**) and nanocomposite (**b**) cured at 2°C/min with 4% imidazole

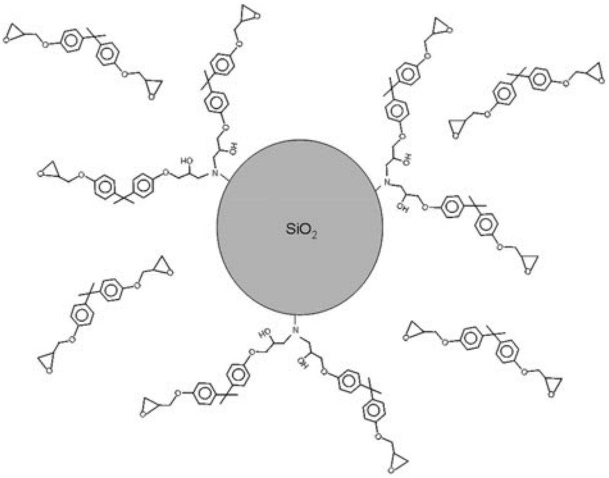

Fig. 3 Illustration of the surface epoxy shell around silica nanoparticles

Dynamic mechanical tests were carried on samples cured at 2°C/min in order to measure the dynamic storage modulus (E') and the loss factor (tanδ) reported as a function of temperature in Fig. 4. The values of dynamic storage modulus (E') in the glassy state and glass transformation temperatures are reported in Table 1. The values of E' in the glassy state indicate that the silica nanoparticles had a reinforcing effect, as the filled samples clearly exhibited an increase in elastic modulus with respect to the unfilled matrix. This can be ascribed [13, 36, 37] to a homogeneous dispersion of silica nanoparticles in the epoxy matrices on nanoscale, due to the effective coupling between the surface amino groups and the epoxy resin. The T_g values were affected by the presence of nanoparticles; however, a stronger effect is related to the imidazole content. That is, as the percent weight of imidazole is increased from 2 to 4 wt%, a reduction higher than 25°C is observed for glass transition values both in the plain resin and in the composite.

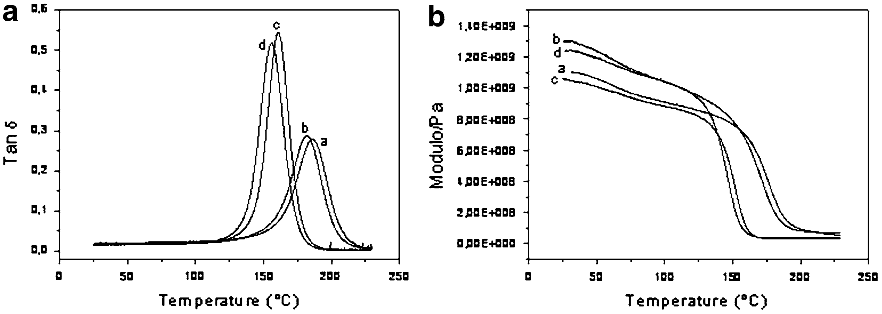

Fig. 4 Plot of tanδ and dynamic storage modulus, E' versus temperature: polymer 2% (*a*), nanocomposite 2% (*b*), polymer 4% (*c*), nanocomposite 4% (*d*)

Table 1 Glass transformation temperature, T_g, and dynamic storage modulus, E', taken from DMA curves

	Polymer 2% imid	Polymer 4% imid	Nanocomposite 2% imid	Nanocomposite 4% imid
T_g (°C) DMA 2°C/min	186	160	181	155
E' (Pa)[a]	1.09×10^9	1.04×10^9	1.29×10^9	1.23×10^9

[a] E' values were taken at $T = 35°C$

Thermogravimetric (TG) results confirm that silica content in the matrix is 5 wt%, as expected.

Cure kinetic

The cure activation energy was evaluated by Kissinger [23] and Ozawa [24] equations largely used in the literature [25–28]:

$$\ln \beta/T_p^2 = -E/RT_p + \text{const} \tag{1}$$

$$\ln \beta = -E/RT_p + \text{const} \tag{2}$$

where β is the heating rate, E is the cure activation energy, and T_p is the cure exo peak temperature. When plotting ln β as a function of $1/T_p$ (Fig. 5), straight lines were obtained, according to Eq. 2. According to Eq. 1, straight lines (not shown) were also obtained when plotting $\ln(\beta/T_p^2)$ as a function of $1/T_p$. According to Eqs. 1 and 2, activation energies of the cure process can be driven from the slopes of the plots. Their values are reported in Table 2. A slight increase of the activation energy with the imidazole content is observed, as already reported in the literature [38]. Cure processes of nanocomposites and plain polymer show close values of activation energy.

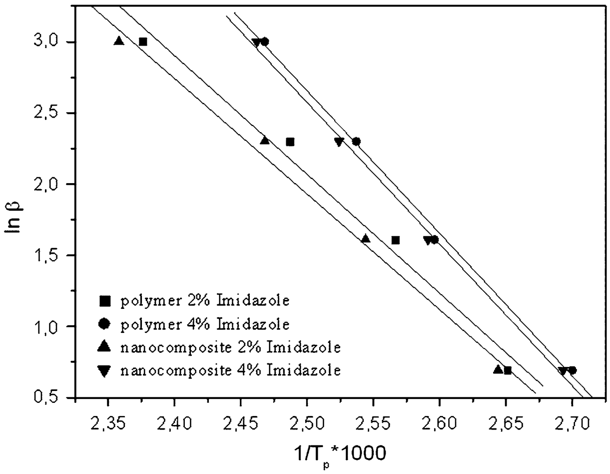

Fig. 5 Ozawa plot: ln(β) versus $1/T_p$

Figure 5 also shows that: (a) temperature of the cure exo-peak shifts downwards as the percent weight introducing nanoparticles, whatever the imidazole content and the heating rate. However, the effects of the filler on the peak temperature are much lower. The former effect is easily explained considering that the greater the imidazole content the faster the cure kinetics and, therefore, the lower the cure temperature in DTA. On the other hand, as reported in the experimental section, the imidazole content is related to amount of the organic phase. Therefore, the introduction of nanoparticles has imidazole volume concentration reduced, thus shifting to higher temperature the DTA cure exo-peak. This result suggests that silica filler has only indirect influence on the epoxy cure. This is confirmed by the cure activation energies reported in Table 2, changing with the imidazole content, not with the filler content.

Glass transformation temperature and structural hypothesis

Figure 6 and Table 1 report the glass transformation temperatures, T_g, of the cured samples as taken from DTA curves. Their values are consistent with those obtained through DMTA, also reported in Table 1. They show that T_g depends on both the cure schedule (heating rate and imidazole content) and silica content. The T_g of both plain polymer and the nanocomposite (whatever the imidazole content) generally decreases as the heating rate of non-isothermal cure process is increased, as already reported [39] for polymers. As already found [25], polymer T_g decreases as the imidazole content is increased, and the shift depends on the heating rate. It is worth pointing out that T_g changes as high as 40°C were detected as a function of the cure schedule that is heating rate and imidazole content. Moreover Fig. 6 and Table 1 show that the effect of silica addition depends on the imidazole amount. At lower imidazole content (2%), whatever the heating rate, T_g decreases upon addition of silica, as already reported in the literature [14, 18, 36], whereas it does not change if the imidazole content is increased to 4%.

T_g depends on several factors [22]: degree of cure, catalyst concentration, network structure/curing history, purity of monomer, physical ageing. In ranking the importance of these effects, Chang estimates, for cross-linked polymers the following T_g changes: 200 K for the degree of cure, >50 K for catalyst concentration, >50 K for network structure/curing history. In our case, the purity of monomer was the same, and no physical ageing was to be taken into account. However, differences in both the degree of cure and network structure/curing history may explain the strong influence of heating rate on T_g.

Table 2 Cure activation energies determined by the Kissinger and Ozawa methods as a function of the imidazole and silica content

Imidazole (wt%)	SiO_2 (wt%)	E_a (KJ/mol) by Kissinger	E_a (KJ/mol) by Ozawa
2		63	66
2	5	61	64
4		77	79
4	5	76	79

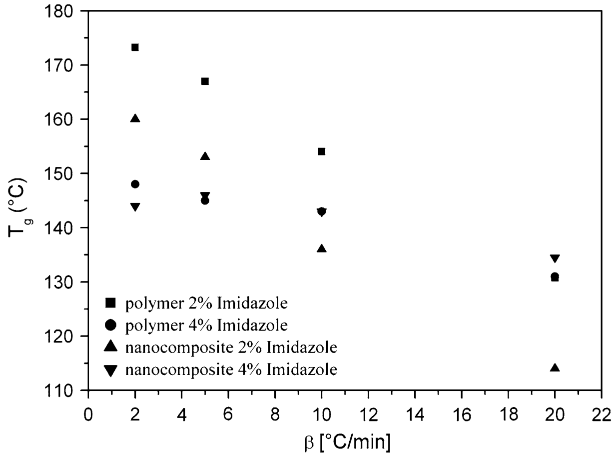

Fig. 6 Plot of the glass transformation temperature, T_g, versus cure process heating rate, β

Strong effect on T_g values, related to the imidazole content were already observed. Chang reported that [22] up to 3–5% wt of imidazole there is little T_g increase as the result of high cross-linking density. When catalyst concentration is further increased, more DGEBA is consumed by DGEBA-imidazole adduct formations and less DGEBA is available for etherification. However, Chang [22] estimates that, when the imidazole content is limited to 2–4 wt%, influence of its concentration on T_g should be within 10 K.

In our case, when curing at 2 K/min as the percent weight of imidazole is increased from 2 to 4 wt%, a reduction higher than 27°C is observed for glass transition values, far beyond Chang's predictions.

The T_g decrease when adding nanoparticles might be due to the plasticizing effect of the silica particles in the epoxy domains. Introduction of silica particles might also increase the free volume at the polymer-filler interface, as already proposed [14, 18, 36]. However, a T_g change is actually observed at low imidazole content (2 wt%). It is interesting to observe that no significant T_g changes between unfilled polymer and the nanocomposite are observed, at 4 wt% imidazole content. This can be the result of a better interconnection. In fact, as reported above, a good compatibilization (leading to the well-dispersed silica nanoparticles into the polymer) was achieved, due to the formation of an epoxy shell around the nanoparticles, through reaction of APTS and epoxy. We can, therefore, expect that the greater the imidazole content the better could be the interconnections of the nanoparticles epoxy shell and epoxy matrix.

Conclusions

DGEBA/SiO_2 nanocomposites with a 5 wt% in SiO_2 and a good dispersion of silica nanoparticles, within fully cured DGEBA matrix were easily produced through the proposed synthesis route. Silica addition reduces cure kinetics. Cure activation energy is not influenced by the silica presence, whereas it changes with the imidazole content.

The nanocomposite glass transformation temperature depends on the heating rate of cure process, the imidazole and silica content. At higher imidazole content there is no difference in T_g values between plain polymer and nanocomposite.

It is known that properties of nanocomposites depend [2] on both interfacial interactions and nanocomposites structure, that is on the nanoparticle size, size distribution, and surface chemistry. Therefore, the new route may allow to project the nanocomposite:

(1) By exploiting the extended correlations between nanoparticles size and synthesis experimental conditions widely ascertained, for the Stöber method, in the literature [4–6, 8] even if the effect of mixing alcoxides must be taken into account [40];
(2) By controlling the surface density of aminopropyl groups through changes of the TEOS/APTS ratio in the starting mixture.

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