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Influence of the Curing Temperature in the Mechanical and Thermal Properties of Nanosilica Filled Epoxy Resin Coating

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Summary: 0.5–3 wt% nanosilica was added to an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) and cured at 25, 40 or 60 °C using isophoronediamine (IPDA) as hardener. Aggregates of nanosilica were properly dispersed into the DGEBA-IPDA resin and agglomerates formation was avoided. Addition of nanosilica increased the storage modulus E′ and the area and height of the tan δ curve of DGEBA-IPDA resin cured at 25 °C, but no significant differences were found by curing at higher temperature. Gel time measurements and the results obtained by applying the Kamal model to isotherm DSC curing of DGEBA-IPDA-nanosilica revealed that nanosilica catalysed the curing reaction between DGEBA and IPDA, in less extent by increasing the curing temperature.

Keywords: differential scanning calorimetry (DSC); epoxy; gel time; kinetics; nanosilica

Introduction

In spite of epoxy resins are more expensive than other resins used as coatings (polyurethane, phenolic, polyester), they are widely used due to their exceptional adhesive properties, their ability to cure without volatile matter formation, their excellent mechanical properties, and their low shrinkage during their curing.

Several factors determine the epoxy coating performance, mainly the molecular architecture, the curing conditions, the nature of the reactants, the epoxy/curing agent(s) ratio, etc [1]. Furthermore, reactive or non reactive diluents, plasticizers, elastomers and inorganic fillers determine the final properties of epoxy coatings [2–5].

Fumed silica (nanosilica) is one of the most common inorganic additives used as thickener of epoxy resin, providing thixotropy and pseudoplasticity, and increasing their mechanical properties. They are obtained by thermal hydrolysis of chlorosilanes in an oxygen-hydrogen flame [6]. The result of this reaction is a non-porous amorphous silicon dioxide having a primary particle size between 7 and 40 nm [7]. Due to the small particle size, primary nanosilica particles stick together by physico-chemical forces forming aggregates and agglomerates.

The performance of nanosilica as filler of epoxy depends on the compatibility between them and the choice of an adequate method to disperse the nanosilica into the epoxy matrix. If an adequate dispersion is reached, improved thermal and mechanical properties of epoxy coatings can be obtained.

Despite nanosilica is widely employed as filler in epoxy industry, and some studies have been carried out in nanosilica filled epoxies, most of them deal with commercial epoxies and with high concentrations levels of filler. In this study the nanosilica–epoxy resin interactions were analyzed in a low filled simple epoxy resin based on diglycidyl

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ether of bisphenol A (DGEBA). The rheological, viscoelastic and thermal properties, and the curing kinetic at different temperatures were studied.

Experimental

The coating system selected was a simple epoxy resin based on DGEBA with an equivalent epoxy index of 5.2 mol/kg, and isophoronediamine (IPDA) hardener; 21 parts of hardener were added to 100 parts of DGEBA to allow curing (stoichiometric ratio). The chemical structures of DGEBA and IPDA are given in Fig. 1. 0.5–3 wt% hydrophilic non-porous nanosilica *Aerosil 200* was used as filler; this nanosilica has a specific surface of 200 m^2/g and a primary particle size of 12 nm.

The nanosilica was dispersed in DGEBA in a *Cowles* mechanical stirrer *Dispermix DL-B* (Oliver y Battle S.A., Badalona, Spain) by adding all nanosilica amount to 35 wt% DGEBA at a stirring speed of 2005 rpm for 20 minutes; afterwards, the remainder DGEBA was added and the final solution was stirred at 1500 rpm for 30 minutes, until an homogeneous mixture was obtained.

The extent of dispersion of the nanosilica in the DGEBA-IPDA matrix was obtained by means of transmission electronic microscope (TEM) in a *JEOL JEM-2010* (Jeol, Tokyo, Japan) by using at an acceleration voltage of 100 kV.

The variation of the viscosity of the filled DGEBA as a function of the shear rate was obtained in a *Rheolab MC Physica* rheometer (Paar-Physica Messtechnik GmbH, Stuttgart, Germany). Experiments were carried out by using 100 ml of nanosilica-DGEBA solutions in rotational mode using concentric cylinders type Z2 DIN. The shear rate was varied from 5 to 25 s^{-1}.

The viscoelastic properties of the cured nanosilica-DGEBA-IPDA for 72 hours at 25, 40 or 60 °C were studied in a Dynamical Mechanical Temperature Analyser (DMTA) *Rheometric Scientific Mk III* (Rheometric Scientific Ltd, Surrey, England). The cured material had dimensions of $2 \times 10 \times 20$ mm^3 and the two bending-point mode; a heating rate of 5 °C/min was used.

Gel time was measured by using a novel procedure based in the use of a *Texture Analyzer TA.XT2i system* (Stable Micro Systems, Surrey, England). The procedure consists in the penetration of a cylindrical steel probe (5 mm diameter) in 60 g nanosilica-DGEBA-IPDA solution placed in an aluminum baker; the probe was sequentially placed in and out of the solution by using a cyclic rate of 1 mm/s, and allowing a maximum penetration of the probe into the solution of 10 mm. The force necessary to pull out the probe from the solution was monitored as a function of time. Because of the gel formation implies a sudden increase in the solution viscosity, the force necessary to pull out the probe from the solution rapidly increases, the gel time was taken when the strength necessary to pull out the probe was equal to 0.2 N. Although strengths between 0.05 and 1 N were tested, 0.2 N was chosen due to reproducibility and experimental convenience. To measure the gel point at 40 and 60 °C, an infrared lamp connected to a thermocouple placed into the solution mixture was used.

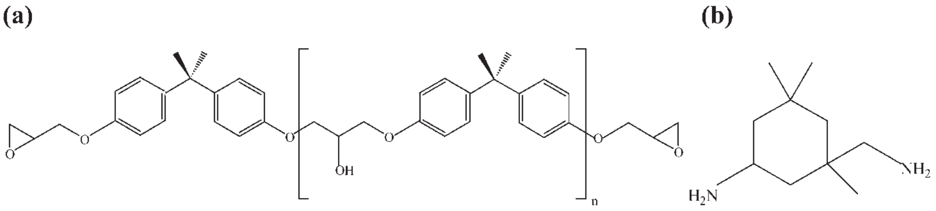

Figure 1.
Chemical structure of (a) DGEBA, (b) IPDA.

The cure kinetics of the nanosilica-DGEBA-IPDA mixtures were studied in a *Differential Scanning Calorimeter (DSC) Q-100 TA instrument* (TA instruments, New Castle, EEUU). About 10 mg nanosilica-DGEBA-IPDA freshly prepared solution was placed into a hermetic pan sealed by means of a *TA Sample Encapsulating Press*. Then, the mixture was placed into the DSC oven, using an empty identical hermetic pan as reference. The nanosilica-DGEBA-IPDA mixture was isothermally cured inside the DSC oven for 360 min at 25, 40 or 60 °C, followed by a dynamical DSC run (heating rate = 5 °C/min) to fully cure the epoxy resin. All experiments were carried out under nitrogen atmosphere using a flow rate of 50 ml/min. The integration of the isothermal curve allows recording the heat flow involved during the reaction at a given temperature (ΔH_{iso}), and the integration of the peak obtained during the dynamical run produces the residual enthalpy of the reaction (ΔH_{res}). The sum of both enthalpies corresponds to the total heat involved for a conversion degree of one ($\alpha = 1$). Finally, the reaction rate (v) can be obtained from equation (1):

$$v = \frac{d\alpha}{dt} = \frac{(dH/dt)}{\Delta H_{iso} + \Delta H_{res}} \qquad (1)$$

Results and Discussion

Filler morphology and dispersion in the polymer matrix determine the viscosity, the thermal and the mechanical properties, among other, of the nanosilica-DGEBA-IPDA mixtures [8].

In this work the nanosilica dispersion in the DGEBA-IPDA matrix was estimated through TEM micrographs, Fig. 2. Two phases are clearly distinguished in the TEM micrographs, the clear zone corresponds to the DGEBA-IPDA matrix, and in dark colour, the nanosilica domains are identified. As the nanosilica content in the DGEBA-IPDA matrix increases a greater number and larger size of filler domains are found. By means of measuring the particle size of nanofiller in several magnified TEM micrographs, the size distribution of the nanosilica domains in the DGEBA-IPDA matrix was obtained, Fig. 3.

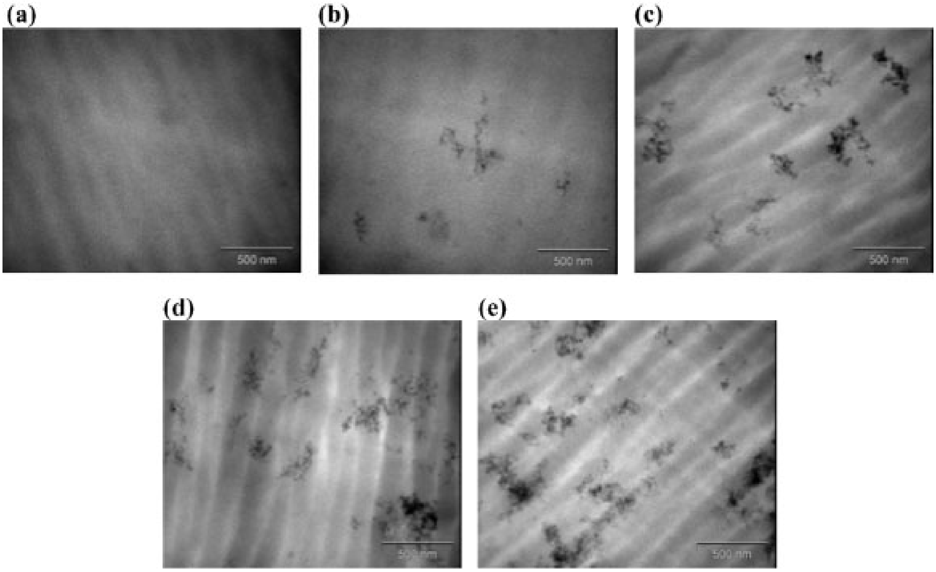

Figure 2.
Nanosilica-DGEBA-IPDA cured film micrographs x60000. (a) 0 wt% SiO_2/DGEBA-IPDA, (b) 0.5 wt% SiO_2/DGEBA-IPDA, (c) 1 wt% SiO_2/DGEBA-IPDA, (d) 2 wt% SiO_2/DGEBA-IPDA, (e) 3 wt% SiO_2/DGEBA-IPDA.

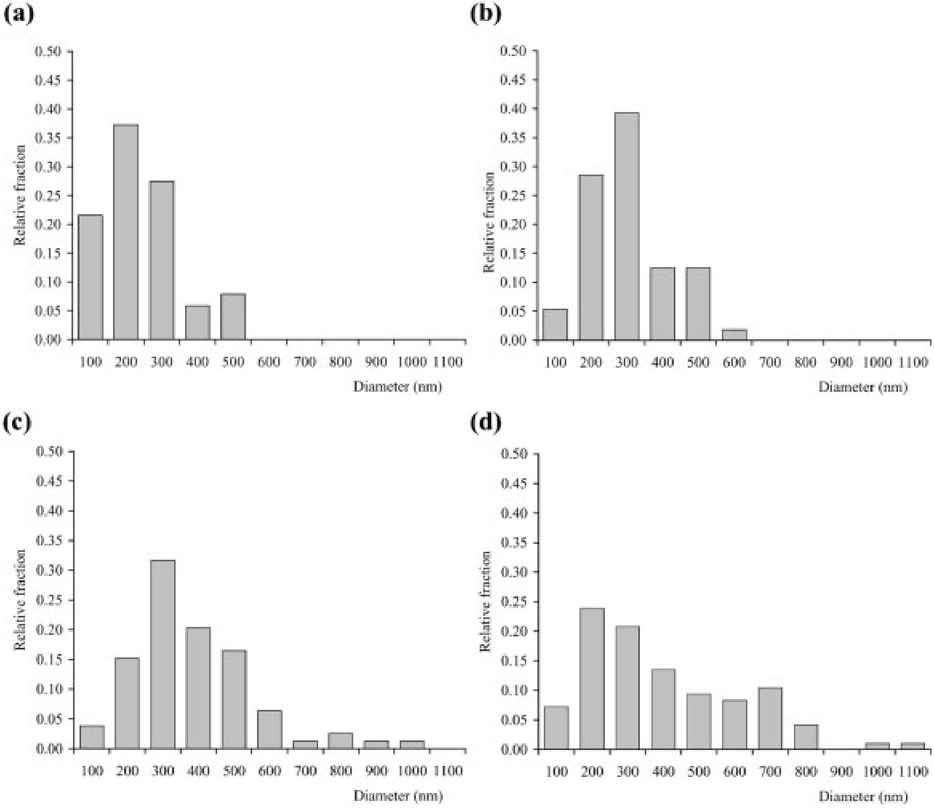

Figure 3.
Nanosilica aggregates size distribution in the DGEBA-IPDA matrix. (a) 0.5 wt% SiO_2/DGEBA-IPDA, (b) 1 wt% SiO_2/DGEBA-IPDA, (c) 2 wt% SiO_2/DGEBA-IPDA, (d) 3 wt% SiO_2/DGEBA-IPDA.

According to Fig. 3, the increase of the nanosilica content produces wider size distributions in the DGEBA-IPDA matrix, however, the maximum of the curves corresponds to 200 and 300 nm of particle diameter. Attending to DIN 53 206 part 1 (08/72) standard [9] that considers an aggregate as a collection of primary particles with a diameter comprised between 100 and 500 nm, and an agglomerate as an aggregate network connected at discrete points through physical forces (Van der Waals and/or H-bond), with a diameter comprised between 10 and 50 μm, the greater part of the nanosilica domains in the DGEBA-IPDA matrix are aggregates. Only for the bigger nanosilica concentrations, 1 wt% SiO_2/DGEBA-IPDA, 2 wt% SiO_2/DGEBA-IPDA and 3 wt% SiO_2/DGEBA-IPDA, a slight relative fraction of nanosilica domains ($\leq 10\%$) shows a diameter up to 500 nm, but agglomerates were not obtained.

Fig. 4 shows the variation of the viscosity of the nanosilica-DGEBA solutions as a function of the shear rate. An increase in the viscosity of DGEBA is produced by adding nanosilica and in a greater extent by increasing its amount. The increase in viscosity is due to the existence of nanosilica aggregates in the DGEBA matrix [10,11] which are formed as a consequence of the small primary particle size (12 nm) of filler that promotes the interactions of the surface silanol groups between them through H-bond. The number of aggregates grows as the nanosilica concentration increases, and therefore a greater increase in viscosity in nanosilica-DGEBA solutions is obtained. In addition, all nanosilica-

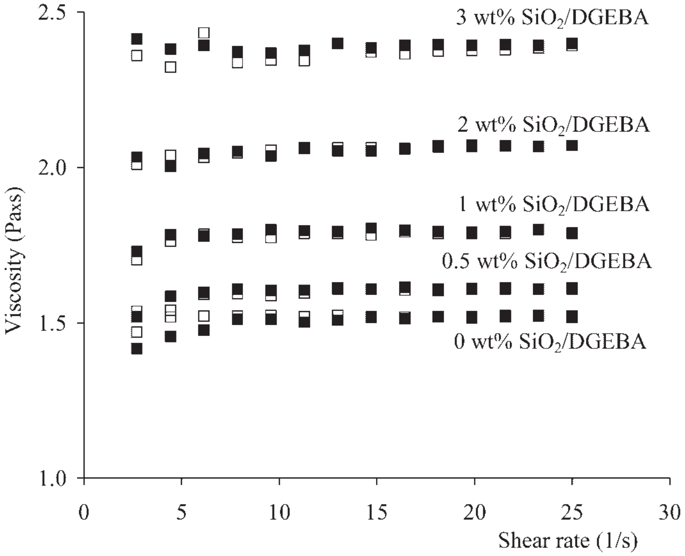

Figure 4.
Flow curves of nanosilica-DGEBA solutions. Solid points correspond to the increase in shear rate and open points to the decrease in shear rate curves.

DGEBA solutions show Newtonian behaviour (i.e. the viscosity is constant by increasing the shear rate).

Table 1 shows some viscoelastic properties (obtained from DMTA curves) of nanosilica-DGEBA-IPDA mixtures cured at 25 °C for 72 hours. Addition of nanosilica increases the elastic modulus of DGEBA-IPDA at 25 °C (E′ 25 °C, Pa), likely due to steric hindrance caused by the nanosilica aggregates embedded in the DGEBA-IPDA matrix. Although, the T_g of DGEBA-IPDA is not affected by nanosilica addition (Table 1, Fig. 5), an increase in the height and area under the tan δ curve is obtained when nanosilica is added to the epoxy (Fig. 5), this variation is more marked as the nanosilica loading increases. Therefore, addition of nanosilica disturbs the crosslinking of the epoxy chains, in a greater extent by increasing the nanosilica loading, confirming the steric hindrance produced by the filler in the polymer matrix. In fact, the tan δ values in the maximum of the curves in Fig. 5 are bigger than one, indicating that a high conversion degree is not reached in the nanosilica-DGEBA-IPDA mixtures cured at 25 °C.

The increase of the curing temperature to 40 °C produces an increase in T_g values in the DGEBA-IPDA mixtures (Table 2) in relation to the nanosilica-DGEBA-IPDA coatings cured at 25 °C (Table 1), and as a consequence, the values of the elastic moduli at 100 °C (E′ 100 °C, Pa) also increase, and the area under tan δ curves decrease. Therefore, addition of nanosilica does not greatly changes the DMTA

Table 1.
Some DMTA parameters of the nanosilica-DGEBA-IPDA mixtures cured at 25 °C for 72 hours.

SiO_2/DGEBA-IPDA (wt%)	E′(25 °C) (Pa)	Area$_{\tan\delta}$ (arb. units)	$h_{\tan\delta}$	$T_{g\ \tan\delta}$ (°C)	E′(100 °C) (Pa)
0	2.0×10^8	30	1.1	68.8	1.1×10^6
0.5	4.1×10^8	38	1.6	65.3	7.4×10^5
1	6.4×10^8	42	1.5	68.8	5.5×10^5
2	3.8×10^8	45	1.7	67.4	3.0×10^5
3	3.8×10^8	45	1.8	66.5	4.9×10^5

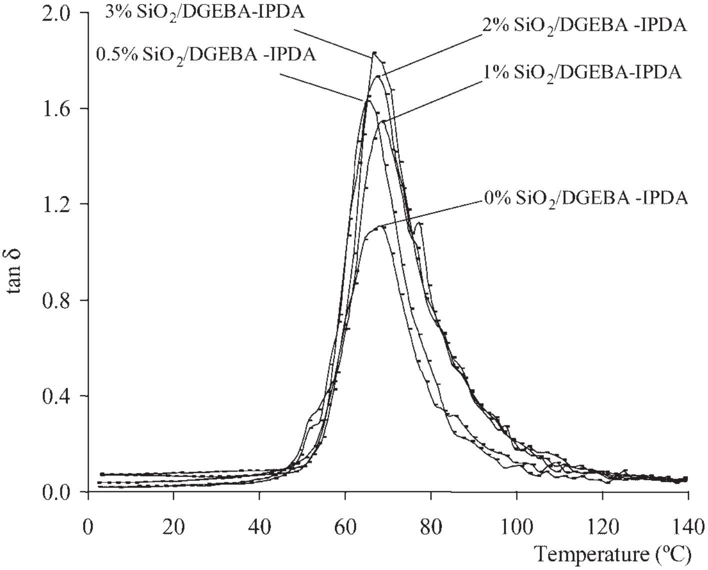

Figure 5.
Variation of tan δ as a function of the temperature for nanosilica-DGEBA-IPDA mixtures cured at 25 °C for 72 hours.

parameter values due to the higher conversion degree obtained in the nanosilica-DGEBA-IPDA coatings cured at 40 °C. The DMTA curves of the nanosilica-DGEBA-IPDA mixtures cured at 60 °C are similar to those obtained at 40 °C.

Fig. 6 shows the plots obtained during gel point measurements of the nanosilica-DGEBA-IPDA mixtures cured at 25 °C, 40 °C and 60 °C. Addition of nanosilica decreases the gel point of DGEBA-IPDA mixtures, this decrease is more marked as the nanosilica content increases for curing temperatures of 25 °C and 40 °C. For 60 °C as curing temperature, the addition of the nanosilica decreases the gel point irrelevant to the nanosilica loading. Therefore, interactions of the nanosilica with DGEBA-IPDA can be produced, leading to faster gelification of the epoxy mixture, in a greater extent by increasing the nanosilica loading. In fact, as the curing reaction progress, the movement of the nanosilica aggregates is restricted and the formation of H-bond between the nanosilica aggregates and the DGEBA-IPDA chains can be promoted. Thus, the H-bond formation could be responsible of the formation of a nanosilica-DGEBA-IPDA network (Fig. 7) which leads to an increase in viscosity as the curing reaction progress, accelerating the gelification of the mixtures.

It can be anticipated that the higher number and wider size distribution of nanosilica (i.e. by increasing the nanosilica loading in the DGEBA-IPDA mixture) will favour the formation of the nanosilica-DGEBA-IPDA network during curing. In

Table 2.
Some DMTA parameters of the nanosilica-DGEBA-IPDA mixtures cured at 40 °C for 72 hours.

SiO_2/DGEBA-IPDA (wt%)	E′(25 °C) (Pa)	Area $_{\tan\delta}$ (arb. units)	$h_{\tan\delta}$	$T_{g\ \tan\delta}$ (°C)	E′(100 °C) (Pa)
0	3.3×10^8	26	1.3	78.8	1.1×10^6
0.5	3.3×10^8	29	1.4	78.4	5.5×10^5
1	4.5×10^8	27	1.3	77.3	1.1×10^6
2	6.1×10^8	29	1.4	77.7	9.9×10^5
3	3.9×10^8	27	1.2	77.7	1.1×10^6

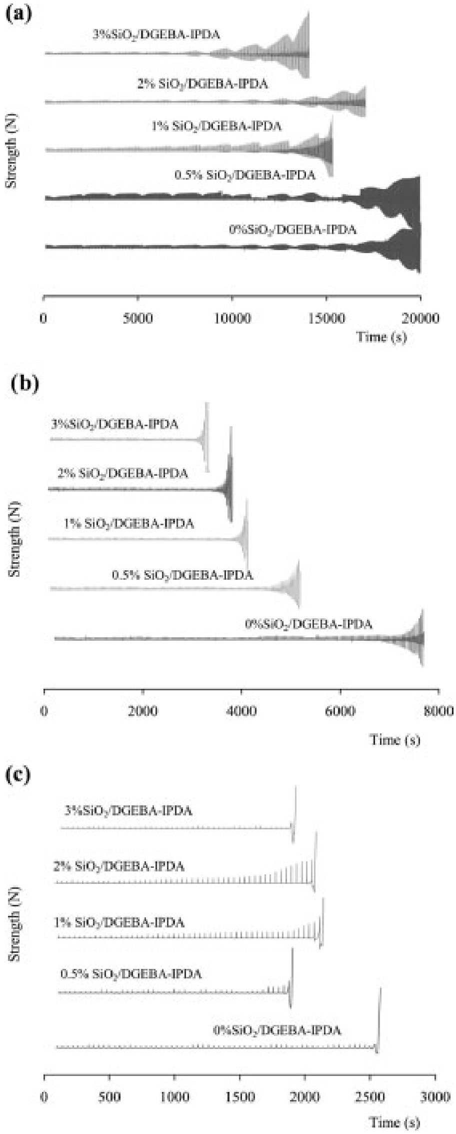

Figure 6.
Gel point measurements of the nanosilica-DGEBA-IPDA mixtures cured at (a) 25 °C, (b) 40 °C, and (c) 60 °C.

addition, this network will be more crosslinked as the nanosilica content increases. On the other hand, a raise in the curing temperature up to 60 °C should facilitate the weakening of the H-bond between the nanosilica and the DGEBA-IPDA matrix, and therefore the gel point becomes independent of the nanosilica loading.

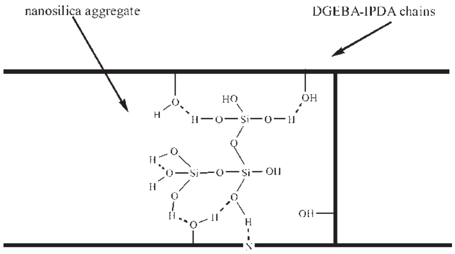

Figure 7.
Scheme of nanosilica-DGEBA-IPDA network.

On the other hand, addition of the nanosilica not only affects diminishing the gel point of the polymer matrix, but also a catalytic effect should be considered in the curing reaction. In fact, it has been reported[12] the catalytic effect produced are catalyzed by Lewis basis, phenols and alcohols in the reaction of epoxies with primary and secondary amines. Nanosilica may also acts as a catalyst in the curing reaction of DGEBA-IPDA mixture.

According to Fig. 8, the hydroxyl group resulting of the oxirane ring opening during the curing reaction of DGEBA with IPDA can act as a catalyst. As a consequence, the rate of the curing reaction between the epoxy resin and the amine increases at low temperature and short time, i.e. autocatalysis is produced [12].

Therefore, in the same way that hydroxyl groups act as catalyst for the curing reaction between the DGEBA and the IPDA, the free silanol groups on the nanosilica surface can produce the same catalytic effect. Fig. 9 shows that the H-bond formation between the oxygen of the oxirane ring and the free silanol group on the nanosilica surface results in an active complex with a deficit of charge in the antimakornikov position, which is more sensitive to nucleophilic attack by the amine. Thus, the curing reaction is speeded. The catalytic effect during the curing reaction should be more marked as the number of active complex sites increases, in other words, as more crosslinked the nanosilica-DGEBA-IPDA network is, i.e. by increasing the nanosilica concentration in the DGEBA-IPDA matrix.

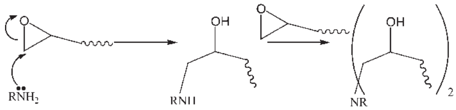

Figure 8.
Curing mechanism of epoxy resin with primary and secondary amines.

In addition, the interaction between the nanosilica, DGEBA and IPDA may produce a filler-polymer interphase enriched in DGEBA monomer and IPDA hardener, increasing the probability of interactions among the reactants, and therefore, increasing the curing reaction rate [13].

To determine the effect of the nanosilica addition in the curing kinetics of DGEBA-IPDA mixture, the Kamal model was applied to isothermal and dynamic DSC curves. Kamal *et al*[14,15] developed a semi-empirical model which consider that the curing reaction between an epoxy resin and an amine occurs through two simultaneous mechanisms, one of them depending on the reactants (n order kinetics), and the other one depending on the products, i.e. hydroxyl groups (autocatalytic curing). Likewise, both the hydroxyl groups produced during the curing reaction and the silanol groups of the nanosilica surface have a catalytic effect in the kinetics. The Kamal model is described by Eq. 2

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (2)$$

where m and n are the kinetics exponents of the reaction, and k_1 and k_2 are the n order and autocatalytic reaction rates constants, respectively.

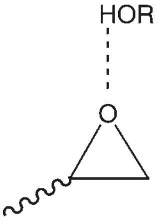

Figure 9.
Oxirane/silanol complex formed during the curing reaction of DGEBA with IPDA.

Table 3.
Reaction rate constants and kinetics exponents for n order and autocatalytic mechanism for nanosilica-DGEBA-IPDA mixture cured at 25 °C.

SiO_2/DGEBA (wt%)	k_1 (min^{-1})	K_2 (min^{-1})	m	n
0	4.2×10^{-3}	2.2×10^{-4}	1.2	1.8
0.5	4.4×10^{-3}	5.4×10^{-4}	1.2	1.8
1	4.6×10^{-3}	6.4×10^{-4}	1.2	1.8
2	4.6×10^{-3}	5.5×10^{-4}	1.2	1.8
3	5.4×10^{-3}	6.8×10^{-4}	1.2	1.8

According to Table 3, although nanosilica addition does not affect the kinetics exponents of the DGEBA-IPDA mixture cured at 25 °C, an increase in the reaction rate constants is obtained, more noticeable for k_2, which is related to the hydroxyl/silanol autocatalytic effect. However, this autocatalytic effect practically disappears by increasing the curing temperature to 40 and 60 °C (Table 4).

The autocatalytic effect in the nanosilica-DGEBA-IPDA mixture can be ascribed to the creation of filler-polymer interactions between the silanol groups on the nanosilica surface and the oxirane ring in the epoxy during curing reaction. Thus, as the curing temperature increases, the filler-epoxy interaction becomes weaker, the filler-polymer interphase increases in size, and then, the catalytic effect is less marked. It is consistent with the gel time measurements, and the reaction rate constants obtained by applying the Kamal model.

Finally, the relationship between the reaction rate constants and the temperature established by the Arrhenius equation allows determining the activation energies of the nanosilica-DGEBA-IPDA mixtures,

Table 4.
Reaction rate constants and kinetics exponents for n order and autocatalytic mechanism for nanosilica-DGEBA-IPDA mixture cured at 40 °C.

%SiO_2/DGEBA (wt%)	k_1 (min^{-1})	k_2 (min^{-1})	m	n
0	9.8×10^{-3}	9.3×10^{-4}	1.2	1.8
0.5	1.0×10^{-2}	2.0×10^{-3}	1.2	1.8
1	9.7×10^{-3}	1.9×10^{-3}	1.2	1.8
2	9.2×10^{-3}	2.1×10^{-3}	1.2	1.8
3	1.1×10^{-2}	2.1×10^{-3}	1.2	1.8

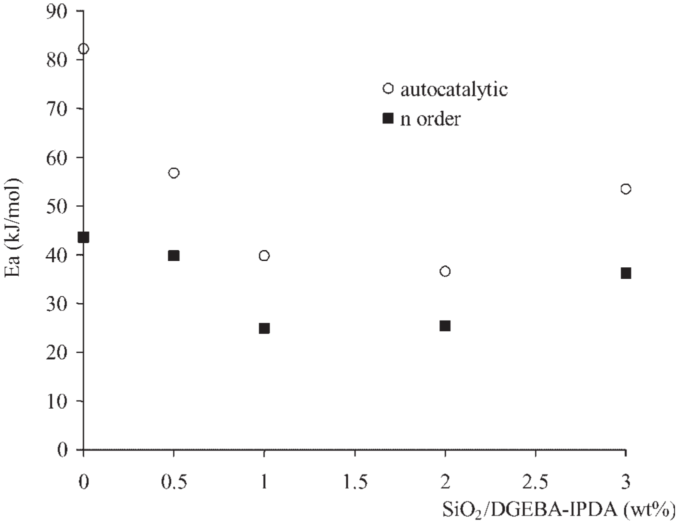

Figure 10.
Activation energy dependence of SiO_2/DGEBA as a function of the nanosilica content.

for both the n order and the autocatalityc curing mechanisms (Fig. 10). Addition of the nanosilica decreases the activation energies in both curing mechanisms. This decrease implies that nanosilica addition produces an alternative curing pathway, which is energetically more favorable. This pathway is related to the nanosilica-DGEBA-IPDA network model proposed in this work, which is also related to the active complex postulated in Fig. 9.

Conclusions

The addition of small amounts of nanosilica allowed a homogeneous distribution in DGEBA-IPDA matrix. The increase in the nanosilica concentration generated a greater number and wider size distribution of filler aggregates and agglomerates were not found. Addition of nanosilica increased the viscosity of the DGEBA solutions in a greater extent by increasing the filler loading, and a Newtonian behaviour was obtained. Furthermore, the addition of nanosilica decreased the gel time at any curing temperature, and catalysed the curing reaction of epoxy at room temperature leading to an increase in the reaction rate constants and a decrease in activation energy. The catalytic effect due to the addition of the nanosilica was ascribed to the formation of a nanosilica-DGEBA-IPDA network, which facilitated the creation of a silanol/oxirane ring active complex that was responsible of the autocatalytic effect.

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