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Effect of sub-micron silica fillers on the mechanical performances of epoxy-based composites

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Abstract

Solid state thermo-mechanical properties, as well as low and large strain mechanical behaviour, of epoxy composites filled with sub-micron pyrogenic silica are discussed in this paper. The reinforcement mechanisms involved are investigated. Two distinct series of pyrogenic silica were used: hydrophilic silica with various specific surface areas and silica grafted with various organo-modifications. Furthermore, two series of networks, having either a high or low crosslink density, and resulting thus either in glassy or rubbery materials at room temperature, were considered. Dynamic mechanical analysis, uniaxial tensile tests and fracture mechanic tests were performed.

All our results showed that pyrogenic silica leads to an improvement of network mechanical properties both in the glassy and rubbery states. The simultaneous increase of stiffness and toughness was observed, demonstrating the great potential of pyrogenic silica for the reinforcement of thermosetting systems. This exceptional behaviour has been interpreted in terms of the interactions and morphology developed.

Keywords: Epoxy networks; Silica; Mechanical properties

1. Introduction

Inorganic particulate filled epoxy composites have been the object of many scientific and technical studies for the last two decades due their use in a variety of applications. However, the particles considered in these composites were most of the time of micrometer size [1–3]. In fact neat epoxy networks are known to be brittle polymers with poor resistance to crack propagation, therefore most of the time some modifiers are needed. This is the reason why the use of sub-micron particles as fillers in epoxy matrices is attracting special interest as a promising and new route for improving polymer properties such as thermo-mechanical behaviour and fracture toughness, but also wear behaviour, optical performance, fire resistance etc. Indeed, it has been shown that the well-known typical trend, i.e. increase in stiffness but decrease in fracture resistance, observed in the case of addition of conventional filler into thermosetting matrices is not checked at the sub-micron scale [4,5]. The property enhancements obtained by the addition of sub-micron fillers are due to (i) the large specific surface area offered by the sub-micron fillers, i.e. the large amount of resulting interfacial zones in which the polymer chains can interact or react with the filler and display unexpected properties and (ii) the assembling of these sub-micron particles in multi-scale arrangements such as aggregates and agglomerates which can form percolated networks.

Among the sub-micron fillers, pyrogenic silica is one of the most versatile. Pyrogenic silica has been extensively used in order to reinforce rubbers, mostly silicone rubbers, as well as for rheology control, but only a few studies deal with the use of pyrogenic silica in thermosetting polymers [6–9]. Pyrogenic silica is a finely divided amorphous silicon dioxide produced by high temperature hydrolysis of silicon tetrachloride in oxygen–hydrogen flame [10–12]. Silica particles can be

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seen at three scales: primary particles of around 5–30 nm in size formed at high flame temperature, these particles are not stable, and do not exist individually. They fuse together to form stable aggregates of around 100–250 nm, then leaving the flame the silica aggregates stick together under the action of physico-chemical surface interactions (mainly Van der Waals forces), building up large micrometer size agglomerates and finally fluffy flocks of 10–1000 μm. Because of the huge specific surface area (50–400 m^2/g) of these particles, their surface silanol functional groups and the surface siloxane bonds play a major role in the surface behaviour of pyrogenic silica. The grafting of the silica surface from the reaction of silanols offers the possibility of designing both the level of interactions with the matrix (physical vs. covalent bonds) and the assembling of the sub-micron particles in the polymer medium from the balance between particle–particle and particle–polymer interactions.

In this work, novel composites based on epoxy-amine matrices filled with pyrogenic silica were considered. Two distinct series of pyrogenic silica were used: in the first one, the silica specific surface area (SSA) was varied and in the second one a chemical modification of the silica surface (amino- or epoxy-modified silica) was used. In the second case, the formation of a covalent bond between the silica and the matrix was checked [13]. Moreover, two distinct types of epoxy matrices were considered: the first one refers to networks having a high glass transition temperature T_g, i.e., such networks are in the glassy state at room temperature; the second one refers to networks having a low T_g, i.e., such networks are in the rubbery state at room temperature. Playing with the chemical structure of the curing agent allows us to vary the architecture of the network and also the nature of the interactions that could be involved between silica particles and the precursors of the networks. These networks were filled with different types of silica at a loading varying from 5 to 36 wt%. Silica particles have shown a positive effect on the mechanical and thermal properties of the materials. The final objective of this work is to develop epoxy–silica formulations which can be used as matrices in high performance composite materials, adhesives or coatings exhibiting enhanced thermomechanical behaviour.

2. Experimental section

2.1. Materials

The thermosetting matrix considered in this work was obtained via the polycondensation of an epoxy-amine system. The diepoxy prepolymer used was a DGEBA (diglycidyl ether of bisphenol A, DER330 from Dow Chemicals). It is liquid at room temperature so that the fillers can be dispersed into this part of the reactive system. Its viscosity is equal to ca. 10 Pa s at 25 °C. The first curing agent used in this study, MDEA (4,4′-methylene bis(2,6-diethylaniline) from Lonza), is a primary aromatic diamine. It presents a short and rigid chain so that the network obtained in combination with DGEBA DER330 presents a high crosslink density, and is glassy at room temperature [13]. The second curing agent used in the study, Jeffamine D2000 (bis-(2aminopropyl) poly propylene glycol from Huntsman), is an aliphatic primary diamine, presenting long and flexible chains. Its molar mass is equal to 2000 g/mol. From the combination of DGEBA DER330 with Jeffamine D2000, a network having a low crosslink density is obtained, and at room temperature this network is in the rubbery state. The reactivity of aliphatic amines is generally higher than that of aromatic ones, however, due to its long chains and also due to the presence of methyl groups close to the amine functions, kinetics of the reaction between DER330 and Jeffamine is rather slow. The presence of oxygen atoms in the chain has to be pointed out because it induces a high polarity that influences the interactions with silica. Chemical structures of components are displayed in Table 1.

Various hydrophilic silicas of specific surface area varying from 50 to 200 m^2/g (measured by BET [14]) were studied (silica D, S, N and T, see Table 2). These silica were all delivered by Wacker-Chemie AG and were commercially available. The silica N, exhibiting a specific surface area of 200 m^2/g, was used as reference among unmodified silica for most experiments. For any SSA, the silanol content on silica surface is considered constant with a value of 1.8 Si–OH per nm^2 [15]. At given silica content, the variation of the silica SSA implies a variation of the overall number of silanol groups able to develop interactions with the epoxy matrix.

Table 1
Chemical structure of monomers

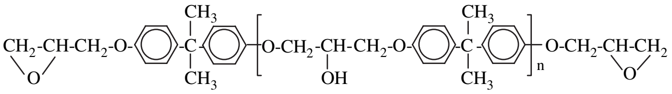
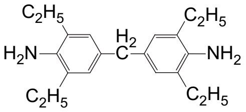
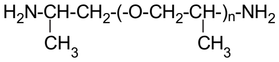
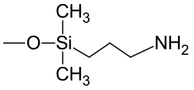
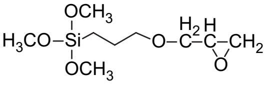
Monomers	Structural formula	Molecular weight (g/mol)
DER330 (D)		$M_n = 360$
MDEA (M)		$M = 310.5$
Jeffamine (J)	 $H_2N\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}(\text{-}O\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-})_n\text{-}NH_2$	$M_n = 2000$

Table 2
Characteristics of the different pyrogenic silica used in the study

Silica	Ref. Wacker	SSA BET (m^2/g)	Residual silanols (%)	Surface modification	Modification content (per 100 g of silica)	Structure
T	HDK T30	300	100	None	0	
N	HDK N20	200	100	None	0	
S	HDK S13	125	100	None	0	
D	HDK D05	50	100	None	0	
A	H30RA	300	10–15	Amino-modified	0.09 mol NH_2	
E	HKSA	300	30–40	Epoxy-modified	0.067 mol epoxy	

Two main categories of organo-modifications were used, i.e. amino-modified and epoxy-modified silica (references A and E, Table 2). Each of these potentially reactive modified silica was grafted from hydrophilic silica with a specific surface area of 300 m^2/g, with a controlled grafting content. The amount of grafting was checked thanks to elemental analysis of the carbon content and titration of the residual silanols on the silica surface.

2.2. Composite processing

The process implemented for the filler dispersion allows to de-agglomerate pyrogenic silica as individual aggregates and counteract their reflocculation in the organic medium under the action of colloidal forces. The standard process used for the preparation of the silica suspensions into liquid media used a high speed disk dissolver (Turbotest 33/300P from Rayneri) with a 65 mm diameter stirring disk. The silica was introduced progressively into the epoxy monomer. A mixing speed of about 500 rpm was first applied and after complete incorporation of the silica, the mixing was performed at maximum rate (3300 rpm) for 1 h. Then the silica–epoxy suspension was out-gassed and the curing agent was added. For MDEA-based systems, the suspension was heated to 90 °C in order to melt MDEA and then the mixture was poured in a mold. The curing cycle was 4 h at 135 °C followed by a post-cure for 4 h at 190 °C. For Jeffamine-based system, the comonomer was added at room temperature (Jeffamine D2000 is a liquid) and the curing cycle was 4 h at 120 °C followed by a post-cure for 4 h at 150 °C. Each of these curing cycles allowed a complete reaction of amino and epoxy groups. All composites were synthesized in stoichiometric conditions (amino-hydrogens over epoxy groups = 1, adjusted in case of amino- or epoxy-modified silica) with a silica content of 5, 10 or 15 wt% or more when feasible. The phenomenological criterion for maximum silica content is related to a limit viscosity allowing further processability of the suspension. Using the standard protocol described above, the maximum silica content dispersible was found equal to 27, 20, 15 and 13.5 wt% for silica D, S, N and T, respectively [13]. Note that if the dispersion of silica is performed in the Jeffamine D2000, which is liquid, the maximum content becomes higher because of the initial low viscosity of the medium and particular interactions developed. Except in one case (highest content of silica D), all composite materials were prepared from the dispersion of silica in the epoxy prepolymer in order to have the same protocol for the two series of networks. The nomenclature used to label the different samples is DM or DJ for the neat epoxy matrices based on MDEA or Jeffamine, respectively, and *y*X-DM or *y*X-DJ for the sub-micro composites where *y* is the wt% of silica, and X is the type of silica used (Table 2). The samples were flat panels of thickness varying between 2 and 5 mm.

2.3. Characterization of composites

Transmission electron microscopy (TEM) examination was completed using a Philips CM120 microscope. The samples were cut, at room temperature, as thin layers (between 60 and 80 nm) using an ultra-microtome with a diamond knife. The thin layers were then placed on a carbon foil on copper grids for observation.

The dynamic thermo-mechanical behaviour was characterized using a Rheometric Dynamic Analyser (RDAII) device to measure the conservation modulus, G', loss modulus, G'' and loss factor, tan δ, as a function of the temperature, at a given strain. The samples were rectangular bars measuring approximately $2 \times 5 \times 40$ mm^3. The temperature sweeps were performed at a rate of 2 °C/min and a frequency of 1 Hz, generally between 80 and 230 °C for MDEA-based systems, and between −100 and 30 °C for Jeffamine-based systems. The strain applied was checked to belong to the linear domain in all the temperature range; it was typically 1% for Jeffamine-based systems and 0.5% for MDEA-based systems. The temperature of the main mechanical relaxation, T_α, was evaluated at the temperature of the maximum of the peak of loss factor and the rubbery modulus was measured at $T_\alpha + 50$ K.

Mechanical tests were performed in uniaxial tensile configuration. In order to characterize MDEA-based systems, which are glassy at room temperature, tensile tests were performed using straight strain gages (from Vishay Micro-measurements). Stress–strain curves in the elastic region at low strain (typically $< 0.5\%$) were recorded using a tensile machine of the Instron Company, at a cross-head speed of 1 mm/min, on samples measuring approximately 3 × 15 × 120 mm^3. Tensile tests on Jeffamine-based samples were carried out on normalized samples (cut using a dye type H3) with a thickness between 2 and 3 mm, using a tensile machine 2/M from MTS. The measurements were performed at room temperature, at a speed of 10 mm/min, and continued until the sample fracture. The samples were fixed using pneumatic clamping tools with a clamping pressure of 3 bars.

Linear elastics fracture mechanics (LEFM) measurements characterize the resistance of the sample to crack propagation; it assumes that the fracture behaviour of the materials is due to the larger defect present in the sample [16]. First, the sample is notched at room temperature using a diamond saw, a fine crack is then generated due to the impact of a thin blade. The fracture strength is then measured by 3-point bending tests on the pre-notched samples and the mode I critical stress intensity, K_{Ic}, can then be deduced. Results were all obtained from a sufficient number of measurements in order to obtain a statistically reliable and accurate average.

Fractured surfaces were observed with an optical microscope, Leica Laborlux 12 POLS, and a scanning electron microscope (SEM), Philips XL 20.

3. Results and discussion

The solid state behaviour of materials is generally modified upon filler addition [17,18]. These modifications were studied as a function of silica surface characteristics (hydrophilic vs. organo-modified surface) and solid content, in order to investigate silica interactions with the network and filler influence on the dynamic thermo-mechanical behaviour, i.e., before and after glass transition, as well as on the elastic and ultimate properties at room temperature.

3.1. Silica/MDEA-based epoxy composites

3.1.1. Influence of the specific surface area of silica

First of all the TEM images shown in Fig. 1 reveal that silica is optimally dispersed into the epoxy matrix (at the level of the elemental aggregates) whatever the specific surface area. This morphology is attributed to the good interactions developed between the polar epoxy matrix and the highly polar silica surface. These images also show that the primary particle size is larger and the size distribution is broader for the lowest specific surface area (50 m^2/g).

Examples of the variations of the storage modulus, G', and loss factor, tan δ, as a function of temperature are plotted in Fig. 2 for the neat epoxy matrix, DM, and for the composite 5N-DM, filled with 5 wt% of hydrophilic silica N. Silica addition results in a large increase in T_α of about 20 °C and a decrease of the magnitude of the peak of the main mechanical relaxation, as well as an increase in the rubbery modulus, G_R'. The strong effect of silica on T_α was related to a reduction in the molecular mobility of the macromolecular chains around the filler due to strong Van der Waals interaction established between the silica surface and the epoxy matrix, including dispersion and dipolar interaction and hydrogen bonds to silica silanols. Additionally, T_α no longer increases when the silica content is increased up to 10 wt% (Table 3). This observation is in agreement with the trend observed in the literature

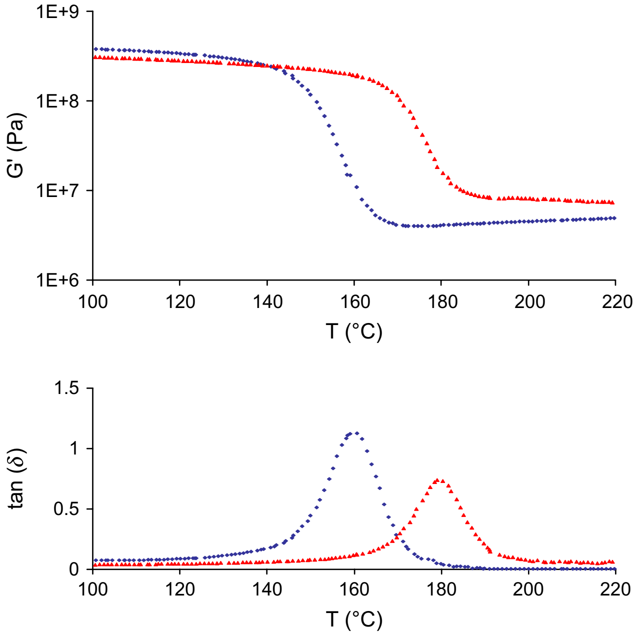


Fig. 2. Variation of G' and tan δ as a function of temperature for: (◆) neat epoxy network DM, (▲) composite 5N-DM.

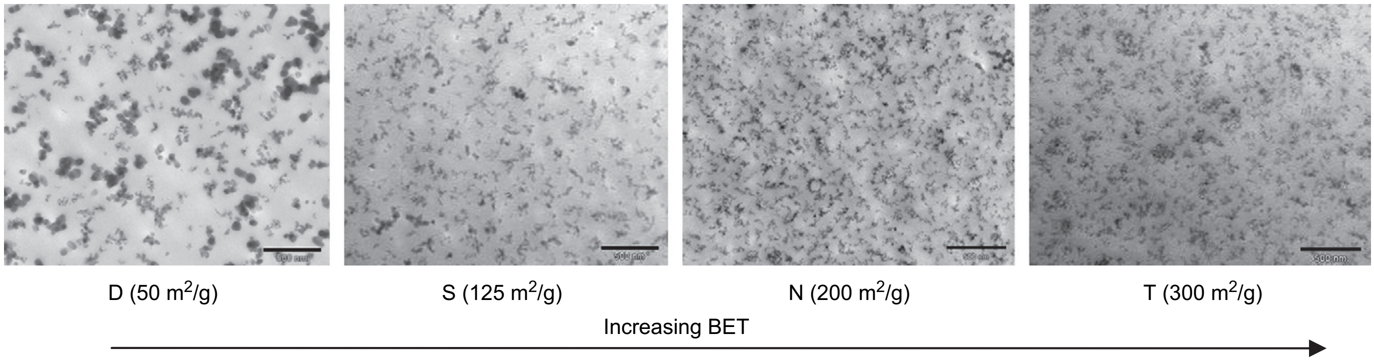


Fig. 1. TEM photographs of silica (5 wt%)/MDEA-based epoxy composites: effect of the specific surface area (BET) on the size distribution and aspect of silica aggregates. Scale bar: 500 nm.

Table 3
Results for DM matrix and silica-DM composites

Network	T_α (°C)	G_R' (MPa)	E/E_0	K_{Ic} (MPa m$^{1/2}$)	G_{Ic} (J m^2)
DM	161	10	$E_0 = 2.63$ GPa	0.71	231
5N-DM	180	11	1.01	0.85	328
10N-DM	177	19	1.08	0.75	239
10T-DM	180	27	1.21	–	–
10S-DM	–	–	1.17	0.77	231
10D-DM	148	13	1.26	0.74	203
21D-DM	162–177	28	1.46	–	–
5A-DM	177	17	1.01	0.74	248
10A-DM	174	20	1.08	0.78	259

[19]. A decrease in the magnitude of tan δ peak is observed when silica content increases, as well as a slight broadening of this peak related to a larger distribution of relaxation times. The only values and curves quoted here are not sufficient to illustrate the overall changes induced by silica addition on MDEA-based systems. Indeed, it is worth mentioning that rather straightforward effects of silica dispersion state were observed on the mean value and shape of the relaxation peak: the poorer the dispersion, the lower the impact of silica on the magnitude of the peak and T_α.

Only a slight enhancement of the Young's modulus, E, of silica-filled systems was observed as expected in the glassy state due to the low silica contents used: the increase was of less than 10% with 10 wt% (~5.4 vol%) of silica N20 (Table 3).

However, the specific surface area of silica exhibits a strong influence on the values of the Young's modulus and rubbery modulus. At a given silica content, for example 10 wt%, the Young's modulus of MDEA-based systems in the glassy state does not vary monotonically as a function of the silica specific surface area (Fig. 3). Between 50 and 200 m^2/g, there is a decrease in the modulus as the silica specific surface area increases. This effect might be either related to the existence of a critical size of the particles for the reinforcement in the glassy state, or to the high polydispersity of particle sizes displayed by the silica of lowest specific surface area, i.e., 50 m^2/g (Fig. 1). The result obtained for the composite filled with 10 wt% of silica of the highest specific surface area T, i.e., 300 m^2/g, does not follow the same trend: the Young's modulus increases and reaches a value in the same range as that for the lowest specific surface area. However, the fractal-like nature of pyrogenic silica must be taken into consideration: indeed, silica both display a mass and a surface fractal structure, expressed by the mass fractal dimension D_m and the surface fractal dimension D_s. These parameters were measured using small angle neutron scattering (SANS) [13,20] on the different epoxy/silica composites under study. The mass fractal dimension, D_m, expressed by "Guinier-like" behaviour observed on SANS patterns, characterizes the distribution of the aggregates (up to ca. 200 nm). D_m is inversely related to the openness of the structure and might thus be associated to the capacity of the silica to occlude important quantities of matrix between the "branches" of the aggregate. It is observed (Fig. 3) that the dependence of the Young's modulus in the glassy state is linear as a function of the apparent mass fractal dimension of the silica aggregates, D_m. Therefore, the relevant parameter for mechanical properties in the glassy state might result from both effects, i.e. particle size and openness of the structure. With the highest silica content that could be reached using silica D (50 m^2/g) into the DGEBA–MDEA network, the Young's modulus was furthermore improved: by almost 50% for 21 wt% (~12 vol%) of silica D.

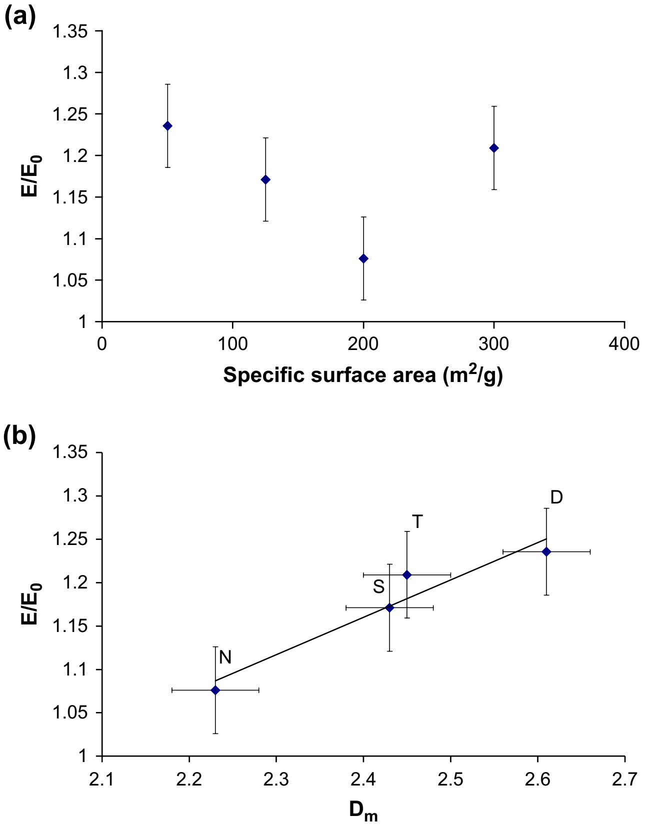


Fig. 3. Normalized Young's modulus in glassy state for MDEA-based systems filled with 10 wt% of hydrophilic silica: (a) effect of the specific surface area, (b) effect of mass fractal dimension D_m.

In the rubbery state, among all the hydrophilic silica used, better properties were achieved for those of higher specific surface area, T and N, showing the importance of the interfacial area in which polymer and silica can interact and stiffen the matrix. This might be furthermore related to the higher fractality as the SSA increases, offering greater capacity to occlude and immobilize the matrix locally. Fig. 4 shows a good correlation between the rubbery modulus, the specific surface area and the surface fractal dimension of the silica aggregates, D_s, measured by SANS at room temperature [13,20]. The surface fractal dimension, D_s, expressed by "Porod-like" behaviour observed on SANS patterns, could be measured at the scale of the primary particles (below 10 nm). D_s is related to the roughness of the surface. It was shown to vary strongly as a function of silica specific surface area: D_s increases as the SSA increases which is perhaps also due to the known presence of micro-porosities on pyrogenic silica surface at high SSA above 250 m^2/g. Locally, silica is expected to interact more with the matrix as D_s increases.

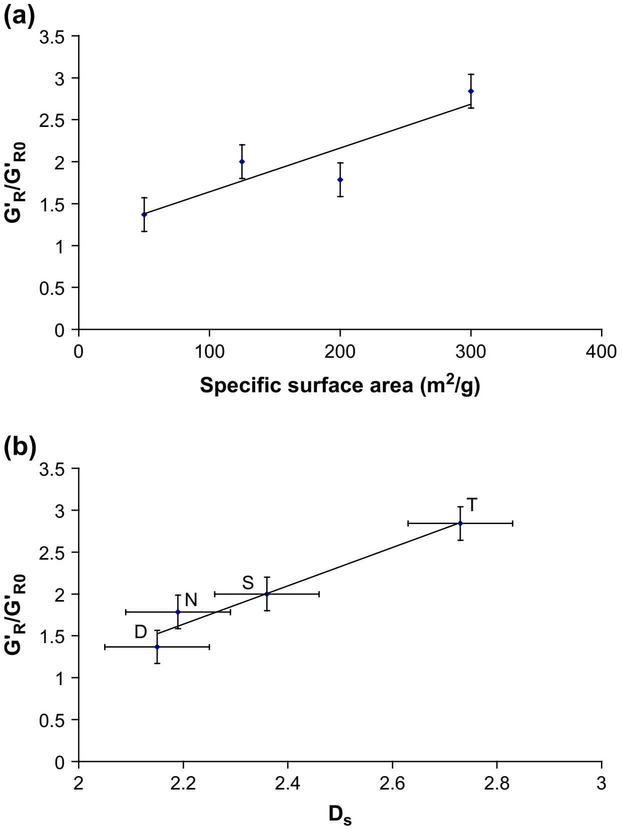


Fig. 4. Normalized storage modulus at the rubbery plateau for MDEA-based systems filled with 10 wt% of hydrophilic silica: (a) effect of the specific surface area, (b) effect of surface fractal dimension D_s.

Results from the linear elastic fracture mechanism are displayed in Table 3. The critical stress intensity factor K_{Ic} of the neat network was found to be at 0.71 MPa m$^{1/2}$, a very typical value for a highly cross-linked epoxy network. Then for all composite materials, an increase in K_{Ic} is observed. This improvement depends on the type and wt% of silica added. The toughening enhancement was up to 20% for an addition of 5 wt% of silica N. It may appear relatively moderate; however, it must be remembered that a decrease in fracture resistance is traditionally expected from the addition of stiff fillers. Additionally, the lower specific surface area appeared less efficient, maybe due to the larger particles of the size distribution leading to the traditional trend and compensating the toughening due to smaller particles. As often observed in the literature for the toughness, there might exist an optimum silica content for the enhancement of this property, which depends on the silica surface chemistry and turns out to be around 5 wt% for hydrophilic silica of specific surface area 200 m^2/g. From the measurements of the modulus and crack propagation resistance, the fracture energy, G_{Ic}, of MDEA-based systems was calculated, assuming that the Poisson coefficient was not significantly modified by the silica addition ($\nu = 0.41$ for the neat matrix). Due to the highest increase in K_{Ic} and low variation in the Young's modulus, E, the network filled with 5 wt% of hydrophilic silica N presents the greatest improvement of the fracture energy whereas the system filled with 10 wt% of hydrophilic silica D presents a decrease in fracture energy due to its higher modulus. The aspect of the fractured surface was observed by optical and electronic microscopies for the sample exhibiting the highest value of fracture energy in comparison with the neat system (Fig. 5). The surface of the neat epoxy after K_{Ic} measurements is rather mirror-like presenting distant river lines, whereas in the case of filled system, the density of the lines is greater. At a higher magnification the fractured surface appeared rougher for the filled system. This means that the surface developed has increased during the fracture of the sample leading to a higher dissipation of energy. Two main mechanisms are generally

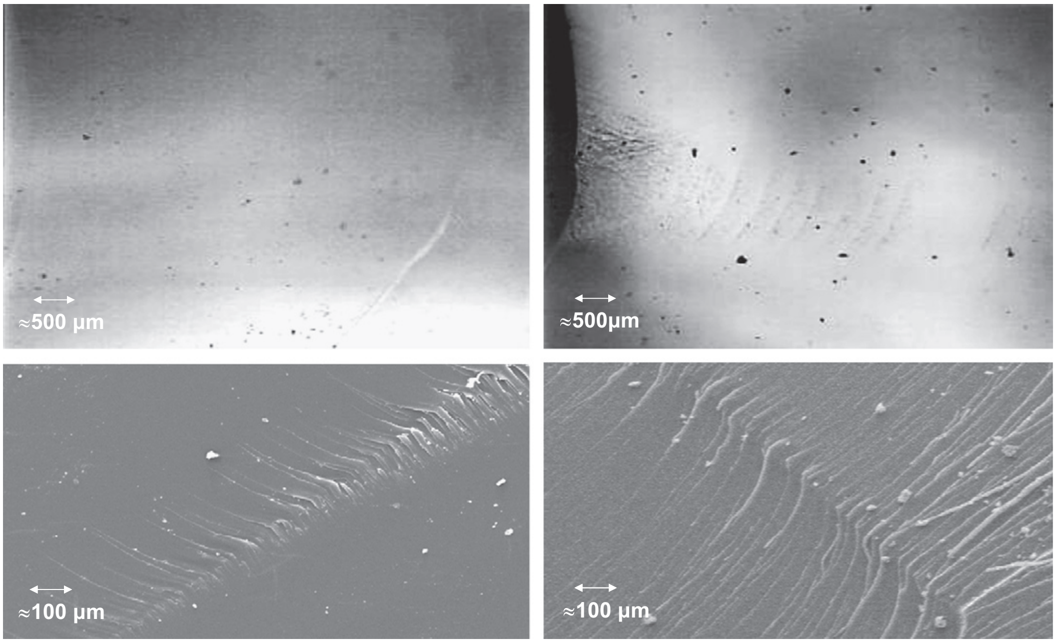


Fig. 5. Aspect of fractured surface. Left: neat epoxy matrix DM, right: silica/epoxy composite 5N-DM. Top: optical microscopy, bottom: SEM.

referred to when considering the reinforcement of epoxy resins by rigid particles: the first one is crack pinning and the second is crack tip blunting [1,2,21]. For the former, the propagation of the crack is impeded by the stiff particles that act as obstacles slowing down the advancing of the crack front, whereas the latter takes place in a localized shear yielding, with the formation of a damaged zone due to crack diversion, particle fracture and debonding of the particle/matrix interface. For the epoxy/silica composites under study, a crack pinning mechanism seems rather likely to happen, whereas there was no evidence of the occurrence of crack blunting.

3.1.2. Influence of surface modification

When the amino-modified silica, A, is used in the silica composites (5 and 10 wt%), some differences in the behaviour of the composites appear. It was proven by ^{14}N NMR and high resolution thermo-gravimetric analysis (TGA) coupled with GC/MS that this silica is able to react, at least partially, with the epoxy monomer during the dispersion step [13]. Covalent bonds between the filler and the epoxy matrix are created. However, the dispersion of silica A is not as perfect as in the case of the hydrophilic silica: some micrometric and relatively compact agglomerates remained in the material whatever the dispersion procedure used (Fig. 6). It is believed that these structures were frozen from the beginning of the dispersion process due to the reaction of the amino groups on the surface of the agglomerates with the epoxy groups from the prepolymer. Another reason is the possible back bonding of some organic segments, $-(CH_2)_3-NH_2$, which can impart a hydrophobic character to the silica surface. The variation of G' and $\tan\delta$ of 5A-DM and 10A-DM composites is very similar to the one obtained on composites based on silica N. The increase of T_α is slightly lower in the case of amino-modified silica than in the case of hydrophilic silica maybe due to the coarser dispersion state, i.e., lower interface developed. The values of rubbery modulus and Young's modulus are not significantly different. In the present study, the direct effect of the filler/matrix adhesion is difficult to distinguish from that of the dispersion state generally worse in the case of reactive silica. Apparently, the presence of agglomerates, observed for amino-modified silica, was not critical for the elastic properties neither in the rubbery nor in the glassy state as long as a fair proportion of silica aggregates was evenly and individually dispersed to participate in the reinforcement of the matrix-rich phase. The adhesion between the silica surface and organic matrix may compensate the effect of the lower dispersion state on the mechanical properties, so that they might be expected to be even slightly better for reactive silica in the case of a good dispersion. Nevertheless, even if mechanical properties are not systematically more improved for reactive silica than for unmodified silica, the interfacial adhesion developed between epoxy and silica can be furthermore important for other physical properties such as resistance to hydrothermal aging, solvent uptake, gas barrier or scratch resistance.

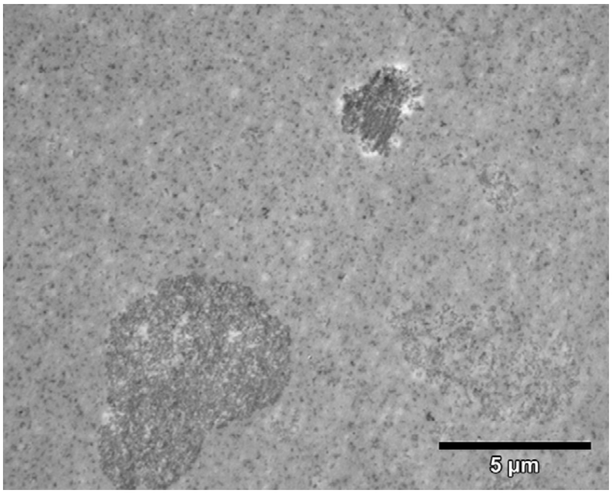


Fig. 6. TEM micrograph of the MDEA-based systems filled with 5 wt% of amino-modified silica (5A-DM).

3.2. Silica/Jeffamine-based epoxy composites

3.2.1. Influence of the specific surface area of silica

TEM observations conducted on Jeffamine-based composites show that the dispersion of hydrophilic silica is very similar to the one observed in MDEA-based composites, i.e., uniform dispersion of silica at the level of elemental aggregates into the organic medium [13]. The hardener nature did not appear as a first order parameter governing the type of morphology developed.

Dynamic mechanical behaviour for Jeffamine-based neat system, DJ, in comparison with the composite material 5N-DJ, can be seen in Fig. 7 and Table 4 to highlight the filler effect. In contrast to MDEA-based systems, the addition of 5 wt% of silica N into a Jeffamine-based network, does not lead to an increase of the temperature of the peak of main mechanical relaxation, T_α. However, like MDEA-based systems, an increase of the rubbery modulus and a decrease of the magnitude of the $\tan\delta$ peak are shown due to silica addition. When the silica content increases further (10 and 15 wt%, Table 4), G_R' shows a continuous increase while T_α remains rather constant. This latter behaviour was attributed to the soft interphase formed by the long and mobile polyoxypropylene diamine chains preferentially adsorbed on the hydrophilic silica surface due to strong dipolar Van der Waals interactions. In addition, this phenomenon might have led to a slight stoichiometric defect in the bulk, thus contributing to a slight decrease in the value of T_α of the matrix. This effect may compensate the increase of T_α that would expectedly result from the reduction of the chain mobility due to filler presence when interactions between fillers and organic matrix are created (as was the case in MDEA-based systems). Indeed, this effect does not have to be associated directly to the rubbery state of Jeffamine-based networks (at room temperature) but to the nature of the interactions generated. It can also be noted that no narrowing of the width of the peak was observed due to silica addition. This parameter represents the distribution of relaxation times of the polymeric chains and characterizes macroscopically

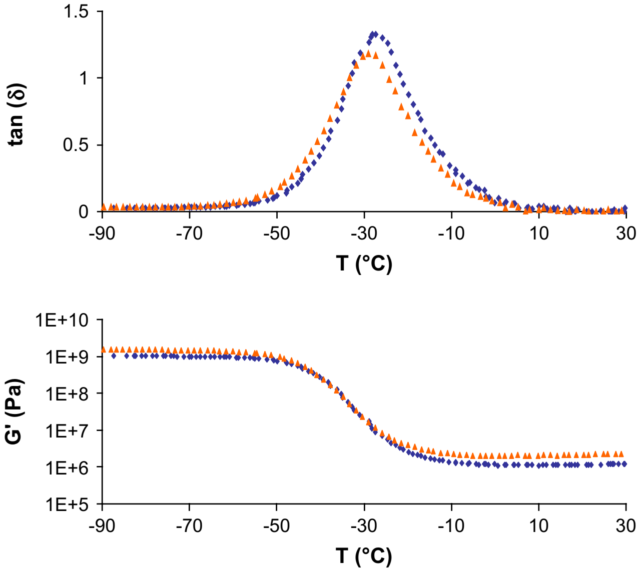


Fig. 7. Variation of G' and tan δ as a function of temperature for: (◆) neat epoxy network DJ, (▲) composite 5N-DJ.

the damping ability of the materials. The magnitude of the tan δ peak decreases as the silica content is increased. Several parameters can be involved in this phenomenon: obviously, there is the decrease of the matrix content as the silica volume fraction increases, but due to the low volume fraction of silica added, this is not a leading parameter; the volume of matrix that could be immobilized in the inner volume of the silica aggregates or in the tiny agglomerates leads also to a decrease of tan δ_{max} because it does not contribute to the relaxation.

The Coulomb modulus at room temperature, G, could be obtained from the slope of the curve of the true stress σ^* as a function of $(\lambda^2 - \lambda^{-1})$, where λ is the extension ratio ($\lambda = l/l_0$). The Young's modulus, E, was then equal to $3G$ according to the theory of rubber elasticity. The tensile curves are shown in Fig. 8 and the values of elastic modulus, strain at break, ε_{max}, stress at break, σ_{max}, and fracture energy, W, for the N-DJ composites can be found in Table 4 (in relative units). Basically, it turns out that all the mechanical properties are increased upon addition of silica N. As the filler content increases, the modulus increases, the stress at break first increases and then decreases slightly and the elongation at break decreases. The overall effect of silica addition on fracture energy resulted from the opposite variation of the stress and strain at break as a function of the silica content, so that optimal silica content was generally observed, for example ca. 10 wt% of silica N.

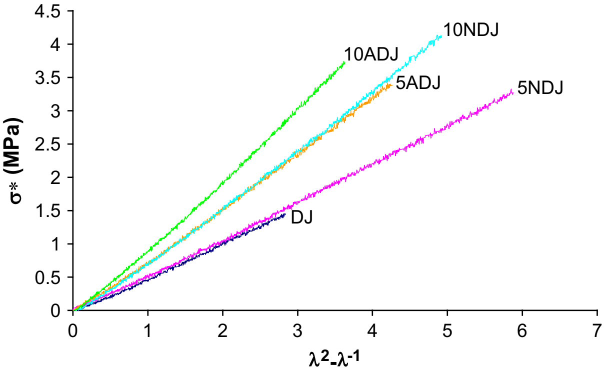


Fig. 8. Effect of the nature and content of silica on the tensile curves of Jeffamine-based systems at room temperature.

Then, as the SSA of silica is decreased, for a given content of hydrophilic silica, for example 15 wt%, it is noticed that T_α shows a tendency to increase. Such an observation is in agreement with the hypothesis previously made of a slight stoichiometric defect due to preferred adsorption of amino hardener on silica surface, i.e. with a low SSA, less surface silanols are available to create specific H-bonding interactions between Jeffamine amino groups. This phenomenon increases as the overall interfacial area displayed increases in the system. At the same time and for the same reason, the rubbery modulus shows a decrease (due to a lower stiffening of the matrix). However, whatever the system considered (silica type or weight fraction) the modulus remains always higher than the one of the neat DJ network. The ultimate properties are clearly improved when low SSA silica is used. With this silica, D, it becomes possible to add up to 36 wt% into the DJ network because of its lower influence upon viscosity. With such a high loading, a really pronounced increase in modulus is observed, however the elongation at break becomes close to the value found on the neat network. It is not really surprising as we noticed already this trend on the N-DJ networks as the silica

Table 4
Results for DJ matrix and silica-DJ composites

Network	T_α (°C)	G_R' (MPa)	E/E_0	$\varepsilon_{max}/\varepsilon_{max0}$	$\sigma_{max}/\sigma_{max0}$	W/W_0
DJ	−27	0.9	$G_0 = 0.51$ MPa	$\varepsilon_{max0} = 78.76\%$	$\sigma_{max0} = 0.74$ MPa	$W_0 = 318$ kJ/m^3
5N-DJ	−29	1.1	1.14	1.93	1.53	2.96
10N-DJ	−28	1.7	1.73	1.55	2.30	3.53
15N-DJ	−30	2	2.53	1.06	1.94	2.03
15S-DJ	−29	2	–	–	–	–
15D-DJ	−28	1.5	1.55	1.84	2.21	4.06
36D-DJ	−29	4.5	5.65	1.07	4.17	4.20
5A-DJ	−28	1.7	1.63	1.46	2.13	3.11
10A-DJ	−30	1.9	2.37	1.30	2.52	3.19
5E-DJ	−29	1.9	1.51	1.46	2	2.92
15E-DJ	−30	2.1	–	–	–	–

content was increased. This trend follows the typical toughness–stiffness as the silica loading increases.

3.2.2. Influence of surface modification

The effect of the addition of amino-modified silica or epoxy-modified silica, in comparison with hydrophilic silica, is illustrated in Table 4. There is no specific influence on the values of T_α. Some differences are observed on the mechanical properties: it appears that the enhancement of the modulus is greater for reactive silica than for unmodified silica, whatever the silica content is. This might be due to a better transfer of the load at the filler–matrix interface.

For the same systems, the effect of the formulation on the ultimate properties is shown in Table 4. It is rather opposite to that of the modulus: that is to say, for a given silica content, the elongation at break was lower in the case of amino- or epoxy-modified silica than in the case of hydrophilic silica. The lower value unexpectedly obtained for 5A-DJ or 5E-DJ composites was attributed to the presence of agglomerates or to the larger particles of the size distribution, respectively, acting as defects initiating the fracture at high strain. In general, the elongation at break was really sensitive to the dispersion state, and it decreased when increasing further the silica content. The stress at break is slightly higher in modified silica-DJ composites, and as observed before on the N-DJ composites, it increased with the silica content. Finally, the fracture energy does not show a strong dependence on the silica surface modification.

The range of the enhancement of the mechanical properties of Jeffamine-based systems in the rubbery state at room temperature is obviously much larger than that of MDEA-based systems in the glassy state at room temperature. However, this result does not depend directly on the type of hardener considered, but more on the respective state in which the samples are considered. Indeed, when MDEA-based systems are considered in the rubbery plateau, then the same conclusions arise and the range of increase of the modulus is equivalent to that for Jeffamine-based systems at room temperature. According to some mechanical models [22,23] implemented on these results, it was shown that in order to predict the influence of silica on the material stiffness in the rubbery state, an apparent volume fraction of filler including the matrix occluded and immobilized within the silica aggregates has to be taken into account. Thanks to image analysis performed on TEM photos, this parameter was estimated from the bulkiness (ratio of the convex area over area of an aggregate); the apparent volume fraction was found to be close to twice the real filler volume fraction. Thus, it appears that the open fractal structure of silica is responsible for the great enhancement of the mechanical properties in the rubbery state.

4. Conclusions

To conclude, the effects of sub-micron silica aggregates on the mechanical behaviour of epoxy matrix composites were studied in the glassy and rubbery state. Two types of epoxy matrices were considered: Jeffamine-based matrix and MDEA-based matrix. Silica specific surface area, content and surface treatment of silica were varied. Uniform dispersion of silica, at the level of the individual aggregates, in both organic matrices was shown by TEM, with only one exception in the case of the fully amino-modified silica where some agglomerates remained.

The dynamic mechanical behaviour could well be connected to the morphology and to the structure of organic-modifier grafted on silica surface. Silica addition resulted in a decrease of the mobility of the macromolecular chains. Glass transition temperature was constant in Jeffamine-based networks and strongly increased in the case of MDEA-based networks; the changes were closely related to the interactions developed in the system.

The most important result of this study is that, upon addition of pyrogenic silica, all mechanical properties are improved as compared to the neat matrices. This increase is observed in the linear region as well as in the fracture region of the composites. However, the range of these enhancements was much greater in the rubbery state than in the glassy state. Adhesion was shown as an important factor in the rubbery state especially in the elastic region. Ultimate properties were furthermore sensitive to the dispersion state.

In all the silica/epoxy composites considered in this study it has been possible to increase simultaneously stiffness and toughness, contrary to the traditional trend observed on micron sized composites. Pyrogenic silica demonstrated thus a strong potential for the mechanical reinforcement of thermosetting epoxy networks.

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