Epoxy Composites Based on Amino-Silylated MMT: The Role of Interfaces and Clay Morphology

Filomena Piscitelli,[1] Anna Maria Scamardella,[1] Valentina Romeo,[1] Marino Lavorgna,[1] Giuseppina Barra,[2] Eugenio Amendola[1]

[1]*Institute of Composite and Biomedical Materials, National Research Council, P.le Fermi 1, 80055 Portici (NA), Italy*
[2]*IMAST-Scral, P.le Fermi 1, 80055 Portici (NA), Italy*

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ABSTRACT: Epoxy-based composites containing sodium montmorillonite (MMT) modified by silylation reaction with 3-aminopropyltriethoxysilane (A1100) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (A1120) were prepared. The effect of MMT chemical functionalization, as well as inorganic content and dispersion method (i.e., sonication or combination of sonication and ball-milling) on the morphology and mechanical and thermal properties of composites was thoroughly investigated by X-ray diffraction analysis, dynamic mechanical and tensile static analysis, nanoindentation measurements and cone calorimeter tests. Morphological characterization showed that the MMT particles are only slightly intercalated by epoxy molecules. Tensile stress, elongation at failure, and toughness of the epoxy composites based on silylated MMT were found to be improved. The presence of 1 and 3% wt/wt of A1100 and A1120 silylated MMT clays allowed the tensile elastic modulus to increase respectively, of about 10 and 15% with respect to the pristine epoxy matrix. The overall results showed that (1) the silylation of MMT clays is a valuable method to improve the interfacial interaction between filler and epoxy matrix and (2) the interfacial interaction plays a role more significant than the clay morphology (i.e., the extent of clay intercalation/exfoliation) over the composite properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 616–628, 2012

Key words: composites; clay; silylation; interfaces; indentation

INTRODUCTION

Polymer/layered silicate nanocomposites (PLSNs) have attracted great industrial and academic interests, because at low filler content (i.e., lower than 5% wt/wt) they show a remarkable improvement of mechanical, thermal, and physical properties compared with the pristine polymer or conventional micro or macrocomposites.[1,2] Among the PLSNs, the epoxy-based nanocomposites are very attractive to be used as innovative materials for adhesives, coatings, and matrix for structural fiber reinforced composites. Montmorillonite (MMT) clay, available as micron size tactoides consisting of nanometric silicate layers, has been widely used as inorganic filler to modify epoxy-based materials. This is mainly due to the large availability of sodium MMT at relatively low cost. The compatibility between epoxy matrix and hydrophilic silicate layers which is mandatory to obtain high mechanical and functional performances, may be improved through an exchange of ions located into the clay structure with organophilic moieties such as alkyl ammonium ions. Zerda and Lesser[3] showed that the epoxy-based nanocomposites with MMT physically modified by alkyl ammonium salts exhibited improvements in tensile modulus but simultaneously reduction in tensile strength and strain at failure. Similar results were observed by Yasmin et al.[4] and by Velmurugan and Mohan.[5] It was suggested that the main drawback of using organic moieties as modifiers of the MMT silicates is the introduction of dangling chains that reduces the degree of polymer crosslinking and weakens the interfacial adhesion between filler and epoxy matrix. To improve this compatibility, it has been recently proposed a new approach based on the chemical silylation of silicate clays with suitable silanes as coupling agents.[6–9] In fact, along with the exchangeable interlayer ions, MMT clays exhibit hydroxyl groups on the broken edges of the silicate layers which represent reactive sites available to perform the MMT chemical modification by silylation reaction.[10] Depending on the components nature, i.e., polymer, clay and the interfacial modifier, as well as the dispersion method, the addition of clays to the epoxy matrix leads to different structures: (a) a phase separated clay-resin composite, in which the clay acts as conventional filler of the organic matrix; (b) an intercalated structure, where the epoxy resin is present within the silicate galleries allowing the inorganic layers to retain the original parallel

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Correspondence to: M. Lavorgna (mlavorgn@unina.it).
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packing; and (c) an exfoliated structure, where the silicate layers are randomly distributed into the organic matrix. The properties of the resulting materials seem to be markedly enhanced by the presence of well dispersed and exfoliated structures which, for epoxy-based nanocomposites, are favored by the *in situ* polymerization as well as the acid-catalyzed additional crosslinking reaction within the silicate galleries.[11] Unfortunately dispersion and homogenization of the MMT is hindered by the strong electrostatic interaction between the single layers as well as the epoxy crosslinking reaction which, externally to the silicate galleries, causes a fast epoxy gelation that, in turns, does opposite to the intercalation and exfoliation of the clay. To improve the MMT dispersion, particular attention has been drawn to the filler dispersion methods, i.e., either the sonication or alternative methods such as the three-roll mill[4] or the ball milling, used to apply external shearing force to clay tactoides.[12] Indeed the ball milling method is claimed to promote clay delamination preserving the lamellae structure[13] as well as resulting more effective when surface initiated curing reaction improves the shear transfer to the tactoides.[14]

However, although the results concerning dispersion, intercalation, and exfoliation of MMT in epoxy-based composites are often puzzling, it is worth noting that the improvement of mechanical properties strongly depends on the clay dispersion degree. As a matter of fact, Koerner et al.[15] stated that "the processing of thermoset layered silicate is still more an art than science" and the relative importance of morphology, interfacial strength, and extent of nanometric dispersion for improvements of physical and mechanical properties have still not been ascertained. Recently Schimidt and Giannelis[16] has verified through solvent uptake experiments that in the case of MMT dispersed into polidimethylsiloxane (PDMS) the edge interactions originated between the hydrophilic surface of the clay and the OH end-terminated polymer play a role more significant than the extent of clay exfoliation. In this context Shi et al.[17] have been the first to explicitly note the potential importance of the polymer/layer edge interactions in nanocomposites as well as the need to further evaluate their role in affecting mechanical properties.

In this work we have studied the effects of MMT silylation reaction with aminosilanes, namely 3-aminopropyltriethoxysilane (A1100) and *N*-(2-aminoethyl)-3aminopropyltrimethoxysilane (A1120), on the interfacial adhesion with the epoxy matrix. The amine moieties anchored by silylation to the pristine MMT are able to further react with epoxy rings concurring to the organic network building. The influence of different dispersion methods i.e., sonication and a combination of sonication and high energy ball-milling, on the morphology as well as mechanical and thermal properties of the composites was investigated by X-ray diffraction (WAXD), scanning electron microscopy (SEM), dynamic-mechanical analysis, nano-indentation, tensile tests, and fire resistance properties. We found that the exfoliation or intercalation of MMT clays is not a key parameter and the synergistic effect of good filler dispersion and reactive amino-organic moieties anchored to the silicate surface is more effective in enhancing mechanical properties of epoxy-based composite.

EXPERIMENTAL

Materials

Sodium montmorillonite (denoted as Na-MMT), with cation exchange capacity (CEC) of 92 meq/100g, was purchased from Southern Clay Products Inc. Diglycidyl ether of bisphenol-A (DGEBA) with epoxy equivalent weight of 187 g/mol and the hardener *meta*-xylylenediamine (MXDA) were purchased from Sigma Aldrich; 3-aminopropyltriethoxysilane (A1100) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (A1120) with a purity of 98% were obtained from GE Advanced Materials. Glycerol was purchased from Fluka. All chemicals were used as received.

Functionalization of montmorillonite

Montmorillonite (MMT) functionalization was carried out by means of the silylation reaction of sodium MMT with 3-aminopropyltriethoxysilane (A1100) and *N*-(3-(trimethoxysilyl)propyl)ethylenediamine (A1120). In particular Na-MMT was stirred in glycerol with each aminosilane (50/50 wt/wt is the Na-MMT to aminosilane weight ratio) at 80°C for 3 h. Then the solid product was separated by centrifugation, washed in distilled water, and dried for 3 h at 80°C in vacuum condition. More details about the effectiveness of silylation reaction were reported in a previous article by some of the authors.[18]

Preparation of the epoxy nanocomposites

The epoxy nanocomposites were prepared by using two different procedures, namely sonication mixing (S) and a combination of sonication and high energy ball-milling (SB). A schematic representation of the procedures is reported in Figure 1.

Sonication mixing (S)

The modified and unmodified clay was first mixed with DGEBA by using the Thinky planetary vacuum

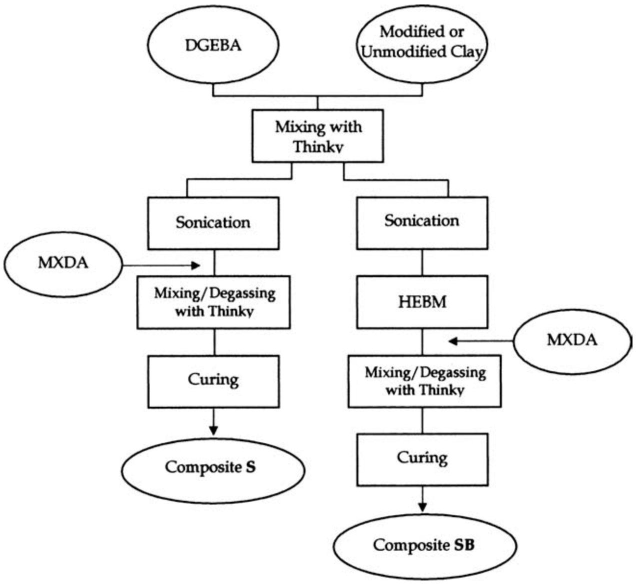

Figure 1 Processing methods of epoxy/MMT nanocomposites.

mixer for 2 min at 2000 rpm. The resulting mixture was sonicated for 30 min (Probe Sonicator Misonix mod. S4000). Afterwards, the hardener was added and the mixture was degassed for 4 min in the planetary vacuum mixer, poured in special molds, and finally cured at 30°C for 1 h, 60°C for 1 h, 90°C for 1 h, 100°C for 1 h, 120°C for 1 h, and finally at 150°C for 1 h. This curing cycle allowed the conversion of the epoxy groups to be completed as confirmed by FT-IR and DSC analysis (data not reported for the sake of brevity). An epoxy control matrix was prepared by using this procedure without the addition of clay.

Sonication and high energy ball-milling mixing (SB)

In this method, the mixture of DGEBA and modified or not-modified clay, was first processed by sonication and then submitted out to a second high shear dispersion process by using a high energy ball milling (PM100 from Retsch (Germany)) for 1 h at 580 rpm. Afterwards the hardener was added, the reacting mixture was degassed and cured by using the thermal curing process previously described for composites prepared by sonication method. An epoxy control matrix was prepared by using this procedure without the addition of clay.

Composites with 1 and 3% wt/wt of net inorganic clay content (i.e., exclusive of organic content due to the moieties introduced by silylation) were prepared. In the case at hand, the content of aminosilane organic moieties was 8.1% and 8.8% wt/wt for MMT-A1100 and MMT-A1120 powders, respectively.[19,20] The composite materials prepared by using unmodified Na-MMT clay are simply labeled as Na-MMT, whereas those obtained by using silylated MMT are labeled as MMT-A1100 and MMT-A1120 for samples including clays functionalized respectively, with A1100 and A1120. Additional numbers and letters complete the labels of the samples by indicating the weight content of clay (i.e., 1 and 3%) and the preparation method (i.e., S and SB).

Characterization

Wide angle X-ray scattering (WAXD) spectra were collected by using a SAXSess Instrument manufactured by Anton Paar (Cu-Kα radiation, $\lambda = 0.1542$ nm) to determine the basal spacing of the silylated and pristine Na-MMT clays, both as powders and as fillers in the epoxy composites. Counts were accumulated by means of an imaging plate detector in the 2θ range between 2 and 40°. The scattering data were dark current and background subtracted and then normalized for the primary beam intensity.

Dynamic-mechanical measurements (DMA) were performed with a DMA Q800 manufactured by TA Instruments, using the single cantilever geometry, an oscillation frequency of 1 Hz and a strain amplitude of 25 μm. The specimens were dried at 80°C for 24 h before testing, and then tested from 0 to 180°C at a heating rate of 3°C/min.

Tensile properties were measured with a SANS CMT universal testing machine in accordance with the ASTM-D638-03 by using a load cell of 1 kN, a crosshead speed of 1 mm/min and an initial preload of 0.2 N. All measurements were carried out at room temperature. The results were averaged on five values.

Scanning electron microscope (SEM, Leica mod. S440) was used to observe the morphology of samples fracture surface after tensile tests. A thin layer of gold was sputtered on the fracture surface of specimens before SEM investigation, for providing electrical conductivity.

The indentation experiment was performed with a NanoTest^{TM} Platform made by Micro Materials, aimed to evaluate mechanical properties including modulus, hardness, and creep behavior. A Berkovich diamond tip with three-side pyramidal geometry is driven to indent the surface of sample. The nano-indentation tests were conducted at a maximum load of 100 mN, with an initial load of 0.02 mN. The load was then held at maximum value for 60 s and the creep behavior was simultaneously monitored. Finally the indenter was withdrawn from the sample with the same rate used during the loading cycle until the value of 10 mN was reached. At least 20 indents were performed on each sample and the distance between the indentations was about 100 nm to avoid interaction effects. The hardness was evaluated as the indentation maximum load (i.e., 100 mN) divided by the projected contact area, which for a perfectly sharp Berkovich indenter is calculated as:

$$A = 24.56h_c^2 \tag{1}$$

where h_c is the contact depth.

The elastic modulus was derived from the reduced elastic modulus by using the following formula:

$$\frac{1}{E_r} = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i} \tag{2}$$

where E and v are respectively, the elastic modulus and the Poisson's ratio ascribed to the tested sample, whereas E_i and v_i are the same parameters for the indenter. In this work v was set as 0.35,[21] E_i and v_i are equal to 1140 GPa and 0.07, respectively.[22]

Thermogravimetric analysis (TGA) was carried out by using a TA Instruments Q5000 TGA. The samples were heated from 30 to 800°C at a heating rate of 10°C/min in air flux.

Combustion studies were performed by using an oxygen consumption calorimeter (Fire Testing Technology, FFT dual cone calorimeter model) in the vertical orientation mode. The rectangular samples $10 \cdot 10 \cdot 0.5$ cm^3 were irradiated with a Heat Flux equal to 35 kW/m^2. Heat release rate (HRR) was measured in triplicate and the results are shown as the average of the curves. It is worth mentioning that usually the HRR measurements with cone calorimeter are performed by adopting the horizontal orientation mode, with sample oriented horizontally with respect the irradiating metal jackets. However, due to the intrinsically inhomogeneous microstructure of the epoxy resins, the horizontal configuration does not provide reliable results, whereas the vertical orientation allows the heat boundary layer to be well established around the sample, providing more consistent results. The experimental error was evaluated to be ranged in 5 to 10%.

RESULTS AND DISCUSSION

WAXD characterization of powders and epoxy-clay pastes and composites

To investigate the effect of the silylation reaction on the typical layered morphology of Na-MMT, WAXS analysis of unmodified and silylated powders was performed. The spectra are reported in Figure 2 as intensity versus the scattering vector, $q = (4\pi/\lambda)\sin\theta$ where λ is the X-ray wavelength and θ the scattering angle. As shown, the Na-MMT diffraction pattern exhibits the characteristic (001) diffraction peak at 4.94 nm^{-1} corresponding to the basal interlayer spacing, d calculated as $2\pi/q$ equal to 1.27 nm.[23] As for the silylated powder, this peak shifts to lower scattering vector, indicating an enlargement of the MMT gallery between the silicate layers. In fact the MMT-A1100 powder shows the diffraction (001) peak at 4.10 nm^{-1}, corresponding to an interlayer spacing of 1.53 nm, whereas it increases to 1.89 nm for the MMT-A1120. It is worth noting that for MMT-A1120 powder, a second reflection peak at a basal spacing value of 0.93 nm appears, probably corresponding to the (002) diffraction peak.[24] Clearly the interlayer spacing of MMT increases with the organic dangling length of aminosilanes and the results confirm that aminosilanes have been intercalated in the silicate gallery of Na-MMT.

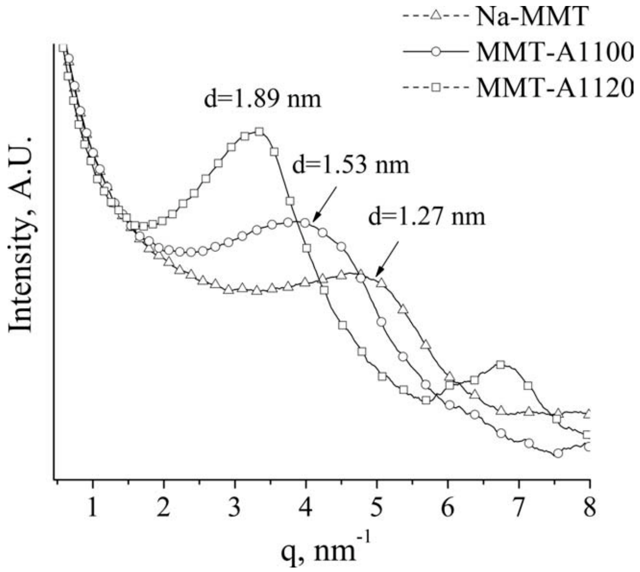

Figure 2 X-ray diffraction patterns of the pristine and silylated Na-MMT powders.

Since the experimental procedures for the preparation of epoxy-based composite materials consisted of an *in situ* polymerization achieved by means of a preliminary sonication mixing step (S) or a combination of sonication and ball-milling (SB) before the subsequent curing step, it is worth to investigate the materials morphology at two stages of the synthesis, namely before and after curing.

In Figure 3 the spectra of the pastes obtained by dispersing the MMT-A1120 powders through both sonication (S) and sonication/ball milling (SB), the spectrum of MMT-A1120 powders and the spectrum of completely cured composite MMT-A1120 3% SB are reported.

The interlayer spacing of the silylated MMT is not significantly affected by the sonication mixing procedure, whereas it is markedly reduced due to the synergistic effect of sonication and ball-milling. It is also worth noting that the shape of the diffraction peak, i.e., the full width at half maximum, exhibited

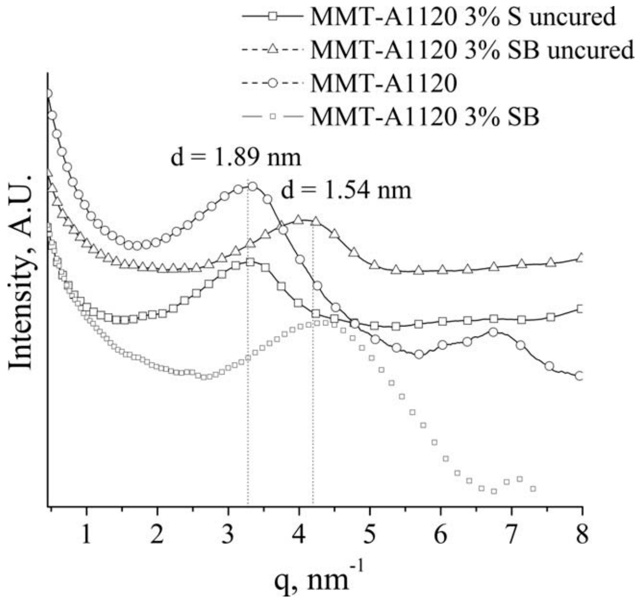

Figure 3 X-ray diffraction spectra of the epoxy pastes containing MMT-A1120 obtained by sonication and sonication/ball-milling mixing procedures compared with the spectra of MMT-A1120 powder and MMT-A1120 3% SB composite.

by the functionalized MMT powders processed by sonication and sonication/ball-milling mixing procedure is somewhat unchanged in comparison with the neat powder. This indicates that the organic moieties grafted or intercalated by silylation allow the clay to retain the tactoide internal structure as well as the aggregation of the original constituting silicate layers.[25] Similar WAXD features have been collected for the pastes obtained by dispersing modified and unmodified MMT in epoxy resin through S and SB mixing procedures and also for cured composites (they are omitted for sake of brevity). The characteristic interlayer spacing for all materials, namely powders, pastes, and composites, with 3 wt % of pristine and silylated MMT clays are reported in Table I.

Since the epoxy monomer van der Waals dimensions are 1.46·0.4·0.35 nm^3,[26] it is reasonable to expect that no intercalation of epoxy monomer is able to occur into the galleries of Na-MMT. As a matter of fact, by subtracting the layer thickness of 0.96 nm from the interlayer spacing, the remaining separation of about 0.33 nm is too small to have been penetrated by the epoxy monomer. On the other side, despite the silylated clays show only a slight increase of the interlayer spacing upon mixing with DGEBA resins, the galleries size is compatible with the intercalation of the epoxy monomers. In particular for the MMT-A1100 and MMT-A1120 clays dispersed in epoxy matrix by sonication method, the remaining separations equal respectively, to 0.75 and 0.93 nm, are namely large enough to host the epoxy monomers.[27,28]

Moreover, as reported in Table I, the sonication mixing procedure favors an enlargement of silicates layers due to the penetration of epoxy monomers only for the MMT-A1100, since its interlayer spacing increases from 1.53 nm to 1.71 nm. On the other hand, since the interlayer spacing of MMT-A1120 was not modified by the sonication it can be expected that the intermolecular interactions between the amine groups of grafted and intercalated organic moieties prevent the epoxy monomers to further enter into the silicate galleries.[18]

Additionally, the interlayer spacing of pristine and functionalized MMTs in the composites are quite comparable with the ones of the epoxy pastes before the curing process. The difficulty in achieving further increase of the interlayer spacing can be ascribed to the sonication mixing which probably enhances the reaction between the amine groups grafted to the edge of the surface of the silicate layers and the epoxy monomers. Probably this crosslinking reaction occurring preferentially on the outside of the silicate galleries, allows the epoxy gelation time to be locally decreased, and the viscosity increased. As a consequence the silicate layers aggregate, not allowing the interlayer spacing to be further increased.[29]

In summary the results obtained by the X-ray diffraction characterization performed on the powders, pastes and composites can be resumed as following:

- The interlayer spacing of the modified Na-MMT increases with the length of aminosilanes used for the silylation reaction;
- During dispersion of modified clays in epoxy resin, the sonication mixing procedure allows the interlayer spacing to increase only for the MMT-A1100 clay whereas the ball-milling dispersion method compacts the layered structure;
- The crosslinking reaction which takes place during the dispersion of silylated MMT in the resin hinders the intercalation of epoxy monomers in the silicate galleries. Thus the retention of layer-layer correlations leads to composites with micron scale reinforcing particles.

TABLE I
Interlayer Spacings for Modified and Unmodified Clay, Pastes, and Composite Materials

	Interlayer spacing (nm)				
		Paste		Composite	
	Powder	S	SB	S	SB
Na-MMT	1.27	1.29	1.30	1.26	1.51
MMT-A1100	1.53	1.71	1.57	1.70	1.45
MMT-A1120	1.89	1.89	1.54	1.89	1.48

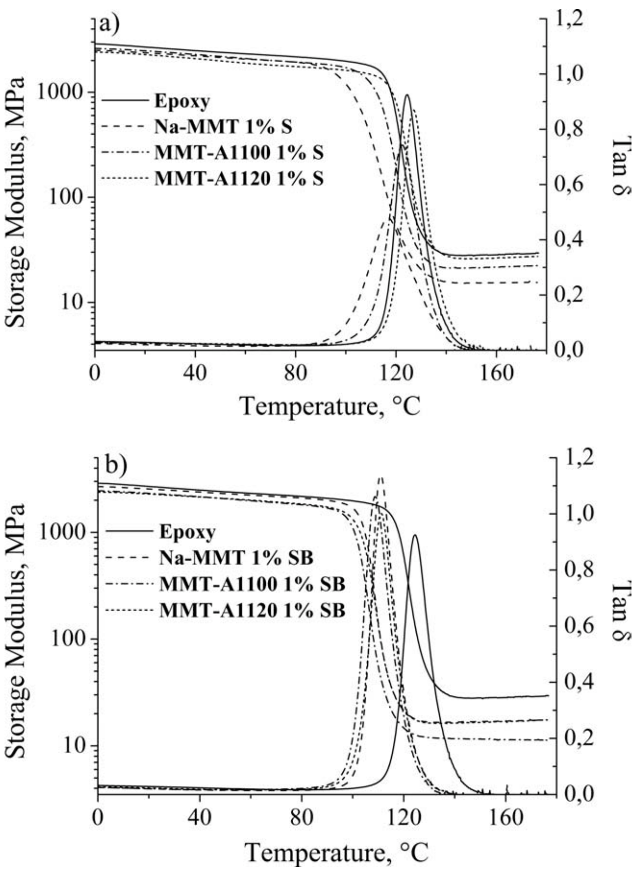

Figure 4 Storage modulus and tan δ versus temperature for epoxy resin and composite with 1% wt of modified and not-modified MMT obtained by sonication (a) and sonication and ball-milling mixing procedure (b).

DMA analysis

Representative dynamic-mechanical plots for neat epoxy resin and epoxy-clay composite containing 1 wt % of pristine and modified MMT, prepared by adopting both S and SB methods, are shown in Figure 4(a,b). The elastic modulus at 150°C, the crosslinking density and the T_g values, as maximum of tanδ curves, are showed in Table II. The elastic modulus from DMA analysis has not been taken into account since several variables, i.e., loading mode, experimental conditions, machine compliance and specimen span-to-thickness ratio and alignment, affect its measurement.[30,31]

It is worth noting that both the T_gs and the elastic modulus at 150°C of epoxy-clay composites with 1 and 3% wt/wt of pristine Na-MMT clays result markedly lower than the values characteristic of neat epoxy matrix. This reduction could be ascribed to poor interfacial interactions between the inorganic fillers and the polymeric matrix as well as to both the plasticization effects due to residual water onto the silicate lamellae and the modification in the organic network building-up.[15] In fact, the sonication process likely favors the base catalyzed homopolymerization reaction at the silicate layers edges leading to an organic network with greater chain mobility.[32] In this case a portion of epoxy groups could be reacted by homopolymerization and consequently an excess of MXDA curing agent remains unreacted in the systems as free dangling, causing a reduction in T_g values.[33] The same properties, i.e., T_g and elastic modulus in the rubbery region, increase for the composites prepared with silylated clays, approaching the values of neat epoxy. Moreover, this behavior is quite evident for composites prepared through the sonication procedure (S method), which display the more pronounced epoxy monomers intercalation in the silicate galleries. Hence, these results highlight the crucial role of the interfacial interactions in the final properties of composites. In fact, in the silylated MMT composites the improved properties with respect to the composite

TABLE II
Elastic Modulus at 150°C, T_g, and Crosslinking Density Values for Neat Epoxy and Epoxy-Clay Composites Determined by DMA Analyses

	T_g (°C)	Elastic modulus at 150°C (MPa)	Crosslinking density[a] (mol/m^3)·10^{-3}	T_g (°C)	Elastic modulus at 150°C (MPa)	Crosslinking density[a] (mol/m^3)·10^{-3}
	Preparation method					
Samples	(S)	(S)	(S)	(SB)	(SB)	(SB)
Epoxy resin	124	28.1	2.66	123	27.1	2.56
Na-MMT 1%	117	15.3	1.45	110	16.9	1.60
MMT-A1100 1%	123	21.4	2.02	108	11.6	1.10
MMT-A1120 1%	127	26.0	2.46	111	16.6	1.57
Na-MMT 3%	104	11.6	1.10	91	3.0	0.29
MMT-A1100 3%	117	23.4	2.22	98	11.0	1.04
MMT-A1120 3%	122	23.1	2.18	99	5.7	0.54

[a] According to the assumption of rubbery theory, above T_g, the rubbery modulus is directly related to the crosslinking density of the epoxy resin which can be expressed as $\nu_e = E/3RT$ where E is the modulus at 150°C, R is the gas constant, and T is the absolute temperature.[34]

based on pristine clay could be ascribed to the chemical interactions which establishes between the amine moieties of silylated clays and the epoxy resin. These interactions could be either covalent bonds originated by the nucleophilic addition of amine group onto the epoxy ring, namely the crosslinking reaction, or hydrogen bonding between the amine and the hydroxyl groups. The latter are both originated by the opening of epoxy rings or located at the edge of MMT lamellae.[10] Moreover, in the case of epoxy-clay composites prepared by means of the combination of sonication and ball-milling procedures, the clay silylation is not able to improve the composite properties. Probably the compacting effect of the silicate layers due to the ball-milling process as well as the aggregation of the tactoides counteract the improved interfacial compatibility, resulting detrimental on the mechanism of load transfer between the filler and the polymeric matrix. Similar results, namely the reduction of both the T_g values and elastic modulus in the rubbery region, were also observed by Brawn et al.[32] for epoxy matrix filled with Cloisite 6A, a dimethyldehydrogenated tallow, quaternary ammonium chloride modified clay. In that case the detrimental effect was associated to the organic moieties present inside the modified clay which in view of the authors resulted chemically not compatible with the epoxy resins and easily released plasticizing the epoxy network.

Irrespective of the experimental procedures adopted to disperse the filler, the epoxy composite materials show a crosslinking density lower than those of epoxy resins. Furthermore, the modulus at 150°C as well as the crosslinking density (see Table II) exhibited by the composite based on amino-silylated clay does not increase linearly with the filler amount. Since these clays are reactive and can participate to the network formation, by increasing the filler concentration a proportional increase in the crosslinking density would have been expected. This trend is clearly not observed in Table II. All that may be indicative of several factors cooperating to further strengthen the epoxy network of the composite based on amino-silylated clay as the polymer absorbed on the filler surface (i.e., increase of entanglements) or the polymer-stabilized filler network rather than any filler-induced changes in the crosslinking density.[35] However, as already stated, the epoxy network is also affected by the extent of homopolymerization promoted by the neat clay as well as amino-silylated clays and the consequent modification of epoxy resin groups/crosslinking agent ratio during crosslinking reaction.

Tensile test

Figure 5(a,b) show some stress-strain curves of composites with 1 and 3% wt/wt of both pristine and silylated MMT; the related curve of the neat epoxy resin is reported as comparison. The curves displayed are the most representative with characteristics comparable with the average values of elastic modulus, ultimate tensile strength, and elongation at break reported in Table III.

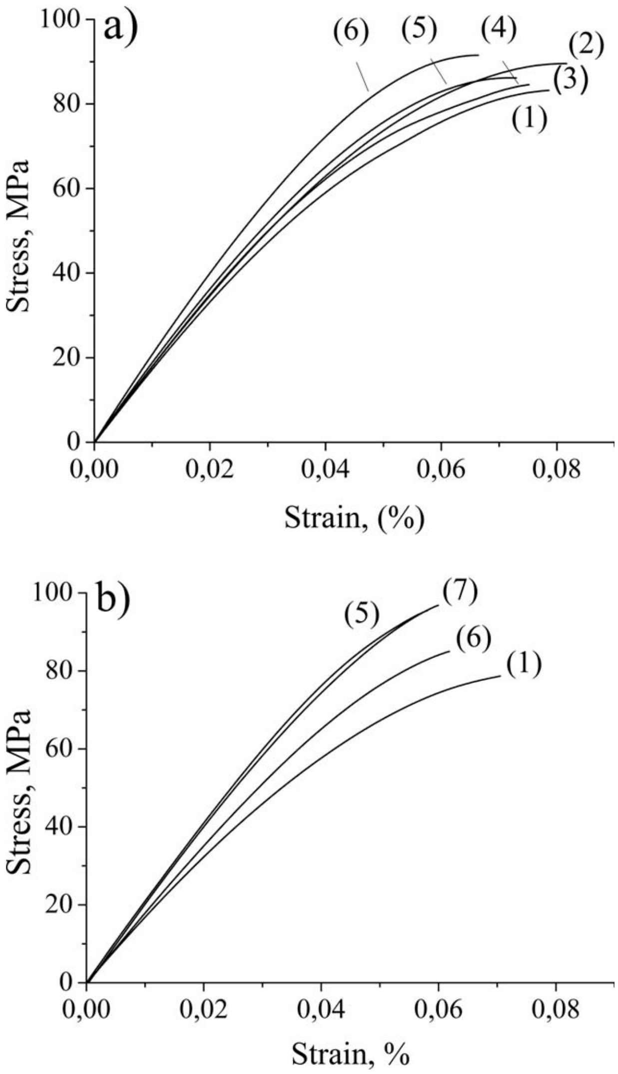

Figure 5 Stress-strain curves of neat epoxy matrix and of epoxy-clay composites (a) with 1% wt/wt and (b) 3% wt/wt of clays: (1) neat epoxy resin, (2) Na-MMT S, (3) MMT-A1120 S, (4) MMT-A1100 S, (5) MMT-A1120 SB, (6) Na-MMT SB, and (7) MMT-A1100 SB. S stands for sonication method and SB for sonication-ball milling method.

The epoxy-clay composites prepared with 1 and 3% wt/wt of pristine and silylated MMT clays exhibit improved tensile strengths and elastic moduli with respect to the neat epoxy resin; whereas the strain at break decreases for composites with 3% wt/wt and slightly increases for those with 1% wt/wt of clays. Moreover, it is evident that since the clay layers were not highly intercalated by the epoxy resins (as showed by WAXD analysis), the improvements observed in mechanical properties derive

TABLE III
Tensile Properties of Pristine Epoxy Resin and Epoxy-Clay Composites

	Tensile strength (MPa)	Elastic modulus (MPa)	Strain at break (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Strain at break (%)
	Preparation method					
Samples	(S)	(S)	(S)	(SB)	(SB)	(SB)
Epoxy resin	76.5 ± 2.3	1670 ± 20	7.0 ± 0.5	76.3 ± 2.3	1668 ± 20	7.0 ± 0.5
Na-MMT 1%	87.0 ± 2.5	1760 ± 20	7.7 ± 0.6	87.4 ± 4.4	1710 ± 20	6.6 ± 0.5
MMT-A1100 1%	84.3 ± 4.5	1800 ± 20	7.9 ± 0.3	87.5 ± 5.2	1780 ± 20	7.2 ± 0.5
MMT-A1120 1%	83.2 ± 2.5	1850 ± 20	7.8 ± 0.6	88.0 ± 4.0	1805 ± 20	7.5 ± 0.6
Na-MMT 3%	77.7 ± 1.5	1785 ± 20	6.3 ± 0.5	84.5 ± 1.9	1825 ± 20	6.3 ± 0.8
MMT-A1100 3%	80.5 ± 4.5	1930 ± 20	6.0 ± 0.3	90.0 ± 2.6	1842 ± 20	6.7 ± 0.5
MMT-A1120 3%	79.0 ± 2.4	1935 ± 20	6.5 ± 0.3	89.0 ± 2.5	1866 ± 20	6.5 ± 0.5

mainly from the better interfacial interactions between the epoxy matrix and the silylated filler. In fact the epoxy-clay composites filled with silylated MMT show a further enhancement of the mechanical properties compared to those prepared with pristine MMT, for which the overall effect is mainly due to the presence of stiffer inorganic particles. Similar results were obtained by Ha et al.[9] for nanocomposites prepared with epoxy resin and clays silylated with A1100. They found that both the elastic modulus and ultimate tensile strength increase with the clay content and ascribed this behavior to both the better filler dispersion and the improved interfacial strength, which in turn restrained the epoxy matrix cracking.

Aimed to highlight the mechanical behavior of composites at varying the organic moieties grafted on the clay layers, the elastic moduli and tensile strengths are reported in Figures 6 and 7, respectively, for either composites with 1 and 3% wt/wt of clays.

The elastic tensile modulus of the epoxy-clay composites increases with the clay content regardless the processing procedures (i.e., S or SB method). This response is characteristic of composite materials reinforced with particles stiffer than the neat matrix. Furthermore the elastic modulus of composites with 1% wt/wt of clays increases with the organic molecules chain length used for the silylation reaction. Improvements of about 10 and 15% with respect to the neat epoxy resin are observed for the samples containing 1 and 3% wt/wt of clays functionalized with A1100 and A1120, respectively. This behavior is superior to that exhibited by conventional composites where low concentrations (i.e., lower than 10% wt/wt) of the inorganic filler induce no or negative effects to the tensile mechanical properties.[36] An improvement of the elastic modulus equal to 10% with respect to the neat epoxy resin was obtained by Xidas and Triantafyllidis[37] through the complete exfoliation of the inorganic layered filler at a filler content of 3% wt/wt for the epoxy resin in the glassy region and 6% wt/wt in the rubbery state. These results confirm that the silylation approach is greatly able to improve the interfacial interactions polymer/filler in comparison with the simple

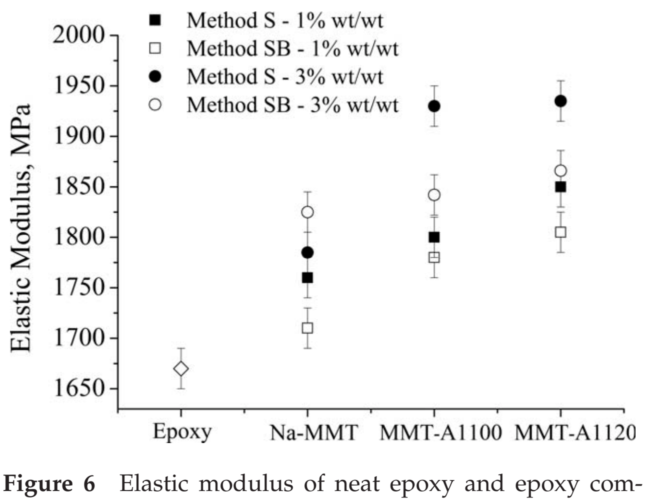

Figure 6 Elastic modulus of neat epoxy and epoxy composites based on clay and ammino-silylated MMT.

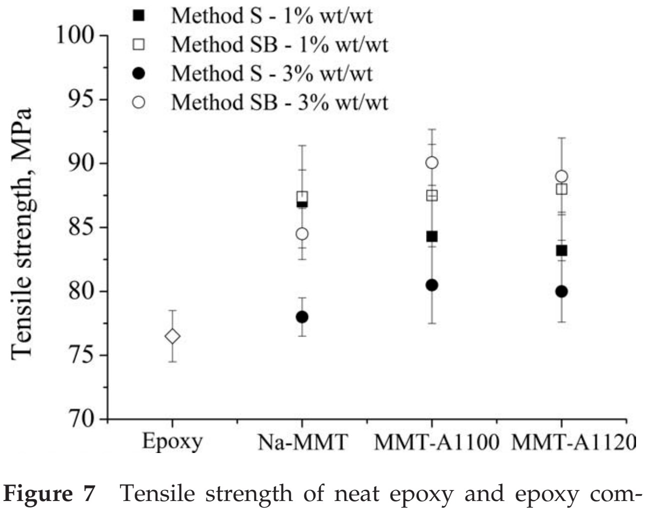

Figure 7 Tensile strength of neat epoxy and epoxy composites based on clay and ammino-silylated MMT.

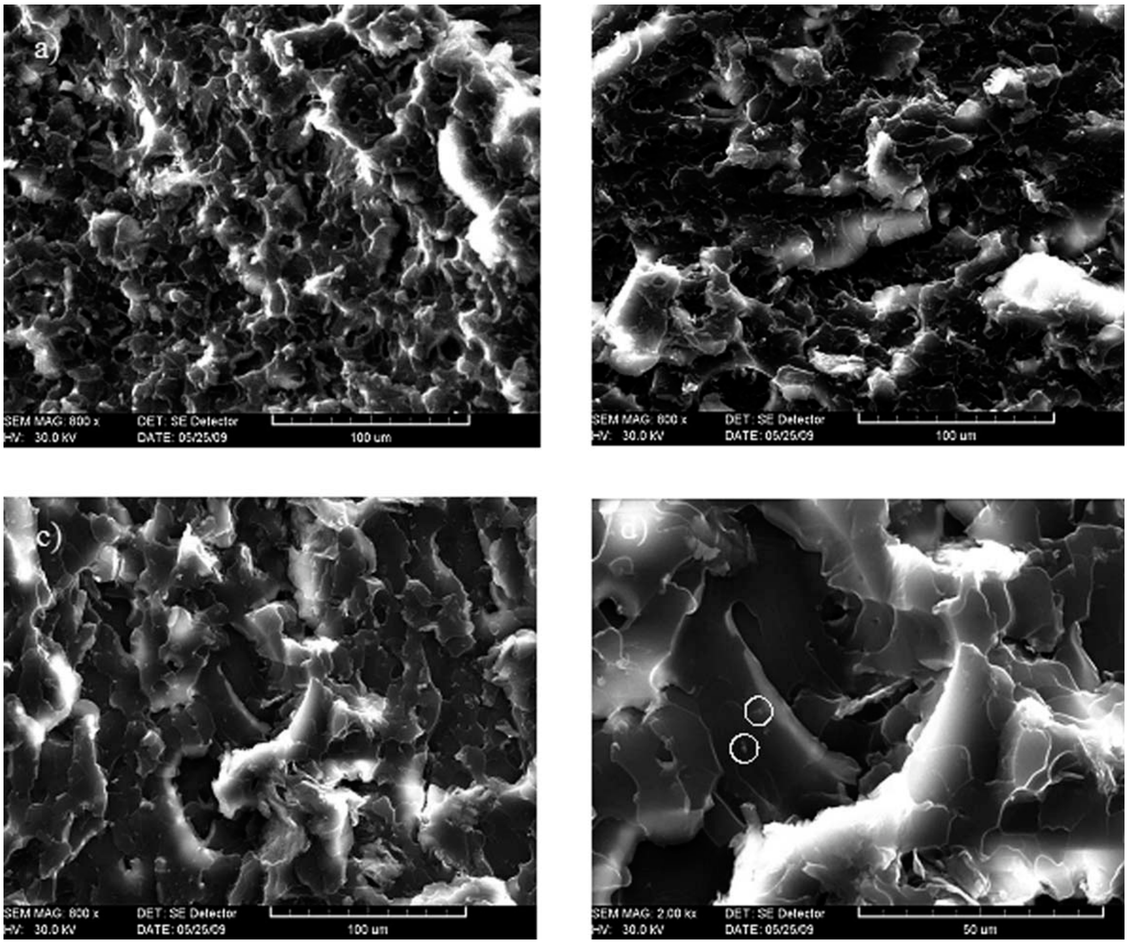

Figure 8 Typical fracture surfaces of epoxy resin (a), MMT-A1120 3% SB (b), MMT-A1120 3% S (c) samples at ×800 magnification and MMT-A1120 3% S sample at ×2000 magnification (d).

dispersion of microsized fillers as well as, in some case, the intercalation/exfoliation of organo-modified clays. Recently, Schimidt and Giannelis[16] have showed that in polysiloxane/layered silicate nanocomposites the interactions between the OH groups owing to the polysiloxane and MMT layers play a more significant role than exfoliation in reinforcing the composites. These edge-interactions can also contribute to restrict the mobility of polymer chains under loading, improving the mechanical behavior.[38] Finally, the ultimate tensile strength of epoxy-clay composites is higher than that of the neat epoxy matrix; in particular it has been found that for composites with 1 wt % of filler the ultimate tensile strength does not depend on the mixing procedure whereas for those at 3 wt % the combination of sonication and ball-milling assures the highest values.

Since the area under the stress-strain curves corresponds to the toughness in kJ/m^3 units, the curves in Figure 5 were also used to estimate the toughness of both the neat epoxy resin and the epoxy-clay composites. The toughness estimated for the epoxy matrix is equal approximately to 3300 kJ/m^3. The composites with 1% wt/wt of filler exhibited a toughness markedly increased (about 4000 kJ/m^3) with respect to that of the neat epoxy, since they exhibit higher ultimate tensile strength and similar or slightly increased strain at break. On the other side the composites with 3% wt/wt of filler, exhibited reduced toughness (about 3000 kJ/m^3) since their strain at break is lower compared to that of the neat epoxy resin.

Therefore, it can be suggested that the presence of reactive organic moieties (i.e., grafted amine groups) represents a feasible approach to overcome the detrimental effect on the mechanical properties due to the inorganic particles dispersed on the microscale range (i.e., tactoides or aggregates of tactoides) in the epoxy network.

SEM analysis

Figure 8 shows the fracture surfaces for neat epoxy resin, MMT-A1120 S, and MMT-A1120 SB composites with 3% wt/wt of filler. These images have

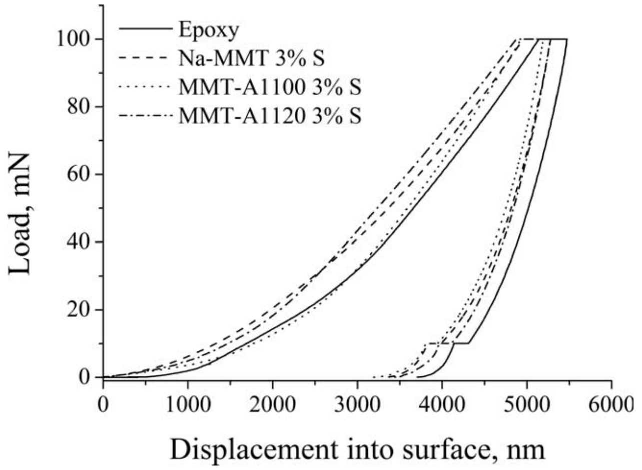

Figure 9 Load-displacement curves of both the neat epoxy and epoxy-clay composites prepared by sonication method (method S).

been selected as the most representative of the fracture behavior exhibited by the several samples.

The neat epoxy system shows a wrinkled fracture surface typical of a ductile behavior. Contrary the composites exhibit a less wrinkled fracture surfaces characteristic of a more fragile fracture behavior. In the specific case of composites containing 3% wt/wt of clay, the fracture behavior could be due to the presence of clay aggregates, which acting as a crack initiation sites cause the failure of the samples to be occurred at lower strain in comparison with the epoxy resin [as shown in the stress-strain curves of Fig. 5(b)]. It is worth noting from higher magnification image reported in Figure 8(b) that there is not voids formation in the vicinity of particles as consequence of the good interaction between silylated particles and the epoxy matrix.

Nanoindentation analysis

Although the fracture and mechanical behavior of epoxy-clay composites has been extensively investigated over the past years, less attention has been paid to the study of stress transfer mechanism between clay and epoxy. In this respect Shen et al.[22] have verified the ability of the nanoindentation technique to evaluate the time dependent mechanical properties of epoxy nanocomposites. In particular, they showed that a clay loading level of about 2.5% wt/wt maximized the creep resistance. At higher clay loadings, the creep resistance decreases due to the plasticization effect of the alkyl ammonium chains which reduced the crosslinking density in proximity of the silicate layers.

Typical loading-hold-unloading profiles under a maximum load of 100 mN, are showed in Figure 9 for both the neat epoxy and composites with 3% wt/wt of clay, prepared by sonication method (i.e., method S). Similar profiles were obtained for the composites prepared through the combination of sonication and ball-milling procedure (i.e., method SB). The results show that the neat epoxy resin possesses the lowest resistance to indentation force and the highest maximum indentation depth before and after the holding segment, respectively. For the epoxy-clay composites the load-displacement curves is shifted upward (i.e., it is necessary a higher force for the indentation depth) and the composites with MMT-A1120 shows the highest indentation load at depths higher than 2500 nm.

In Table IV the elastic modulus, the creep displacement at 60 s and the hardness values measured from indentation tests for pristine epoxy and epoxy-clay composite materials are reported.

The composites obtained through sonication method clearly show creep resistance higher than neat epoxy matrix. On the other side the composites obtained by combination of sonication and ball-milling dispersion procedure, exhibit a lower creep resistance. This may be ascribed to the worse dispersion of clay tactoides and to the lower crosslinking density of the epoxy network.[22] Additionally, the nanoindentation results show that the hardness increases with the addition of clay, since all composites exhibit hardness values higher than that of the neat epoxy. Moreover, the hardness value seems to depend on the dispersion procedures, the clay loadings as well as the clay silylation. In details, the composites prepared through sonication by using MMT-A1100 and MMT-A1120 clays show an increment of hardness of about 35 and 50%, respectively, with respect to the pristine epoxy. This result could be ascribed to the dispersion method, since the sonication seems to allow a better dispersion and then a better interface interaction between clay tactoides and the epoxy matrix. On the other hand, the combination of sonication and ball-milling increases the

TABLE IV
Mechanical Parameters from Indentation Test

Samples	Elastic modulus (GPa)	Creep displacement at 60 s (nm)	Hardness (GPa)
Epoxy resin	4.01 ± 0.33	348.90 ± 12.40	0.145 ± 0.05
Na-MMT 3% S	4.10 ± 0.19	297.18 ± 15.46	0.162 ±0.02
MMT-A1100 3% S	4.30 ± 0.34	298.83 ± 13.73	0.195 ± 0.06
MMT-A1120 3% S	4.34 ± 0.23	336.65 ± 11.67	0.220 ±0.05
Na-MMT 3% SB	3.70 ± 0.32	352.53 ± 15.88	0.169 ±0.03
MMT-A1100 3% SB	4.20 ± 0.39	363.10 ± 16.07	0.178 ±0.04
MMT-A1120 3% SB	4.29 ± 0.15	347.91± 18.02	0.157 ±0.05

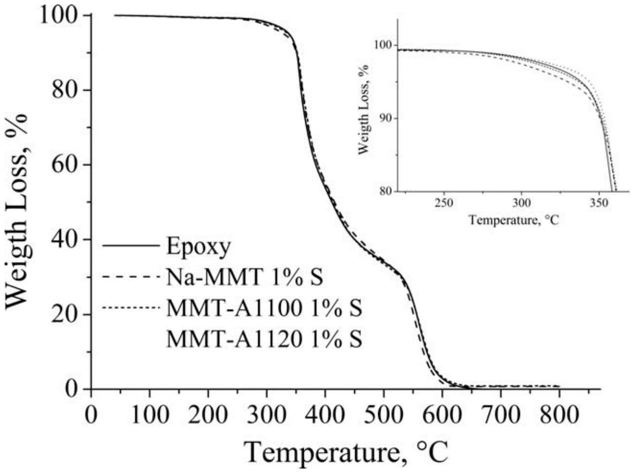

Figure 10 TGA curves in air flow of the neat epoxy resin and composites with 1% wt/wt of Na-MMT, MMT-A1100, and MMT-A1120 prepared by sonication method.

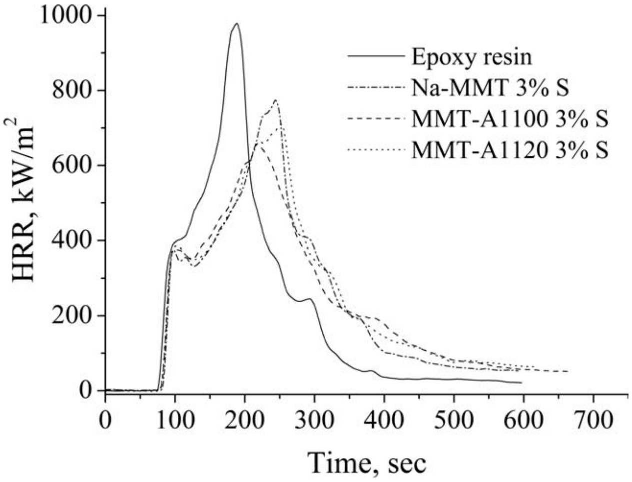

Figure 11 HRR from cone calorimeter test for both the neat epoxy and composites prepared by sonication method.

aggregation of clay tactoides, reducing the interfacial interaction between clay tactoides and the organic matrix despite the silylation reaction.

It is worth noting that the values of elastic modulus obtained by nanoindentation tests are different from those obtained by tensile measurements, although each techniques show that the introduction of clays stiffens the matrix. The differences in terms of absolute values have to be ascribed to the different experimental conditions, i.e., applied loading rate.[39]

TGA and cone calorimeter analysis

Thermal properties of neat epoxy resin and epoxy-clay composites have been investigated by thermogravimetric analysis and cone calorimeter tests. In Figure 10 the thermal gravimetric curves of the neat epoxy resin and epoxy-clay composites with 1% wt/wt of both the modified and unmodified MMT obtained through sonication are reported. In the inset, an enlargement of the first degradation region is reported. Similar plots are achieved for all the other composites.

Pristine epoxy resin shows a thermally oxidative degradation which occurs through a three step process with maximum rates at around 300, 410, and 520°C due to the degradation of the epoxy network, the charring formation and the complete oxidation of the char, respectively. It is worth noting that the presence of clay filler does not significantly affect the thermal oxidative degradation mechanism of the epoxy matrix, probably because of its low content. The degradation temperatures are listed in Table V as the onset temperatures at which a mass loss of 3% wt/wt occurs.

Figure 11 shows the average trend of the heat release rate (HRR) as a function of the time for both the neat epoxy and the composites.

Fundamental parameters are the maximum value of the HRR and the time corresponding to the peak. These parameters, together with the ignition time, are shown in Table VI.

TABLE V
On-Set Degradation Temperatures of Epoxy Resin and Epoxy-Clay Composites

	T_{id} (3% weight loss) (°C)	
Samples	S dispersion method	SB dispersion method
Epoxy resin	321	320
Na-MMT 1%	306	311
MMT-A1100 1%	316	316
MMT-A1120 1%	328	324
Na-MMT 3%	308	326
MMT-A1100 3%	309	324
MMT-A1120 3%	303	302

TABLE VI
Comparison of Time to Ignition, t_{ig}, and HRR of Pristine Epoxy and Epoxy-Clay Composites

		HRR		
Sample	t_{ig} (s)	Time (s)	HRR (max) kW/m^2	Percentage in comparison with epoxy resin (%)
Epoxy resin	80	187	970	100
Na-MMT 3% S	80	240	766	79
MMT-A1100 3% S	83	220	650	67
MMT-A1120 3% S	83	253	712	73

Regardless the silylation of MMT clays, the addition of 3% wt/wt of clay in the epoxy resin causes a significant delay in the HRR peak and a reduction of the intensity at maximum of HRR peak. However, compared with the neat Na-MMT, the addition of MMT-A1100 and MMT-A1120 results in two different effects: (1) a further reduction of the HRR peak depending on the improvement of the dispersion of MMT-A1100 tactoides, and (2) a slight increasing of the time necessary to reach the HHR peak when MMT-A1120 clays is used as filler. The reduced flammability of composites with silylated clays can be ascribed to the more effective dispersion of particles throughout the samples which causes an enrichment of layered silicate at the surface, acting as gases and heat barrier. It is also worth noting that the reduction of the HRR maximum obtained for composite materials with silylated clays is an important insight since in most of the epoxy composites filled with organomodified clays, i.e., clays modified with alkyl ammonium salts, it has been often observed an increase of HRR with respect to the neat epoxy resin.[40] Conversely to the composites with organo-modified clay, the presence of silylated filler and the enhancement of the interfacial interactions between filler and epoxy resin, does not affect negatively the fire resistance behavior.

CONCLUSIONS

Epoxy-based composites have been produced by using sodium montmorillonite (Na-MMT) untreated and modified with two different aminosilanes, i.e., 3-aminopropyltriethoxysilane (A1100) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (A1120) via a silylation reaction. Two different dispersion methods have been employed to prepare epoxy/clay composites, namely sonication and a combination of sonication and high energy ball-milling. The basal spacing of the modified Na-MMT increased with the aminosilanes organic chain length, suggesting that the organic moieties were intercalated into the clay galleries. However, despite no exfoliation was observed in the composite materials, the physical, thermal, and mechanical properties of composites with silylated clays are particularly interesting. As a mater of fact, DMA results confirmed that silylation of clay tactoides improved the interfacial interaction between the micro-sized filler and epoxy matrix, since the composites with silylated MMT exhibited T_g higher than composites with pristine clay. Moreover, tensile modulus and toughness of composites with silylated MMT were improved significantly with respect to both the neat epoxy and composites with pristine clay. This behavior can be ascribed to the chemical interaction between epoxy molecules and amine groups of grafted silane on MMT particles. All results strengthen the idea that the interfacial interactions between the ammine moieties anchored to the clay surface and the epoxy matrix play a more significant role than the degree of clay exfoliation in determining the properties of the epoxy base composites.

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