

Epoxy–silica polymers as restoration materials

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Abstract

The epoxy monomer 3-glycidoxypropyltrimethoxysilane reacts, under non-hydrolytic conditions, with the primary amine (3-aminopropyl)triethoxysilane in 2:1 (**1**), 5:1 (**2**) and 10:1 (**3**) molar ratios leading to epoxy–silica materials which were characterized by TGA, DSC, Raman, and NMR investigations. The epoxy ring opening and the hydrolysis reactions of the Si(OR)₃ groups were examined by means of ¹³C NMR before gelation occurs. The identification of the different types of silicate substructures present in the solids **1**, **2** and **3** was accomplished by ²⁹Si CP-MAS NMR spectroscopy which also provides a quantitative measure of the degree of condensation through the relative abundance of *T*⁰ [RSi(OR)₃], *T*¹ [RSi(OR)₂OSi], *T*² [RSi(OR)(OSi)₂] and *T*³ [RSi(OSi)₃] silicon nuclei. The combined results of the Raman and ²⁹Si CP-MAS investigations clearly show that all the mixtures, especially the higher ratio ones, are characterized by a high degree of cross-linking; in addition, for **2** and **3**, residual epoxy fragments are still present in the solid structure. The absence of residual enthalpy curing peaks in the calorimetric analysis indicates that the volatiles are simply released from all the samples. The thermogravimetric analysis shows that, among all the mixtures, **1** is featured by different structural properties which cause a higher degradation temperature and a longer decomposition time.

To evaluate the effect of different experimental conditions on the properties of the final products, the reactions were also performed in the presence of small amounts of KOH and of a stoichiometric amount of water to effect hydrolysis of Si(OR)₃ groups. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Consolidation and surface protection of historical buildings [1,2] is today attained by treating decayed stones with polymerizable monomers such as Si(OCH₂CH₃)₄, RSi(OCH₃)₃ (R = CH₃, C₂H₅) [3] or organic polymers [4, 5]. Although featured by tunable mechanical and adhesion properties the latter species suffer, as a common feature of most of the polymers used in conservation and restoration activity, from a marked tendency to yellowing, lower durability than silicon compounds and higher susceptibility to weathering. Furthermore they do not meet other requirements such as low viscosity (less than 10 mPa s) and high penetration depth. The penetration depth is a key factor of a conserving material since it must be deep enough to exceed the maximum moisture zone as well as go beyond the damaged thickness. Only low-molecular weight

materials diffuse and penetrate rapidly inside the pores while larger molecules are confined in the surface region. ‘In situ polymerization’ [6], following stone impregnation with a polymerizable low-molecular weight monomer, was suggested as an alternative technique to the capillary absorption of the polymeric solution or suspension.

Aimed to develop new materials with chemical, physical and mechanical properties adapted to the specific needs of cultural heritage, we report here on the synthesis, TGA, DSC, Raman and NMR investigations of epoxy–silica materials obtained by inducing polymerization on the epoxy 3-glycidoxypropyltrimethoxysilane (GLYTS) through the primary amine (3-aminopropyltriethoxysilane) (ATS) (Fig. 1). The above materials offer two merits: (i) the polymerization process can be carried out inside the stone starting from low-molecular weight monomers; (ii) the Si(OR)₃ groups, after hydrolysis and condensation, allow to insert hard inorganic micro-domains into the epoxy polymeric network.

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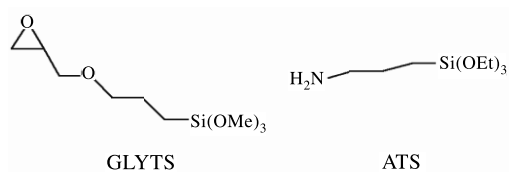


Fig. 1. GLYTS and ATS.

2. Experimental section

3-Glycidoxypropyltrimethoxysilane (GLYTS) and (3-aminopropyl)triethoxysilane (ATS) were purchased from Fluka and used as received. ^{13}C NMR spectra were recorded on a Bruker AMX R-300 spectrometer operating at 75.47 MHz. Solid state ^{29}Si CP MAS NMR spectra were recorded with a Bruker AMX 300WB spectrometer operating at 59.62 MHz. FT-IR spectra were obtained on Perkin-Elmer FT 1720X on KBr disks. Micro-Raman measurements ($300\text{--}1700\text{ cm}^{-1}$) were carried out with 632.8 nm (He-Ne laser) excitation and a Jobin Yvon HR460 spectrometer equipped with a liquid-nitrogen cooled CCD detector. A TA Instruments TGA-DTA 2960 thermal analyzer was employed for thermogravimetric analysis under either nitrogen or air flow at 100 ml/min and heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Thermo-oxidation residues were analyzed by an FT-IR spectrometer Thermo Nicolet Nexus with Smart Endurance accessory. Differential scanning calorimetry (DSC) experiments were run with a TA Instruments DSC 2910 under nitrogen flow at 60 ml/min and heating rates of 10 or $20\text{ }^\circ\text{C}/\text{min}$. Polymer heatings were also performed in a coil-type flash pyrolysis apparatus operating at $250\text{ }^\circ\text{C}$, with direct analysis of volatiles in a combined gas chromatography/mass spectrometry (GC/MS) system. A CDS Pyroprobe was used and the volatile products were analyzed by a Hewlett-Packard HP5890A gas chromatograph interfaced to a HP5970 quadrupole mass spectrometer. Separation was obtained by a HP5-MS, methyl silicone coated column.

3. Results and discussion

GLYTS has been widely used as a coupling agent in the preparation of a variety of cross-linked inorganic-organic hybrid polymers but its properties have been mainly exploited under hydrolytic conditions [7–11]. It may react either with the appropriate catalyst or co-reactant leading, via oxirane ring cleavage, to a polymeric network or via hydrolysis of the $\text{Si}(\text{OR})_3$ groups leading to species containing the Si–O–Si core. On the other hand, ATS is able to interact with both the active sites of GLYTS. In fact it may catalyze the hydrolysis of the $\text{Si}(\text{OR})_3$ groups via nucleophilic attack of hydroxyl anions [12] or, alternatively easily react with the oxirane ring leading to the formation of secondary or tertiary amines. Epoxy cross-linking and inorganic cross-linking are therefore concomitant processes,

which may occur when GLYTS and ATS are reacting. Independently from the reaction sequence, organic polymer chains covalently linked to inorganic domain size may be expected.

Room temperature reaction of GLYTS, in an open system, with net ATS in 2:1 (**1**) molar ratio leads, a few minutes after mixing the reactants, to the formation of a high viscosity mixture which rapidly (24 h) assumes a rubbery consistence. The rate of the sol-gel phase transition decreases when high ratios, 5:1 (**2**) and 10:1 (**3**), mixtures are used. On the contrary, the reactions are slow when performed in a closed system, either as a bulk or in solution implying that air moisture provides the necessary water to effect the hydrolysis reaction. The epoxy ring cleavage and the hydrolysis reactions of the $\text{Si}(\text{OR})_3$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) groups have been monitored by ^{13}C NMR spectra at different stages of the reaction just after mixing the reactants and until the liquid phase was present. The ^{13}C NMR spectra in CDCl_3 of the 2:1 bulk mixture show the progressive disappearance of the resonances associated to the methylenic group of the epoxy fragment and the methylene neighbor to the NH_2 groups centered at 43.72 and 44.63 ppm, respectively. The signals of the $\text{Si}(\text{OCH}_3)_3$ fragment at 50 ppm gradually disappear being replaced by new superimposed resonances, in the 50–55 ppm region, very likely due to partially hydrolyzed $\text{RSi}(\text{OR})_{3-x}\text{OH}_x$ ($x = 1, 2, 3$) species. No signals attributable to poly(ethylene oxide) or diol species were detected indicating that the oxirane ring is not involved in secondary reactions such as homo-polymerization or hydrolytic cleavage [9]. On the contrary, the resonances of the epoxy fragments are still well detectable in the ^{13}C NMR spectra of the 5:1 and 10:1 mixtures even after 30 days clearly showing that not all the epoxy groups are involved in the process. The glassy solids, obtained after curing ethanolic solutions of **1**, **2** and **3** for four months at $30\text{ }^\circ\text{C}$, were studied by a number of spectroscopic techniques. FT-IR spectra were not of much help to get information on the degree of cross-linking as well as the cleavage of the epoxy ring. In fact the absorptions due to residual silanol groups, which represent a useful indication of the extent of the inorganic network formation, or to uncleaved oxirane rings, cannot be confidently assigned due to several medium and weak-intensity bands in the range $900\text{--}980\text{ cm}^{-1}$. The only valuable information is found in the absorption domain ranging from 1000 to 1200 cm^{-1} were two broad bands culminating at 1027 and 1124 cm^{-1} , assigned to Si–O–Si stretching vibrations, are detected [13,14].

Differently from FT-IR, Raman spectroscopy is a powerful tool to detect the epoxy ring cleavage since the absorption of the inplane expansion and contraction of all three ring bonds, an active Raman mode, appears as a strong polarized band at 1256 cm^{-1} . Furthermore two absorption domains, lying in the range $600\text{--}700$ and $400\text{--}500\text{ cm}^{-1}$, are diagnostic of the presence of partially hydrolyzed $\text{Si}(\text{OR})_3$ groups and Si–O–Si network formation,

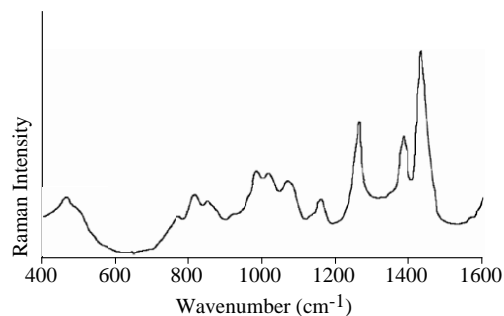
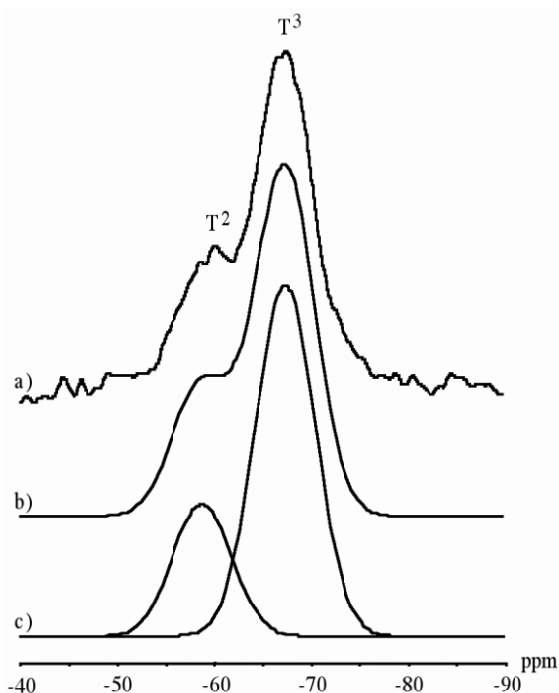
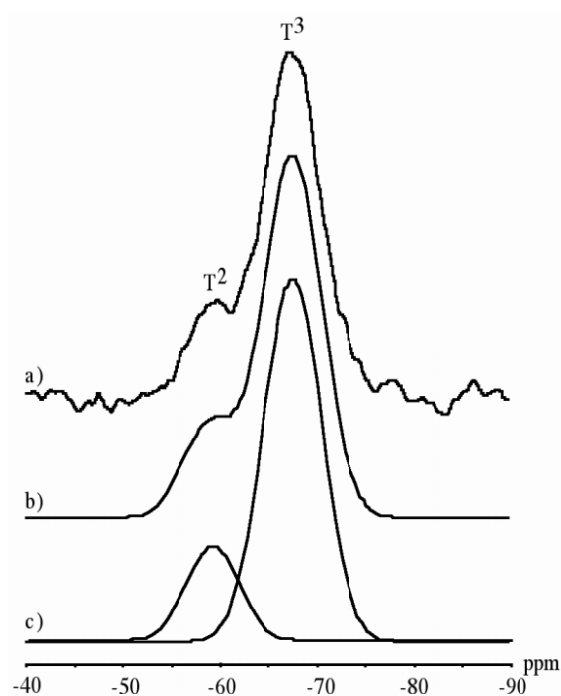


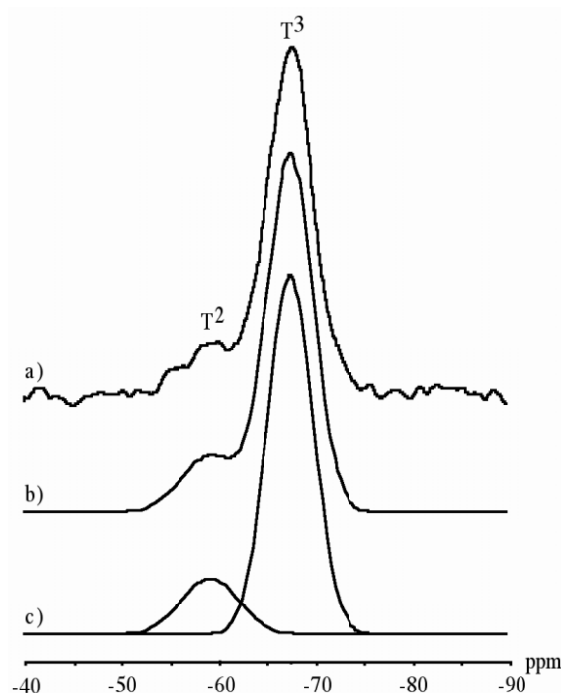
Fig. 2. Raman spectrum of sample 1.

respectively. The Raman spectra of the 2:1 (**1**) mixture (Fig. 2), in the 600–700 cm^{-1} region, do not show the strong polarized bands due to the symmetrical $\nu(\text{SiO}_3)$ stretching of the $\text{Si}(\text{OR})_3$ groups of GLYTS (641 cm^{-1}) and ATS (651 cm^{-1}) as well as any absorption attributable to partially hydrolyzed $\text{RSi}(\text{OR})_{3-x}\text{OH}_x$ ($x = 1, 2, 3$) [15] strongly suggesting a high degree of cross-linking. A broad absorption, culminating at 467 cm^{-1} , due to the $\nu(\text{Si}-\text{O}-\text{Si})_n$ stretching of siloxane fragments, is also observed. The epoxy breathing absorption at 1256 cm^{-1} , no more observable in the Raman spectrum of **1**, is still detectable in the spectra of **2** and **3** confirming that not all the epoxy rings are involved in the cleavage reaction and that the ring cleavage reaction is dependent on ATS concentration. These findings suggest that the reaction occurring in the high ratio GLYTS/ATS mixtures mainly involves the hydrolysis and condensation of the $\text{Si}(\text{OR})_3$ groups more than the epoxy ring cleavage. This suggestion is in agreement with the Micro-Raman study of a gel obtained by reacting a 19:1

Fig. 3. ^{29}Si CP-MAS NMR spectrum of sample 1 (a); global (b) and single peak (c) fitting curves obtained with SPORT-NMR.Fig. 4. ^{29}Si CP-MAS NMR spectrum of sample 2 (a); global (b) and single peak (c) fitting curves obtained with SPORT-NMR.

GLYTS/ATS mixture under hydrolytic conditions. The spectra of this material do not show evidence of uncondensed $\text{Si}(\text{OR})_3$ groups but the epoxy ring-breathing vibrational band is only little decreased in intensity [16].

The identification of the different types of silicate substructures present in **1**, **2** and **3** was accomplished by

Fig. 5. ^{29}Si CP-MAS NMR spectrum of sample 3 (a); global (b) and single peak (c) fitting curves obtained with SPORT-NMR.

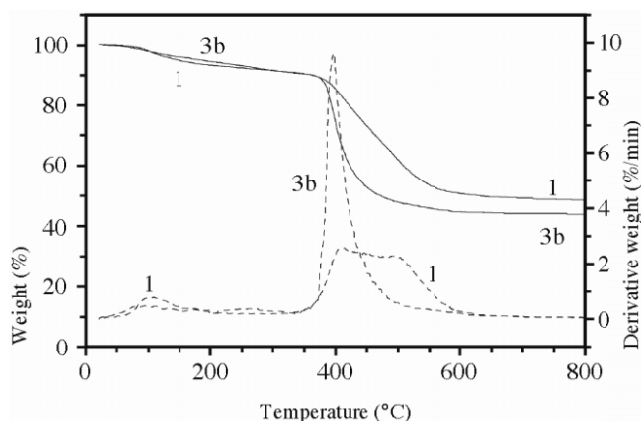


Fig. 6. Thermogravimetric curves (solid lines) and corresponding derivative curves (dashed lines) of the samples **1** and **3b** under nitrogen flow, at a heating rate of 10 °C/min.

^{29}Si CP MAS NMR spectroscopy which also provides a quantitative measure of the degree of condensation through the relative abundance of T^0 [$\text{RSi}(\text{OR})_3$], T^1 [$\text{RSi}(\text{OR})_2\text{-OSi}$], T^2 [$\text{RSi}(\text{OR})(\text{OSi})_2$] and T^3 [$\text{RSi}(\text{OSi})_3$] silicon nuclei [17]. The ^{29}Si spectra of the three mixtures (Figs. 3–5) show, as a common feature, only two peaks, the main lying at -70 ppm and the minor one at -60 ppm. The position of these signals is in agreement with those of homo-condensed siloxane fragments in T^3 and T^2 arrangements, respectively. Furthermore the spectra do not show evidence of peaks associated to T^0 species, namely uncondensed materials trapped in the solid network, as well as signals attributable to $\text{SiO}_{4/2}$ substructures indicating that no Si–C cleavage had occurred. The condensation degree (percentage of siloxanes bonds formed), was calculated from the signal intensity of ^{29}Si CP MAS NMR spectra fitted with SPORT-NMR software [18] according to the formula c.d. (%) = $\{(0.5) [\text{area } T^1] + (1.0) [\text{area } T^2] + (1.5) [\text{area } T^3]\}/1.5$. The c.d. ranges from 91 to 94.7 and clearly shows that the inorganic network formation occurs for a larger extent in the high ratio mixtures. Figs. 3–5 also show that the intensity of the T^3 resonances in all the three mixtures is much higher than T^2 , so on the inorganic side, the polymer exhibits a predominating content of the tetrafunctional building group $\text{RSi}(\text{OSi})_3$.

It is worth to mention that GLYTS, when left on standing in the air, solidifies after months while, under hydrolytic conditions, it reaches a condensation degree, on the inorganic side, of 5% with a very low extent of epoxy ring cleavage (10%) [11]. On the contrary, ATS leads to a white solid after a few days although the hydrolysis of the ethoxy groups is usually ten times slower than methoxy [19]. Since the rate-determining step in the formation of Si–O–Si linkages is the hydrolysis of the $\text{Si}(\text{OR})_3$ groups, the transition sol–gel–solid phase of ATS is very likely accelerated, via autocatalysis, by the amino group present in the same molecule. In the same way, the amino groups of ATS accelerate the hydrolysis of the methoxy groups of

GLYTS. As long as the organic side is concerned, the oxirane ring cleavage seems to be dependent on the ATS concentration so that the higher ratio mixtures correspond to a higher percentage of uncleaved rings.

To evaluate the effect of changes of the experimental procedure on the physical properties of the final products, the reactions were also performed in the presence of small amounts of KOH to accelerate the epoxide ring cleavage (**1a**, **2a**, **3a**) and of stoichiometric amount of water to effect hydrolysis of the $\text{Si}(\text{OR})_3$ (**1b**, **2b**, **3b**). All the mixtures were left on standing in a Petri dish for six months during which time an increase of viscosity occurs up to the formation of a solid, transparent phase. The FT-IR, Raman and ^{13}C NMR spectra of all the mixtures, independently from the molar ratio, appear very similar and only experience a modification of the band shape.

Other information on the structural complexity of the networks was obtained by thermal analysis. As a first approximation, the relative degradation behavior of networks having very similar chemical structures may be considered as indicative of the development of the network itself, i.e. the degree of cross-linking.

The thermogravimetric (TG) curves of thermal decomposition of epoxy–silica networks show a common behavior exemplified in Fig. 6, relative to samples **1** and **3b**, where the corresponding derivative TG curves are also reported. In general, thermal degradation in dynamic nitrogen occurs in at least two steps, and may be schematized as follows:

- a low temperature weight loss, with maximum volatilization rate between 85 and 110 °C, depending on the sample;
- a main decomposition process taking place in either one or two partially superimposed steps;
- at 800 °C a charred residue is left, accounting for more than 40% of the initial sample weight.

Quantitative characterization of degradation process is better illustrated by the values reported in Table 1, i.e. temperatures of maximum volatilization rate of the different steps, and residues at 300 and 800 °C, expressed as weight percent on the initial amount of sample.

The products volatilized at the low temperature step, approximately corresponding to one tenth of the initial weight, were analyzed by GC/MS. As expected water is the main product, together with smaller amounts of methanol and ethanol. The absence of residual enthalpy curing peaks in the calorimetric analysis in such range of temperatures (DSC traces not reported) indicates that the volatiles are simply released from the samples, after being trapped in the network during the initial curing procedure as secondary products of polymerization. The lack of enthalpy peaks is in full agreement with the high percentage of siloxane bonds and the consequent low amount of residual silanol groups, as found by ^{29}Si NMR measurements. On the other hand, the

Table 1
Thermogravimetric analysis parameters of epoxy–silica networks

	$T_{\max 1}$	Res _{300 °C}	$T_{\max 2}$	$T_{\max 3}$	Res _{800 °C}	Res _{(air) 800 °C}
1	100	92	414	498	48	39
1a	100	87	424	–	42	37
1b	115	89	426	–	44	39
2	101	92	429	–	42	34
2a	96	90	420	–	42	37
2b	115	89	384	419	43	35
3	85	92	427	–	41	31
3a	98	90	397	–	44	34
3b	85	88	~390	–	38	34

T_{\max} is the temperature of maximum of volatilization rate from derivative TG curves of the corresponding step of weight loss. Res is the residue at the indicated temperature, expressed as weight percent of the initial sample. Data refer to degradation in dynamic nitrogen, except when otherwise indicated.

limited weight decrease between 200 °C and the beginning of decomposition, particularly evident in **2**, **2a**, **2b**, **3**, **3a** and **3b**, is possibly related to the progressive reaction of small amount of unreacted active groups [20].

The onset of polymer decomposition is observed at around 350 °C independently on the sample composition, whereas further decomposition takes place in a wide range of temperature in all the epoxy–silica networks except **3a** and, particularly, **3b**. In the latter ones such process occurs in less than 100 °C. During degradation the rate of weight loss tends to increase rapidly as a temperature effect but the ensuing bond scission gives more stable structures and the rate of volatilization decreases. The final solid structure corresponds to a char stable at higher temperatures, at least up to 800 °C.

Moreover, it is worth noticing that only in the case of sample **1** (Fig. 6) the rate of volatilization, herewith expressed as weight loss%/min, is limited to small values in the whole range of decomposition. Thus indicating a higher complexity of such network, which requires higher temperature and longer time for degrading to the same charred material.

The presence of oxygen during heating does not entail substantial differences in the degradative behavior of the epoxy–silica networks. Only at temperatures higher than 600 °C a further decomposition step appears, which is tentatively attributed to the formation of oxygen containing volatiles. The little influence that oxygen has on the degradation at lower temperature has been already reported for traditional epoxy systems [21]. The peculiar behavior of sample **1** was also confirmed by the chemical nature of the residue, which is almost exclusively formed by silica. Thus indicating a total disappearance of the organic material by thermo-oxidation. On the contrary, in all the other cases the residue has a carbonaceous aspect and maintains a hybrid structure.

The data gathered in Table 1 allow some conclusions to be drawn on the effect of the different curing agents on the

thermal stability of **1**, **2** and **3**. The temperature of maximum volatilization rate of **1**, following the treatment with KOH or KOH/water, slowly increases while the different curing procedures cause a decrease of the above parameter when the higher ratio mixtures are involved. The different network structure of **1** may be invoked to explain the different behavior when KOH and water are added to the original mixtures. It is worth to mention that the structural and textural properties of these materials are affected by a number of factors such as pH, concentration and amount of water. Furthermore the catalyst nature, beside to influence the kinetic of the hydrolysis and condensation reactions, also modifies the network structure [22,23].

4. Conclusions

The reaction of the epoxy 3-glycidoxypropyltrimethoxysilane with the primary amine (3-aminopropyltriethoxysilane), under non-hydrolytic conditions, leads to the formation of highly branched materials. The combined results of the Raman and ²⁹Si CP MAS investigations suggest that all the GLYTS/ATS mixtures are featured by a very high degree of inorganic cross-linking which increases on going from the 2/1 to the 10/1 mixture. The epoxy cross-linking follows an opposite trend. Its density decreases by decreasing the amine content. While the 2/1 mixture does not evidence uncleaved oxirane rings, the lower amine content mixtures still show the presence of unreacted epoxy groups. The very high inorganic condensation level in the absence of added water may be due to the curing procedure, which involves a long stay at 30 °C for four months (usually composites are prepared under hydrolytic conditions and cured at temperature higher than 100 °C), as well as to the catalytic activity of the primary amino group of ATS. The higher temperature and longer time to degrade **1**, as found by thermogravimetric analysis, indicate that **1** is featured by different structural properties. Accordingly, the addition of KOH or water does not appear to significantly affect the nature of **1** while it acts as a network modifiers when added to **2** and **3**. **1**, **2** and **3** are expected, on the inorganic side, to be quite rigid and with a fewer residual silanole groups. They are then expected to be hydrophobic and moderately porous with consequent effects on other properties such as sorptivity and permeability.

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