

Environmental Aging of Cold-Cured Epoxy-Silica Hybrids Prepared by Sol–Gel Process

Francesca Lionetto, Mariaenrica Frigione

Department of Engineering for Innovation, University of Salento, via Arnesano, 73100, Lecce, Italy

Correspondence to: M. Frigione (mariaenrica.frigione@unisalento.it)

ABSTRACT: The article investigates the effects of long term environmental aging on thermal and mechanical properties of epoxy-silica hybrids. These nanostructured materials, prepared by non-aqueous sol-gel process and in situ generation of nanosilica during epoxy curing at room temperature, present the potential to be used as cold-cured adhesives for civil engineering and Cultural Heritage applications. A specifically developed conditioning procedure for these cold-cured nanostructured materials was applied before moisture/water absorption tests. The work evidenced the superior durability of the studied epoxy-silica hybrid, which kept its performances in severe, but realistic, environmental conditions with respect to traditional epoxy adhesives. The reduction in the glass transition temperature and mechanical properties of the studied epoxy-silica hybrid, observed in the first weeks of environmental aging, was followed by a significant recovery. This was attributed to two concomitant phenomena: the reactivation of the incomplete curing reactions in the epoxy domains and the continuation of the condensation reactions in the siloxane domains activated by the absorbed water. Finally, the Fickian behavior, presented by the studied epoxy-silica hybrid, was used as an indirect indication of the homogeneity of achieved microstructure, with well dispersed silica nanostructures in the epoxy network. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40093.

KEYWORDS: ageing; adhesives; nanostructured polymers; thermosets; glass transition

Received 31 July 2013; accepted 21 October 2013

DOI: 10.1002/app.40093

INTRODUCTION

Organic-inorganic (O-I) polymers with in situ generated nanostructures are a special category of nanostructured materials extensively studied for their unique characteristics arising from the integration of compatible organic and inorganic components at a molecular scale.^{1–11} Recently, O-I polymer nanocomposites based on epoxy systems with interpenetrating silica domains have been optimized by the authors.^{12,13} The methodology for their production is based on solvent-free nonaqueous sol–gel process, involving the hydrolysis and condensation of metal alkoxides, which is able to bind chemically, at nanometric scale, the organic phase with the inorganic one. The solventless technique made it possible to avoid drawbacks of the classical aqueous procedure. These novel epoxy-silica hybrids present superior properties than those of the parent epoxy resins mainly due to the interaction of the silica nanodomains with the thermosetting matrix at a molecular level and by the restriction of molecular dynamics at the interface. In particular, higher glass transition temperatures and greater mechanical properties than those experienced by epoxy resins have been previously reported by the authors.^{12,13}

The presence of nanostructured co-continuous organic and inorganic domains is expected to give an enhanced adhesion of the

hybrids to different substrates. For such a reason, these epoxy-based hybrid systems have been investigated by the authors as potential “cold-cured” adhesives, i.e. to be cured at ambient temperatures and to be used in civil engineering or in Cultural Heritage applications, for restoration of artefacts and consolidation of concrete or masonry structures instead of the cold-cured epoxy resins, traditionally used in these applications as adhesives and matrices for FRP (Fiber Reinforced Plastics).¹⁴ To the best of our knowledge, there are no studies in literature on the evaluation of epoxy hybrids as cold-cured adhesives, apart from recent works of the authors.¹⁵ The few reports available on literature concern, in fact, hot-cured systems for industrial applications.^{16,17}

The main advantages in using epoxy-silica hybrids as cold-cured adhesives for civil engineering and Cultural Heritage applications lie, in particular, in the possibility of overcoming the main limitations of conventional cold-cured epoxy resins associated to the very long curing times (in order of months) required at room temperature, often not sufficient to complete the curing reactions and achieve a full development of physical and mechanical properties.^{18,19} Due to the incomplete cure at ambient temperatures, the cold-cured epoxy systems typically display a glass transition temperature (T_g) never greater than 65–70°C.^{20–22}

Moreover, when used in outdoor applications, the humid environment often acts as a degrading agent for the epoxy resin, with detrimental effects on glass transition temperature (T_g) and mechanical properties. Epoxy adhesives exposed to a wet environment absorb water because they possess polar groups attracting water molecules. Once inside, water may alter the properties of the polymer both in a reversible manner, through plasticization phenomena caused by strong association of OH groups of water with NH groups of the epoxy,²³ and in an irreversible manner if hydrolysis, cracking, or crazing occur.²⁴ The lowering of the T_g due to water ingress into epoxy resins can be particularly harmful for cold-curing epoxies whose typical T_g is not much higher than the service temperature. Therefore, if the service temperature approaches the T_g of the system, a lowering of the adhesion strength and of the mechanical properties of the adhesive could occur.

Although the great interest of the scientific community towards epoxy-silica hybrids, to our knowledge no studies on the water uptake behavior of these novel materials have been performed. This lack of information on the durability of O-I hybrids limits the spreading of these materials. The present work is aimed to overcome the lack of data on the kinetics of moisture uptake and the influence of water on the physical properties of epoxy-silica hybrids.

The underlying idea of this work arises from the experimental results obtained by the authors on an optimized formulation of epoxy-silica hybrid (silica content 15 wt %) aged at room temperature at 55% R.H. up to 1 year. It has been observed that the little ambient humidity is sufficient to reactivate the sol-gel reactions in the inorganic domains by hydrolysing the residual alkoxy silane groups and promoting further condensation reactions within siloxane domains.¹³ Starting from this information, an experimental study has been devoted to the effects of water absorption on thermal and mechanical properties of an optimized formulation of epoxy-silica adhesive either immersed in water or exposed to high level of relative humidity.

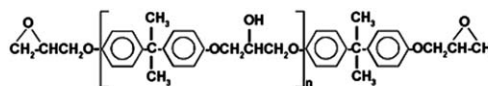
In order to better understand the independent effects of water on the studied resin, the synergistic influence of moisture and temperature has been avoided. To this aim, a novel conditioning procedure before exposure to water/moisture has been tailored to these cold-cured epoxy-silica hybrids. The proposed procedure is aimed to overcome the difficulty to assess the long-term performance of cold-curing epoxy-silica systems, amplified by the lack of appropriate standards for durability tests for these particular systems curing at ambient temperature.

EXPERIMENTAL

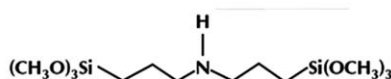
Materials

The epoxy-silica hybrid was prepared starting from diglycidylether of bisphenol A (DGEBA) with an epoxy equivalent weight of 184–190 g/mol, commercially known as Epikote 828 (supplied by Resolution Performance Products). A bis-(γ -propyltrimethoxysilane) amine obtained from Aldrich (purity > 90%) was used to partially functionalize the DGEBA resin.

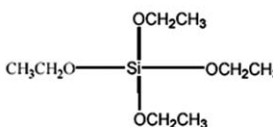
An alkoxy silane mixture was used as alkoxide precursors for the hydrolysis and condensation reactions. The mixture was based on a fixed combination of tetraethoxysilane (TEOS) and γ -glycidyloxypropyltrimethoxysilane (GOTMS) in amounts that



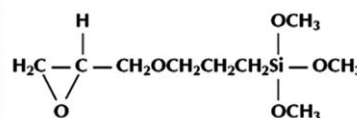
DGEBA epoxy resin



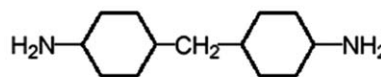
bis-(γ -propyltrimethoxysilane)



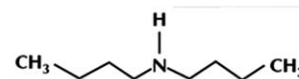
Tetraethoxy silane (TEOS)



Gamma-glycidyloxypropyltrimethoxysilane (GOTMS)



4-4' methylene bis-cyclohexaneamine (PACM) - hardener



Dibutylamine (DBA)

Scheme 1. Chemical structure of: DGEBA epoxy resin; bis-(γ -propyltrimethoxysilane); TEOS, tetraethoxysilane; GOTMS, Gamma-glycidyloxypropyltrimethoxysilane; PACM, 4-4' methylene bis-cyclohexaneamine; DBA, Dibutylamine.

would produce a nominal silica content of about 15 wt %. Both TEOS and GOTMS were obtained from Aldrich (purity > 97%).

The hardener was 4-4' methylene bis-cyclohexaneamine (PACM), a cycloaliphatic amine supplied by Aldrich and used at molar ratio epoxy/amine = 1 : 0.75.

The epoxy control system was a DGEBA resin modified with a tertiary amine, dibutylamine (DBA, supplied by Aldrich) at molar ratio DGEBA/DBA = 10 : 1. The hardener for the control resin was 4-4' methylene bis-cyclohexaneamine (PACM), as in the case of O-I epoxy hybrid.

The chemical formula of the materials used is reported in Scheme 1. The compositions of the systems prepared are reported in Table I.

Synthesis of Epoxy-Silica Hybrid

The epoxy-silica hybrid was prepared by a two-step procedure starting from the functionalization of the DGEBA resin with the

Table I. Formulation of the Analyzed Epoxy Systems, Cured Using a Molar Ratio (Amine/Epoxy) of 0.75/1

System	Resin	Hardener	Exposure conditions	Exposure time(weeks)
Control -1	DGEBA-DBA	PACM	75% R.H.	25
			Immersion in water	25
Hybrid-1	Hybrid DGEBA with 15 wt % of SiO ₂ in-situ generated	PACM	75 % R.H.	25
			Immersion in water	25
Control -2	DGEBA-DBA	PACM	Immersion in water	3
Hybrid-2	Hybrid DGEBA with 15 wt % of SiO ₂ in-situ generated	PACM	Immersion in water	3

bis-(γ -propyltrialkoxysilane) amine at 10 : 1 epoxy/silane molar ratio, under continuous stirring at 90°C for 2 h. It was previously found by the authors that, under anhydrous conditions, the reaction of epoxy groups with the amine groups of a silane coupling agent enhanced considerably the formation of co-continuous phases by balancing the rate of reactions for the evolution of the epoxy network to the condensation reactions between the alkoxy silane species present in the system.¹³

A mixture TEOS/GOTMS (molar ratio 1 : 0.12) was prepared at 90°C for 2 h in amounts that would produce a nominal silica content of about 15 wt % in the final epoxy-silica hybrid system. This procedure was adopted as a means of inducing a limited extent of condensation reactions between the two alkoxy silane components so that products of low volatility could be obtained and prevent losses by evaporation during curing. The small amount of GOTMS in the siloxane precursor was used to provide functional groups for the reaction with the amine hardener in the resin, as a means of enhancing the compatibilization drive derived from the reactions between the components of silane-functionalized epoxy resin and the alkoxy silane groups in the siloxane precursor mixture.

The prepared TEOS/GOTMS mixture was then stirred with the silane-functionalized resin at 90°C for 2 h. After cooling down to ambient temperature, the PACM hardener was added and mixed for 30 min.

Curing Procedures

For both the studied systems, twenty specimens were cast in teflon moulds, cured for 14 days at ambient temperature in a controlled environment (23 ± 2°C and 55 ± 5% relative humidity) and then aged in open air for one year in the same controlled environment. The specimens' shape and dimensions (100 x 10 x 4 mm³) were chosen on the basis of ASTM D790 standard for flexural mechanical tests.²⁵ After this period, they were exposed to two different aging regimes, as described in the next section. The necessity of a such long aging period (1 year) arises from the very long time required from the cold-cured systems (both conventional epoxy structural adhesives used in civil engineering and novel epoxy-silica hybrids) to complete their cure process. It should be kept in mind that low-temperature curing leads to an incompletely cured adhesive system, with a greatly decelerated development of full physical and mechanical properties, which can only be achieved after significantly longer curing

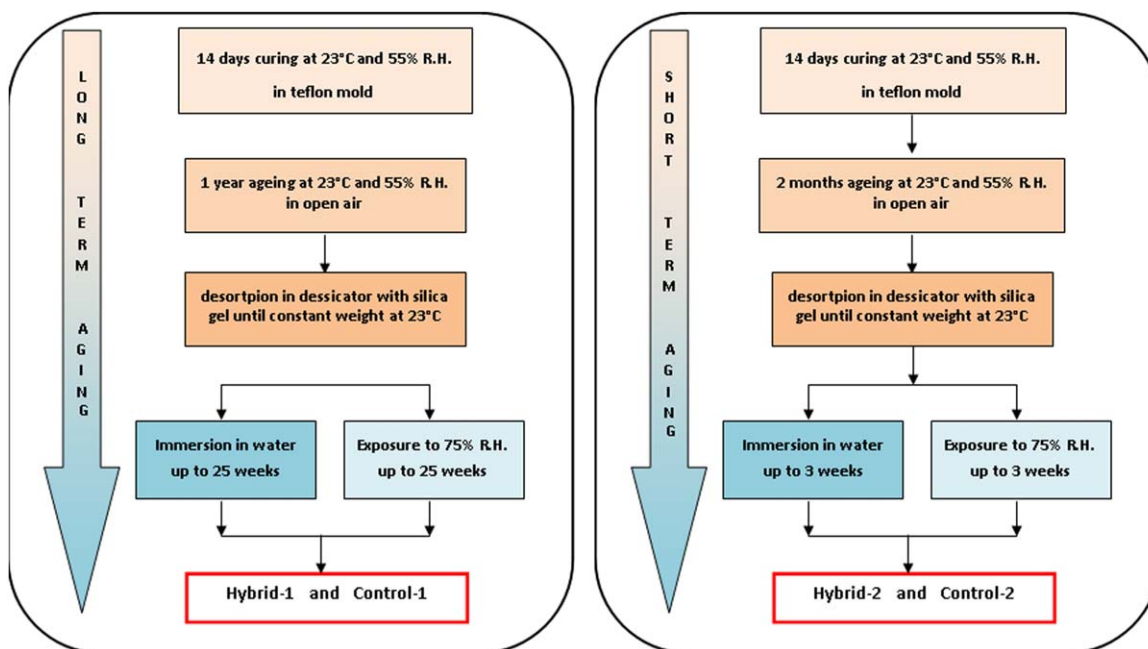
periods, since thermal post-curing is not practically possible to be realized in civil engineering applications. As recently demonstrated by Moussa et al.,¹⁸ the long-term development of thermo-physical and mechanical properties of cold-curing structural adhesives can be predicted until periods of up to 17 years.

As concerning the short term environmental ageing, twenty specimens of hybrid and control systems, possessing the same dimensions (100 x 10 x 4 mm³), were cured in a teflon mold at 23 ± 2°C and 55 ± 5% relative humidity for 14 days and 2 months in open air. They were, then, immersed in water, as following explained.

The experiments of long-term and short-term aging would compare the behavior of both epoxy-based systems, i.e. hybrid and control systems, if exposed to severe, but realistic, wet/moist conditions when their cure is roughly completed since the degree of cure is 0.95 (long-term aging) or, conversely, during the proceeding of the cross-linking process (short-term aging). The aging conditions and times for the analyzed systems are reported in Table I.

Water/Moisture Tests

Tests of moisture/water absorption were performed on cured samples according to a novel procedure specifically developed for cold cured epoxy-silica hybrids. It consisted in storing the samples in a desiccator with silica gel at ambient temperature until their weight achieved a constant value, i.e. when the difference between two consecutive weighing was less than 1% of the original weight of the sample. This procedure, even if time-consuming, allows to eliminate the water contained in the specimens without the use of a thermal treatment performed in oven at 50°C, as indicated by the ASTM D 570 standard,²⁶ which is the solely code available to measure the water absorption for plastics. The latter, in fact, is absolutely inadequate for cold-cured systems that, as previously underlined, are not fully cured even when the cure at ambient temperature is performed for a long time (several months). As a consequence, the thermal treatment used to dry the specimens, carried out at a temperature close to the T_g of cold-cured systems, is able to post-cure them, affecting their behavior towards the water absorption. Moreover, in civil engineering applications, as those thought for the novel epoxy-silica hybrids studied in this work, the thermal post-cure is not practically possible. The conditioning procedure proposed, therefore, is able to overcome the mentioned limits



Scheme 2. A schematization of the procedure used for long term and short term aging is reported in Scheme 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the standard in respect of the peculiarities of cold-cured epoxy-based structural adhesives.

After the drying of the specimens was completed, they were placed in a climatic chamber at $23 \pm 2^\circ\text{C}$ and $75 \pm 5\%$ relative humidity or immersed in distilled water at a constant temperature of $23 \pm 2^\circ\text{C}$. In both cases, the samples were periodically taken from the storage box, wiped with a dry cloth and weighed to calculate the percentage of water absorption using an analytical balance with an accuracy of ± 0.1 mg. After the measurements, the samples were replaced in the container. From the weight variations of all the samples subjected to these two treatments, the moisture content absorbed during any exposure was assessed. The moisture content M_t at time t was expressed as the increase in weight percent, i.e.:

$$M_t = \frac{W_t - W_0}{W_0} * 100(\%) \quad (1)$$

where W_t was the weight of the specimens at exposure time t and W_0 the weight of the dry specimen before the exposure procedure to water/moisture.

This procedure continued until the increase in weight for three subsequent periods, as shown by two consecutive weightings, was less than 1% of the original weight of the sample. At this point, the samples were considered to have reached the saturation condition. The reported weight data were calculated as the mean value of measurements performed on 10 samples for each system.

As concerning the short-term environmental ageing, twenty specimens of hybrid and control systems, cured at $23 \pm 2^\circ\text{C}$ and $55 \pm 5\%$ relative humidity for 14 days in a teflon mold and for 2 months in open air, were immersed in water for 3 weeks.

A schematization of the procedure used for long-term and short-term aging is reported in Scheme 2.

Characterization

The thermal properties of the hybrid and control epoxy systems at each time of exposure to water/moisture were determined by Differential Scanning Calorimetry (DSC). A DSC 822 Mettler Toledo was employed to this aim. Each sample, with an average weight around 10–14 mg, was heated under nitrogen atmosphere (flow rate = 80 mL/min) from 5° to 200°C at a $10^\circ\text{C}/\text{min}$ heating rate. The glass transition temperature was determined as the transition midpoint; the relaxation enthalpy and the residual heat of cross-linking reactions were evaluated from the peak area delimited by the tangent line to DSC curve. In order to prove the repeatability of results, the calorimetric experiments were repeated at least three times and the results averaged.

The effect of water on the mechanical properties of the analyzed systems was investigated by mechanical tests performed on specimens at different times of exposure to water/moisture. Three point bending test were performed following the ASTM D790 standard²⁵ in order to determine the flexural properties of the adhesives. Specimens with a span/thickness ratio of 16 : 1 were tested using a LR5K Lloyd Instruments Machine with displacement control, at a cross-head speed of 2 mm/min. Flexural modulus of elasticity and flexural strength were calculated by performing the tests at room temperature. The reported results were the average values of at least five experiments.

The light transmittance characteristics of the samples were determined in the spectral range of wavelength 300–1100 nm, using a Varian CARY 50 SCAN UV-Vis spectrophotometer.

Wide-angle X-ray diffractions (WAXD) were collected on a Rigaku Ultima+ diffractometer. The X-ray generator was

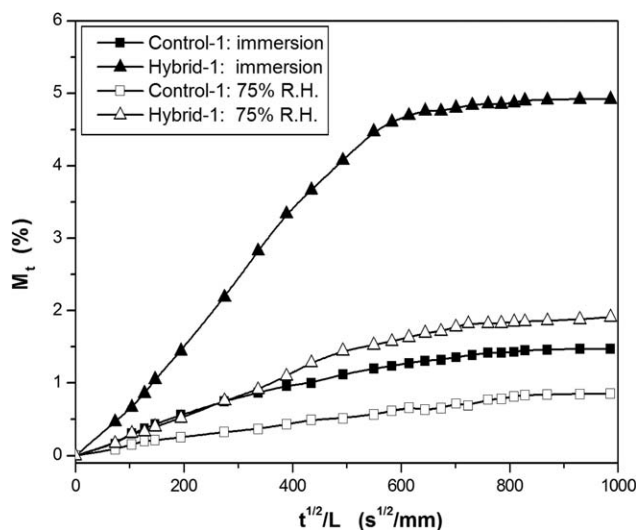


Figure 1. Water absorption profiles of the hybrid and control systems exposed to 75% R.H. or immersed in distilled water.

equipped with a copper tube operating at 40 kV and 26 mA and irradiating the sample with a monochromatic CuK_α radiation with a wavelength of 0.154 nm. XRD spectra were acquired at room temperature over the 2θ range of 1° – 15° at 0.05° intervals with a measurement time of 1 s per 2θ intervals.

The morphology of the fractured samples was examined by scanning electron microscopy (SEM) using a Zeiss EVO 40 SEM instrument at variable pressure operating with a voltage of 20KV. Control and hybrid samples, aged in air or immersed in water up to saturation, were analyzed.

RESULTS AND DISCUSSION

Water/Moisture Absorption in Long-Term Aging Behavior

The water/moisture absorption profiles of hybrid and control systems, immersed in distilled water or exposed to 75% relative humidity, are shown in Figure 1, where the values of water gain are reported as a function of the square root of the exposure time. Weight gain M_t due to water/moisture absorption increases proportionally to $t^{1/2}$ before beginning to level off to a saturation level, M_∞ , which depends on the material structure and on the exposure conditions. As expected, increasing the humidity level causes a corresponding increase in the saturation level. From Figure 1 it can be also noted that control and epoxy-silica systems exhibit differences both in the water/moisture uptake behavior and saturation level.

The experimental data from gravimetric measurements have been fitted by the single Fickian model given in eq. (2), commonly used to model the diffusion behavior of water into adhesive polymers²⁷:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right] \quad (2)$$

where M_t represents the mass of water absorbed at time t , M_∞ is the absorbed water in correspondence of the saturation condition, D is the diffusion coefficient, and L is the sample thickness.

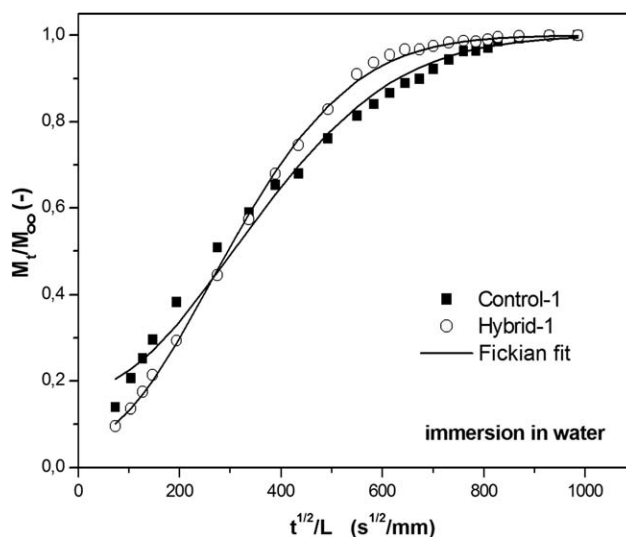


Figure 2. Water absorption profiles of the hybrid and control systems immersed in distilled water. The fitted curves represent Fickian water absorption.

The comparison between experimental results and fit with the single Fickian model are reported in Figures 2 and 3. The response of the epoxy control system, immersed in deionized water or exposed to 75% R.H., is roughly Fickian with some anomalies. Approaching the saturation level, in fact, the diffusion rate does not decrease to zero but seems to reach a constant value. Deviations from the Fickian behavior in the studied control epoxy system are in agreement with literature data on different epoxy resins, mostly for specimens thickness lower than 2 mm.^{27–30} In particular, Vanlandingham et al.²⁸ has related the non-Fickian effects in the moisture diffusion behavior of epoxy systems to the existence of a two-phase morphology consisting of a nodular or microgel phase with high

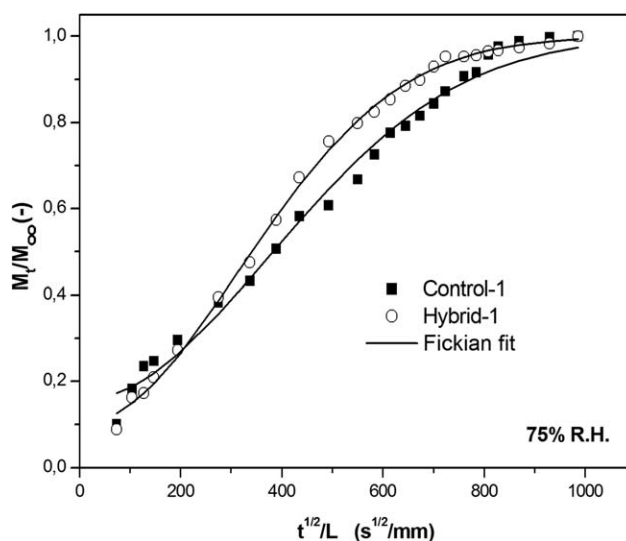


Figure 3. Water absorption profiles of the hybrid and control systems immersed in distilled water. The fitted curves represent Fickian moisture absorption.

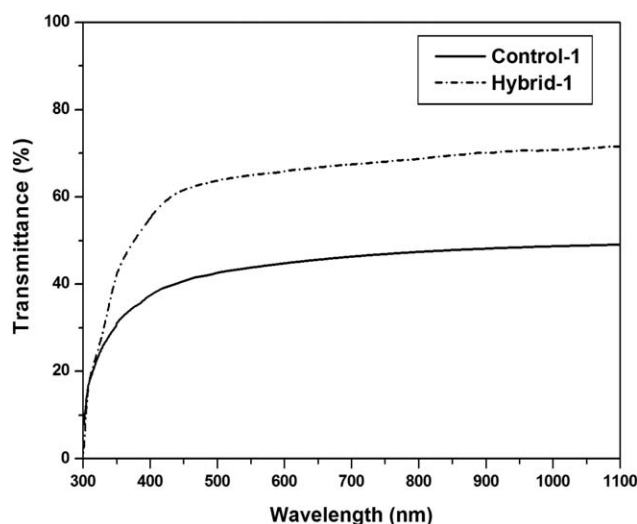


Figure 4. Glass Variation of light transmittance as a function of the wavelength of incident light for hybrid and control specimens.

crosslinking density, surrounded by a low-density phase, which is composed of unreacted and/or partially reacted material.

On the other hand, epoxy–silica hybrids show a Fickian behavior, with the Fickian curve well fitting the experimental results. In fact, a slow and steady increase in water/moisture level is observed after the initial linear increase of M_t with $t^{1/2}$ until a stable saturation level is achieved. It is not possible to compare this behavior with literature data since, to the best of our knowledge, this is the first time that the absorption behavior of an epoxy–silica hybrid has been studied in detail. In the present case, the Fickian uptake behavior of the studied organic–inorganic hybrid can be considered an indication of a homogeneous morphology. This conclusion is confirmed by Wide Angle X-Ray Diffraction (WAXD) and transmittance measurements, performed on the studied systems. The plots of the transmittance against wavelength of the incident light, shown in Figure 4, evidence that at low wavelengths (<350 nm) all samples exhibit a very low light transmittance, whereas at the upper end of the visible spectrum the Hybrid sample displays about 40% higher level of transparency than the control sample. This result indicates the presence of fluctuations in density in the control samples, which may cause a loss of transparency through internal light scattering. The important result is the absence of these density fluctuations in the epoxy–silica hybrid, as also confirmed by the absence of the broad band with a maximum at $2\theta = 6^\circ$ observed in the epoxy control from WAXD measurements (Figure 5).

Epoxy–silica hybrids show much higher values of water uptake than the control system at the same exposure conditions, as also reported in Table II. The reason of this can be related to the higher polymer–water affinity and free volume of the studied hybrid system, which, as known from literature,^{28,31,32} are the major parameters governing the absorption and diffusion of water in polymers. In epoxy–silica hybrids the polymer–water affinity is higher than in neat epoxy resins, since is caused by: (i) the polar hydroxyl (-OH) groups created by the epoxide

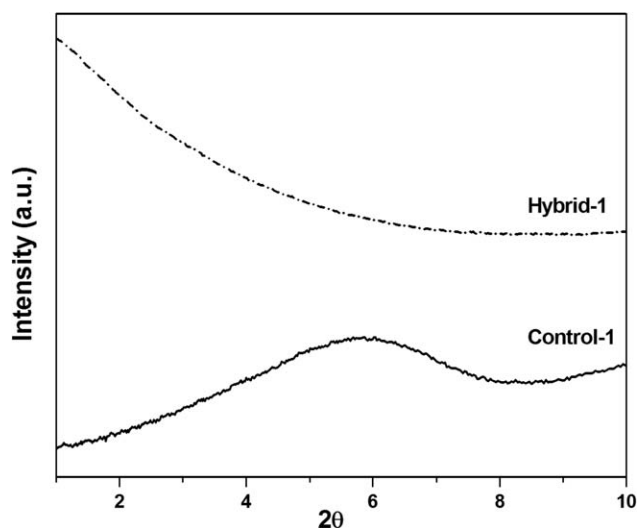


Figure 5. WAXD patterns for the hybrid and control samples.

ring-opening reaction with primary and secondary amines, and (ii) the highly hydrophilic nature of the siloxane networks, that may act as the major recipient of the water absorbed by the system.

The amount of free volume is affected by both the cross-linking density and “physical aging” process.^{21,33} In the studied epoxy–silica hybrids, the free volume is higher than that of the parent epoxy resin due to: (i) a reduced physical aging, as evidenced by the value of relaxation enthalpy (ΔH_{rel}) in Table III, and (ii) a higher cross-linking density along with the presence of more polar groups. Steric hindrances at the cross-link junctions, in fact, introduce unoccupied volume elements coincident with the polar hydroxyls and amines. This opens the matrix and facilitates the access and the association of water molecules with the polar groups, thus increasing the water uptake.

The values of the coefficient of diffusion D , estimated from the fit with the single Fickian model, are reported in Table II together with the water content in correspondence of the saturation condition M_∞ and the time required to reach the saturation condition. The values obtained in the present study for the control system are in line with those available from previous works²¹ on different epoxy adhesives which are commercially

Table II. Water/Moisture Absorption of Epoxy–Silica Hybrid and Control Systems Cured 1 Year

	Exposure condition	Water content at saturation (%)	Time to saturation (weeks)	Diffusion coefficient (cm^2/s)
Control-1	75% R.H.	0.85	25	$3.47 \cdot 10^{-9}$
	Immersion in water	1.47	25	$5.35 \cdot 10^{-9}$
Hybrid -1	75% R.H.	1.91	25	$5.12 \cdot 10^{-9}$
	Immersion in water	4.92	25	$7.28 \cdot 10^{-9}$

Table III. Thermal Properties Measured by DSC on the Epoxy Adhesives During Their Exposure to Water/Moisture Environment

	Exposure condition	Exposure time (weeks)	ΔH_{rel} (J/g)	ΔH_r (J/g)
Control-1	75% R.H.	0	8.7 ± 0.7	15.4 ± 0.2
		4	6.6 ± 0.6	12.5 ± 0.3
		25	7.6 ± 0.5	11.9 ± 0.1
	Immersion in water	0	8.7 ± 0.7	15.4 ± 0.2
		4	5.5 ± 0.5	13.4 ± 0.2
		25	5.4 ± 0.3	12.1 ± 0.1
Hybrid-1	75% R.H.	0	2.5 ± 0.1	5.3 ± 0.4
		4	2.2 ± 0.1	2.5 ± 0.4
		25	2.1 ± 0.1	2.0 ± 0.2
	Immersion in water	0	2.5 ± 0.1	5.3 ± 0.4
		4	1.9 ± 0.4	4.3 ± 0.1
		25	2.6 ± 0.2	3.6 ± 0.1

ΔH_{rel} , relaxation enthalpy; ΔH_r = residual heat of reaction.

available and have a similar molecular structure of the control epoxy resin studied in this work, apart from the DBA functionalization. Commercial cold-cured epoxy-based adhesives present, in fact, a water content at saturation ranging from 1 to 7%, a time to reach saturation between 19 and 24 weeks and diffusion coefficients with an order of magnitude of 10^{-9} cm^2/s . The D and M_∞ values of the hybrid system cannot be

compared with literature data, since no absorption studies has been undertaken, up to our knowledge, on this novel type of structural adhesives.

Thermal, Mechanical, and Morphological Properties During Water/Moisture Absorption

In Figure 6, the glass transition temperatures, T_g , calculated on the two analyzed systems, are reported as function of the exposure/immersion time. An initial T_g value (about 73°C) substantially higher than the cure temperature is found for the hybrid system. The T_g measured on the control epoxy-based system, on the other hand, is roughly in line with those reported for commercial products, never higher than $65\text{--}70^\circ\text{C}$, as already underlined. The higher T_g values represent a first distinctive advantage offered by organic-inorganic hybrid systems over the traditional cold-cured epoxy adhesives.

With increasing water/moisture uptake, the T_g decreases due to the plasticization of the network. A drop in the T_g values is observed for hybrid and control system in the first week of immersion in distilled water (Figure 6(a)). The T_g reduction is around 13°C and 8°C for immersed hybrid and control systems, respectively, with respect to the initial T_g measured on dry specimens. The specimens exposed to 75% R.H. [Figure 6(b)] show a similar behavior than those immersed but present a delayed (of about 5 weeks) and alleviated drop in T_g values. Again, the decrease in T_g is more pronounced for the hybrid system (about 11°C) with respect to the control one (about 4°C).

After reaching a minimum, the T_g begins to increase with exposure/immersion time, irrespective to the system analyzed. This phenomenon is due to the further cross-linking reactions during

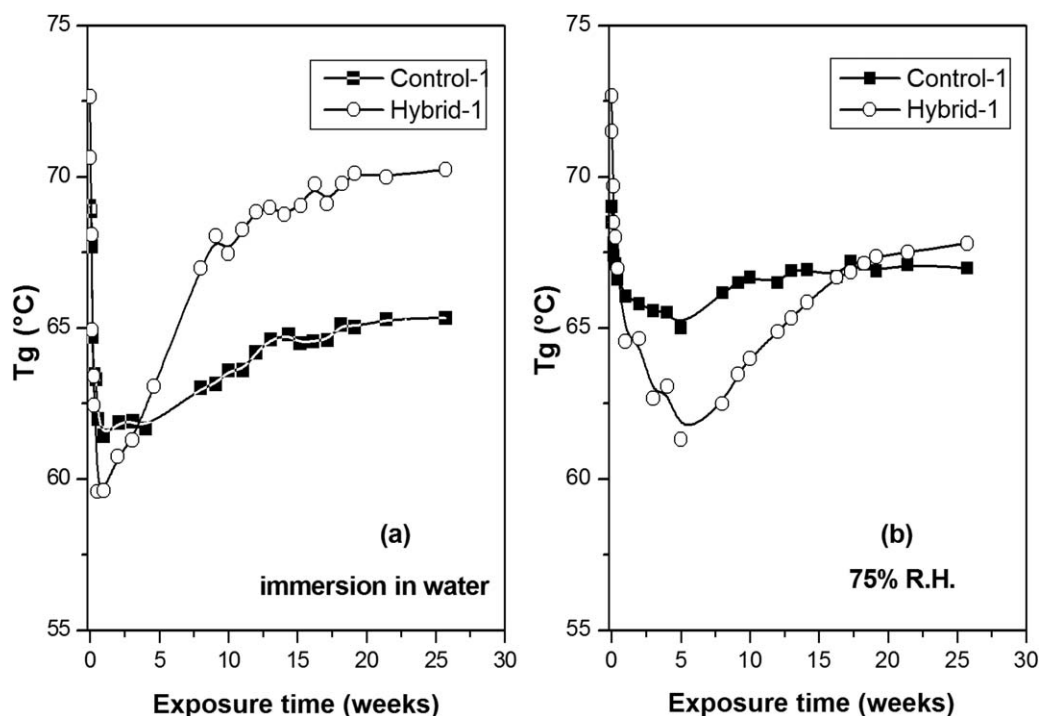


Figure 6. Glass transition temperatures of hybrid and control systems versus exposure time for: (a) specimens immersed in distilled water; (b) specimens exposed to 75% R.H.

environmental aging. It is reported that the lower T_g allows the polymer chains to become mobile, increasing the probability of a contact between the unreacted groups.²³ This leads to the reactivation of the incomplete curing reactions for the not fully cured samples, as testified by the substantial reduction of residual heat of reaction (Table III), or the formation of pseudo or secondary cross-linking brought about by water molecules forming bridging between chain segments. In that case, an increase in T_g is expected. This phenomenon has been observed both in heat cured^{34,35} and cold cured epoxy resins.²² The further cross-linking brings about additional restrictions to the molecular relaxations within the network, thus counteracting the plasticization effect of the bound water and contributing to lessen the T_g depression. Due to the competition between plasticization and further cross-linking, the T_g recovery in control epoxy system is not complete and the control resin does not achieve the original T_g value of the dry state. In Figure 6 it is also evident the effect of the structure of epoxy and the exposure conditions on the kinetics of the T_g recovering. The T_g increase is faster for samples immersed (Figure 6a) than for sample exposed to 75% R.H. [Figure 6(b)].

The literature on water sorption in epoxy resins indicates that the water molecules into the resin have a double nature: unbound molecules, confined into the free volume of the system, and molecules bound to hydrophilic sites along the polymer.^{34,36,37} In the absorption process of epoxy networks, water molecules firstly bind with the hydrophilic groups, then, diffuse into free volume elements as unbound water. As the water concentration increases, the number of polar groups on the network available for hydrogen bonding remains unvaried, but they result saturated by water and additional water molecules prefer to form hydrogen bonds with other water molecules rather than with the polar groups in the polymer.^{38–40}

The hybrid system shows a peculiar behavior with a much faster and complete T_g recovery than that experimented by the control system. The final T_g , in fact, is only 2°C lower than that of the initial dry state. The different behavior of hybrid and control systems is well evidenced in Figure 7, where the T_g 's for the two immersed systems are reported as a function of water content. After the minimum achieved in the T_g for a water uptake of about 1%, the epoxy silica hybrid presents a T_g recovery of about 11°C accompanied by a water gain of 4%. The control resin presents a minimum at a water uptake of about 0.5%, followed by a T_g recovery of 4°C and a water gain of 1%. A similar behavior has been observed for the samples exposed to 75% R.H., even though the T_g recovery is reduced (ΔT_g of 8° and 2°C, for epoxy silica and control resin, respectively).

The reductions in T_g observed at low amounts of absorbed water can be ascribed to the prevailing of plasticization effects on the post-curing. At low amount of absorbed water, in fact, strong water–resin interactions are more likely to occur: in this case, bound molecules, which are responsible of T_g decrease, prevail. On the other hand, as the water content increases, the occurrence of a more rigid molecular structure, caused by both the post-curing process and doubly hydrogen-bonded water molecules, is able to counteract the decrease in T_g due to the plasticization.

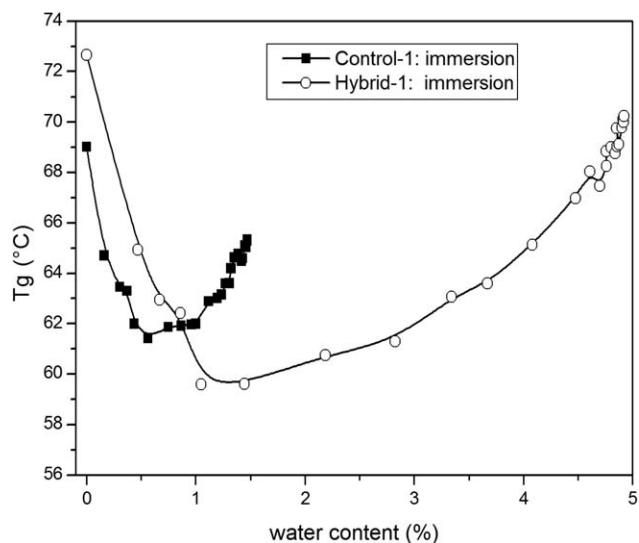


Figure 7. Glass transition temperatures versus water gain of hybrid and control system immersed in distilled water.

The T_g recovery of hybrid system cannot be explained only in terms of reactivation of incomplete curing of the organic domains, since the residual heat of reaction of the hybrid adhesive is three times lower than the value of the control resin reported in Table III, indicating a very small further cross-linking. The high T_g recovery of the hybrid system is, then, attributed to two concomitant processes: the (small) further cross-linking of the organic domains and, for the most part, the prosecution of the sol–gel process activated by the absorbed water. This latter, in fact, hydrolyses the residual alkoxy silane groups and promotes further condensation reactions within siloxane domains, as already observed by the authors on samples aged at room temperature for 1 year but not immersed, in which the humidity of the storage ambient was sufficient to reactivate the sol–gel reactions in the inorganic domains.¹³

The key result of the work is that, during immersion in water or aging at high humid conditions, the siloxane domains of epoxy-silica hybrids cured at ambient temperature undergo further sol–gel reactions, causing a nearly complete recovery of T_g and mechanical properties which mitigates their initial reductions due to plasticization phenomena. This constitutes a distinct advantage of epoxy-silica hybrid systems over corresponding conventional cold-cured epoxy resins for outdoor applications.

In Table IV the results of flexural tests performed on both cold-cured epoxy-based resins at the saturation conditions are presented. For comparison purposes, the properties calculated on the samples before the immersion or exposure to 75% R.H. are reported in order to assess the influence of the aging on the final properties of the adhesives. The mechanical characteristics displayed by the epoxy control are very similar to those calculated on commercially available unfilled epoxy systems.²¹ On the other hand, a very large improvement, especially in flexural strength, over the control epoxy is provided by the efficient reinforcement and toughening effects of the siloxane domains, as already underlined in a previous study.¹³

Table IV. Mechanical Properties of the Epoxy Adhesives Before and During Their Aging at 75% R.H. or Immersion in Distilled Water

	Exposure condition	Exposure time (weeks)	σ_y (MPa)	$\Delta\sigma_y$ (%)	E (GPa)	ΔE (%)
Control-1	75% R.H.	0	36.6 ± 6.3		2.6 ± 0.2	
		25	29.6 ± 4.5	-19	2.1 ± 0.1	-18
	Immersion in water	0	36.6 ± 6.3		2.6 ± 0.2	
		25	24.3 ± 7.3	-34	2.2 ± 0.4	-15
Hybrid-1	75% R.H.	0	76.3 ± 4.7		3.5 ± 0.1	
		25	66.3 ± 8.1	-13	3.1 ± 0.1	-9
	Immersion in water	0	76.3 ± 4.7		3.5 ± 0.1	
		25	58.5 ± 12.5	-23	3.0 ± 0.3	-13

σ_y , strength at yield; E, flexural modulus of elasticity. For each data set the maximum deviation is reported. $\Delta\sigma_y$ and ΔE are calculated respect to the values of the corresponding system before the exposure to water/moisture (i.e., at 0 weeks).

The obtained results confirm the behaviour observed for cold-cured epoxy resins at longer immersion or exposure times,²¹ whose flexural strength and modulus significantly decrease to values lower than those of the unaged polymer as the result of the degradation produced by moisture or water. As expected, and well documented in literature, the decrease in mechanical properties is more appreciable after a prolonged immersion in water than upon exposure to 75% R.H. In both cases, however, the decrease in flexural properties shown by hybrid specimens is

lower than that of control samples. Moreover, the superior performance of the hybrid system is confirmed since when it is exposed to 75% R.H. or immersed in water its mechanical performance still remain well above those relative to the control resin. This result corroborate the indubitable advantages offered by hybrid systems over parent epoxy systems, since their properties, measured in presence of severe environments (as long-term immersion in water) always overcome those measured in standard conditions on the corresponding parent epoxies.

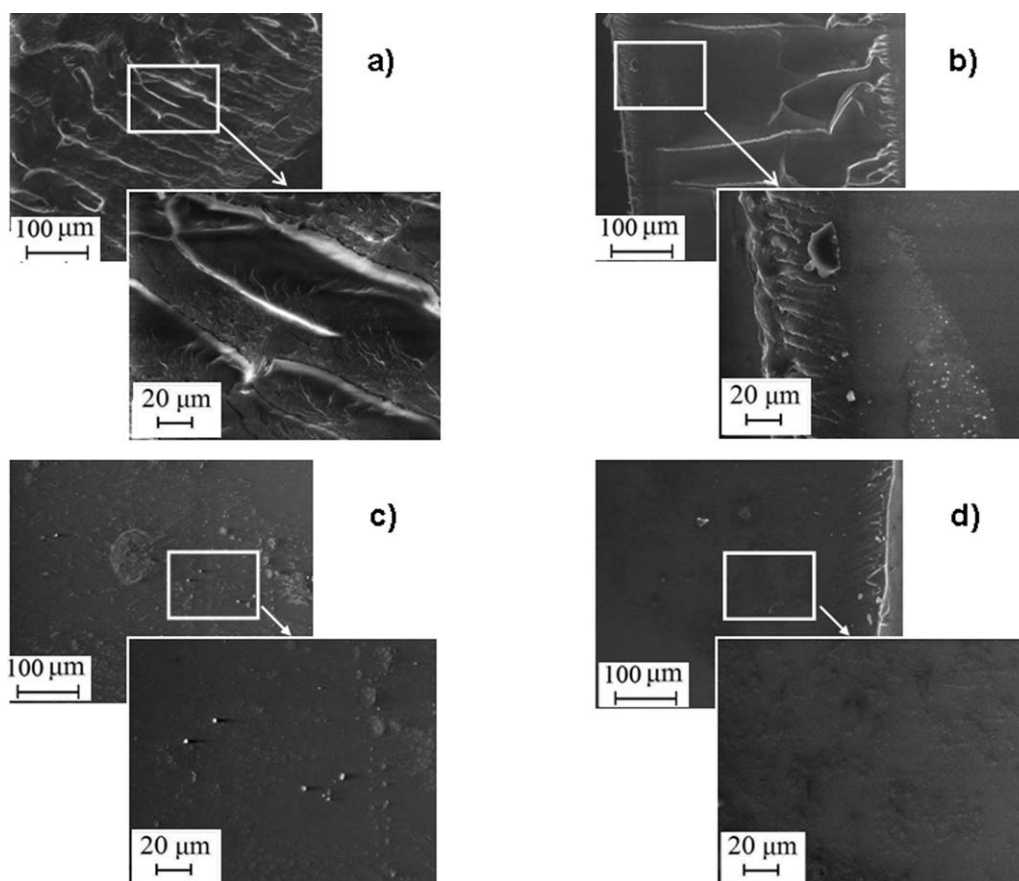


Figure 8. SEM micrographs of fractured samples of: (a) control aged in air; (b) control immersed in water; (c) hybrid aged in air; (d) hybrid immersed in water.

The observation of the morphology of the fractured samples, presented in Figure 8(a–d), can provide a qualitative view of the effect of the sorbed water inside the studied systems. The control sample aged in air [Figure 8(a)] presents distinct fracture lines, characteristics of brittle resins. The cracks mainly orient in one direction, i.e. the direction of the applied load. The control sample immersed in water [Figure 8(b)] evidences two distinct zones: an external zone that appears had fractured in a ductile manner [as better evidenced by the micrograph in Figure 8(b) at higher magnification] and an internal zone with thinner fracture lines which can be however ascribed to a brittle failure.

The SEM micrograph of the hybrid sample aged in air [Figure 8(c)] displays the typical features of organic-inorganic hybrids, which consists of diffuse silica domains very well dispersed within an organic matrix without fracture lines. Some microscopic and irregularly shaped agglomerations are also discernible as dark shades. The effect of water on the morphology is far less evident in the hybrid sample than in the control one. As shown in Figure 8(d), in fact, the morphology of the hybrid sample immersed in water is not significantly altered by this agent.

Short-Term Aging Behavior

The good thermal and mechanical performance in the long-term immersion in water achieved by the novel hybrid system in comparison to a standard cold-cured epoxy, pushed the researchers to analyze the short-term aging behaviour of samples not yet fully cured, being the latter a more realistic environmental condition that cold-cured adhesives can experience. To this aim, 2-months cured specimens of both hybrid and control systems were immersed in distilled water for 3 weeks.

Table V. Thermal Properties Measured by DSC on the Epoxy Adhesives Cured 2 Months Before and After Their Immersion in Water

	Immersion time (weeks)	T_g (°C)	ΔH_{rel} (J/g)	ΔH_r (J/g)
Control-2	0	63.1 ± 0.5	6.1 ± 0.5	42.9 ± 0.6
	3	59.4 ± 0.8	4.1 ± 0.5	41.5 ± 1.2
Hybrid-2	0	62.6 ± 0.7	1.8 ± 0.1	5.8 ± 0.5
	3	58.7 ± 0.6	1.2 ± 0.1	4.7 ± 0.8

T_g , glass transition temperatures; ΔH_{rel} , relaxation enthalpy; ΔH_r = residual heat of reaction.

The results from thermal analysis performed on the specimens, just before and after the aging procedure, are reported in Table V. As expected, the T_g values of both the control and hybrid adhesives before the immersion (time=0 in Table V), are lower than those obtained after 1 year of curing at room temperature (time = 0 in Table II). In accordance, the residual heat of reaction of both systems are appreciably higher, especially in the case of the control, than those measured of the same systems cured for one year. As already stated in the Introduction, this is due to the peculiar behaviour of cold-cured epoxy resins, whose cross-linking reactions needs several months at room temperature to be almost completed, or at least frozen by energetic barriers (the cross-linking reaction became diffusion controlled). As further indirect indication of systems in which the cure process is still in progress, it can be noticed that the physical aging process has not yet achieved its maximum level, testified by the relaxation enthalpy values (ΔH_{rel} in Table V) lower for both systems than those measured on the same systems after one year

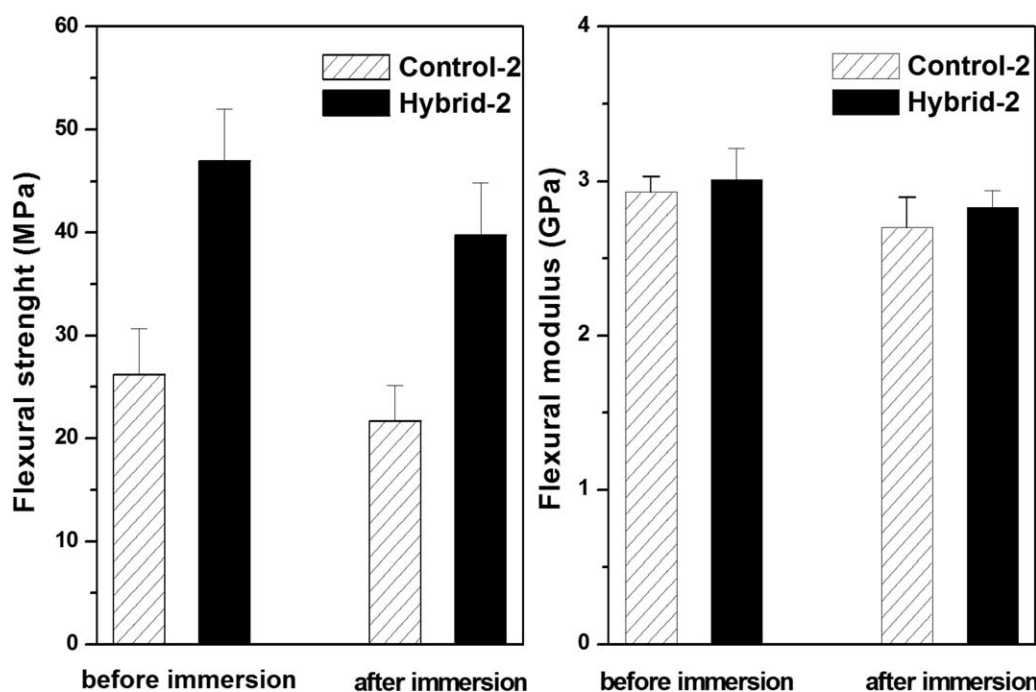


Figure 9. Flexural properties of the epoxy adhesives cured for 2 months, before and after their immersion for 3 weeks in distilled water.

of cure. Both systems, therefore, are still able to arrange their molecular structure towards the last thermodynamic equilibrium.

The T_g value of hybrid-2, reported in Table V, is comparable at this time to that developed by the control-2 system. This has been attributed to a phenomenon already observed by the authors in 4 mm thick specimens of O-I epoxy-silica hybrid, where the entrapment of ethanol formed into the specimens as by-product during the hydrolysis of TEOS, acting as a plasticizer for the epoxy network, has been found to slow down the condensation reactions.¹² It is necessary a longer curing period at room temperature to obtain for the hybrid a T_g higher than that of the control sample, as found for hybrid-1 samples.

Despite the negligible difference of T_g , the difference in the mechanical response is significant, as observed in Figure 9. The hybrid system, in fact, exhibits comparable stiffness but appreciably higher flexural strength (almost doubled) than the control one, being both systems cured for “only” two months. This constitutes another distinct advantage of a cold-cured epoxy-based hybrid over the parent epoxy resin.

Finally, the effects of a short immersion (3 weeks) in water on the T_g and on the flexural mechanical properties of hybrid and control systems have been assessed. Referring to the T_g values, a little reduction (never exceeding 4°C) has been found as consequence of a short-term immersion, irrespective to the system analyzed. More impressive are the results of flexural tests performed on immersed specimens: the superior mechanical performance of the hybrid system, in fact, is confirmed also in the short term ageing in water. The reductions in flexural properties are, in fact, much smaller than those measured on the control system. Furthermore, the immersed hybrid system maintains a flexural strength much higher than that measured on unimmersed control one.

CONCLUSIONS

The durability in water of an experimental cold-cured epoxy-silica hybrid, prepared by sol-gel process, has been analyzed. A tailored conditioning procedure of the specimens before exposure to water/moisture has been developed in order to overcome the well known lack of standard conditioning procedures for epoxy structural adhesives cured at room temperature. The conclusions of the study are summarized as follows:

1. Epoxy-silica hybrid have a Fickian sorption behaviour, characterized by higher saturation level and diffusion coefficient compared to the epoxy control at the same exposure conditions due to a higher polymer-water affinity and free volume.
2. The siloxane domains of epoxy-silica hybrids cured at ambient temperature undergo further sol-gel reactions during aging under high humidity conditions, causing a nearly complete recovery of T_g and mechanical properties which mitigates their initial reductions due to plasticization phenomena. This constitutes a distinct advantage of epoxy-silica hybrid systems over corresponding conventional cold-cured epoxy resins for outdoor applications.

3. Cold-cured epoxy-silica hybrids can be formulated and processed to provide a tailored “dual curing” mechanism, i.e. relative to the organic (thermosetting) and inorganic (silica constituents), which takes even advantage from environmental conditions to enhance their service performance.

To conclude, the enhanced performance of the novel epoxy-silica hybrids may open the possibility of overcoming some of the well known deficiencies of conventional epoxy adhesives in concrete/masonry repairing and structure strengthening applications: for the latter, in fact, environmental factors have a significant detrimental effect on the performance of the adhesives in service. Further studies are in progress to evaluate the desorption behaviour of the investigated systems.

ACKNOWLEDGMENTS

The experimental research and the instrumentations used were partially financed by PON 2007–2013 “IT@CHA - Italian Technologies for Advanced Applications in Cultural Heritage Assets” and Apulia Regional funds in the framework ‘Network of Public Research Laboratories’, Project: Applied Innovation Technologies for Diagnosis and Conservation of Built Heritage – A.I.Te.C.H. (2010-12), respectively. Mr. U. Falcone is kindly acknowledged for the specimens’ preparation and aging.

REFERENCES

1. Mascia, L. In *Functional Fillers for Plastics*; Xanthos, M., Ed.; Wiley-VCH Verlag: Weinheim, **2010**; p 469.
2. Piscitelli, F.; Lavorgna, M.; Buonocore, G.; Verdolotti, L.; Galy, J.; Mascia, L. *Macromol. Mater. Eng.* **2013**, *298*, 896.
3. Matejka, L. In *Hybrid Nanocomposites for Nanotechnology*; Merhari, L., Ed.; Springer: New York, **2010**; p 3.
4. Donato, R. K.; Donato, K. Z.; Schrekker, H. S.; Matejka, L. *J. Mater. Chem.* **2012**, *22*, 9939.
5. Afzal, A.; Siddiqi, H. M. *Polymer* **2011**, *52*, 1345.
6. Ochi, M.; Matsumura, T. *J. Polym. Sci. Pol. Phys.* **2005**, *43*, 1631.
7. Afzal, A.; Siddiqi, H. M.; Saeed, S.; Ahmad, Z. *RSC Adv.* **2013**, *3*, 3885.
8. Bondioli, F.; Darcchio, M. E.; Luyt, A. S.; Messori, M. *J. Appl. Polym. Sci.* **2011**, *122*, 1792.
9. Malucelli, G.; Priola, A.; Sangermano, M.; Amerio, E.; Zini, E.; Fabbri, E. *Polymer* **2005**, *46*, 2872.
10. Alonso, B.; Massiot, D.; Valentini, M.; Kidchob, T.; Innocenzi, P. *J. Non-Cryst. Solids* **2008**, *354*, 1615.
11. Spirkova, M.; Brus, J.; Hlavata, D.; Kamisova, H.; Matejka, L.; Strachota, A. *J. Appl. Polym. Sci.* **2004**, *92*, 937.
12. Lettieri, M.; Lionetto, F.; Frigione, M.; Prezzi, L.; Mascia, L. *Polym. Eng. Sci.* **2011**, *51*, 358.
13. Lionetto, F.; Mascia, L.; Frigione, M. *Eur. Polym. J.* **2013**, *49*, 1298.
14. Meier, U. *Constr. Build. Mater.* **1995**, *9*, 341.
15. Frigione, M.; Lionetto, F.; Mascia, L.; Antonacci, A. *Adv. Mater. Res.* **2013**, *687*, 94.

16. Ochi, M.; Takahashi, R.; Terauchi, A. *Polymer* **2001**, *42*, 5151.
17. May, M.; Wang, H. M.; Akid R. *Int. J. Adhes. Adhes.* **2010**, *30*, 505.
18. Moussa, O.; Vassilopoulos, A. P.; de Castro, J.; Keller T. *J. Appl. Polym. Sci.* **2013**, *127*, 2490.
19. Moussa, O.; Vassilopoulos, A. P.; Keller, T. *Int. J. Adhes. Adhes.* **2012**, *32*, 15.
20. Frigione, M.; Naddeo, C.; Acierno, D. *J. Polym. Eng.* **2001**, *21*, 23.
21. Frigione, M.; Lettieri, M.; Mecchi, A. M. *J. Mater. Civil. Eng.* **2006**, *18*, 715.
22. Frigione, M.; Lettieri, M. *J. Polym. Sci. Pol. Phys.* **2008**, *46*, 1320.
23. Perrin, F. X.; Nguyen, M. H.; Vernet, J. L. *Eur. Polym. J.* **2009**, *45*, 1524.
24. Xiao, G. Z.; Delamar, M.; Shanahan, M. E. R. *J. Appl. Polym. Sci.* **1997**, *65*, 449.
25. ASTM Standard D 790-92, ASTM International: West Conshohocken, PA, 1992.
26. ASTM Standard D570, ASTM International: West Conshohocken, PA, 1988.
27. Loh, W. K.; Crocombe, A. D.; Abdel Wahab, M. M.; Ashcroft, I. A. *Int. J. Adhes. Adhes.* **2005**, *25*, 1.
28. Vanlandingham, M. R.; Eduljee, R. F.; Gillespie, J. W. *J. Appl. Polym. Sci.* **1999**, *71*, 787.
29. Popineau, S.; Rondeau-Mouro, C.; Sulpice-Gaillet, C., Shanahan, M. E. R. *Polymer* **2005**, *46*, 10733.
30. Wong, T. C.; Broutman, L. *J. Polym. Eng. Sci.* **1985**, *5*, 521.
31. Duda, J. L.; Zielinski, J. M. In *Diffusion in Polymers*; Neogi, P., Ed.; Marcel Dekker: New York, **1968**.
32. Van der Wel, G. K.; Adan, O. C. G. *Prog. Org. Coat.* **1999**, *37*, 1.
33. Struik, L. C. E. *Pol. Eng. Sci.* **1977**, *17*, 165.
34. Zhou, J., Lucas, J. P. *Polymer* **1999**, *40*, 5505.
35. Zhou, J.; Lucas, J. P. *Polymer* **1999**, *40*, 5513.
36. Musto, P.; Ragosta, G.; Mascia, L. *Chem. Mater.* **2000**, *12*, 1331.
37. Mensitieri, G.; Lavorgna, M.; Musto, P.; Ragosta, G. *Polymer* **2006**, *47*, 8326.
38. Wu, P.; Siesler, H. W. *Chem. Phys. Lett.* **2003**, *374*, 74.
39. Soles, C. L.; Chang, F. T.; Gidley, D. W.; Yee, A. F. *J. Polym. Sci. Pol. Phys.* **2000**, *38*, 776.
40. Wu, C.; Xu, W. *Polymer* **2007**, *48*, 5440.