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Environmental effects on the adhesion properties of nanostructured epoxy-silica hybrids

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ABSTRACT: A nanostructured epoxy-silica hybrid based on epoxy systems with interpenetrating silica domains was designed for a possible use as a structural adhesive for civil engineering applications. Silica domains were obtained *in situ* during the curing of the thermosetting matrix by means of the sol-gel process, which was able to chemically bind the organic phase with the inorganic one. To assess the ability of the developed epoxy-silica hybrid system of overcoming some of the well known deficiencies of conventional epoxy adhesives used in civil engineering field, the environmental effects on the adhesion properties of these novel systems were investigated. First, flexural tests were undertaken on cast epoxy-silica specimens to determine the mechanical properties of the nanostructured adhesive when exposed to different environmental conditions, that is, moderate temperature or immersion in water. For comparison purposes, a control sample of epoxy resin, representative of a commercially available adhesive, was tested after the same exposure regimes. In order to assess their durability in service, concrete/concrete joints, bonded or with the hybrid epoxy-silica or with the control epoxy adhesive, were exposed to the same environmental conditions and subjected to adhesion tests according to the "slant shear test." The results obtained on both cast specimens and concrete/concrete adhesive joints proved the significantly better retention of properties of the nanostructured organic–inorganic adhesive compared to the control resin after exposure to moderate temperature or immersion in water. This constitutes a distinct advantage of the hybrid system over the corresponding conventional epoxy resins cured at ambient temperature for civil engineering applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42514.

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INTRODUCTION

Over the past 15 years fiber reinforced polymer (FRP) composites have been increasingly considered for concrete strengthening thanks to the great advantages over conventional repair materials.[1–4] Among thermosetting polymers, epoxy resins are the most widely used as a matrix for FRP materials, as well as bonding adhesives for FRP used for retrofitting of concrete structures. The reason of this widespread use is due mostly to their excellent adhesion to different materials, their ability to set and harden at ambient temperature with a minimum shrinkage and the outstanding mechanical properties. During the application, epoxy adhesives undergo a chemical reaction, called "curing" or "cross-linking," upon mixing with a proper hardener, whose amount and type control the rate of cross-linking and, consequently, the final properties of the adhesive. These latter are highly dependent on the curing temperature and curing duration, too.[3,5] For economic and practical reasons, the epoxy resins used in civil engineering applications must cure on site at ambient temperature, which strongly differentiates their performance compared to those of hot-cured epoxy adhesives.[6,7]

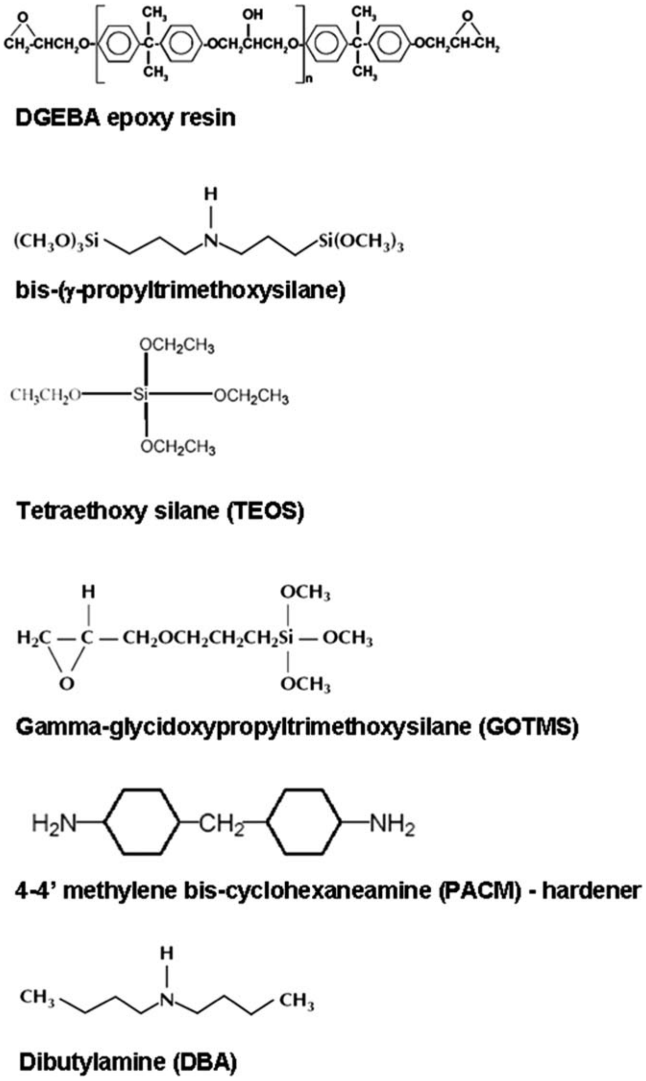
A curing process carried out at ambient temperatures, that is, in conditions which are very often unpredictable and uncontrolled, presents several drawbacks that can seriously affect the FRP performance: (i) the glass transition temperature, Tg, of the adhesive is not much higher than the ambient temperature[8,9] and, when this latter raises approaching the Tg, a dramatic decrease in the resin stiffness, strength and adhesion strength occurs;[10] (ii) long curing times (in the order of weeks) are necessary to achieve sufficient mechanical properties: the lower the curing temperature, the longer will be the curing time;[11] (iii) the cross-linking reactions are often not complete and the adhesive has residual reactive groups which potentially can continue the cure process if gain enough molecular mobility.[12–14]

The outstanding performance of epoxy resins and, consequently, FRP may be also negatively affected by the changing and hostile environmental conditions to which they can be exposed during their service life. These conditions usually involve large variations of temperature and humidity or presence of liquid water (i.e., rain).[15–17] Water may easily penetrate through a permeable adherent like the concrete, which possesses from 10 to 40% of volumetric fraction of voids and capillary pores,[18] and it can diffuse or be transmitted along the interfaces through capillary action.[19] After having accessed the joint, water may cause deterioration of the bond by altering the adhesive mechanical properties with a consequent adhesive displacement at the interface.[6] Epoxy resins are able to absorb water since they have polar groups linking water molecules. Once inside, water may alter the properties of the polymer both in a reversible manner, through plasticization phenomena caused and in an irreversible manner if hydrolysis, cracking, or crazing occur.[20] The plasticization phenomenon, responsible of a lowering of the Tg, is particularly harmful for epoxies curing at ambient temperature, whose typical Tg, as already underlined, is not much higher than the service temperature.[2,6,21] If the service temperature exceeds Tg, the adhesive will absorb more moisture at a faster rate than at ambient temperature. Several authors reported that substantial decreases in bond strength are experienced under wet and moist environments on epoxy resins used to bond FRP and concrete.[8,17,22–32]

An increase of the environmental temperature can also reduce the performance of epoxy adhesives cured at ambient temperature. A service temperature close to its Tg is able, in fact, to appreciably reduce the adhesion strength and the fatigue resistance of the adhesive.[8,16,33] For this reason, the environmental temperature under working conditions for adhesives cured at ambient temperature should be at least 20°C below the glass transition temperature.[17]

The great uncertainty about the durability of the epoxy adhesives cured at ambient temperature, especially when used for outdoor applications, has pushed research towards new advanced epoxy systems, able to overcome all the limitations above outlined. For example, some additives, such as silanes or organotitanates, added to the matrix prior to the setting up[34] or nanofillers, introduced into the polymer at the time of manufacture, have been proposed to reduce the moisture absorption, thus improving mechanical properties and durability.[35,36] Since contradictory results have been found by different authors,[37–42] it is unclear whether the addition of nanofillers improves the mechanical properties or not.[43] Consequently, there is uncertainty about the usefulness of these materials in civil engineering applications. Moreover, the utilization of additives and nanocomposites is expensive for the construction industry and currently it could be used only under very special circumstances.

Recently, hybrid organic–inorganic O-I epoxy resins have been optimized by the authors.[44,45] This new class of nanostructured materials is characterized by a strong integration between compatible organic and inorganic components at a molecular scale. The optimized hybrids are based on epoxy systems with interpenetrating silica domains obtained *in situ* during the curing of the thermosetting matrix by means of the sol-gel process, which is able to chemically bind, at nanometric scale, the organic phase with the inorganic one.



Scheme 1. Chemical structure of the materials used for the preparation of the investigated adhesives.

Unlike other O-I hybrid epoxies reported in literature,[46–50] the hybrid epoxy-silica systems proposed by the authors are the only ones able to polymerize at ambient temperature, thus developing superior performances compared to unmodified epoxy resins cured at ambient temperature at comparable production costs. From previous studies has been, in fact, verified that the presence of inorganic co-continuous domains in epoxy-silica hybrids enhances the load-bearing properties of the adhesive cured at ambient temperature.[44,51,52]

The present study is aimed to assess the suitability of the recently developed and optimized O-I epoxy-silica resin as a structural adhesive in civil engineering applications. To this aim, the nanostructured O-I epoxy-silica adhesive has been synthesized with the goal to improve the adhesion performance under severe but realistic service conditions. The short term durability of the O-I adhesive has been evaluated exposing the specimens to different realistic environmental conditions, such as moderate temperature and immersion in water. Finally, the experimental

Table I. Details of Concrete Composition Together with Compression and Tensile Strength

Sand (kg/m^3)	Gravel (kg/m^3)	Cement (kg/m^3)	Water (kg/m^3)	Filler (kg/m^3)	Additive (%)	Compression strength (MPa)	Tensile strength (MPa)
930	1610	360	214	480	0.60	55.0 ± 0.3	3.56 ± 0.7

formulation has been also applied to concrete/concrete joints, which have been exposed to middle temperature or water to analyze the retention of its properties in true service conditions.

MATERIALS

Adhesives

The experimental hybrid adhesive was a two-part formulation. One component (part A) consisted of a mixture containing a silane-functionalized epoxy resin and an alkoxysilane component based on tetraethoxysilane and γ-glycidoxypropyltrimethoxysilane. Part A of the experimental hybrid adhesive was synthesized through a procedure described elsewhere.[44] The second component (part B) was the hardener for the hybrid epoxy resin, which was 4-4′ methylene bis-cyclohexaneamine, a cycloaliphatic amine known with the PACM acronym. All the reagents for the production of the epoxy-silica hybrid adhesive were purchased by Aldrich (purity > 97%) apart from the liquid bis-phenol (DGEBA) epoxy resin, obtained from Resolution Performance Products with the commercial name of Epikote 828 (epoxy equivalent value of 184–190 g/mol). Before application, part A and part B were mixed at laboratory temperature for 10 min. After curing, the hybrid adhesive had a nominal silica content of about 15 wt %, which, from previous work of the same authors, has been found be the optimal silica content able to provide the adhesive in isolation with the highest mechanical strength and the maximum retention of properties when the adhesive is exposed to mild temperatures or immersed in water.[44,45,52–54]

The epoxy control system was a DGEBA resin modified with a tertiary amine, dibutylamine (DBA, supplied by Aldrich) at a 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 formulae of the materials used are reported in Scheme 1.

Concrete

The concrete mix used for the adhesion tests was provided by Italiana Calcestruzzi srl. Details of compositions of the concrete mix are reported in Table I. The mechanical properties (compression and tension strengths) of the concrete were evaluated according to the UNI EN 12390-3 and UNI EN 12390-6 standard tests,[55,56] respectively. The average compressive and tension strengths and the corresponding standard deviations are reported in Table I. As reported in Table I, a high strength concrete has been used for this study.

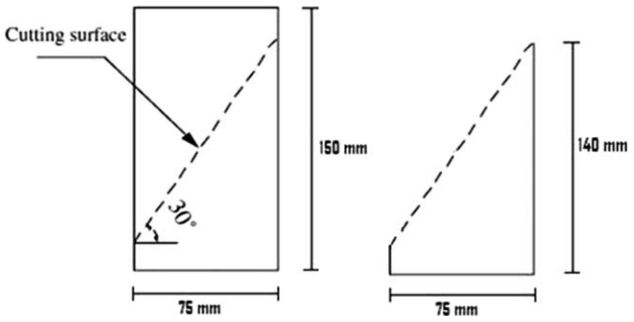


Figure 1. Concrete/concrete adhesive joint specimen.

Adhesive Joints

The experimental hybrid adhesive were used to join concrete cylindrical specimens, tested according to the ASTM C 882-91 standard.[57] The hybrid adhesive was used to bond together two equal sections (75 × 150 mm^2) of concrete cut at a 30° angle from vertical of a concrete cylinder (Figure 1). Before the application of the adhesive, any concrete surface was carefully dried and cleaned. The thickness of the final adhesive layer was set at 3 mm. The concrete/concrete epoxy-silica joints were allowed to cure at ambient temperature for 2 months, which was the time required to achieve an excellent setting of the resin, since, as obtained from a previous study performed on the same hybrid adhesive,[44] after 2 months of cure the 90% of final Tg was achieved. For comparison purposes, concrete/concrete epoxy joints, bonded with neat epoxy resin, were prepared as a control.

A total of 60 concrete cylinders, bonded either with the experimental either with the control adhesive, were prepared. A sample of the concrete/concrete adhesive joint after adhesive setting is reported in Figure 2.

Figure 2. Concrete/concrete adhesive joint specimen after adhesive setting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

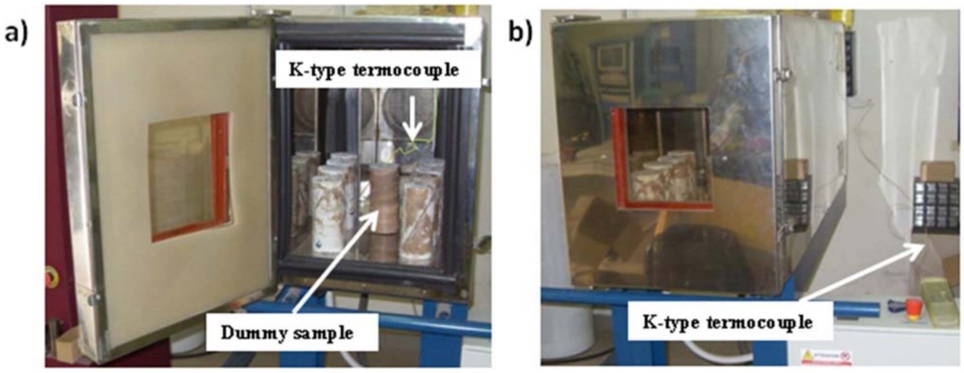


Figure 3. Oven for the conditioning of concrete/concrete joints at 50°C: (a) open with the specimens inside; (b) closed; the arrow indicates the digital temperature reader displaying the internal temperature of adhesive at the adhesive/concrete interface of a sacrificial sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of Adhesive

Specimens of hybrid epoxy adhesive were cast in Teflon moulds with $100 \times 10 \times 4$ mm^3 dimensions. The specimens were cured for 7 days at ambient temperature in a controlled environment (23°C and 55% relative humidity) and, then, demolded and aged for 2 months in the same controlled environment. For comparison purposes, specimens of neat epoxy resin were prepared as a control.

Three point bending test were performed at laboratory temperature following the ASTM D790 standard[58] 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. The reported results were the average values of at least 10 experiments.

Moreover, flexural tests were also performed at 50°C on specimens previously heated at 50°C for the time necessary to reach a uniform temperature inside the sample, monitored by two K-type thermocouples, placed both on the surface and on the inside of a dummy sample. This conditioning temperature was chosen because it represents a value both reachable in the summer period either close to the Tg of samples cured at ambient temperature. The reported results were the average values of at least 10 experiments for each kind of adhesive.

Finally, for each kind of adhesive, 10 specimens were immersed in distilled water for 3 weeks and then tested in three point bending mode at laboratory temperature.

Adhesion Tests at Different Environmental Conditions

The strength of the bond between each epoxy adhesive and the concrete was studied in accordance with the "slant shear test" reported in the ASTM C 882-91 standard[55] using a Metro Com Engineering compression testing machine with a crosshead speed of 1 mm/min. The slant shear test has become the most widely accepted test for evaluating the bond of adhesive repair materials to concrete substrates.[59] During axial compression loading, the interface surface was under compression and shear stresses.

The bond strength (σ) of the composite cylinder was determined as the ratio between the load carried by the specimen at failure and the effective area of the elliptical bonded surface. Each measure was performed on 10 specimens, at least, and the results averaged.

To investigate the effect of the service temperature on the bond strength, 10 concrete/concrete epoxy-silica joints and 10 concrete/concrete epoxy joints were conditioned for at least 2 h at 50°C in an oven and, then, tested at the same temperature. This conditioning temperature was chosen because it represents a value both close to the Tg of samples cured at ambient temperature and reachable in the summer period. It has been found that in summer periods with air temperature around 40°C, the temperature of an epoxy resin inside a concrete element with the surface irradiated by sun, can be about 7°C higher.[19] The conditioning time at 50°C was determined by means of K-type thermocouples inserted inside a sacrificial joint specimen, on the adhesive-concrete interface and inside the concrete, which monitored the adhesive and concrete temperature, as shown in Figure 3.

The effect of water exposure on the bond developed between any adhesive and concrete was also studied. The samples of concrete/concrete joints bonded with the experimental or the control adhesive were immersed in distilled water at a temperature of 23°C ± 1°C for 21 days. Then, the samples were left for 2 days in air at ambient temperature and finally subjected to compression tests at laboratory temperature.

The thermal properties of the hybrid and control adhesive after the adhesion tests were determined by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 822. Some small fragments of adhesive, taken from the concrete/concrete adhesive joints, with an average weight around 10–14 mg, were heated under nitrogen atmosphere from 5 to 200°C at a 10°C/min heating rate. The glass transition temperature was determined as the midpoint of the change in the endothermic heat capacity step. The calorimetric experiments were repeated at least three times and the results averaged.

RESULTS

Characterization of the Nanostructured Epoxy-Silica Adhesive

The effect of environmental factors on the flexural characteristics of the novel nanostructured hybrid adhesive is reported in

Table II. Flexural Properties Evaluated on both Epoxy–Silica and Control Adhesive at Room Temperature, at 50°C and after Water Immersion for 21 days (σ = flexural strength; E = flexural modulus)

	Control			Hybrid		
	23°C	50°C	Water	23°C	50°C	Water
σ (MPa)	26.2 ± 3.8	12.3 ± 4.3	20.3 ± 3.5	47.0 ± 5.1	30.1 ± 5	40.2 ± 5.7
E (GPa)	2.9 ± 0.1	2.4 ± 0.1	2.6 ± 0.2	3.0 ± 0.2	2.6 ± 0.1	2.8 ± 0.2

Table II. For comparison purposes, the flexural properties of a control epoxy resin, representative of a commercial resin cured at ambient temperature, are reported too. The results of three-point bending tests at ambient temperature evidence the significant enhancement in mechanical properties resulting from the hybridization of the epoxy resin. The O-I epoxy-silica hybrid system, in fact, exhibits a comparable stiffness but a noticeable improvement in flexural strength (almost doubled) compared to the control one, which presents mechanical properties comparable with those found in commercial epoxy adhesives tested in previous works.[60] This distinct advantage of the O-I hybrid cured at ambient temperature over the parent epoxy resin is due to the unique morphology of the nanostructured adhesive, resulting from the chemical interaction of the silica nanodomains with the thermosetting matrix at a molecular level and the restriction of molecular dynamics at the interface between the organic and inorganic regions of the adhesive, as previously found by the authors.[44,52]

In addition, when the mechanical tests are performed at 50°C, the expected decrease in flexural characteristics is limited in the case of the hybrid system, as observable in Figure 4, where the retention of flexural properties of the control and hybrid adhesive, obtained as the ratio between the property measured in each environmental condition and the corresponding property at ambient temperature is reported. At 50°C about 64% of the initial flexural strength of the O-I hybrid adhesive is retained. This result is particularly important if compared with the control resin, where the initial flexural strength is more than halved when it is measured at 50°C. In addition, the strength at 50°C of the O-I hybrid resin (30.1 MPa) is about 15% higher than the strength of the control resin measured at laboratory temperature (26.2 MPa). As concerning the flexural modulus, the retention of the initial value of the hybrid resin is slightly higher than the value of the control resin.

The retention capability of flexural strength and modulus of the hybrid adhesive is remarkable even after immersion in water for 3 weeks, as reported in Table II. As expected, the plasticization effect of water brings about an appreciable decrease in strength and stiffness of both adhesives cured at ambient temperature. However, the superior performance of the hybrid system is confirmed by a reduction in flexural mechanical properties much smaller than that measured on the control system. After a short term immersion in water, about 85% of the initial flexural strength of the O-I hybrid adhesive is retained against about 77% in the case of control resin.

Moreover, the strength after water immersion of the O-I hybrid resin (40.2 MPa) is about 53% higher than the strength of the un-immersed control resin (26.2 MPa). This remarkable result is due to the fact that the siloxane domains of the epoxy-silica hybrid cured at ambient temperature undergo further sol–gel reactions during aging under high humidity conditions, which counteracts the plasticization phenomena.[52] This constitutes a distinct advantage of epoxy-silica hybrid systems over

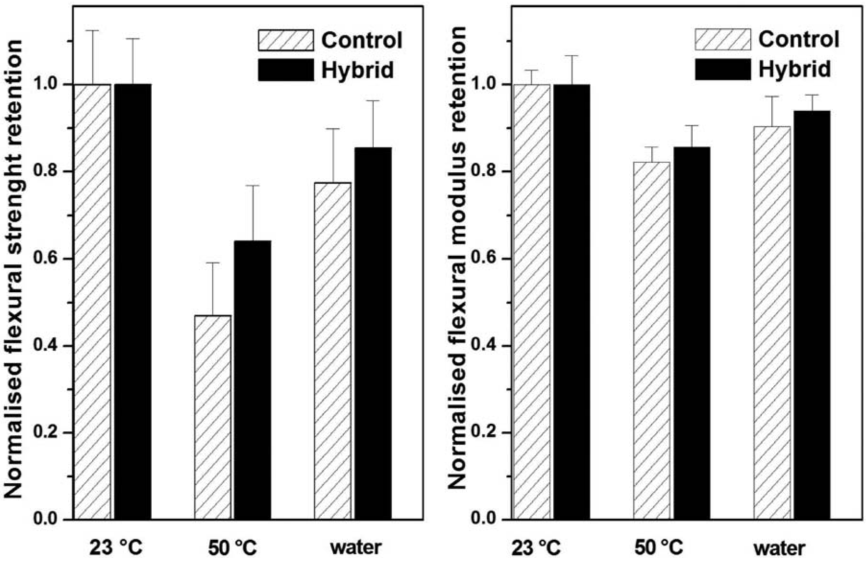


Figure 4. Normalized retention of flexural properties of control and hybrid adhesive.

Table III. Adhesion Strength of Adhesives to Concrete in Different Environmental Conditions

Adhesive	Adhesion strength in std. condition (MPa)	Adhesion strength at 50°C (MPa)	Adhesion strength after a 21-days immersion (MPa)]
Control	9.9 ± 1.4	5.7 ± 1.3	6.8 ± 1.1
Hybrid	13.7 ± 2.0 (+ 38%)	8.8 ± 1.8 (+ 54%)	11.0 ± 2.3 (+ 62%)

corresponding conventional epoxy resins cured at ambient temperature for outdoor applications.

The outstanding mechanical performance achieved by the experimental hybrid system in comparison to the standard epoxy cured at ambient temperature pushed the research toward analyzing the short term durability of the hybrid adhesive when it is used to bond two concrete surfaces, as in real service applications.

Adhesion Tests at Laboratory Temperature

The results of the adhesion tests performed on concrete cylinders, bonded with hybrid or control adhesives and exposed to different environmental conditions, are reported in Table III. In brackets the percentage difference in adhesion strength of the concrete joints bonded with the hybrid adhesive compared to that of the joints bonded with the control adhesive, measured in the same environmental conditions, are reported. In Figure 5 the retention of the adhesion strength of the concrete/concrete joint, obtained as the ratio between the property measured in each environmental condition and the corresponding property measured at ambient temperature, is shown.

The adhesion strength and the kind of failure observed in the concrete/adhesive specimens are mainly influenced by the strength of the adhesive. In all the performed tests, a higher adhesion strength has been achieved by using the more resistant adhesive, that is, the hybrid one. In fact, the adhesion strength of the joint with the O-I epoxy-silica resin is more than 38% higher than that observed in the joint with the control resin. Therefore, the experimental results obtained at laboratory temperature, showing a clear improvement of the adhesion performance of the O-I hybrid adhesive, confirm the usefulness of the use of this nanostructured adhesive for civil engineering applications.

The dominant failure mode has been determined on the basis of the visual examination of the fracture surfaces of the tested specimens. Since in this work a high strength concrete has been used, the expected failure mechanism should be of a mixed type, consisting both of simultaneous crushing within the concrete and inside the adhesive and debonding at the interface. However, some interesting differences have been observed among specimens bonded with control and hybrid adhesives, in accordance with the obtained mechanical results.

In the case of concrete joints with control resin, adhesion failure has been recorded in almost all samples, as can be observed in Figure 6. The failure has been primarily attributed to debonding of the adhesive along the concrete/adhesive interface with the total slip of the two halves forming the elliptical concrete joint. This indicates that the adhesion strength between the control adhesive and the concrete adherent is lower than the cohesive strength of the polymer and of the concrete.

On the other hand, the adhesion behavior of the concrete/concrete joints bonded with the hybrid adhesive was found to be excellent. As reported in Figure 7, a collapse typical of the entire concrete specimen under compression load, that is, vertical cracks within the whole samples, without detachment and slip

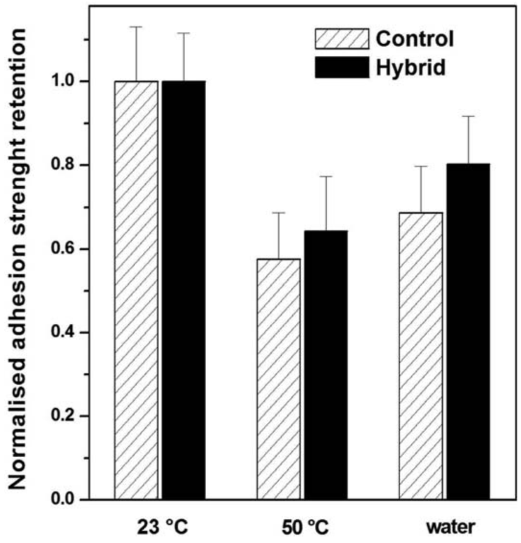


Figure 5. Normalized retention of adhesion strength of concrete–concrete joint.

Figure 6. Failure mode in a joint bonded with control resin; the arrow indicates the fracture inside concrete. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Failure mode in a joint bonded with O-I hybrid resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on the interface, has been observed. This is due to the higher mechanical strength and adhesive strength of the O-I hybrid adhesive compared to that of the concrete. This result is a distinct advantage of the experimental hybrid resin compared with the control, which exhibits the typical behavior of the commercial available products previously tested.[58]

After adhesion tests at laboratory temperature, from the adhesive/concrete interface some small fragments of adhesive have been taken and analyzed with DSC. An example of calorimetric thermograms is reported in Figure 8. From the heat scanning of both control and hybrid adhesive an endothermic peak at the upper temperature side of the glass transition region is observable. This phenomenon, very common in epoxy resins cured at ambient temperature, is due to the physical ageing of the adhesive stored at ambient conditions, that is, at temperature lower than its Tg but close to it.[61,62] The endothermic peak results, in fact, from the disruption of short range molecular order between cross-links, manifested as a relieve of the enthalpy acquired by physical ageing during curing. In the thermograms of Figure 8, the glass transition region is followed by an exothermic peak at higher temperatures arising from the reactivation of the incomplete curing of the residual reactive groups of the organic domains. These latter, previously frozen in the glassy state, can continue to react very slowly with a diffusion controlled kinetics for several months and even years during ageing at ambient temperature, as reported in literature.[52,63,64] The residual heat of reaction of the hybrid system, evaluated as the area of the exothermic peak, is smaller than that of the control system, indicating the achievement of a higher degree of cross-linking and of a more stable system.

The Tg value for each sample has been taken as the temperature at the mid-point of the curve between the onset of the transition and the enthalpy peak associated with the erasing of physical ageing. The values of glass transition temperature have been reported in Table IV. Although the significant higher mechanical properties, the Tg values are surprisingly lower in the hybrid adhesive than in the control adhesive. This is most likely due to the presence of low molecular weight products (water and ethanol) arising from the condensation reaction of the nanosilica slowly formed inside the concrete/concrete joint, which cannot evaporate and give some plasticization effect on Tg. This phenomenon has been also observed in laboratory experiments on thick samples of epoxy-silica hybrid resin.[45]

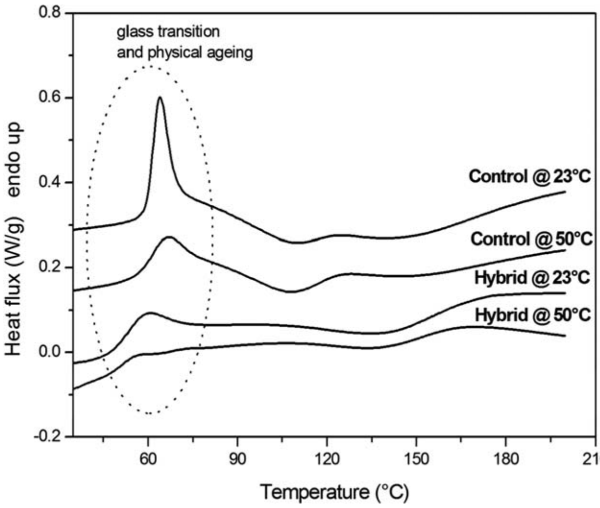


Figure 8. DSC thermograms of the adhesive taken from the concrete/concrete joints after adhesion test at 23 and 50°C.

Adhesion Tests at 50°C

In order to verify the effect of environmental exposure to moderately high temperatures, some concrete/adhesive joints have been conditioned in an oven at 50°C for 2 h and, then, tested at the same temperature. In Table III the results of the adhesion tests at 50°C are reported. In brackets the percentage difference in adhesion strength of the concrete joints bonded with the hybrid adhesive compared to that of the joints bonded with the control one, measured at the same temperature, are reported. As observed from Figure 5, upon exposure at 50°C the O-I hybrid adhesive is able to retain about 64% of its adhesion strength to concrete at laboratory temperature while the control adhesive retains only the 57% of the initial value. However, the concrete joint bonded with the hybrid adhesive exhibits a significantly higher (about 54%) adhesion strength compared to that measured on the concrete joint bonded with the control adhesive in the same environmental condition.

Table IV. Glass Transition Temperature Evaluated on both Epoxy–Silica and Control Adhesives after Adhesion Test Performed on Joints Exposed to Different Environmental Conditions

	Tg after adhesion test (°C)		
Adhesive	At room temperature	At 50°C	After immersion in water
Control	61.1 ± 1.0	59.6 ± 0.7	59.1 ± 0.8
Hybrid	54.2 ± 0.9	53.1 ± 1.0	52.6 ± 0.8

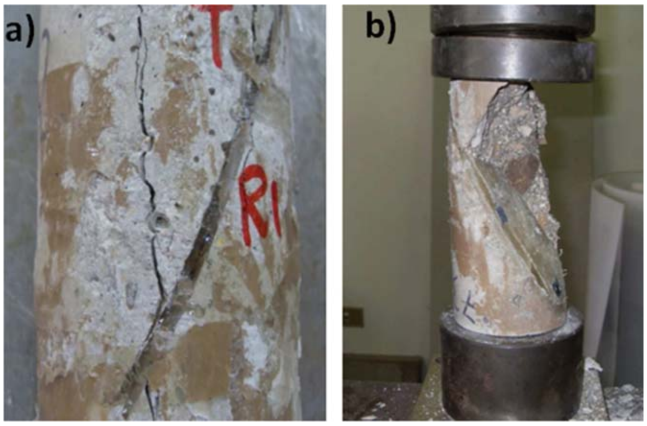


Figure 9. Failure modes in joints bonded with O-I hybrid resin tested after exposure at 50°C (a) and after immersion in water (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The heating of the cross-linked adhesives for a short time at a temperature close to the Tg causes the erasing of physical aging, as confirmed by the reduction of the height of the endothermic peak for both adhesives in Figure 8. However, the exposure time has not been enough to cause the post-curing of the resin, as confirmed by the Tg values reported in Table IV, which do not seem to be affected by the exposure condition.

The decrease in mechanical properties occurring when the range of glass transition temperature is approached, agree with the findings of other authors on FRP/concrete samples tested with single lap shear tests.[65,66]

By approaching the Tg of the adhesive, the mechanical properties of the resin dramatically drop, and as a consequence the adhesive layer becomes the weakest part of the composite cylinder. This results in a loss of bond between concrete and adhesive which affects the failure mode. The concrete samples bonded with the hybrid adhesive tested at 50°C present fractures in the concrete and partial slip at the interface between concrete and adhesive, as reported in Figure 9(a). In the case of the control adhesive, the complete debonding at the interface has been more frequently observed. The obtained results confirm the superior properties of the O-I hybrid adhesive over the control one even at moderately high temperatures.

Adhesion Tests after Immersion in Water

In order to complete the analysis on the concrete/adhesive bond strength when subjected to short term severe environments, the effect of water immersion on the bond developed between both adhesives and the concrete has been studied. Some half-cylinders of concrete bonded with hybrid or control adhesives have been immersed in distilled water for 21 days and then tested after drying 2 days in air. The main results of adhesion tests are given in Table III, where in brackets the percentage difference in adhesion strength of the concrete joints bonded with the hybrid adhesive compared to that of the joints bonded with the control adhesive, measured after the same environmental exposure, are reported.

As stated in the Introduction, a reduction in the adhesion strength due to the plasticizing effect of water on the adhesive is expected. However, the hybrid epoxy-silica adhesive demonstrates once again an excellent retention of properties. Compared to the values measured at ambient temperature, the hybrid resin is able to retain the 80% of its adhesion strength, which, after the water immersion, is however more than 62% higher than the value displayed by the control adhesive after immersion.

The crisis mechanism changes with the environmental test condition due to the plasticization of adhesive induced by moisture ingress, which is responsible of the decrease of the adhesion strength and the interfacial capacity. After immersion in water for 3 weeks, some of the concrete specimens with O-I adhesive display a mixed fracture, characterized not only by failure within the concrete but also by slip at the interface and failure of the resin, as reported in Figure 9(b), while adhesion failure due to the complete debonding at the interface has been the failure mode of all the specimens prepared with the control adhesive.

CONCLUSIONS

The effects of environmental factors on the adhesion characteristics of an experimental nanostructured O-I hybrid adhesive have been studied. On the basis of the performed experimental investigation and the related obtained results, the following considerations can be remarked:

1. The *in situ* production of siloxane domains during curing at ambient temperature of an epoxy resin leads to the formation of a nanostructured O-I adhesive, characterized by a significant enhancement of the mechanical properties at ambient temperature over the parent epoxy resin. In particular, the obtained flexural strength at 20°C has been almost doubled.
2. When the epoxy-silica hybrid adhesive is exposed to realistic environmental conditions, a good retention of properties is further shown by the hybrid adhesive.
3. The outstanding performance of the O-I epoxy resin has been also confirmed when it is applied to join two concrete elements through the slant shear method. The adhesion strength to concrete of the epoxy-silica adhesive is about 38% higher than that exerted by the control epoxy resin. In addition, an excellent retention of properties has been obtained after exposure to environmental conditions, in particular to water immersion.
4. The significant difference between the adhesion behavior of control and hybrid adhesive are reflected also on the failure mode of the concrete/concrete joints under adhesion tests. The prevalent failure mode is within the concrete for the joints bonded with the O-I hybrid adhesive, while it is characterized by slip at the interface or debonding in the case of the joints bonded with the control adhesive.

The enhanced performance of the novel epoxy-silica hybrids may, therefore, open the possibility of overcoming some of the well known deficiencies of conventional epoxy adhesives in civil engineering applications: for the latter, in fact, environmental factors have a significant detrimental effect on the performance of the adhesives in service. It must be underlined, finally, that the production costs of the hybrid systems based on epoxy resins are comparable to those of commercial adhesives cured at ambient temperature.

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