Innovative nanostructured materials as cold-cured adhesive/matrix of FRP for strengthening of building structures

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ABSTRACT: Thermosetting cold-cured resins are largely used as structural adhesives and/or matrix to manufacture and apply fiber reinforced polymer (FRP) composites employed in retrofitting technique. The slow development of their mechanical, adhesive and physical properties due to a cold-cure process represents a serious inconvenience in the repair procedures of large structures. Furthermore, the durability of these materials is still unclear, especially when they are outdoor exposed to common or harsh environmental conditions. These issues are likely to hamper the enormous potential of structural adhesives in construction field and their composites employed for strengthening and rehabilitation of infrastructures. The development of innovative nanostructured (hybrid) materials based on thermosetting (mainly epoxy) resins to be used as structural adhesives, and possibly as matrices for FRP composites, has been recently explored in the view to overcome some of the well-known drawbacks of traditional structural adhesives and matrices for construction industry. Some of the recent findings in this field will be illustrated.

1 INTRODUCTION

Structural thermosetting resins, largely based on "cold-curing" epoxies, in view of their superior properties with respect to those of traditional repairing materials, are commonly used as either adhesives and matrices for fiber reinforced polymers (FRP) for the strengthening and rehabilitation of civil engineering structures. One of the main consequences of a cold-cure, i.e. a cross-linking process of the resin carried out at ambient temperature, is that very long curing times (even months) are necessary to achieve sufficient adhesive and mechanical properties, the lower the curing temperature, the longer the curing time. Furthermore, the cross-linking process of the cold-cure resin is often not completed due to kinetic restrains. Finally, there is great concern regarding the long-term behavior of the rehabilitated structures for outdoor applications, since environmental factors can bring about severe deterioration of cold-curing epoxies, in particular on their glass transition temperature (Tg), Frigione et al (2001). A characteristic feature of the commercial cold-cured epoxy systems is, in fact, that their Tg is usually limited to about 50-60°C; this latter property can even decrease in service through water induced plasticization, Frigione (2018). The Tg, on the other hand, represents the superior limit beyond that the adhesive resin behaves as a rubber, with a dramatic loss of mechanical and adhesive properties at temperatures around 15°C below the Tg. Thus, even though already employed in many structural applications, the performance and durability of cold-cured epoxy adhesives/matrices for FRP exposed to external environment is still a highly debated issue, Hollaway (2010). These considerations hamper the enormous potential of adhesives and FRP in construction applications, since the acceptable lifetime of the products employed in this field should be at least 50-100 years, Frigione (2016).

Among the innovative solutions explored in the last years by academic and industrial research in the view to overcome the deficiencies displayed by commercial cold-cured epoxy-based adhesives/matrices for FRP, nanostructured hybrid systems, based on epoxy resins containing interpenetrating silica nano-domains, raised a major interest. Organic-inorganic (O-I) hybrids are characterized by a morphology consisting of co-continuous domains in the region of 5–20 nm of organic chains chemically linked to the inorganic phase, composed by nanometric silica with hydroxyl groups and obtained through sol-gel method. Starting from previous studies on organic-inorganic hybrids by Mascia et al (2006), it was believed that the presence of inorganic co-continuous domains in epoxy-silica hybrids would greatly enhance the load-bearing properties of the resins and their adhesion to construction materials (concrete, masonry, bricks), even under harsh service conditions. Furthermore, shorter curing times to achieve sufficient physical properties, such as glass transition temperature, were expected.
Different hybrid epoxy-silica formulations were, then, produced and cold-cured. The development in time of their physical properties (Tg, mechanical properties, adhesion to concrete/masonry), as well as their durability if exposed to different exposure regimes, were studied. It was found that these novel O-I epoxy-based hybrids display significant advantages, in terms of development of short- and long-term properties and durability performance, over the typical epoxy structural adhesives at competitive costs: thus, they could represent a viable solution towards the well-known durability issues of the commercial cold-cured epoxies.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Hybrid formulations

Different experimental two-part formulations, summarized in Table 1, were realized and studied, as detailed described in Lettieri et al (2011), Lionetto et al (2013), Lionetto et al (2019).

Table 1: Details of composition of the formulations realized.

System	Resin (Part A)	Curing agent (Part B)	Amine/epoxy ratio
Control B0	DGEBA	PACM + M851	0.75/1
BSi	DGEBA – 7.5% SiO_2	PACM + M851	0.75/1
BSiMo	DGEBA – 7.5% SiO_2	PACM + M851 + $(NH_4)_2Mo_2O_7$	0.75/1
Control DGEBA	DGEBA	PACM	0.75/1
Hybrid DGEBA	DGEBA – 15.0% SiO_2	PACM	0.75/1
Epoxy-A	DGEBA	TETA	1:1
Hyb-L-A	DGEBA 5.1% SiO_2	TETA	1:1
Hyb-H-A	DGEBA 5.3% SiO_2	TETA	1:1
Epoxy-B	DGEBA	PACM	0.75/1
Hyb-L-B	DGEBA 7.0% SiO_2	PACM	0.75/1
Hyb-H-B	DGEBA 7.1% SiO_2	PACM	0.75/1

They were all based on silane functionalized bis-phenol A (DGEBA) resins (Part A) cured with different amine systems (Part B), i.e.: 4-40 methylene bis-cyclohexaneamine (PACM) plus small amounts of catalysts and ammonium molybdate powder, when applicable; aliphatic amine

(Triethylenetetramine, TETA). In the last produced epoxy-silica precursors, a deep eutectic solvent (DES) based on a mixture of choline chloride (ChCl) and urea (U) was added in low, i.e. 2.5 phr (Hyb-L-A or Hyb-L-B) or high, i.e. 5 phr (Hyb-H-A or Hyb-L-B) amounts.

Table 1 reports the composition of all the formulations realized, with the indication of the nominal SiO_2 content in the final cured epoxy-siloxane hybrid and the employed molar ratio (amine/epoxy). For each hybrid formulation, For comparison purposes an epoxy-based non-hybrid control was produced.

2.1.2 Preparation and curing of specimens

For each formulation, Part A and Part B were carefully mixed manually for 5 min, in proper amounts. The liquid mixtures were then poured in Teflon molds and cured for 24 hours in a controlled laboratory environment (i.e. 23°C ± 2°C, 55% ± 5% R.H.). Further curing was carried out on the ‘‘free’’ specimens, i.e. removed from the mold, in the same conditions for prolonged times (up to one year, depending on the formulations).

2.1.3 Concrete/masonry elements and adhesive joint

The concrete mix used for the adhesion tests with the epoxy-silica hybrids were characterized by compressive and tensile strength of 55.0 MPa and 3.6 MPa, respectively. The stone selected for the adhesion strength to masonry was Calcarenitic *Leccese stone*, characteristic of masonry construction of Salento region (South Italy) and characterized by a compressive strength of 15 MPa. Some of the experimental hybrid adhesives were used to join concrete/masonry cylindrical specimens. The hybrid adhesive was used to bond together two equal sections (75 x 150 mm^2) of concrete cut at a 30° angle from vertical of a concrete cylinder, being 3 mm the thickness of the final adhesive layer. The concrete/concrete epoxy-silica joints were allowed to cure at ambient temperature up to two months. For comparison purposes, concrete/concrete epoxy joints, bonded with neat epoxy resin, were also prepared.

2.2 Characterization Techniques

2.2.1 Tests performed on epoxy-silica formulations

Different physical properties were evaluated on experimental organic–inorganic epoxy-silica hybrids, as a function of the employed curing time. The evolution of the glass transition temperature of the produced hybrid systems was monitored (by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 822) during curing at room temperature in a controlled humidity environment, even varying the thickness of specimens (from 0.2 to 4.5 mm), in order to assess the behavior of the adhesive in true applications. The mechanical (flexural and dynamic-mechanical) properties of the hybrid systems, cured for different time spans, were evaluated using a LR5K Lloyd Instruments Machine with displacement control (grip separation rate of 2 mm/min, span/thickness ratio of 16:1) to determine the flexural characteristics, and an ARES rheometer (Rheometric Scientific) in the torsion rectangular configuration (using a constant heating rate of 2°C/min, from 30°C to 200°C, frequency of 1 Hz) to assess the dynamic-mechanical properties, respectively. The flexural properties were also measured after exposure to different levels of humidity (varying between 55 and 100 %) or immersed in distilled water, representing these latter realistic service outdoor conditions. Flexural tests were also performed at temperatures slightly higher (50°C) than the typical ambient temperature. This temperature was chosen since it represents a value both close to the Tg of samples cured at ambient temperature and also achievable in summer. It was found, in fact, 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 achieve even 50°C. Thermogravimetric analysis (TGA/DSC1 Stare System, Mettler Toledo) was performed up to 800°C on some of the produced hybrids. The TGA experiments were performed in air in order to assess the true decomposition temperatures for each system. The latter information, in fact, can give a useful indication of the thermal resistance and the fire behavior of the resins.

2.2.2 Adhesion strength to concrete/masonry in standard and severe conditions

The cylindrical concrete joint specimens, prepared as described in 2.1.3, were tested according to the ASTM C 882-91 "slant shear test" standard, the most widely accepted test for evaluating the bond of adhesive repair materials to concrete substrates. The strength of the bond between each, hybrid or standard, epoxy adhesive and the concrete was studied using a Metro Com Engineering compression testing machine with a crosshead speed of 1 mm/min. 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. To investigate the effect of the service temperature on the bond strength, some concrete/concrete epoxy-silica joints were tested at 50°C, again in order to simulate a realistic condition, i.e. characteristic of Mediterranean region during summer, according to previous studies performed on commercial adhesives, Aiello et al (2002). The effect of water exposure on the bond developed between any adhesive and concrete was also studied, according to same previous research. 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 for three weeks. Then, the samples were left for 2 days in air at ambient temperature and finally subjected to compression tests at laboratory temperature. Similar experiments were also performed on masonry/epoxy-based hybrid joints.

3 RESULTS AND DISCUSSION

3.1.1 Development of glass transition temperature in hybrid epoxy adhesives

As already underlined, one of the main issue related to the use of structural cold-cured adhesives is the slow development of their Tg, whose value results slightly above the ambient temperature, even after prolonged curing times. Therefore, the first parameter measured on the different hybrid systems under analysis was their Tg after short and long cold-curing times.

In Figure 1, the average values of Tg (obtained by DSC analysis) as a function of the curing time for some of the systems realized, are reported. For all the experimental systems, it was found that the Tg of the hybrid formulations significantly increases over the control resins in reduced curing times (i.e. time to achieve a stable structure). In particular, the Hybrid DGEBA formulation developed a glass transition temperature even greater than 70°C after a cold-curing of about four months, which represents a significant advancement over the commercial epoxy-based systems. The hybrid systems containing DES and cured with TETA amine display comparable Tg values but at longer curing times, while Tg much greater than 70°C were measured for both Hyb-L-B and Hyb-H-B after a prolonged cold-cure. An adverse effect of the thickness of the specimens on Tg was observed for BSi and BSiMo hybrids and attributed to the entrapment of some alcohol formed during the hybridization of the epoxy component.

As a first main conclusion of the present study, the produced cold-cured hybrid epoxy-silica adhesives were able to provide the desirable increase in Tg with respect to typical epoxy adhesives, with an additional advantage in reducing the curing times. The observed advantages seem to arise even in presence of a low amount of silica in the hybridized epoxy.

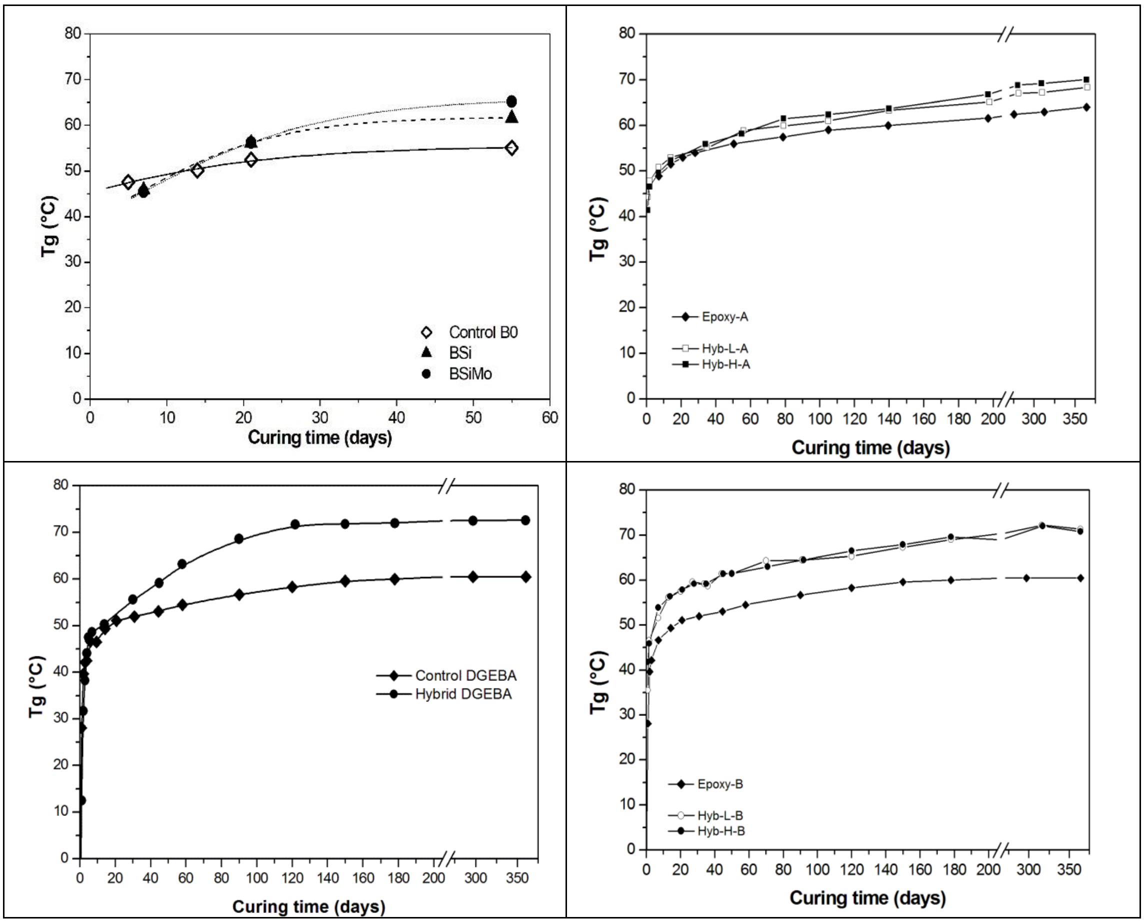

Figure 1. Tg values as a function of curing time for the studied, hybrid or control, epoxy systems.

3.1.2 Mechanical (dynamic-mechanical and flexural) properties of hybrid epoxy adhesives

The results of the DMTA tests, performed on Hybrid DGEBA system after a seven-month cold-cure, indicate an appreciable improvement in the mechanical properties of this new system compared to the same properties displayed by the corresponding unmodified epoxy-based adhesive, i.e. Control DGEBA, cold-cured in the same conditions. The inclusion of silica in the epoxy matrix produces clear changes in the dynamic mechanical parameters. This hybrid system, in fact, shows the smallest magnitude of the loss factor and the broadest range of relaxations within the glass transition region. Evident increases in storage modulus at ambient temperature and in the rubbery-plateau region were observed. This enhancement is higher in the rubbery state, ensuring a better high temperature performance of the hybrid system with respect to the corresponding epoxy resin. For the same system, it was observed an appreciable increase in Charpy impact test toughness (+92%), with respect to the unmodified resin, demonstrating that the siloxane domains are also able to provide a toughening effect to the resin.

Similar results were found for the hybrid systems containing DES and cold-cured for four months. The presence of siloxane domains in these hybrid systems leads to a significant increase in the storage modulus G’, which is more evident at high temperatures, i.e., in the rubbery plateau region. The tanδ curves of the hybrid systems show a significant increase in Tg along with a reduction of the peak height. These results indicate a hindering of the molecular motion of the organic chains brought about by the presence of nano-structured silica domains.

The flexural mechanical data shown in Table 2 for the different systems examined testify the significant enhancement in mechanical properties resulting from the modification of the epoxy resin. Appreciable improvements in mechanical properties, i.e. both in strength and stiffness, were provided by the efficient reinforcement of the inorganic phase (siloxane domains) in Hybrid DGEBA. The hybrid systems containing DES component display a general increase in strength with respect to the control resins, representative of commercial cold-cured adhesives, even doubled when a cycloaliphatic curing agent was employed. Smaller were the increases in flexural modulus observed in such hybrids, once again the best results were those measured on Hyb-B systems. Finally, the hybrid systems cold-cured in presence of an accelerator and containing ammonium molybdate displayed the lowest flexural mechanical characteristics, even lower than those measured on typical cold-cured epoxy adhesives, testifying the key-role of the chemical formulation in the production of successful epoxy-silica hybrids. The comparison between different hybrid systems suggests that the amount of silica has a certain effect on their mechanical data. A quantitative comparison, however, is not feasible since the procedures to obtain the different hybrids substantially differ.

Table 2. Mechanical properties of specimens cured for 2-4 months at ambient temperature

System	Test Temperature (°C)	Flexural strength (MPa)	Flexural modulus (GPa)
B0	23	46.8 ± 2.9	1.2 ± 0.1
BSi	23	16.8 ± 0.7	0.5 ± 0.1
BSiMo	23	20.9 ± 5.4	0.8 ± 0.1
Control DGEBA	23	30.9 ± 4.5	2.2 ± 0.1
	50	12.1 ± 4.3	1.8 ± 0.1
Hybrid DGEBA	23	75.2 ± 4.7	3.6 ± 0.1
	50	45.9 ± 5.5	3.1 ± 0.1
Epoxy A	23	42.5 ± 2.0	2.3 ± 0.1
Hyb-L-A	23	64.4 ± 4.1	2.1 ± 0.9
Hyb-H-A	23	56.3 ± 3.2	2.2 ± 0.1
Epoxy B	23	30.9 ± 4.5	2.2 ± 0.1
Hyb-L-B	23	61.8 ± 2.4	2.6 ± 0.1
Hyb-H-B	23	37.8 ± 0.9	2.9 ± 0.2

3.1.3 Properties of hybrid epoxy adhesives in different environmental conditions

Some tests were performed on the produced hybrid systems after their exposure to severe environments in order to assess their durability in realistic outdoor conditions.

As observable in Table 2, when the mechanical tests were performed on the Hybrid DGEBA system at 50°C, the expected decrease in flexural characteristics, since the glass transition range of temperatures of the adhesive is approached, was somehow limited. For this system, the strength and the stiffness measured at 50°C were even greater than the same properties displayed by the control resin, representative of a commercial structural epoxy adhesive.

A peculiar behavior of hybrid systems was especially revealed during an aging in moisture/water. The typical deterioration in mechanical properties, as well as in Tg, due to water plasticization, that is normally observed with conventional epoxy resins, was not found for BSi and BSiMo formulations, as shown in Figure 2 (only for the system BSiMo). The water absorbed during aging in moist environments, or immersion in water, is likely to provide considerable improvement in mechanical properties as a result of the increase in network density of the siloxane domains.

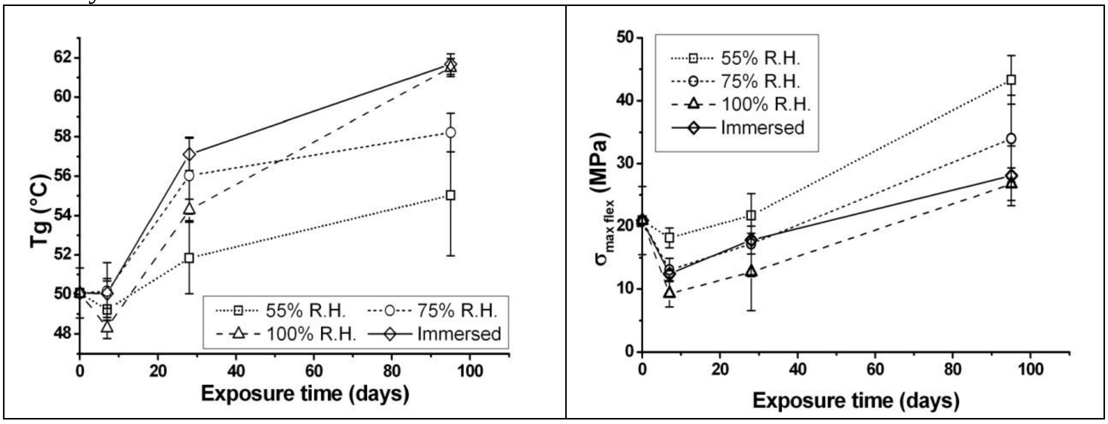

Figure 2. Tg and flexural strength of BSiMo hybrid specimens exposed to different levels of humidity or immersed in distilled water.

Similar results were also found for Hybrid DGEBA system that, after an initial decrease (at shorter exposure times) of Tg upon immersion in water/exposure to 75% RH, experienced a complete recovery in this characteristic, attributed once again to the prosecution of the sol–gel process activated by the absorbed water, thus leading to a greater densification of the siloxane network. The superior mechanical performance of this hybrid is confirmed if it is exposed to 75% R.H. or immersed in water, since its mechanical characteristics (flexural E modulus and strength) still remain well above the same properties measured on unexposed control resin.

Referring to the behavior at high temperatures, the hybrid systems Hyb-A and Hyb-B exhibited a higher thermal resistance at very high temperatures with respect to control ones; in particular, the hybrid systems containing ionic liquid cured with cycloaliphatic amine (i.e. Hyb-L-B and Hyb-H-B) showed the highest thermal resistance. The observed enhanced thermal stability can be attributed to the presence of the inorganic siloxane structure which forms siliceous barrier layers able to inhibit, or at least limit, heat and mass transfer. This could represent another additional advantage displayed by cold-cured epoxy-silica hybrids with respect to typical epoxy-based adhesives to be used in construction industry.

3.1.4 Adhesion strength to concrete/masonry of hybrid epoxy adhesives in different environmental conditions

The adhesion tests were performed on concrete/masonry cylinders bonded with Control DGEBA and Hybrid DGEBA, performing the tests also in different environmental conditions, i.e. at 50°C and after a three-week immersion in water. The results of adhesion strength tests (to concrete only) are reported in Table 3 with, in brackets, the percentage difference in properties with respect to Control DGEBA adhesive measured in the same conditions.

Table 3. Adhesion strength (MPa) to concrete in different environmental conditions

System	Standard Conditions	T = 50°C	Three-weeks immersion in water
Control DGEBA	9.9 ± 1.4	5.7 ± 1.5	6.8 ± 1.1
Hybrid DGEBA	13.7 ± 2.0 (+38%)	8.8 ± 1.8 (+54%)	11.0 ± 2.3 (+62%)

The adhesion strength of the hybrid system to concrete resulted higher than that measured on the control system, especially when the bonded specimens were subjected to severe, but realistic, environmental conditions. An excellent retention of the adhesive properties can be, then, attributed to the presence of siloxane domains in the epoxy network. Similar results were found when the same adhesive was applied to masonry. This behavior confirms the outstanding performance displayed by hybrid silica-epoxy adhesives when bonded to construction materials.

4 CONCLUSIONS

The thermal, mechanical and adhesive characteristics of different experimental organic-inorganic hybrid cold-cured formulations were evaluated in order to propose these new systems as efficient adhesives for structural applications. The attainment of Tg higher than 70°C in shorter cold-curing times is an obvious indication of the superiority of O-I hybrid systems above the traditional epoxy adhesives. Some of the proposed hybrids were also able to develop greater mechanical (flexural) characteristics with respect to the un-modified epoxy resins, even when tested to temperatures not much lower than their Tg, testifying their superior properties in such severe conditions. A unique feature was the further increase in Tg of the hybrids and improvements in mechanical properties during their aging in presence of moisture/water. In addition, the epoxy-based hybrid systems display greater adhesion strength with concrete and masonry at moderate temperatures and in presence of water. The peculiar characteristics of epoxy-silica hybrids can be attributed to the presence of co-continuous siloxane reinforcing domains and to their ability of undergoing further densification through hydrolysis/condensation reactions during aging in humid environments. The enhanced performance of the epoxy-silica hybrids opens the possibility of overcoming some of the well-known deficiencies of conventional epoxy adhesives employed for concrete repairing and structure strengthening.

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