

Improved mechanical properties of CFRP laminates at elevated temperatures and freeze–thaw cycling

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ABSTRACT

Externally bonded Fiber Reinforced Polymer (FRP) laminates are recognized as an effective system to repair or strengthen existing structures in the field of buildings. Despite the evident advantages of FRPs over traditional materials, the greatest impediment to worldwide utilization is represented by the limited knowledge of composites behavior at elevated temperature and/or freeze–thaw cycling exposure. In order to investigate this aspect, a series of mechanical tests have been carried out on innovative epoxy based-matrices and on carbon FRP coupons exposed to different temperature and humidity conditions in an environmental chamber. Since commercially available resins exhibit a reduced capacity to transfer loads over fibers around glass transition temperature (T_g) which, for cold-cured systems (i.e. systems cured around the ambient temperature), is somewhat comparable to the operating temperature, the innovative matrices have been formulated with the aim to attain T_g values significantly higher than those exhibited by presently used epoxy based-systems. The strategy adopted for the formulation of such resins is based on the key idea that for cold-cured epoxy resin, it is essential to increase the exothermal cross-linking reaction heat allowing the curing reaction in the bulk of the material to be carried out at temperatures higher than ambient temperature.

The results of Differential Scanning Calorimetry (DSC), Dynamic-Mechanical Analysis (DMA) and Thermo-Gravimetric Analysis (TGA) as well as results of tension tests on FRP laminates subjected to severe operating conditions are presented and widely discussed in this paper. The experimental results pointed out that the innovative epoxy-based formulations provide significant improvements on the mechanical properties of FRP laminates exposed to elevated temperatures or to freeze–thaw cycles.

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1. Introduction

Over the last years, effectiveness of externally bonded Fiber Reinforced Polymer (FRP) laminates for flexural and/or shear strengthening or for confining reinforcement of structural members has been clearly confirmed experimentally [1]. Despite evident advantages of FRP technique over other strengthening methods, some aspects concerning the use of carbon or glass fiber reinforced epoxy composite materials under elevated temperatures and freeze–thaw cycling need to be further investigated [2,3]. The exposure to these conditions might lead to a significant reduction in the mechanical properties of the polymeric matrix thus limiting its ability to transfer forces between fibers with consequent failure of the FRP strengthening system. Until now the detrimental effect

of elevated temperatures on FRP mechanical properties has been mainly studied with reference to fire exposure [4–6]. Experimental studies conducted on FRP strengthened reinforced concrete columns, beams and slabs during exposure to fire have pointed out that thermal protection is strictly required to preserve interaction between FRP and concrete and to guarantee the same fire endurance as for the original members [7–9]. However, only few studies have been conducted to investigate the FRP mechanical properties at elevated temperature or after freeze–thaw cycling related to service conditions (i.e. FRP external application exposed to sun in hot regions, cycling exposure in Mediterranean climates), in spite of the ACI 400.2R-08 [10] prescription states the service temperature should not exceed the value corresponding to the T_g decreased of 15 °C (i.e. $T_g - 15$ °C).

The performances at elevated temperatures and/or at freeze–thaw cycling exposure of structural members strengthened by using externally bonded FRP laminates are mainly related to two

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aspects: (a) the adhesion between FRP and the member substrate; (b) the mechanical properties of laminates themselves. Available experimental tests aiming at investigating the latter aspect are still lacking; only few tests have been performed to evaluate the residual tension strength of FRP coupons after exposure to elevated temperatures [11] or freeze–thaw cycling.

Motivated by these premises, the present paper deals with a three series of experimental tensile tests on uniaxial carbon FRP laminates (CFRPs) impregnated with both commercially available resins and innovative reformulated epoxy systems. Before tensile tests, the CFRPs were exposed to both controlled temperature and relative humidity (RH) conditions and freeze–thaw cycles. In particular, due to reduced capacity of commercially available resins to transfer loads over fibers around glass transition temperature, T_g two new innovative epoxy systems for the field of buildings (i.e. suitable to be cured at temperature conditions compatible with the materials and construction process) were formulated and exhaustively characterized by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA). In details, in order to improve the T_g value a new epoxy system was formulated to be cured at 60 °C after an hour at ambient temperature (i.e. 22 ± 1 °C). Furthermore, in order to improve the thermo-mechanical behavior of epoxy matrix to be cured at ambient temperature, a nanocomposite system was formulated by dispersing preformed nano-sized silica particles into the neat epoxy resin.

The mechanical properties of commercially available matrices and new formulated ones as well as their influence on the mechanical properties of FRP coupons under axial load at different temperature values and after exposure to freeze–thaw cycles are herein extensively presented and discussed.

2. Innovative epoxy systems: strategy for new formulations

The T_g of an epoxy matrix is the key parameter of epoxy-based composites, since it establishes the service exposure temperature for materials' use. In practical applications, the epoxy matrices are used at temperature well below T_g (i.e. in the glassy state). However, when cold-cured epoxy matrices are exposed to a hydrothermal environment the materials' T_g dramatically depresses because of the plasticizing effect of absorbed water; hence the state of cold-cured epoxy matrices may change from glassy to rubbery during their operative life [12], being their T_g values as low as 45–60 °C [13]. Furthermore the curing time to reach stable T_g values and arrest the epoxy cross-linking reaction, has been verified to be as long as about 5 months compared to the few weeks suggested by the suppliers of cold-epoxy resins [14].

In thermoset materials the achievement of a defined T_g value is a complex process. As known [15], during the first stage of the curing reaction the reacting viscosity is low, therefore the rate reaction is controlled only by the chemical reactivity of epoxy rings [16]. Once the gelation point is reached, the three-dimensional network is built-up, then the further cross-linkings progressively

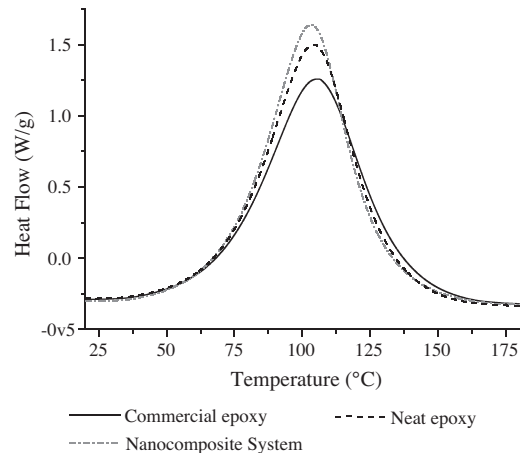


Fig. 2. Total heat of curing reaction for the commercial epoxy, and both reformulated neat epoxy and nanocomposite system.

slow down, until the reaction becomes diffusion controlled (i.e. vitrification phenomenon). During the epoxide curing, the T_g and the conversion degree progressively increase as a result of the growth of the network cross-linking density. This rise stops when the T_g of the reacting system approaches the actual material temperature, which in turns is slightly higher than the curing temperature because of the exothermicity of curing reaction [17].

As a consequence of vitrification, the attained T_g of the cold-cured epoxy system results to be well below the T_g corresponding to the fully cured sample, $T_{g\infty}$ and the cross-linking reaction is arrested before the fully epoxy conversion [17]. To allow the commercially available epoxy systems to be completely cured, a relatively high amount of reactive solvent, namely an epoxide aliphatic component with low molecular weight (e.g. aliphatic mono or diglycidyl ether) is normally added in the initial formulation [13,17]. This solvent reduces the viscosity of the reacting mixture, allowing then the epoxy macromolecules to have the necessary mobility to further react, reaching the maximum conversion degree value, also at low curing temperatures. Nonetheless the reactive solvent reduces the rigidity of the network and consequently the T_g of the cured material [13,18] being part itself of the epoxy network and having higher molecular flexibility.

For cold-cured epoxy systems Kroutilova et al. [17] suggested to increase the cross-linking reaction rate in order to have a heat generation faster than heat dissipation towards the external environment. In this way, the temperature of the reaction medium grows, becoming higher than that at which the curing reaction occurs and the T_g increases consequently.

On the basis of these considerations, firstly, an innovative epoxy system was formulated by reducing the amount of reactive solvent with respect to the epoxy DGEBA [18]. In details a new epoxy system (afterwards referred to as Neat epoxy system) was formulated and then post-cured at 60 °C after 1 h curing at ambient temperature. Additionally, in an attempt to improve the mechanical properties of the epoxy matrix, a crosslinked matrix was realized by curing at ambient temperature a nanocomposite system prepared by dispersing a low amount (i.e. 3.3% wt/wt) of preformed nano-dimensioned silica particles into the tailor-made epoxy formulation described right above (this system is referred to as Nanocomposite system). In these systems, due to the high value of the heat associated to crosslinking reaction along with the high reactivity of the innovative epoxy systems, the heat generation rate is higher than its dissipation. In this way the temperature of the reaction medium increases considerably above the ambient temperature. As a consequence, the T_g values of the innovative epoxy systems are higher as compared to commercial epoxy system. Furthermore, the newly

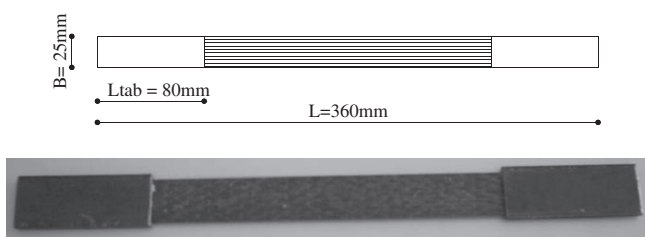
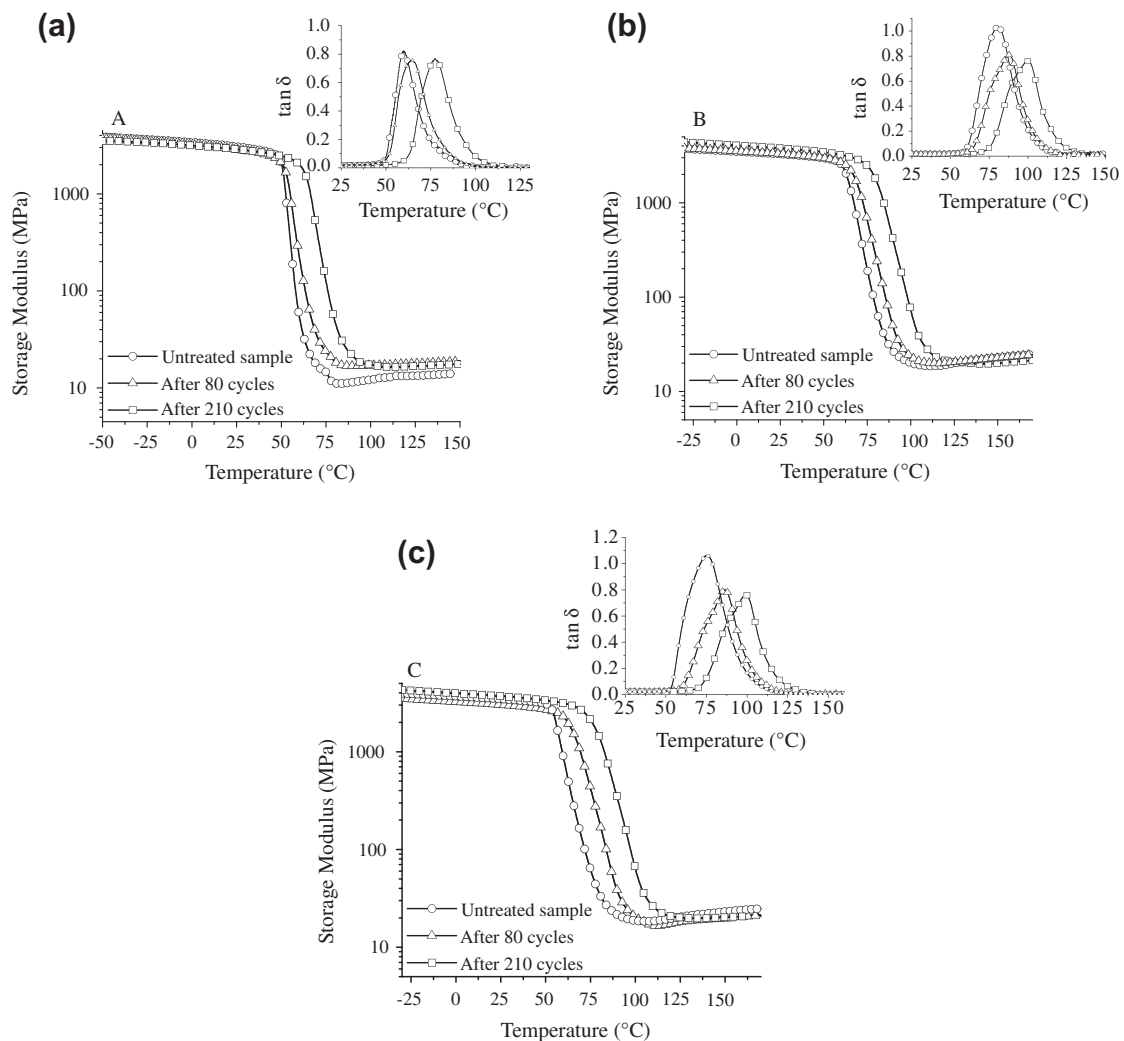


Fig. 1. Specimen geometry.

Table 1Residual heat ΔH_{res} and conversion degree α values of epoxy systems before and after freeze–thaw cycles.

Sample	0 Cycle	80 Cycles	210 Cycles
Commercial epoxy ($T_{\text{max}} = 106.5 \pm 0.5$ °C) ($\Delta H_{\text{Tot}} = 424 \pm 3$ J/g)	$\Delta H_{\text{res}} \approx 4.5 \pm 0.6$ J/g $\alpha = 0.990$	^a	^a
Neat epoxy ($T_{\text{max}} = 104.1 \pm 0.5$ °C) ($\Delta H_{\text{Tot}} = 451 \pm 3$ J/g)	$\Delta H_{\text{res}} = 20.2 \pm 0.9$ J/g $\alpha = 0.955$	$\Delta H_{\text{res}} = 7.8 \pm 0.6$ J/g $\alpha = 0.983$	$\Delta H_{\text{res}} = 4.0 \pm 0.2$ J/g $\alpha = 0.991$
Nanocomposite system ($T_{\text{max}} = 103.3 \pm 0.5$ °C) ($\Delta H_{\text{Tot}} = 467 \pm 3$ J/g)	$\Delta H_{\text{res}} = 20.9 \pm 0.8$ J/g $\alpha = 0.955$	$\Delta H_{\text{res}} = 2.3 \pm 0.7$ J/g $\alpha = 0.995$	$\Delta H_{\text{res}} = 0.91 \pm 0.2$ J/g $\alpha = 0.998$

^a ΔH_{res} not detectable by DSC method.**Fig. 3.** DMA analyses of (a) commercial epoxy, (b) neat epoxy, and (c) nanocomposite system.

formulated epoxy systems reach also the important goal of increasing the elastic modulus in the rubbery region, thus improving the performances of CFRPs at elevated temperatures and/or under freeze–thaw cycles exposure.

3. Materials and samples preparation

The epoxy resin components used in this work were (a) resins consisting of diglycidyl ether of bisphenol-A (DGEBA) with EEW 187 g/mol eq or a blend of DGEBA and diglycidyl ether of bisphenol-F (DGEBF) in the ratio 30/70 wt/wt (EEW 180 g/mol

eq) provided from Shell Chemicals; (b) reactive solvent consisting of 1,6 hexanediol diglycidyl ether (from Fluka) and nonylphenol as curing accelerator (from Fluka); (c) hardener consisting of metaxylilene diamine, MXDA (AEW = 35.56 g/mol eq) (from Fluka); (d) preformed silica particles (average diameter equal to 20 nm) provided by Hanse Chemie Nanoresins as a dispersion of silica particles in DGEBA with 40% wt/wt of solids content (trade name C450, EEW = 295 g/mol eq).

The commercial epoxy system consists of DGEBA, DGEBF and 1,6 hexanediol diglycidyl ether as reactive diluents, cured with a mixture of polyethylenamine-xylenediamine and nonylphenol as accelerator (from data sheet; viscosity 300 MPa s; tensile strength 30 N/mm²; elongation at break 1.2%; flexural strength 55 N/mm², compression elastic modulus 2000 N/mm²; flexural elastic modulus 55 N/mm²).

Table 2
Storage modulus in the glassy and rubbery regions, glass transition temperatures calculated as maximum values of (a) loss modulus and (b) $\tan \delta$, and relaxation strength values of epoxy systems submitted to the freeze–thaw cycles.

	Freeze–thaw cycles	Storage modulus at 25 °C (MPa)	Storage modulus at 150 °C (MPa)	$T_g^{(a)}$ (°C)	$T_g^{(b)}$ (°C)	Relaxation strength
Commercial epoxy	0	3062 ± 30	14 ± 2	52 ± 1	60 ± 1	0.82 ± 0.08
	80	2867 ± 30	19 ± 2	55 ± 2	65 ± 2	0.76 ± 0.10
	210	2895 ± 30	18 ± 2	67 ± 2	78 ± 2	0.76 ± 0.07
Neat epoxy	0	3278 ± 30	23 ± 2	67 ± 3	80 ± 3	1.03 ± 0.12
	80	3315 ± 30	23 ± 2	72 ± 3	88 ± 3	0.81 ± 0.04
	210	3787 ± 30	20 ± 2	84 ± 3	100 ± 3	0.76 ± 0.04
Nanocomposite System	0	3472 ± 30	23 ± 2	58 ± 2	76 ± 2	1.06 ± 0.11
	80	3024 ± 30	20 ± 2	69 ± 4	86 ± 4	0.80 ± 0.07
	210	3700 ± 30	20 ± 2	81 ± 3	100 ± 3	0.76 ± 0.08

Epoxy systems were prepared [18] at ambient temperature (i.e. about 22 ± 1 °C) by mixing resins, reactive diluents, eventually the nano-silica, and, finally, the amine curing agent MXDA in stoichiometric amount with respect the total epoxide groups. Then the reactive mixtures were out-gassed under vacuum and then cured. According to this procedure, the Neat epoxy system was cured for 1 h at ambient temperature followed by 1 h at 60 °C. This curing protocol allowed reaching a conversion degree of epoxide groups approximately equal to 0.955 (see later for more details concerning conversion degree).

Moreover, the nanocomposite system, prepared by dispersing 3.3% wt/wt of preformed silica into the above mentioned Neat epoxy system as matrix, was cured for 1 week at ambient temperature exhibiting a ultimate conversion degree equal to 0.955.

The same curing cycle adopted to realize the Nanocomposite system was used to prepare the commercial epoxy films, characterized by the highest conversion degree, namely 0.990.

By using the three above mentioned epoxy systems (i.e. commercial epoxy, Neat epoxy system and Nanocomposite system), several films and FRP laminates were prepared according to ASTM D3039/D 3039M specifications [19]. The matrix films exhibited a thickness equal to about 0.5 mm. Whereas for the preparation of FRP laminates, carbon fibers sheets with unit weight of 600 g/m² (thickness,

$t_f = 0.33$ mm), length L and width B equal to 360 mm and 25 mm, respectively (see Fig. 1), were impregnated with the different epoxy systems, finally cured between two steel plates used to ensure a uniform, smooth surface of the final cured FRP.

Further, both the matrix films and FRP laminates were submitted to freeze–thaw cycles which consisted in cyclically exposing samples at -5 °C and 0% RH for 6 h and then at 40 °C and 80% RH for 15 h, with a time to pass from one condition to the other equal to 1.5 h. Such 24 h cycle simulates the typical temperature and moisture time profile which takes place in a typical Mediterranean day. Both the films and the FRP laminates samples were removed from the climatic chamber after 80 and 210 cycles, respectively, and then tested. For comparison, also the untreated samples were characterized.

4. Experimental characterization

4.1. Tests on epoxy matrices

Differentials Scanning Calorimetry (DSC) measures have been performed using a TA Instruments model Q1000. The samples

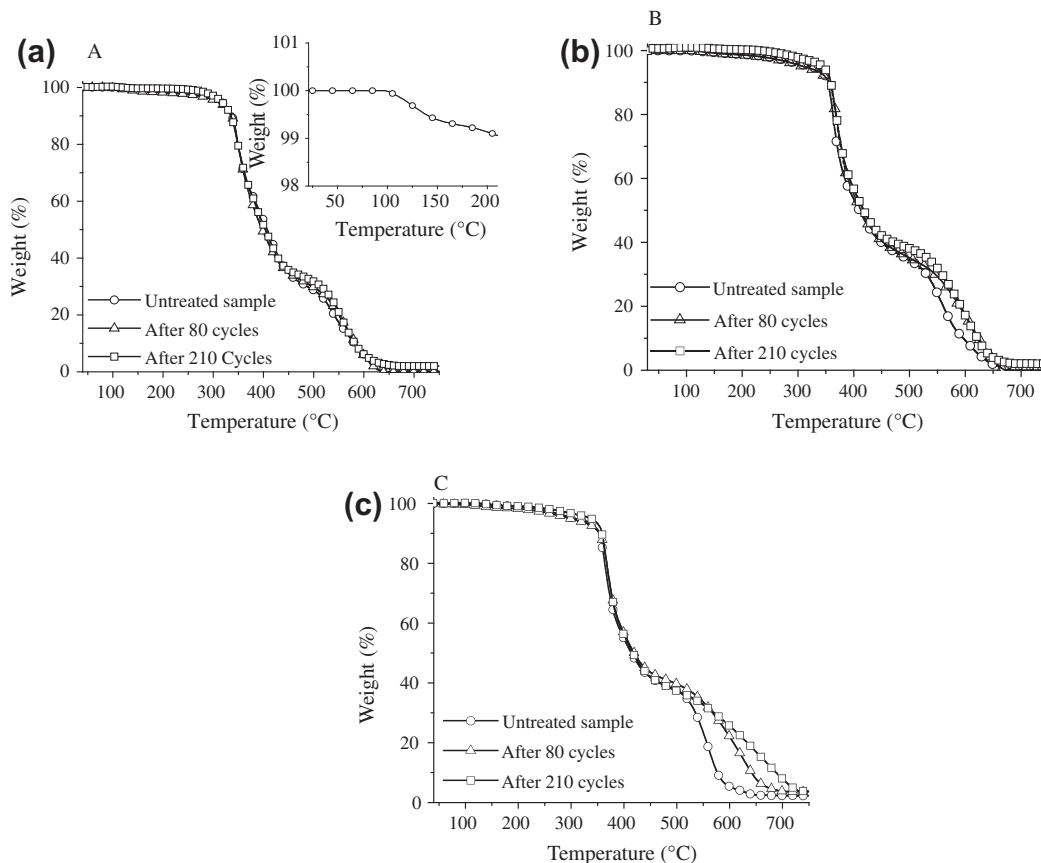


Fig. 4. TGA analyses in air flow of (a) commercial epoxy, (b) neat epoxy, and (c) nanocomposite system.

Table 3
Experimental results tensile tests at ambient temperature.

Fibers	Matrix	Spec. ID	f_{fu} (MPa)			E_f^{chord} (GPa)			ϵ_{fu} (%)				
			Exp.	Mean	CV (%)	Exp.	Mean	CV (%)	Exp.	Mean	CV (%)		
Carbon (unit weight 600 g/m ²)	Commercial epoxy	#1	2585	2890	10.7%	228	220	3.5%	1.13	1.31	10.2%		
		#2	2879			219			1.32				
		#3	2638			227			1.16				
		#4	2748			208			1.32				
		#5	3480			230			1.52				
		#6	3073			222			1.38				
		#7	2626			214			1.23				
		#8	3089			215			1.43				
	Neat epoxy	#9	2898	3168	10.0%	227	214	6.1%	1.28	1.49	12.2%		
		#10	2702	(+10%) ^a		214			(-3%) ^a			1.26	(+13%) ^a
		#11	2903	236		1.23							
		#12	3052	218		1.4							
		#13	3141	200		1.57							
		#14	3227	196		1.65							
		#15	3464	213		1.62							
		#16	3438	210		1.63							
		#17	3689	212		1.74							
		#18	3532	3228		6.1%			267			215	10.3%
	#19	3184	(+12%) ^a	215	(-3%) ^a		1.48	(+16%) ^a					
	#20	3289	182	1.81									
	#21	3229	236	1.37									
	#22	2867	202	1.42									
	#23	3226	196	1.65									
	#24	3222	214	1.5									
	#25	3423	206	1.66									
	#26	2924	213	1.37									
	#27	3233	210	1.54									
	#28	3380	220	1.54									

^a Percent difference with respect to mean values related to commercially epoxy.

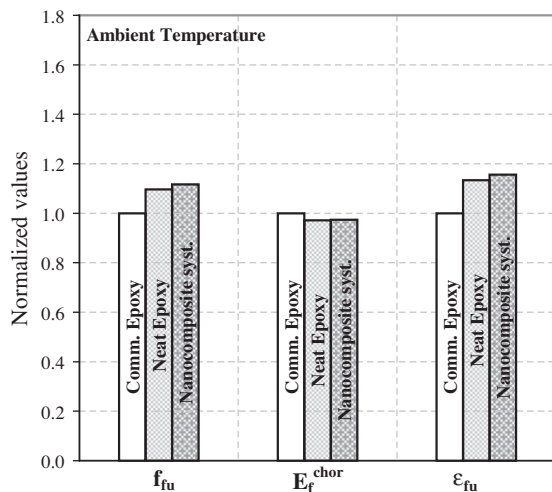


Fig. 5. Normalized strength, Young's modulus and ultimate strain at room temperature.

(about 10 mg) were heated in hermetic aluminum pans from -40 to 250 °C at a heating rate of 10 °C/min.

The DSC method was used to calculate the conversion degree of epoxy matrix, because it can quantitatively detect the heat evolved from the exothermic curing process, thus indirectly supplying information about unreacted species [16]. In particular, the degree of conversion, α was calculated by the following formula [16,20]:

$$\alpha = \frac{\Delta H_{\text{Tot}} - \Delta H_{\text{res}}}{\Delta H_{\text{Tot}}}$$

where ΔH_{Tot} corresponds to the total heat evolved during the complete curing of just prepared epoxy systems, whereas ΔH_{res} represents the residual curing reaction heat of samples both after

different curing times and freeze–thaw cycles. Both heats were determined by collecting the heat flow versus temperature for samples submitted out to a dynamic heating running from -50 to 250 °C. According to the α definition, the value equal to 1 is expected for fully cured epoxy system.

Dynamic mechanical analysis (DMA) were performed using a Q800 apparatus by TA Instruments on tension clamped samples varying the temperature from -50 °C to 250 °C, at a heating rate of 3 °C/min. The experiments were carried out at a fixed frequency of 1 Hz and 5 μm strain amplitude. The temperatures at the maximum values of loss tangent $\tan \delta$, i.e. the ratio between loss modulus (E'') and storage modulus (E'), as well as at the maximum values of the loss modulus were taken to represent T_g s.

Thermogravimetric analysis (TGA) was carried out on a TGA 2950 thermobalance (TA Instruments). Samples were heated from 30 to 750 °C at a heating rate of 10 °C/min under air flow.

4.2. Tests on CFRP coupons

The experimental program consisted of 78 tensile tests on CFRP one ply coupons samples. Four series of tests were performed: (1) at ambient temperature (i.e. 20 °C) and relative humidity (i.e. RH = 55%), 28 tests; (2) at elevated temperature, $T = 70$ °C and RH = 65%, 15 tests; (3) on specimens pre-treated by exposure to 80 freeze–thaw cycles, 13 tests and (4) on specimens pre-treated by exposure to 210 freeze–thaw cycles, 22 tests.

Two strain gages were applied on each FRP sample, one for each face, symmetrically attached about the mid-span and mid-width location of the sample. Strain gages were protected with a plastic insulating coating; in case of tests at elevated temperatures a further protection was applied by using a butyl rubber layer covered by a neoprene and then aluminum film. The FRP samples were axially loaded in the fiber direction at a displacement rate of 0.033 mm/s.

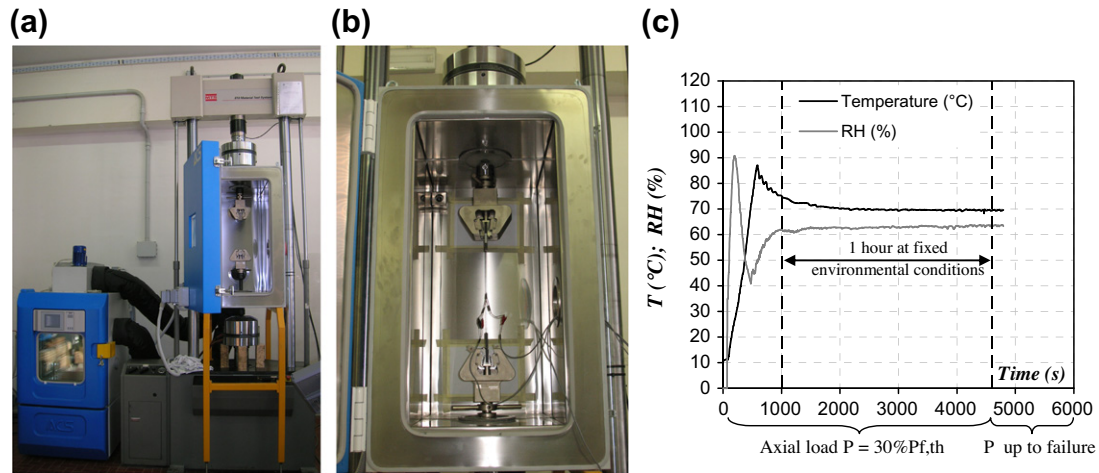


Fig. 6. Test setup view (a); CFRP sample under MTS testing machine and climatic chamber (b); temperature and relative humidity exposure profile (c).

Table 4

Experimental results tensile tests at $T = 70\text{ }^{\circ}\text{C}$ and RH 65%.

Fibers	Matrix	Spec. ID	f_{fu} (MPa)			E^{chord} (GPa)			ε_{fu} (%)		
			Exp.	Mean	CV (%)	Exp.	Mean	CV (%)	Exp.	Mean	CV (%)
Carbon (unit weight 600 g/m ²)	Commercial epoxy	#1	2048	2056	6.1%	207	219	11.9%	0.99	0.95	14.4%
		#2	2179			246			0.89		
		#4	1886			235			0.80		
		#5	2112			189			1.12		
		#6	3026			233			237		
	Neat epoxy	#7	3064	(+57%) ^a	234	(+8%) ^a	1.31	(+44%) ^a			
		#8	3101	247	1.26						
		#9	3427	231	1.48						
		#10	3391	234	1.45						
		#11	3325	242	1.38						
		#12	3527	264	242	5.9%	1.33	1.35	13.0%		
	Nanocomposite system	#13	3598	(+58%) ^a	229	(+10%) ^a	1.58	(+42%) ^a			
		#14	3395	237	1.43						
		#15	2740	247	1.11						
		#16	2965	231	1.28						

^a Percent difference with respect to mean values related to commercially epoxy.

5. Results and discussion

5.1. Properties of epoxy matrices

Fig. 2 shows the heat flow related to the complete curing reaction for just prepared Commercial epoxy, Neat epoxy system and Nanocomposite system. As expected (see Fig. 2 and Table 1), the ΔH_{tot} values corresponding to the newly formulated epoxy systems were higher than the commercial epoxy. Therefore, supposing the heat dissipation of matrix films depends only on the formulation components, due to the exothermicity of the cross-linking reaction the bulk temperature for the innovative epoxy systems is expected to be higher than that related to the commercial epoxy. Additionally, the innovative epoxy systems result to be more reactive, since (see Fig. 2) the temperatures corresponding to the maximum of heat flow (T_{max}), are slightly lower as compared to that observed for the commercial product.

In details, in Table 1 are listed the residual heat and the corresponding conversion degree for the newly formulated epoxy matrices, both before and after different freeze–thaw cycles, respectively. As for the commercial epoxy system, the residual heat of the samples submitted out to freeze–thaw cycles was not easily detectable by DSC method (i.e. it approaches the zero value). This result suggests that this system was already almost completely cured before the aging cycles. As for the new formulated epoxy matrices, the

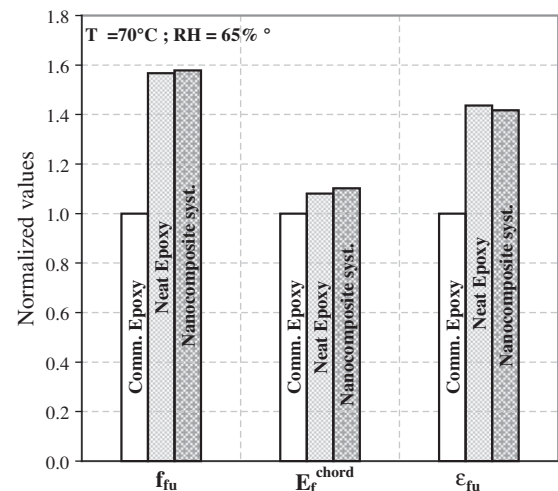


Fig. 7. Normalized strength, Young's modulus and ultimate strain at 70 °C and 65% RH.

freeze–thaw cycles treatment creates the conditions to allow further proceeding of the cross-linking reaction. Thus the conversion degree, α reaches the maximum values after 210 cycles (see

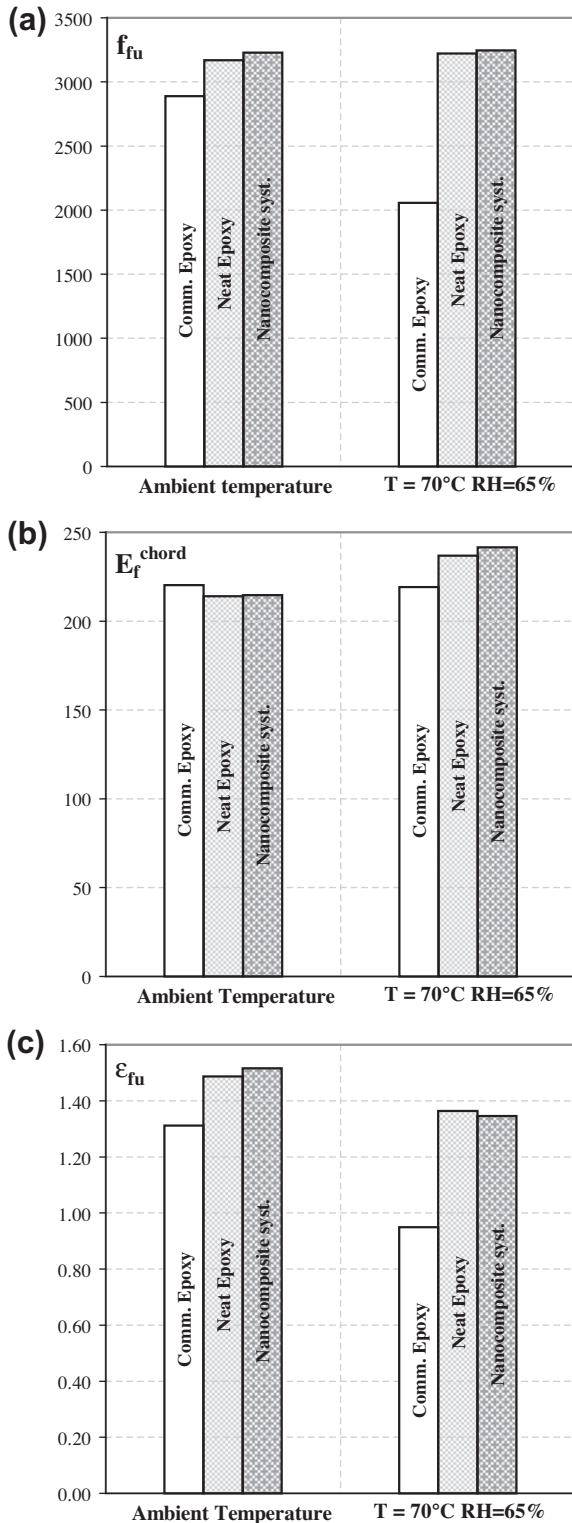


Fig. 8. Tensile strength profiles (a), Young's modulus profiles (b), and ultimate strain profiles (c).

Table 1). However, despite the low temperatures operated during freeze–thaw cycles, such a finding corresponding to a post-curing process is not unexpected. Indeed, depending on the interacting nature of water molecules with epoxy backbone, the moisture absorption might show two opposite effects. On one side, the water molecules which are single hydrogen bonded to the epoxy backbone break the initial Van der Waals interchain forces resulting in

increased chain mobility [20,21]. This plasticizing effect causes an obvious decrease of the T_g of cured epoxy resins and allows the crosslinking reaction to start again. On the other side, water molecules which form multi-site interconnective bond complexes do not plasticize the resin but, on the contrary, create bridging between chain segments resulting in a secondary cross-linking network [21–23]. A detailed spectroscopic study [24] highlighted that in epoxy systems equilibrated at different water vapor conditions three different water species can be distinguished. In particular, the water species were labeled as S_n , being n the number of hydrogen bonds that water establishes with proton acceptor groups on the epoxide backbone. According to this nomenclature, S_0 and S_1 water species contribute to plasticize the epoxy network, whereas S_2 can possibly act as additional cross-linker when water molecule bridges two neighboring polymeric chains. In particular for epoxy matrices submitted to hydrothermal aging, the amount of S_2 species increases with the exposure time and conditioning temperature [25].

According to the above reported findings [20,21,23,25], the hydrothermal exposure during the freeze–thaw cycles allowed the samples to absorb water molecules which plasticized the epoxy systems (i.e. S_1 species) then increasing the macromolecular mobility. In these conditions, the cross-linking reactions start again in those samples which were not completely cured, i.e. both Neat epoxy and Nanocomposite systems. In fact, after the hydrothermal aging process the new formulated systems reached the complete cure (Table 1). However, in these systems the presence of water molecules tightly hydrogen bonded to form additional cross-linkers (i.e. S_2 species) cannot be excluded.

In Fig. 3, are reported the DMA spectra, expressed in terms of storage modulus and loss tangent, for the commercial epoxy product (A), Neat epoxy system (B) and Nanocomposite system (C), respectively. Both the new formulated systems exhibit T_g values as well as storage moduli in the rubbery plateau (i.e. at 150 °C) higher than those of the commercial resin (see Table 2). After the freeze–thaw cycles, the T_g values of all the epoxy systems increased with respect to the untreated samples. The higher the number of freeze–thaw cycles the higher the T_g . In details after 210 freeze–thaw cycles the T_g of the formulated epoxy systems increased of about 20 °C. Since the thermo-mechanical performances of commercial epoxy system (Fig. 3a) improved significantly during the aging process in spite of the unmodified value of curing degree α , the T_g enhancement has to be ascribed to the crosslinking effect of the water molecules tightly bonded between adjacent epoxy chains which retain inside the epoxy samples over the T_g transition [21]. In fact, as reported by TGA analysis in the inset of Fig. 4 the tightly bonded water molecules are retained inside the epoxy samples and they are released only in the 80–150 °C temperature range. Hence, in the formulated epoxy systems the improvement of the thermo-mechanical properties may be ascribed both to the plasticizing effect of absorbed water, which provides the epoxy chains to move and further react during aging treatment, and the tightly hydrogen bonded water molecules, which are effective in the cross-linking of epoxy resin molecules.

The effect of additional cross-linkings due to hydrothermal post-curing of epoxy reaction may be detected also by the TGA analysis. In fact the degradation temperature during the second thermo-oxidation step (Fig. 4) of the formulated epoxy systems increased suggesting the presence of an organic network with higher crosslinking density. This enhancement appeared to be more pronounced in the nanocomposite system, probably because of an additional thermal stabilizing effect due to the presence of silica nanoparticles.

In conclusion, the formulation strategy adopted in this work guarantees that both the T_g and rubbery modulus of new epoxy systems improve in comparison to the commercial epoxy system.

Table 5
Experimental results tensile tests after 80 freeze–thaw cycles.

Fibers	Matrix	Spec. ID	f_{fu} (MPa)			E_f^{chord} (GPa)			ε_{fu} (%)					
			Exp.	Mean	CV (%)	Exp.	Mean	CV (%)	Exp.	Mean	CV (%)			
Carbon (unit weight 600 g/m ²)	Commercial epoxy	#1	3139	3077	4.5%	230	225	7.7%	1.37	1.37	9.8%			
		#2	3091			199			1.55					
		#3	2879			235			1.22					
	Neat epoxy	#4	3196	3151	5.8%	235	213	7.9%	1.36	1.49	13.2%			
		#5	3102			226			1.37					
		#6	3336			(+2%) ^a			200			(-6%) ^a	1.67	(+9%) ^a
		#7	3183			207			1.54					
		#8	2866			234			1.22					
		#9	3270			195			1.67					
	Nanocomposite system	#10	3182	3251	6.0%	271	235	16.1%	1.57	1.52	16.6%			
		#11	3024			(+6%) ^a			263			(+4%) ^a	1.15	(+11%) ^a
		#12	3479			210			1.66					
		#13	3319			195			1.70					

^a Percent difference with respect to mean values related to commercially epoxy.

Table 6
Experimental results tensile tests after 210 freeze–thaw cycles.

Fibers	Matrix	Spec. ID	f_{fu} (MPa)			E_f^{chord} (GPa)			ε_{fu} (%)					
			Exp.	Mean	CV (%)	Exp.	Mean	CV (%)	Exp.	Mean	CV (%)			
Carbon (unit weight 600 g/m ²)	Commercial epoxy	#1	2518	2643	9.3%	224	232	11.8%	1.12	1.00	12.1%			
		#2	2758			219			1.26					
		#3	3135			265			1.18					
		#4	2559			251			1.02					
		#5	2715			196			1.39					
		#6	2172			237			0.92					
	Neat epoxy	#7	3199	3063	8.2%	227	210	9.7%	1.41	1.47	14.5%			
		#8	3263			(+16%) ^a			177			(-10%) ^a	1.84	(+28%) ^a
		#9	3276			226			1.45					
		#10	2611			215			1.21					
		#11	3012			221			1.36					
		#12	3015			192			1.57					
	Nanocomposite system	#13	3282	3167	5.6%	255	225	9.1%	1.29	1	7.3%			
		#14	3311			(+20%) ^a			220			(-3%) ^a	1.51	(+23%) ^a
		#15	3349			255			1.31					
		#16	3014			240			1.26					
		#17	2970			210			1.41					
		#18	3221			229			1.41					
		#19	3114			205			1.52					
		#20	3236			213			1.52					
		#21	3334			240			1.39					
		#22	2840			186			1.52					

^a Percent difference with respect to mean values related to commercially epoxy.

Furthermore, during the freeze–thaw cycles treatment the water sorption contributes to enhance the thermal–mechanical properties of epoxy matrices due to the synergetic effect of plasticization of epoxy network and increase of physical cross-linking density.

5.2. Properties of CFRP coupons at ambient temperature

The tensile tests were carried out at ambient temperature (i.e. 20 °C) and humidity conditions (i.e. RH = 55%) under a servo-hydraulic MTS testing machine under displacement control according to ASTM D 3039/D 3039M guidelines [19]; the results of 28 tests, processed according to ACI 440.3R [26] provisions, are summarized for each series of specimens (i.e. CFRP samples impregnated with commercial matrix, neat epoxy or nanocomposite system) in Table 3. The ultimate tensile strength, f_{fu} , has been computed dividing the maximum experimental force by the average specimen cross-sectional area, $A_f = t_f B$; the Youngs' modulus, E_f^{chord} was computed between the longitudinal strain range 1000–3000 $\mu\epsilon$, respectively. Note that the strain values were based on the average of the two strain gages readings. The ultimate tensile strain, ε_{fu} , has been computed as $f_{fu}/E_f^{\text{chord}}$.

Experimental outcomes showed that the newly formulated matrices display increased performances in terms of mean tensile strength (10% and 12% increase for neat epoxy and nanocomposite system, respectively) and ultimate strain (13% and 16% increase respectively). The comparison in terms of tensile strength, ultimate strain and Young's modulus are shown in Fig. 5, which reports their mean values normalized with respect to those related to samples impregnated with commercial epoxy resin.

Table 3 and Fig. 5 show that the Youngs' modulus, mainly related to the fibers type, was not significantly influenced by the matrices used to impregnate the specimens. Further, the lower values of coefficient of variation, CV, were those related to the Youngs' modulus (i.e. in the range 3–10%).

5.3. Properties of CFRP coupons at elevated temperature, i.e. $T = 70$ °C, RH 65%

To simulate field conditions of externally bonded FRP laminates on structural members, the experimental tests on CFRP coupons have been conducted in three steps: (1) coupon pre-load at about 30% of the theoretical coupon failure load, $P_{f,th}$; (2) 1 h under

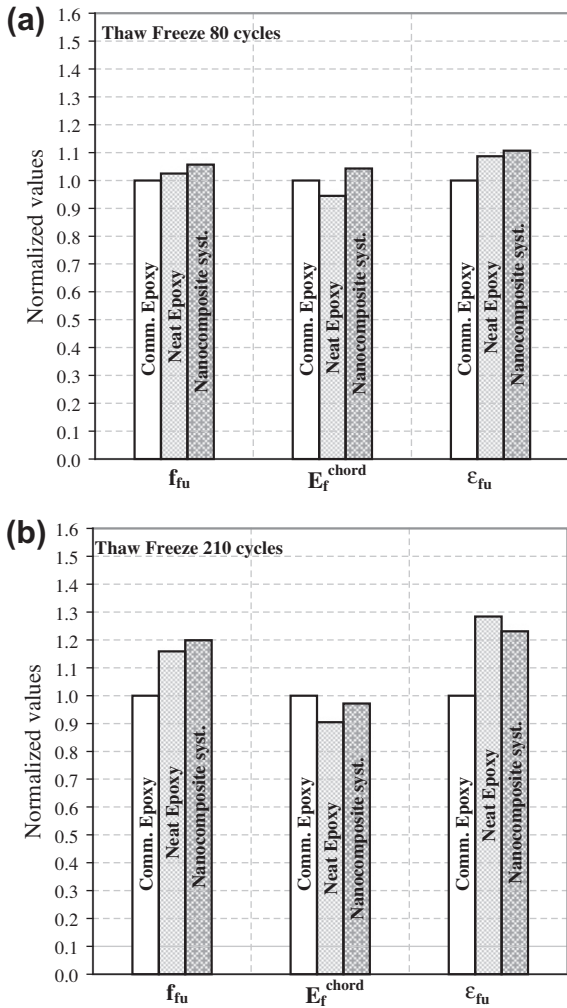


Fig. 9. Normalized strength, Young's modulus and ultimate strain after 80 cycles (a), 210 cycles (b).

controlled conditions (i.e. $T = 70\text{ }^\circ\text{C}$, RH 65%) in the environmental chamber and constant axial load $P = 0.3 P_{f.th.}$; (3) uniaxial tensile test up to the coupon failure at $T = 70\text{ }^\circ\text{C}$, RH 65%.

The tensile tests were carried out under a climatic chamber equipped with a thermoregulatory unit, two insulated pipes (capable of sustaining temperature in a range of -60 to $120\text{ }^\circ\text{C}$), and a thermostatic test room hosting a servo-hydraulic MTS 810 universal test machine (maximum stroke ± 75 mm and maximum load ± 500 kN). In particular, the thermoregulatory unit (AT250TC) allows achieving a temperature range of -75 to $180\text{ }^\circ\text{C}$ with a moisture rate between 0% and 95%.

In this way, samples were allowed to condition at well defined temperature and moisture conditions for a fixed period of time prior loading under controlled environmental conditions.

Fig. 6 illustrates the whole test setup and the temperature and relative humidity exposure profile during the test.

The experimental results of 15 tensile tests are summarized in Table 4. The experimental outcomes show that the impregnation of carbon fibers with Neat epoxy or Nanocomposites system led to significant gains both in terms of tensile strength (57% and 58%, respectively) and ultimate strains (44% and 42%, respectively); the Young's modulus slightly increased by using the new matrices (i.e. 6% and 8%, respectively). The percentage increase in terms of tensile strength, ultimate strain and Young's modulus are shown in Fig. 7.

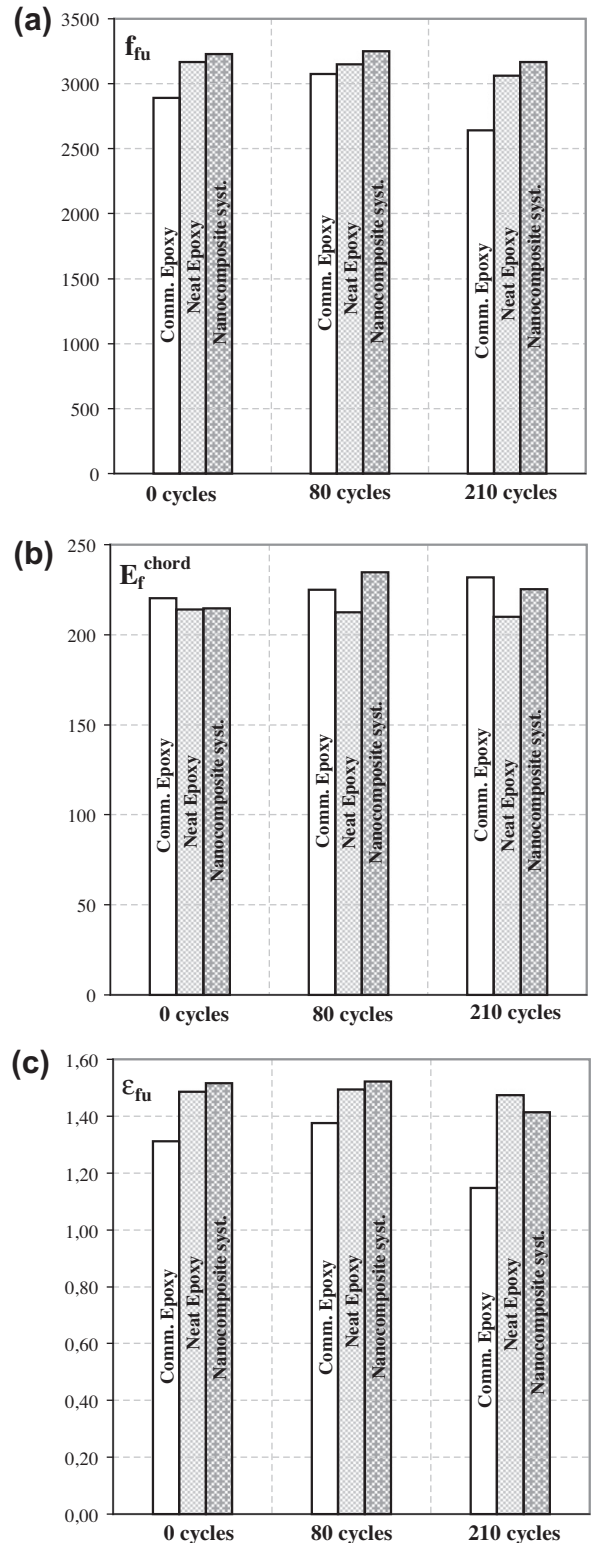


Fig. 10. Tensile strength profiles (a), Young's modulus profiles (b), and ultimate strain profiles (c).

The comparison between mechanical properties of coupons impregnated with commercial epoxy or with new formulated matrices tested at ambient temperature or at $T = 70\text{ }^\circ\text{C}$, RH 65% is reported in Fig. 8. It is worth noticing that exposure at elevated temperature implied a strong degradation of mechanical properties of coupons impregnated with a commercial epoxy (decrease

of about 29% and 27% for tensile strength and ultimate strain, respectively) as opposed to the slightly increased (in terms of f_{fu} and E_f^{chord}) or almost unchanged performances of specimens with new formulated matrices. Such effect could be clearly related to the increased T_g values of new formulated matrices beyond 70 °C (see Table 2); since the new formulated matrices remained in the glassy region they were able to uniformly transfer loads to fibers during the tests preventing localized concentration of stresses and thus premature FRP laminate failure. Further, the Young's modulus gains recorded on specimens impregnated with new matrices at $T = 70$ °C with respect to tests performed at ambient temperature could be explained as a post-curing effect of matrix.

Figs. 7 and 8 clearly show that the new matrices could allow to better exploit the potential of FRP laminates both in case of service conditions and especially in case of elevated temperature. Both the innovative matrices are able to improve the FRP laminates' mechanical properties, however, the Nanocomposite system seems to be the most promising matrix since its curing process is at ambient temperature and thus can be easily used in field applications.

5.4. Properties of CFRP coupons after exposure at freeze–thaw cycles

The tensile tests were carried out at ambient temperature and humidity conditions on CFRP specimens after exposure to 80 freeze–thaw cycles (i.e. 13 tests) or to 210 cycles (i.e. 22 tests). Experimental tensile strength, Young's modulus and ultimate strain are summarized in Tables 5 and 6; the mean values of such properties normalized with respect to those related to samples impregnated with commercial epoxy resin are plotted in Fig. 9. The results in terms of tensile strength, Young's modulus and ultimate strain confirmed the trends recorded on the previous series of tests: newly formulated matrices impregnation improved the tensile strength and ultimate axial strain of CFRP laminates. In particular, they slightly increase the tensile strength and ultimate axial strain after exposure to 80 freeze thaw cycles; the maximum percentage increase was achieved on flat coupon tests impregnated with nanocomposite systems (i.e. tensile strength increase of 6% and ultimate axial strain increase of 11%). Further by increasing the number of freeze thaw cycles up to 210, the tensile strength and axial strain were remarkably higher on specimens impregnated by using Neat epoxy or Nanocomposite systems. The new matrices improved the mechanical properties in terms of tensile strength and axial strain by a factor of about 20% with respect to specimens impregnated with commercial epoxy (see also Table 6).

The comparison with results obtained at ambient temperature condition without freeze–thaw cycling treatment, is reported Fig. 10. Fig. 10a and c shows a decreasing trend of commercial epoxy impregnated CFRP coupons in terms of tensile strength and ultimate axial strain as the number of freeze thaw cycles increases; in particular, the mechanical properties of coupons were not particularly influenced by the exposure to 80 freeze–thaw cycles while a significant degradation was observed after 210 cycles. By contrary, the performances of FRP coupons impregnated both with Neat epoxy or Nanocomposite system were not substantially affected by the freeze thaw cycling. This result is clearly related to the improved performances of new formulated matrices after freeze thaw cycling which promotes their residual curing. The detrimental effect of freeze thaw cycling is counterbalanced by the benefits provided by the residual curing which ensures a uniform stress distribution along fibers and thus delays the fiber failure due to stress local concentration. Less significant is the influence of freeze thaw cycles on the Young's modulus independently of matrix used to impregnate fibers (i.e. a low increase was recorded only on specimens impregnated by using nanocomposite system). This can be explained considering that the Young's modulus value

of FRP flat coupons is mainly governed by fibers, especially in case of high values of volumetric fraction of fibers.

6. Conclusions

The paper summarizes the outcomes of a preliminary investigation on CFRP coupons, prepared by using commercially available epoxy resins or new matrices (Neat epoxy or Nanocomposite system), and subjected to uniaxial tensile tests under controlled temperature conditions. The innovative matrices were mainly formulated with the aim to increase T_g with respect to resins traditionally available on the market. Experimental tests indicate that the adopted strategy to tailor-make the new systems enhanced T_g values of approximately 25% for both neat epoxy and nanocomposite system. This could allow increasing the minimum service temperature from 45 to 60 °C, according to ACI 440.2R-08 [10].

The experimental results on CFRP coupons pointed out that the developed formulations of epoxy resins provide a significant increase of ultimate strength and axial strain of CFRP coupons at elevated temperatures with respect to commercial systems, without significant change of the elastic modulus. Their use is also effective in case of environmental exposure which simulates the typical temperature and moisture in Mediterranean climates, since the upper bound exposure temperature must be $T_g - 15$ °C [10]. Despite commercial epoxy resin, new formulated matrices were also able to prevent the detrimental effect of freeze–thaw cycling on FRP coupons' mechanical properties. Particularly promising could be the use of nanocomposite system to impregnate fibers since it significantly improve the FRP mechanical properties without requiring curing process at elevated temperature.

Experimental outcomes strongly confirmed that the use of the innovative matrices could allow overcoming one of the main limit of FRP laminates related to their poor performances under elevated temperatures and/or freeze–thaw cycling. Further experimental researches are need in order to investigate on the bond behavior between FRP laminates, obtained by impregnating fibers with the new formulated matrices, and the member substrate.

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