SMAR 2015

Effects of curing temperature on pull-out behavior and stiffness evolution of epoxy adhesives for NSM-FRP applications

Andrea Benedetti[1], Pedro Fernandes[1], José Granja[1], Miguel Azenha[1], José Sena-Cruz[1]

[1] ISISE, University of Minho, Guimarães, Portugal

ABSTRACT: The efficiency of the FRP-concrete strengthening system is strongly influenced by the mechanical properties of the epoxy adhesive, which depend on the curing temperature.In the present work, the influence of temperature on the curing process of the epoxy was examined. Two different temperatures were studied: 20 and 30 °C. The elastic modulus of the adhesive was continuously monitored by using a variant of the classical resonant frequency methods, called EMM-ARM (Elasticity Modulus Monitoring through Ambient Response Method). A simultaneous study of direct pull-out tests with concrete specimens strengthened with NSM carbon FRP laminate strips was carried out at the same two different temperatures to compare the evolution of bond performance with the E-modulus of epoxy since early ages. The results showed that increasing the curing temperature significantly accelerated both the curing process of the epoxy adhesive and the evolution of bond performance. Moreover, the EMM-ARM technique revealed its ability in clearly identifying the hardening kinetics of epoxy adhesives, allowing measurements since very early ages and in different environmental conditions.

1 INTRODUCTION

The use of near-surface-mounted (NSM) carbon-fiber reinforced polymer (CFRP) reinforcement is emerging as a strengthening technique and a valid alternative to CFRP reinforcement externally bonded to the surface of a concrete member (De Lorenzis et al., 2007). Although a large number of experimental investigations has been carried out on the structural behavior of NSM FRP strengthened structures, the effect of the curing conditions on the development of the bond performance is one of the less investigated issues. In spite of this, it is largely acknowledged that the bond performance of NSM FRP systems is mainly governed by the mechanical properties of the two-component epoxy resin-based adhesive used as a groove filler (Borchert et al., 2008). Previous research works have shown that the evolution of mechanical properties (both strength and stiffness) of structural epoxy adhesives strongly depend on the curing temperature: lower curing temperatures considerably decelerate the curing process and consequently the rate of development of mechanical properties of the epoxy resin (Lapique et al., 2002; Moussa et al., 2012a). However, such research works were focused mainly on the adhesive.

The aim of the work presented in this paper is to investigate the evolution of both adhesive stiffness and interface behavior of NSM systems under different curing conditions in terms of temperature and duration. In this context, quantifying the effect of curing temperature on the bond performance of CFRP/adhesive/concrete systems could significantly improve the quality of preparation and installation procedures for the strengthening applications. The curing process of the epoxy resin was monitored by means of an innovative technique, termed EMM-ARM (Elasticity Modulus Monitoring through Ambient Response Method) that has been developed for study the early stiffness evolution of cement-based materials such as cement paste, concrete or cement-stabilized soils (Azenha et al., 2010). After the encouraging results obtained in the first applications to epoxy adhesives (Granja et al., 2015), the present work extends the capability of the methodology to thermal activation testing for both the epoxy itself and the interface behavior of the NSM system.

2 EXPERIMENTAL PROGRAM

The experimental program is summarized in Table 1. Two different types of tests were carried out at two distinct temperatures (20 and 30°C): (i) EMM-ARM tests were performed on samples of epoxy resin cured under different temperatures with the objective of describing the evolution of the adhesive stiffness since early ages; (ii) monotonic direct pull-out tests were carried out on CFRP strips embedded in concrete blocks, for evaluation of the influence of curing conditions on the interface relationship between shear stresses and interface slip. In order to validate the capability of the EMM-ARM for evaluating the elastic modulus of the hardened epoxy, static E-Modulus was determined through tension tests, according to ISO 527-2:2012 (ISO, 2012). Finally, a comparison between the evolution of epoxy E-modulus and the maximum pull-out force was performed, evaluating the possibility of a correlation between these two entities in regard to their temperature dependent kinetics at early ages.

Table 1. Experimental program

	Curing temperature: 20°C		Curing temperature: 30°C	
Testing method	Testing Time	Denomination	Testing Time	Denomination
Pull-out	6h	DPT1_6h_T20	6h	DPT1_6h_T30
	9h	DPT2_9h_T20	8h	DPT2_8h_T30
	11h	DPT3_11h_T20	10h	DPT3_10h_T30
	13h	DPT4_13h_T20	12h	DPT4_12h_T30
	24h	DPT5_24h_T20	24h	DPT5_24h_T30
		DPT6_24h_T20		DPT6_24h_T30
	72h	DPT7_72h_T20	72h	DPT7_72h_T30
		DPT8_72h_T20		DPT8_72h_T30
	168h	DPT9_7d_T20	168h	DPT9_7d_T30
		DPT10_7d_T20		DPT10_7d_T30
EMM-ARM	0h-144h	EMM1_T20	0h-168h	EMM1_T30
		EMM2_T20		EMM2_T30
Tensile test	168h	TT_T20	168h	TT_T30

The mixing and strengthening procedures took place in laboratory environment (with temperature of 20 ±1ºC) and all the tests were performed at the same respective curing temperature (either 20 or 30ºC). It should be mentioned that new tests are currently going on at a temperature of 40°C, in order to enhance the conclusions that can be withdrawn from this experimental program.

2.1 EMM-ARM Tests

The EMM-ARM is a variant of the traditional resonance frequency methods that allow the measurement of the E-modulus of the tested material since mixing and was already adapted for the study of epoxy adhesives by Granja et al. (2015). This method is based on the identification of the first resonance frequency of a cantilever composite beam filled with the material to be tested. The beam is composed by a 33 cm long acrylic tube with external and internal diameters of 20 mm and 16 mm, respectively (see Figure 1). In one of the extremities, a custom made clamping device is attached to the composite beam, in order to ensure the structural system, which is a cantilever with a span of 25 cm.

In order to identify the natural frequency of the beam, a lightweight accelerometer (mass: 5.8 g; sensitivity: 100 mV/g) is attached to the free end of the cantilever beam that is solely excited by environmental noise. However, in order to increase the intensity of the environmental noise, a fan is placed in the vicinity of the beam. Based on the vertical accelerations measured by means of the Welch procedure (Welch, 1967) and a peak picking method (Oppenheim et al., 2009), the resonance frequency is identified through the peak with highest intensity in the response spectrum (for more detailed information see the paper of Granja et al., 2015). The measured accelerations are acquired by a 24-bit data logger (NI-USB-9233) with a frequency of 500 Hz, and divided into sets of 5 minutes every 10 minutes.

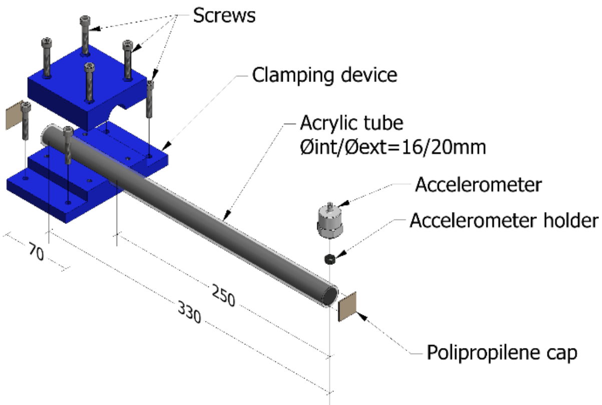
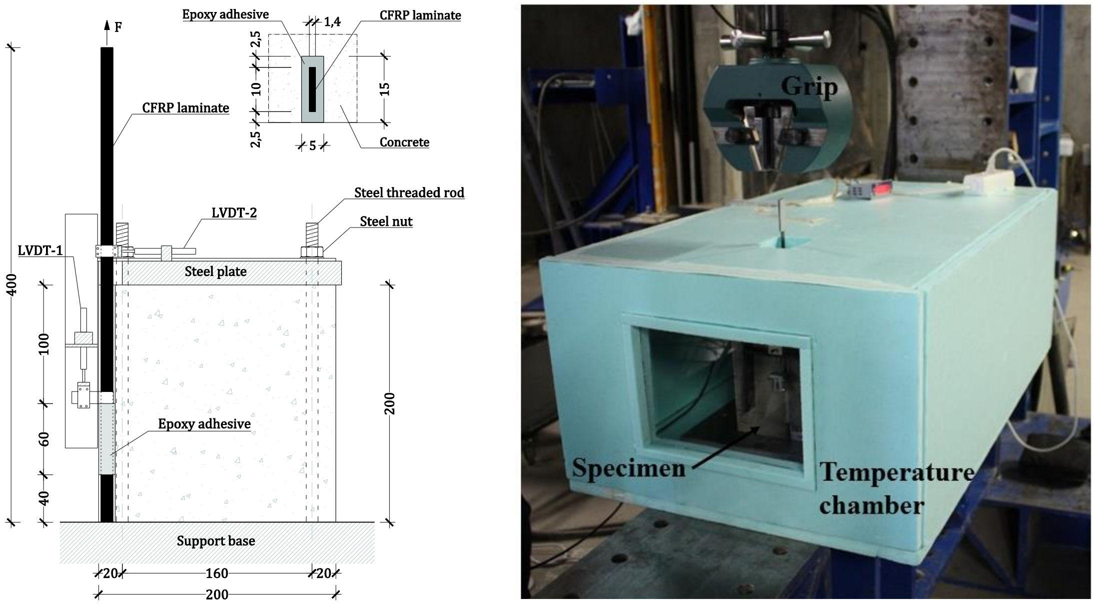


Figure 1. Experimental setup of EMM-ARM tests (exploded view). Note: dimensions are in millimeters.

After the identification of the resonance frequency, the E-modulus of the epoxy adhesive can be analytically correlated to the resonance frequency of the composite beam through the dynamic equations of the cantilevered structural system. The whole set of equations used for the characterization of E-modulus is explained in Azenha et al., 2012.

2.2 Pull-out Tests

In order to study how the interface relationship between shear stresses and interface slip is influenced by the curing conditions on NSM CFRP systems (20 and 30 °C curing temperatures), twenty monotonic direct pull-out tests were performed for the ages of testing specified in Table 1. Figure 2 shows the specimen geometry and test setup adopted for the monotonic direct pull-out tests. The specimens consisted on concrete cubic blocks of 200 mm edge, into which a CFRP laminate strip with 1.4 mm of thickness and 10 mm of width was inserted according to the NSM technique. A fixed bond length of 60 mm, filled with the epoxy adhesive was adopted. More detailed information related to the specimen, monitoring and test configuration is available elsewhere (Fernandes et al., 2015). As previously referred, the testing temperature was the same as that of the corresponding curing. For this purpose, a custom-made temperature controlled chamber was created with Expanded Polystyrene plates (see Figure 2b), comprising a heating element and a thermostat. For both studied temperatures, the strengthening was performed at laboratory environment, and then (after approximately 3 minutes) the specimens were kept under controlled temperature until the age of testing, together with the EMM-ARM specimens.



(a) (b)

Figure 2. Configuration of direct pull-out tests: (a) cross-section of the specimen; (b) photo of the experimental setup. Note: all dimensions are in millimeters.

3 RESULTS AND DISCUSSION

3.1 Epoxy E-modulus

The development of the epoxy E-modulus at different curing temperatures (20 and 30ºC) obtained by the EMM-ARM are presented in Figure 3. The results of tensile tests are also presented in the same chart. The modulus of elasticity in tension was calculated at the highest slope of the stress-strain curve, in accordance with the work of Moussa et al., 2012a. From observation of Figure 3, it is possible to verify that the E-modulus curves corresponding to the two specimens tested at the same temperature have very good coherence with each other, with absolute stiffness differences under 3.0% (~0.27 GPa at the age of 144 hours at 20ºC), demonstrating adequate repeatability of EMM-ARM. Furthermore, there is a good agreement between the EMM-ARM results and the E-modulus estimated through the tensile tests, with stiffness differences under 2.0% (~0.18 GPa for the 20ºC test) validating the possibility to use the EMM-ARM to test the curing of adhesives at different isothermal conditions.

In addition, the results show that the reaction kinetics is increased with the increase of the curing temperature, since it can be observed that, for example, the elastic modulus of 4 GPa is achieved at approximately 10.7 hours at 20ºC as opposed to the approximately 6.2 hours at 30ºC. This effect can also be observed in the duration of the dormant period.

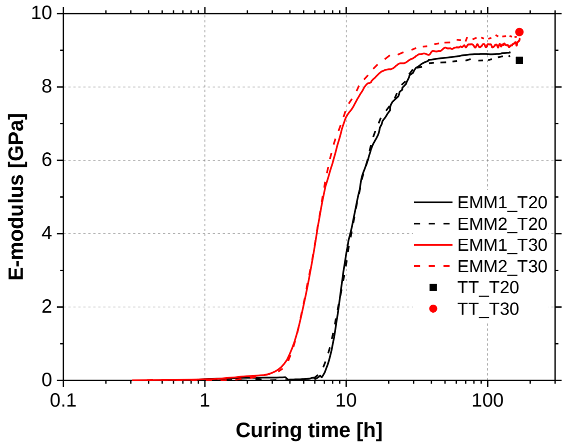


Figure 3. Evolution of epoxy E-modulus along curing time.

It should also be noted that the final E-Modulus of the epoxy increased slightly with the increase of the curing temperature, reaching near-stabilized final values of 8.9 and 9.3 for the tests at 20 and 30ºC, respectively, in accordance to several previous works on epoxy adhesives (e.g. Sun et al., 2002, Moussa et al., 2012b, Lionetto et al., 2013).

3.2 Bond behavior of NSM systems

The relationship between the pull-out force and slip at loaded end ($F_l - s_l$) for all tested specimens at two different temperatures (20 and 30ºC) of curing are presented in Figure 4a and b. It is possible to observe the increase on bond stiffness along the curing of epoxy adhesive, i.e., the evolution process seems to be strongly governed by the state of hardening of the adhesive. For the two analysed temperatures, the bond stiffness has a significant increase from 6 to 24 hours, showed by the sharp slope difference of the curves obtained by the tests performed between 6 and 24 hours. However, the speed of the thermosetting reactions depends mainly on the temperature, i.e. the higher the temperature the faster the curing process, as can be seen in Figure 4 comparing both temperatures of curing. The final values of pull-out force, $F_{l,max}$ at 30ºC were higher (9.5 % on average) than those of 20ºC, that is consistent with the obtained final values of epoxy E-modulus (see Figure 3). As expected, the slip at loaded end corresponding to $F_{l,max}$ was much higher during the early hours, due to early stage of curing of the epoxy at such period.

Two failure modes were observed in this experimental program (see the codes between parentheses for each specific ages in Figure 4): cohesive shear failure in epoxy (FE) and debonding at adhesive/laminate interface (D). It is possible to observe that the FE occurred at the early ages until 13 and 6h for 20 and 30ºC, respectively, confirming the low mechanical properties of the adhesive at the beginning of the curing. When the epoxy presented a significant maturity level, the failure mode occurred by pure interfacial debonding.

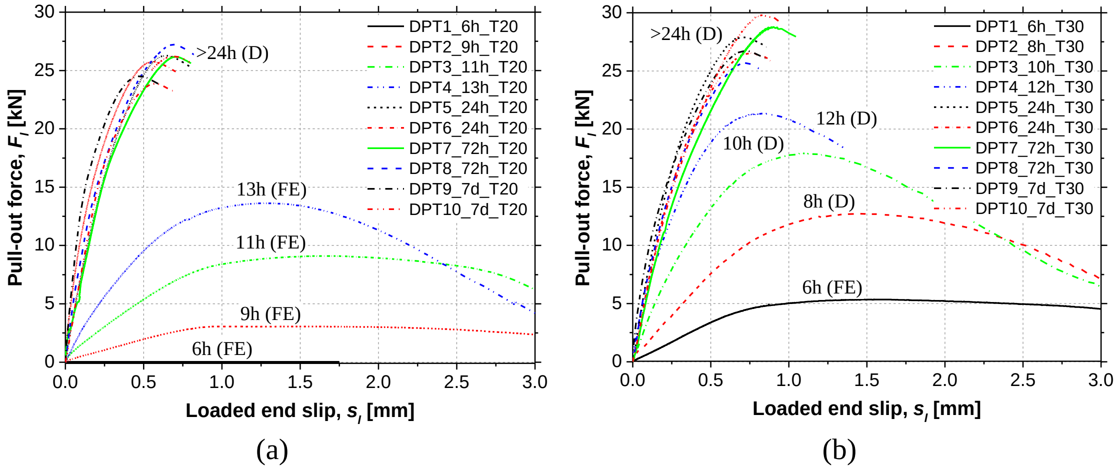


Figure 4. Pull-out force *vs.* loaded end slip during curing time at different temperatures: a) 20°C and b) 30°C.

3.3 *Comparison between E-modulus and maximum pull-out force*

With the purpose of evaluate the possibility of a correlation between the interface behavior of NSM systems and the epoxy stiffness, a comparison between the peak pull-out force and the adhesive E-modulus is carried out for the two studied temperatures, as shown in Figure 5. In order to better compare the results pertaining to different temperatures, all the values were normalized to their 72 hours value. Figure 5a highlights that the peak pull-out force and the epoxy E-modulus obtained by EMM-ARM exhibit very similar evolution kinetics, thus indicating that the bond performance of NSM CFRP system strongly depends on the stiffness of the adhesive. The increase on bond stiffness is consistent with the stage at which the rate of thermosetting reactions is higher, although its development was slightly delayed compared to E-modulus development.

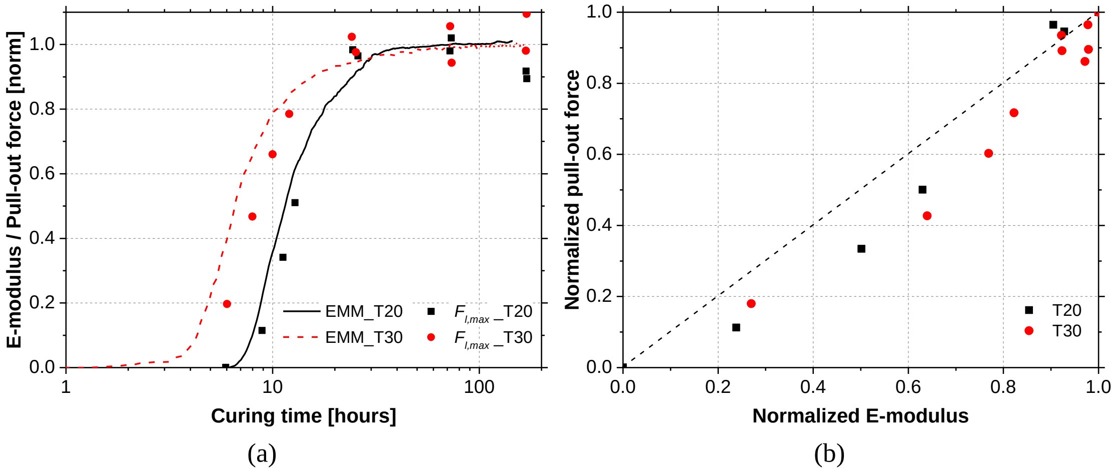


Figure 5. Comparison between epoxy E-modulus and peak pull-out force: (a) Epoxy E-modulus and peak pull-out force along time, normalized to 72 hours; (b) Relationship between epoxy E-modulus and pull-out force.

Figure 5b illustrates the obtained relationship between the E-modulus of the epoxy-resin and the maximum pull-out force for the two different curing temperatures: the scatter in the measured properties tended to be highest when the slope of the curves in Figure 5a was steepest and then decreased for longer durations. The slightly different evolution kinetics of the two properties seems to be similar for both temperatures and may be attributed to a delay in the development of the molecular bond quality, which usually has less influence on the stiffness of the epoxy resin than on its strength (Moussa et al., 2012a). Based on this kind of relationship, EMM-ARM can be employed for estimating the maximum pull-out force and the minimum curing time to reach a threshold value of pull-out force. In this manner it is possible to know the time required to put the strengthened structure in service, taking into account the influence of different environmental curing conditions.

4 CONCLUSIONS

The present paper aimed to investigate the evolution of the adhesive stiffness and the bond behavior of NSM systems for different curing conditions in terms of both temperature and duration. For this purpose, the capability of the EMM-ARM technique was extended to thermal activation testing. The tests described in this work have demonstrated encouraging results: (i) the possibility of using the EMM-ARM for monitoring the curing of adhesives at different isothermal conditions was assessed (the experimental program is currently going on with further curing temperatures); (ii) higher curing temperature considerably accelerated the curing process and consequently the rate of development of both epoxy E-modulus and pull-out force of NSM systems, showing that the bond stiffness is completely dependent on the mechanical properties of adhesive.

In conclusion, EMM-ARM has potential to be employed for in-situ monitoring of the hardening of an epoxy adhesive curing in un-controlled conditions, as may be those of a construction site, as basis for decisions concerning the waiting periods prior to putting strengthened structures into service.

5 ACKNOWLEDGEMENTS

This work is supported by FEDER funds through the Operational Program for Competitiveness Factors - COMPETE and National Funds through FCT - Portuguese Foundation for Science and Technology under the project FRPreDur PTDC/ECM-EST/2424/2012 and the project VisCoDyn EXPL/ECM-EST/1323/2013. The authors also like to thank all the companies that have been involved supporting and contributing for the development of this study, mainly, S&P Clever Reinforcement Ibérica Lda. The second and third authors wish also to acknowledge the grants SFRH/BD/80338/2011 and SFRH/BD/80682/2011, respectively, provided by FCT.

REFERENCES

Azenha, M., R. Faria, F. Magalhães, L. Ramos, and Á. Cunha, 2012, Measurement of the E-modulus of cement pastes and mortars since casting, using a vibration based technique, *Materials and Structures*, 45(1-2): 81-92.

Azenha, M., F. Magalhães, R. Faria, and Á. Cunha, 2010, Measurement of concrete E-modulus evolution since casting: A novel method based on ambient vibration, *Cement and Concrete Research*, 40(7): 1096-1105.

Borchert, K., and K. Zilch, 2008, Bond behaviour of NSM FRP strips in service, *Structural Concrete*, 9127-142.

De Lorenzis, L., and J. G. Teng, 2007, Near-surface mounted FRP reinforcement: An emerging technique for strengthening structures, *Composites Part B: Engineering*, 38(2): 119-143.

Fernandes, P., J. L. Granja, A. Benedetti, J. Sena-Cruz, and M. Azenha, 2015, Quality control and monitoring of NSM CFRP systems: E-modulus evolution of epoxy adhesive and its relation to the pull-out force, *Composites Part B: Engineering*, 7595-103.

Granja, J. L., P. Fernandes, A. Benedetti, M. Azenha, and J. Sena-Cruz, 2015, Monitoring the early stiffness development in epoxy adhesives for structural strengthening, *International Journal of Adhesion and Adhesives*, 5977-85.

ISO 527-2:2012 Plastics - Determination of tensile properties - Part 2: Test conditions for moulding and extrusion plastics. International Oganization for Standardization, Genève, Switzerland.

Lapique, F., and K. Redford, 2002, Curing effects on viscosity and mechanical properties of a commercial epoxy resin adhesive, *International Journal of Adhesion and Adhesives*, 22(4): 337-346.

Lionetto, F., and A. Maffezzoli, 2013, Monitoring the Cure State of Thermosetting Resins by Ultrasound, *Materials*, 6(9): 3783-3804.

Moussa, O., A. P. Vassilopoulos, J. de Castro, and T. Keller, 2012a, Early-age tensile properties of structural epoxy adhesives subjected to low-temperature curing, *International Journal of Adhesion and Adhesives*, 359-16.

Moussa, O., A. P. Vassilopoulos, J. de Castro, and T. Keller, 2012b, Time–temperature dependence of thermomechanical recovery of cold-curing structural adhesives, *International Journal of Adhesion and Adhesives*, 3594-101.

Oppenheim, A. V., and R. W. Schafer, 2009. "Discrete-Time Signal Processing," Prentice Hall Press.

Sun, L., S.-S. Pang, A. M. Sterling, I. I. Negulescu, and M. A. Stubblefield, 2002, Thermal analysis of curing process of epoxy prepreg, *Journal of Applied Polymer Science*, 83(5): 1074-1083.

Welch, P. D., 1967, The use of fast Fourier transform for the estimation of power spectra: A method based on time averaging over short, modified periodograms, *Audio and Electroacoustics, IEEE Transactions on*, 15(2): 70-73.