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EFFECTS OF DIFFERENT ENVIRONMENTAL CONDITIONS ON THE MECHANICAL CHARACTERISTICS OF A STRUCTURAL EPOXY

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Abstract: With the aim of characterising a commercially available epoxy adhesive used for fibre-reinforced polymers strengthening applications, when submitted to different environmental conditions, mainly thermal (TC), freeze-thaw (FT), and wet-dry (WD) cycles and immersion in pure (PW) and water with chlorides (CW) for periods of exposure that lasted up to 16 months, an experimental program was carried out. Several methodologies were used in its characterization, mainly the scanning electron microscope (SEM), dynamic mechanical analysis (DMA), standard tensile tests (STT) coupled with digital image correlation (DIC). In general the results revealed that the chemical composition was not affected by the environmental conditions. Nevertheless, it was verified through DMA and STT that the modulus of elasticity and tensile strength of the epoxy adhesive increased in the TC, while the specimens submitted to PW and CW faced a high degradation in terms of its mechanical properties. Eventually, the glass transition temperature (T_g) was not affected by the environmental conditions, apart from the specimens subjected to TC and FT, presenting a higher and lower T_g, respectively, when compared with the reference specimens.

Keywords: A. Thermosetting resin; B. Chemical properties; B. Mechanical properties; D. Thermal analysis; Durability.

1 INTRODUCTION

In last decades, the use of fibre reinforced polymer (FRP) materials on the strengthening of existing structures has been becoming a viable alternative to conventional materials like steel and concrete. The bond between the strengthened structural elements and the FRP material plays an important role on the success and efficiency of a strengthening system. Structural epoxy adhesives are commonly used as bonding agent because they provide the required load transfer between both materials, i.e. reinforcing material and the substrate. Several studies have shown that these FRP materials applied with proper strengthening techniques (e.g. externally bonded or near-surface mounted), improve the ultimate load carrying capacity and the serviceability aspects of the reinforced concrete (RC) elements e.g. [1-4].

The long-term performance (including the durability) of the retrofitted structures is a critical issue in terms of keeping the structural safety, since these structures are subjected to environment conditions and, consequently, its performance can be compromised due to the degradation of the composing materials. Furthermore, potential synergies can exist between individual physical and environmental factors when, for example, the material/structural element is subjected a sustained load and moisture simultaneously [5].

The temperature is one of the main environmental factors that limits the application range of structural epoxy adhesives. When the material achieves a temperature equal or above the glass transition temperature (T_g), a sudden change in its properties occurs: from a hard and relatively brittle state into a rubber-like state. However, this value only limits applicability, since the transition from solid to a viscous state is a continuous process over a certain temperature range (of about 10-20 °C) [6].

Mechanical properties such as strength and stiffness of epoxy adhesives are directly influenced by curing conditions, under which cross-linking of the polymer chains has to take place. The curing temperature plays an important role on the curing of epoxy adhesives [6, 7]. Moreover, depending on the type of epoxy adhesives it is usually observed a post-curing process when the material is submitted to a temperature higher than the one at the first cure. The post-curing phase can increase the mechanical properties of the material, even though the curing degree increase only marginally [7, 8]. The same process of post-curing is observed when the temperatures in the epoxy temporally exceed the T_g, and the T_g also increases itself [6]. Moreover, cooling the adhesive from temperatures above T_g to temperatures below T_g result into a full recovery of its mechanical properties [9].

Other environmental factors, such as humidity, salinity and UV radiation, can lead to the ageing and consequently, affecting the long-term performance of adhesive due to the reduction of its mechanical properties [10]. Moisture and water penetration can lead to properties changes as a consequence of physical and chemical

transformations [11, 12]. Epoxy adhesives absorb water because they contain polar groups which attract water molecules. Consequently, water can change in a reversible manner the polymer properties through plasticization. This phenomenon involves a considerable reduction of stiffness and strength. Moreover, water can also change the mechanical behaviour of thermosetting resins in an irreversible manner, if hydrolysis or cracking occur [11-14]. Hydrolysis of epoxies involve chemical reactions at the molecular level, which include chain scission. It should be stated that the effects of water absorption are only harmful for humidity levels higher than 75% [11]. El Yagoubi *et al.* [12] performed a research work with the aim of studying the hygrothermal ageing of an anhydride-cured epoxy under temperature and hygrometry conditions, in which the epoxy adhesive was submitted to thermal cycles (12 h at 70 °C and 90% of relative humidity (RH) following by 15 min at –40 °C) up to a maximum of 3000 cycles. They observed that the water uptake caused a rapid increase of about 1% of mass after the soak time in epoxy, resulting in a decrease (about 13%) of the T_g during the first 200 cycles, and a slowly increased between 250 and 1000 cycles was observed. After that, the T_g remained constant until the end of the ageing action. The authors of this work also observed a correlation between the evolution of the modulus of elasticity (E-modulus) and the T_g during the ageing action, which it lead to conclusion that the evolution of both parameters resulted from the same processes.

Lin and Chen [15] performed a research work where the moisture sorption-desorption-resorption characteristics of an epoxy system was investigated by hydrothermal ageing in order to verify the effects of moisture on the mechanical behaviour. Uniaxial tensile tests were carried out in specimens submitted to following conditions: (i) not aged; (ii) saturated (preconditioned under hygrothermal conditions: 85 °C and 85%RH); (iii) completely desorbed (dry under thermal conditions of 85 °C); and, (iv) re-saturated (re-preconditioned under hygrothermal conditions, 85 °C/85%RH). They verified that the E-modulus and tensile strength were reduced at about 42% and 54% respectively in the case of resorption, due to the hygrothermal effect. Also, the fractographic analysis showed that the absorbed moisture can modify the type of failure mode of the polymer from brittle to ductile for the not aged and saturated specimens.

In the study performed by Fonseca *et al.* [16] some specimens of epoxy adhesive were placed during 18 months at different environmental conditions: (i) continuous condensation; (ii) immersion in demineralised water; (iii) immersion in salt-water; and, (iv) immersion in alkaline solution. Furthermore, these wet environments were performed at temperatures of 40 °C and 60 °C. The results showed a decrease in mechanical

properties in all immersion conditions, and higher temperatures caused further degradation. Alkaline immersion at 40 °C revealed as the most aggressive condition presenting a tensile strength retention of about 14%.

Yang *et al.* [17] carried out a similar experimental program to the one performed by Fonseca *et al.* [16] over a maximum period of 24 months. They concluded that immersion in deionized water at 60 °C causes a significant decrease in strength (about 69%) and E-modulus (about 68%) within the first 6 months, much higher than under others conditions (deionized water at 23 °C and 38 °C; salt-water and alkaline solution at 23 °C). The main reason for such decrease pointed out was related to the temperature used for ageing the specimens. And like others authors [16, 18], Yang *et al.* [17] concluded that the temperature is an important factor that increase the rate of diffusion and amplifies the degradation caused by the different immersion conditions, suggesting a greater level of damage development at the interfaces of the fillers and resulting in matrix microcraking. Comparing only water immersion environments at 23 °C, over a period of 24 months of immersion, the samples in alkali solution showed the maximum deterioration in both tensile strength (about 53%) and E-modulus (about 41%) [17].

The aeronautic industry and other advanced industries/technologies have been studying in an exhaustive manner epoxy adhesives. The conclusions came up from these investigations cannot be directly extended to FRP/epoxy systems applied to structural rehabilitation, since the corresponding environmental conditions, substrate and loading are distinct. Furthermore, the curing period and temperature are two important characteristics of structural adhesives that should be taken into account in the global behaviour. The existing information about the most used epoxies in the ambit of FRP/epoxy systems applied to structural rehabilitation is scarce. Therefore, the main goal of the present work is the assessment of a commercial structural epoxy adhesive commonly used in FRP strengthening systems when submitted to different environmental conditions. For this purpose, an experimental program was carried out in which epoxy specimens were submitted to different environmental conditions (thermal, freeze-thaw and wet-dry cycles and immersion in pure and water with chlorides) during periods of exposure up to 16 months. Several methodologies were used in its characterization, mainly the scanning electron microscope, dynamic mechanical analysis and standard tensile tests coupled with digital image correlation. The experimental program is described and the main results are presented and discussed.

2 EXPERIMENTAL PROGRAM

2.1 General characteristics of the epoxy adhesive

The structural epoxy adhesive studied, widely used in retrofitting existing reinforced concrete structures with CFRP laminate strips, is produced by S&P® Clever Reinforcement Company and its trademark is "S&P Resin 220 epoxy adhesive". This epoxy adhesive is a solvent free, thixotropic and grey two-component (Component A = resin, light grey colour and Component B = hardener, black colour). According to the available information provided by the manufacture, the chemical composition of component A includes Bisphenol A (20% to 25%) and 1,3-bis(2,3-epoxypropoxy)-2 2-dimethylpropane (5% to 10%), whereas the Component B includes Poly (oxypropylene) diamine (20% to 25%), Piperazine (1% to 2.5%) and 3,6-diazaoctanethylenediamin and Triethylenetetramine (20% to 25%). According to the manufacturer, after mixing the two components, the homogenized compound density is 1.70 to 1.80 g/cm^3 and has the following mechanical properties [19]: (i) compressive strength >70 MPa; (ii) tensile E-modulus >7.1 GPa; (iii) shear strength >26 MPa; (iv) adhesive tensile strength to concrete or CFRP laminate >3 MPa (after 3 days of curing at 20 °C). The recommended application temperature is between +10 °C and +35 °C. Recent studies [20] proved that this epoxy at 20 °C exhibits during the first 6 hours a dormant period with a nearly null stiffness, followed by a drastic increase in the stiffness in the next 18 hours, reaching at the end of this period 90% of its maximum value.

2.2 Specimens and environmental exposure conditions

The specimens used in the present work were produced according to "type 1A" defined in EN ISO 527-2:2012, as represented **Fig. 1a**. The mixture of two resin components was made manually and then the homogenized compound was cast into a Teflon moulds. Then, it was placed an acetate sheet on the top surface and pressed with a steel roller. All these procedures were carefully performed in order to assure specimens with nominal geometry and homogeneity by avoiding as much as possible voids. The specimens were removed from the moulds one day after casting and then they were kept in lab with an average temperature around 22 °C and relative humidity close to 55% during at about one year before being submitted to the corresponding ageing actions.

Table 1 summarizes the thirteen series of the present experimental program being each series composed of 6 specimens. A total of 78 specimens were submitted to different environmental conditions for a period of time that lasted up to 480 days, depending the type of environmental exposure.

During the experimental program all the reference specimens (REF) were kept in the lab environment. Reference specimens were tested at the beginning (REF0), middle (REF240) and end of the experimental program (REF480).

To evaluate the moisture effect on the performance of the studied epoxy adhesive, the additional three environmental actions were considered: (i) specimens immersed in pure water at 20 °C (PW); (ii) specimens immersed in water with 3.5% chlorides at 20 °C (CW); and, (iii) specimens submitted to wet-dry cycles in water with 3.5% chlorides at 20 ºC (WD). The percentage of chlorides adopted was based on the ASTM D1141-98 [21], which recommends a concentration of 2.453% of NaCl in order to simulate a seawater. However, with the aim of obtaining a more severe and aggressive environment and accelerate the degradation mechanisms, 3.5% concentration of NaCl was adopted since the salinity of seawater is around 3.5% [22]. For these series half the specimens were submitted to these actions during 240 days (PW240, CW240 and WD240), whereas the other half continued this ageing tests up to 480 days (PW480, CW480 and WD480).

The effect of thermal actions were analysed through two different environmental exposures, namely, thermal (TC) and freeze-thaw (FT) cycles. For each test, the specimens were aged during 120 days (TC120 and FT120) and during 240 days (TC240 and FT240), and each cycle lasted a 24 hours of duration. The TC program was based on EN 13687-3:2002 standard and the applied temperatures ranged between −15 °C and +60 °C, with plateaus that lasted 12.5 and 10 hours, respectively. The transitions between these two temperatures took 1.5 hours. In the FT program, temperatures ranged from −18 °C to +20 °C according to CEN/TS 12390-9:2006 standard, with plateaus that lasted 3 and 13 hours, respectively. The transitions from positive to negative and negative to positive temperatures took 3 hours and 5 hours, respectively. The specimens were immersed in water at positive temperatures.

2.3 Methods of characterization

2.3.1 Scanning electron microscope

Observation in Scanning Electron Microscope (SEM) was done on reference specimens (REF0 and REF480) and specimens submitted to environmental actions (TC, FT, PW CW and WD). The observation has been done in back-scattered electrons mode (BSED), to provide information about the chemical structure of the present phases, in the inorganic charges. The observation was complemented by the possibility of doing micro-analysis by energy dispersive spectrometry (EDS). The surface of the samples was prepared for observation by grinding

(SiC paper) and polishing (with diamond particles of 6 and 1 μm). Phase distribution in the composite and the presence of internal defects were verified for samples with different types of environmental actions.

2.3.2 Dynamic mechanical analysis

The Dynamic Mechanical Analysis (DMA) is a technique most useful for studying the viscoelastic behaviour of polymers, where an oscillating force is applied to the sample and the corresponding material's response to that force is analyzed [23]. With the DMA, the complex modulus, elastic modulus (E-modulus) and loss modulus are determined from the material response to the sine wave. These moduli allow a better characterization of the material properties since it is possible to observe the capacity of the material to store energy (E' – storage modulus) and to lose energy (E'' – loss modulus) [23]. With DMA it is also possible to evaluate the (tan δ) by calculating the ratio between E' and E'' entities which is usually denominated by damping.

The determination of the viscoelastic behaviour represented by the E' and E'' and their damping characteristics of the specimens, was performed with the TA DMA Q-800 equipment, using a single-cantilever configuration. The specimen's geometry was 35 mm long, 5 mm wide and 1 mm thick. These tests were performed by the application of a constant amplitude (5 μm) with a frequency sweep (1, 5 and 10 Hz) at a temperature of 24 ºC. The aim of these frequencies was comparing the response at low frequency (close to a static test) to intermediate and very high and frequencies. Additionally, the dynamic E-modulus (E^*) of the samples was determined using Eq. (1) [23].

$$E^* = \sqrt{E'^2 \cdot E''^2} \tag{1}$$

In order to determine the glass transition temperature (T_g), the specimens were subjected to a temperature ramp from room-temperature to 120 °C with a heating rate of 2 °C/min in an inert nitrogen atmosphere. These tests were carried out by the application of a constant amplitude (5 μm) with a frequency of 1 Hz. The T_g was calculated from two distinct methods: (i) the onset of the storage modulus curve drop, as represented in **Fig. 4a**; and (ii) the peak value of loss modulus curves as shown in **Fig. 5**. The first and second methods will be represented in the following sections by means method E' and E'', respectively. More information about these methods can be found in [6, 24].

2.3.3 Standard tensile test

The standard tensile tests (STT) were performed according to EN ISO 527-1:2012. The epoxy samples were tested on universal testing machines under displacement control of 1 mm/min. The applied load was measured with a load cell of 50 kN maximum carrying capacity. In order to measure the longitudinal strain, a strain gauge (SG) (TML BFLA-5-3-3L) was installed at mid-length of the specimen, as can be seen in **Fig. 1b**. Before performing the tensile tests, the thickness and width of each single specimen were measured with a digital calliper (0.01 mm of precision) in three distinct sections (middle height and two at 1 mm apart to the former). Based on these measurements the average cross-section area was determined for assessing the longitudinal normal stress. E-modulus was calculated as the slope of the secant line between strain values of 0.05% and 0.25% on the stress-strain curve.

2.3.4 Digital image correlation

The digital image correlation (DIC) technique was used in this work as a complementary method for monitoring the deformations and strains during the standard tensile tests (STT), instead of using strain gauges. DIC provides full-field displacements of a target objects. Therefore, it can allow to verify the existence of homogeneous strain field of the tested material and measure the strains in both directions in contrast to the single element strain gauge used in the present work. DIC has been increasingly used in experimental mechanics, being, however, its relevance more emphasised when gradient deformation fields are expected to occur across the region of interest. The STT of the series REF480 were coupled with DIC as shown in **Fig. 1d**. In this optical method, the displacements of a speckled surface are measured by correlating images recorded at successive deformation stages. In the matching (correlation) process, the reference (undeformed) image is divided into subsets whose size defines the displacement spatial resolution. The specimens monitored with DIC were prepared by applying a speckle pattern on the region of interest (ROI), produced by applying a thin coating of white matt followed by a spread distribution of black dots using spray paint, see **Fig. 1c**. The ARAMIS DIC-2D software was used in this work [25, 26]. The optical system was equipped with an 8-bit Baumer Optronic FWX20 camera coupled with an Opto-Engineering telecentric lens TC 23 09, yielding a magnification factor of 18 μm/pixel. Two Raylux 25 white-light LED sources were used to assure uniform illumination with suitable image contrast. The target ROI was set to10×30 mm^2 at the centre of the specimen (see **Fig. 1c**). The DIC parameters were carefully chosen in order to obtain the best compromise between spatial resolution and accuracy. A subset size of 15×15 pixels^2, a subset step of 13×13 pixels^2, and a strain gauge length of 5 subsets were therefore selected. This set of

parameters defined a displacement spatial resolution in displacement and strain of 0.27 mm and 1.35 mm, respectively. Moreover, a resolution in displacement and strain of 1.12×10^{-2} pixel (0.2 µm) and 1.34×10^{-2} was achieved, respectively.

3 RESULTS AND DISCUSSION

3.1 Chemical composition

Two typical SEM observations are shown in **Fig. 2**, namely the reference specimen (REF0) and specimen after being submitted to pure water (PW480) immersion. High density and uniform distribution of mineral fillers and some air bubbles were observed. The existing main phases in this studied epoxy adhesive are: (i) silica (very likely quartz); (ii) Ca, Na, Mg silico-aluminates, probably a micaceous mineral; (iii) barium sulphate; and, (iv) titanium oxide. The maximum particle size is around 200 µm. The SEM observations showed that the specimens submitted to environmental conditions over long periods of time did not present changes in chemical composition, when compared to reference.

3.2 Dynamic thermomechanical properties

Fig. 3 represents the evolution of average dynamic E-modulus (E^*) and damping (tan δ) obtained by frequency sweep at 1, 5 and 10 Hz. For 1 Hz of frequency, the values of dynamic E-modulus are presented in **Table 2** and were calculated according to the equation (1). Dynamic E-modulus slightly increased with the increase of the frequencies. This observation was confirmed by previous works, e.g. [27]. Similar trend was observed for all the tested series. Comparing the values of dynamic E-modulus of reference specimens (REF480) with the aged ones, it is possible to point out (i) a significant decrease for the series PW, CW and WD, approximately 19%, 13% and 5% respectively, and (ii) a significant increase for the series TC240 of about 22%.

The dynamic E-modulus of reference specimens (REF0, REF240 and REF480) did not approximately present the same values. These differences can be related to the fact that the samples have been obtained from distinct mixtures. According to other research works [20, 28] performed with the same epoxy adhesive, the mechanical properties of this adhesive presents slight variations for different mixtures even carried out from the same container and with the same curing conditions.

The decrease of the dynamic E-modulus in series PW, CW and WD may be directly related to the level of plasticization of the adhesive when water uptake occurs [14]. Additionally, it can be also concluded that the chlorides decelerated the degradation (in comparison with series PW) since the molecules of salts work as a

semipermeable membrane. Regarding to the series TC, the post-curing of the epoxy adhesive caused by applied thermal cycles yielded an improvement in its mechanical properties [9, 29]. More details about these observations will be discussed in further sections. Regarding to the evolution of (tan δ), similarities in terms of results for all the series (reference and aged) are observed, as shown in **Fig. 3b**, mainly on series PW480 and CW480 being out of this trend. The damping decreased with the increase of frequencies, which indicates a higher energy dissipation at low frequency. Probably, the damping behaviour is sensitive to the polymer-particle interaction state and hence mainly governed by the structure of epoxy network (crosslink density). The higher dissipation of energy of specimens PW480 and CW480 can be justified by degradation of these connections due to the environmental conditions.

Fig. 4 shows the evolution of the storage modulus with temperature obtained from DMA tests of all the tested series, whereas **Fig. 6** presents the T_g assessment through the two distinct methods described in Section 2.3.2, i.e. (i) the onset of the storage modulus curve drop (method E') and (ii) peak of loss modulus (method E''). In general the storage modulus exhibit a large decrease with the increase of the temperature, particularly when the glass transition region is reached, which reflects the changes in the viscoelastic polymer matrix of adhesive with the increase of the temperature. When compared with the reference specimens, the shape of the storage modulus curves of specimens submitted to environmental conditions did not present so remarkable drop. However, it is possible to be observed for all aged specimens a lower slope in the glass transition region comparing to reference one. For the specimens subjected a higher period of exposure, this aspect is more pronounced, apart from the TC series. This change in the slope can be attributed to the physical degradation (plasticization) in the network chains promoted by water absorption. However, the filler content seems to show an important factor on the elastic properties in vitreous and rubbery regions since the specimens exhibited a considerable initial moduli in spite of the high degradation of network chains [30, 31].

From **Fig. 6**, it is possible to observe that the assessment of T_g is highly dependent on its evaluation technique, as can be verified in others works, e.g. [6]. Comparing the two methods, the most conservative approach is when the onset point T_0 at the tangent intersection is used. The maximum difference found when the two approaches are used for assessing the T_g is at about 15 °C (specimen TC120). These conclusions underline the need of a clarification and unification of the guidelines about the procedure on how to determine T_g, as pointed out by other researchers [6].

In spite of T_g had been assessed by two distinct methods, for the present analysis values obtained from method E' are selected since this method is the most widely used. The results of T_g obtained for different periods

of exposure were lower than the reference specimen, being the higher variations of about 21% for CW240 (T_g=42.4˚C) and 23% for FT (T_g=41.5˚C) series. The results of T_g obtained for specimens submitted to water environments would be expected due to the plasticization phenomenon occurred during the period of exposure. In the case of specimen FT240, the lower T_g can be related with an interruption of the curing along time [32]. As expected, the T_g of TC240 was slightly higher than reference specimen (REF240), of about 3%. This is consequence of stronger chain cross-linking as pointed out in bibliography [9, 33].

3.3 Tensile mechanical properties

Fig. 7 shows typical stress-strain curves obtained from the tensile tests. The average values of the main parameters obtained from the tensile tests mainly, the tensile strength (f_{ult}), the ultimate strain (ε_{ult}) and the E-modulus (E_{std}) are presented in **Table 2**. The average curves presented in **Fig. 7** were obtained averageing all the specimens composing the series (6 specimens per series); however, the average curve is interrupted at onset of the failure of the first specimen in the series. This figure does not include the strain-stress curves of series TC due to the technical problems faced at the very beginning of the corresponding tests during the acquisition of the strains. When compared with the reference series, the mechanical properties (tensile strength and E-modulus) of aged series presented distinct trend: (i) increased for the series TC120 and TC240; (ii) slightly decreased for the series FT120 and FT240; and, lastly, (iii) significant decreased for the series PW, CW and WD. These conclusions are also underlined by the observation of the curves presented in **Fig. 7** and the results summarized in **Fig. 8**. The differences in terms of the mechanical properties observed for the series REF0, REF240 and REF480 have been previously justified (see section 3.2).

The tensile strength increased on the series TC120 and TC240 at about 25% and 33%, respectively, when compared to REF240. Although the technical data sheet of the epoxy adhesive does not give any information regarding the curing and post-curing process, this behaviour has been reported in the literature. Moussa *et al.* [9] observed for another epoxy adhesive similar behaviour, i.e. a post-curing phase which improved its mechanical properties. This process occurs when temperatures higher than the ones experienced at the first curing are achieved. **Fig. 8** also highlights higher increase of strength than stiffness, due to the following main reasons: (i) strength is more related with the polymeric structure regarding an increase in chain branching and molecular bond strength; (ii) the fillers incorporated in the epoxy adhesive contribute more to the stiffness than the strength. Consequently, the changes in the polymeric structure influenced more the changes in strength than the changes in stiffness [33].

Regarding to the series FT, the expected tendency was observed, i.e. some degradation on the mechanical properties with the ageing. In fact, the tensile strength on specimens with 120 and 240 days of ageing decreased 11% and 17%, respectively. In spite of both ages presented an important decrease in terms of such mechanical property, apparently higher rates of degradation occurs at early stages, since the series FT120 presents a higher degradation for a period of 120 days than the FT240 for a period of 240 days. The stiffness also decreased 11% and 17% with 120 and 240 days of ageing, respectively. The degradation processes of stiffness can be the same of strength since the decrease of stiffness follows the trend of strength variation. Although the adhesive had been submerged in water, and the hydrolysis phenomenon had occurred, the diffusion and reaction processes are significantly slower for negative temperatures [12]. Finally, it should be referred for these series a post-curing phase was not occurred since the applied temperatures ranged in between –18ºC and +20ºC.

The remaining three series (PW, CW and WD) presented the higher degradation ratios, when compared with series TC and FT. As previously stated, time can be a major factor on the evolution of the mechanical properties because these specimens were aged for longer periods of time. All comparisons have been made to the REF480 (kept in lab environment for 480 days). Results show that specimens immersed on pure water had the greatest degradation ratio (35% and 38% for PW240 and PW480, respectively). Epoxy adhesives absorb water and, as a consequence, they plasticize, increase their volume and their mechanical properties are enfeebled, namely stiffness, tensile strength and the glass transition temperature [12, 14, 32]. El Yagoubi *et al.* [12] explains that the hydrolysis phenomenon observed on materials exposed to wet-dry cycles, is characterized by a chemical reaction at the molecular level that destroys the mollecular chains.

Comparing the results obtained for the specimens submitted to pure water (PW) with specimens immersed in water with chlorides (CW), the stiffness of the formers was more affected than the lastests (47% and 35% for PW480 and CW480, respectively). The reason for such behavior is related to the fact that in aqueous environments the cross-linked matrix behaves as semi-permeable membranes, where only the water can permeate and the large inorganic ions are obstructed, as previuously stated [34]. In essence, the mechanical properties of the epoxy adhesive are affected due to the presense of water. An exception was observed on series S4 where the a post-curing phase might be responsible for the increse on the mechanical properties.

The E-modulus (E_{std}) obtained by standard tensile test are very close to the dynamic E-modulus (E^*), as can be demonstrated by the E^* / E_{std} ratio (see **Table 2**). By default higher values for E-modulus are expected when dynamic methods are used, as reported by the literature. In general, for the present case this trend was observed.

As previous mentioned, the DIC method was used for simultaneously measuring the axial and transverse strains in tensile tests of an epoxy adhesive for the series REF480. **Fig. 9** shows the typical relationship between axial (1) and transversal (2) strains obtained for one specimen of series REF480. The Poisson's ratio (v) was calculated as the slope of the linear trend line of the experimental values of the strains in both directions, gathered until 0.2% of the axial strain (ε_1) values, as can be seen in ***Fig. 9***. From the tested specimens of the series REF480, an average of Poisson's ratio value of 0.27 with a coefficient of variation (CoV) of 2.59% was obtained (see **Table 3**). Moreover, **Table 3** includes the coefficient of determination (R^2) values for each curve obtained by the fitting method, resulting in an average value of 0.995. This value demonstrates that, in the considered range of strain values, the experimental curve is almost linear.

4 CONCLUSIONS

In the present study, the effects of the different environmental conditions on a commercial epoxy adhesive used on the strengthening of RC structures were analysed and discussed. From the obtained results the following main conclusions can be pointed out:

(i) The observations in Scanning Electron Microscope revealed that all the tested specimens were very similar. The specimens submitted to environmental conditions did not present changes in their chemical composition when compared with the reference specimens;

(ii) Dynamic E-modulus increased with the increase of the frequencies. Moreover, the specimens submersed in pure water and water with 3.5% of chlorides presented a higher decrease of dynamic E-modulus, of about 19% and 13%, respectively, comparing to the reference specimens. As opposed the thermal cycles caused a increase of about 22%.

(iii) For all specimens, the damping decreases significantly with the increase of frequencies. The specimens exposed to pure water and water with the chlorides showed a higher dissipation of energy than the remaining specimens. The higher dissipation of energy of these specimens can be justified by degradation of connections between polymer-particle due to the environmental conditions since the damping behaviour is sensitive to the structure of epoxy network.

(iv) The storage modulus curves of all aged specimens presented a lower slope in the glass transition region comparing to reference ones. For the specimens subjected a higher period of exposure, this aspect is more pronounced, apart from the TC series. This change on the slope can be attributed to the degradation in network chains promoted by water absorption. The filler content seems to show

an important factor on the elastic properties in vitreous region since the specimens showed a considerable initial moduli in spite of the high physical degradation (plasticization) in the network chains.

(v) The T_g values of specimens submitted to different environmental conditions were negatively affected, mainly the specimens exposed to chlorides water and freeze and thaw cycles, with a relative decrease of about 21% and 23%, respectively. The exposure to wet environments may have had as consequence the plasticization of adhesive and the negative temperatures might have interrupted the curing along time.

(vi) From the tensile tests, it was observed an increase up to 33% and 15% on the ultimate tensile stress and E-modulus for the series submitted to thermal cycles, respectively. The thermal cycles might have caused a post-curing phase that could explain the increase on the epoxy specimens strength and stiffness, as verified in dynamic thermomechanical analysis. In addition, it was observed a decrease on the tensile strength and E-modulus for the freeze-thaw cycles samples.

(vii) A generalized decrease on the ultimate tensile stress and E-modulus for series PW, CW and WD up to 47% and 38%, respectively. These reductions of mechanical properties were observed due to the presence of water. This epoxy material seemed susceptible to the degradation mainly when it is immersed in pure water due to the occurrence of plasticization phenomena.

(viii) The DIC method was used for assessing to the axial and transverse strains during the tensile tests of the studied epoxy adhesive: from the tests carried out a Poisson's ratio of 0.27 was obtained.

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Table 1 — Environmental exposure conditions.

Environmental condition	**Series ID**
Reference	REF0, REF240, REF480
Immersion in pure water	PW240; PW480
Immersion in water with chlorides (3.5% NaCl)	CW240; CW480
Wet and dry cycles in water with chlorides (3.5% NaCl)	WD240; WD480
Thermal cycles (between −15 °C and +60 °C)	TC120; TC240
Freeze-thaw cycles (between −18 °C and +20 °C)	FT120; FT240

Table 2 — Tensile mechanical properties and dynamic E-modulus.

Environment exposure	f_{ult} **[MPa]**	ε_{ult} **[%]**	E_{std} **[GPa]**	E^* **[GPa]**	E^* / E_{std}
REF0	22.0 (4.5%)	0.36 (15.2%)	7.15 (3.7%)	7.02 (0.2%)	0.98
REF240	20.7 (1.0%)	n/a	n/a	6.14 (0.2%)	n/a
REF480	20.8 (2.2%)	0.43 (6.1%)	6.66 (3.4%)	5.94 (0.2%)	0.89
PW240	13.6 (4.9%)	0.55 (23.8%)	4.10 (3.0%)	5.03 (0.1%)	1.23
PW480	13.0 (2.1%)	0.75 (14.1%)	3.52 (3.3%)	4.81 (0.1%)	1.37
CW240	15.3 (2.9%)	0.50 (10.6%)	4.72 (3.5%)	5.47 (0.2%)	1.16
CW480	15.0 (1.7%)	0.68 (11.4%)	4.36 (1.5%)	5.14 (0.3%)	1.18
WD240	16.6 (4.2%)	0.39 (18.2%)	5.43 (2.8%)	5.80 (0.1%)	1.07
WD480	16.5 (2.5%)	0.51 (13.6%)	5.20 (3.2%)	5.66 (0.1%)	1.09
TC120	25.9 (4.0%)	0.39 (10.8%)	7.50 (3.2%)	n.a.	n/a
TC240	27.3 (2.3%)	0.43 (5.3%)	7.64 (4.7%)	7.22 (0.2%)	0.95
FT120	18.6 (0.6%)	0.48 (6.1%)	5.93 (1.4%)	n/a	n/a
FT240	17.2 (2.5%)	0.45 (11.8%)	5.54 (1.8%)	6.21 (0.1%)	1.12

Notes: The values between parentheses are the corresponding coefficients of variation.

Table 3 — Poisson's ratio assessment.

Specimen	Poisson's ratio, ν	R^2
REF1	0.26	0.997
REF2	0.26	0.996
REF3	0.28	0.998
REF4	0.28	0.992
REF5	0.27	0.994
REF6	0.26	0.996
REF7	0.27	0.991
Average	0.27 (CoV=2.59%)	-

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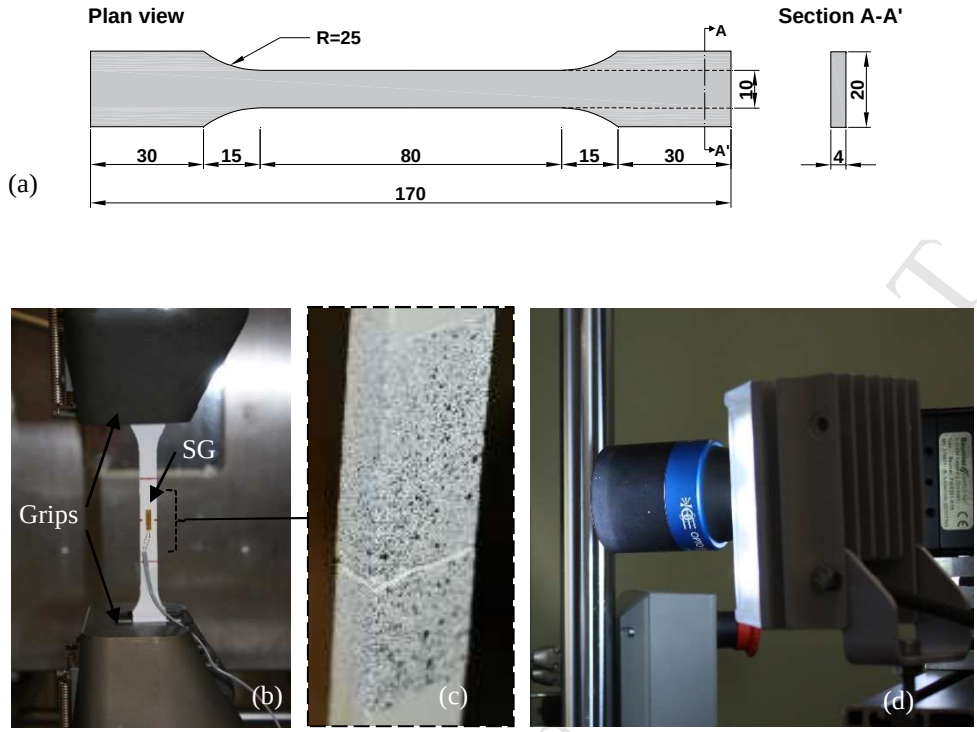

Fig. 1 — (a) Specimen's geometry (all units are in millimetres); (b) Tensile test overview; (c) Detailed view of pattern use with DIC method; (d) DIC set-up.

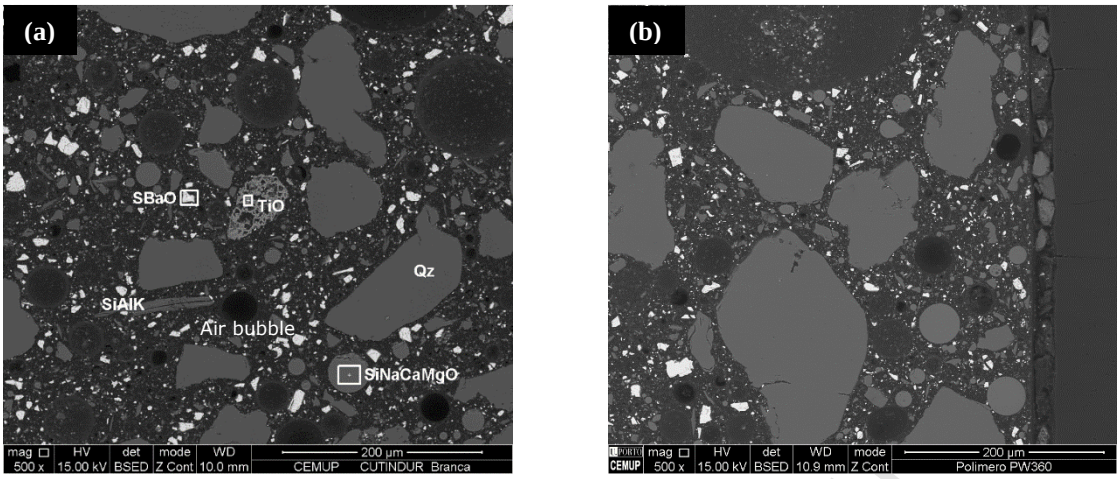

Fig. 2 — SEM images: (a) chemical composition of reference specimen; (b) specimen after being submitted to pure water environmental action.

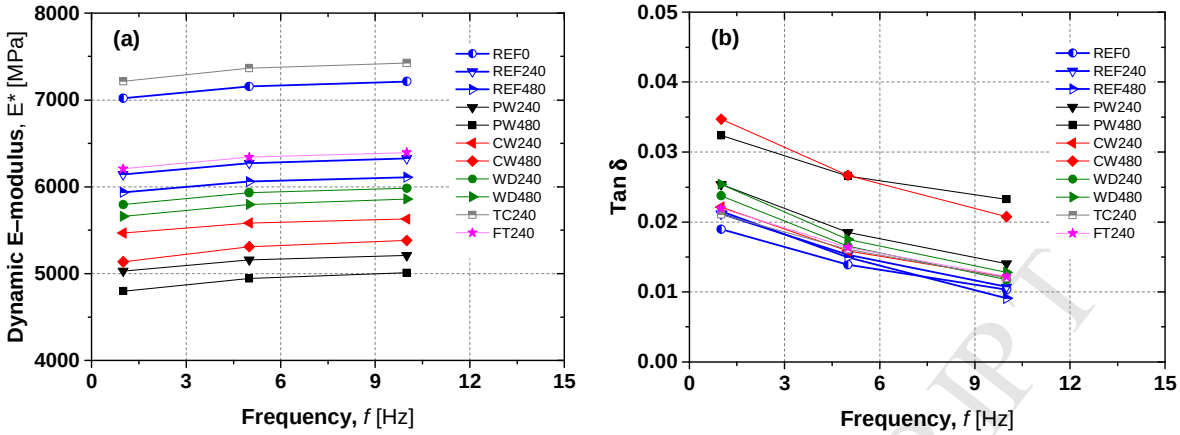

Fig. 3 — Viscoelastic properties at different frequencies: (a) dynamic E-modulus and (b) Tan δ.

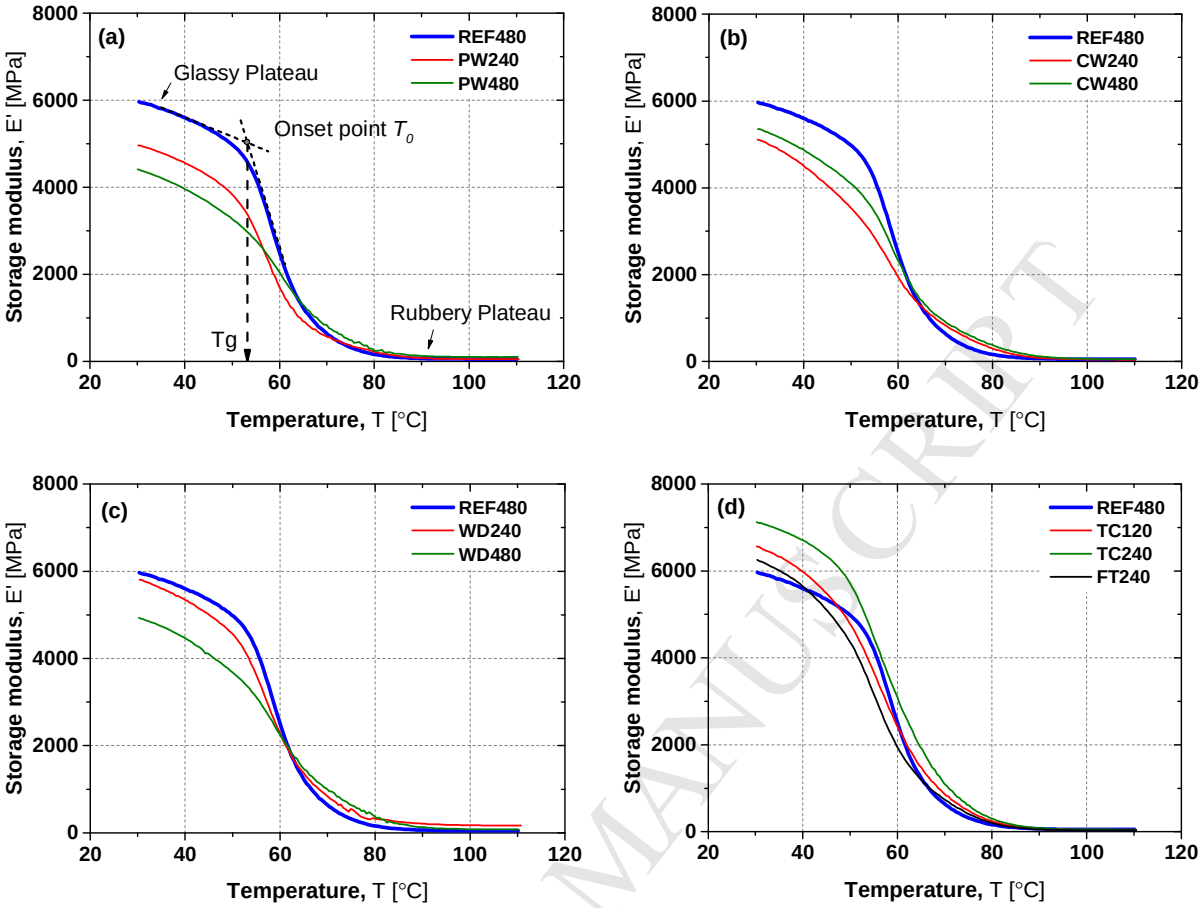

Fig. 4 — Evolution of the storage modulus with the temperature for specimens submitted to: (a) pure water; (b) water with chlorides; (c) wet and dry cycles in water with chlorides; (d) thermal and freeze-thaw cycles.

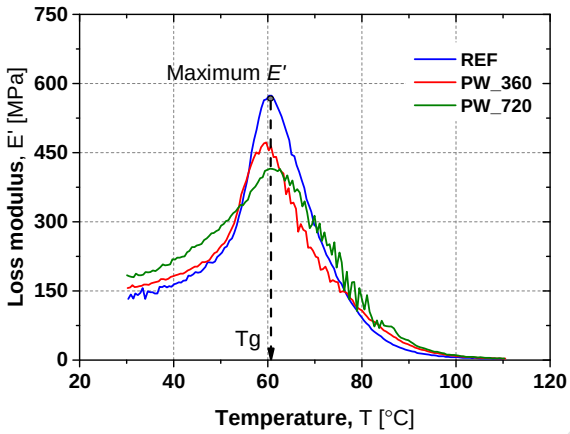

Fig. 5 — Evolution of the loss modulus with the temperature for specimens submitted to pure water.

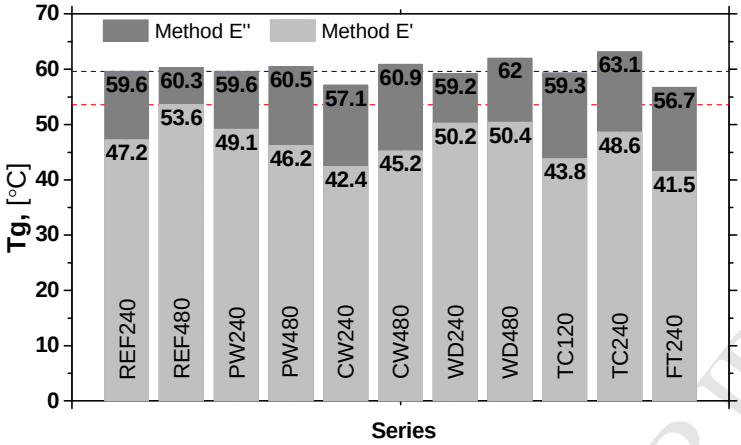

Fig. 6 — Glass transition temperature (T_g).

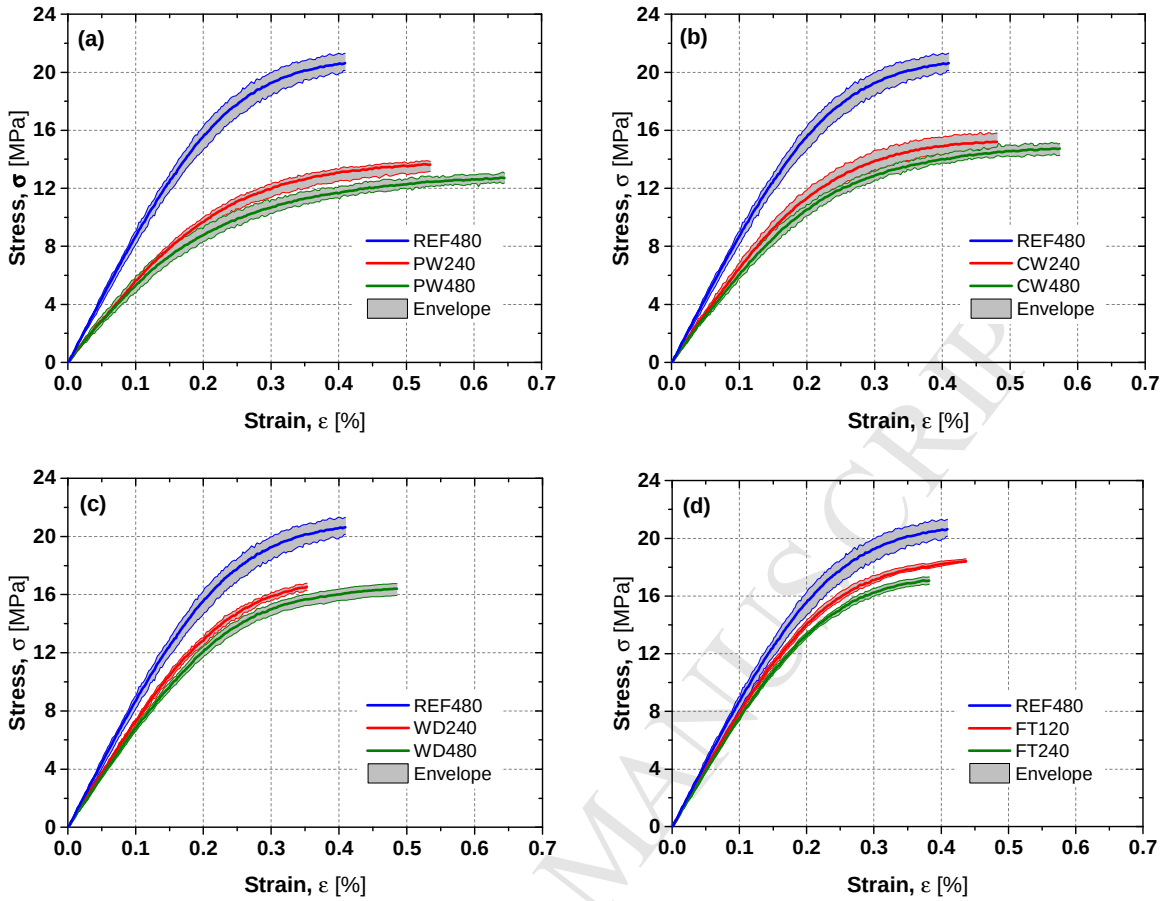

Fig. 7 — Stress *versus* strain relationships of specimens submitted to: (a) pure water; (b) water with chlorides; (c) wet and dry cycles in water with chlorides; (d) freeze-thaw cycles.

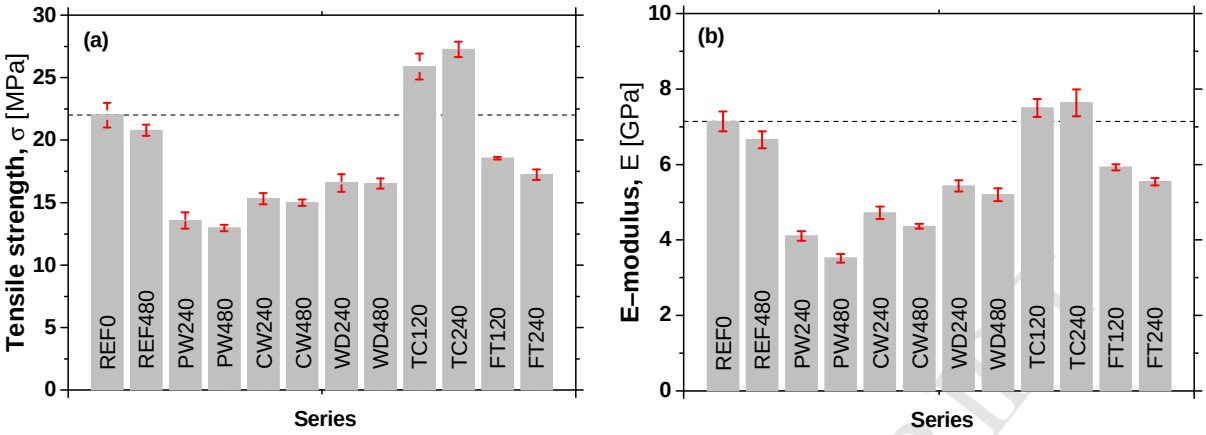

Fig. 8 — Tensile mechanical properties: (a) tensile strength; (b) E-modulus.

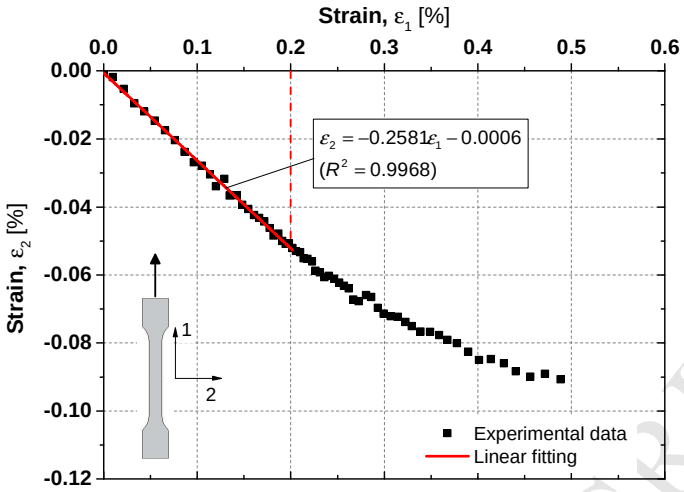

Fig. 9 — Example of determination of the Poisson's ratio for the REF480 series.