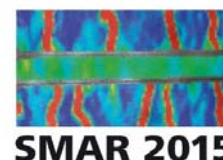


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Thermo-mechanical properties of commercially available epoxy resins for structural applications

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ABSTRACT: Externally bonded (EB) or Near-Surface-Mounted (NSM) composite reinforcements are often bonded to a cementitious substrate by means of commercially available epoxies. These two-component-resins are generally ‘cold-curing’ (at room temperature), having however the ability to cure faster under elevated temperatures. One application requesting such an accelerated curing process is the gradient anchorage for strengthening of concrete structures with prestressed CFRP laminates, based on a purely concrete/epoxy/CFRP connection without any mechanical devices.

This paper resumes the investigation on several crucial thermo-mechanical parameters of different epoxy resins, such as glass-transition temperatures, directional tensile strength and elastic modulus. It is for instance demonstrated that an accelerated curing process or an increasing specimen age implicate a higher glass transition temperature. Strength and stiffness development is faster in case high temperatures are applied; the final values with growing age however are below the ones for specimens cured only at room temperature. Initial mixing under vacuum on the other hand induces higher strength and stiffness values. Eventually, it is shown that an accelerated curing of a cold-curing epoxy increases the porosity of the latter, possibly implying durability issues.

1 INTRODUCTION

In structural engineering, CFRP strips or sheets are mostly bonded to their respective substrate by means of epoxy resins, Bakis et al. (2002). Once cured at a certain temperature, they are responsible for a proper shear stress transfer of the composite material to the structure and vice-versa. The efficiency of these polymer resins is strongly depending on the surrounding temperature. Especially elevated temperatures might cause a certain weakening of the epoxy, mainly the loss of its stiffness. This happens when the so-called *glass transition* temperature range is exceeded, Michels et al. (2015). For practical purposes, a glass transition temperature T_g is defined in order to characterize the service temperature at which a product can be used. Besides its thermal stability, mechanical performance is another key point when judging about the suitability of a product for a specific application. In this sense, tensile strength and stiffness are among the most important.

This paper presents results obtained from Dynamic Mechanical Analysis (DMA) tests in order to derive the previously presented T_g as well as from tensile tests. For this investigation, a special focus was put on the adopted curing procedure for the epoxy resin after mixing. For the application of a gradient anchorage for prestressed CFRP strips (Michels et al. (2013)), it is for

instance necessary to apply accelerated curing of the epoxy resin at elevated temperature during a defined time span. This configuration is compared to epoxy specimens conventionally cured at room temperature prior to testing. A second important parameter taken into account for both the glass transition and the mechanical tensile properties is the specimen age at which testing was performed. Regarding T_g , two additional test parameters (i.e. heating ramp and maximum temperature during testing) were investigated.

2 EXPERIMENTAL INVESTIGATIONS

2.1 Materials

Tests have been performed on three commercially available epoxy resins, namely S&P Resin 220 (Resin 1), Sikadur30 (Resin 2), and Sikadur30 LP (long pot, Resin 3). All product types are two-component pre-batched thixotropic epoxy resins.

2.2 Dynamic Mechanic Analysis (DMA)

2.2.1 Curing configurations

Curing configurations differentiate between the following parameters: a) initial accelerated curing (AC) of the epoxy at high temperature during 25 minutes (application of the gradient anchorage, Michels et al. (2013)) or only at room temperature (RT), b) specimen age (3 or 28 days, see Figure 1, left), c) maximum temperature reached during the DMA test (T_{max} of 100 or 150°C), and d) heating rate (0.5 or 2°C/min).

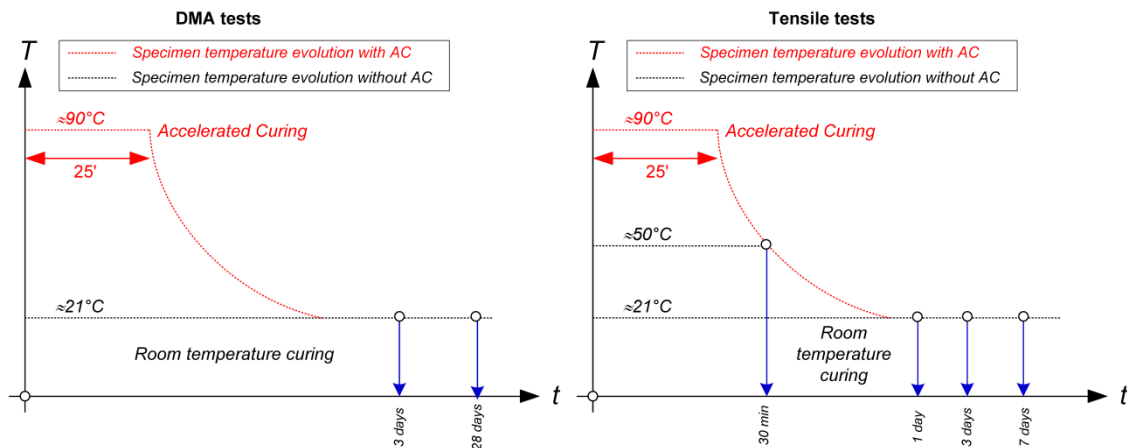


Figure 1 Curing configurations (Epoxy temperature T vs. time t) for the DMA tests (left) and tensile tests (right)

2.2.2 Test Setup (DMA)

The three-point bending test setup and the complete testing installation are shown in Figure 2. Specimens had the dimensions of $45 \times 5 \times 3 \text{ mm}^3$ with a span length of 40 mm. Testing involved the application of an oscillatory strain over a temperature range (T_{min} to T_{max}). Loading frequency was 1 Hz. Liquid nitrogen was used to cool the inner chamber part for temperatures below zero. Apart from one test in the end, which was conducted with a heating velocity of 0.5°C/min, all tests were performed with a ramp of 2°C/min.

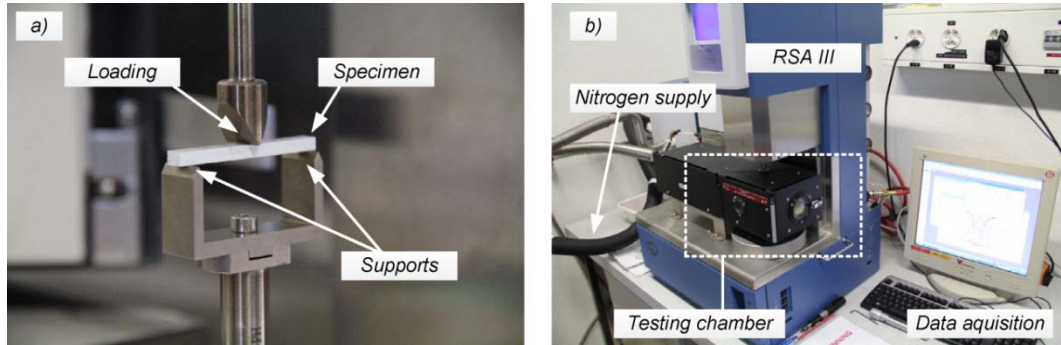


Figure 2 Three-point bending test setup for DMA analysis (left), and complete testing installation (Type 'RSA III' by TA Instruments)

2.3 Tensile tests

2.3.1 Curing configurations

Curing configurations are presented in Figure 1 (right). A first group of specimens was cured at constant room temperature, a second one was initially cured under high temperature for 25 minutes followed by a cooling phase and an additional curing period at room temperature. Testing ages were the following: a) 30 minutes (specimens tested very shortly after the accelerated curing process), b) 1 day, c) 3 days, and d) 7 days. Additionally, epoxy mixing under vacuum was performed for two test series, one with and one without an initial accelerated curing. A photo of the mixing device is given in Figure 3.

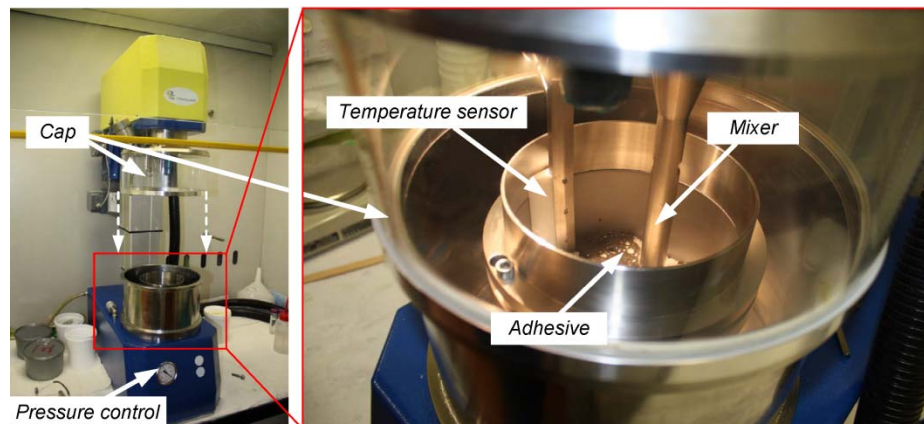


Figure 3 Vacuum mixing device

2.3.2 Test setup

The ISO527-2:1993(E) was followed in order to evaluate the tensile properties of the epoxy specimens (Figure 4). The dogbone specimens were tested under controlled displacement at a velocity of 1 mm/min in a servo-controlled machine. A 50 mm-clip gauge was used in the central part of the specimens to assess the strain and hence evaluate the elastic modulus. A digital caliper was used to measure the specimen's thickness and width in the center as well as

in two locations 25 mm apart at each side. The average values were subsequently taken to define a mean cross-section ($A_{avg}=(A_1+A_2+A_3)/3$) in order to derive the tensile stress values. A photo of the test setup is shown in Figure 5.

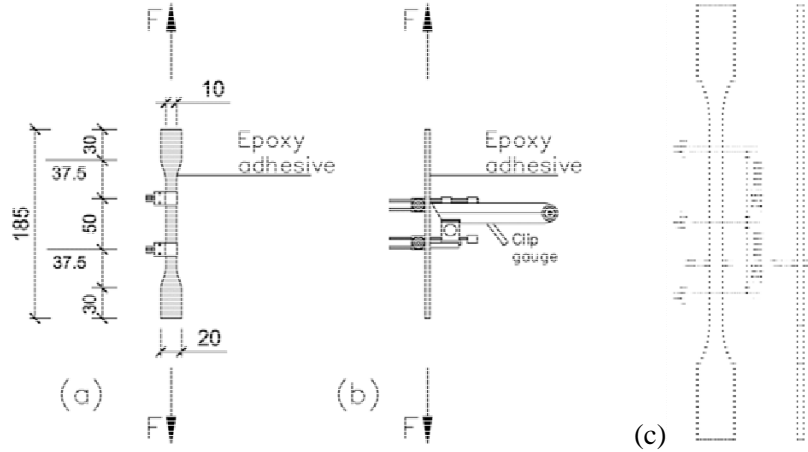


Figure 4 Test configuration according to the ISO527-2:1993 standard (a,b) and cross-section definition (c)

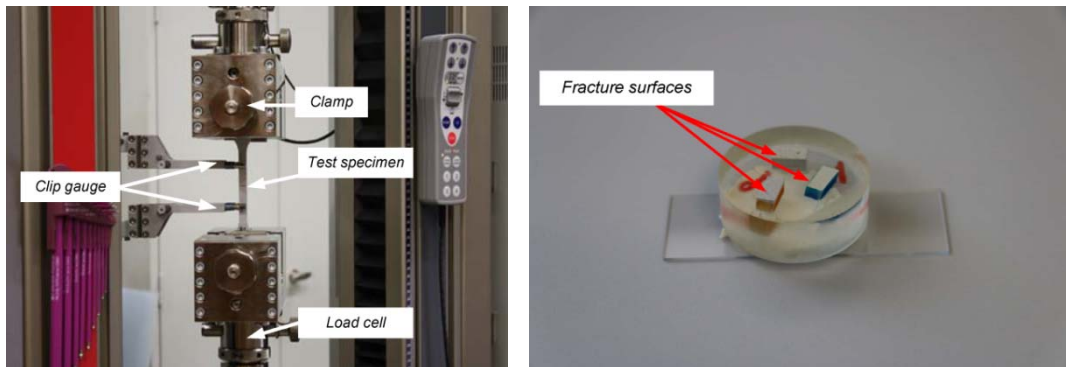


Figure 5 Test setup for the tensile test (left), and microscope specimens for the porosity analysis (right)

In Figure 5 (right), an example of a microscope sample is shown. After the tensile tests, these samples were used to investigate more closely the fracture surfaces under the microscope.

3 RESULTS

3.1 Glass transition temperature

In this paper, glass transition temperature T_g is evaluated with the maximum value of the loss factor $\tan(\delta)$, which itself is defined by the ratio between the loss modulus E'' and the storage modulus E' and hence varies over the applied total temperature range. It is noteworthy to mention that the glass transition is a thermochemical reaction over a certain temperature range, and the definition of a precise glass transition temperature is a simplification for characterization purpose. It is referred to Michels et al. (2015), where it is shown that the chosen results evaluation method has a strong influence on the eventually obtained value. Results of the present campaign are shown in Figure 6 to Figure 8 (Michels et al. (2015)). Figure 6 (left) presents the chosen temperature evolutions during the tests. Firstly, two different maximum temperatures T_{max} of 100 and 150°C as well as two different ramps of 0.5 and 2°C/min were

investigated. Secondly, every DMA test was run in two steps with an increasing and a decreasing branch. This implicates that for each specimen, two values for the glass transition temperature are obtained, one for the initial stiffness decreasing on the rising temperature branch and one for the re-setting with decreasing temperatures.

Figure 6 (right) shows that growing age results in a higher glass transition temperature. For the investigated case, an initial value of 53.1°C is increased by approximately 14°C after 28 days, indicating that cross-linking of the polymer chains at room temperature takes place over a time span longer than 3 days. In practical applications, an initial curing time of 1 to 3 days is often considered necessary to properly use the adhesive properties regarding load transfer. Both tests show very similar results on the decreasing branch. For both specimen ages, these values are clearly higher than the ones on the increasing temperature branch. When surpassing the glass-transition range during the DMA test, cross-linking is further improved and hence higher values for T_g are obtained. Hence, if a post-curing of the epoxy resin once put in place is possible, it leads to an improved behavior regarding elevated temperature exposure.

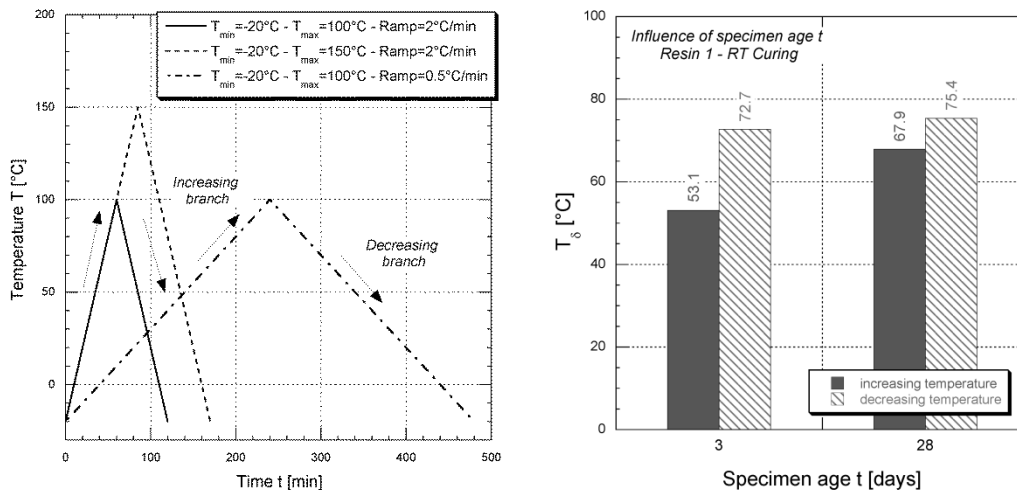


Figure 6 Heating ramps during the DMA testing (left), and influence of the specimen age t on T_g (right)

In Figure 7, the influence of the initial curing condition on T_g is presented for two different resins with different curing procedures. In both cases, the initial accelerated curing (AC) during 25 minutes implicates higher values for T_g compared to the specimens fully cured at room temperature (RT). The previously presented effect of higher glass transition values on the decreasing temperature slope is also confirmed in this case. The effect is a bit less pronounced for the AC specimens compared to the RT specimens ($\Delta T_2 < \Delta T_1$).

Figure 8 presents both the effect of the chosen maximum temperature during the DMA test and the slope of the heating ramp on the glass transition. As expected, the maximum temperature T_{max} does not influence the obtained values on the increasing temperature branch, since glass transition occurs at lower values. Regarding the decreasing temperature branch, however, 150°C as maximum temperature (compared to 100°C) induces higher values for T_g . This is due to a further extended cross-linking due to the increased temperature. The investigated case for Resin 1 regarding the slope of the heating ramp shows that a slower heating velocity (0.5°C/min) implicated higher values for T_g compared to a faster heating at 2°C/min. This

observation is contrary to information found in the literature, Jankowsky et al. (1994). However, the cited references cover a broader temperature range with mostly higher values. In this case, further testing with several specimens per category is mandatory.

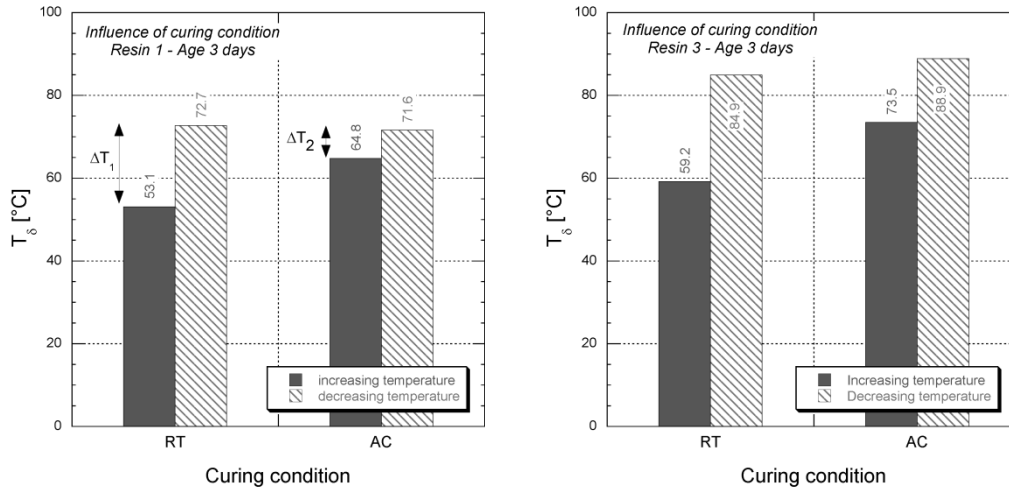


Figure 7 Influence of the curing conditions (AC or RT) on T_g for Resin 1 and 3

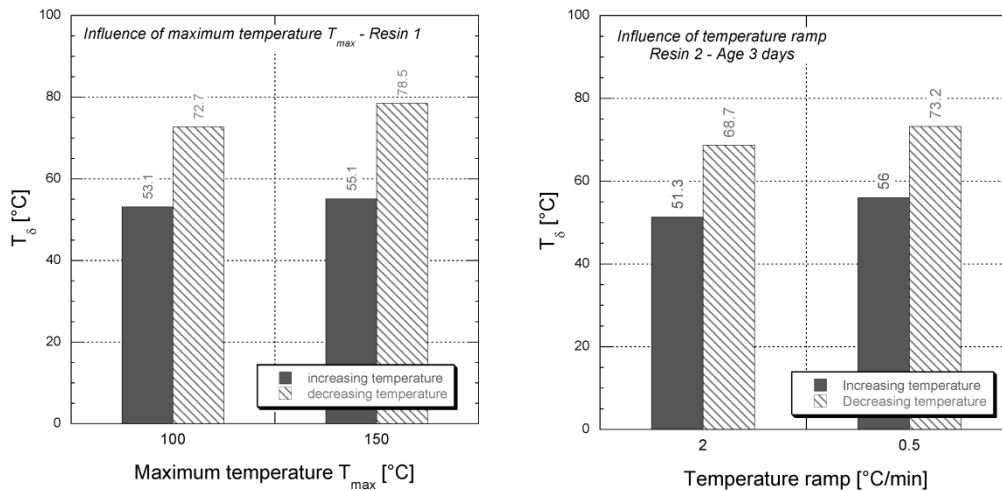


Figure 8 Influence of the maximum temperature T_{max} (left) and of the temperature ramp (right) on T_g for Resin 1 and 2

3.2 Tensile tests

The nominal tensile strength $f_{a,u}$ is defined by the maximum force at failure F_u divided by the previously mentioned average cross section A_{avg} . The elastic modulus $E_{a,m}$ was defined by using nominal stresses and the measured strains according to the ISO527-2:1993(E) standard. Both the strength and elastic modulus $E_{a,m}$ as a function of the curing time are presented in Figure 9.

A first observation is the fact that the specimens with an initial accelerated curing at high temperatures are able to develop their strength and stiffness already at a very young age. In the present case, one series of specimens was tested approximately at $t=30$ minutes after the end of the accelerated curing process. At that moment, a tensile strength of about 12 MPa and an

elastic modulus of 5 MPa could already be observed. Regarding the strength, a slight increase in time towards a limit value can be noticed. The elastic modulus also slightly increases. Due to the scatter, further tests have to be performed. Specimens cured at room temperature exhibit noticeable strength after 1 day, being higher than the maximum that can be reached with an accelerated curing. However, the elastic modulus after 1 day remains inferior to the former AC specimens. Only after 3 days, the RT specimens are stiffer compared to the AC ones. Both curing configurations eventually lead to an upper limit plateau, also observed by Moussa et al. (2012). Interesting information is obtained for the specimens where the epoxy resin has been mixed under vacuum. In both cases, whether an initial accelerated curing has been performed or not, the nominal measured strength and stiffness values are clearly above the ones with mixing at air.

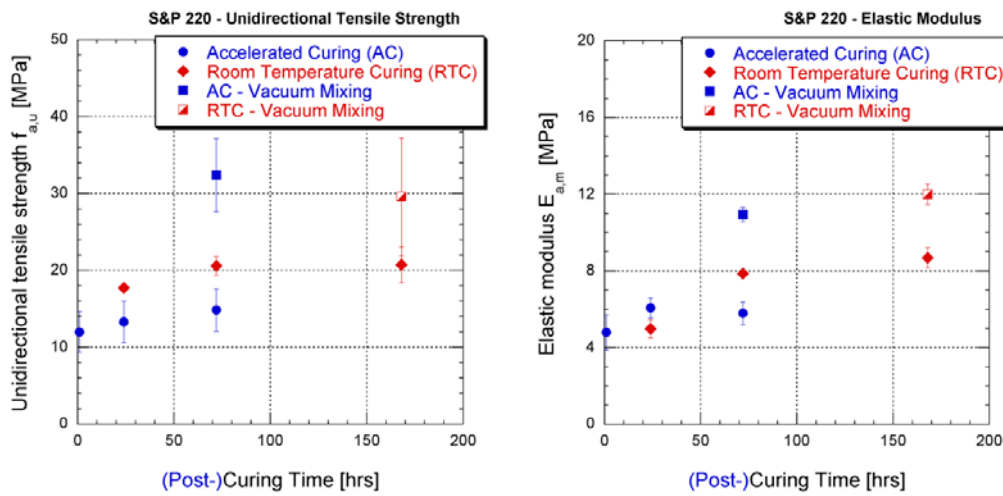


Figure 9 Tensile strength f_{au} (left) and elastic modulus E_{am} (right) depending on the curing time at room temperature for Resin 1 (S&P Resin 220)

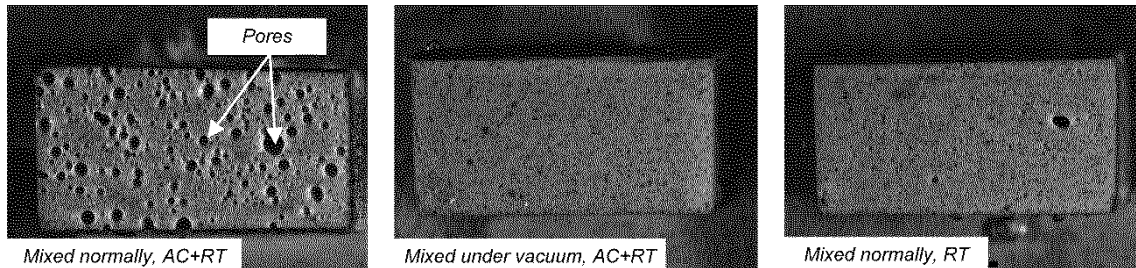


Figure 10 Microscope photos of the failure cross-sections for Resin 1 tested at three days after different curing and/or mixing configurations

Figure 10 shows microscope photos of three different mixing and curing configurations. It arises that for epoxy mixing at air, porosity of the material is drastically increased when an initial accelerated curing under elevated temperature is performed (comparison between Figure 10 left and right). This might be due to a certain amount of air inclusion and subsequent expansion and well as various components of the resin that might try to evaporate at high temperature. However, when a mixing under vacuum is performed, as shown in the photo in the middle, porosity is almost reduced to zero. Such a mixing procedure might represent an interesting technique in order to avoid high porosity and subsequent durability issues. The observed

porosity and the related reduced cross-sections are one of the reasons why lower strength values are observed for specimens with an accelerated curing procedure and without mixing under vacuum.

4 CONCLUSIONS

Several conclusions can be drawn from the presented investigation, mainly:

- The glass transition temperature is depending on the specimens' age. Especially at early age, the obtained values are lower than at a more progressed age at for instance 28 days.
- Post-curing of the partly cured adhesive can induce higher values for the glass transition temperature. This can be helpful when a repaired construction might be exposed to elevated temperatures under service. Generally, the higher the temperature and exposure time for the post-curing, the better the subsequent glass transition values. One should however take care that the applied temperature for the post-curing stays within the limits for not provoking any damage to the surrounding substrate (e.g. microcracks in concrete).
- An initial accelerated curing at elevated temperatures with the purpose of a faster strength and stiffness development can have a positive effect on the glass transition temperature when comparing it to the values obtained with reference specimens at the same age. However, accelerated curing at high temperatures increases the porosity of the epoxy resin. This can be well observed by have a close look under the microscope at the fracture surfaces of specimens tested in tension. This has a direct influence on the nominal tensile strength, which decreased compared to epoxy resins conventionally cured at room temperature with the same age.
- Even if the mechanical performances of the epoxy resins with an increased porosity seem satisfying at short-term, durability issues due to an increased risk for instance water and chloride penetration might appear on the long-term.
- To summarize, a structural designer should carefully judge the exposure situation of the epoxy in service and should afterwards define precise parameters for both the curing and testing (epoxy age, temperature ramp, curing temperature, etc.) in order to obtain valuable information that well reflect the reality.

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