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A coupled thermal-analytical and mechanical approach to investigate the behavior of bonded anchors cured at sub-zero temperatures

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ABSTRACT

In post-installed connection in reinforced concrete structures, bonded anchors are commonly adopted when elevated mechanical performances are required. Such performances may be significantly impaired by adverse service conditions, above all temperature variations with respect to room ambient one. It is also generally acknowledged that the curing temperature may impact on the anchor performances, to the extent that all the main existing qualification procedures assess the anchor behavior when cured at different temperatures, in particular below zero Celsius degree. However, among the few investigations focusing on the impact of a low curing temperature on the long term behavior of an anchor, a low effort exists in addressing the relationship between the anchor mechanical behavior and the thermal properties of the bonding agent. The paper proposes a coupled thermal-analytical and mechanical approach to detect potential critical issues in the long term mechanical behavior of the anchor as a function of the adhesive behavior, as investigated by thermal or thermo-mechanical analyses. To the scope, a wide investigation on two adhesives is carried out comprising MDSC, DMA, pull-out and sustained load tests. On the basis of the obtained results, it is concluded that some thresholds in the variations of degree of conversion and phase transition temperatures may indicate a negligible impact of a low curing temperature on the anchor mechanical behavior, but also that existing qualification procedures are not able to capture the anchor behavior, when cured at low temperatures and subjected, during its service life, to temperatures higher than room ambient one.

1. Introduction

In cold regions, it is crucial to have the chance of creating a post-installed connection in reinforced concrete structures by adopting a bonding agent even when the curing temperatures are below zero Celsius degree, typically acknowledged as the threshold for so-called ‘low installation temperatures’.

Up to few years ago, existing qualification procedures in Europe [1] and US [2] accounted for such possibility on the basis of a simple pull-out test where the mortar was cured in a concrete member kept at a specific target temperature. In case the test results (in terms of capacity) would not indicate a significant deviation with respect to the behavior at room ambient temperature, the specific bonding agent was considered as suitable to be installed at the investigated temperature.

Lately, several investigations pointed out how the impact of curing at low temperatures on the final behavior of a bonded anchor could not be captured solely and entirely be a mechanical pull-out test.

Given for granted that the glass transition temperature of a bonding agent T_g can be seen as a property of a given bonding agent (but not discussing, as for moment, the relationship between the mechanical properties of the cured agent at a given temperature with a specific value of T_g), it is interesting to report that Alig et al. [3] and Barrere et al. [4] put in evidence how, for epoxy resins, the T_g for a fully cured agent is limited in an isothermal reaction and it may exceeds the value of temperature at which curing occurred only by a constant value ΔT.

In fact, the glass transition temperature is dependent on both curing temperature and time, which can be described in a Time-Temperature-Transformation (TTT) diagram [5,6]. Each polymer matrix system has an “ideal” glass transition temperature, $T_{G,\infty}$, corresponding to the complete conversion of reaction, which occurs when T_g tends to $T_{g,\infty}$; the so-called “post curing effect”. Glass transition temperature can also be understood in term of free volume theory [7]: if curing temperature is below T_g, the polymer has no free volume to allow chains movements, which corresponds to a so-called “vitrous” state. Curing can be further completed by time (diffusion) or kicked by increasing temperature over T_g, thus allowing to increase chains mobility, and consequently increase reaction conversion. Depending on the sample

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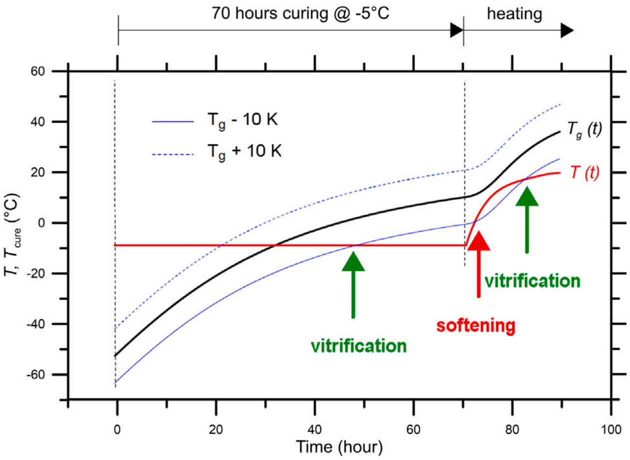

Fig. 1. Time evolution of the glass transition temperature of a thermosetting adhesive cured at low temperatures and then heated up to room ambient temperature.
Source: Reproduced after [3].

curing history [8,9], the effect of post-curing can be predominant versus temperature softening, or vice versa.

Alig et al. [3] also pointed out that, when the curing temperature T_C evolves through time (as it could happen in reinforced concrete structures subjected to night/day temperature variations), there is a sort of 'competition' between the effect of increasing the degree of curing and the softening due to a T_C higher than T_g.

Fig. 1 reports the time evolution of a glass transition temperature $T_g(t)$ of a thermosetting adhesive with a scatter band of ± 10 K, which may account for uncertainties in the adhesive behavior. It is shown how vitrification is observed as long as $T_g(t)$ is higher than curing temperature $T(t)$. However, if during an heating process the increase in curing temperature is more rapid than the corresponding increase in the glass transition temperature, softening may be induced.

Should the bonding agent be able to 'complete' its curing process, a second vitrification occurs till reaching the final level of conversion. However, when dealing with bonded anchors, the issue consists in that temperature increase may occur while the system is loaded, should one assume the initial curing time (e.g. 70 h in Fig. 1) is the one for which the anchor can be loaded.

Such result represents the main reasons for having introduced in ICC-ES AC308 [10] a specific test procedure where a sustained load is applied prior to a temperature increase from the value at which curing is carried out till normal ambient temperature. Stabilization of displacement during an observation time period after having reached room temperature is the main criterion to consider the product as "suitable" to be installed at low temperatures. Such test method can be labeled as 'low-temperature sustained test'.

The test, which was later introduced also in Europe (EAD 330499 [11]), is characterized by several parameters, whose background is synthetically reported hereinafter:

- 5 K/hour as heating rate: such rate is based on Alig et al. [3] on the basis of an estimation of heating rate in a concrete member exposed to solar radiation;
- 150 h as test duration at room ambient temperature (observation time period): some background is available in Fuchs et al. [12]; by comparing results obtained for two specific epoxy-based and vinylester-based adhesives for different times, it was found that 150 h was sufficient to expect stabilization of displacements.

The following criticism can be detected. As first, none of the investigation which claim that the simple pull-out test is not sufficient to verify suitability of anchors to be installed at low temperatures reports a case where results of pull-out tests indicate suitability but the anchor failed in a low-temperature sustained test. Additionally, it is not clear why one should expect stabilization (or not) during a 150 h time window when, when checking the creep behavior at normal ambient temperature (ACI 355 [13], EAD 330499 [11]), the standard test duration is 2000 h.

Consequently, the following research questions arise:

- is the low-temperature sustained test appropriate to determine the suitability of an adhesive anchor to be installed at low-temperatures? Or, in other words, can all the relevant information be extracted from such test?
- Is it possible to establish a correlation between the anchor mechanical behavior and chemo-physical properties of the bonding agent (as glass transition temperature or degree of curing)?
- Should the answer to previous question be positive, should or can we ignore such information, in alternative or in combination with the information obtained from mechanical tests?

The research programme presented in this paper aims to address such questions.

2. Methodological approach

Carrying out a mechanical test, as the low-temperature sustained one, has the scope of directly testing a system in its final configuration, i.e. a structure, under conditions which intend to be representative of the action that structure will face during its service life. In line of principle, no specific knowledge regarding the single elements which contribute to load transfer could be required once the overall testing conditions are sufficiently representative of real application scenarios.

However, typically, preliminary evaluations on the properties of the bonding agent are carried out, as the cited glass transition temperature T_g and degree of curing (DoC). Even in absence of a mechanical model correlating such properties to the behavior of an adhesive anchor under a tensile loading, it is asked if a change in both T_g and DoC can be coupled with information coming from mechanical tests and if the two sets of information are complementary or mutually exchangeable.

Table 1 reports the complete test programme, which aims to investigate, for different curing temperatures and curing times:

- two different classes of product: epoxy (Product #1) and vinyl ester (Product #2);
- the degree of curing (DoC) through (Modulated) Differential Scanning Calorimetry (DSC) ;
- the glass transition temperature (T_g) through Dynamic Mechanical Analysis (DMA) and – when reliable – also through DSC;
- the short term pull-out behavior of an anchor — test codes labeled according to EAD 330499 [11] as A1 (ambient temperature) or B4 (low temperature);
- the pull-out behavior of an anchor subject to a constant load and to a raising temperature regime — test codes labeled according to EAD 330499 [11] as B20, also accounting for a different target temperature (B20M).

Details of the testing methods and background for the selection of testing parameters will be provided in the following section.

3. Materials and methods

3.1. Materials

The adhesives used in this study are two-components thermoset resins with different curing properties listed in Table 2 (for both products the minimum storage temperature is equal to −5 °C). Product 1 is a pure epoxy-amine reacting by poly-addition, while Product 2 is a vinyl-ester reacting by radical polymerization initiated by dibenzoyl peroxide.

Table 1
Test programme.

Product	Test	Storage (°C)	Cure temp. (°C)	Curing time (hh:mm:ss)	Total per series
#1	DSC	20	20	0:00:00	3
#1	DSC	20	20	7:00:00	2
#1	DSC	20	20	24:00:00	3
#1	DSC	5	5	24:00:00	2
#1	DSC	5	0	48:00:00	3
#1	DSC	5	−5	168:00:00	3
#1	DMA	20	20	7:00:00	2
#1	DMA	20	20	24:00:00	2
#1	DMA	5	5	24:00:00	2
#1	DMA	5	0	48:00:00	2
#1	DMA	5	−5	168:00:00	3
#1	A1	20	20	7:00:00	3
#1	B4	5	−5	168:00:00	2
#1	B20	5	−5	168:00:00	2
#1	B20M	5	−5	168:00:00	2
#2	DSC	20	20	0:00:00	3
#2	DSC	20	20	01:00:00	3
#2	DSC	20	20	24:00:00	4
#2	DSC	5	0	4:00:00	3
#2	DSC	5	−5	24:00:00	3
#2	DSC	5	−10	24:00:00	2
#2	DMA	20	20	01:00:00	2
#2	DMA	20	20	24:00:00	2
#2	DMA	5	0	4:00:00	2
#2	DMA	5	−5	24:00:00	2
#2	DMA	5	−10	24:00:00	2
#2	A1	20	20	1:00:00	3
#2	B4	5	−10	24:00:00	3
#2	B20	5	−10	24:00:00	2
#2	B20M	5	−10	24:00:00	2

Table 2
Materials curing temperatures and curing times.

Product 1		Product 2	
Curing temperature	Curing times	Curing temperature	Curing times
		−10 °C to −5 °C	24 h
−5 °C to −1 °C	168 h	−4 °C to 0 °C	240 min
0 °C to 4 °C	48 h	1 °C to 5 °C	120 min
5 °C to 9 °C	24 h	6 °C to 10 °C	90 min
10 °C to 14 °C	16 h	11 °C to 20 °C	60 min
15 °C to 19 °C	12 h		
20 °C to 24 °C	7 h	21 °C to 30 °C	45 min
25 °C to 29 °C	6 h		
30 °C to 34 °C	5 h		
35 °C to 39 °C	4.5 h	31 °C to 40 °C	30 min
40 °C	4 h		

3.2. Modulated Differential Scanning Calorimeter (MDSC)

Differential Scanning Calorimetry (DSC) is the most frequent thermal analysis technique [14] used to measure enthalpy changes due to physical and chemical properties changes of a material as a function of temperature or time. The technique is based on the measurement of energy necessary to maintain a null temperature difference between an analyzed sample and the reference. If the sample absorbs some amount of heat during phase transition, the reaction is said endothermic, while exothermic reactions generate heat during phase transition.

The equipment used to carry out the program is a MDSC (Modulated Differential Scanning Calorimeter), working on heat-flux principle. The equipment is the MDSC Q20 model from TA Instruments, range -40 °C to 450 °C.

Unlike the standard mode, modulated mode (as described in [15–17]) allows to separate thermodynamic events (glass transition temperature T_g, for instance) from kinetic events (polymerization reaction enthalpy, for instance). When T_g is located in the area of the peak, it is not possible to measure it; in that case, switching to modulated mode is useful as it allows to separate and distinguish phenomena which are dependent on temperature from events which are not dependent on temperature.

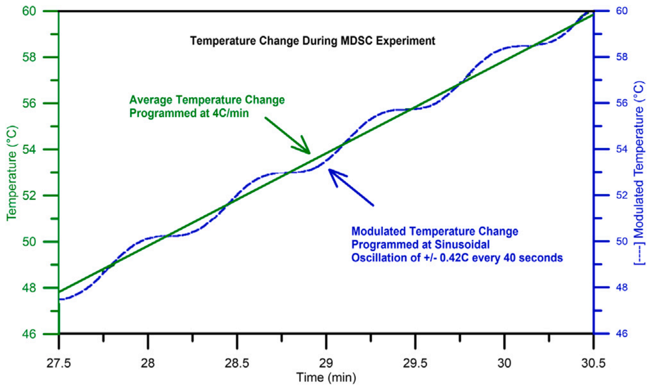

Fig. 2. Typical temperature profile from a MDSC experiment.
Source: Reproduced after [16].

Modulated Temperature Differential Scanning Calorimetry (MTDSC) is a family of techniques where a temperature modulation is overlaid on a linear heating (or cooling ramp) resulting in a modulated heat flow [18]. The operating principle of MDSC differs from standard DSC in that MDSC uses two simultaneous heating rates - a linear heating rate that provides information similar to standard DSC, and a sinusoidal or modulated heating rate that permits the simultaneous measurement of the sample's heat capacity. Creation of the sinusoidal temperature change requires the operator to select a modulation period (seconds) and modulation temperature amplitude.

Fig. 2 shows a typical temperature profile from an MDSC experiment. MDSC allows the separation of overlapping thermal events. In general, use of MDSC allows the separation of reversing and non-reversing effects from the total heat flow. The total heat flow is the sum of all the thermal events and similar to the heat flow seen in conventional DSC. The reversing heat flow encompasses thermal events that respond to changes in the ramp rate. Events that are reversing are heat capacity and glass transition. Conversely, those events that do not follow the modulation in the ramp rate will go into the non-reversing heat flow. For thermosets these are the cure exotherm and the enthalpy relaxation endotherm [16,18,19].

Provided sample preparation is conducted in a repeatable manner as described in Section 3.2.1 (as for mass, protocol, curing temperature and time, storage temperature, sample picking), measurement of enthalpy is reliable and provides accurate information on the degree of conversion of the reaction [20].

3.2.1. MDSC test procedure

DSC specimens are taken from resin/hardener mixture extruded from cartridge through mixing nozzle. First extruded centimeters of product are discarded, in order to have an optimal ratio between resin and hardener. For any specific target temperature, specimen are picked at a specific curing time, as reported in Table 2. Sample were previously stored at 20 °C for 12 h or 5 °C for 12 h for curing temperatures higher or lower/equal than 5 °C, respectively. Sample mass is equal to 15 +/− 1 mg. Aluminum non-hermetic pans are used to allow volatile substances to escape during the heating ramp. Pans and samples are weighed on an auto-calibrated scale, with sensitivity 0.01 mg. Repetition is made at least on 3 different samples produced from the same cartridge. The time elapsed from sample preparation to beginning of test is not more than 3 min.

The equipment is preliminary calibrated according to manufacturer instructions. The testing procedure consists in:

- equilibrate temperature to −40.00 °C;
- modulate temperature 1.00 °C for 60.0 s;

Fig. 3. Confined test setup for sustained load tests — global view in the climatic chamber.

- start isothermal for 5.0 mins;
- start ramp at 3 °C/min up to 250.00 °C;
- mark End of Cycle;
- jump to 20.00 °C;
- equilibrate at 20.00 °C;
- mark End of Cycle.

3.3. Differential Mechanical Analysis (DMA)

The Dynamic Mechanical Analysis (DMA) technique is based on a rather simple principle: when a sample is submitted to a sinusoidal oscillating stress, its response is a sinusoidal oscillation with similar frequency provided the material stays within its elastic limits. When the material responds to the applied oscillating stress perfectly elastically, the responding strain wave is in-phase (storage or elastic response), while a viscous material responds with an out-of-phase strain wave (loss or a viscous response).

For a Newtonian liquid the phase angle will be 90 degrees and for Hookean solid it will be 0 degrees, whereas the phase angle of viscoelastic material falls in between these two extremes. The storage modulus G' measures the elastic component while the loss modulus G'' measures the viscous component of the material. Tangent delta ($tan\delta$) is the ratio G''/G'.

The equipment used to carry out the program is a rheometer form Anton Paar, MCR301, equipped with a DMA device and convection temperature device CTD 180, range -20 °C to 180 °C.

Even though various glass transition temperature determination methods are available [21–23], preliminary comparative studies conducted according to ASTM [24] or ISO [25] standards on both products confirmed alignment to literature data; the most appropriate thermal technique is, by far, DMA and the most accurate method [26,27] to evaluate T_g for chemical anchors is based on maximum of $tan\delta$ curve, characteristic of first order transition or α-transition T_α. Consequently, in this study, T_g is associated to the peak of $tan\delta$ curves (T_α).

3.3.1. DMA test procedure

DMA test specimens are prepared with a dedicated Teflon rectangular-shaped mold which dimensions are (50 mm)x(10 mm)x(3 mm). First extruded centimeters of product are discarded, in order to have optimal ratio between resin and hardener. Specimens are prepared according to storage and curing conditions as defined in Table 2. Time elapsed from sample preparation to start of test is about 10 min, because the apparatus has first to drop to the initial temperature of test, equal -5 °C first. This is achieved by a water refrigerated system.

The equipment is preliminary calibrated according to manufacturer instructions. The testing procedure consists in:

- clamp the sample vertically;
- set oscillation at 0.01%, constant profile.
- set frequency at 1 Hz, constant profile;
- start temperature ramp from −10 °C to 190 °C at 2.6 °C/min.

T_g is the value read at max $tan\delta$ curve. In the case of multiple peaks, the T_g has to be related to peak characteristic of α transition, as described in Pascault et al. [28]. First order or α-transition can be indeed considered, as previously discussed, as the glass transition temperature of the thermoset material, which is the transition from glassy state to liquid state. Verification can be performed by second DMA-scan: if this second peak remains, it means that the transition is reversible, typically as T_g transition is. A drastic softening of the material is observed after T_g.

3.4. Mechanical tests

Mechanical tests were carried out according to the procedures described in EAD 330499 [11] for:

- confined pull-out tests at room ambient temperature and standard curing time (A1 code);
- confined pull-out tests at minimum curing temperature and minimum curing time (B4 code);
- sustained loading testing starting from minimum curing temperature at minimum curing time (B20 code).

For all the tests, M12 anchors were considered embedded 72 mm or 84 mm for Product 1 and 2, respectively. The embedment depth was selected through preliminary tests as the minimum one to prevent steel failure. All the bars were in 10.9 carbon steel. For A1 and B4 tests, the reaction frame was equipped with a 100 kN capacity hydraulic jack, the applied load was monitored by a 100 kN load cell, while anchor displacements were monitored at both sides of each anchor by 50 mm LVDTs. The test was displacement controlled at a rate such to achieve failure within 1 to 3 min from the starting of the test.

The B20 testing procedure accounts for the application of a sustained load after samples cured at the minimum curing time for the target curing temperature in a climatic chamber (Fig. 3). Successively, the temperature in the chamber is raised up to 20 °C during 96 h and stabilized for 150 h. Should the anchor not fail during the constant load portion of the test, a residual pull-out tests is carried out (with the same procedure adopted for A1 tests). The load applied to the anchor during the constant load portion was estimated according to EAD 330499 [11] on the basis of the results of previous qualification procedures. Such load was equal to 50.0 kN and 35.5 kN for Product 1 and 2, respectively. Temperature evolution within concrete was monitored through two thermocouples placed on an unloaded steel bar placed in the concrete in the proximity of the loaded anchors. Such bar was embedded approximately 70 mm and the thermocouples were installed at 10 mm (TC1) and 70 mm (TC2) from the concrete surface.

Authors also propose to carry out a modified sustained tests (B20M code), currently not accounted by qualification procedures, where – differently from standard B20 – the temperature is raised not up to room ambient one, but to the maximum long term temperature the products are actually qualified for (which is equal to 43 °C and 50 °C for Product 1 and 2, respectively). This is done assuming that, during its service life, the anchor cured at minimum ambient temperature can be subjected to a load and temperature regime which is captured by a sustained test at the maximum long term temperature. It is noticed that such combination is currently not accounted by existing qualification procedure, which separately assess (a) the effect of long term temperature by sustained loading and (b) the effects of minimum curing temperature by the described B20 test. In such framework, it is still assumed that the anchor cured at minimum temperature can, during its service life, be subjected to temperatures higher than ambient one. However, the effect of the ability of the anchor to sustain a load

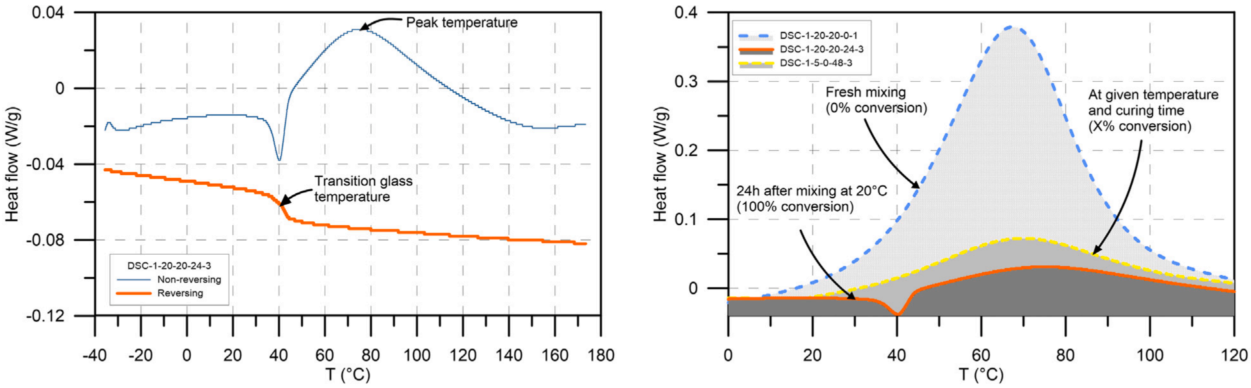

Fig. 4. Heat flow vs temperature curves from MDSC tests, typical curve showing reversing and non-reversing components (left) and comparison of non-reversing components for different curing time and temperatures.

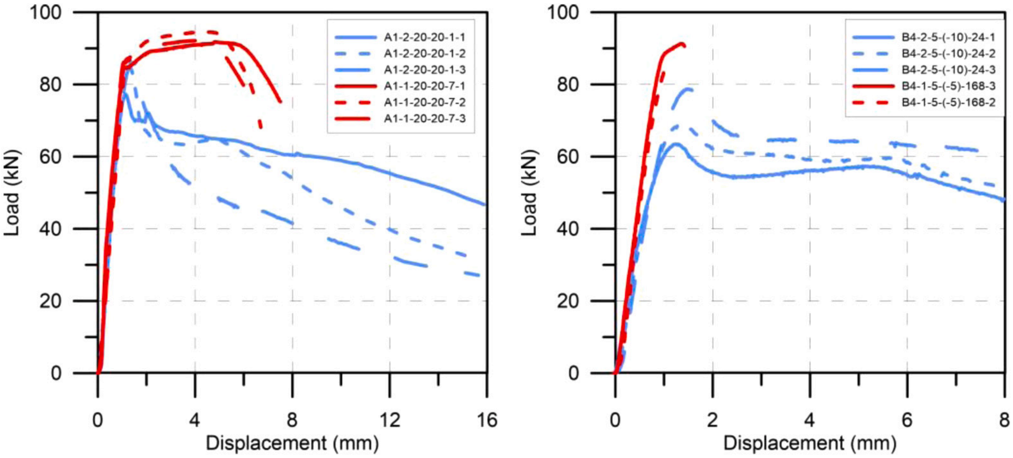

Fig. 5. Load vs displacement curves for tests at room ambient temperature (left) and at minimum curing temperature and curing time (right).

at 'high' temperatures when cured at 'low' temperature is not directly checked, which is the aim of the proposed modified sustained tests. The authors recognize that the applied temperature rise is quite steep and that, in most design cases, such significant temperature change may not occur in such short time. As a consequence, in such cases, curing of the product during the temperature rise phase may be different and more favorable with respect to the proposed testing procedure. However, acknowledging that, at least for epoxy resins, the T_g for a fully cured agent may exceeds the value of temperature at which curing occurred only by a constant value ΔT ([3], as previously discussed in the Introduction), such testing procedure may represent an upper bound for the estimation of the low temp curing/max temp service effect (see Fig. 3).

4. Test results

Tables 3 and 4 reports all the obtained test results for each testing procedure (DSC, DMA, A1, B4, B20, B20M), storage temperature, curing temperature and time in terms of reaction enthalpy (δH), peak temperature T_{peak}, first transition temperature (T_1); glass transition temperature (T_g), mean uniform bond stress (τ).

Test code is composed as [Test series]-[Product ID]-[Storage temperature]-[Curing temperature]-[Curing time]-[Repetition].

Fig. 4 reports some typical heat-flow vs temperature curves as obtained by testing. Peak temperature and an estimation of the glass transition temperature are shown with reference to the plots of non-reversive and reversive components, respectively.

The reversing heat flow encompasses thermal events that respond to changes in the ramp rate, for example heat capacity, glass transition, relaxation [18]. The non-reversing heat flow (NHF) is simply calculated from the difference between the total heat flow (THF) and the reversing heat flow (RHF).

Generally, a drop in the reversing component corresponding to the glass transition temperature can be hardly noticed for Product 2 (as typical in vinyl-ester agents). Similarly, for Product 1, as the curing temperature decreases, such processing showed to be less robust. Consequently, even if T_g values estimated by MDSC are reported for completeness, they will not be processed or discussed later.

Additionally, it is shown how different values of reaction enthalpy (the integral of the non-reversive component, [25]) are associated to different curing temperatures and times.

Fig. 5 reports all the load vs displacement curves for both tests at room ambient temperature and at minimum curing temperature (and minimum curing time).

At room ambient temperature both products show similar stiffness and a similar value of load at the loss of proportionality. After such load level, Product 2 shows a steep decay with a long descending branch, while Product 1 shows a pseudo-hardening behavior. Low temperatures have a negligible influence on the strength of Product 1, but induce a significantly more brittle post-peak behavior. As for Product 2, strength is affected by low temperatures, but not the ability of redistributing stresses, as evident by the still extended descending branch.

Figs. 6 and 7 report the displacement evolution in time for the sustained tests (one relevant curve for each product) and the relevant residual load vs displacement curves. It can be noticed how

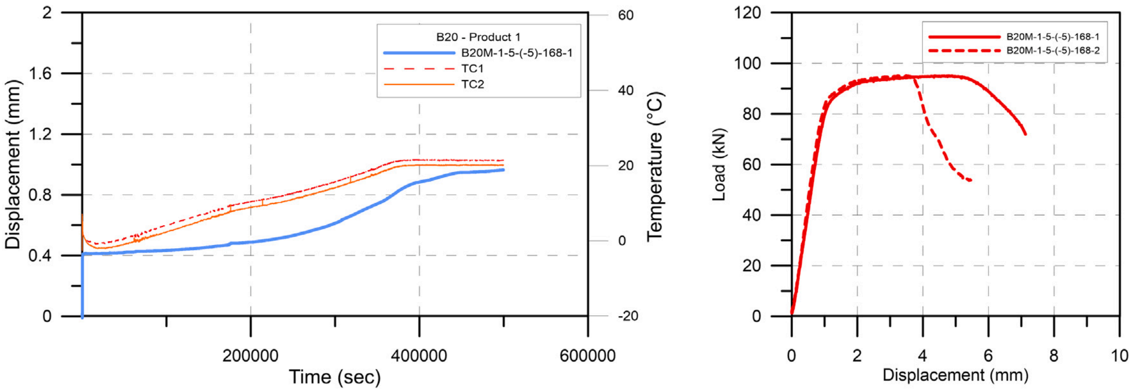

Fig. 6. Displacement and temperature vs time curves for B20 tests and corresponding load vs displacement curves for residual tests, Product 1.

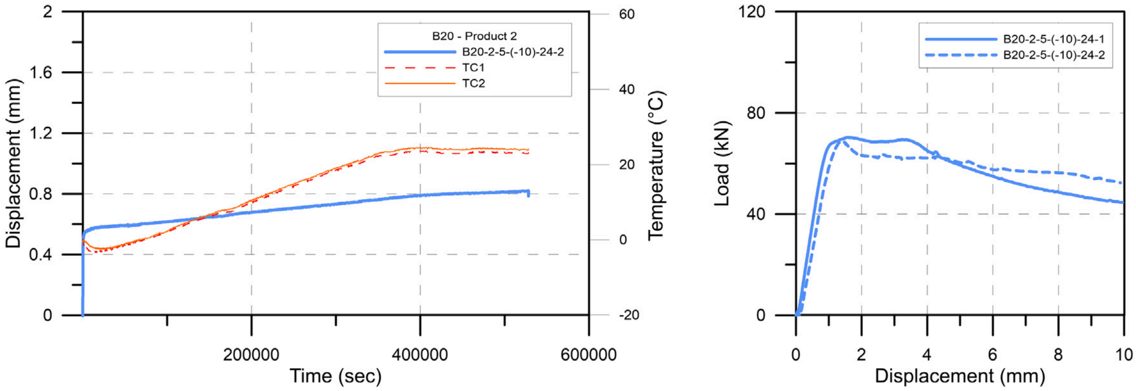

Fig. 7. Displacement and temperature vs time curves for B20 tests and corresponding load vs displacement curves for residual tests, Product 2.

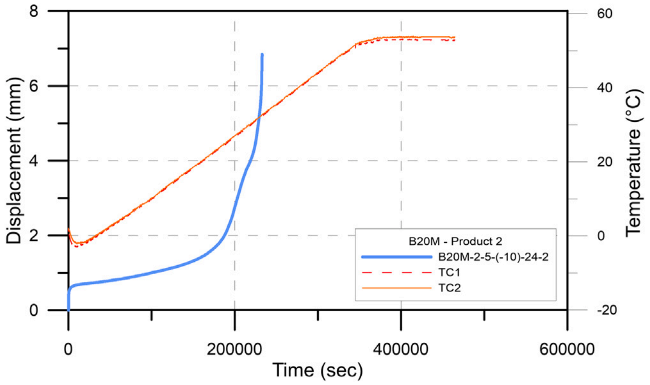

Fig. 8. Typical displacement and temperature vs time curve for B20M tests.

the temperature distribution along the embedment (as measured by the 'control' bar locations 'TC1' and 'TC2') was quite uniform and steadily evolved through time till the stabilization phase. After initial load application, displacements constantly increase tending, but not reaching, stabilization in the final phase.

As it can be noticed by test results no value of residual bond strength is reported in Tables 3 and 4, no anchor was able to pass the modified B20 testing regime, having failed during the constant load portion of the test. Fig. 8 reports an example of an evolution of displacement through time for such testing regime. It can be seen how, during the temperature increasing phase, an evident tertiary creep induces failure in the system.

5. Discussion

As first, data obtained from DMA and MDSC tests can be interpreted as follows.

5.1. Effect of curing temperature and time on glass transition temperature, as estimated by DMA

Figs. 9 and 10 report the evolution with temperature of the storage modulus and of the ratio between the loss and the storage moduli ($tan\delta$) for Product 1 and 2, respectively. For Product 1 the effects of curing at temperatures below 0 °C on the storage modulus is quite negligible; a significant increase is noticed when the product cures at room ambient temperatures. Looking at the evolution of $tan\delta$ a clear peak can be identified, which is associated to the glass transition temperature T_g. When the product cures below 0 °C, a significant reduction in T_g is detected.

Product 2, on the contrary, shows more significant differences in the storage modulus evolution for different curing temperatures. As for the $tan\delta$, two peaks can be observed. As previously discussed, the second peak is characteristic of α transition and, in the context of the current paper, is associated to the glass transition temperature (T_g).

After T_g, softening of the material is observed. At the contrary, first peak is characteristic of the system reactivity, increased by molecular relaxation (kicked by temperature). This phase transition is irreversible, as peak disappears at second DMA-scan. Over this phase transition, material does not soften, and G' storage modulus decreases only half a decade, while over T_g, material starts softening and G' modulus decreases 1.5 to 2 decades. We can ascribe this first peak of $tan\delta$ curve to monomers unreacted double bonds.

Consequently, looking at the second peak, associated to the glass transition temperature, there is a negligible effect of the minimum curing temperature.

Table 3
Test results, Product 1.

Code	Product	Test	Storage (°C)	Cure temp. (°C)	Curing time (hh:mm:ss)	Repetition	ΔH (J/g)	T_{peak} (°C)	T_1 (°C)	T_g (°C)	τ (MPa)
DSC-1-20-20-0-1	#1	DSC	20	20	0:00:00	1	378,8	67,5			
DSC-1-20-20-0-2	#1	DSC	20	20	0:00:00	2	333,1	65,6			
DSC-1-20-20-0-3	#1	DSC	20	20	0:00:00	3	368,3	66,4			
DCS-1-20-20-7-1	#1	DSC	20	20	7:00:00	1	53,7	74,5		31,6	
DCS-1-20-20-7-2	#1	DSC	20	20	7:00:00	2	56,3	76,5		30,1	
DSC-1-20-20-24-1	#1	DSC	20	20	24:00:00	1	34,3	79,3		43,6	
DSC-1-20-20-24-2	#1	DSC	20	20	24:00:00	2	56,3	74,4		41,8	
DSC-1-20-20-24-3	#1	DSC	20	20	24:00:00	3	51,5	75,5		41,7	
DSC-1-5-5-24-1	#1	DSC	5	5	24:00:00	1	70,5	63,9		19,8	
DSC-1-5-5-24-2	#1	DSC	5	5	24:00:00	2	79,1	64		19,8	
DSC-1-5-0-48-1	#1	DSC	5	0	48:00:00	1	86,8	66,3		16,0	
DSC-1-5-0-48-2	#1	DSC	5	0	48:00:00	2	92	70,7		13,1	
DSC-1-5-0-48-3	#1	DSC	5	0	48:00:00	3	99	69,8		14,5	
DSC-1-5-(−5)-48–1	#1	DSC	5	−5	168:00:00	1	110,5	68,9		16,2	
DSC-1-5-(−5)-48–2	#1	DSC	5	−5	168:00:00	2	64,3	67		16,4	
DSC-1-5-(−5)-48–3	#1	DSC	5	−5	168:00:00	3	85,8	71,5		21,0	
DMA-1-20-20-7-1	#1	DMA	20	20	7:00:00	1				43,6	
DMA-1-20-20-7-2	#1	DMA	20	20	7:00:00	2				43,6	
DMA-1-20-20-24-1	#1	DMA	20	20	24:00:00	1				50,1	
DMA-1-20-20-24-2	#1	DMA	20	20	24:00:00	2				50,1	
DMA-1-5-5-24-1	#1	DMA	5	5	24:00:00	1				33,3	
DMA-1-5-5-24-2	#1	DMA	5	5	24:00:00	2				32,0	
DMA-1-5-0-48-1	#1	DMA	5	0	48:00:00	1				30,7	
DMA-1-5-0-48-2	#1	DMA	5	0	48:00:00	2				30,1	
DMA-1-5-(−5)-168–1	#1	DMA	5	−5	168:00:00	1				30,1	
DMA-1-5-(−5)-168–2	#1	DMA	5	−5	168:00:00	2				30,7	
DMA-1-5-(−5)-168–3	#1	DMA	5	−5	168:00:00	3				32,6	
A1-1-20-20-7–1	#1	A1	20	20	7:00:00	1					33,2
A1-1-20-20-7–2	#1	A1	20	20	7:00:00	2					33,8
A1-1-20-20-7–3	#1	A1	20	20	7:00:00	3					33,7
B4-1-5-(−5)-168–1	#1	B4	5	−5	168:00:00	2					30,9
B4-1-5-(−5)-168–2	#1	B4	5	−5	168:00:00	3					33,7
B20-1-5-(−5)-168–2	#1	B20	5	−5	168:00:00	1					34,4
B20-1-5-(−5)-168–3	#1	B20	5	−5	168:00:00	2					34,6
B20M-1-5-(−5)-168–1	#1	B20M	5	−5	168:00:00	1					–
B20M-1-5-(−5)-168–2	#1	B20M	5	−5	168:00:00	2					–

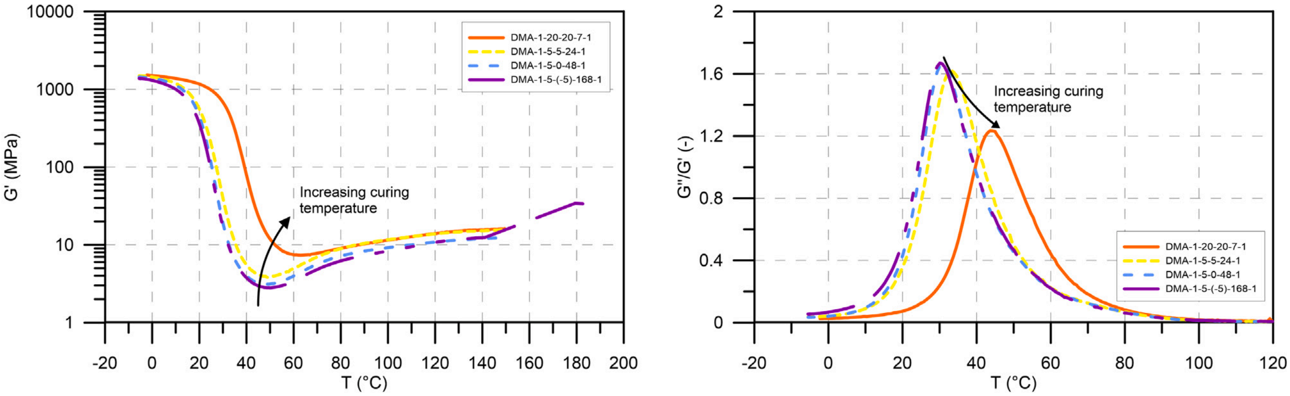

Fig. 9. DMA tests, evolution of storage modulus and ratio loss to storage moduli, Product 1.

5.2. *Estimation of degree of conversion from MDSC results*

An ideal thermoset net is hardly achievable in practice, being associated to a case where only when controlled conditions are applied, i.e. temperature raised over T_g and a speed rate allowing predominant effect of post-curing versus material softening. In this section, degree of conversion is estimated considering as reference conversion (100% conversion) the one at 20 °C for 24 h curing time. Thus, the conversion is calculated comparing the residual enthalpy $\Delta H_{t_{min},T}$ (for given curing temperature and time) with the enthalpy at the starting point of reaction ΔH_{tot} (right after mixing), both minored by reference residual enthalpy (at 20 °C for 24 h, $\Delta H_{24\ \mathrm{h},20\ ^\circ\mathrm{C}}$), as reported in Fig. 4, right.

Consequently, the degree of conversion χ may be evaluated according to Eq. (1)

$$\chi = 1 - (\Delta H_{t_{min},T} - \Delta H_{24\ \mathrm{h},20\ ^\circ\mathrm{C}})/(\Delta H_{tot} - \Delta H_{24\ \mathrm{h},20\ ^\circ\mathrm{C}}) \quad (1)$$

Regarding such definition of the degree of the conversion, the following may be noted:

- theoretically, a 100% converted material would show an ‘ideal’ net density, requiring perfect curing conditions in terms of time, speed of curing, temperature, level of moisture, etc. Some of these conditions could be artificially replicated by submitting the material to a second ramp of temperature up to temperature values exceeding 50 °C to 100 °C the glass transition value. However,

Table 4
Test results, Product 2.

Code	Product	Test	Storage (°C)	Cure temp. (°C)	Curing time (hh:mm:ss)	Repetition	ΔH (J/g)	T_{peak} (°C)	T_1 (°C)	T_g (°C)	τ (MPa)
DSC-2-20-20-0-1	#2	DSC	20	20	0:00:00	1	127,3	35,8			
DSC-2-20-20-0-2	#2	DSC	20	20	0:00:00	2	110,8	34,6			
DSC-2-20-20-0-3	#2	DSC	20	20	0:00:00	3	120,4	34,7			
DSC-2-20-20-1-1	#2	DSC	20	20	01:00:00	1	12,1	107,4			
DSC-2-20-20-1-2	#2	DSC	20	20	01:00:00	2	16,6	107,8			
DSC-2-20-20-1-3	#2	DSC	20	20	01:00:00	3	10,4	107,4			
DSC-2-20-20-24-1	#2	DSC	20	20	24:00:00	1	15,9	107,9			
DSC-2-20-20-24-2	#2	DSC	20	20	24:00:00	2	8,4	107,7			
DSC-2-20-20-24-3	#2	DSC	20	20	24:00:00	3	14,8	107,4			
DSC-2-20-20-24-4	#2	DSC	20	20	24:00:00	4	10,7	107,9			
DSC-2-5-0-4-1	#2	DSC	5	0	4:00:00	1	25,7	107,9			
DSC-2-5-0-4-2	#2	DSC	5	0	4:00:00	2	35	108			
DSC-2-5-0-4-3	#2	DSC	5	0	4:00:00	3	31,5	107,9			
DSC-2-5-(−5)-24–1	#2	DSC	5	−5	24:00:00	1	30,4	107,5			
DSC-2-5-(−5)-24–2	#2	DSC	5	−5	24:00:00	2	30,6	107,4			
DSC-2-5-(−5)-24–3	#2	DSC	5	−5	24:00:00	3	26,8	107,4			
DSC-2-5-(−10)-24–1	#2	DSC	5	−10	24:00:00	1	26,7	107,3			
DSC-2-5-(−10)-24–2	#2	DSC	5	−10	24:00:00	2	28,3	107,6			
DMA-2-20-20-1-1	#2	DMA	20	20	01:00:00	1			44,9	121,2	
DMA-2-20-20-1-2	#2	DMA	20	20	01:00:00	2			44,3	122,7	
DMA-2-20-20-24-1	#2	DMA	20	20	24:00:00	1				118,6	
DMA-2-20-20-24-2	#2	DMA	20	20	24:00:00	2				116	
DMA-2-5-0-4-1	#2	DMA	5	0	4:00:00	1			29,4	123,7	
DMA-2-5-0-4-2	#2	DMA	5	0	4:00:00	2			32,7	120,5	
DMA-2-5-(−5)-24–1	#2	DMA	5	−5	24:00:00	1			30,1	121,7	
DMA-2-5-(−5)-24–2	#2	DMA	5	−5	24:00:00	2			30	119,8	
DMA-2-5-(−10)-24–1	#2	DMA	5	−10	24:00:00	1			26,9	117,9	
DMA-2-5-(−10)-24–2	#2	DMA	5	−10	24:00:00	2			28,8	121,1	
A1-2-20-20-1–1	#2	A1	20	20	1:00:00	1					24,4
A1-2-20-20-1–2	#2	A1	20	20	1:00:00	2					26,8
A1-2-20-20-1–3	#2	A1	20	20	1:00:00	3					27,2
B4-2-5-(−10)-24–1	#2	B4	5	−10	24:00:00	1					20,1
B4-2-5-(−10)-24–2	#2	B4	5	−10	24:00:00	2					21,7
B4-2-5-(−10)-24–3	#2	B4	5	−10	24:00:00	3					24,4
B20-2-5-(−10)-24–1	#2	B20	5	−10	24:00:00	1					22
B20-2-5-(−10)-24–2	#2	B20	5	−10	24:00:00	2					21,7
B20M-2-5-(−10)-24–1	#2	B20M	5	−10	24:00:00	1					–
B20M-2-5-(−10)-24–2	#2	B20M	5	−10	24:00:00	2					–

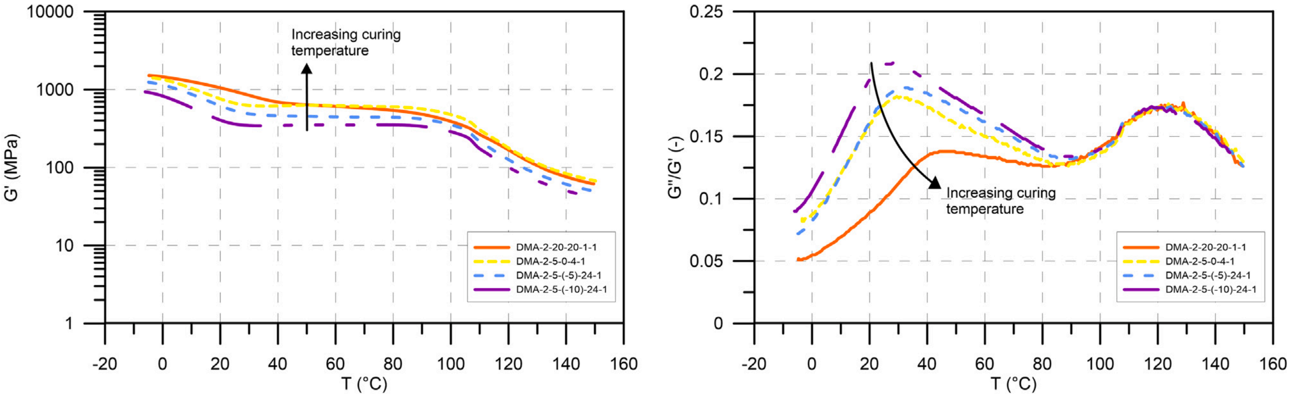

Fig. 10. DMA tests, evolution of storage modulus and damping factor (ratio loss to storage moduli), Product 2.

such conditions are hardly achievable neither in standard chemical anchors curing conditions nor when post-curing is applied in conditions defined by mechanical guides and, therefore, are not representative of the situation discussed in the current paper;

- literature [20,28] typically suggest as state reference 20 °C for 24 h curing. In the current study, no significant further development of adhesion after post curing was observed. Hence, such parameters were confirmed as reference ones;
- other conversion calculation methods could be adopted indeed. Authors compared various conversion calculation methods, and the chosen one showed up to be the most representative and accurate, considering at the same time mechanical testing rules, product specifications and behavior in practical conditions of use.

5.3. Comparative analysis of results from thermal analyses and mechanical tests

Initially, the information retrieved from MDSC testing in terms of degree of conversion and from DMA testing in terms of glass transition temperatures is compared. Fig. 11 reports, for both products, the variation in reaction enthalpy and glass transition temperature for all the investigated curing temperature. Additionally, for room ambient temperature, the enthalpy 'after mixing' (that is, when the two

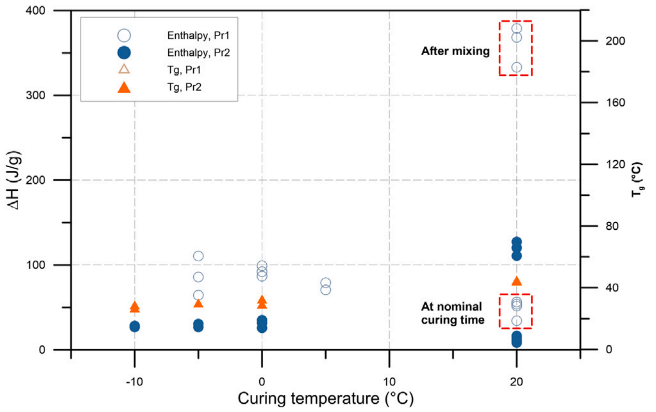

Fig. 11. Evolution of degree and conversion and glass transition temperature as a function of the curing temperature.

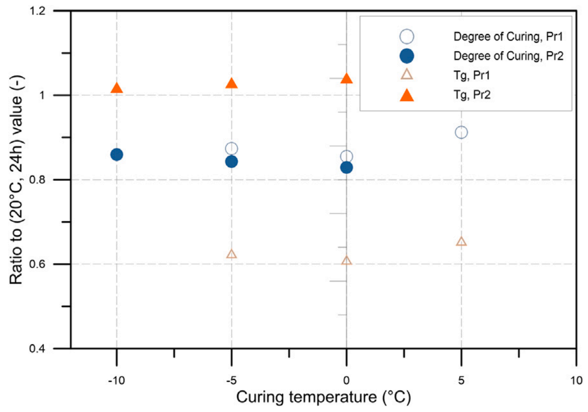

Fig. 12. Degree of conversion and glass transition temperature as a function of the curing temperature, ratios with respect to values at room ambient temperature at 24 h curing time.

components of the bonding agent are mixed) is also plotted such to provide to the reader the order of magnitude in the difference in the reaction enthalpies between the initial one and at nominal curing time (as declared by the manufacturers and reported in Table 2). For Product 1 a higher residual enthalpy and a lower glass transition temperature are detected for low values of curing temperature, while for Product 2 only T_g seems not affected by variation in curing temperatures.

Such trend is more evident if both the degree of curing, evaluated according to Eq. (1), and the glass transition temperature are plotted in terms of relative values with respect to the ones for 'maximum conversion' (20 °C for 24 h), as in Fig. 12.

A clear 'drop down' in χ is detected for both products; additionally, for Product 1, T_g is around 60% of the one associated to the full cured status. By comparing such findings with the results of mechanical tests, we observe that χ and T_g tend to correlate mechanical performance for curing condition at minimum curing temperature. For Product 1, for which no reduction after pull-out tests at low temperatures is detected (both in B4 and B20 case) a relatively small reduction in degree of curing is detected (around 90% degree of conversion is reached). Conversely, Product 2 showed a reduction in bond capacity of 15% with respect to room ambient temperature case and, in parallel, a decrease below 85% in degree of curing. Consequently, it seems that a 90% ratio between degree of curing at a given temperature with respect to the fully cured status may represent a significant threshold level for assessing potential impairment in the mechanical performances of the bonded anchor (similar conclusions can be reached by taking as reference the degree of curing for nominal curing time rather than for 24 h). Ad adiuvandum, it is also noticed that when such '90% conversion' is not reached, in sustained tests (B20) an unstabilized displacement at 150 h is detected.

Finally, a focus is made on the correlation with the modified sustained tests (B20M) results. As previously mentioned (Section 3.4), such procedure is proposed to simulate the case when an anchor cured at minimum ambient temperature is subjected to a load and, during its service life, to a temperature higher than room ambient one. In such case it is noticed that the maximum temperature accounted in the test (43 °C) is lower than the glass transition temperature of Product 1 cured at room ambient temperature (50.1 °C) for the 'full' cured state, but definitely higher than the one when curing occurs at the minimum installation temperature (31.1 °C). In fact, when during the test T_g is reached, failure occurs.

It is noticed that also Product 2 was not able to complete the sustained load portion during the modified sustained tests, even if its glass transition temperature was always higher than 110 °C. A potential explanation is the following one. Having discussed how the first peak in *tanδ* curves can be ascribed to monomers unreacted double bonds (Fig. 10), their presence can explain a partial performance (drop of storage modulus) depending on the history of the sample and the temperature at which is it tested. For the product cured at −10 °C, such peak (T_1) is around 28 °C. Consequently, during the heating ramp, the material is in an intermediate state, where molecular relaxation is important enough to 'soften' the material (descending branch after T_1 in Fig. 10), which is not the case when the material cures at 20 °C (basically constant *tanδ* after T_1). If the history of the sample is determinant on the final behavior, also the predominant behavior between post-curing and softening during temperature increase is [4,29]. For example, a change in the heating rate would change the history of the sample, and could modify competition between post-curing and softening of the material, and consequently temperature profiles. Product 2 is a product qualified for maximum short temperature equal to 80 °C with no significant performance decrease with respect to room ambient temperature. However, in such standard test procedures, the product cures at 20 °C before being subjected to 80 °C; hence, the reactivity of the product is less impacted.

6. Conclusions

To the scope of investigating the behavior of bonded anchors cured at sub-zero temperatures, the paper introduces and discusses an extended experimental programme on two different bonding agents including both thermal and thermomechanical tests on the bare material and mechanical tests on the bonded anchors. With respect to the initial research questions, the following conclusions are drawn.

It was shown that the degree of conversion (evaluated through MDSC) and the glass transition temperature (evaluated through DMA) tend to correlate the results for both short-term (i.e. pull-out) and long-term (i.e. sustained loading) mechanical testing. As for the tested products, a reduction in the degree of conversion when passing from room to sub-zero temperatures is associated to both a reduction in bond strength and to a lower tendency to stabilize displacements in sustained tests.

On the contrary, the correlation with the glass transition temperature is less direct. It is noticed that its evolution can be a few degrees to more than a decade when degree of conversion increases a few points, especially when the thermoset material reaches a high degree of conversion. By analyzing the results of mechanical tests accounted by current qualification procedures, a change in the glass transition temperature seems to have no impact on the global mechanical performances of the bonded anchors. However, for both analyzed products, the maximum temperature reached during such tests is lower than the glass transition temperature or even the first transition temperature. In fact, if the temperature reached during a sustained load test is higher than any of such values (as in the test regime proposed by the authors), the increased molecular mobility of the bonding agent triggers a tertiary stage of creep.

Following the initial criticism with respect to the existing qualification procedures aiming to assess the effects of curing at low temperatures, it was asked if all the relevant information to determine the suitability of an adhesive anchor in such conditions could be extracted from such tests. The obtained results incline authors towards a negative answer. Even though a relationship between the anchor behavior and the bonding agent thermal properties can be detected, a positive correlation can be sustained only if, when passing from room ambient to low (typically sub-zero) temperatures, the degree of conversion is not significantly affected (a reduction lower than 10%) AND glass transition temperature does not fall below the long term value the anchor is expected to be subjected during its service life. Similar remarks apply also to the first transition temperature if the material softens after reaching such value.

In case of a negative correlation, a full mechanical characterization of the bonded anchor is required, also exploring the anchor behavior for maximum long term temperatures higher than room ambient one. Once again, it is remarked that existing qualification procedures do not assess the anchor behavior at temperatures higher than room ambient one considering the possibility that the anchor cures at low temperatures. Consequently, authors recommend an evolution in such direction.

Founding

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

G. Muciaccia: Writing – original draft, Validation, Supervision, Methodology, Formal analysis, Conceptualization. **A. Consiglio:** Investigation, Data curation. **S. Quercy Jouvet:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **V. Rostaind:** Supervision, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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