EARLY STAGE TEMPERATURE CONDITIONS INFLUENCE ON MICROMECHANICAL FEATURES OF THERMOSET POLYMER-BASED COMPOSITE

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ABSTRACT

The application of thermoset polymer-based composites is very common in many engineering fields, such as automotive, aerospace or bioengineering industry. More recently, such composites found their utilization in the civil engineering, for instance as post-installed anchoring systems or in concrete and masonry reconstructions. Regardless of the use, environmental conditions imposed on a typical thermoset polymer matrix during casting and early curing stage predetermine properties of the composite in a hardened state. Moreover, inconsistent environmental conditions that usually occur in civil engineering practice, may lead to structural service life reduction or, in the worst case, to abrupt failure due to alternated mechanical features. In general, the modeling and optimization of polymer-based composites is decisively dependent on an understanding of two basic aspects; heat generation during the initial chemical reaction of the polymer and the material formation reflected in a strength gain. To capture initial environmental fluctuation, this contribution presents an experimental evaluation of a thermoset polymer-based composite cast and cured at different temperatures. The reaction heat generation is monitored by an isothermal calorimetry and both viscoelasticity and strength gains are measured on the material microscale using nano-indentation. Supported by described experimental work, bottom-up uncoupled multi-scale homogenization is used to estimate temperature impact on material properties. Furthermore, the data can be applied in both curing kinetics and heat generation models or stress evolution and structural integrity development simulations.

Keywords: thermoset, polymer, composite, environmental conditions, temperature, curing degree, indentation, viscoelasticity, creep compliance

1 INTRODUCTION

Optimization and long-term performance prediction of structural material are inevitable consequences of risen demands for high-performance construction, accelerating the construction speed and reducing the cost of buildings. Recently increased requirement for building reconstructions prompted the development of new composite materials, broadly implemented in aerospace, automotive or bioengineering industry. Structural member strengthening or partial construction rehabilitation are typical examples of small-scale polymer-based composite application in civil engineering. Other application of thermoset polymers can be found in fast-growing post-installed fastening and cohesive anchoring systems in existing concrete or masonry structural members. Regardless of the composite application, a polymer-based matrix is subjected to congruent manufacturing issues defining overall features in hardened state. The most significant influencers of final material state are environmental conditions (temperature, humidity and/or chemical conditions) and their stability during early stage curing process.

Environment impact on composite curing is reflected in results of heat generation (conduction) during inner chemical reaction and the gain of material integrity and strength. The optimization of a thermoset polymer is dependent on proper understanding of both these aspects. The curing kinetics and heat generation modelling proposed by a number of studies [1 - 4] incorporate Kamal's approach to the phenomena paired with standard heat equation

and temperature field defined by Fourier's law. One of early approaches describing stress evolution during the hardening and structural integrity development was proposed by Plepys et al. [5,6]. In his study, the development of elastic properties and curing stresses was described as a function of curing degree. Despite introducing linear mixing rule relevant to the curing degree (based on elastic moduli of both non-cured and fully hardened polymer), Bogelli and Gillespie [7] did not incorporate the viscoelasticity of thermoset while forming its structure. More recent modelling of polymer mechanical features with respect to the curing degree proposed by Adolf and Chambers [8] use an advanced model to reflect cracking of the polymeric matrix on the microscale.

The attempt of this contribution is to experimentally evaluate the mechanical response of thermoset polymer-based composite casted and cured in different temperatures. Moreover, by testing the material at various curing stages using nanoindentation, the evolution of microscopic viscoelastic features can be established. Obtained data can be further incorporated in the bottom-up uncoupled multi-scale homogenization strategy, such as Mori-Tanaka method or advanced FEM analysis of representative volume element.

2 THEORETICAL BACKGORUND

The nano- or micro-indentation developed over the past three decades has been considered an effective investigation technique for time-independent elastic-plastic materials. The basis of indentation relies on continuous load-displacement record of rigid, axisymmetric probe propagation into a homogeneous, linearly elastic and isotropic half-space [9 - 12].

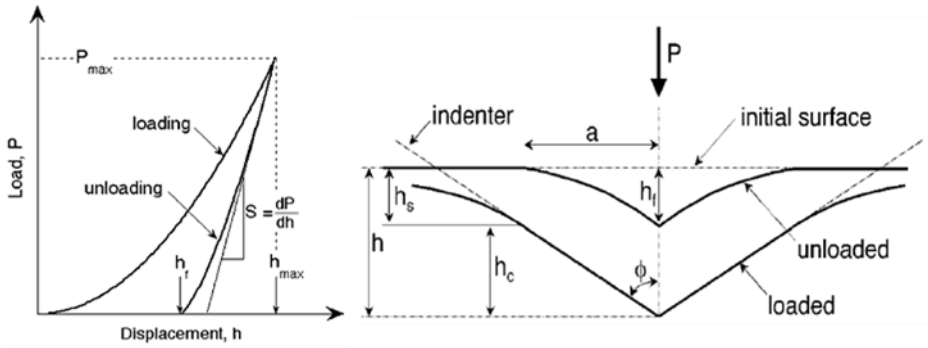


Figure 1: Indentation load-displacement record and relevant contact parameters characterization

The fundamental elastic-plastic material features derived from nanoindentation tests are hardness (H) and indentation modulus (E_r). Both are determined from an indentation record with respect to the probe shape and contact parameters of deformed material half-space (see Fig. 1). Hardness is defined as the maximum contact pressure under the indenter in the loading phase of measurement as

$$H = \frac{P}{A_C}. \tag{1}$$

The P is the maximum implied load (defined and detected by instrument sensors) and A_c corresponds to projected contact area, determined for each variety of probe shape from the contact depth h_c (see [11 – 14]).

The most often used probe contact depth formula proposed by Oliver & Pharr [11] is defined as

$$h_c = h - h_s = h - \varepsilon \frac{P_{max}}{S}, \quad (2)$$

where ε represents probe shape constant and S is the material stiffness defined by curve fitted regression function from unloading phase (see Fig. 1).

The indentation (or reduced) modulus E_r is also derived based on probe contact area and material stiffness with respect to probe shape (shape correction factor β) as

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_c}}. \quad (3)$$

The rheological behaviour of viscoelastic materials can be incorporated to the fundamental indentation premise of rigid, axisymmetric probe propagation into a linear elastic half space by upgrading to a linearly viscoelastic one. First attempts to characterize viscoelastic attributes of a material under monotonic load used simplified modelling [15, 16]. Due to comparatively large deformations under pointed sharp probe (such as commonly used Vickers or Berkovich probe), nonlinear behaviour of the indented material can be expected. This phenomenon can be captured by sophisticated models, methods founded on viscoelasticity theory or by finite element models [17 - 21].

For the purpose of this study, in which comparison of casting and curing environmental conditions are observed, simplified method of viscoelastic properties measurement via nanoindentation is used. The indentation force imposed on a rigid probe propagating into a homogeneous linearly elastic half space can be defined as

$$P = \frac{4Gh^2}{\pi\,(1-\nu)\tan\alpha}, \quad (4)$$

where G is the shear modulus, ν is the Poisson's ratio and α is effective face semi-angle of the probe [9].

The indentation force $P(t)$ and corresponding indentation depth $h(t)$ for linearly viscoelastic half space can be analogically derived from eqn. (4) as

$$P_{(t)} = \frac{2}{\pi\,(1-\nu^2)\tan\alpha} \int_0^t E(t-\tau) \left(\frac{dh^2(\tau)}{d\tau}\right) d\tau \quad \text{and} \quad (5)$$

$$h^2_{(t)} = \frac{\pi\,(1-\nu)\tan\alpha}{4} \int_0^t J(t-\tau) \left(\frac{dP(\tau)}{d\tau}\right) d\tau, \quad (6)$$

by replacing shear modulus G with relaxation modulus $E_{(t)}$ (resp. creep compliance $J_{(t)}$) at time t [21, 22]. Due to described simplifications, the viscoelastic mechanical features of thermoset polymer matrix of a composite under imposed monotonic load can be directly evaluated. It is obvious that the selection of monotonic load function also directly effects interpretation of viscoelasticity. Basic scenarios of imposed load function and resulting adjustment of eqn. (6) are stated bellow [16, 21, 22].

- Step load function (constant load indentation creep test) with prescribed constant indentation force $P_{(t)} = P_0 H_{(t)}$ (where $H_{(t)}$ is the Heaviside step function) results in direct creep compliance $D_{(t)}$ in form

$$D_{(t)} = \frac{2\,h^2_{(t)}}{\pi\,(1-\nu^2)\,P_0\tan\alpha} \quad (7)$$

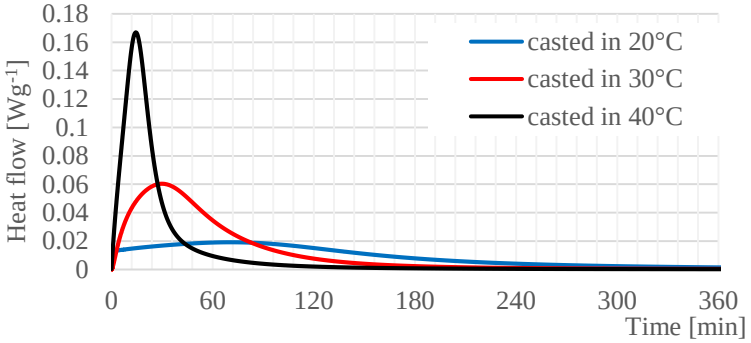
- Constant indentation depth load function (fixed penetration or indentation relaxation) with controlled penetration depth $h_{(t)} = h_0\,H_{(t)}$ from which relaxation modulus $E_{(t)}$ is derived as

$$E_{(t)} = \frac{\pi\,(1-\nu^2)\,\tan\alpha}{2\,h_0^2}\,P_{(t)} \quad (8)$$

Due to limitations of indentation instruments, Heaviside step function in both creep compliance and relaxation modulus measurements is replaced by ramp loading in short beginning of the load function, which are followed by imposed constant indentation load or penetration depth. Such conditions lead to exclusion of certain data set from the analysis (usually interval 5 to 10 times longer than ramp load duration).

3 EXPERIMENTAL SETTINGS

For the purpose of this study, commonly accessible bisphenol-A based two-component epoxy resin (FIS EM Plus 585 S, assumed Poisson ratio $\nu = 0.35$) was selected for casting and curing temperature impact testing on viscoelastic features of hardened composite. The testing set (total of 9 samples) was divided into three main groups (specimens casted and cured in temperatures of 20, 30 and 40°C), each containing thermoset polymers cured to 0.50, 0.70 and 0.99 degree (close to fully cured sample). Investigated samples are identified as FIS_EM_xx_yyy, where xx represents a casting temperature and yyy stands for relevant curing degree. Prior to the resin casting, both of its components were preheated to corresponding temperatures. To prevent further chemical reaction (i.e. curing), all samples were immediately stored in -10°C when reaching appropriate level of curing degree. The timing of production and storage was based on prior isothermal DSC measurements for each selected temperature (see Fig. 2). The samples were place to standard environmental conditions (20°C temperature, 50% humidity) 120 minutes prior to nanoindentation testing (same environmental conditions were kept during the testing).



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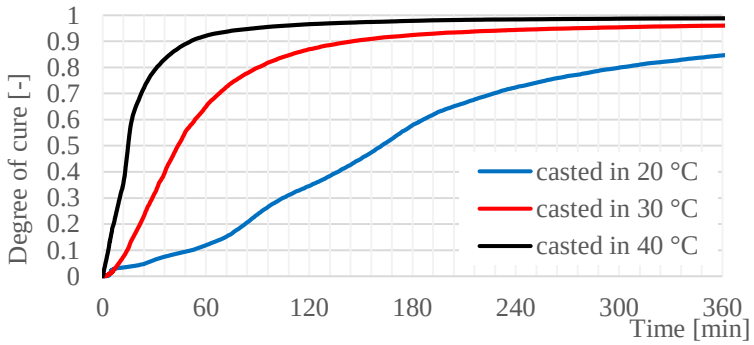

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Figure 2: Thermal analysis of bisphenol-A epoxy resin based composite casted in different temperatures – (a) Isothermal DSC records, (b) Degree of cure records

The nanoindenter Ti 700 series (Hysitron Inc., measured in CET Telc, ITAM) equipped with standard Berkovich probe tip (face semi-angle α = 65.03°, Poisson ratio $\nu = 0.07$) was used for experimental evaluation. The data to evaluate elastoplastic and viscoelastic properties of the composite material were collected separately.

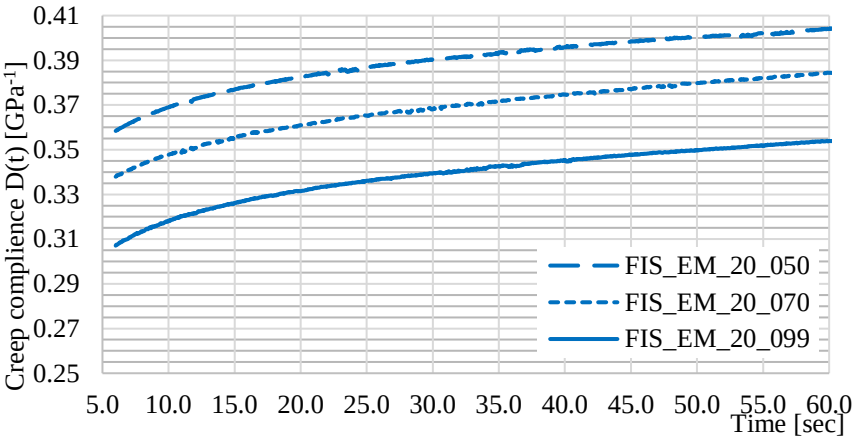
At first, a grid indentation consisting of 5 by 5 indents separated respectively by 50 μm was performed to evaluate hardness and indentation (reduced) modulus. The applied load reached its maximum of 10 mN in 5 seconds and was kept constant over 25 seconds. The unloading, from which elastoplastic features of the composite are calculated, lasted 5 seconds.

For evaluation of viscoelastic properties, the individual indents were placed in 10 by 10 indentation grid with mutual perpendicular separation of 50 microns. The step load function consisted of ramp loading over first 1 second of the measurement in which maximum indentation load of 5 mN was reached. This load was constantly held over the period of 60 second. The unloading of the specimen was identical to the loading segment. Such indentation setting suggests an application of eqn. (7). The first 6 seconds (ramp load segment and first 5 seconds of constant maximum load holding) of the measurement were excluded from the evaluation to avoid incorporated errors that may occur in this period.

4 RESULTS

Both elastoplastic and viscoelastic results of investigated thermoset composite features are summarized in Tab. 1. in the form of mean values and their the standard deviation. The viscoelastic creep compliance results with respect to casting temperature are depicted over the evaluation period as stated in previous section, in Fig. 3. For the ease of interpretation and discussion, results with identical level of cure are included in Fig. 4. It needs to be stated, that approx. 12.4 % results were excluded from the evaluation due to presence of infill particles of the composite.

The impact of both casting / curing temperature and the degree of cure are obvious from presented results. Comparing the two most extreme cases of our study (resin casted and cured in 20°C with curing degree of 50% and fully cured composite treated in 40°C), the quantification of micromechanical features can be stated, that FIS_EM_40_99 creep compliance is about 24.63% lower than FIS_EM_20_50. The same can be written about indentation modulus (E_r) and hardness (H), which are respectively about 188.23% and 33.79% higher for FIS_EM_40_99.



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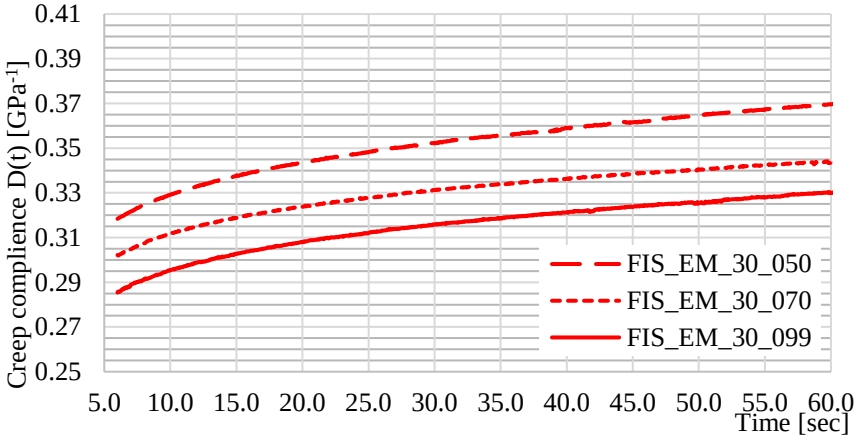

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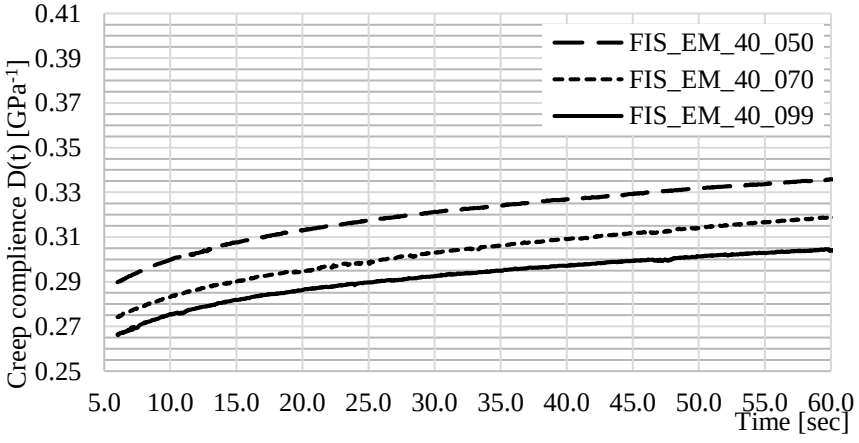

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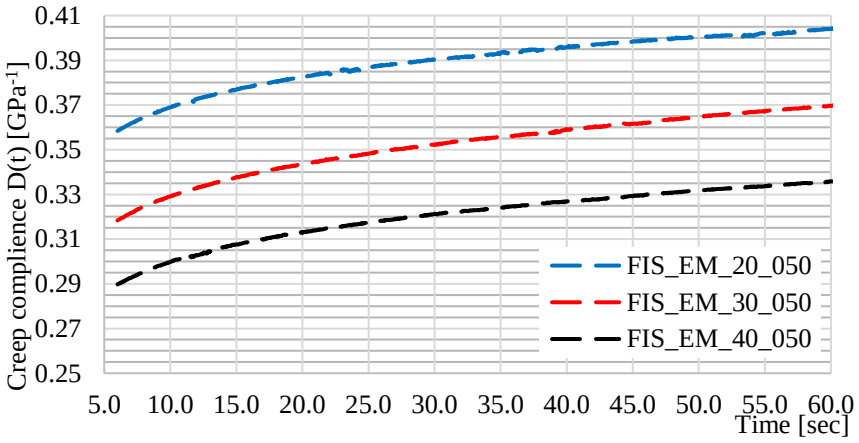
Figure 3: Creep compliance D(t) of bisphenol-A epoxy resin-based samples in different curing stage casted in – (a) 20°C (b) 30°C and (c) 40°C



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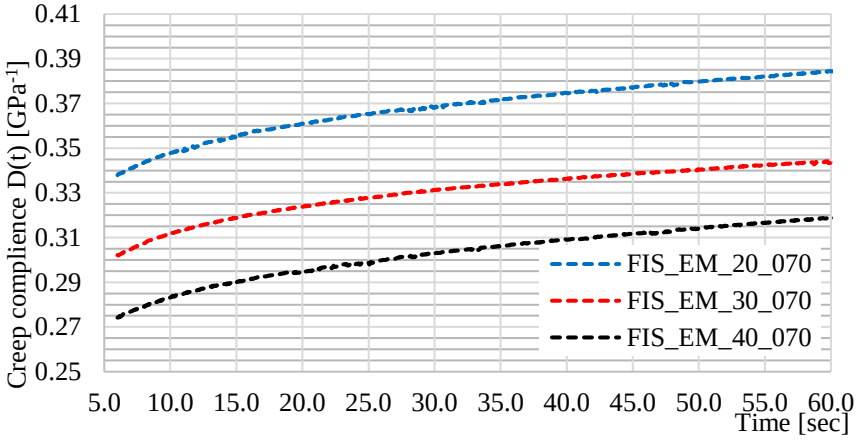

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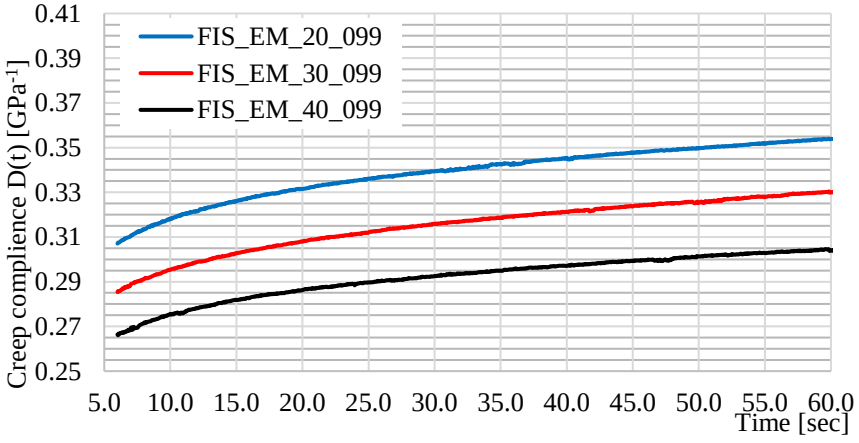

(c)

Figure 4: Creep compliance D(t) of bisphenol-A epoxy resin-based samples casted in different temperatures at level of cure of – (a) 50% (b) 70% and (c) 99%

Table 1: Summary of average indentation results

Measurement denomination	Indentation results			
	Hardness H [GPa]	Ind. modulus E_r [GPa]	Contact depth h_c [nm]	Creep comp. $D_{(t)}$ [GPa^{-1}]
FIS_EM_20_050	0.219 ± 0.11	3.890 ± 0.72	891.701 ± 52.35	0.402 ± 0.21
FIS_EM_20_070	0.235 ± 0.10	4.259 ± 0.80	858.412 ± 47.42	0.383 ± 0.18
FIS_EM_20_099	0.254 ± 0.12	4.746 ± 0.62	823.360 ± 45.17	0.352 ± 0.19
FIS_EM_30_050	0.250 ± 0.09	4.922 ± 0.75	829.960 ± 49.89	0.368 ± 0.19
FIS_EM_30_070	0.258 ± 0.08	5.275 ± 0.87	817.022 ± 51.73	0.341 ± 0.20
FIS_EM_30_099	0.280 ± 0.08	5.842 ± 0.66	780.992 ± 48.21	0.329 ± 0.18
FIS_EM_40_050	0.264 ± 0.10	6.386 ± 0.59	805.384 ± 43.68	0.334 ± 0.16
FIS_EM_40_070	0.281 ± 0.09	6.818 ± 0.84	780.565 ± 43.03	0.318 ± 0.14
FIS_EM_40_099	0.293 ± 0.07	7.322 ± 0.93	766.635 ± 42.56	0.303 ± 0.12

5 CONCLUSIONS

The thermal analysis and micro-mechanical characteristics of thermoset polymer-based composite were investigated. The effects of various casting / curing temperatures and degree of cure on the elastoplastic and viscoelastic behaviour of the material were in focus of this study. Selected nanoindentation method is sufficient to evaluate the environmental impact. Together with macroscopic results, the outcome of this study serves as input data for simplified modelling of polymer-based composite behaviour. For a closer understanding of the material, other intermediate temperatures should be considered for additional testing as well as other types of thermoset polymers. Even though the methodology can be used for simplified modelling, the recommendation is to consider other settings of viscoelasticity nanoindentation testing.

ACKNOWLEDGEMENTS

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