Life-time Modelling of thermoset Polymers in Structural Engineering (LiMoPoSE)

Abstract: Thermoset polymers play an increasingly important role in structural engineering. Compared to classical aerospace or automotive applications the polymers typically do not reach a fully cured state during construction. The material will consequently undergo post-curing during it's life-time, changing significantly it's material characteristics. Currently, the scientific community is lacking modeling concepts for the temperature and curing level dependent mechanical response of set-cast polymers, in particular with regard to visco-elasticity. Due to aging, these materials defy all known concepts for accelerated testing. Hence, the performance prediction for structural life-times of 50 years or longer remains an unsolved challenge. In this proposal an interdisciplinary approach combining experiments and simulations on multiple length and time scales aims at delivering a physically based and thus truly predictive multi-physics multi-scale model for structural applications. The model's quality will be established by three typical and independent case studies, one classical problem from aerospace and two representative cases in structural engineering.

Abstrakt: Polymerwerkstoffe spielen eine zunehmend größere Rolle im Ingenieurbau. Im Vergleich zu den klassischen Anwendungen im Fahrzeug und Flugzeugbau unterscheiden sich die Infrastrukturanwendungen vor allem dadurch, dass die Polymere während der Herstellung nicht vollständig aushärten. Folglich finden Nachhärtungsreaktionen im Laufe der Lebensdauer des Materials statt, welche dessen mechanische Eigenschaften maßgebend verändern, insbesondere das viskoelastische Verhalten. Aufgrund der fortschreitenden Materialalterung können etablierte Konzepte für beschleunigte Tests nicht angewendet werden. Die Zustandsvorhersage für eine Lebensdauer von mehr als 50 Jahren bleibt somit eine ungelöste Herausforderung. Im vorliegenden Projekt soll auf Basis einer interdisziplinären Vorgehensweise bestehend aus Experimenten und Simulationen, die auf mehreren Längenskalen und Zeitskalen statt finden, ein Modell für Strukturanwendungen entwicklelt werden, welches echte Langzeitvorhersagen ausgehend von begrenzten experimentellen Kurzzeitmessungen erlaubt. Die Qualität des Models wird anhand von 3 Fallbeispielen, ein klassisches aus dem Flugzeugbau und zwei repräsentative für den Ingenieuerbau demonstriert.

1 Motivation and significance

In the last century construction engineering as well aerospace engineering was dominated by the materials steel, aluminium, and concrete. Stimulated by the space race during the cold war and the nuclear energy community extensive basic research has been performed leading to major jumps in understanding and modelling capabilities. In the last decade, new forces driving research such as sustainability, or the climate change have emerged stimulating the demand for more (fuel) efficient cars, airplanes and cost-efficient construction techniques. Composite materials are a key element of those, combining the positive characteristics of typically two materials. In many cases these are a bonding matrix made from polymers and an actual load carrying constituent typically in the form of carbon or glass fibers. Indeed, the outstanding properties of thermoset composites are boosting their application in modern aircrafts [23, 54] such as the Boeing 787 and the Airbus 350, in the automotive field accomplishing increased car crashworthiness and reduced fuel consumption [56, 21], and in the wind energy field leading to more durable and efficient turbine blades [18, 57].

In the field of construction mostly cement based or polymer based matrices are combined with high strength fibers. Depending on the application (mechanical loading) and the environmental conditions (aggressive waters, temperature) the type of fiber and their arrangement may vary. Typically, glass fibers, carbon fibers, basalt fibers or classical steel fibers may be used and arranged in unidirectional layers, multi-directional sheets or as a dispersed phase. While in the aerospace industry entire structural members are made from composites, in the construction industry so far polymer-based composites can be found almost exclusively in rehabilitation and strengthening (e.g. glued on laminates, confinement jackets, ...) as well as post-installed fastenings. Even though the products and applications are quite different, the commonly found polymers are of similar characteristics and face analogous challenges: they are typically exothermally reacting **thermoset polymers** (e.g. epoxies or vinyl-esters) and a **high filler content**. In typical applications the polymer is **incompletely cured** and, hence, the mechanical properties are uncertain and depend on the environmental conditions; none of the products reach a fully cured state. The construction industry demands a large range of working temperatures, typically ranging from freezing conditions to 40 degrees Celsius or above. During the life-time, phases of increased temperature lead to post-curing and related changes in mechanical properties. The exception are fully cured industrially produced pipes which are commonly used for many years now. On top of **short-term loads** in almost all applications either the performance under **sustained loads** or cyclic loads are relevant, both of which depend on the actually reached curing degree and potential post-curing during the service life. Pipes are typically pressurized at high levels and subject to earth pressure; strengthening laminates on the tensile face of concrete beams carry significant portions of dead loads; and adhesive anchors are in many applications designed for predominant permanent actions, e.g. carrying the ceiling elements in tunnels. The latter application recently attracted significant public attention after two severe disasters in Boston and Sagano [60, 48] were attributed to the installed anchors. Further complications in structural engineering arise from the pronounced temperature but also humidity dependence of polymers, which are in direct conflict with the practically required large range of environmental conditions during installation but also service.

All engineering structures and construction elements have to satisfy a number of design conditions regarding failure (ultimate load), serviceability and durability considering a given design life-time or operation hours. In some fields (automotive, aerospace) compliance with these requirements can be established by extensive testing of prototypes. In the construction industry this is typically not possible as every structure is unique. Products for the construction market such as anchors or strengthening laminates represent the intermediate case where the product itself cannot be tested independently of the structural member. The current approach of technical approvals based on system level testing of products installed in concrete [2, 32] only incompletely captures their life-time performance. Prominent examples are e.g. the certification of adhesive anchors under sustained loads [33] or fire. In both cases the effective material properties of the polymer are functions of space and time, influenced by installation, curing temperature history, storage and testing conditions. For many years now concepts for accelerated creep tests are available based on temperature time superposition. While these concepts would allow the testing of life-times (e.g. 50 years) in a matter of days or weeks, these concepts fail for incompletely cured products as heating to higher temperatures would trigger post-curing and irrevocably change the materials properties.

Consequently, (1) a meaningful interpretation of fire tests of construction elements involving an incompletely cured polymer component is only possible in combination with a temperature and curing degree dependent (visco-) elastic constitutive model for the polymer component. Such a model is also the pre-requisite for (2), the development of cost-efficient and safe design standards concerning fire and sustained load as the local interaction with the building material and the environmental conditions can be accounted for. Finally, (3) inverse analysis based on an aging visco-elastic model may represent a remedy to the dilemma of accelerated creep tests of aging polymer based materials. Overall, multi-decade predictions during structural design as well as extrapolations to untested environmental conditions and structural configurations can only be trusted if the underlying model is based on solid theory. The proposed research attempts to further the state of the art and science and provide the required basis for future developments.

This investigation focuses on two highly-filled thermoset polymers. One product is vinyl-ester based, the other one is an epoxy system. Both are presentative for a large group of polymer products on the construction market but exhibit substantially different properties due to their chemistry.

2 Objectives

- **Aging constitutive model**: optimized constitutive model for highly filled thermoset polymers depending on the cross-linking level, calibrated/validated by experiments
- **Temperature and humidity dependence**: theoretical and numerical framework for the prediction of temperature and humidity influence, calibrated by experiments
- **Aging visco-elasticity**: extension of the theoretical and numerical framework to include aging visco-elasticity of highly filled thermoset polymers following a hybrid multi-physics and multi-scale modelling and testing concept
- **Hybrid concept for accelerated creep tests of incompletely cured polymers** utilizing the developed framework for aging visco-elasticity in combination with accelerated creep tests at elevated temperatures and standard tests for the aging behaviour

3 State-of-the-art review

3.1 Modelling concepts for curing level

Thermosetting resins offer superior mechanical properties and fracture behaviour compared to conventional mortars thanks to the formation of several inter-chain covalent bonds leading to the emergence of a strong polymer network. A typical example are e.g. the state-of-the-art mortars used in bonded anchors [31] which are composed of a thermosetting polymer (e.g. Bisphenol A diglycidyl ether or Vinyl-ester) combined with a higher filler content such as e.g. 40% in weight of particles.

The thermodynamically irreversible process of network formation is called curing and its understanding is key to fully exploit the advantages of these materials. As extensive studies in the composite community have shown (see e.g. [64, 22, 24, 66], the curing process can produce residual stresses due to differential chemical shrinkage and non-uniform curing degree throughout the structure. If not monitored properly, these stresses can eventually lead to extensive microcracking impacting heavily not only the instantaneous but also the long term macroscopic mechanical properties of the composite. This makes the analysis of the curing process quintessential for the correct prediction of the long term behaviour of polymers in construction.

The scientific literature on the curing process of composites is commonly broken down into two parts: a) analysis of *chemical reaction*, heat generation and heat conduction, and, b) study of the *evolution of stress* and development of structural integrity. However, capturing the emergence of curing stresses and predicting the long term behaviour of the polymer requires a thorough understanding of both issues. The temperature field, highly affected by the exothermic process of network formation, is usually modelled using the standard heat equation and Fouriers law. The phenomenological model proposed by Kamal [46] is generally used for cure kinetics. According to this model, the rate of cure can be described by $\mathrm{d}\phi/\mathrm{d}t = [k_1(T) + k_2(T)\phi^m](1-\phi)^n$, where $k_1(T) = A_1 \exp(-\Delta E_1/TR)$, $k_2(T) = A_2 \exp(-\Delta E_2/TR)$, are two Arrhenius-type functions related to the probability that a reaction might take place after an atom collision, ΔE_1 and ΔE_2 are activation energies, A_1 and A_2 are frequency-like constants, R is the gas constant and, m and n are constants to be determined experimentally. The applicability of this law has been verified by several studies on the curing kinetics of various epoxy and hardener system [3, 74, 68, 61, 1].

3.2 Curing level dependent constitutive models

In recent years, several approaches have been proposed for the evolution of curing stresses. A first attempt was made by Plepys and co-workers [64] who used incremental elasticity to describe the evolution of stresses and elastic properties as a function of cure. Bogetti and Gillespie [14], used a linear mixing rule based on degree of cure, elastic modulus of uncured and fully cured resin moduli and a parameter to quantify stress relaxation and chemical hardening. However, the foregoing contributions completely neglected the viscoelastic behaviour of the polymer during network formation. This is a significant issue considering the viscoelastic nature of the polymer is even more pronounced during curing and it affects highly the development of internal stresses. Attempts to address this issue were made employing linear viscoelasticity [3, 4, 52, 77]. Recently, researchers [41, 27] have proposed to model the evolution of the cure dependent (and therefore time dependent) material properties with the aid of integral linear elastic constitutive equations where a simple Tresca criterion is coupled to the crack band model [10] to capture matrix microcracking.

Even if the introduction of damage in the foregoing model represents a step forward, there are still some fundamental issues which need to be addressed. In particular, (1) the model neglects the *viscoelastic behaviour* of the polymer as a function of degree of cure although viscous effects play a huge role in the development of internal stresses, (2) the model oversimplifies the *mechanical interactions* between network chains by assuming a simple parallel coupling with no interactions or strain localizations, (3) the simple damage criterion used cannot capture the complex mechanical behaviour of the polymer under *multi-axial state* of stress which is likely to develop during the curing process; (4) the failure criterion itself should be recast within a non-linear viscoelastic framework to capture the effects of temperature and moisture which are known to highly affect the mechanical behaviour. This is of utmost importance for the applications considered in the present research.

3.3 Visco-elastic models for thermo-set polymers

The viscoelastic behaviour of thermosets and thermoplastic polymers has attracted increasing interest from both the scientific and industrial communities. Notable contributions are represented by the pioneering works by Argon [5] and later Boyce [16, 17] and Arruda [6] in the field of glassy polymers (thermoplastic and rubber-like) and, most recently, of thermosets [45]. Probably the most general nonlinear viscoelastic theory was proposed in the pioneering works by Schapery [71, 72]. His formulation leverages on the use of convolution integrals of linear viscoelasticity with the nonlinearities appearing only in the measures of stress and strain and in the reduced time. Although very elegant and comprehensive, Schapery theory implementation is complex. Further, the experimental characterization of the main parameters is very difficult and, most often, one needs to rely on indirect estimations. To address these issues, Knauss and Emri [51] proposed a special case of the Schapery model called free volume approach. The underlying assumption is that the free volume, while not explicitly defined, controls the molecular mobility, directly affecting the inherent time scale of the material. Introducing a physically well-defined quantity such as the free-volume makes the formulation clearer and makes it easier to account for e.g. temperature effects. In fact, the dependence of the volumetric effects of temperature [34], solvent concentration [50] and mechanical pressure [35], which have all been shown to influence the time scale, can be described by the Doolittle expression [28] relating free volume to the time scale of the material.

To improve the prediction of the viscoelastic behaviour in shear, Popelar and Liechti [65] introduced a distortional term into the free volume in a phenomenological manner, without explicitly indicating what molecular mechanism might be involved. This resulted in a good agreement with experimental tensile and shear stress-strain curves, also in the presence of strain softening.

The *"free-volume approach"* is considered the ideal platform for the implementation of the viscoelastic model required for polymer-based mortars. However, it's successful use urges the solution of the following important issues: non-linear softening behaviour in shear needs to be captured accurately. Even if successful in some selected case studies, the distortional term introduced by Popelar and Liechti represents only a phenomenological way to fix the problem. Further, the connection between this term and the free-volume is somewhat obscure from a physical standpoint. The proposers of this research believe that an accurate prediction of the non-linear behaviour in shear will be made possible by the use of a more physically-based approach to effectively capture the local dilatational strain at the mesoscale and capture its effects at the macroscale. Thanks to its semi-multiscale nature, it is believed that the *microplane modelling framework* [8] coupled with the free-volume concept will provide accurate results without the need of artificial distortional terms. Finally, another aspect to be considered is the emergence of cohesive cracks in the material, a phenomenon which is currently not captured by the current viscoelastic models. This latter issue needs (1) the definition of viscoelastic cohesive laws, and (2) the introduction of a characteristic length scale into the formulation to guarantee mesh objectivity during strain localization. These tasks will be made relatively easy by the microplane framework and the crack band model [10, 8] as described in the following sections.

3.4 Multiscale modelling

The development of new and better understanding of traditional materials requires insights into complex systems which almost all show multiple scales. Things are made up of atoms and electrons on the atomic scale, and at the same time are characterized by their own geometric dimensions which are usually several orders of magnitude larger. This is true for both engineering and natural materials. Specifically, there are different length scales of importance depending on the type of material and its use. Many examples of materials which exhibit a strong dependence on the various length scales can be found in literature, e.g., composite materials, soils, rocks, biological materials and even metals. When considering composite materials, the information on the fibre or filler length scale is crucial to the material response of the continuum on the macroscale. On the other hand, metals are made up of grains and from a damage and failure point of view this length scale is important. Also concrete can be considered as a combination of constituent phases with different properties (aggregate, mortar and interface material). The process, in which the effects of the different length scales are included, is commonly termed as multiscale modelling.

Multiscale modelling has the potential to improve the simulation-based design and performance assessment of materials and structures. In some cases, multiscale techniques allow for investigating problems for which experiments are either impractical or impossible. The need for the correct prediction of material behaviour and properties is arising in association with many applications. In most practically relevant cases these predictions constitute extrapolations to unobservable durations (life-time of structures) or untestable geometries (prototype dams) which cannot rely on empirical models formulated and calibrated on one scale. Multiscale modelling allows to consider the source of a phenomenon at the scale at which it originates, thus introducing the correct physics into predictive simulations. Many experimental tests are carried out at the system but also material scale to learn more about a given problem. Numerical (multiscale) modelling represents a toolset for the interpretation of experimental data which can provide unprecedented insights into material / structural response and mechanisms. The border between material and structure is blurry and a matter of the investigated problem. Particularly, multiscale modelling enables us to capture the influence of the heterogeneous material microstructure on the macroscopic behaviour, see [43] for more details.

Traditionally, multiscale modeling of heterogeneous materials is performed either within the framework of homogenization methods (hierarchical modelling) for problems in which the scales are clearly separated or within the framework of concurrent methods when the scales are coupled [59]. The first approach will be employed in the current study, where the computational homogenization (method studying discrete microstructure) or homogenization based on the mean field approaches [15] (methods based on statistical information), i.e. Mori-Tanaka method, self-consistent method, etc., will be employed at lower scales and the obtained material properties will be utilised for the macroscale simulation (scale of structure) based on finite element or discrete element methods.

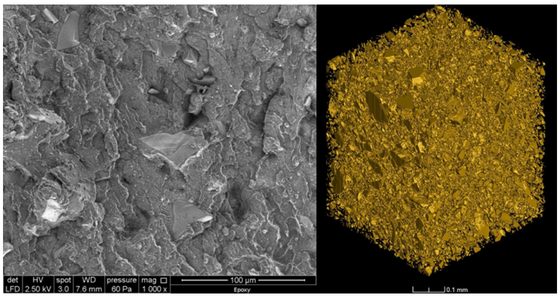

Figure 1: SEM-image and CT scan of a typical highly filled epoxy

3.5 Material characterization

In order to study the long-term performance of composites in the construction industry, a number of experiments have to be performed at various length scales. Essential inputs apart from the composition are the meso- and micro-structure of the material. Microscopy, (micro and nano) CT scans, see also Fig. 1, together with e.g. porosity measurements can provide insights into the multi-phase nature of these materials. Further properties of interest concern the reaction kinetics and associated curing degrees. Mechanical material properties (elastic, fracture mechanical) can be obtained at the macro-scale by standard code based tests. At lower scales micro- and nano indentation combined with e.g. *environmental scanning electron microscopy* (ESEM) pictures for the characterization of the individual constituents properties and the respective interfaces. Especially the latter is potentially crucial for multi-scale modelling.

3.5.1 Thermo-analytical methods

Differential scanning calorimetry (DSC) and *Differential thermal analysis* (DTA) are thermo-analytical methods where information about the curing process and the degree of cure of thermoset polymers can be obtained. Basically, both techniques measure the temperature difference (ΔT) between sample and reference material during a present temperature gradient or an isothermal process. This temperature difference is actually measured as a thermoelectric voltage with a thermocouple, which is proportional to ΔT. The provided information of both methods is quite similar but there is a slight difference. DTA simply measures ΔT whereas the DSC uses the signal to keep both the sample and the reference material at the same temperature during the measurement by individual heaters. Therefore, two different types of DSC are distinguished: The power-compensated DSC measuring the electrical power difference and the heat-flux DSC that measures the heat-flux difference between a sample and a reference material to maintain $\Delta T = 0$ [19]. However, both methods will yield the same thermodynamic data such as enthalpy, Gibbs energy, entropy, specific heat and also information about the kinetics is obtained [67]. A conventional DTA would have to be calibrated by an appropriate substance for this purpose.

For polymers characteristic temperatures of the glass-transition (T_g), melting point (T_m) or thermal degradation are very important, that provide information about the molecular weight (MW), crystallinity or degree of cross-linking. Also the influence of the environment during the measurement is relevant, since it can be reactive (air, O_2) or inert (vacuum, N_2). Thermoset polymers show a certain degree of cure that influences the glass-transition temperature as well as material properties like brittleness, impact resistance, creep behaviour or long term stability [78]. The resin cure is dependent on both time and temperature [30]. Therefore, it is essential to investigate their curing state and curing kinetics. Especially thermosets containing fillers such as cement can show very complex curing properties, since the system includes a further reactive component that forms hydrates in the presence of moisture and represents inclusions in the composite.

3.5.2 Visco-elastic characterization

Dynamic mechanical analysis (DMA) is a very frequently used method to study the viscoelastic behaviour of polymers by exposing it to a periodic alternating, usually sinusoidal, stress. Stress and strain can be applied to a specimen in an axial or torsional mode. The variation of the frequency allows the characterization of the time dependence within a short testing time and also the temperature dependency can be studied using a *dynamic mechanical thermal analysis* (DMTA). There are several methods varying in the type of stimulation such as forced and natural damped oscillation or resonance vibration [39].

Amplitude and phase shift of the material deformation during the measurement give information about characteristic parameters such as glass-transition temperature, Youngs modulus and shear modulus. Since the curing state of thermosets depends on time and temperature, post-curing heat treatments are often used to increase the mechanical performance. Stark et al. [75] used a 3-point bending arrangement of a DMTA for online-monitoring of thermoset post-curing to find optimal conditions. A combination of both techniques, DSC and DMTA can be very useful to get a relationship between chemical and mechanical conversion of thermoset polymers [69].

A commonly applied concept to obtain creep compliance data for decades is the temperature time superposition principle [42], applicable only for non-aging (fully cured) materials. The basic idea is to relate the temperature-dependent mechanical properties of linear viscoelastic materials to a known reference state by “simple” shifting in a suitable plot.

3.5.3 Mechanical characterization at microscale

The materials considered for this project have a hierarchical structure. While the materials appear homogeneous at the macro scale at the microscale they are more like *multi-phase-composites* (see Fig. 1). To predict the material behaviour over time, detailed knowledge of mechanical data at a reference time and their temporal changes are necessary. This implies a characterization of homogenous mechanical as well as rheological properties at the macro-scale as well as the properties of the constituents at the microscale. The materials under consideration are compounds of thermoset polymers filled with inorganic particles from sand, stone, and cement. During the curing process the resin hardens, changes its viscosity, mechanical parameters and strength. Due to the curing process also residual stresses occur at particle resin interfaces, reducing the macroscopic strength of the hardened polymer. To access these properties, micro- and nanomechanical testing can be used. *Microhardness testing* is a very useful method to determine the local hardness by pressing an indenter onto a material surface with pre-defined load and by determining the size of the indent as a measure of the materials hardness [13]. With *nanoindentation* local hardness as well as the indentation modulus can be easily accessed [36, 62]. Point-measurements as well as profiles provide clear insights into the curing level dependent micro-scale material properties at clearly defined times. The method is also suitable for mapping of properties in inhomogeneous phases and has been successfully applied to bones and implants [40]. Nanoindentation has to be carried out with great care in order to avoid errors introduced in the zero point determination (the depth when the recording of the load displacement curve is started) and in the area function that is influenced by the exact shape of the indenter which is usually rounded and exhibits some irregularities around the tip and by material effects such as sinking in or piling up. Furthermore, there may be influences of thermal drift that can be largely excluded by letting the setup equilibrate before the test [36].

An overview of the nanoindentation technique applied to polymers is given in [76]. Creep properties can also be measured by nanoindentation by modification of the standard testing procedure [55, 36, 58, 38]. In combination with suitable *microscopy* methods (e.g. AFM or SEM) nanoindentation can be performed in precisely pre-defined locations to obtain information about interfaces, inclusions and voids, which is essential in inhomogeneous materials such as composites. A comprehensive overview of advances in the nanoindentation of polymer composites is found e.g. in [37].

3.5.4 Mechanical characterization at the macro-scale

The macroscopic mechanical properties of polymers and polymer-based composites can be tested by a variety of standard testing methods. This includes classical tensile testing for the determination of Young's modulus, Poisson ratio and tensile strength. Fracture toughness can be determined by compact tension tests. For this purpose, a notched sample with a pre-crack is loaded at controlled rate and the resulting load-displacement data is recorded. The data can be used to calculate the energy release rate related to the stress intensity factor K or the J-integral (see e.g. [47, 79]). Furthermore, the quasi-brittle nature of the material and related phenomena like the mechanical size effect will be explored. Three point or four-point bending tests are another way to assess the fracture behaviour by employing a notched specimen. They are also used to determine the flexural modulus and flexural strength of the material (e.g. [29]). Naturally, the aforementioned dynamic mechanical analysis (DMA) is part of any (visco-elastic) characterization at the macro-scale. In combination with suitable theoretical concepts such as temperature time super position [53], classical tension tests performed at different temperatures can also provide access to a polymer's multi-decade behaviour.

4 Research methodology

4.1 Overall approach

This research proposal is sub divided into 5 work packages. In WP1 the basics for modelling aging visco-elastic polymers are collected in an extensive literature review followed by the implementation and basic validation of the most suitable modelling approach. In parallel to the analytical and numerical work, in WPs 2 and 3 the necessary micro-scale and macro-scale experimental tests are performed to provide the inputs on reaction kinetics, material micro-structure, and material properties on the different scales and for different curing levels and temperatures. In parallel to the experimental characterization of the matrix the interface properties of the respective curing states are determined. WP4 focuses on the formulation and later calibration / validation of a multi-scale multi-physics computational framework. In WP5, ultimately, all research efforts are amalgamated into a set of case studies - one case in aeronautics and two cases of practical relevance for the construction market (an adhesive anchor and a strengthening measure with a glued on laminate).

4.2 Detailed work program

4.2.1 Constitutive models for thermoset polymers (WP1)

The process of crosslinking of thermoset mortars can have critical effects on the long term behaviour. Curing can induce differential chemical shrinkage whereas temperature gradients caused by the highly exothermic chemical reaction might lead to thermal residual stresses. As can be noted from Fig. 2, these internal stresses not only affect the creep behaviour of mortars through relaxation but they might also lead to damage. This, considering the complex microstructure composed by the thermoset polymer and quartz microparticles, can occur in the form of particle debonding and matrix microcracking. Finally, temperature gradients and environmental effects might lead to incomplete and non-uniform curing. This is a serious issue because it means that cure stresses and damage might

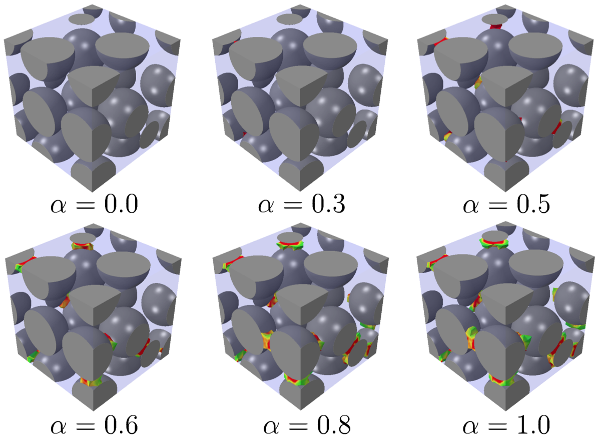

Figure 2: Curing simulation of a polymer showing microstructural damage. Fully developed cohesive cracks are shown in red. α is defined as time/total curing time

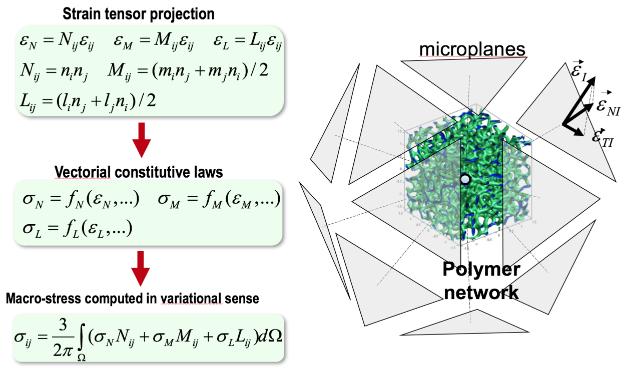

Figure 3: Microplane: a) flow chart for model calculations; b) schematic representation of microplane description of viscoelastic behaviour of a polymer network

rise also later during service life, putting at risk the integrity of the structural element. The foregoing issues are of utmost importance, nevertheless none of the models available in the literature address them within a comprehensive viscoelastic framework. The present research effort aims at filling this knowledge gap. Towards this end, the following tasks will be performed:

Literature study: The PIs will carry out a comprehensive literature review of the main modelling approaches. The study will focus on (1) getting a thorough understanding of the main modelling issues regarding the curing and the non-linear viscous modelling of thermosets and (2) select the most suitable models currently available and identify areas of improvement.

Model selection: Modelling the long term, time dependent behaviour of thermoset mortars needs the identification of suitable models for (1) the cure kinetics, (2) heat transfer, (3) internal stress development and (4) the non-linear viscous damage behaviour.

Cure kinetics can be described phenomenologically by Kamals equation [46] whereas standard heat equations with internal heat generation caused by curing can be adopted for the temperature field. An area which is expected to require improvement is the modelling of cure stresses. To date, a viscoelastic framework capable not only of modelling the emergence of cure stresses but also of capturing damage and then long-term effects on the creep behaviour is lacking.

To address these issue, the PIs will develop a novel computational framework based on the idea of the microplane model which has already been successfully applied to the simulation of several quasi-brittle materials including concrete, rock and polymer composites [8, 7, 9, 49, 44, 70, 11, 12, 20].

In the microplane formulation the elastic and inelastic behaviour is described not by tensors and their invariants but by stress and strain vectors on planes (called microplanes) of various representative orientations in the material microstructure. The microplane approach has a number of advantages that make it the perfect candidate for modelling the onset of cure stresses and their effect on the viscous behaviour of thermoset mortars. Thanks to the application of different microplane orientations, the stresses generated during polymer network formation as well as the various curing-induced physical inelastic phenomena such as matrix microcracking or shear banding are easier to formulate (Fig. 3). Furthermore, interaction of microplanes provides cross effects such as the shear dilatancy and the pressure sensitivity which are aspects highly affecting the non-linear time dependent behaviour as shown in [65].

Consolidation into a unified computational framework: The newly developed formulations will be consolidated into one comprehensive computational framework in the FE software MARS and ABAQUS. Particular emphasis will be devoted to optimizing the code for parallel computing on large computational clusters. This task will provide the *first numerical suite* to model mortars from manufacturing to 50-80 years of service.

Validation and verification: the development of the model will be coupled tightly to the experimental tasks proposed in this project. The formulation of the anticipated physically-based model will deeply rely on the information regarding the main deformation and damage mechanisms at the mesoscale. On parallel tracks, coupon level tests will be used to provide basic validation of the model throughout the entire development process.

D1.1 The comprehensive literature study will lead to a thorough understanding of the main modelling issues. Considering the lack of studies grasping all aspects at the same time, the authors expect to write a state of the art review paper. It is expected that the model implementation and basic verification will lead to at least two international journal papers and as many conference contributions.

4.2.2 Basic and lower-scale material characterization (WP2)

Curing-protocol and -time have direct influence on the crosslinking level of polymers, adhesion to fillers and the development of residual stresses. Consequently, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) will be performed, measuring the temperature difference and the heat flux, crosslinking of polymers and thermal stability of polymers. The composites will be prepared using 3 different curing programs and samples characterized with DSC and DTA. Results will be correlated to mechanical, as well as rheological properties.

Insights into the microstructure as well as a qualitative characterisation of material properties at the microscale will be made by optical- and scanning-electron-microscopy. With these methods the amount of fillers, shape and structure of particles can be accessed. Additional EDX-analysis will be used to discriminate between different kinds of filler particles. For later modelling stages the raw data of nano-CT scans for both products will be made available by the products producers.

The macroscopic shrinkage experiments and standard mechanical tests in tension, compression and shear (see WP3) will be supported by in-situ-SEM-heating experiments up to 100°C in order to study the material under thermal stress and identify possible particle delamination and cracking.

Quantitative data on the microscale as further input for multi-scale simulations will be obtained by nanoindentation. In particular, local hardness and indentation moduli will be measured. A mismatch of Youngs-moduli might be the cause of delamination and crack growth due to thermal fatigue. Nanoindentation provides also access to the postulated curing degree gradients in larger specimens and can be used to probe the interfaces between solid inclusions and polymer matrix. For selected curing levels a modified nanoindentation protocol may be used to determine the local microscale creep compliance as one of the essential input quantities for the visco-elastic multi-scaling, the output of which can be validated against macroscale creep tests, see WP3. Finally, digital image correlation (DIC) will be used in the ESEM to measure the shrinkage of the resin at the microscale and directly observe the developing incompatible strains and potentially also delamination. This information will be used together with the results from nanoindentation to access possible residual stresses.

D2.1 The results of WP2 are the basic material properties of all relevant constituents, information about the meso/micro-structure of the material and the reaction kinetics. The results are expected to lead to at least 1 international journal paper and will be developed in 1-2 master thesis.

4.2.3 Macro-scale material characterization (WP3)

For a long time, the actual material properties of thermoset polymers were considered of subordinate interest in the construction industry and especially the field of fastenings as the behaviour of entire structural systems, involving the polymer as adhesive, were tested. Consequently, only limited data is available going beyond system properties such as e.g. an average bond strength τ. However, the few existing investigations such as e.g. [63] indicate a pronounced temperature but also humidity dependence, on top of the dependence on the level of cross-linking.

Dynamic Mechanical Analysis (DMA) will be used to measure the viscoelastic properties of the assumed homogenous materials and characterize the different curing schemes. Data will be correlated to micro (see WP2) and other macro mechanical tests in order to understand the influence of the curing level on the long term performance of the investigated thermosets. A potential degradation due to thermal load and humidity variations will be also studied systematically with DMA.

In order to characterize the expected volume changes during curing, free shrinkage tests starting with the specimen production and supported by DIC will be performed. The temperature evolution inside the specimen will be measured in parallel.

The macro-scale material characterization in WP3 will entail also a complete set of quasi-static standard tests for tensile strength, Youngs modulus, Poissons ratio, and fracture properties including a dedicated shear test. For each test at least 5 specimens each of at least three curing levels will be tested. The influence of testing temperature and humidity will be covered by 2 additional sets of tests, once for a temperature variation and one for a humidity variation. These environmental variations will be performed for the practically most relevant curing level. The specific temperature and humidity levels will be product and application dependent and will be based on a preliminary screening including DSC and DMA measurements.

For the calibration of the visco-elastic model properties standard 24-hour tensile creep tests performed on dog-bone specimens [26] are required for different curing states as well as testing temperature and humidity conditions. Here, generally the same conditions as described above for the quasi-static characterization will be considered. Additionally, for 1-2 selected material conditions creep tests at different loading levels will be performed to study the non-linear visco-elastic response.

D3.1 The results of WP3 are a full curing degree dependent fracture mechanical and visco-elastic characterization at the macro-scale as basis for the model development, calibration and validation. Data of this quality for the investigated materials are currently not available in the scientific literature. Consequently, 1-2 international journal paper can be expected.

4.2.4 Multi-scale Multi-physics modelling (WP4)

To characterize and capture the behaviour of thermoset polymers at different length scales, multiscale modelling techniques will be utilized. Such approach can provide the means for virtual testing of structural capacity, performance, and, ultimately, also life-time, if structural analysis is coupled with multi-physics and deterioration modelling. The multiscale approach can be based on the analytical micromechanical approach as proposed by [73] or finite element methods. The multiscale multi-physics modelling of polymers has to take into account not only the direct and indirect mechanical loading by curing related eigenstresses but also the evolution of the material properties in course of time, on top of non-mechanical loading e.g. by temperature and humidity. The result of such complex multi-scale material models will be the necessary inputs for the simulation of structural components made of a thermoset polymer such as the mortar layer in adhesive anchor systems or the bonding agent in glued-on laminates for strengthening measures. The mechanical behaviour of the material model will be based on the microplane model [10, 20, 49, 70] and the time, temperature and humidity influence will be taken into account based on the free volume approach [51]. The input information for model setup and calibration but also *validation* will be provided by the appropriate experimental tests found in published reports or provided through additional experimental investigations including but not limited to nanoindentation, macroscopic tension/compression tests, and compact tension test.

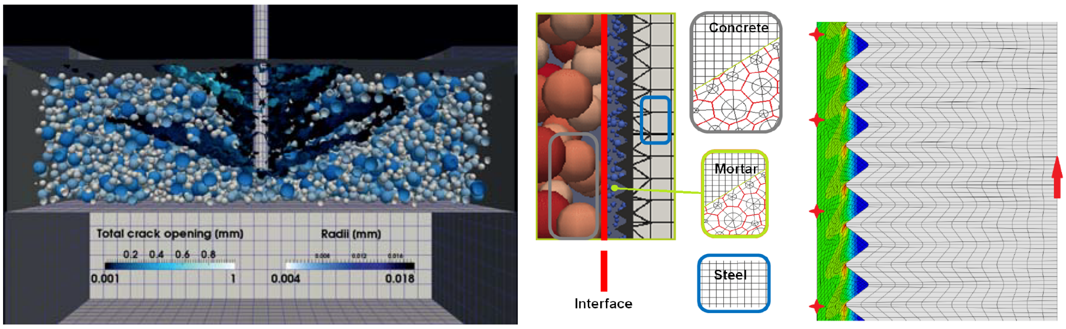

Figure 4: Numerical multi-scaling for polymers in structural engineering, here bonded anchors

D4.1 The results of WP4 are analytical and/or numerical multi-scale models for thermoset polymers, calibrated and validated by experiments. These models are based on the physics of the relevant lower scale phenomena and mechanisms. As such, they are expected to be predictive and allow life-time extrapolations. 1-2 international journal papers can be expected.

4.2.5 Application to complex real-life problem (WP5)

Once implemented, and validated, the capabilities of the proposed computational framework will be showcased by analysing complex engineering problems which require a thorough understanding and accurate modelling of the curing process and creep behavior of thermoset polymers. The study will include an investigation of the onset of defects generated during the curing process of thick carbon fibre unidirectional (UD) composites used for several primary structural components in aeronautics (e.g. window frames or floor grids). A $[0/90]_{10s}$ lay-up will be considered to study the effects of e.g. (1) curing time, (2) curing temperature, (3) composite thickness on the onset of microcracks, and (4) the overall macroscopic properties. The results will be compared to data available from the literature to get a preliminary verification of the model for the application to complex engineering problems.

After the qualitative assessment of the predictive capabilities of the model based on (1) the composite-only case from the field of aeronautics, a comprehensive study on the model's applicability to the prediction of the time-dependent behaviour of (2) bonded anchors (see Fig. 4), and (3) glued-on laminates in interaction with concrete will be carried out. In these cases, a real life design scenario will be simulated. First, the tests required to characterize the model inputs will be carried out on simple laboratory specimens following the procedures suggested in the foregoing sections. Then, the polymer model will be calibrated and used to provide blind predictions (no a posteriori adjustment of the parameters allowed) on the time-dependent behaviour of the structural problem (bonded anchor / laminate). Concrete will be represented by the state of the art discrete multi-physics model LDPM [25] which will be independently calibrated on standard laboratory specimens following an analogous procedure. The results of the system simulations will be compared to time-dependent experimental data on system response performed in a controlled environment (humidity and temperature data will be recorded during the tests and compared with model predictions to provide additional verifications to the theory). The ability to predict the structural response in the proposed three case studies does not only confirm the quality of the model but also provides major insights into the mechanisms and phenomena on lower cases. Finally, the lower scale experiments will allow assessing the ability of the model to capture the real physics of deformation and damage at the lower scale.

D5.1 WP5 will yield validated models for structural applications that in consequence are the basis for further basic research on structural aspects, product development, and improved design codes in the respective fields. Considering the complexity of the three chosen case studies, it can be expected that each leads to a journal paper.

Table 1: Working and dissemination plan; personnel involved and its expertise/interaction (work load according to initials, see Section 5.2)

	Time schedule			Work load [%]						Dissemination of results
WP	1st year	2nd year	3rd year	RW	HL	JV	GS	MS	PS	(intended)
WP 1				10	10	40		10	30	*Review paper on models*
WP 2				10	10		20		60	*Journal paper on aging material characteristics*
WP 3				10	10		20		60	*Journal paper on multi-scale experiments*
WP 4				10	5	20		10	55	*Journal paper on multi-scale modelling/prediction*
WP 5				10		30		10	55	*Journal paper on structural applications*

4.3 Time schedule

The time schedule is organised along the main themes of the project. The work program is extensive, however, the authors believe that the scope of the proposed work is feasible within the project duration of three years considering the prior work of the applicants in related areas. This project will provide both novel contributions and a synthesis of previous work, exploiting fully the existing modelling capabilities, computational frameworks, and data sets.

5 Project management and resources

5.1 Research Institution

The Institute of Structural Engineering (IKI) as well as the Institute of Physics and Material Sciences (IPM) at the University of Natural Resources and Life Sciences (BOKU) are equipped with all the required experimental tools and scientific software applications.

IPM offers a broad range of state-of-the-art materials characterization methods from the macroscopic to the nanometre scale such as: fully equipped mechanical testing laboratory with testing devices on various scales, ultrasonic fatigue testing devices, micro-deformation stage, micro hardness, contact angle measurements, etc. A dedicated nanostructure characterization laboratory has been established in 2012 and features a modern field emission environmental scanning electron microscopy (ESEM, FEI Quanta 250 FEG) equipped with in-situ deformation stages and nanoindenter and small- and wide-angle X-ray scattering (RIGAKU S-Max 3000). A digital image correlation (DIC) system is available for use in mechanical testing or also in the ESEM (local deformations, cracking, anisotropic materials shrinkage etc.). DMA and DSC equipment are available at BOKUs department of Material Sciences and Process Engineering, Institute of Wood Technology and Renewable Materials, and will be made available for this investigation free of charge.

IKI offers a state of the art structural laboratory, equipped with load frames and sensors suitable for material characterization and testing on the system scale, and has access to state of the art software applications and numerical analysis tools for structural investigations: ABAQUS, ATENA, SOFISTIK, and MARS to name a few. Further applications include the high language environments Matlab and Mathematica, and FREET and VAP for statistical evaluation and reliability analysis. Finally, for demanding multi-scale multi-physics simulation tasks and parametric studies the Austrian initiative on high performance computing, the Vienna Scientific Cluster, specifically VSC3, is available.

5.2 Human resources

The project team LiMoPoSE is an interdisciplinary group of internationally active researchers, including a structural engineer (Wendner), material scientists (Lichtenegger, Sinn), a computational mechanician (Vorel) and a composite expert (Salviato).

The project leader is **Roman Wendner** (RW, 20%), currently Director of the Christian Doppler Laboratory LiCRoFasT at the University of Natural Resources and Life Sciences Vienna, Austria, where he received his PhD degree in Structural Engineering in 2009. In the years 2011 to 2013 he worked as research fellow at Northwestern University (NU) on topics related to the long-term performance prediction of concrete structures, fracture, and creep. After his return to BOKU he completed his habilitation in 2015. Dr. Wendner authored more than 27 SCI journal papers, 90 conference papers and 7 book chapters. He received several awards for his early research work, among others the award of excellence from the Austrian Ministry of Education and a Erwin Schrödinger Fellowship in 2011. Dr. Wendner is member of several technical committees of *fib*, ACI and RILEM, and is the chair of ACI 209-D on numerical methods in creep.

Co-PI. **Helga Lichtenegger** (HL, 20%): Prof. Helga Lichtenegger is head of the Institute of

Physics and Materials Science (IPM) and deputy chair of the Department of Materials Sciences and Process Engineering at BOKU. She received her Physics PhD at the University of Vienna in 2000 and has gained research experience at the University of Leoben, Austria, the University of California Santa Barbara (U.S.), the Vienna University of Technology (where she completed her habilitation in 2005) and industry experience at RUAG space GmbH (Austria). Her research is focused on micro- and nanocomposite materials from biological and non-biological origin, with special emphasis on the relationship of nanostructure and mechanical properties. She has worked on wood, bone, and bio-inspired polymer composites. Lichtenegger has top ranking journal publications and has been awarded the Erwin Schrödinger (2001) and the Hertha Firnberg (2003) fellowships by FWF. She is a member of several committees, e.g. the scientific advisory boards of the Institute of New Materials in Saarbrücken (Germany), the Helmholtz Zentrum Geesthacht (Germany) and the beamtime allocation committee at The European Synchrotron (ESRF, Grenoble).

Jan Vorel (JV, 50%) is an assistant professor at the Czech Technical University (CTU) in Prague, Faculty of Civil Engineering. He graduated from CTU in 2006 (Master of Civil Engineering), and obtained the doctoral degree at Faculty of Civil Engineering in 2009. He spent one year as research fellow at the Stellenbosch University and one year as postdoctoral fellow at the Northwestern University (NU). His research activities fall into the field of computational mechanics. A special interest is focused on the multi-scale analysis of heterogeneous materials and composites.

Gerhard Sinn (GS, 20%) is a PostDoc researcher at the institute of Physics and Materials Science (IPM) in the filed of materials science. He graduated 1998 in technical physics at Technical University of Vienna and received his PhD 2005 from BOKU University with a thesis on the surface properties of machined wood. His special interest is in micromechanics of hierarchical materials, machining of materials and electron microscopy.

Marco Salviato (MS, 20%) received his PhD degree in Mechanical Engineering from the University of Padova (Italy) in 2013. His doctoral research focused on multi-scale computational models for and the experimental characterization of polymer nanocomposites. Before joining the University of Washington in 2015 as Assistant Professor, Dr. Salviato worked at Northwestern University as a Postdoctoral Fellow, and later as Research Assistant Professor. Currently, he leads the Laboratory for Multiscale Analysis of Materials and Structures at the William E. Boeing Department of Aeronautics and Astronautics. His research focuses on the development of materials with unprecedented properties and computational models for the design of next-generation aerospace structures.

Two PhD students will be funded by the project (both 75%) who will be responsible for preparing and running the experimental and numerical studies and simulations, where extensive manpower is expected. These will be supported by at least 6 Master students.

5.3 Collaboration and synergies

The applicants bring to the table the experience and skill set to successfully complete the proposed research. Dr. Wendner, Dr. Vorel and Dr. Salviato have a long history of successful collaboration tracing back to their research fellowships at NU during which they developed close ties with one of the foremost experts in creep, fracture mechanics, mechanics of composites and the inventor of the microplane model, **Prof. Z.P. Bažant**. Further collaborators in the United States as well as Europe who work in related fields will bring in additional insights and stimulate research.

All computational models will be prototyped as ABAQUS user subroutines and later implemented in a computational simulation framework that was developed for grid-computing and the solution of large-scale multiphysics simulations in a discrete or continuum framework. Related efforts will be supported by the Engineering and Software System Solutions (ES3 inc., Sand Diego, United States), a company with which the applicants pursue a productive collaboration for already several years.

This project idea was motivated by the ongoing research within the Christian Doppler Laboratory on the Life-Cycle Robustness of Fastening Systems which focuses on the SYSTEM behaviour and especially the concrete component. During that work a significant lack of basic models and understanding regarding the aging visco-elastic behaviour of thermoset polymers was identified. While this is an independent project synergies in the application WP can be expected.

5.4 Costs

The majority of costs (85%) is dedicated to human resources which are required to perform the necessary amount of simulations and experiments. The remaining requested funds cover mainly materials for testing, travel costs for project meetings and conference attendance, costs for open access publication and a minimum of costs for the support in model implementation and grid computing. The financial planning is described in detail in the attached financial table.

Personnel: Given the extensive work programme, one Post-Doctoral researcher (Dr. Vorel) and two PhD Students are needed. The mathematical formulations and numerical solution schemes proposed in the work packages for aging visco-elasticity in a multi-scale framework are highly complex and, because of this, a researcher with substantial prior modelling experience is essential. Dr. Vorel is an ideal choice as he has indeed extensive experience in the subject area (see his publication list). It would be very difficult for a PhD student to acquire the required level of expertise during the project duration. Two 75% positions for PhD students are applied for, one focusing on the development, calibration and validation of the computational models, the other one on the material testing. It is anticipated that the PostDoc and the PhD students will closely collaborate under the supervision of the applicant (Doc. Wendner) and Professor Lichtenegger. Professor Salviato will contribute his expertise free of charge, profiting from the interdisciplinary approach. Dr. Sinn will support the experimental work on nano-indentation and ESEM as senior researcher at the Institute of Physics.

Supplies and expendables: The technical infrastructure and software equipment of the institutes provide most of the tools required. Only very few tasks need to be outsourced. One such task are CT scans. An additional amount is requested for highly specialized external support in implementing the multi-scale and multi-physics simulation schemes making use of grid computing. Machine hours are contributed generally free of charge by the applying parties and their partners with the exception of the ESEM, due to the high costs for the quickly degrading light source.

5.5 Dissemination of results

The results of this project will be disseminated through two main channels. The first are publications in peer reviewed journals of international rank, see Table 1. The second channel are technical reports and pre-normative documents. Furthermore, two PhD theses and further 6 master theses are expected which will contribute to strengthening the University as a competence centre for the life-time prediction of construction materials

5.6 Ethical aspects

In all phases of the project the research team will strive for quality and integrity. Where applicable the confidentiality and intellectual property rights of third parties will be respected, also with regard to publications. Experimental work in this project will be limited to basic material characterisation on small scale samples with minimum environmental impact. No substantial direct harm to the nature or human life is expected. Potential positive effects on the economy due to the increased accuracy in performance assessment and cost-efficiency in e.g. maintenance planning and life-time / life-cycle design will compensate by far the environmental impact of the work in this research project.

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