Composite and Multi-material Joints in Body Applications

Tim Welters, Christian Holtgrewe, Manuel Schiel
Henkel AG & Co. KGaA

Abstract
Numerical modeling of materials and processes has become more and more important for automotive applications. This in particular applies to materials like composites which are in many cases selectively used where they are most effective and therefore thus are often combined with more traditional materials like steel, aluminum or magnesium. Joining these material combinations by adhesive bonding raises two major challenges. First, these are related to the complex anisotropic properties of the fiber reinforced materials. Therefore in the first part of this paper the impact of this anisotropy on the stress state in a bond line is discussed. Second, the mismatch of thermal expansions between different materials plays an increasingly important role, especially if assembly in the body shop and thus oven cure is required. A lot of effort was recently put into the development of modeling techniques which are able to take into account the curing processes and are able to predict residual stresses which are locally superimposed with the stresses from external loads. Thus the second part of this paper starts with a discussion of the implementation of a kinetic model to predict the conversion level of an adhesive for arbitrary temperature histories and the determination of the model parameters from experimental data. On this basis a viscoelastic material model which takes into account the current level of conversion and assumes a chemo- and thermo-rheological simple material behavior is presented. After adding a plastic contribution to this model a calculation and validation example is shown.

Introduction
There is a clear trend visible in automotive and also other industrial applications to utilize the full lightweight and performance potential of all available materials. Two main trends can be identified in this context: The utilization of lightweight metals like aluminum or magnesium and the introduction of fiber reinforced materials. Figure 1 shows the relative costs and the weight saving potential of different materials and solutions. To maximize the weight saving at reasonable costs most of the new designs will use expensive materials only for these applications with a maximum weight saving potential. Consequently the number of components made from a mix of dissimilar materials and therefore also the number of multi-material joints will increase. Adhesive bonding is the favorable method in many cases since the fiber-matrix system stays unaffected.

The new materials and material combinations require optimized joining technologies and create new challenges for designers, material developers and modeling specialists. Technical challenges which have to be mastered from the perspective of the bonded joint are e.g.

- the simultaneous adhesion to dissimilar substrates,
- the thermal sensitivity of composites which often prevent standard oven processes and drives bonding processes into the assembly lines
- residual stresses from processes and thermal stresses from service loads due to incompatible thermal elongation properties and
- the anisotropic strength and stiffness and specific failure modes of substrates made from fiber-reinforced plastics (FRP).

Today most product development and innovation strategies heavily depend on reliable and validated models and numerical tools to reduce the number of development cycles. In case of the development of new materials these numerical methods are often the only possibility to understand the underlying principles and relationships. This in particular applies to the development of new adhesives and bonding solutions because the adhesive is only a small yet, in particular if it fails, important part of a large component. As performance requirements are mostly defined on a component level it is necessary to translate these into a material specification for adhesives. It is even more difficult if residual stresses are important because an experimental approach will rely on the size of a tested structure. Scaling the size of the test specimens down to a typical laboratory scale is in general not possible.
In addition residual stresses are difficult or even impossible to measure in thin bond lines and if the residual stress does not exceed the strength of the material it is only recognized if its superposition with service loads produces an unexpected early failure.

In the following two of the above aspects of adhesive joints between dissimilar substrates or between substrates made from fiber reinforced materials are discussed in more detail with a focus on strength assessment and numerical methods: The interaction of laminate design and stresses in the adhesive and the formation of residual stresses in bondlines in the presence of a curing adhesives.

**Bondline stresses and strength in consequence of the composite design**

A typical joint geometry for bonding is that of a single- or double-lap joint. The valuable VDI guideline 2014 [1] already includes a section discussing some of the aspects which are relevant for bonded joints between composites. Composite joints run the risk of failing by delamination within the laminate if an unfavorable lay-up or adhesive is used. Using a wrong design may very well produce intra- and interlaminar stresses which are more critical than the load in the adhesive due to e.g. the effect of local strain magnification. When these stresses exceed the resistance against inter-fibre fracture the laminate fails [2]. Thus from the perspective of the laminates the bending moment and the normal stresses which are transferred into the laminates should be minimized.

The first advice which is given in the VDI 2014 guideline is that of using a double-lap joint to prevent normal stresses at the adherend edges. In case of a large-volume production which is required for automotive applications this will be prohibitive in many cases. This guideline also suggests to use a tapered overlap for single-lap joints to moderate the peel stresses at the adherend edges if these are causing the joint failure. Again, the feasibility for automotive applications is at least questionable. In general it can be concluded that the peel stresses at the end of a single-lap joint are inversely proportional to the adherend stiffness. If reasonable properties of the adhesive and the composite material are assumed the equations given in the guideline show that flexible adhesive joints will result in lower shear and normal stresses when loaded by a constant force despite the increase in load eccentricity created by a typically thicker bond line. This is also in line with the latest adhesive developments for FRP bonding which are all rather tough and flexible materials.

However, the VDI 2014 guideline primarily looks onto the problem from the perspective of the laminate and not the adhesive and thus an important aspect of composite bonding is not discussed but should nevertheless be considered when designing composite parts with bonded joints. Much of the critical load components in a bonded joint are out-of-plane loads from the laminate perspective. In combination with an in many cases significant bending load caused by an eccentric load application the specific layups of the substrates becomes important also for the stress state in the bondline. If the substrates are not only simple uniaxial laminates with the fibers oriented along the overlap direction the potential couplings of the different in-plane and out-of-plane deformations of the laminates can generate a complex inhomogeneous stress state in the adhesive. Also a bending deformation along the width direction of the overlap, i.e. with the well-known stress peaks at the edges, will be present. This is quite unfamiliar compared to the situation for metallic substrates and adds significant complexity. The typical assumption of the independence of the lap-shear strength from the width of the specimen which used for testing is no longer valid.

Today the assessment of composites is mostly based on the classical laminate theory (CLT) and different strength criteria are available, e.g. based on the theory of Puck using stress action planes [1,2] or also global stress criteria based on the work of Tsai and Wu [3]. Today these approaches allow a sufficiently accurate prediction of laminate failure at least for the plane stress situation while three dimensional stress states and out-of-plane loads like they are often observed at points of load application and joints pose still a challenge.

To understand the implications of the laminate layup onto the stress state in the adhesive it is helpful to utilize the tools provided by CLT for thin plates, i.e. assuming a plane-stress situation and neglecting the shear deformation in the planes aligned with the thickness direction so that straight line elements which are initially perpendicular to the mid-plane remain straight and perpendicular during deformation (Kirchhoff hypothesis). In laminate theory in many cases fluxes are used, i.e. forces normalized to the width dimension, instead of stresses, i.e. forces normalized to the cross-section. The fluxes can be determined by integrating the laminate stresses over all layers. If \( \sigma_x \) and \( \sigma_y \) are the in-plane normal stresses and \( \tau_{xy} \) is the in-plane shear stress then the in-plane \( \mathbf{n} \) and out-of-plane fluxes \( \mathbf{m} \) are given by

\[
\begin{align*}
\begin{pmatrix}
  n_x \\
  n_y \\
  n_{xy}
\end{pmatrix} &= \int_i \begin{pmatrix}
  \sigma_x \\
  \sigma_y \\
  \tau_{xy}
\end{pmatrix} \, dz \equiv \mathbf{n} \quad \text{and} \quad \\
\begin{pmatrix}
  m_x \\
  m_y \\
  m_{xy}
\end{pmatrix} &= \int_i \begin{pmatrix}
  \sigma_x \cdot z \\
  \sigma_y \cdot z \\
  \tau_{xy} \cdot z
\end{pmatrix} \, dz \equiv \mathbf{m}.
\end{align*}
\]

Here \( i \) is the thickness of the laminate and \( z \) corresponds to the thickness direction of the laminate. Due to the potential inhomogeneity of the laminate along the \( z \)-direction the integrals have to be evaluated layer by layer and the result is not independent from the choice of the origin. In case of a symmetric laminate usually the mid-plane or a neutral plane is aligned with the origin in the \( z \)-direction. The out-of-plane shear distortions and shear stresses are missing because of the assumptions of the Kirchhoff plate theory. Normal stresses in \( z \)-direction are also missing because for an isolated laminate the total integral over the thickness should vanish if the forces in the laminate are balanced. This is no longer true in the neighborhood of a bond line because here the adhesive will carry normal loads and may transfer significant out-of-plane shear loads into the laminates and the forces are only balanced over the joint as a whole. In a first step it is really helpful to stay with the laminate itself and the plane-stress assumption because the complex geometry of a bonded joint
can no longer be handled in this simple way and numerical methods are necessary to determine the complex stress state like it will be shown below.

The deformation of a laminate for the plane stress situation is usually expressed via the deformation measures shown in Figure 2 which can be combined in one vector containing all distortions relative to a reference plane denoted by the index “0”:

\[
\begin{pmatrix}
\varepsilon_x \\
\varepsilon_y \\
\gamma_{xy} \\
\kappa_x \\
\kappa_y \\
\kappa_{xy}
\end{pmatrix}_0
\]

(2)

The elastic law of the plane-stress laminate can now be written in the following form

\[
\begin{pmatrix}
\nu \\
\mu
\end{pmatrix}
= 
\begin{pmatrix}
A_{11} & A_{12} & A_{16} \\
A_{12} & A_{22} & A_{26} \\
A_{16} & A_{26} & A_{66}
\end{pmatrix}
\begin{pmatrix}
\varepsilon_x \\
\varepsilon_y \\
\gamma_{xy}
\end{pmatrix}_0
\]

The different sub-matrices are

- the membrane (extensional) stiffness matrix \( A \),
- the (extension-bending) coupling stiffness matrix \( B \) and
- the plate or bending stiffness matrix \( D \)

which can be calculated if the elastic properties of the individual layers are known.

The sub-matrices are

- \( A \) for in-plane (shear and extension)
- \( B \) for out-of-plane (bending or twisting)
- \( D \) for plate (bending)

Within this relationship between distortions and stresses couplings may exist between

- in-plane (shear and extension) and out-of-plane (bending or twisting) directions if \( B_{11} \neq 0 \),
- in-plane shear and extension if \( A_{16} \neq 0 \) and/or \( A_{26} \neq 0 \) and
- out-of-plane bending and twisting if \( D_{16} \neq 0 \) and/or \( D_{26} \neq 0 \).

In case of the bondline stresses in the above lap-shear joint it would be preferred to suppress all this couplings, eventually with the exception \( B_{11} \neq 0 \), so that only a curvature along the x-axis is generated by in-plane loads. Unfortunately this is unrealistic for most real applications. As an example a quasi-isotropic layup like it is commonly used in e.g. aerospace applications may be used. The smallest quasi-isotropic layup possible is a symmetric stacking of six unidirectional layers with 60° angles between the fiber directions e.g. a laminate with the configuration (0/+60/-60). Although this is a symmetric and balanced laminate either the in-plane and out-of-plane directions are coupled or the out-of-plane bending and twisting modes. If now such a laminate is bonded, the load in the adhesive will strongly depend on the local fiber directions because, depending on the joint location and geometry, the loading is not necessarily aligned with the 0° direction of the laminate.

As was already mentioned above, the stress state in the neighborhood of a single-lap joint is too complicated to handle it analytically and thus an elastic FEA model was used for this purpose like it is shown in Figure 3. A simple single lap-shear specimen is fully clamped...
at one end and a constant force is applied to the other end which also takes up bending moments. The substrates are modeled with six transverse isotropic elastic layers with typical properties of carbon fiber reinforced materials. The adhesive is isotropic elastic with common values of a structural epoxy material. The detailed numbers are not documented here because only the principal relations are in the focus.

Exemplarily the equivalent stress along a line perpendicular to the loading and at the center of the bond line close to the edge of the adhesive was evaluated for three different orientations of the laminate each rotated by 60°. Figure 3 shows the corresponding layups with the 0° direction aligned with the load application and figure 4 contains the stress results.

It is clearly visible that depending on the laminate orientation the stresses are very different and in most cases far away from being homogeneous along the width direction. The average stress level strongly depends on the bending stiffness of the substrates. Configuration 3 with the 0° layers at the surface of the laminate provide the highest bending stiffness as was to be expected. For configuration 2 the asymmetry along the width direction is at a maximum because the coupling coefficient $D_{26}$ is large and produces a strong coupling between the bending distortions $\kappa_x$ and $\kappa_{xy}$ and the corresponding moments $m_x$ and $m_{xy}$.

![Fig. 3: Bonded joint between two different configurations of quasi-isotropic laminates](image)

**Fig. 3:** Bonded joint between two different configurations of quasi-isotropic laminates

![Fig. 4: Equivalent stresses at the edge of the bondline along a line in the width-direction of the specimen](image)

**Fig. 4:** Equivalent stresses at the edge of the bondline along a line in the width-direction of the specimen.

In summary the following may be noted: The complexity of a good joint design significantly increases when fiber reinforced substrates have to be bonded. In contrast to the design process of a fiber reinforced component which is usually optimized with regard to the service loads and with sufficient accuracy based on the assumption of a plane-stress situation the bond lines often require a more sophisticated approach for both the adhesive and the substrates. Depending on the local fiber orientation in the direct neighborhood of the bond line the stress state in the adhesive may change drastically which has to be taken into account during strength assessment and design optimization. Furthermore the common approach of reducing the complexity of experimental testing by using small lap-shear specimens is limited due to the potential inhomogeneity of the stress along the width direction with significant stress peaks at the edges. Simultaneously the normal stresses transferred from the adhesive into the laminate require a complex three-dimensional assessment methodology. Classical nominal stress concepts will reach their limits immediately. Numerical methods with a high spatial resolution will be helpful to handle this situation which combine advanced models of the laminated including out-of-plane loads with detailed models of the adhesive. The latter ones are already highly developed for many types of adhesives, e.g. the elastoplastic continuum mechanics models including damage which are often used for structural adhesives [14-16]. For large structures with thin bond lines this will pose a problem due to the strong demand for computing power required for the high spatial resolution. Some work still has to be done to investigate how approaches like e.g. cohesive zone elements can be reliably combined with advanced laminate models.
Numerical modelling methodology for curing induced residual stresses in a bond line

In order to numerically predict the mechanical behavior of a thermosetting adhesive during the BIW process it was necessary to develop a material law for adhesives, implemented in form of a user material subroutine for commercially available FEA programs, which takes into account the time, temperature and conversion depended properties of the adhesive.

In order to describe the material behavior during the process as a function of the curing state of the adhesive a measure reflecting the progress of the curing reaction us needed. A typical value of this type is the conversion \( \alpha \) which can be determined e.g. from differential scanning calorimetry (DSC) measurements. The result of such measurements which were carried out exemplarily for a two-component epoxy based adhesive is shown in figure 5 on the left side. The heat flow through an adhesive sample is measured against the flow through an identical but empty cup when heated with a constant temperature rate \( \beta \) (10 K/min in this case). The difference signal \( \Phi \) is the measurement signal shown in figure 5.
From this information it is now possible to determine the conversion under the assumption that the degree of curing is proportional to the heat generated by the reaction. If \( H_0 \) is the reaction enthalpy and \( \Delta H \) the heat generated by the curing reaction until some given point in time \( t \) then the conversion can be defined in the following way:

\[
\alpha(t) = \frac{\Delta H}{H_0} = \frac{\int_0^t \phi(t') dt'}{\int_0^\infty \phi(t') dt'}
\]  

(4)

The result of this evaluation is shown in the right diagram of figure 5.

For this way of determining the conversion it is required that the reaction enthalpy is to a high degree independent of the heating rate which is also important for the subsequent selection of an adequate kinetic model in the following. This was up to now the case for several different types of adhesive we tested including one- and two-component epoxy based adhesives and also hot-curing rubber based systems.

Although it is possible to measure the conversion progress for nearly arbitrary heating rates this is not sufficient to determine the curing progress in a large component. In this case the local time-temperature history is not known a priori and possibly strongly inhomogeneous and a model to predict the conversion rate as a function of this history is needed. There are dozens of different methods existing which are often applicable only to specific types of reactions. Nearly all of them are based on the following basic equation which relates the conversion rate to two functions splitting the dependencies multiplicatively in a temperature dependent and a conversion dependent part. The temperature dependent part is usually assumed to follow the Arrhenius equation, i.e.

\[
\frac{d\alpha}{dt} = K(T) f(\alpha) = A e^{\frac{E}{RT}} f(\alpha)
\]

(5)

with the kinetic triplet of activation energy \( E \), temperature \( T \) and pre-exponential factor \( A \) (\( R \) is the ideal gas constant). For the reaction model \( f(\alpha) \) a lot of different equations exist. A typical problem is that it is difficult to estimate the absolute scale of the activation energy because not only changing \( E \) but also changing \( A \) and \( f(\alpha) \) has a direct impact on the conversion rate.

Two general types of approaches exist to model the curing reaction on this basis. On the one hand the so called differential approaches are used. This allows directly using equation (5) as the starting point and the experimental values can be used without further integration, i.e. with \( \dot{\alpha} = \phi/H_0 \). Although these equations are often easier to handle the disadvantage is the scatter of differential measurement signals. In many cases the integration of the heat flow over time and the corresponding integral kinetic equations provide a more stable situation. To determine an absolute value for the activation energy iso-conversional methods are helpful. Both, the differential approach based on the work of e.g. Friedman [4] and an integral method based on the work of Vyazovkin [5] were used with good success several times for different adhesives.

Friedman [4] and others [6,7] used the logarithm of eq. (5), i.e.

\[
\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT}
\]

(6)

to determine \( E \) from the slope of the curve \( \ln(d\alpha/dt) \) versus \( 1/T \). The isoconversional aspect of equation (6) gets clear when realizing that at a constant extent of conversion the conversion rate is only a function of the temperature. Using DSC experiments at different heating rates it is now easy to obtain data on the variation of the conversion rate at a constant extent of conversion which allows directly the determination of the activation energy with the help of equation (6). Figure 6 shows the data for the adhesive already discussed above. The four black lines in the left diagram denoted with the different heating rates in the legend are the curves calculated from the logarithm of the conversion rate. These curves are shown for selected measurements only to provide a better overview. The symbols are points of constant conversion on these type of curves derived from all available measurement data (seven different heating rates in this case). Finally the black dashed lines are least squares fit to the points shown. The slopes of the dashed lines are proportional to the activation energy for this conversion value. Similar energies can also be determined for all other conversion values. The final result of this evaluation is shown in figure 6 on the right.
This value can now directly be used in the equation (5) i.e. the activation energy is taken to be a function of the conversion $E_\alpha$. Another possibility is to use a single value for the activation energy, e.g. the average, and include the dependency on conversion into the function $f(\alpha)$. This was done for the results presented in the following. Now the remaining parts of equation (5) have to be determined. To do this an assumption for the reaction model is necessary. Helpful in this context is the following function which can be easily evaluated for the experimental data:

$$y(\alpha) = \frac{d\alpha}{dt} = \frac{\nu}{e^{RT}} = Af(\alpha)$$

Figure 7 shows the values for all the experimental data at different heating rates (thin lines in the left diagram). To get rid of the experimental scatter and simplify the evaluation not the experimental values themselves but a fifth order polynomial approximation to each experimental curve was used. To separate a potential dependency of the pre-exponential factor on the heating rate and the reaction model the values of $y(\alpha)$ are plotted in a normalized form. This is possible because the reaction function is by definition normalized to 1.

The curves obviously do not strongly depend on the heating rate and the curve shape is typical for a two-parameter autocatalytic reaction model of the Šesták-Berggren type [8], i.e.

$$f(\alpha) = \alpha^n(1-\alpha)^m$$

The auto-catalytic behavior is provided by $\alpha^n$ term which increases the conversion rate with progressing conversion. The $(1-\alpha)^m$ part accounts for the decreasing probability to find reaction partners. A problem of this simple type of model is the vanishing conversion rate for an initial $\alpha$ of 0. To avoid this situation a zero conversion rate value $k_1$ can be added to the equation:

$$f(\alpha) = (k_1 + k_2\alpha^n)(1-\alpha)^m$$

**Figure 6**: Arrhenius plots and isoconversion lines (left) and variation of the activation energy with the conversion (right)

**Figure 7**: Left: Variation of the function $y(\alpha)$ with the conversion for measurements at different heating rates (solid lines) and the best fit of the kinetic model (dashed line) Right: Pre-exponential factor $A$ calculated from $y(\alpha)/f(\alpha)$
In a first step the values for the two conversion rate constants can be simply assumed to be $k_1 = 0.0001$ and $k_2 = 1$, i.e. the first constant is only used to kick-off the conversion and the impact of the exact value on the further progress of the reaction is small. Using a least-squares non-linear fitting algorithm to adjust the parameters of equation (9) optimal values for the parameters $n$ and $m$ can be determined. Figure 7 shows the function $f(\alpha)$ based on these parameters in form of the dashed black line.

Now all terms in equation (5) are known except for the pre-exponential factor. Simply dividing $y(\alpha)$ by the now known reaction model $f(\alpha)$ gives an estimate for its value. The evaluation for all the experimental data points is shown on the right side of figure 7 as a function of $\alpha$. An average value can be used as a starting point for further optimization. At the beginning and the end of the reaction the values of $A$ which are calculated in this way typically show a large scatter because here the divisor $f(\alpha)$ is rather small and thus small deviations from the ideal curve shape have a strong impact on the value of $A$.

The parameters of equation (5) which were estimated in the described way were now used as a starting point for a last additional non-linear multivariate optimization step. The optimization function was defined by directly comparing the experimental $\alpha(t)$ curves with the predicted ones on an error square basis. For this the kinetic differential equation was integrated using Romberg’s method [9].

The conversion curves for a constant heating rate based on the final set of optimal values are shown in figure 8 together with the experimental data. In addition to the tests with constant rate several tests at isothermal conditions were done and the corresponding curves are also shown in figure 8. These curves were not used for the optimization but only for validation.

Using this kinetic model it should now be possible to predict the conversion for arbitrary temperature-time histories. The full equation and its numerical integration was implemented in an FEA user material law slightly extended to the following form:

$$\frac{d\alpha}{dt} = A_\alpha e^{\frac{E_\alpha}{RT} \left(k_1 + k_2 \alpha^m \right)} (1 - \alpha)^n \frac{2}{1 + e^{D(T)(\alpha - \alpha_c)}}$$

The last additional term accounts for a diffusion controlled reaction kinetics when the conversion exceeds a critical value $\alpha_c$ although this was not required for the above experimental results because the curing took place at elevated temperatures, i.e. where temperature is always above the temperature of vitrification and the reaction is not driven by diffusion. For a 2C adhesive this is no longer true when it is cured at lower temperatures. The activation energy and the pre-exponential factor were defined as function of $\alpha$ to allow the reproduction of other model-free approaches and arbitrary reaction models with the same implementation.

![Figure 8: Comparison of predicted (solid) and measured (dashed) conversion vs. time plots for different heating rates and different isothermal curing conditions (on a logarithmic time scale).](image)

The next step is now to define a relation between the degree of conversion and the mechanical behavior of the adhesive. The approach presented here is based on the following two assumptions:

- The conversion dependent material behavior can be modeled on the basis of a linear viscoelastic material description.
- The typical temperature dependent elastoplastic behavior of adhesives takes place on another time scale, i.e. the plastic deformation is instantaneous in comparison to the viscoelastic processes.

The first of the two above assumptions was already made by several authors and presented in various publications [10,11].

Figure 9 shows this material behavior in form of a rheological analogy using springs, dampers and a friction element. The left part consisting of springs and dampers is a typical generalized Maxwell model often used as a phenomenological approach for polymers
while the friction element represents an elastoplastic part. The Maxwell model represents a linear viscoelastic material for which the Boltzmann superposition principle is valid.

The general strategy to develop the necessary constitutive equations is now the following: The total strain is additively decomposed into the following strain contributions:

\[ \varepsilon = \varepsilon^e + \varepsilon^v + \varepsilon^p + \varepsilon^{th} + \varepsilon^{sh} \tag{11} \]

with the elastic strain \( \varepsilon^e \), the viscous strain contribution \( \varepsilon^v \), plastic strain \( \varepsilon^p \), thermal strain \( \varepsilon^{th} \) and the curing shrinkage \( \varepsilon^{sh} \).

This way of separating the strains is a consequence of the second assumption above. If the time scales of viscous and plastic deformations become similar this separation is no longer possible and the strain decomposition has to be done by using a combined viscoplastic strain \( \varepsilon^{vp} \) instead of \( \varepsilon^v + \varepsilon^p \) and a full viscoplastic model has to be implemented.

Both thermal strain and curing shrinkage act purely volumetric, i.e. for the thermal strain the following equation is used:

\[ \varepsilon^{th} = \alpha^{th}(T - T_{\text{ref}}) \mathbf{1} \tag{12} \]

if \( \alpha^{th} \) is the coefficient of thermal expansion and \( T_{\text{ref}} \) the reference temperature which corresponds to a zero thermal strain. The curing shrinkage is acting in a similar manner. The difference is that it is assumed to be proportional to the conversion \( \alpha \) instead of the temperature, i.e.

\[ \varepsilon^{sh} = \alpha \varepsilon^{sh}_{\text{vol}} \mathbf{1} \text{ with the value for volume shrinkage } \varepsilon^{sh}_{\text{vol}} = \frac{\Delta V}{V_0}. \tag{13} \]

The implementation of the generalized Maxwell element, i.e. the left part of the mechanical model shown in figure 9 is relatively easy. Figure 10 shows this part of the mechanical model together with the material parameters typically used to characterize the individual springs and dampers, i.e. the equilibrium shear modulus \( \mu_i \) and the shear modulus \( \mu_i \) and viscosity \( \eta_i \) for each branch \( i \) of the Maxwell element.

The constitutive equation for each single part of the Maxwell element, i.e. the elastic relations \( \sigma_j = \mu_j \varepsilon_j \) and the viscous \( \sigma_j = \eta_j \dot{\varepsilon}_j \) for the stresses in the individual branches, in combination with the Boltzmann superposition principle delivers the well-known integral representation of linear viscoelasticity \([12,13]\) which can be solved with the help of a Laplace transform. In a one-dimensional stress case this can be written as

\[ \sigma(t) = \int_0^t \mu(t - t') \varepsilon(t') dt' \tag{14} \]

with the relaxation function.
To implement a user material law for finite element codes an incremental stress update algorithm is needed which meets the requirements of common FEA codes. For a purely isochoric viscoelastic behavior the stress in the Maxwell element in time step \( n + 1 \) is the sum of a purely elastic stress and a modification taking into account the viscous contribution from each of the \( N \) branches of the generalized Maxwell element

\[
\mu(t) = \mu_s + \sum_{j=1}^{N} \mu_j e^{-t/\tau_j} \quad \text{and the relaxation times } \tau_j = \eta_j / \mu_j .
\]  

(15)

The evolution equation for the history variables of a generalized Maxwell element can be calculated in the following way for the isochoric part \([12,13]\)

\[
h_{n+1}^j = e^{-\Delta t / \tau_j} h_n^j + \gamma_j \frac{1 - e^{-\Delta t / \tau_j}}{\Delta t / \tau_j} \left[ \text{dev} \sigma_0^{n+1} - \text{dev} \sigma_0^n \right].
\]  

(19)

and in a completely similar way for the volumetric part.

In this expression the relaxation functions are defined in a normalized form, i.e. instead of the shear modulus the following dimensionless values are used:

\[
\gamma_j = \frac{\mu_j}{\mu_s} \quad \text{and} \quad \sum_{j=1}^{N} \gamma_j + \gamma_\infty = 1
\]  

(20)

What is still missing in the viscoelastic formulation here is the dependency on the level of conversion. One possibility is to assume that the relaxation times in the above equations are conversion dependent in terms of a shift factor \( a_{\tau, \alpha} \) which is a function of the temperature and conversion rate and that is used as a scaling coefficient for the relaxation times \( \tau_j \) measured at a given reference temperature \([10]\).

\[
\tau_j = \tau_{j0} a_{\tau, \alpha}
\]  

(21)

The material is assumed to exhibit a so-called thermo- and chemo-rheological simple behavior, i.e. the shift factor does not only contain the temperature dependency but also the dependency on the level of conversion. The formulation in terms of a scaling factor for the relaxation times is fully equivalent to the introduction of a reduced time scale \( \xi \) by

\[
\xi(t) = \int_0^t \frac{ds}{a_{\tau(s), \alpha(s)}},
\]  

(22)
There are already different ways published to estimate and model the dependency on temperature and conversion of the shift factor. Some authors try to identify the conversion dependency directly by carrying out DMA measurements at different conversion values [17, 18]. Another approach is to define the shift factor not as a function of the material temperature $T$ but as a function of the difference $T - T_G$ between the material temperature and the current glass transition temperature $T_G$ which increases with ongoing conversion [10], i.e.,

$$\tau_j = \tau_0 a_T^\alpha a_{T - T_G}$$ \hfill (23)

The advantage of the latter is that the dependency of the glass transition temperature on the degree of conversion can be determined by relatively simple differential scanning calorimeter (DSC) measurements. A disadvantage is that the material has to follow this assumption. For hot-curing epoxies with a low initial glass transition temperature (e.g. $< 10 \, ^\circ\text{C}$) and a final value above $100 \, ^\circ\text{C}$ this proved to be a successful assumption. For two-component epoxy systems with a low final $T_G$ or rubber based systems where the glass transition temperature always stays below the room temperature this is not appropriate. For the dependency of $T_G$ on the conversion different parametrizations are available like that based on the work of DiBenedetto [19]. Here a simple multiplicative split into two independent shift factors was used, i.e.,

$$\tau_j = \tau_0 a_T^\alpha a_{\alpha}$$ \hfill (24)

The typically non-linear dependency of the glass transition temperature on the conversion from equation (23) has now to be reproduced by the shift factor $a_{\alpha}$.

In the following exemplary data again for a two-component epoxy adhesive is discussed. In figure 10 on the left side the result of a dynamic mechanical analysis at 25 °C (DMA) in a parallel plate rheometer (diameter 15 mm) is shown. The liquid adhesive is placed between the plates directly after mixing ($t = 0 \, s$) and a measurement at constant frequency ($\omega = 1 \, \text{rad} / s$) is started. After approximately 62000 s the torque limit of the machine was exceeded and the measurement is stopped. The measurement can for sure also be done with a smaller plate diameter until full cure but then the resolution for low modulus values drastically decreases. The important information here is that of the gel point. If defined as the point where the ratio of storage modulus and loss modulus becomes larger than 1, the gel point of this material is reached rather late, i.e. after 47000 s at a conversion of 91%. A similar picture was obtained by determining the glass-transition temperature with DSC measurements. The glass transition temperature increases only pretty late for conversion values of more than 90%. The kinetic equation which was determined for this adhesive delivers the information about the conversion in dependency of the time which is the dotted line in figure 10. At the gel point the conversion is 91% in this case. The same measurement result is shown also in the right diagram (gray line) but now as a function of the conversion. The black line is based on another DMA measurement with a rectangular bar loaded in torsion direction. This bar was clamped into the machine after pre-curing for approximately 50000 s. The dotted lines show the uncertainty in conversion due to a ± 2 $K$ temperature change.

![Fig. 10: Left: Storage modulus, loss modulus (measured in a plate/plate setup) and conversion as a function of time, the straight lines denote the gel point / Right: Storage modulus during isothermal (25 °C) curing as a function of conversion, measured in a plate/plate configuration (gray lines) and with a rectangular bar under torsional load (black lines).](image)

To find a suitable approximation for the shift factors of equation (24) another DMA experiment with a pre-cured rectangular torsion bar was executed. Again the experiment was isothermal at 25 °C but now the frequency of loading was varied during the experiment. Frequency sweep between $0.1 \, \text{rad} / s$ and $100 \, \text{rad} / s$ were carried out continuously. With this experiment it is possible to obtain data for the curing material at a minimum conversion of slightly below 90%. This is sufficient here because for the models discussed above the shift factors are required after gelation only. Before gelation took place the material is still a liquid and stresses are released mainly by mass transport which is not a viscoelastic effect. The data from the individual sweeps was shifted along the logarithmic frequency axis to form a continuous curve like it is often done and well-known to form a viscoelastic master curve for the material with the difference...
that in this case not the temperature is the varying parameter but the conversion. This result is shown in figure 11 for two independent measurements (gray lines). The black line shown in the same diagram is a master curve of the fully cured material, i.e. the result of a typical temperature- (starting at -80 °C) and frequency-sweep (0.1–100 rad/s) experiment and a subsequent shifting operation. The reference temperature was chosen to be 25 °C and the reference conversion was 1.

Fig. 11: Viscoelastic (black) and curing master curves (gray) for isothermal curing at 25 °C

For both shifting operations the corresponding shift factors are shown in figure 12 for several independent measurements. The black line in the left diagram is based on the combined data set from the parallel plate and the rectangular bar measurement already shown in figure 10 on the right while the two gray lines are the shift factor curves belonging to the data shown in figure 11.

Fig. 12: Shift factors for the conversion $\alpha_a$ (left) and temperature dependency $\alpha_T$ (right)

If now the relaxation times and the moduli of a Prony series approximation for the master curve from figure 11 are determined (which is a well-known technique but not shown here) everything which is needed to calculate the shift factor from equation (24) and thus the conversion and temperature dependency of the relaxation times is contained in figure 12.

Looking again at equation (15), although the moduli $\mu_j$ and relaxation times $\tau_j$ are now known the dependency of the equilibrium shear modulus $\mu_e$ on the level of conversion still has to be determined. Several other authors used the following phenomenological relation [10,20] which was also implemented for this material routine:

$$\mu_e(\alpha) = \mu_{e,fc} \left( \frac{\alpha^2 - \alpha_{gel}^2}{1 - \alpha_{gel}^2} \right)^{8/3} \quad \text{for} \quad \alpha \geq \alpha_{gel}, \ 0 \ \text{else} \quad \tag{25}$$

where $\mu_{e,fc}$ is the equilibrium shear modulus of the fully cured adhesive and $\alpha_{gel}$ is the level of conversion at the point of gelation. The general shape of the dependency on the conversion fulfills two conditions: On the one hand first shear stresses can only develop after the polymer network is complete i.e. $\alpha = \alpha_{gel}$ and on the other hand the above function has a value of $\mu_{e,fc}$ if $\alpha$ is 1. The shape of the curve between these two points is purely phenomenological and comes from experimental observations. The equilibrium shear modulus of the fully cured material is already fixed by the Prony series parameters. The isochoric part of the curing dependent viscoelastic behavior is thus fully specified now. For the volumetric part again different choices exist. One possibility is to assume a constant Poisson ratio and thus directly correlate the bulk modulus with the shear modulus. This is not realistic because a liquid is known to be nearly...
incompressible while the shear resistance vanishes. Another possibility is the assumption of a simple linear dependency of the equilibrium bulk modulus on the conversion, i.e. 

\[ K_x(\alpha) = K_{x0} + (K_{xfc} - K_{x0})\alpha \]  

(26)

if \( K_{x0} \) and \( K_{xfc} \) are the equilibrium bulk moduli of the uncured and the fully cured material respectively. Equation (26) was the choice for the implementation here. The other parameters of the Prony series for the volumetric part can be determined in the same way as for the isochoric one if sufficient experimental data containing volume changes is available. In the simplest approximation the relative moduli and the relaxation times can be assumed to be the same in both cases.

As a last step the plastic part \( \varepsilon^p \), the last contributor to the sum of equation (11) which is still missing, has to be determined. For this we need a yield function \( F \) which is here defined in the following form:

\[ F = \sqrt{3J_2 + a_1Y_1 I_1 + a_2I_1^2} - Y \leq 0 \]  

(27)

This equation is based on the work of Schlimmer [14,16] and Mahnken [15] and contains contributions from the first invariant \( I_1 \) of the stress tensor and the second invariant \( J_2 \) of the stress deviator. \( a_1 \) and \( a_2 \) are two material parameters and \( Y \) is the current yield strength.

The yield strength \( Y \) is not assumed to be constant but a function of the equivalent plastic strain \( \bar{\varepsilon}^p \) in the following form

\[ Y = Y_0 + q(1 - e^{-b\bar{\varepsilon}^p}) + H\bar{\varepsilon}^p \]  

(28)

This equation allows to account for different hardening effects.

To define the evolution and direction of plastic strains a flow rule is necessary:

\[ d\varepsilon^p = d\lambda \frac{\partial G}{\partial \sigma} \]  

(29)

The flow potential \( G \) is not restricted to an associative type here because adhesives typically do not exhibit this behavior. Actually it is not only defined with similar although independent parameters like these of the yield function, i.e.

\[ G = \sqrt{3J_2 + a_1' I_1 + a_2' I_1^2} \]  

(30)

but moreover \( a_i' \) is even fixed to 0 to achieve a thermodynamically consistent behavior as Mahnken showed in [15]. To obtain the plastic strain evolution the principle of the equivalence of dissipated power like shown in [16] was used, i.e.

\[ \dot{\varepsilon}^p Y = \sigma : \varepsilon^p \]  

(31)

Equations (27) to (31) can now be used to setup a system of non-linear algebraic equations which provides the required solution in terms of stress and plastic increment. All the material parameters used in these equations are principally temperature dependent.

To determine the incremental stress formulation which is required for the FEA implementation the stress update form the viscoelastic calculation, i.e. equation (18), is taken as the trial stress \( \sigma^n \) in terms of the terminology of elastoplastic material laws. In terms of incremental stress updates the viscoelastic stress result is thus the predictor stress of a subsequent plastic corrector step if the yield limit is exceeded. The following set of four incremental equations has to be solved numerically to determine an appropriate stress increment if the yield condition \( F(\sigma^n) - Y^n \geq 0 \) is true:

\[ F(\sigma^{n+1}) = Y^{n+1} \]  

(32.1)

\[ Y^{n+1} = Y_0 + q(1 - e^{-b(\bar{\varepsilon}^p + \Delta \bar{\varepsilon}^p)}) + H(\bar{\varepsilon}^p + \Delta \bar{\varepsilon}^p) \]  

(32.2)

\[ F(\sigma^{n+1})\Delta \varepsilon^p = G(\sigma^{n+1})\Delta \lambda \]  

(32.3)

\[ C^{-1}(\sigma^n - \sigma^{n+1}) = \Delta \lambda \frac{\partial G}{\partial \sigma} \mid_{\sigma^{n+1}} \]  

(32.4)

The first equation is simply the requirement that after the stress update the stress is on the yield surface. Equation (32.2) ensures the correct update of the yield strength in accordance with the hardening rule. Equation (32.3) is the above requirement from equation (31) and (32.4) determines the plastic strain increment where \( C^{-1} \) is again the elasticity tensor from equation (17).
This system is solved using a Newton-Raphson iteration scheme [9]. To carry out the Newton-Raphson iteration the Jacobian matrix of system (25) has to be determined which is not shown here.

The elastoplastic parameters of the material can e.g. be determined from tensile tests at different temperatures which allows the evaluation of the parameters as a function of temperature, which was done but is not shown here. The conversion dependency of the elastoplastic behavior can be taken into account by making the yield strength a parameter which depends on the conversion, i.e. $Y_0(\alpha)$. Tensile tests at different levels of conversion could then be used to determine this parameter. Still absolutely unclear is the dependency of the hardening equation, the flow potential and the yield function on the conversion level. The experimental work which has to be done to get the required insights into the material behavior will be neither short nor easy.

Figure 13 shows a simple model of an aluminum sheet which is bonded onto a steel section. The adhesive is modeled between two layers of shell elements like it is shown in the schematic on the right. A contact formulation is used to connect the solid adhesive elements with the shell of the metallic substrates. The purpose of this model is to show the way of modelling and demonstrate how residual stresses develop. A validation case with a comparison to measured values is shown below. In this case the adhesive is a hot-curing one-component epoxy.

![Fig. 13: Simple model of a sheet made from aluminum (blue) bonded onto a section made from steel (green)](image)

The component is heated up to 200 °C homogeneously and after 12 minutes the cooling starts. The temperature history and the corresponding conversion obtained from the integration of the kinetic equation for this adhesive is shown in figure 14 on the left. The main shear and the equivalent stress for the element in the center of the bond line marked in figure 13 is shown on the right. Until the gel point is reached after 400 s there are no stresses present. Then the equilibrium shear and bulk moduli increase and the material shows some resistance against the shear deformation induced by the larger thermal elongation of the aluminum sheet compared to the steel. This happens still on a low level of stresses because the stiffness of the adhesive at 200 °C is small. After the cooling starts the metals shrink again and the adhesive, now solid, tries to maintain its shape with increasing stiffness and decreasing relaxation ability. What remains at the end is the residual stress.

![Fig. 14: Conversion as a function of time (left) and stresses (right) in a selected element in the bond line](image)

Another example of a panel component is shown in figure 15. A flat aluminum sheet is bonded onto a frame made from steel sections with a one-component, hot-curing structural epoxy adhesive. Figure 15 shows a view on the top surface of the aluminum sheet. The gray patterned areas show the locations where the bond lines are placed below the surface. The displacements shown in the figure where measured with an optical measurement technology after curing the adhesive, i.e. with the component cooled down to room temperature again.
The calculation result shown on the right was obtained using a quarter model of the component, i.e. the result is in every case fully symmetric. This is not perfectly the case for the experimental results where a global torsion is superimposed to the distortion caused by the curing adhesive and the incompatible thermal elongations. A measurement of the state of deformation of the panels before curing showed that a panel of this size (approximately 450 by 600 mm) and stiffness (the sheet thickness of the steel was 1.5 mm and that of the aluminum 1.2 mm) does not perfectly match the nominal geometry. Figure 16 shows the out-of-plane displacement along selected lines on the aluminum surface. This time the global torsional deformation was removed from the measurement signal.

Although the agreement is not perfect the shape is reproduced with satisfying accuracy when considering that all materials and process conditions of such a complex and large component are subject to scatter. It is furthermore important to realize that the shape looks completely different if the adhesive is modeled purely elastically with stresses set to zero at maximum temperature, i.e. taking into account only the cooling step. In the latter case there would be a single maximum of displacements at the center of the panel and the displacement curves in the diagram on the left in figure 16 would continuously decrease towards the edges of the panel.

Summary

Two different key aspects of multi-material joints and joints including composite substrates were discussed. The stress distribution in a bond line between composite materials was analyzed and the importance of a detailed consideration of the laminate layup and loading direction was demonstrated. For the common problem of incompatible thermal elongations of substrates in multi-material joints the implementation of a visco-elastoplastic material law for finite element methods was shown which takes into account the level of conversion based on a kinetic equation. The numerical approach presented allows the prediction of residual stresses and distortions caused by the curing of an adhesive. The determination of characteristic material parameters for the viscoelastic behavior is shown in detail. A validation example is briefly discussed at the end to show the applicability of the method.

References


