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Determination of cure-dependent properties of adhesives by thermal analysis using reaction kinetics and a novel experimental apparatus

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ABSTRACT

This work deals with the determination of cure-dependent mechanical properties, especially the modulus, and the degree of cure. Therefore kinetic methods will be used to determine this degree of cure in addition to the direct measurement by differential scanning calorimetry. Furthermore, the experimental part focuses on the reproducible preparation of samples for dynamic mechanical analysis at different states in the curing reaction. In combination with additional rheological data these different techniques of thermal analysis show a good correlation and offer a deeper understanding of the development of the mechanical properties during cure.

1. Introduction

Today the mechanical characterization of fully cured adhesives is state of the art [1]. Within this context established methods for the determination of stiffness and strength under different loading speeds are available [2,3]. All of these methods only characterize the adhesive in a fully cured condition as it is used during a product's lifetime. Most of the work focuses on the description of the adhesive's structural behavior during the lifetime of a product or, in the case of numerical approaches, regarding its failure. Since these stages of a product are well described, one of the major issues of the adhesive bonding technology is related to the adhesive behavior during the application phase where it is in a mostly viscous state. Within this phase the build-up of the modulus is of large interest. The industrial processes have to be optimized regarding the pot life as well as the gelation of the adhesive. This can only be achieved by an accurate description of the adhesive's properties during processing, such as viscosity or modulus. Furthermore, the development of new products or manufacturing methods is mostly conducted by means of computer-assisted methods, such as the finite element method. These methods also offer the possibility of optimizing the manufacturing process by adapting the curing cycle to the adhesive's special needs or by reducing the fixing times after adhesive application. Therefore, the mechanical behavior, such as the strength of the material, has to be sufficiently known in dependence on the degree of cure.

The optimization of the curing cycle of paste adhesives [4] in order to reduce curing times [5] as well as to minimize residual stress is a relevant field in adhesive bonding. Sanchez et al. [6] as well as Frauenhofer et. al. [7] have shown that an accelerated curing cycle by means of inductive heating is possible in the field of composite material structures. Ruiz [8] proposed a model to evaluate the elastic and viscoelastic properties of glass-polyester composites during cure by using kinetic reaction model.

The need to know the mechanical properties of adhesives during cure can be explained by different coefficients of thermal expansion of the adherends that cause residual stresses in an adhesively bonded joint after the curing cycle is completed [9]. An optimization of this process could lead to a change in the temperature related to the gel point of the material and therefore to minimized residual stresses.

For this reason, this work presents a methodology for correlating the mechanical properties determined by rheological and dynamic mechanical measurements with the degree of cure that was measured in differential scanning calorimetry. Therefore, kinetic approaches are used to calculate the degree of cure in dependence on the temperature profile the sample is submitted during the curing phase. Furthermore, a novel experimental procedure for the preparation of the samples is presented which is mainly focused on the temperature profile the samples are submitted to.

1.1. Determination of cure-dependent properties of adhesives

The determination of cure-dependent properties of adhesives has to be split into two separate parts. On the one hand the degree of cure has to be measured, for example by differential scanning

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calorimetry, or modeled by kinetic analysis. On the other hand the dependent properties, as the glass transition temperature, the viscosity or the modulus, have to be determined by adequate techniques. The challenge is to combine the data from these different methods which will be explained in more detail.

The kinetic analysis can be divided into model-fitting and isoconversional approaches. Both approaches are based on the Arrhenius equation

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) = A \cdot e^{-\frac{E}{RT}} \cdot f(\alpha) \tag{1}$$

where α is the degree of cure, t is the time, $f(\alpha)$ is the reaction model, R is the universal gas constant, T is the temperature, A is the pre-exponential factor and E is the activation energy [10]. The last two are also called Arrhenius parameters. Commonly used models are for example presented by Galwey and Browncan [11]. The isoconversional kinetic analysis is often related to the works of Friedman [12] who introduced the differential isoconversional kinetics and the works of Ozawa [13] and Flynn and Wall [14] who used an integral method. The most recent approach of isoconversional kinetics has been promoted by Vyazovkin [15,16]. Both approaches and the application within the context of this paper were explained and compared in an earlier paper in more detailed manner in [17]. Therefore a detailed discussion is omitted here.

Besides the kinetic approach the degree of cure can also be measured by differential scanning calorimetry where it is determined from the fractional integral over temperature. This leads to Eq. (2) where ΔH is the residual enthalpy and ΔH_0 is the reaction enthalpy of an uncured material [18].

$$\alpha = \left(1 - \frac{\Delta H}{\Delta H_0}\right) \cdot 100\% \tag{2}$$

Nevertheless, most of the work that was published during the past years in adhesive bonding used a model-based approach for the description of the curing behavior of commonly used adhesives. Jendrny [19], Eichleiter [20] and Menzel [21] measured the curing behavior of different adhesives at different constant heating rates. Starting from a model-free kinetic analysis for the determination of the activation energy, model-based approaches were chosen. In every case, good correlation between experimental and predicted data was reported.

Subsequently different specimens were used by Jendrny [19] and Eichleiter [20] to characterize the mechanical behavior, in particular loading conditions of structural adhesives with respect to the determined degree of cure. A more comprehensive characterization of both, stiffness and strength can be achieved using the butt-bonded hollow cylinder [22] that proved to give reliable results regarding the elastic-plastic behavior of structural adhesives that are used in the automotive industry. Menzel [21] used this specimen to determine the mechanical behavior of an adhesive at relatively high levels of cure (75–98%).

A more recent work is currently conducted by Devaux [23]. Within this work the Kamal and Sourour [24] reaction model is used to describe the reaction kinetics of a cold-curing epoxy-based adhesive during its lifetime in the launcher Ariane [5]. The aim of this work is to describe the nonlinear response of the adhesive by means of finite element simulations and to validate it using the modified Arcan test [25].

In contrast to the work presented above, where bonded specimens were used, it is also possible to characterize the adhesive by means of dynamic mechanical thermal analysis (DMTA) or rheological methods. Within this work the rheometer is used in parallel-plate configuration and operated in continuous oscillation. Therefore and due to the similar measurement principle the rheological approach can also be seen as a dynamic mechanical analysis. Therefore the differentiation is omitted in the following discussions. In both cases the samples are exposed to a harmonic variation of shear stress τ or deformation γ. The complex shear modulus G^*, the elastic shear modulus (storage modulus) G' and the viscous shear modulus (loss modulus) G'' can be calculated according to Eqs. (3)–(5) from these data [26].

$$G^* = \frac{\tau(t)}{\gamma(t)} \tag{3}$$

$$G' = G^* \cdot \cos(\delta) \tag{4}$$

$$G'' = G^* \cdot \sin(\delta) \tag{5}$$

δ being the phase shift between excitation and response.

In the rheological characterization the adhesive is applied in viscous state and cured in between the parallel plates as the measurement in oscillatory mode is going on. In contrast to this approach already – at least partly – cured samples are needed for the characterization by means of dynamic mechanical thermal analysis (DMTA) measurements in shear configuration. A good quality of these samples is essential for the achieved results. It is therefore state of the art to cure the adhesive, for example on an even surface or between two parallel plates. The samples are subsequently stamped, milled or sawn out of the resulting plates [28]. This mechanical treatment could lead to imperfections of the sample geometry or its chemical composition. While the stamping process results in edges, a milling process may result in a chemical change of the specimen due to inserted heat or chemical reaction with the cooling fluid.

Furthermore, any additional treatment of the samples between their preparation and the measurement leads inevitably to errors within the interpretation of the results since the thermal history cannot be controlled during this phase. Additionally these manual steps risk the introduction of handling errors or time variations which interfere with the actual results.

Therefore a novel experimental technique will be presented for the preparation of these samples with a main focus on the temperature control of the curing process and the reproducibility of the geometrical dimensions. Furthermore, this tool will allow the simultaneous preparation of samples for DSC as well as for DMTA. For the subsequent interpretation of the results it is necessary that both types of samples have undergone the same temperature process leading to an equal state regarding the degree of cure.

2. Material and methods

2.1. Adhesive

For the experimental work, a one-part hot-curing epoxy-based adhesive was used. It is the Terokal 5089 crash-toughened adhesive of Henkel for use in the automotive industry. Its typical properties are presented in its corresponding data sheet [27]. The recommended curing cycle is 30 min at 180 °C or at least 10 min at 155 °C to reach minimal mechanical properties.

2.2. Differential scanning calorimetry (DSC)

The kinetic parameters were identified by nonisothermal differential scanning calorimetry. A Mettler differential scanning calorimeter was used to measure the heat flow during the curing reaction at four different heating rates (5 K/min, 10 K/min, 15 K/min and 20 K/min) from a starting temperature of 25 °C up to 260 °C. Out of the measured heat flow the degree of cure was evaluated according to equation (2). Fig. 1 shows the dependence of the degree of cure on the sample temperature. For a better

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