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Cure kinetics of electrically conductive adhesives

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Abstract

Electrically conductive adhesives (ECA) are an alternative interconnection method for crystalline silicon solar cells, providing low thermomechanical stress, being lead-free and applicable to new contact structures. The ability to control their curing reaction in a stringing or lamination process is essential for enabling cost effective and reliable industrial module production. We set up an autocatalyzed model for the curing reaction of ECAs. The model is parameterized using dynamic differential scanning calorimetry (DSC) measurements and isoconversional methods for parameter extraction. We use the model to simulate arbitrary temperature profiles and find a good agreement to experimental data with 5-10 % (abs.) error. Furthermore the model is used to calculate the advancing degree of cure of ECA during a typical lamination process.

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1. Introduction

The application of electrically conductive adhesives (ECA) is an alternative interconnection method for standard H-pattern cells [1] and a key technology for emerging new cell concepts like metal-wrap-through (MWT) [2] and heterojunction cells [3]. ECAs are lead-free, mechanically compliant and can be processed at low-temperatures. Therefore, they reduce the thermomechanical stress of the cells during interconnection. Furthermore, ECAs gain increasing attention to be used for innovative contact structures like back-contact solar cells especially in cases where soldering is difficult. From our experience, processing of ECA (e.g. dispensing, printing and curing) are major challenges to be addressed more

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deeply before large-scale production with ECA using achieved. One major step is the control of the curing reaction so that we can calculate the degree of cure from any time-temperature profile.

Our approach to study the cure kinetics of ECA was to use dynamic differential scanning calorimetry (DSC) measurements for the parameter determination of an autocatalytic reaction model. Then, isoconversional methods are used to calculate the activation energy [4] whereas the remaining parameters are obtained with a method outlined in [5]. After the model is parameterized the differential equation describing the cure reaction is solved for an arbitrary temperature profile with numerical Runge-Cutta methods to validate the model. Finally, the curing of ECA is simulated for the temperature profile of a lamination process.

Nomenclature

\begin{tabular}{ll}
\(a(t)\) & degree of cure at time \(t\) \\
\(a_0\) & initial degree of cure \\
\(A\) & pre-exponential factor \\
\(E\) & activation energy \\
\(E_a\) & \(\alpha\)-dependent activation energy \\
\(f(\alpha)\) & reaction model \\
\(k(T)\) & rate constant of the cure reaction \\
\(m, n\) & exponents of the autocatalytic reaction model \\
\(Q_{part}(t)\) & partial heat generated during DSC up to time \(t\) \\
\(Q_{tot}\) & total heat generated during cure reaction \\
\(R\) & gas constant \\
\(t\) & time \\
\(T\) & temperature \\
\(\Phi\) & heat flow
\end{tabular}
2. Experimental

2.1. Sample preparation

The ECA used for this methodology is an epoxy-based adhesive filled with silver flakes. Fig. 1 shows its cross section on a standard H-pattern solar cell. The dark areas in the ECA layer are the polymer matrix and the elongated brighter shapes are the silver particles forming the electrical network between solar cell busbar and the interconnector.

2.2. Measurement

Differential scanning calorimetry (DSC) is widely used to study the cure kinetics of thermosets [6] including ECAs [7]. The DSC measurements for this study are carried out on a Q200C from TA Instruments. The runs are performed in dynamic mode with heating rates of 6, 8, 10 and 12 K/min and a temperature range between 35 °C and 250 °C respectively. The aluminum pans are filled with approximately 15 mg ECA and are hermatically sealed. After the measurement in which the adhesive is cured the sample is run with the same DSC settings again in order to define an appropriate baseline for later integration of the DSC peak.

2.3. Modeling approach

The degree of cure, $\alpha(t)$ can be calculated from the measured heat flow $\Phi$ when the ratio of the partial heat $Q_{\text{par}}(t)$ generated up to time $t$ and the total heat of reaction $Q_{\text{tot}}$ is determined:

$$\alpha(t) = \frac{Q_{\text{par}}(t)}{Q_{\text{tot}}}$$  \hspace{1cm} (1)

Once $\alpha(t)$ is obtained the rate of cure $d\alpha/dt$ can be calculated by numerical differentiation.
The curing reaction of an ECA can be described with the general rate law,

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$  \hspace{1cm} (2)

where \( \frac{d\alpha}{dt} \) is the rate of cure, \( k(T) \) is the temperature-dependent rate constant of the reaction and \( f(\alpha) \) is a function of the concentration of reactants. \( k(T) \) is usually described by the empirical Arrhenius equation,

$$k(T) = A \exp\left(-\frac{E}{RT}\right)$$  \hspace{1cm} (3)

with \( A \) as the pre-exponential factor, \( E \) as the activation energy, \( R \) as the gas constant and \( T \) as the absolute temperature. Substituting eq. (3) into eq. (2) gives the basic model equation,

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)$$  \hspace{1cm} (4)

According to [8] a useful expression for \( f(\alpha) \) to study the cure reaction of epoxy resins is,

$$f(\alpha) = \alpha^m(1 - \alpha)^n$$  \hspace{1cm} (5)

by assuming zero initial cure rate. This autocatalytic model contains two independent reaction orders \( m \) and \( n \).

In order to solve the differential equation (4) the unknown parameters of the Arrhenius relationship \( E \) and \( A \) as well as the reaction orders of the autocatalytic model \( m \) and \( n \) must be obtained. The first step is to determine the activation energy. If model-free isoconversional methods are used no prior knowledge of \( f(\alpha) \) is necessary. Moreover, they are among the most reliable for this task [9]. After obtaining the activation energy we decide on an appropriate reaction model \( f(\alpha) \) which best describes the experimental data. Then, the pre-exponential factor \( A \) and the remaining parameters of the model can be derived.

With isoconversional methods it is possible to determine a variation of the activation energy \( E_\alpha \) with \( \alpha \). This allows complex reaction processes to be detected. The logarithmic form of eq. (4) is the foundation of the differential isoconversional method of Friedman [10],

$$\ln\left(\frac{d\alpha}{dt}\right)\bigg|_{\alpha} = \ln(A_\alpha f(\alpha)) - \frac{E_\alpha}{RT_\alpha}$$  \hspace{1cm} (6)

The slope of \( \ln(\frac{d\alpha}{dt}) \) versus \( 1/T \) for a fixed value of \( \alpha \) and different heating rates gives the activation energy \( E_\alpha \) at different degrees of cure. For further calculation a mean value of \( E_\alpha \) within \( \alpha \in (0.2, 0.8) \) is used. This assumption is actually a non-physical simplification but we use it as a first approach to solve our applied kinetic problem.

For the remaining quantities \( m, n \) and \( A \) we follow a method described in [5]. Further details are also given in [11]. With all parameters known Runge-Cutta-methods are then used to solve the ordinary differential equation given in (4). For the numerical solution an initial value \( \alpha_0 \) has to be defined. For some parameter sets the solution differs significantly with changing \( \alpha_0 \).
3. Results and discussion

3.1. Dynamic differential scanning calorimetry

The heat flow versus time of the exothermal curing reaction of the ECA for four different heating rates is shown in fig. 2. After defining linear baselines using the second run of the same samples, the degree of cure is calculated according to eq. (1).

![Fig. 2. Heat flow versus time from DSC measurements with different heating rates](image)

3.2. Determination of the kinetic parameters

Using eq. (6) the activation energies with respect to the degree of cure can be obtained. The result of the calculation can be seen in fig 3. It is noticeable, that the activation energy is dependent on the degree of cure which indicates a multiple step cure reaction. In [12] it is suggested that this kind of activation energy variance may be due to competitive reactions. The mean value of the activation energy within \(<0.2, 0.8>\) of \(\alpha\) is 66.26 kJ/mol and will be used for the calculations. As stated earlier, this simplification is probably a source of error in the simulation results seen later. The aim of future work is to expand the model to include a double step reaction to compensate for this effect [13] or to solely use model-free kinetic analysis [14].

Table 1 gives a summary of all obtained parameters of the model.
Fig. 3. Activation energy versus degree of cure

Table 1. Parameters of the kinetic model

<table>
<thead>
<tr>
<th>parameter</th>
<th>mean (+/- std. dev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>activation energy $E$</td>
<td>$66.26 (+/- 7.7)$ kJ/mol</td>
</tr>
<tr>
<td>pre-exponential factor $A$</td>
<td>$1.35 \times 10^9 (+/- 0.26 \times 10^9)$ min$^2$</td>
</tr>
<tr>
<td>exponent $m$</td>
<td>$1.33 (+/- 0.19)$</td>
</tr>
<tr>
<td>exponent $n$</td>
<td>$1.09 (+/- 0.12)$</td>
</tr>
<tr>
<td>initial degree of cure $\alpha_0$</td>
<td>$0.01$</td>
</tr>
</tbody>
</table>

3.3. Model validation and application

The model is validated with empirical $\alpha(t)$ from an arbitrary temperature profile of a DSC measurement and compared with the calculated data from the model. The results can be seen in fig. 4. The black line describes the temperature profile. First the temperature is raised to 120 °C for a short time such that a partial cure of the ECA can take place. Then the temperature is lowered to interrupt the curing reaction and is finally raised to temperatures > 150 °C to finish the reaction. The red line represents the experimental degree of cure as derived from the DSC. The blue line indicates the calculated values.

We conclude that the model is able to predict the degree of cure with reasonable accuracy. The error lies in the range of 5 – 10 % abs. The reasons for the deviations from model to experiment are (a) the variance of the activation energy from the degree of cure that is presently not included in the model, (b) possible inaccuracy in the definition of the initial value $\alpha_0$ for the numerical solution of the differential equation, (c) very likely numerical errors in the baseline approximation when evaluating the experimental
DSC curves of the arbitrary temperature profile. Issues (a) and (b) can probably be overcome if the model is refined according to the approaches indicated earlier in this paper. Problem (c) will remain as a typical source of error for any DSC measurement.

The model was applied to study the cure kinetics during a typical lamination process. In the lamination experiment, the temperature was logged using thermocouples and is indicated by the black line in fig. 5. If this temperature profile is fed to the model the red curve for the degree of cure is calculated. For comparison we calculate an isothermal cure at 140 °C as shown with the blue line in fig. 5. Usually the ECA manufacturer only supplies isothermal cure recommendations with the datasheet. However as can be seen from the chart, the actual time for curing is significantly longer if the laminator or any other equipment that has longer periods of heating and cooling are used for that purpose.

![Fig. 4. Comparison of model with experiment showing the temperature in the DSC, the experimental degree of cure and simulated degree of cure](image1)

![Fig. 5. Degree of cure for an isothermal cure at 140 °C compared to a laminator cure with the given temperature profile](image2)

### 4. Conclusions

The cure process is of major importance for conductive adhesives as an alternative interconnection technology. The mechanical and electrical properties of the adhesive joint depend on that curing process. The cure kinetics of ECA can be modeled using dynamic DSC measurements. We determine the activation energy dependence of the cure reaction over the degree of cure with isoconversional methods and set up an autocatalytic reaction model. It was shown that the reaction contains complex competitive processes causing the activation energy to vary with degree of cure. The model is validated with an arbitrary temperature profile in the DSC and shows good agreement to experimental data within 5 – 10%.

It is used to study the cure reaction within the lamination process. We found that the cure during lamination takes significantly longer than an isothermal cure at comparable set temperatures because of an extended non-isothermal heating phase. The model is applicable to arbitrary temperature profiles and supports the understanding of the cure process in an industrially relevant environment. It shows further potential to be transferable to the cross-linking reaction of EVA.
Acknowledgements

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