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Polymerization of Thin Film Polymers

Markus Woehrmann and Michael Toepper

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/48205>

1. Introduction

Polymeric coatings such as polyurethanes, acrylic, epoxies and silicones have been used for over 40 years to protect printed wiring boards (PWB) from moisture, handling and environmental influences. Special semiconductor grade polymers have been developed for chip passivation layers. Polyimide became the standard passivation layer for memory chips and other devices needing surface protection for handling and testing procedures. Photosensitive resins have been developed to reduce processing costs. Thin film polymers are used widely in the area of electronic packaging and as an interlayer dielectric (ILD) in nearly every electronic device. Typical layer thickness ranges from 5 μm up to 15 μm . These polymers films should be temperature stable up to range of 150°C (permanent), and for a short time up to 250°C and higher, depending on the soldering process of the components. This is the reason to use thermoset polymers in most cases. The coating process is the spin-coating technology. Spray coating and other techniques are only niche processes. The polymer supplied by the chemical company is a so-called pre-cursor consisting of a partially polymerized polymer in an organic solvent. Nearly all of the thin film polymers need a polymerization step, which is done in most cases by a thermal process after the deposition on the wafer. Polymerization changes the pre-polymer into a long-term stable and much more inherent polymerized dielectric layer. The polymerization process is generally called the *cure* or *cure step* of the process. But the definition “cure” does not mean in every case a fully finished polymerization reaction. Also partly cured polymer films are possible and becoming important if multiple layers have to be deposited. Partly polymerized layers have better adhesion to the following layer compared to fully cured ones. To get something more precise the following definitions have been used: partly cured or soft cured polymers for a 60 – 80 degree of polymerization, and full cured or hard cured for a complete polymerized layer.

There are a huge range of different polymer materials which are used as interlayer dielectric such as polyimides, polybenzoxazole and benzocyclobutene [1]. An example of such a polymer layer on a CMOS-wafer is shown in figure 1:

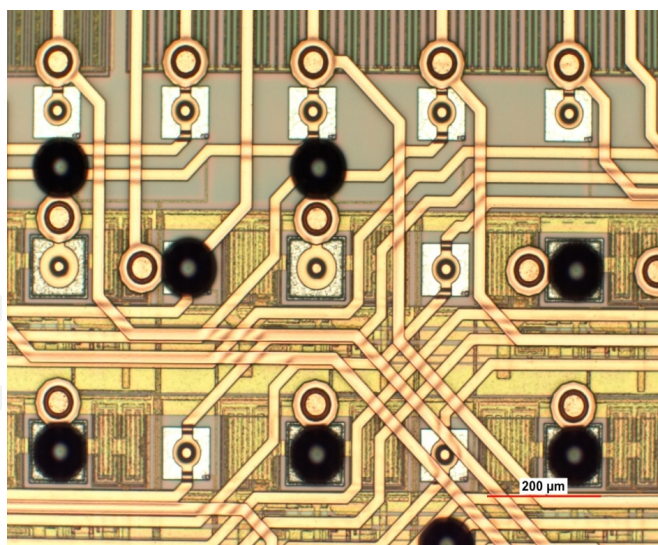


Figure 1. A thin film polymer (BCB from Dow Chemical) as protection layer on a CMOS-wafer

In the last few years, the development of new polymer materials for thin film applications has increased more and more. One main driver for this is the 3-D integration technology which demands optimized material behaviors of the polymers, such as a low coefficient of thermal expansion (CTE) or higher tensile strength. The 3-D technology also demands more and more the low temperature processing. The material combinations get more temperature critical. The reliability will be increased at the same time with low cure temperature, because of a decreased thermal stress in the material stack. In contrast to the demand of low cure temperature, a tough polymer layer is desired with a high decomposition temperature. Analyzing and engineering the polymerization process will help enormous to reach these goals.

This chapter will focus on the benzocyclobutene (BCB) from The Dow Chemical Company being a well-known material for thin-film applications. The full cured BCB has a decomposition temperature well above 350°C. The cure temperature of 250° has been reported in dozens of publications. The analyzing and modeling of the BCB polymerization process will be discussed here in detail. Understanding the behavior of the polymerization process in different states and their kinetic modeling shows the potential for decreasing the cure temperature for a BCB layer which has nearly the same material stability and decomposition temperature as standard processed BCB layers.

2. The relevance of thin film polymers in micro electronics

The Dow Chemical Co. (Midland, MI) has developed a variety of low-dielectric (low-k) polymers which are based on different benzocyclobutene monomers (BCB, also known as biscyclo[4.2.0]octa-1,3,5-triene or 1,2-dihydrobenzocyclobutene). Based on these studies, the Dow Chemical Co. commercializes a BCB-Polymer under the registered trademark CYCLOTENE. CYCLOTENE is a family of thermosetting polymers prepared from 1,3 divinyl-1,1,3,3-teramethyldisiloxane-bis-benzocyclobutene (DVS-bis-BCB) monomer. The structure of the DVS-bis-BCB monomer is illustrated in figure 2. Today CYCLOTENE is just

called BCB in most of the literature. BCB has been developed for electronic coating applications. Based on the low- k characteristic of BCB, the material is very attractive as an interlayer dielectric for RF-components [2] [3]. The BCB has been widely used for multilayer re-distribution on wafer level (wafer level packaging-WLP). Since the early 90's, there are hundreds of application notes for BCB (e.g. bumping and redistributing chips, and for planarization and isolation in flat-panel displays, MEMS hermetization, wafer bonding, passivation, gap filling). The wide field of application is based on the material properties such as good planarization, no outgassing, and low copper migration. The Dow Chemical Co. also releases the chemical structure of the monomer and the final polymer, which is not common for the most commercialized thin film polymers. Knowledge of the structure allows for a better understanding of material behavior and material analyzing, which leads to the fact that BCB is used very often for academic research. Most of the newer polymers are years away from such a comprehensive database. BCB is available as photosensitive (CYCLOTENE 4000 series) and non-photosensitive (CYCLOTENE 3000 series) in the form of a spin-on solution. CYCLOTENE can be purchased in different viscosities to obtain a wide film thickness range of $<1\text{ }\mu\text{m}$ up to $26\text{ }\mu\text{m}$ (see table 1). CYCLOTENE is shipped in a partly cross-linked state in mesitylene solvent (trimethylbenzene). The non-photosensitive CYCLOTENE can be structured by dry etch processes or laser ablation. On account of this, it is often called dry-etch BCB. The initial extent of polymerization is slightly different when comparing dry etch BCB with photo BCB. The dry etch version is stable at room temperature, in contrast to the photosensitive parts of the 4000 series, which have a shelf life of a week at room temperature, due to the photo-sensitizer. In a frozen state, the durability increases up to a couple of years.

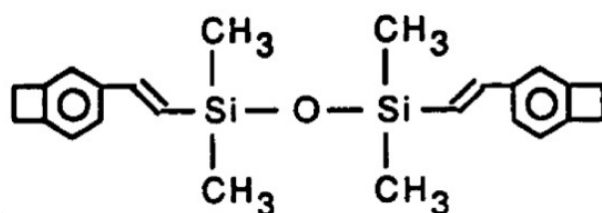


Figure 2. Structure of a DVS-bis-BCB monomer [4]

In contrast to polyimides, which are also often used as thin film layers, BCB has a couple of advantages. BCB is highly cross-linked, based on the small monomer, which leads to higher thermal stability in comparison to the cure temperature [4]. It also leads to a complete isotropic behavior of the polymer film. On the other hand, the long-chain characteristic of the polyimide leads to a higher elongation at break, which is an important factor in reliability [1]. The polymerization reaction of the BCB does not emit any volatile by-products, resulting in low cure shrinkage (less than 5 %). The non-polar chemical structure of BCB leads to low dielectric constant ($\epsilon_r=2.65$) and a high breakdown voltage ($530\text{ V}/\mu\text{m}$) in combination with a low water uptake (less than 0.2 %). The good planarization properties also make BCB attractive for 3-D and adhesive bonding [5] [6].

Notation	Viscosity (cST@25°C)	Thickness (μm)	Solid content (%)	b-stage (%)
3022-35	14	1.0 – 2.4	35	35
3022-46	52	2.4-5.8	46	35
3022-57	259	5.7-15.6	57	35
3022-63	870	9.5-26.0	63	35
4022-35	192	2.5-5.0	35	47
4024-40	350	3.5-7.5	40	47
4026-46	1100	7.0-14.0	46	47

Table 1. CYCLOTENE with different solid content

3. Overview of the polymerization process

3.1. General polymerization behavior of thermosets

BCB is a thermoset like most other ILD polymers. The polymerization is the process which forms the small molecules or monomers into large polymers structures. The chemical reaction (polymerization) of the thermoset during the processing allows an easy processing of thin film layers. In most cases, a liquid solvent is deposited by spin coating on a substrate, and after the polymerization a tough solid state with a high glass transition temperature is formed. In contrast to thermosets, thermoplastics need a physical condition change for the polymerization. The disadvantage of thermoplastics is the low glass transition temperature ranging from below room temperature up to 180°C, which is a result of the low Van der Waals forces between the polymer chains. For the following processes, such as sputtering, a high thermal stability above 200°C is necessary. A softening of the polymer based on low T_g during sputtering could lead to buckling of the deposited metal layer.

The result of the polymerization of thermosets is a more or less strong 3-D cross-linking of the polymer chains with strong covalent connections in combination with solidification of the polymer layer, which leads to an insolubility of the material. In most cases, thermal energy is used for the polymerization reaction, but there are also other methods like radiation or hardener materials which work like a catalyzer being used for other polymers.

The polymerization is not a monotonic reaction, because it progresses through different stages which change the characteristics of the reaction significantly. The reaction starting point is an ideal solvent in which there are only monomer structures in the solvent. The material is in a “liquid phase” (also called an a-stage). With the supply of enough energy in the system, the cross-linking of the monomers starts and polymer chains build up. The degree of cure describes the rate between reacted parts and unreacted parts (reactants and products). In literature there is a different notation which means more or less the same thing, like extent of cure, extent of reaction, extent of conversion and fraction transformation. The reaction rate is nearly constant in a viscous liquid stage up to the gelation point, which described the abrupt and irreversible transformation of the material into an elastic gel or rubber, and the material loses its ability to flow. At this point, there are infinitesimal networks which are more or less cross-linked to each other (b-stage). The

gelation leads only to a small change in the reaction rate, but could be estimated with rheological measurement. The point of gelation is for a thermoset on a fixed degree of cure with the conclusion, that it is independent of the polymerization method (radiation, convection oven or microwave). Because of that, the measurement of the gelation point allows for calculating the activation energy of the polymerization reaction [7].

With the increase in the polymer network, the material becomes more and more rigid. The movement of the monomer reactants slows down abruptly when the glass transition point (T_g) of the polymer overwhelms the process temperature. The material vitrifies as a solid state, for polymers often called the glassy state, based on their more or less amorphous structure. The reaction rate drops down by an order of two or three magnitudes, and is significantly dependent on the mobility of the reactive monomers. In gel state, the polymerization is controlled by a chemical reaction rate, but in glassy formation, the reaction is controlled by the diffusion of the reactants. The glass transition temperature increases with the polymerization degree. Based on that, the glass transition temperature is highly dependent on the cure process. The vitrification is, in contrast to the gelation, reversible by heating. When the process temperature is again above the T_g devitrification occurs. A fully cured thermoset (c-stage) has a glass transition temperature near the dissociation temperature, which makes the measurement of such a T_g in most cases impossible. Based on that it can be postulated that a fully polymerized thermoset does not have glass transition temperature anymore [8].

3.2. The polymerization reaction of BCB

The fully polymerized BCB has a high 3-D cross-linked network, which leads to isotropic properties. The polymerization reaction consists of two steps. The first step is a thermal activated BCB four-membered ring opening reaction. This reactive intermediate readily undergoes a [2+4] Diels-Alder reaction (see figure 3). The Diels-Alder reaction is a reaction where a conjugated diene will be added on a double bond, building a six terms ring. Both reaction partners are named dien and dinophile. The reaction is also called a [4+2] cycloaddition.

After ring opening, the BCB monomer has two diens and dinophiles, which allow a highly cross-linked polymer. The ring opening is a first order reaction, and depends on the concentration of the pre-polymer. The reaction rate of the ring opening and the Diels-Alder reaction was measured by ROTH et. al. The ring opening has a 10 times higher reaction rate constant [9] [10].

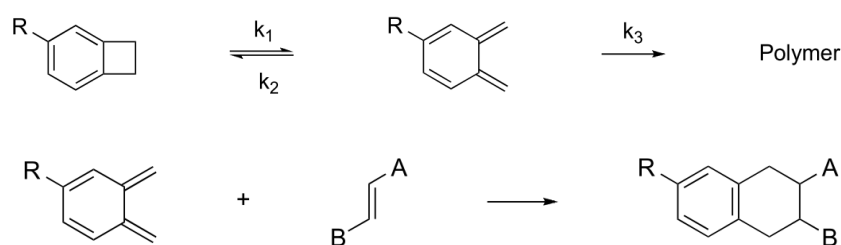


Figure 3. Ring opening reaction and Diels-Alder reaction of BCB

The polymerization reaction could be described by a pseudo first-order reaction equation, because the Diels-Alder reaction is the reaction rate limited factor. The thermal activated polymerization process of BCB or the reaction rate depends on temperature, time and extent of cure. Figure 4 show a Time-Temperature-Transformation diagram (TTT-diagram) for the polymerization reaction of BCB. The numbers in the diagram describes the extent of cure which could be measured by different methods.

The reactions rate is strongly influenced by the mobility of the molecule chains which generally increase with the temperature, but also decrease with the extent of cure, because increased cross-linking decreases the mobility. During the cure, the reaction kinetic runs through different stages, from liquid pre-polymer through a gelation to a vitrification.

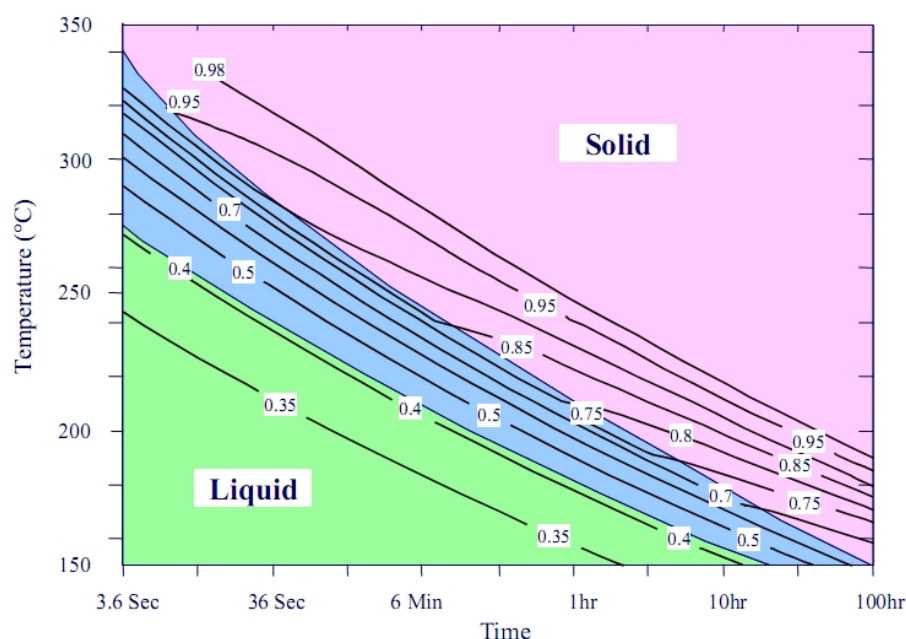


Figure 4. Extent of cure of photo BCB in relation to soak temperature and soak time. The colors describe the material conditions: liquid state (green), gel state (blue) and solid state (red) [11]

The gelation point has no significant effect on the polymerization reaction. The change into the solid state impacts the reaction rate based on the change from a chemical controlled to a diffusion controlled regime. That leads to a significant drop in molecule mobility, which could decrease the reaction rate down to nearly zero. The slowdown factor of BCB is relatively weak because of the small monomers.

The commercially available CYCLOTENE (see table 1) has been pre-cured (b-stage resin). Especially for structured photo BCB layers, a viscous liquid state during processing is avoided by a higher molecular weight of the b-stage state. After the evaporation of the solvent, the polymer layer lost its flow ability and the layer could be structured. A flowing of polymer during the cure would limit the critical structure dimension. The reaction rate is nearly constant during the entire gelation phase. The fully cured BCB has a T_g near the decomposition temperature above 350°C. But the T_g of an uncured CYCLOTENE will exceed approximately 60°C, and will rise dependent upon the degree of cure (figure 5) [6].

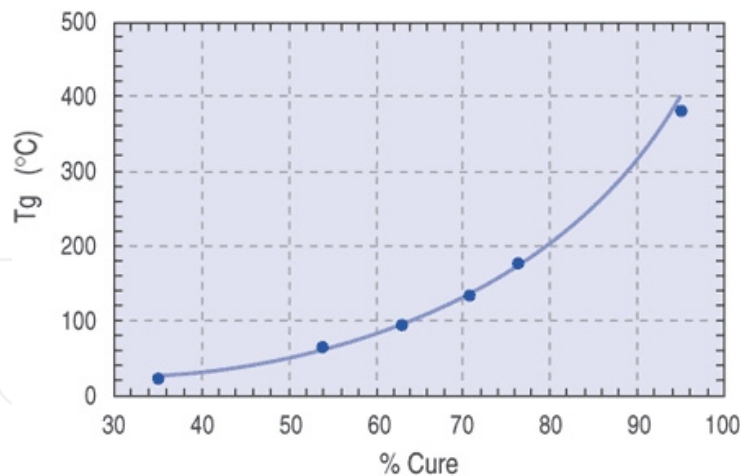


Figure 5. Glass transition temperature of photo BCB [6]

It is shown for some other polymers that the degree of cure is nearly fixed after vitrification without a temperature rise, because of the extremely slow reaction rate [12]. This means for polymerization process optimization a full cure is not possible if the temperature is decreased. A lower processing temperature leads to the glass transition temperature occurring earlier, which can be seen in figure 4. The polymerization process stops at a lower degree of cure, because the reaction changed earlier from a reaction controlled to diffusion controlled characteristic.

The slowdown of the reaction rate of BCB after vitrification has been described in previous publications [13] [14]. However, the reaction does not stop and proceeds to the solid state. In contrast to many other polymers, the diffusion controlled reaction rate is high enough to continue the polymerization process. DIBBS et. al. specifies only that above 95 % the diffusion controlled reaction rate will slow down so that it could be seen as a fixed state [2]. A degree of cure of about 95 % can be accepted as nearly fully cured. There is no significant difference measurable because of the approximation failures of measuring methods for the degree of cure.

4. Measurement of the polymerization degree of BCB

The datasheet of CYCLOTENE describes a cure at 250°C for 90 minutes to get a full cured film. Any change in the cure process or the creation of a kinetic model needs knowledge about the extent of cure. There are a couple of methods to monitor it, like Fourier transformed infrared-spectroscopy (FT-IR spectroscopy), change of the refractive index or the difference scanning calorimetric (DSC).

The determination of the reaction rate, and the extent of reaction by time and temperature are investigated further to develop a kinetic reaction model. Real-time measurements during the cure process are necessary to monitor the degree of cure. DSC measurement was used for kinetic model creation. Based on the kinetic model, cure processes were set-up and the expected extent of cure was controlled by FT-IR spectroscopy. The FT-IR spectroscopy

allows the measurement on product wafers, but for the creation of a kinetic model, a special oven with integrated measurement equipment is necessary. The discrete IR wavelength gets into resonance with the rotation or vibration of some molecule groups. The rate of reactants and products of the polymerization could be estimated by the peak height [15]. The samples were measured before and after the curing by the “FT-IR 2000 System” from Perkin-Elmer.

The broadly used method for the investigation of thermal processes like polymerization is difference scanning calorimetric. The DSC is preferred because of an accurate temperature regulation and good recording of the energy dissipation [12] [16]. The DSC-analysis was done with 7 mg CYCLOTENE 4024-40 in an inert atmosphere using a “Q2000” machine from the TA Instruments Company. The samples were dried and exposed before they were analyzed. The DSC analyzer could perform high heat-up and cool-down rates, up to 300°C/min. Higher heat-up rates leads to more inaccuracy based on a stronger overshoot of the thermal system.

The DSC records the heat flow to a sample during a tempering in comparison to a reference cell. The integration of the heat flow over time gives the heat dissipation of the sample. The polymerization reaction is an exothermic reaction and occurs in DSC plot by a dip/peak of the heat flow curve [14]. The integration of the heat flow peak over time allows the estimation of the heat transformation (enthalpy change) of the reaction.

The DSC experiments for the estimation of the BCB polymerization has been done in isothermal and non-isothermal mode with a constant heat rate. In figure 6 a non-isothermal signal of a BCB DSC sample is shown. The heat of the reaction of 294.4 J/g is calculated by a linear baseline. A more accurate calculation can be done by using a blind curve, which means a second measurement of the fully polymerized sample. The difference between the two curves gives the energy dissipation of the polymerization process. The blind curve also compensates the parasitic endothermic signal which came from heating up the aluminum sample pan [8].

The heat of the reaction could be set in relation to the extent of reaction. The reaction rate $d\alpha/dt$ at any state of the polymerization can be estimated at any stage of the reaction by the following relation:

$$\frac{d\alpha}{dt} = \frac{dH / dt}{\Delta H_{total}} \quad (1)$$

The total heat of reaction ΔH_{total} describes the integral of heat flow from the initiation of reaction up until the full polymerized material form. The constant heat rate β allows for applying the extent of reaction over the heat rate, instead of the extent of reaction over time, which is measured with a higher inaccuracy:

$$\frac{d\alpha}{dT} \beta = \frac{dH / dt}{\Delta H_{total}} \quad (2)$$

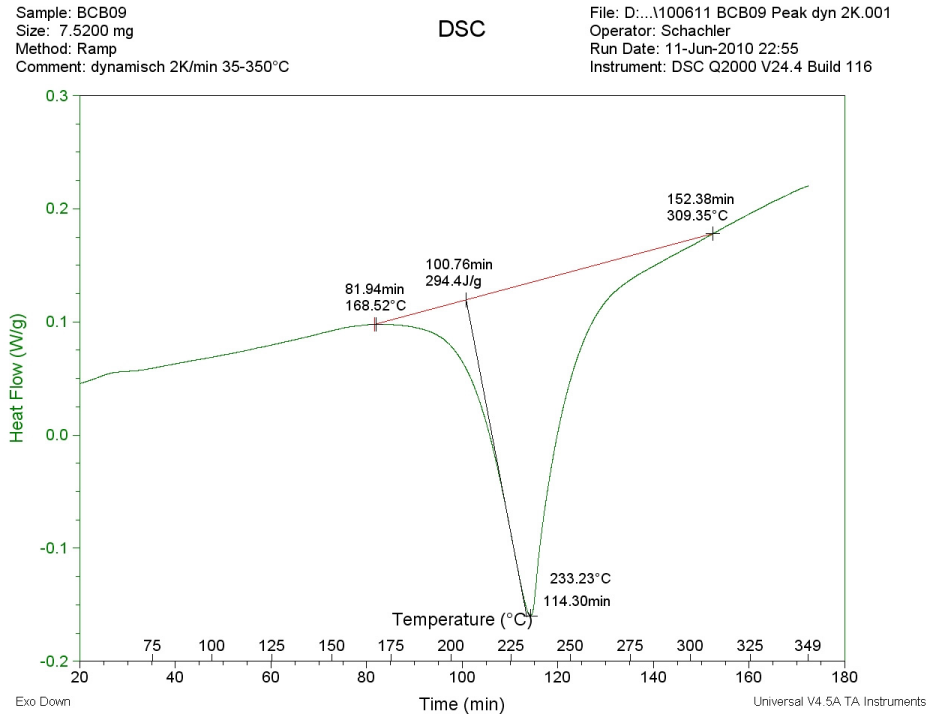


Figure 6. DSC plot of the polymerization of a photo BCB sample during a non-isothermal experiment with a heat rate of 2 K/min

This is the reason why non-isothermal experiments are often used to analyze the reaction. The degree of cure at any state could be estimated by the rate of the heat of reaction ΔH to the total reaction heat ΔH_{total} of a fully cured layer:

$$\alpha = \frac{\Delta H}{\Delta H_{\text{total}}} + \alpha_i = \frac{1}{\Delta H_{\text{total}}} \int \frac{dH}{dt} dt \quad (3)$$

where α_i is the initial degree of cure of the b-stage resin. The estimation has included an inaccuracy by the calculation of the total heat reaction of the complete polymerization. Linear heating experiments at different heating rates are performed. The ΔH_{total} of the non-isothermal experiments with different heat rates are printed in table 2. The blind curve corrected DSC-curves are shown in figure 7. By increasing the heat rate, the reaction is shifted more and more into higher temperatures. The average total heat of reaction of the fully cured BCB film is about 281.8 ± 5.3 J/g. The results are in good correlation to the measurement of CHAN, who measured a heat of reaction for CYCLOTENE 4024-40 of 291.3 ± 8.8 J/g [17]. The measurement of the heat reaction is strongly dependent on base line settings. The estimation of the total heat reaction has in general an inaccuracy of 3 to 5%. It should be noted that the photosensitive CYCLOTENE will be shipped out with an initial degree of cure of about 47 %. Based on this, the true total heat of the reaction is around 531.7 J/g. The value is confirmed by BAIR et. al. which shows a value of 515 ± 10 J/g for the complete polymerization of a monomer BCB resin [18]. An increased heat rate leads to more intensive reaction peak but with less time resolution, which increases the inaccuracy for a kinetic model development.

Heat rate [K/min]	Reaction heat ΔH [J/g]	T_{Peak} [°C]
2	289,6	233,35
5	283,6	245,24
10	276,4	255,52
20	281,8	266,00
40	277,4	277,12
Average ΔH_{total}	$281,8 \pm 5,3$	

Table 2. Heat reaction and the peak temperature of photo BCB

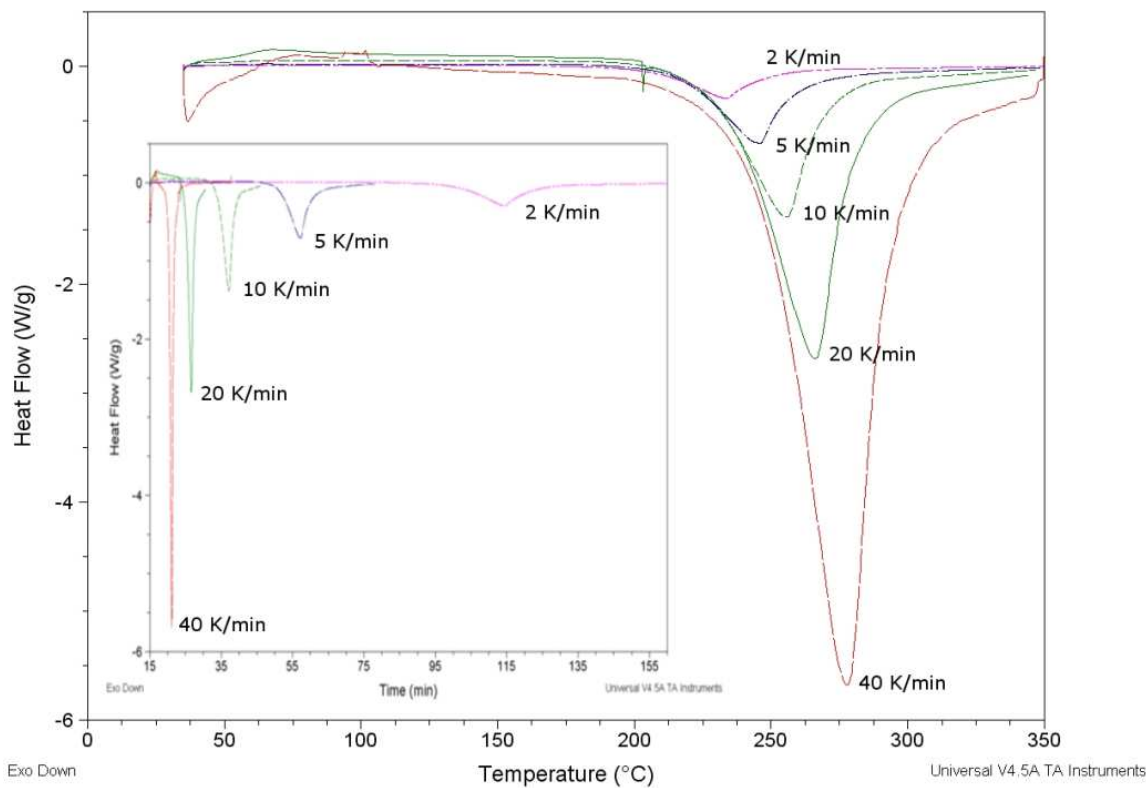


Figure 7. Non-isothermal DSC measurement of CYCLOTENE 4026-46 versus temperature and time

The state change at the glass transition temperature caused more or less a peak in the DSC curve. This peak increases significantly with higher heat rates [19]. The uncured coated BCB has a T_g of around 60°C. In figure 7 the parasitic peak which is caused by the overwhelming of the glass transition temperature (gelation) could be seen for the two heat rates at 20K/min and 40K/min in the temperature range from 60°C up to 100°C.

The vitrification of the polymer is the important factor for the reaction kinetic caused by the gradual decreasing of the rate. When the material returns to a glassy state, the same peak is generated, but the high slope of the reaction signal absorbs the additional peak. The vitrification could only be observed by the gradual change of the reaction rate.

The gradual change is in the case of non-isothermal experiments softened by the permanent increase in the temperature. The heat signal of the state change is calculated into the total heat of reaction.

Based on the knowledge of the T_g (figure 5), the influence of the vitrification could be estimated for the different heat rate experiments. The theoretical development of the T_g for the non-isothermal experiments is plotted in figure 8. The influence of the diffusion controlled part decreases with higher heat rates and has shifted the vitrification to higher temperatures.

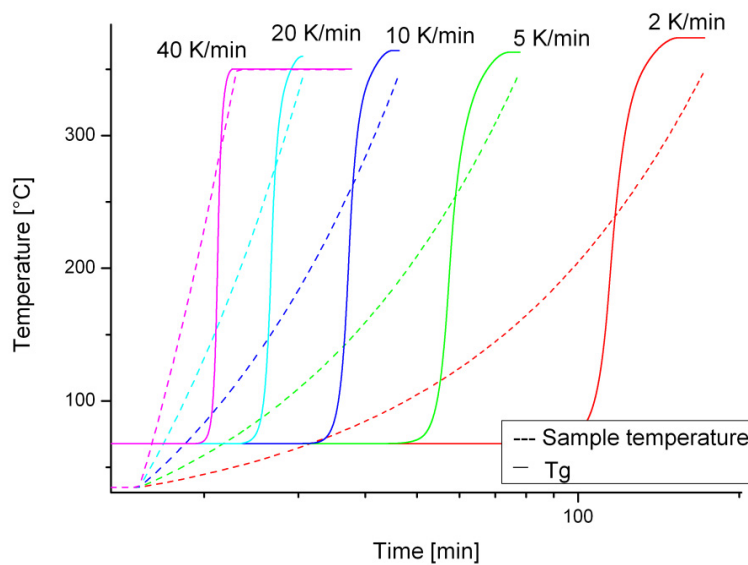


Figure 8. Prediction of the glass transition temperature for the non-isothermal experiments of photo BCB

Low heat rates or isothermal experiments allow to analyze better the influence of the vitrification on the reaction rate. An isothermal measurement is based on a heat up phase, a soak temperature and a cool down phase. An isothermal experiment also gives a better prediction for the real cure process in a convection oven. But an isothermal measurement method has some disadvantages in contrast to an experiment with a continuous heat rate. The extent of cure is calculated by the integration of the reaction peak signal to get the reaction heat ΔH_{ds} over the soak temperature. The higher time resolution of the reaction signal is in relation to a much smaller reaction peak. The small peak and the possibility of not a fully polymerized layer at the soak temperature, caused by vitrification or short process time, are critical impacts in estimating the total heat reaction ΔH_{total} . A simple estimation of the total heat reaction can lead to an inaccurate interpretation of cure degree (see Eq.(3)). The reaction already starts during the heat up and cool down phases, which takes into account the integration of heat flow over time. The discontinuity of the temperature function produce parasitic signals. The DSC signal of a BCB soft cure at 210°C at 30 minutes is plotted in figure 9. The heat flow signal shows that there is a parasitic signal peak between isothermal and dynamic heat phases. The reaction start during the heat up phase, which can also be seen. The short process time leads only to a soft cured layer, which

means that the measured reaction heat does not equates to the total reaction heat. After the soft cure, the sample was again heated up to 350°C with a constant heat rate. A leftover heat of reaction ΔH_{res} can be measured. The sum of ΔH_{ds} and ΔH_{res} leads to the total heat of reaction ΔH_{total} [12].

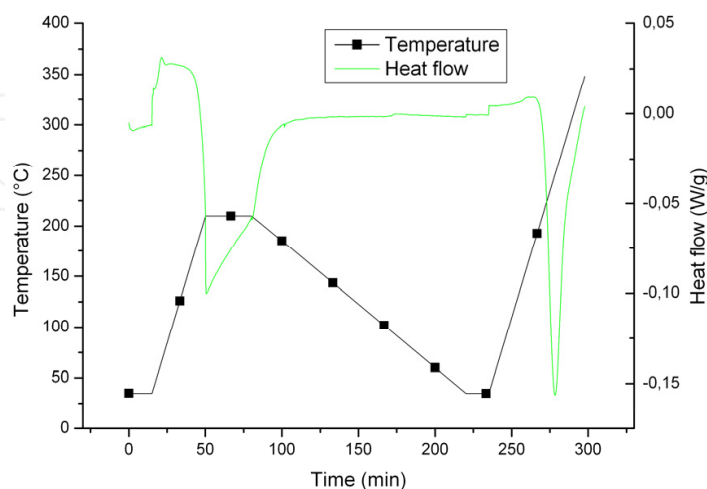


Figure 9. DSC measurement of a BCB soft cure process with additional non-isothermal heat up step to estimate the cure degree.

5. Development of a kinetic model of the polymerization reaction

The extent of cure for a dedicated cure program can be measured by DSC experiments. But the prediction of the extent of cure and the polymerization behavior based on any temperature – time program is necessary for any process optimization with respect to energy consumption, process time or material properties. On account of the DSC experiments, a kinetic model can be set up to characterize the polymerization reaction and can be used to design and optimize the cure process. The reaction is described by a mathematical relation between time, temperature and the extent of cure. In general, special software is required to develop the kinetic equation. The kinetic model in combination with a chemical-rheological model allows a simulation of the complete polymerization reaction [14] [8].

The kinetic models are generally sorted into two types:

- A phenomenological model and
- A chemical model.

The phenomenological model describes the reaction by a relative simple equation. This model type intentionally ignores details of the reaction with the benefit of simple application. Detailed relations and progression of the different chemical reaction steps and the relationship of the reaction groups will be ignored. The chemical reaction model takes into account the chemical steady state of the partial reactions. These types of models have a much better prediction and interpretation potential, but it is often not useable, especially for complex reactions. In contrast to a phenomenological model, the efforts involved for such a

model are much higher, because many more reactions parameters are necessary, and the users need to do a chemical analysis of every reaction step. The phenomenological model can be used without chemical understanding, and can be created only by a comparison of reactants and products. The extent of cure behavior, which has been estimated by DSC experiments, was used to create a phenomenological model for BCB. The simple application makes the phenomenological model the most preferred for polymerization reactions [20] [21].

The two-step polymerization reaction of BCB can be described by a pseudo first-order equation. Based on that simplification, the BCB reaction could be described as follows:

$$\frac{d\alpha}{dt} = k_e(T)f(\alpha) \quad (4)$$

Where α is the degree of cure, $k_e(T)$ is the reaction rate constant which depends on the temperature, and $f(\alpha)$ is the reaction model which describes the reaction order [22]. The kinetic equation such as Eq.(4) is a simplified assumption which describes the reaction rate as a product of a temperature-depending function and a fraction-transformed-depending function. There is a range of empirical mathematical forms for the reaction model [23]. Some particularly idealized reaction models are proposed in table 3.

Reaction model	$f(\alpha)$
Power law	$4\alpha^{3/4}$
Power law	$3\alpha^{2/3}$
One-dimensional diffusion	$1/2\alpha^{-1}$
Mampel (first order)	$1 - \alpha$
Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$
Three dimensional diffusion	$2(1 - \alpha)^{2/3}[- \ln(1 - \alpha)]^{-1}$
Contracting sphere	$3(1 - \alpha)^{2/3}$

Table 3. A range of reaction models which are often used in kinetic analytics

The reaction rate constant could be realized for the simplest case by the Arrhenius relation:

$$k_e = A \exp\left(\frac{-E_A}{RT}\right) \quad (5)$$

Where R is the universal gas constant, E_A is the activation energy, T is the temperature and A is the reaction rate constant at an infinite temperature [24]. The Arrhenius equation describes a reaction in gas phase. In approximation, the relation can be used for liquid and solid materials. But influence by molecule mobility and vitrification are ignored and could be added by the adaptation of the reaction function.

The determination of the three important kinetic parameters, the two Arrhenius parameter E_A and A and the reaction model $f(\alpha)$ is an interlinking problem. The measurement of one of the parameters, and especially the accurate estimation, influence the other two parameters.

Based on this problem they are often called a kinetic triplet [25]. There are many different methods for the determination based on DSC measurements. The method of KISSINGER has been used for the investigation of the polymerization process of BCB. It allows for a simple application with a small inaccuracy, which is also described in detail by STARINK.

The KISSINGER method is focusing on the determination of activation energy as first parameter with the most accuracy possible. The reaction rate in Eq.(4) is calculated by the Eq.(1) from a DSC experiment. The Eq.(5) is inserted into the Eq.(4). The logarithm of Eq.(4) leads to the following equation:

$$\ln \frac{d\alpha}{dt} = -\frac{E}{RT} - \ln f(\alpha) \quad (6)$$

For non-isothermal experiments with constant heat rate ($\beta = dT/dt$) the Eq.(6) could be changed to:

$$\ln \frac{d\alpha}{dT} \beta = -\frac{E}{RT} - \ln f(\alpha). \quad (7)$$

The activation energy could be obtained from the slope of plots of $\ln(d\alpha/dT)$ versus $1/T$. It is estimated without any knowledge of the reaction model $f(\alpha)$. In literature, the principle is also termed model free kinetic (MFK). The slope in the plot should be constant. If there is a change in the slope, it indicates a phase change in the reaction. The calculation of the reaction rate by Eq.(1) leads to an inaccuracy which could have a huge impact on the kinetic equation caused by the triplet relation. The assumption of the reaction rate can be replaced by correlation of a set of non-isothermal DSC experiments. Based on Kissinger, the Eq.(7) is integrated by separation of variables and the following approach was postulated:

$$\int_0^{\alpha_f} \frac{d\alpha}{f(\alpha_f)} = \frac{A}{\beta} \int_0^{T_{100\%}} \exp\left(-\frac{E_A}{RT}\right) dT \approx \frac{AE_A \exp\left(\frac{-E_A}{RT}\right)}{\beta R \cdot \exp\left(\frac{-E_A}{RT}\right)^\kappa} \quad (8)$$

The Eq.(5) have been logarithm and lead to following equation:

$$\ln \frac{\beta}{T_f^\kappa} = -\frac{E}{RT} + C \quad (9)$$

C is a constant for different heating rates at a constant degree of polymerization and belongs to the reaction model. T_f means the temperature of experiments with different heat rates where the same extent of cure occurs. The variable κ is a correction factor in the range of 1,92 up to 2. With the Eq.(9) the E_A can determined as the slope of the plot $\ln(\beta/T_f^\kappa)$ versus $1/T_f$ independent of constant C. Three or more experiments with different heating rate β are necessary to determine the activation energy with MFK. The correct estimation of T_f is the main challenge at this method. For the normal reaction, analyzing the maximum rate method or peak method is used, which is described also in the ASTM E698 norm [26]. The

peak method avoids the defective calculation of cure rate by Eq.(1). It was found that the extent of cure is approximately fixed at the maximum reaction rate, but a small error will be introduced. The peak temperatures of the non-isothermal experiment are shown in table 2. The temperature of the peak is shifted with the heat rate. The results of Eq.(9) for the five non-isothermal experiments are plotted in figure 10.

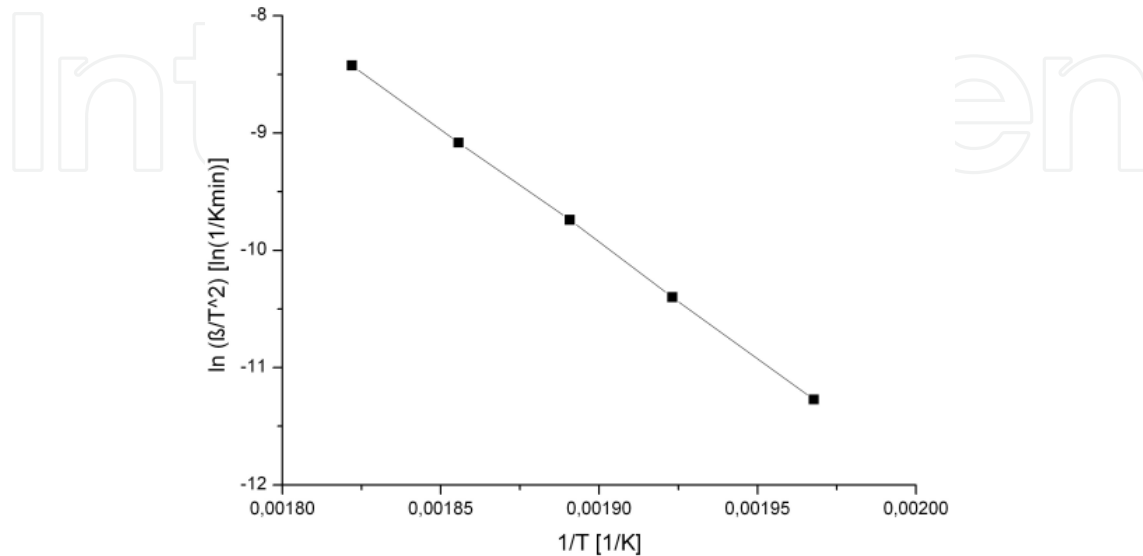


Figure 10. Non-isothermal measurement of BCB. The slope approximate the activation energy of the polymerization reaction cure degree of around 73%

A value of 149.5 kJ/mol \pm 1.75 kJ/mol was measured, which acknowledges the declarations of DIBBS et. al.. Different literature sources describe an activation energy in a range from 146 kJ/mol up to 197,6 kJ/mol [27] [17] [28]. A disadvantage of this method is that the values are only estimated at one degree of cure (around 73 % conversion). Therefore, in relation to the used heat rates, the value describes only the chemically controlled kinetic. With a first-order reaction model, the A has a value of 1,35 h⁻¹ for a reference temperature T₀ of 210°C:

$$\frac{d\alpha}{dt} = 1,35 h^{-1} \exp \left[-\frac{149,5 kJ / mol}{T} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] (1 - \alpha) \quad (10)$$

The plot for the non-isothermal experiments (Figure 11) shows that the model fits the chemically controlled regime very well. The estimated model is in good agreement with the already proposed kinetic model for BCB [2] [6]. There is a poor estimation for the diffusion controlled part, which is also described in previous publications [6] [28]. With the focus on lower cure temperatures, the influence of the diffusion controlled part increases.

The polymerization analysis aims for a better understanding of the influence of the vitrification. That demands a modulation of the normal kinetic model Eq.(10). There are many different methods for correcting the conventional reaction model by a conversion-dependent diffusion contribution. One of the most popular methods for thermosetting systems is to modify the kinetic equation by a “diffusion control function” which is described by SCHAWÉ [29].

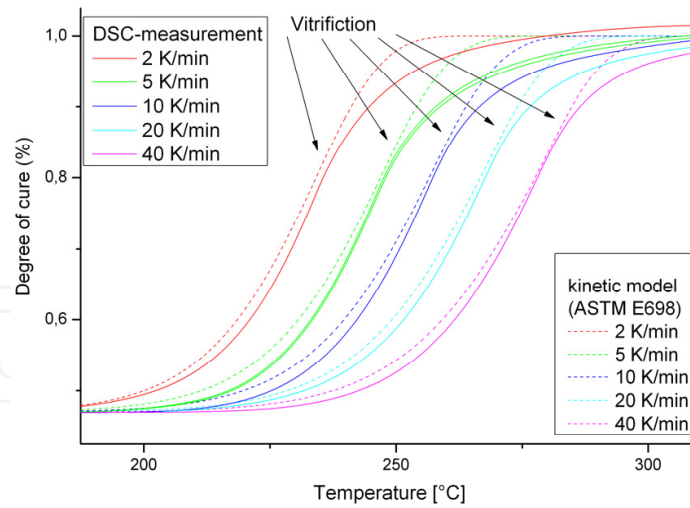


Figure 11. Extent of polymerization based on the non-isothermal experiments and calculation based on Eq.(10)

$$\frac{d\alpha}{dt} = k_e(T)f(\alpha)f_d(\alpha;T) \quad (11)$$

The diffusion control function works in an electro-technical analogy like a low-pass filter. During the polymerization up to the change in the solid state, the function should not influence the reaction which means $f_d(T < T_g) = 1$. After the vitrification, the function decreases down to zero. A function which achieves this condition is proposed by SCHAWÉ:

$$f_d(\alpha;T) = f_d(T_g(\alpha)) = 1 - \left(1 + \left(\frac{T_0 - T_g(\alpha)}{D} \right)^3 \right)^{-1} \quad (12)$$

where T_0 is the temperature at which the diffusion control function is zero and A is an empirical constant to smooth the function. The function is focused for a reaction which is nearly stopped in a glassy state. The difficulty of this method is to estimate the empirical diffusion control function which leads to the best fit. Another problem is the influence of the diffusion control function for the chemically controlled part.

MENCZEL describe an alternative model from RABINOWITCH for small-molecule reactions, where the rate constant k is based on a sum of a chemically controlled and diffusion controlled rate constant [8]:

$$\frac{1}{k_e(T,\alpha)} = \frac{1}{k_r(T)} + \frac{1}{k_d(T,\alpha)} \quad (13)$$

where k_e is the overall rate constant, k_r is the Arrhenius ratio constant for the chemical reaction and k_d is the diffusion rate constant. The overall reaction rate constant k_e is governed prior the vitrification by the Arrhenius rate constant, and after vitrification is dominated by the diffusion rate constant. The disadvantage is an extended interlink problem of the parameters.

A combination of both models from SCHAWÉ and RABINOWITCH has been used to create an advanced model for the polymerization reaction of CYCLOTENE. Two different rate constants ($k_r; k_d$) were calculated. The overall reaction rate constant is the sum of both, but the terms are combined with a step-function, which works like a switch and allows the change between gel and glassy state kinetic models.

$$\frac{d\alpha}{dt} = k_r(T)f(\alpha)f_{step}(\alpha;T) + k_d(T)f(\alpha)(1 - f_{step}(\alpha;T)) \quad (14)$$

The step-function belongs to the process temperature and the glass transition temperature and gets a value between one and zero. For both reaction regimes, a first-order reaction model was used based on a good fit, but the model allows for the declaration of two different reaction models for chemically controlled and diffusion controlled states. The following expression was used for the step-function:

$$f_{step}(\alpha;T) = \frac{1}{1 + \exp(-(T - T_g(\alpha))B)} \quad (15)$$

where B is a parameter to smooth the changeover between the two reaction functions. The value was set at 0.1 to get a change in temperature range of $\pm 5^\circ\text{C}$ around the glass transition temperature. The glass transition temperature depends on the extent of cure (see figure 5), and the following relation was estimated based on the measurements of TOEPPER:

$$T_g = \frac{35}{0.054}\alpha^2 - \frac{10865}{27}\alpha + \frac{3070}{27} \quad (16)$$

For the kinetic model, two Arrhenius terms need to be calculated, one for the chemically controlled part and one for the diffusion controlled part. The Eq.(9) allows the calculation of the activation energy for different extents of reaction. In contrast to the peak method, the extent of reaction need to be calculated by Eq.(3). The consideration of the vitrification-heat rate relation for the estimation of the activation energy of the two regimes is necessary to see any difference. For example, the highest heat rate of 40 K/min leads to a vitrification above 90% in contrast to the slowest heat rate of 2 K/min, which vitrifies around 80%. Therefore the heat rate of 2 K/min is used to calculate the activation energy for the chemically controlled state up to 80%, above this value it is used for the calculation of the activation energy of the diffusion controlled state. The calculated activation energies for different extents of reaction are shown in figure 12.

The change in the reaction kinetic is marked by the change in the activation energy. The activation energy for the chemically controlled region has an approximate value of 157.1 ± 3.6 kJ/mol. The activation energy is slightly higher than the value which was estimated by the peak method /ASTM E698 norm (pointed line). For the diffusion controlled kinetic, a higher activation energy of around 166.1 ± 8.1 kJ/mol was measured. The increase in the activation energy in a diffusion controlled regime shows a higher temperature dependency for the reaction, which could be explained by the more temperature-dependent molecule mobility.

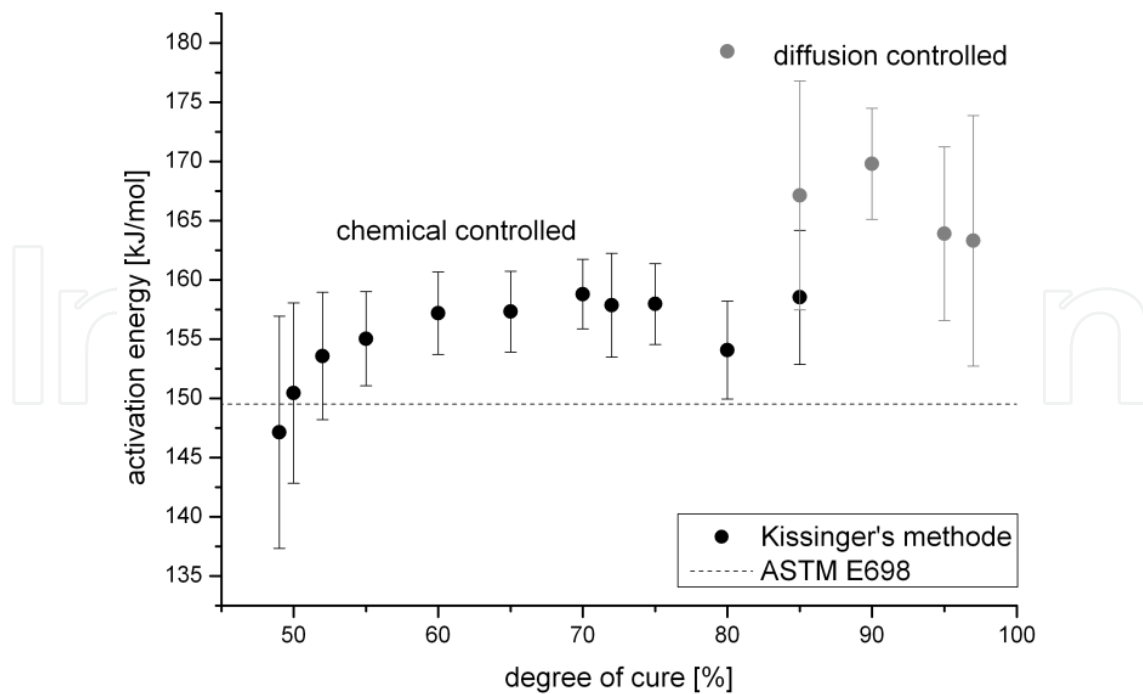


Figure 12. Activation energy estimated by the ASTM E698 norm and dependent of the degree of cure

The results for the reaction rate at the reference temperature are 1.41 hr^{-1} for the chemically controlled regime, and 0.27 h^{-1} for the diffusion controlled regime. In figure 13, the calculated degree of polymerization for the conventional (Eq.(10)) and modified kinetic model (Eq.14) is compared to a measured curve for a cure at 190°C . The modified model shows a much better fit in comparison with the real behavior above a degree of cure of approximately 80 %.

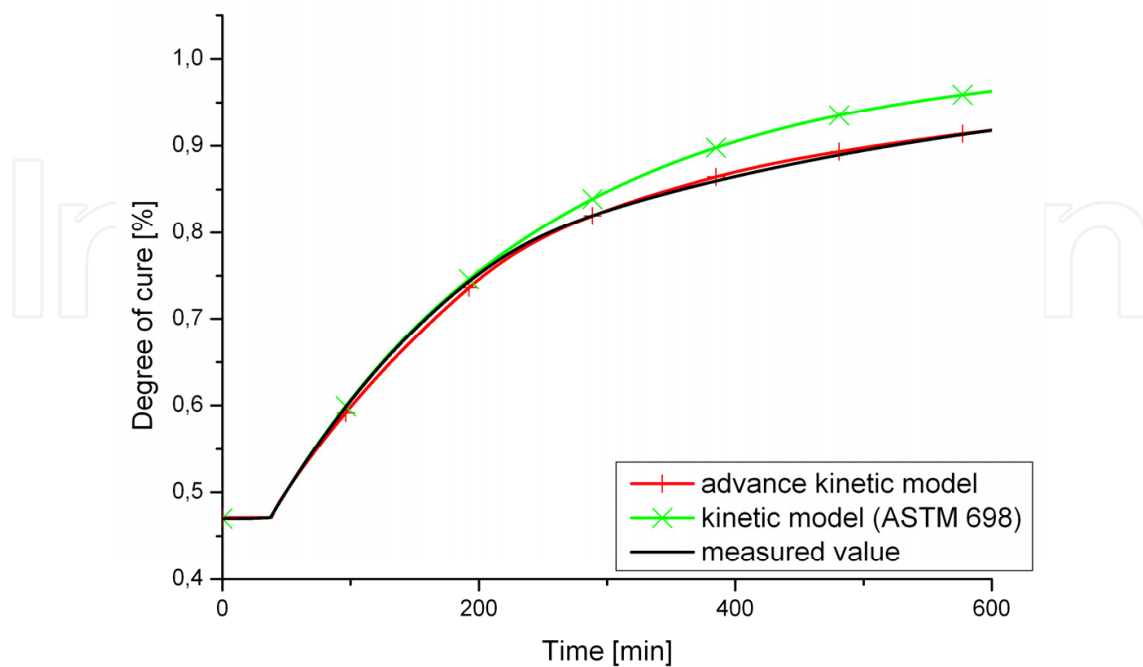


Figure 13. Degree of cure of a photo BCB sample at 190°C

6. Benefits of the kinetic model for the BCB polymerization and the relation for the polymer properties

The investigation of the cure behavior of BCB shows that an ongoing polymerization reaction in solid state is also possible with the requirement of a minimal process temperature above 150°C caused by the thermal activation. The enhanced model which is described in Eq.(14) allows a much better prediction for the polymerization of BCB in glassy state. The polymerization in vitrified state is relative slow and should only use if the device is temperature critical. But the cure in glassy state could be interesting with the focus on the properties of the polymer. The stress development of BCB during the cure at 250°C is plotted in figure 14. The thermal stress of a polymer film on a substrate could be calculated as followed:

$$\sigma_{th} = \frac{E_f}{1 - \nu_f} (\alpha_f - \alpha_s) \Delta T \quad (17)$$

Where E_f and ν_f are the Young's modulus and Poisson ratio of polymer. For silicon as substrate CTE α_s are approximately 2.6 $\mu\text{m/mK}$, and BCB has a CTE of 42 $\mu\text{m/mK}$. Delta T is the temperature difference between ambient temperature and the vitrified temperature. The polymer is in gel phase during the heat up phase and the stress is nearly zero. When the polymer vitrifies, the stress state at that point is set to zero. During the cool down, the thermal tensile stress in the layer increases based on the coefficient of thermal expansion mismatch to the substrate [8] [30] [31]. A nearly fully cured BCB has a T_g near the decomposition temperature, which means the zero stress point could not reset by processing at a higher temperature. A reheating of the BCB after the cure at 250°C above the temperature where the polymer vitrify leads to a compressive stress, which could be seen in figure 15. The stress measurements were done by Toho Technology with a Flexus-2320-S system. In comparing the stress values at room temperature between the measurement of figure 14 and figure 15 a slightly difference occurs. This could be explained by a visco elastic behavior of the BCB which is discussed elsewhere [32].

There are trends in microelectronics towards enlarging the wafer size in combination with thinner wafers to decrease costs. In contrast to this, the signal frequency gets higher and higher, which means packaging thick dielectric polymer layers to assure good signal integrity. It results in two major challenges. The first is in handling, because the stress leads to a bow of the wafer, which is a problem for automatic handling tools and also for the processes because of the topography. The second point is that the stress in the layer stack is a continual problem for reliability. It force cracks through the layers and delamination. The decrease of the stress in the layer stack becomes more and more a focus in the future. This could also be seen by the polymer supplier who presented a couple of new polymers with low temperature cure properties in the last few years.

The stress in the polymer layer can be minimized by the optimization of the cure process with the help of a kinetic model. There are already some works which try to decrease the stress by cure process optimization [33] [34], but they unaccounted the meaning of the vitrification for the stress formation. A set of BCB experiments was done to examine the

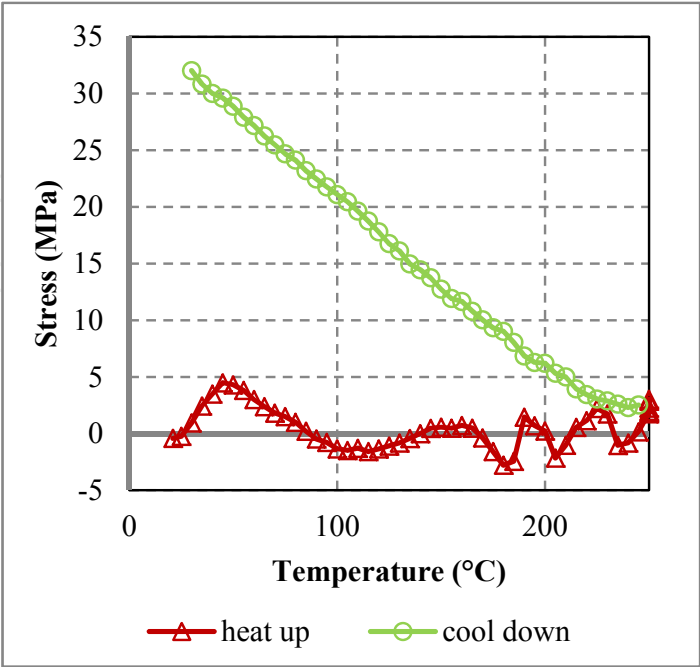


Figure 14. The stress in the material during a cure at 250°C

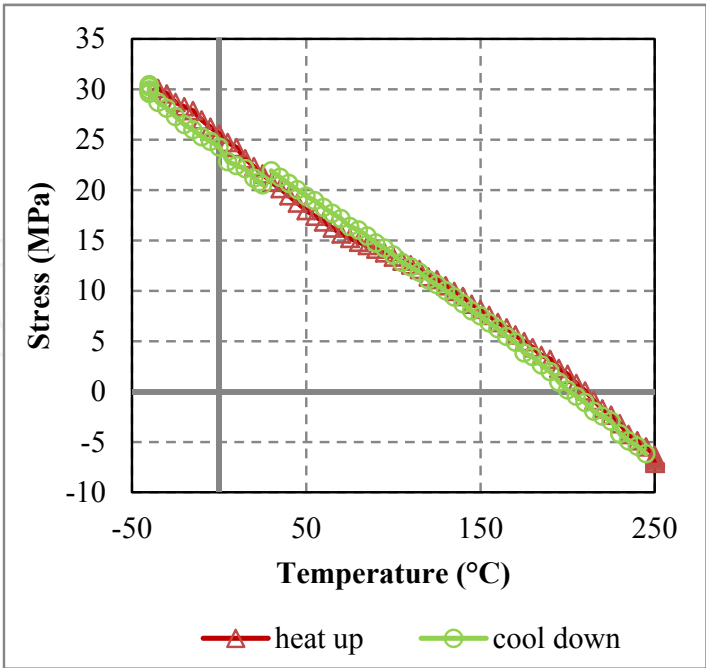


Figure 15. Stress curve of a cured BCB layer on a silicon substrate measured with Flexus-2320-S

potential of stress decreasing by process optimization. In relation to the lowest temperature where vitrification occurs, and a nearly fully cured layer is obtainable, a theoretical minimal stress of around 18 MPa should be achievable. There has been shown a possible decreasing of the stress in a BCB layer from 28 MPa based on a normal cure at 250°C down to a stress value of 19 MPa [32]. Nevertheless, the process time will increase exponentially with a decrease of the temperature, and for higher volumes a decrease of the temperature down to 150°C is not economically feasible. The kinetic model allows for the creation of curing processes with more than one soak temperature, with the benefit that the processing temperature before and after the vitrification is higher to decrease the processing time, and the temperature is set lower in the phase change to a solid state. The cure of the polymer is generally performed in convection ovens. The slow temperature change in a convection oven limits the difference between the high and low temperature levels. A programmable control of the oven makes a dynamic heat process possible, which reaches the shortest possible time in combination with low stress in the polymer layer. Such a theoretical temperature profile is plotted in figure 16.

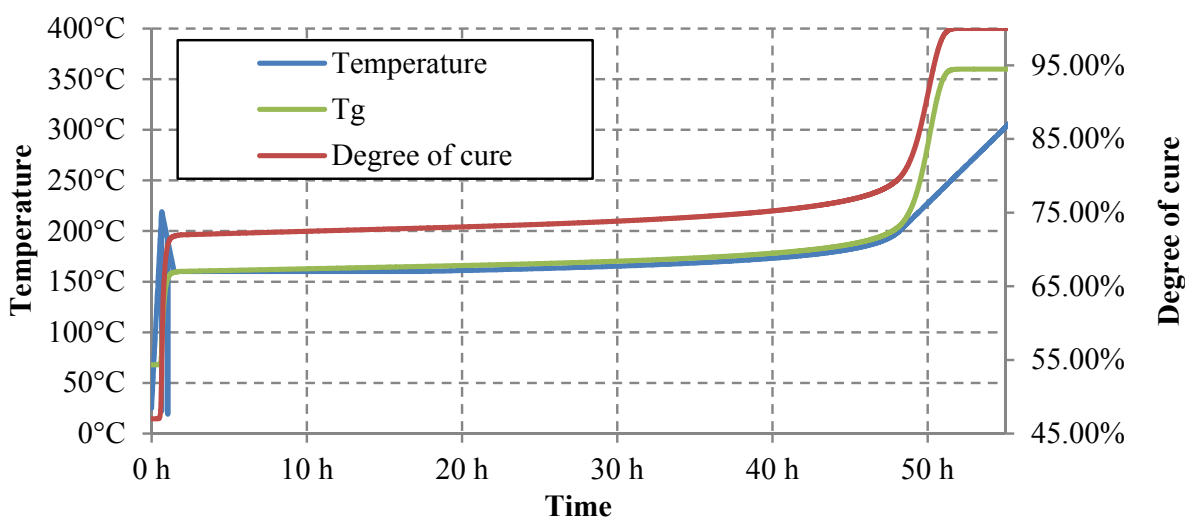


Figure 16. Calculated process profile with a focus on a vitrification at low temperature

The oven will heat up to a high peak temperature to achieve fast polymerization. After that the temperature is decreased to reach a vitrification at low temperature. The temperature will be ramped up after the vitrification, but the process temperature is controlled to be below the glass transition temperature, to decrease the process time and avoid devitrification. The described program aims for a vitrification at low temperature in relation to the stress in the polymer layer. DIBBS described a seven days process, which also aims to get a vitrification at a low temperature and slowly increase the temperature after that [2]. The process involves a long time processing at 150°C, and after that a slow ramp up to 250°C. The expected cure profile of DIBBS process is plotted in figure 17. The long heat up

phase of 6 days results due the lack of a detailed kinetic model for the diffusion controlled part.

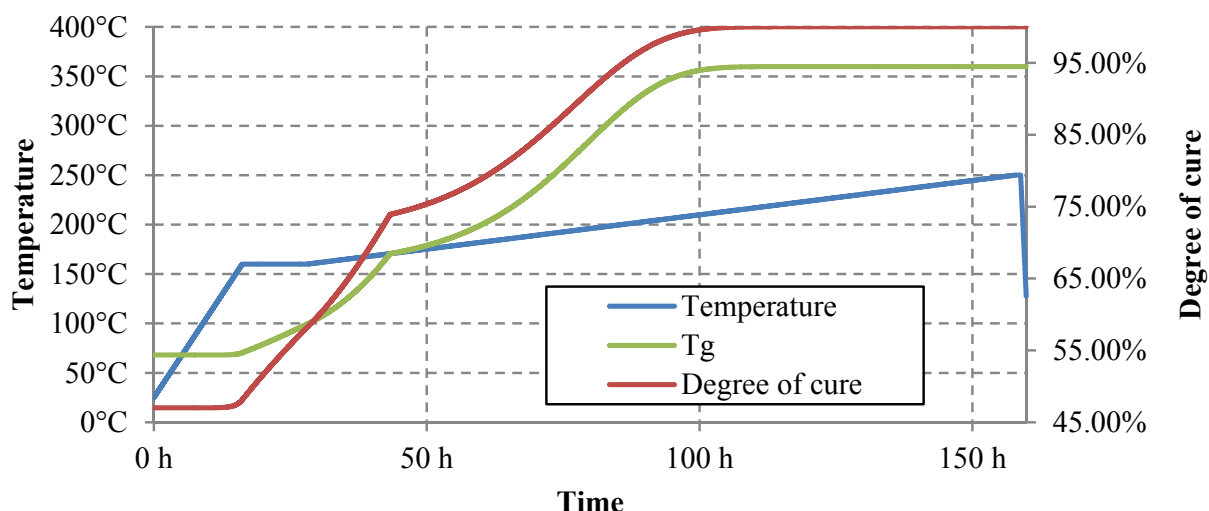


Figure 17. Calculated process profile of the low stress cure of DIBBS

He realized only a small decrease of the stress down to 24 MPa. The results of DIBBS and own experiments lead to the assumption that the ongoing of the polymerization in glassy state also influences the stress. A BCB layer on substrate was soft cured at 210°C up to 70%, which has a T_g of around 190°C. After soft cure, the layer was stored at 150°C for 100 hours and reached 93% polymerization. The stress in the layer decreased during the storage from 24 MPa down to 19 MPa [32]. A layer which was fully cured at 250°C shows no strong relaxation after the storage. This could be explained by two things. First, the partly cured film has a higher viscoplastic behavior and the material relaxed easier. Another possible reason is stress relaxation caused by the ongoing polymerization at low temperature. Further ongoing experiments are necessary to clarify in more detail the stress behavior in solid state BCB layers.

The polymer dielectric layer is an essential component in packaging technology. The temperature-activated polymerization processing of polymers has increasingly become a key parameter for the process workflow. The investigation of polymerization processes allows the optimization of the cure process down to lower temperatures. Based on the example of BCB, a simple model was developed, which also described the polymerization reaction of BCB in a solid state. The model allows for significantly decreasing the stress in the layer and also decreasing down to very low cure temperatures. The mechanical properties like Young's modulus or tensile strength of BCB will not be affected by the processing parameter changes [32]. In combination with the low-temperature curing possibilities of BCB, a decrease in the stress of about approximately 30% is possible.

Author details

Markus Woehrmann

Technische Universität Berlin (TUB), Berlin, Germany

Michael Toepper

Fraunhofer Institute for Reliability and Microintegration (IZM), Berlin, Germany

Acknowledgement

The authors want to emphasize the contributions from the colleagues at Fraunhofer IZM who are not mentioned here by name. Financial support from the Deutsche Forschungsgemeinschaft (International Research Training Group GRK 1215, "Materials and Concepts for Advanced Interconnects") is gratefully acknowledged.

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