# THERMAL ENDURANCE OF UNREINFORCED UNSATURATED POLYESTERS AND VINYL ESTER RESINS

by

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## Abstract

In addition to maximum service temperature as determined from heat deflection temperature (HDT) or glass transition temperature (Tg), thermal endurance is important for composites exposed to high temperatures. Typical applications for such are for electrical components and under the hood automotive. It is beneficial to have accelerated methods for the determination of thermal endurance. Thermogravimetric analysis (TGA) is one such method. Standards exist for estimating life time at elevated temperatures by TGA. ASTM standards E 1641 and E 1877 consider the decomposition kinetics and the estimation of thermal endurance respectively. Determination of relative thermal indexes can then be done according to ISO 2578. In this study selected unsaturated polyester and vinyl ester resins have been studied by TGA. Attempts to interpret results by the procedure of ASTM E 1641 was possible for isophthalic resins, but not for DCPD and vinyl ester resins due to more complex decomposition mechanisms. By an alternative isothermal TGA method and interpretation by basic chemical kinetics we were able to estimate thermal endurance of these resins. The results suggested better thermal endurance at temperatures around and below 200°C for the DCPD resin tested than the isophthalic resin, a fact that could not easily be detected by the ASTM procedures. This behaviour was confirmed in an oven weight loss test at 220°C for 300 hours duration.

## Introduction

In addition to maximum service temperature as determined from heat deflection temperature (HDT) or glass transition temperature (Tg), thermal endurance is important for composites exposed high temperatures. Typical applications for such are for electrical components and under the hood automotive. It is of course beneficial to have accelerated methods for the determination of thermal endurance. Thermogravimetric analysis

(TGA) is one such method. Standards exists for estimating life time at elevated temperatures by TGA. ASTM standards E 1641 [1] and E 1877 [2] consider the decomposition kinetics and the estimation of thermal endurance therefrom respectively. Determination of relative thermal indexes can then be done according to ISO 2578 [3].

A restriction on the use of the ASTM E 1641 method to determine kinetic parameters is that it applies to first order reaction kinetics where the decomposition follows what is described as a smooth continuous mass change with a single maximum rate [1].

In the simple case of a decomposition reaction following first order reaction kinetics one can describe the mass loss by the first order rate equation:

$$\frac{dm}{dt} = -k \cdot m \qquad (1)$$

And with a rate constant, k, described by an Arrhenius relationship:

$$k = Ae^{-E_a/RT} \qquad (2)$$

Operating the TGA in a scanning mode, heating the sample at a preset rate, β [K/min]:

$$T = T_0 + \beta \cdot t \qquad (3)$$

Combining these and attempting to solve we will get:

$$\ln \frac{m}{m_0} = -\frac{A}{\beta} \cdot \int_{T_0}^{T} e^{E_a/RT} dT \qquad (4)$$

ASTM E 1641 calls for running four or more different heating rates all between 1 and 10 K/min. The analysis is not straightforward, as can be seen from equation 4 above. This is because the integral is not easily solved. Thus there is an iterative method involving tabulated numerical integration constants described that will give the activation energy.

An alternative would be to study the decomposition by isothermal experiments. In the case of isothermal decomposition data obeying first order kinetics the analysis is much simpler, as the rate constant now actually is constant during the experiment:

$$\ln \frac{m}{m_0} = -k \cdot t \qquad (5)$$

This will give the rate constant as the slope of a semi-log plot of ln(m) vs. time. The major disadvantage is that the isothermal experiment will generally take longer to run. Also several experiments at different temperatures are needed to give the temperature dependence of the decomposition rate according to equation 2. Another disadvantage is the heating from ambient to test temperature necessary before the isothermal TGA starts. This will hide any deviations from the simple first order model of equation 5 if they take place at very low conversions.

## Experimental

Cured unsaturated polyester samples were prepared. An isophthalic resin and a dicyclo pentadiene (DCPD) resin were tested. Samples were diluted with styrene to a viscosity of 300 mPas to give acceptable castings. The curing system used was the commonly applied redox initiation system with cobalt octoate and MEK peroxide. Samples were cast between prepared glass plates at 2 mm thickness and allowed to cure 24 hours at room temperature followed by postcuring 24 hours at 60°C and 3 hours at 150°C. Similarly a vinyl ester resin casting was also prepared with cobalt octoate and cumene hydroperoxide as curing system.

Samples, all in one piece, approximately 20 mg each and preferably not taken from the edges of the castings were used for the TGA analysis. For the scans at different rates according to the ASTM method, 3, 5, 7 and 10 K/min heating rates were used. Isothermal experiments were performed at temperatures 300, 320, 340 and 360°C, with initial 40 K/min ramping rate from ambient temperature. The decomposition was followed in a nitrogen atmosphere.

## Results: Unsaturated Polyesters

Inital experiments were run according to the ASTM method [1]. A striking difference between the isophthalic resin and the DCPD resin was observed. This is presented in Figure 1. While it shows a smooth continous mass change with a single maximum rate and following first order kinetics probably for the isophthalic resin, it certainly does not for the DCPD resin. The shape of the latter curve suggest multiple reactions taking place.

For this reason isothermal experiments were performed for both resins. The isophthalic resin was tested first as represented by the semi-log plots of Figure 2.

First order rate constants for the four different temperatures have been determined by linear regression of the semi-log data plotted above. Activation energy, Ea, in accordance with the Arrhenius equation, equation 2, have been determined as shown in Figure 3. For all the resins tested the values obtained are listed in Table 1.

Coming back to the comparison between isophthalic and DCPD resin, Figure 4 shows an example taken at one of the temperatures used in the isothermal measurements. This clearly shows the difference between the two resins, and in the case of the DCPD resin the deviation from the behaviour of a single first order reaction. The DCPD resin gives a faster initial decomposition than the isophthalic resin but later it levels out with a slower rate. The isothermal experiments on the DCPD resin are shown in figure 5. The same kind of behaviour can be

observed at all temperatures. This behaviour can be described by a biphasic first order rate equation:

$$\frac{m}{m_0} = ae^{-k_I t} + be^{-k_{II} t} \qquad (6)$$

Typically this is the behaviour of reaction mechanisms involving consecutive or parallell first order reactions.

Based on equation 6 the kinetic parameters for the weight loss data was determined by an iterative least squares method. The experimental data seemed to be very well described by equation 6, this is shown in Figure 6.

Figure 7 shows Arrhenius plots for rate constants, kI and kII determined for the DCPD resin. It has also been attempted for the normalized preexponential factor a. Preexponentials, a and b were normalized to a+b=1, i.e. starting the biphasic curve with no weight loss at time equals 0 minutes. Experimental data have time lags due to the initial temperature ramp. Good linearity in the Arrhenius plot is observed for kI. For kII it is more uncertain. Also the linearity is not impressing, and it should be noted that reaction mechanisms including multiple first order reactions will give linearity of this plot only in certain temperature regions. Thus the linear regression shown above, and especially extrapolations of this, should be treated with great care. The slope of the curve for the preexponential factor, a in Figure 7 corresponds to an "activation energy" of 38 kJ/mol. This is expected be a function of the activation energies of different rate constants in a multiple first order reaction mechanism.

Oven weight loss data at 220°C for the DCPD resin was also obtained, it is of interest to see how the kinetic model is capable of describing these results. This is shown below in Figure 8.

This was obtained using the extrapolations of the above Arrhenius plots for the kinetic model. The result is not conclusive, but the model seems to pick up the general trend and the magnitude of the weight loss. This is notable because much of this effect is really that the crossover between fast initial decomposition and the subsequent slower decomposition takes place at lower weight loss at lower temperatures. This is reflected in the temperature dependence of the preexponential factors of equation 6. Note that the oven weight loss was not really in an inert gas atmosphere. Still it had larger samples so the specific surface for oxygen to have an effect was less than what it would have been for TGA samples at the mg scale.

## Thermal Endurance: Unsaturated Polyesters

The DCPD resin does not show thermal decomposition according to a single first order reaction. Especially since the decomposition "levels out" at different levels at

different temperatures the method described in ASTM E 1877 [2] and ISO 2578 [3] for determination of thermal endurance will not be applicable. These methods use the extrapolation of data in an Arrhenius type plot, from measurements at high temperatures to estimate the temperature that will give a certain lifetime.

To visualize the effect of the observed kinetic model on the lifetime at lower temperatures, the sets of data are extrapolated, even though the extrapolation of the preexponential factors especially is questionable. The resulting lifetime chart for weight losses 5, 10, 15 and 20% is shown in Figure 9. And indeed it can be seen from Figure 9 that the observed decomposition kinetics of the DCPD resin does not give time-temperature plots that can be extrapolated in the manner described in the standards mentioned. A reasonable linear relationship is achieved for the high weight loss data only. Regarding the time necessary to reach a specified weight loss, when going from high to low temperatures a shift towards longer time is observed. And again that reflects the crossover between fast initial and later a slower decomposition.

The simple first order model found to fit for the isophthalic resin, on the other hand, will of course lead to time-temperature Arrhenius type plots as assumed in the standards.

## Vinyl Esters

A standard bisphenol A based vinyl ester resin was also tested in the same way. Figure 10 shows the isothermal TGA weight losses at the same temperatures as for the isophthalic and DCPD resins.

Biphasic kinetics can be observed, but it appears that the faster reactions observed especially at 300 and 320°C has a lower activation energy than what was the case for the DCPD resin. At higher temperatures the biphasic nature disappears possibly as the second rate constant dominates. At 340°C there is a biphasic nature, but at 360°C it can not be observed at all. Note that the scale of figure 10 is very different from figure 5 indicating a better thermal endurance in a vinyl ester. The crossovers are at very low weight losses, and the curves also indicates that this will shift further towards lower weight losses as temperature is reduced. So probably the thermal endurance of this vinyl ester can be estimated assuming the first step observed at 300 and 320°C is neglitible.

A single rate constant was determined for the decomposition at 360°C. This was used together with the kII values for the other temperatures in Figure 11. This seems to fit well with the trend observed, giving good linearity. Values obtained for rate constants and activation energy is at the level as for kII of the DCPD resin shown in Figure 7.

## Thermal Index

Table 1 gives the rate constants determined and the thermal endurance of the resins investigated. The TI used here was the temperature giving 5% weight loss after 20000 hours. Remarkably, a higher thermal index was found for the DCPD resin, even than the vinyl ester. Again this reflects that kII values and temperature dependencies found are quite similar for DCPD and vinyl ester resins. And also that the faster initial decomposition which is much higher on the DCPD resin at 300-360°C becomes less important at lower temperatures, i.e. in the range of 200°C. At 196°C the extrapolated preexponential factor value is only 0.025. A weakness of this comparison is that the data for the DCPD resin depend very much on values for kII and a for which the Arrhenius plots, Figure 7, showed poorer linearity.

## Conclusions

Biphasic first order decompositions was found for the DCPD and vinyl ester resins tested. This was determined in isothermal TGA measurements, which also provided the necessary kinetic parameters for the determination of thermal endurance by extrapolation of time-temperature data. The isophthalic resin studied had a decomposition following the simple first order required in ASTM E 1641 A comparison of the resins' thermal endurance was still determined by the isothermal measurements. Relative performance of the resins in these test showed DCPD and vinyl ester resins being approximately equal, and both outperforms the isophthalic resin.

The use of the ASTM E 1641 method to determine kinetic parameters for thermal decompositions of the DCPD and vinyl ester resins was not possible due to the more complex reaction mechanism.

## References

1) ASTM E 1641 (1998), "Decomposition Kinetics by Thermogravimetry".

2) ASTM E 1877 (1997), "Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data".

3) ISO 2578 (1993), "Plastics - Determination of Time-Temperature Limits after Prolonged Exposure to Heat".
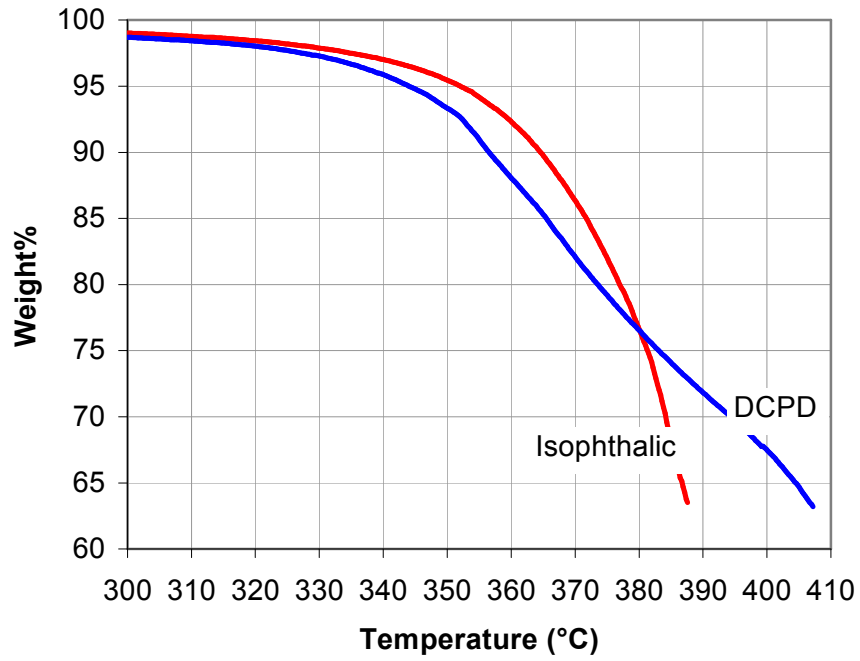
**Figures**



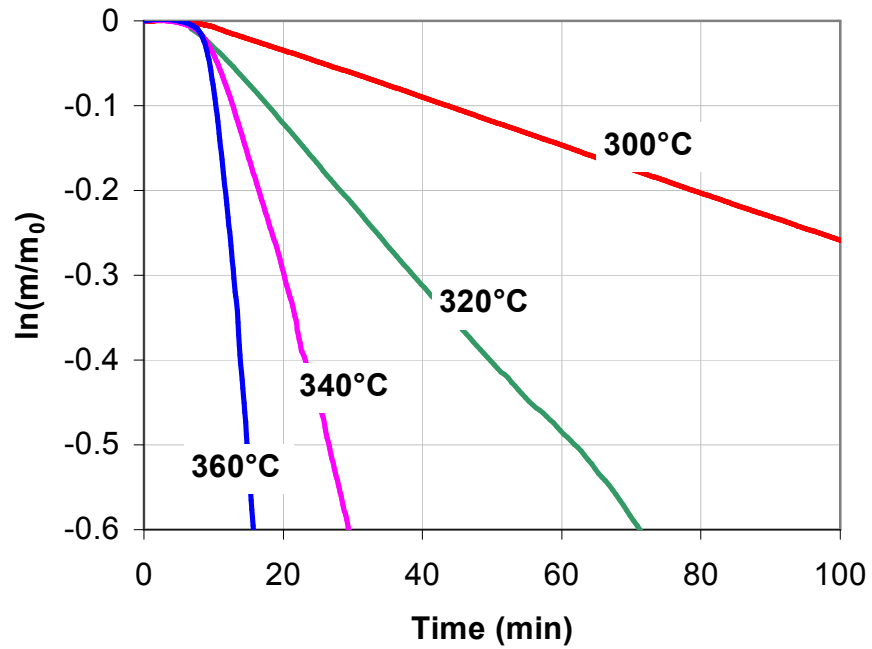Figure 1. TGA scan at 7 K/min for the isophthalic and the DCPD resin.



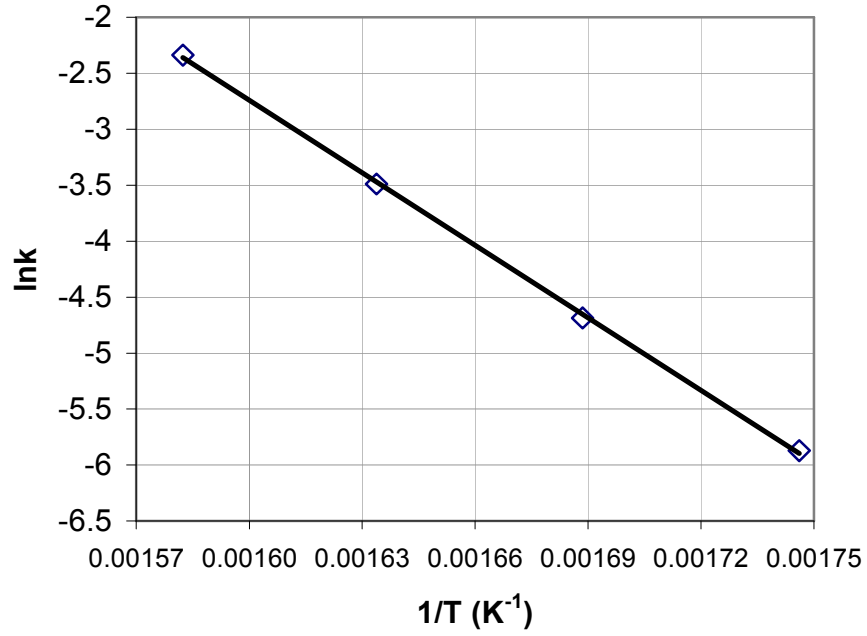Figure 2. Isothermal weight loss data for isophthalic resin.

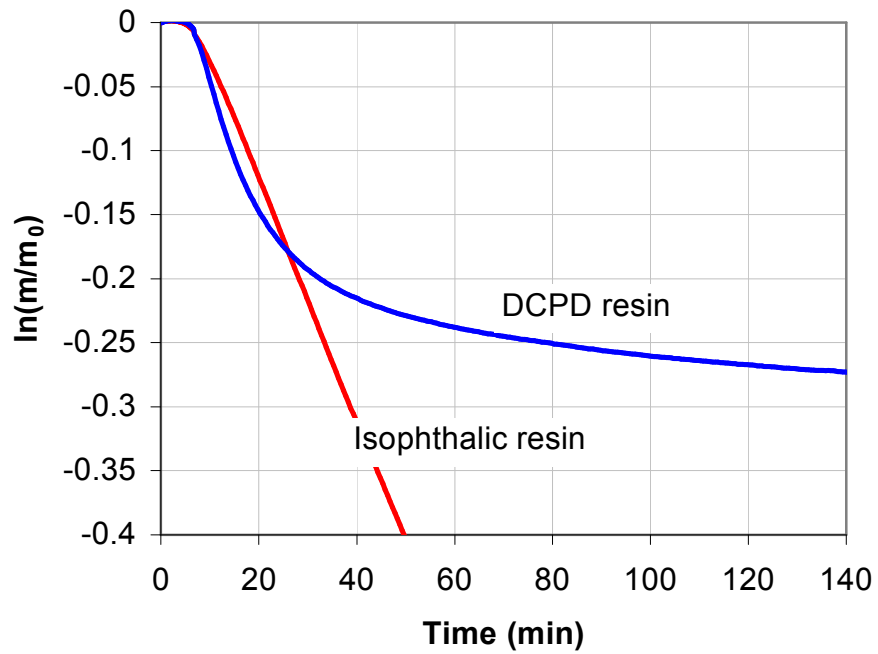**Figure 3. Arrhenius plot of first order rate constant for isophthalic resin decomposition.**



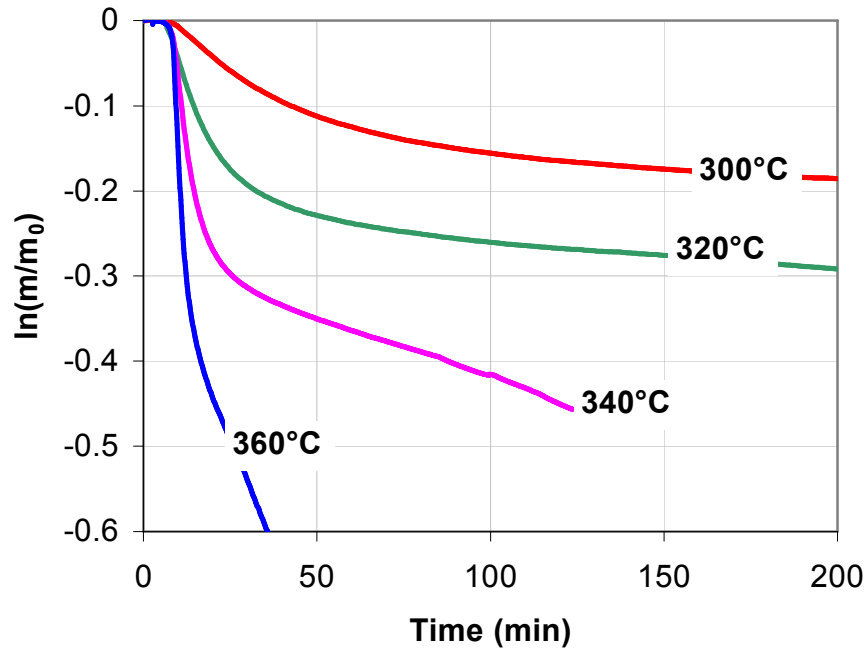**Figure 4. Isothermal data at 320°C on the two different unsaturated polyesters.**

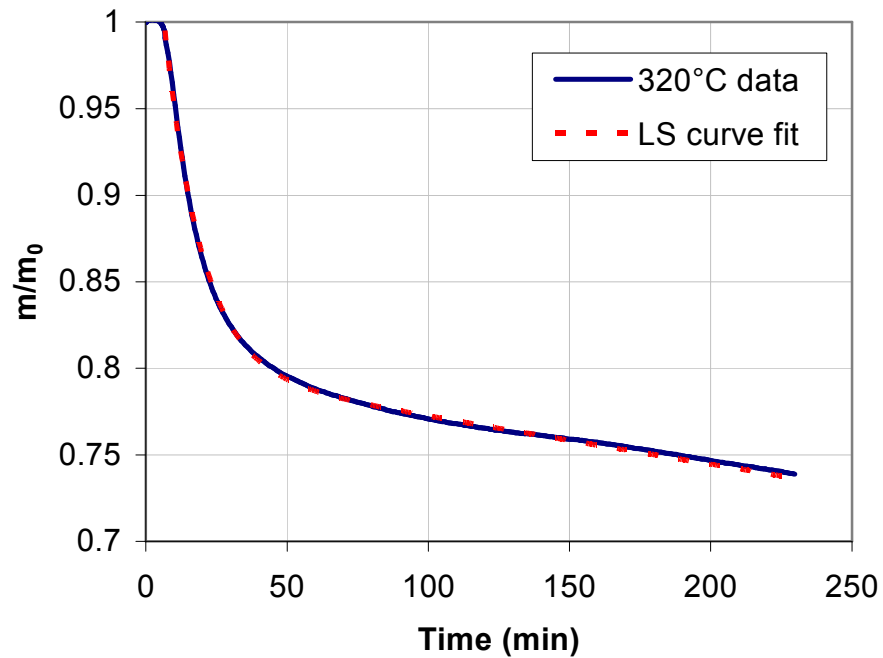**Figure 5. Isothermal weight loss data for DCPD resin.**



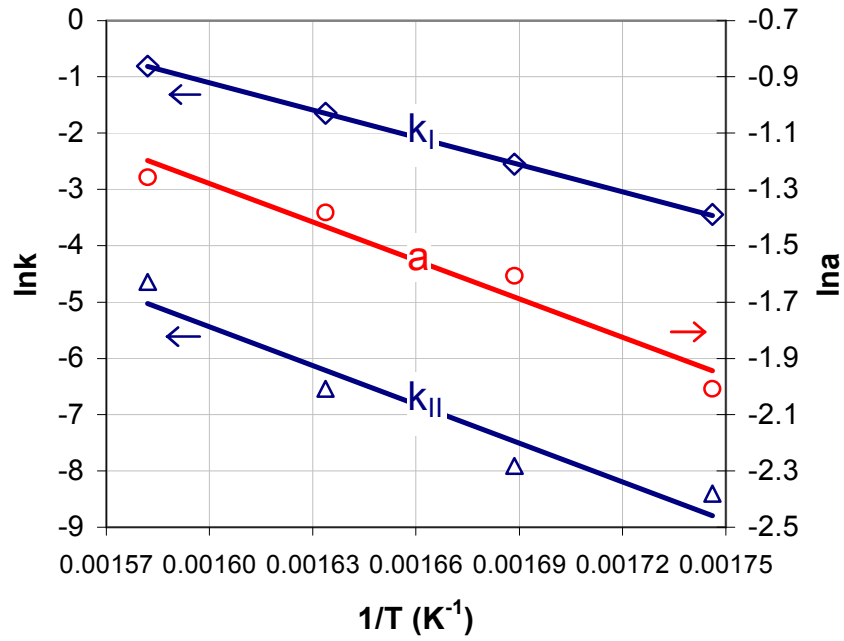**Figure 6. Least squares method curve fit on 320°C weight loss data for DCPD resin.**

**Figure 7. Arrhenius plot of $k_I$ ($\diamond$), $k_{II}$ ($\triangle$) and preexponential a ($\bigcirc$).**
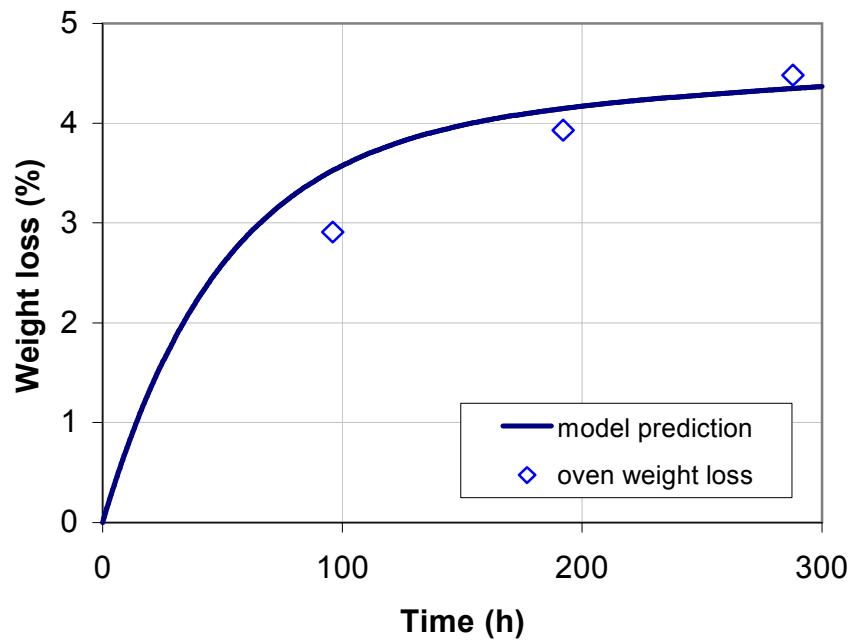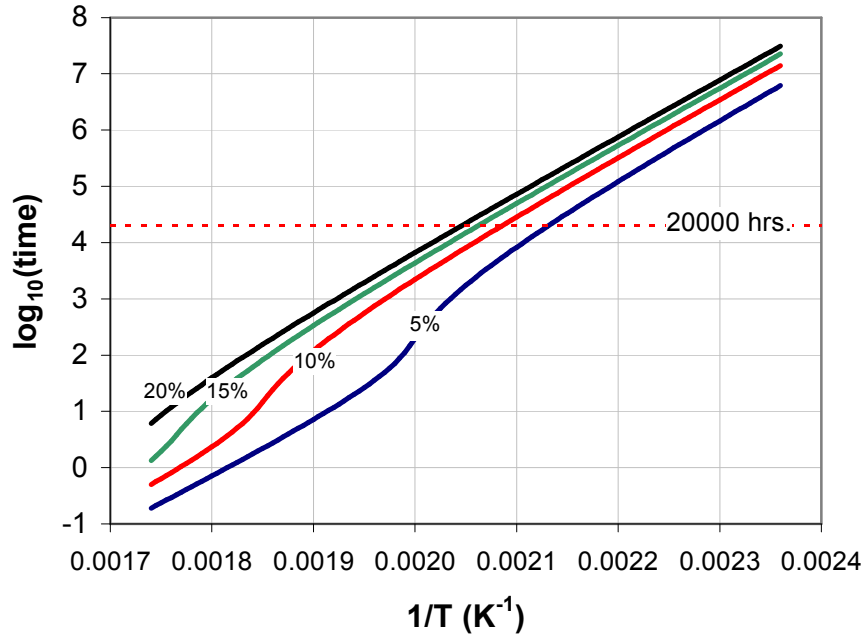


**Figure 8. Oven weight loss for DCPD resin.**

**Figure 9. Lifetime chart for the weight loss of the DCPD resin.**
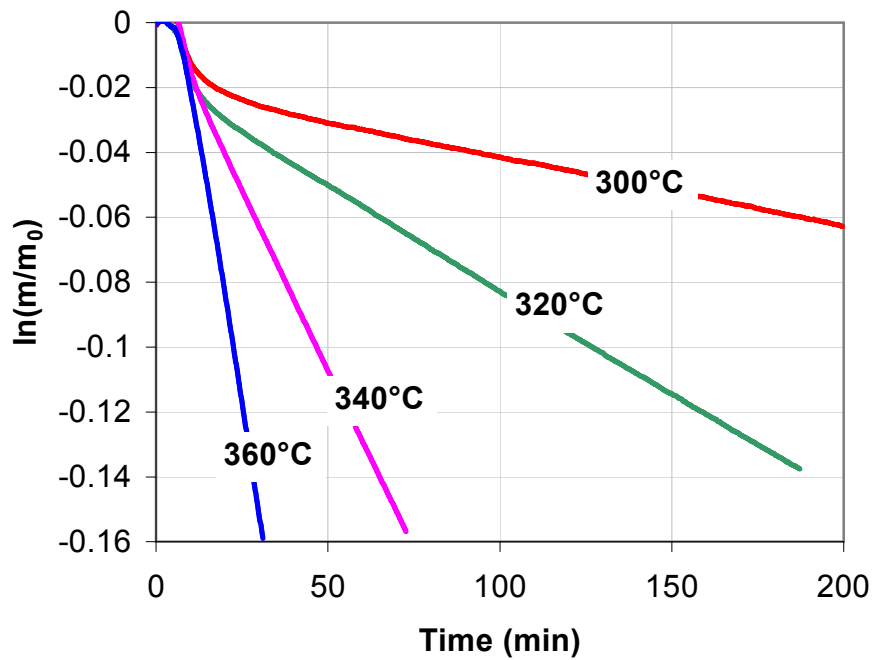

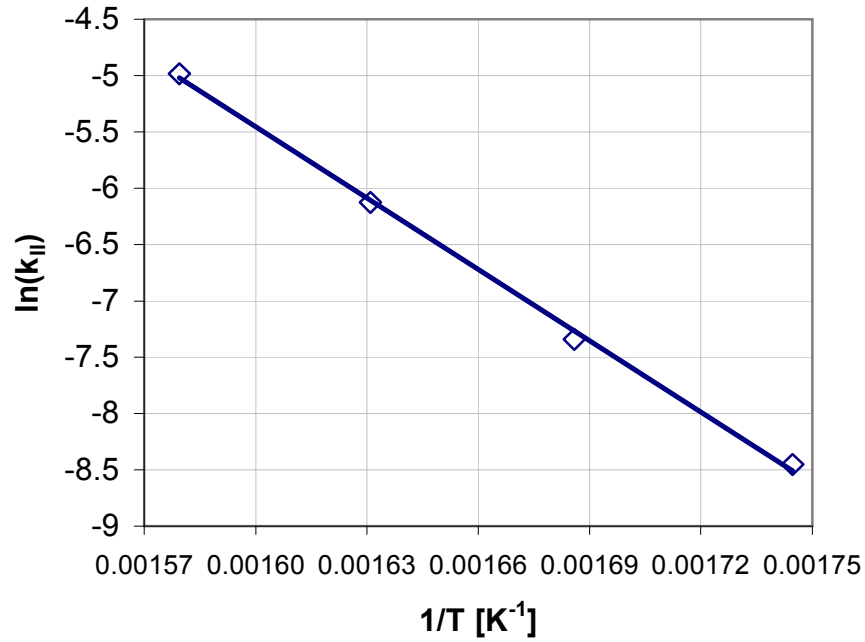
**Figure 10. Isothermal weight loss data for vinyl ester resin.**

**Figure 11. Arrhenius plot of $k_{II}$ for the vinyl ester resin.**

|  | DCPD | | | Iso | VE |
|---|---|---|---|---|---|
|  | a | $k_I$ [min$^{-1}$] | $k_{II}$ [min$^{-1}$] | k [min$^{-1}$] | $k_{II}$ [min$^{-1}$] |
| 300°C | 0.13 | 0.032 | 0.00022 | 0.0028 | 0.00021 |
| 320°C | 0.20 | 0.078 | 0.00037 | 0.0092 | 0.000648 |
| 340°C | 0.25 | 0.193 | 0.00144 | 0.031 | 0.0022 |
| 360°C | 0.28 | 0.45 | 0.0096 | 0.097 | 0.0069 |
| Ea [kJ/mol] | 38 | 134 | 191 | 180 | 175 |
| TI [°C] | → | → | 196 | 170 | 193 |

**Table 1. Data on the different resins tested.**