

# THERMAL ENDURANCE OF UNREINFORCED UNSATURATED POLYESTERS AND VINYL ESTER RESINS

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## ABSTRACT

Selected unsaturated polyester and vinyl ester resins has been studied by thermogravimetric analysis (TGA) for the purpose of estimating life time for their corresponding composites at elevated temperatures.

An initial attempt was made to obtain and interpret thermal weight loss data by TGA using the procedures laid out in ASTM D-1641 "Decomposition Kinetics by Thermogravimetry", ASTM D-1877 "Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data" and ISO 2578 "Plastics-Determination of Time-Temperature Limits after Prolonged Exposure to Heat". The benefit of this methodology being the fast analysis by running TGA temperature scans at 4 different heating rates in the range 1 to 10 K/min. This could be performed on an isophthalic unsaturated polyester.

When attempting the same on a DCPD resin and a vinyl ester the method did not give valid results for thermal endurance since the requirements for the applicability of ASTM D-1641 was not fulfilled. ASTM D-1641 calls for a smooth continuous mass change with a single maximum rate. This was not the case for DCPD and vinyl ester resins.

Isothermal analysis of the weight loss behaviour of these resin was performed at four temperatures in the range 300-360°C. The isophthalic resins again showed less complicated behaviour, and the weight loss data could be fitted to a first order rate law. Weight loss data for the DCPD and vinyl ester resins tested again did not show the same behaviour. Our data suggest a biphasic first order rate law for the weight loss for these resin.

Kinetic data obtained from the analysis of isothermal TGA weight loss data at the four different temperatures were then used to estimate thermal endurance. In similar manner to what is specified in ISO 2578, "Plastics – Determination of time temperature limits after prolonged exposure to heat", data was plotted as logarithm of time versus reciprocal temperature for a specified weight loss. Nonlinearity was then observed for the DCPD resin. Strikingly the data 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 on the TGA scans according to the mentioned ASTM procedures. This behaviour was then confirmed in an oven weight loss test at 220°C for 300 hours duration.

## 1. INTRODUCTION

In addition to maximum service temperature as determined from heat deflection temperature (HDT) or glass transition temperature ( $T_g$ ), 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 D-1641 [1] and D-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 D-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:

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

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

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

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

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

Combining these and attempting to solve we will get:

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

ASTM D-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 being 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:

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

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.

## 2. EXPERIMENTAL

For this study cured unsaturated polyester samples were prepared. An isophthalic resin and a DCPD resin was tested. Samples were diluted with styrene to a viscosity of 300 mPas to give acceptable castings. 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 was also prepared with cobalt octoate and cumene hydroperoxide as curing system.

Samples, all in one piece, approx. 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.

### 3. RESULTS – UNSATURATED POLYESTERS

Initially experiments according to the ASTM method [1] were attempted. A striking difference between the isophthalic resin and the DCPD resin was observed. This is presented below:

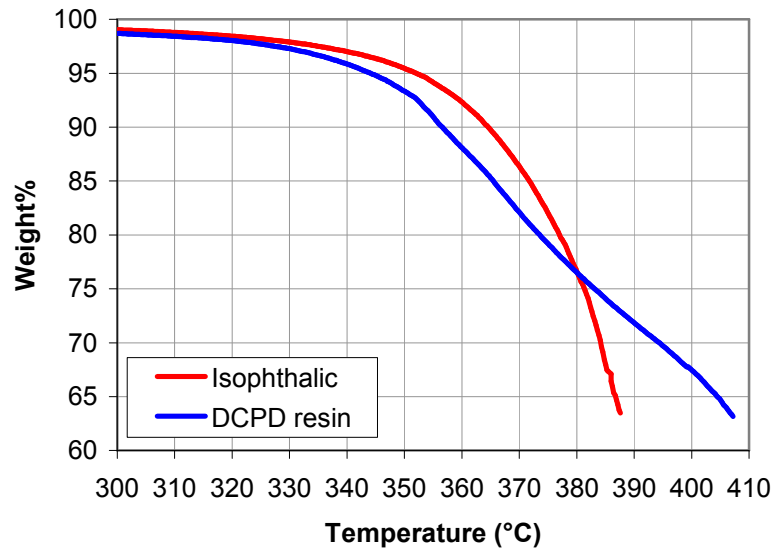


Figure 1. TGA scan at 7 K/min for the isophthalic and the DCPD resin.

From Figure 1 above it can be seen that while the condition of a smooth continuous mass change with a single maximum rate and following first kinetics probably is valid for the isophthalic resin, it certainly is 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. First for the isophthalic resin as represented by the semi-log plots below:

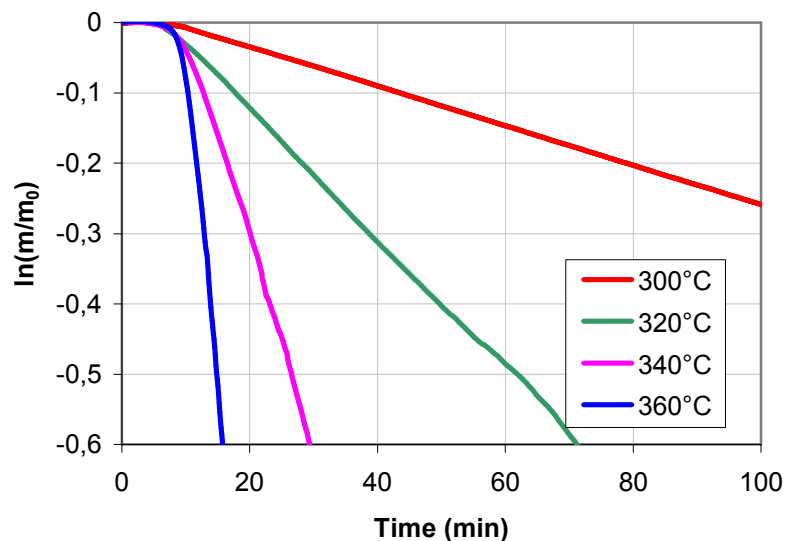


Figure 2. Isothermal weight loss data for isophthalic resin.

First order rate constants for the four different temperatures have been determined by linear regression of the semi-log data plotted above. Activation energy,  $E_a$ , in accordance with the Arrhenius equation, equation 2, have been determined as shown below.

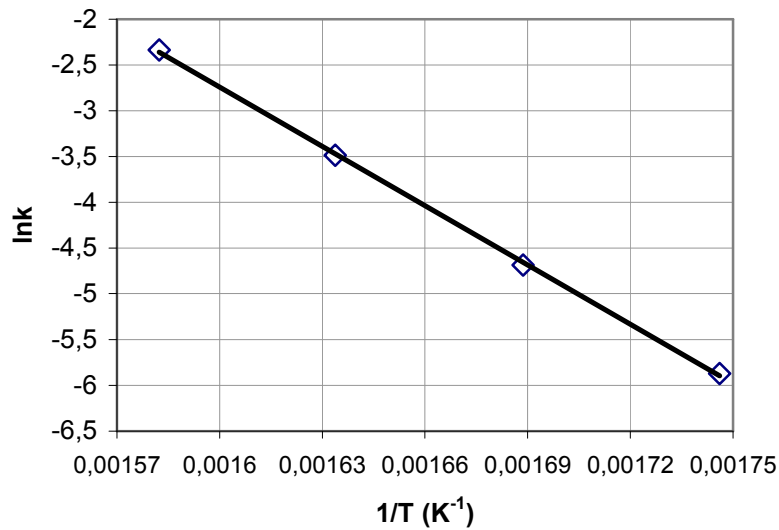


Figure 3. Arrhenius plot of first order rate constant for isophthalic resin decomposition.

Coming back to the comparison between isophthalic and DCPD resin, below is an example taken at one of the temperatures used in the isothermal measurements.

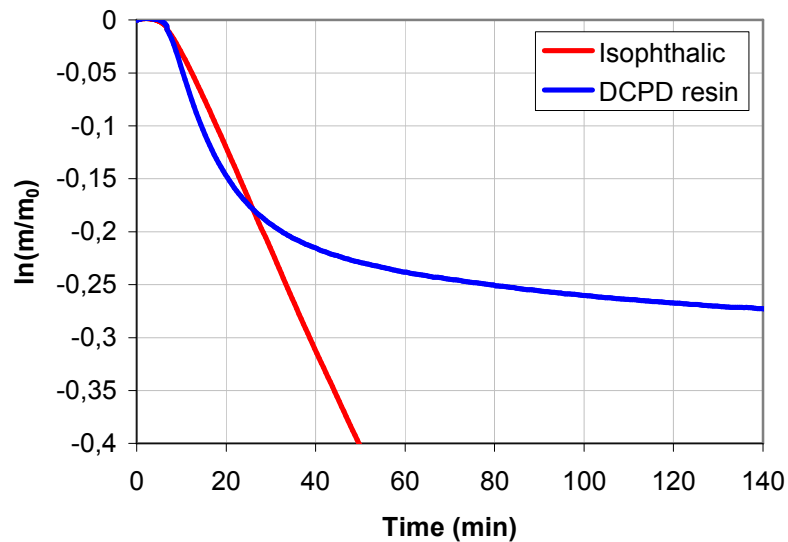


Figure 4. Isothermal data at 320°C on the two different unsaturated polyesters.

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. In figure 6 below are all the isothermal experiments on the DCPD resin. Same kind of behaviour can be observed at all temperatures. This behaviour can be described by a biphasic first order rate equation:

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

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

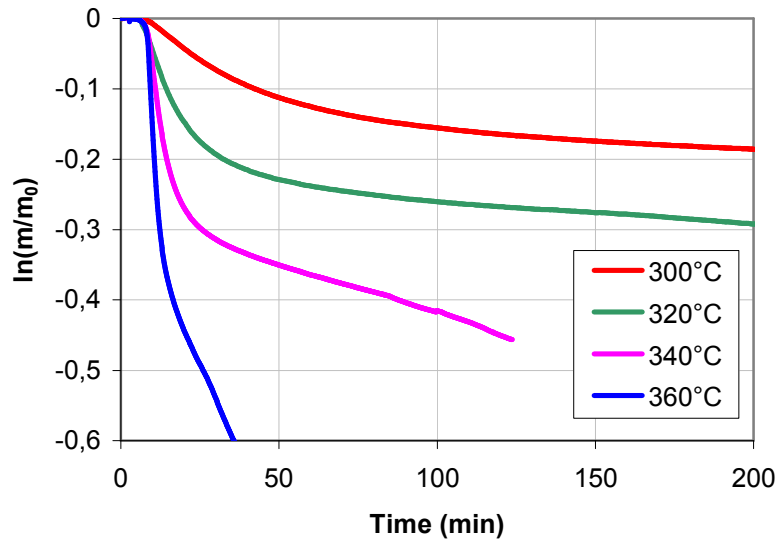


Figure 5. Isothermal weight loss data for DCPD resin.

Based on equation 6 kinetic parameter for the weight loss data has determined by an iterative least squares method. The experimental data seemed to be very well described by equation 6, as is shown below:

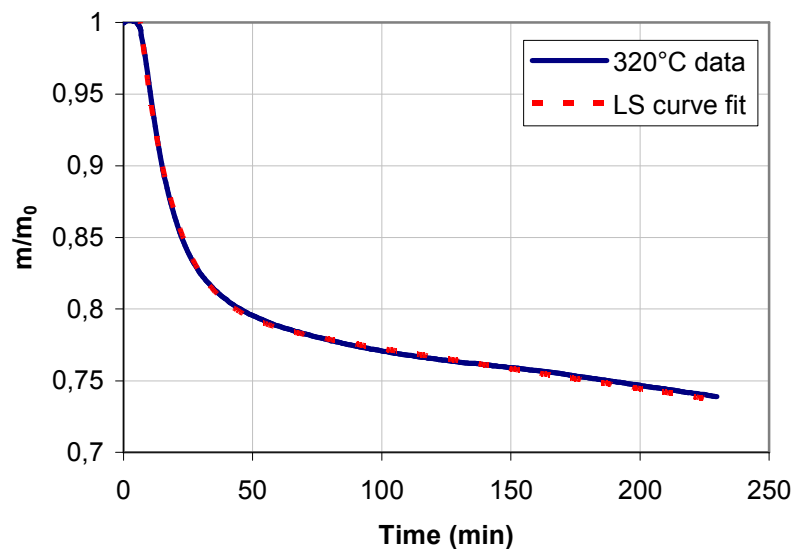


Figure 6. Least squares method curve fit on 320°C weight loss data for DCPD resin.

Below are the Arrhenius relationships for rate constants,  $k_I$  and  $k_{II}$  determined for the DCPD resin. It has also been attempted for the normalised preexponential factor  $a$ . Preexponentials,  $a$  and  $b$  was normalised 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.

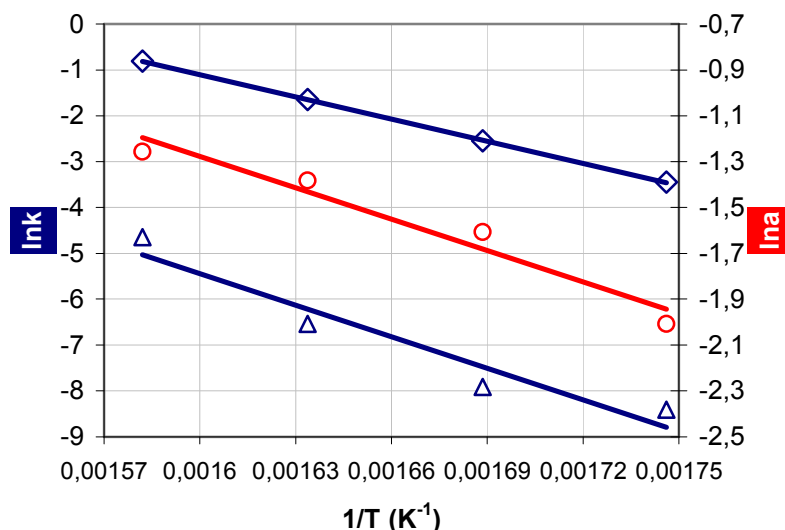


Figure 7. Arrhenius plot of  $k_I$  (◇),  $k_{II}$  (△) and preexponential  $a$  (○).

Good linearity in the Arrhenius plot above is observed for  $k_I$ . For  $k_{II}$  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 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.

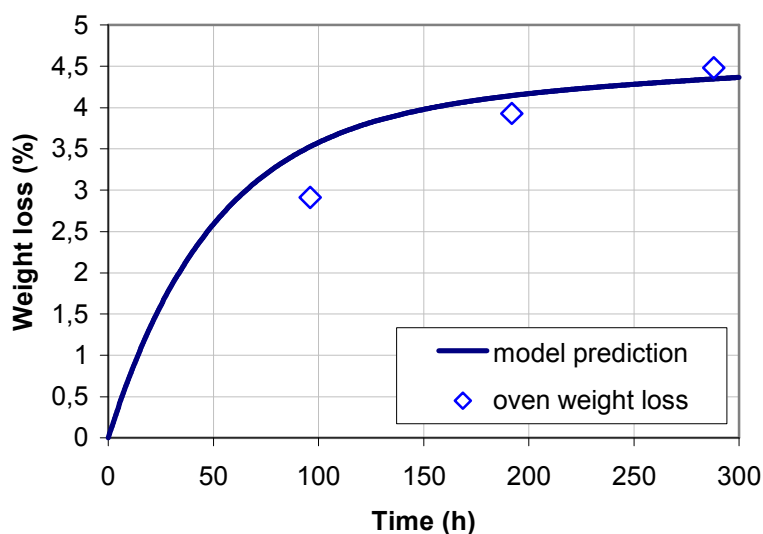


Figure 8. Oven weight loss for DCPD resin.

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 inert gas atmosphere, but 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.

#### 4. THERMAL ENDURANCE – UNSATURATED POLYESTERS

The DCPD resin does not show thermal decomposition according to a single 1.order reaction. Especially since the decomposition "levels out" at different levels at different temperatures the method described in ASTM E1877 [2] and ISO 2578 [3] for determination of thermal endurance will not be applicable. These methods uses 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 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 below.

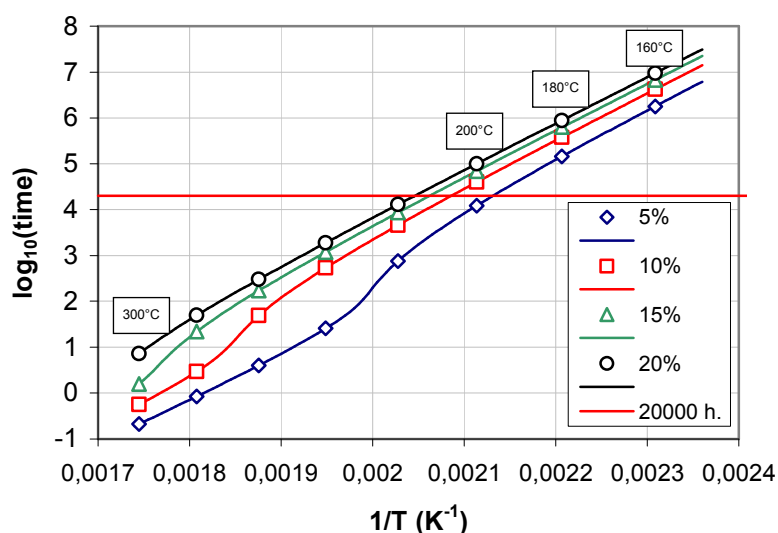


Figure 9. Lifetime chart for the weight loss of the DCPD resin.

And indeed it can be seen from Figure 9 that the observed decomposition kinetics of the DCPD 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. For the time necessary to reach a given weight loss, going from high temperatures a shift towards longer time is observed when reducing temperature. And again that reflects the crossover between fast initial and later a slower decomposition.

The simple 1.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.

## 5. VINYL ESTER PERFORMANCE

A standard bisphenol A based vinyl ester was also tested in the same way. Shown below are the isothermal TGA weight losses at the same temperatures as for the unsaturated polyesters.

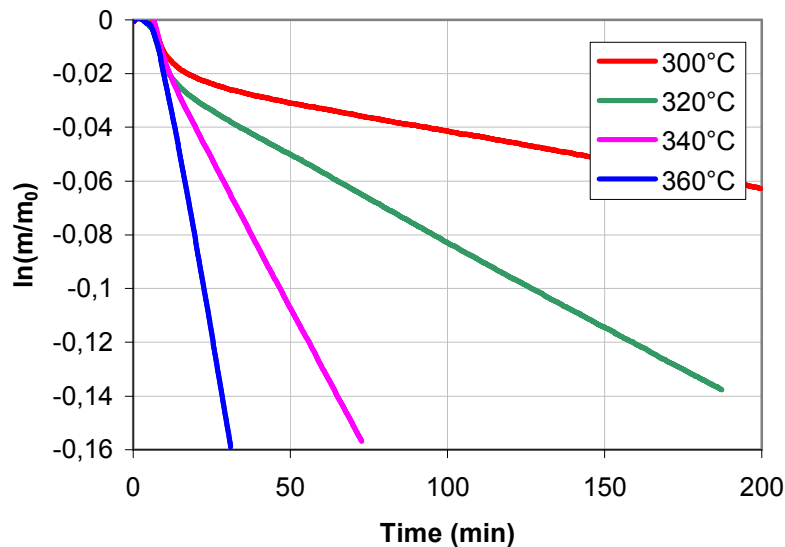


Figure 10. Isothermal weight loss data for vinyl ester resin.

Biphasic kinetics can be observed, but it seems that the faster reactions observed especially at 300 and 320°C has a lower activation energy. At higher temperatures the biphasic nature disappears possibly as the second rate constant then dominates. At 340°C there is a biphasic nature, but at 360°C it can not be observed at all. Note also that the scale of figure 10 is very different from figure 5 indicating a better thermal endurance in a vinyl ester. The crossovers now are at very low weight losses, and also the curves 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 negligible.

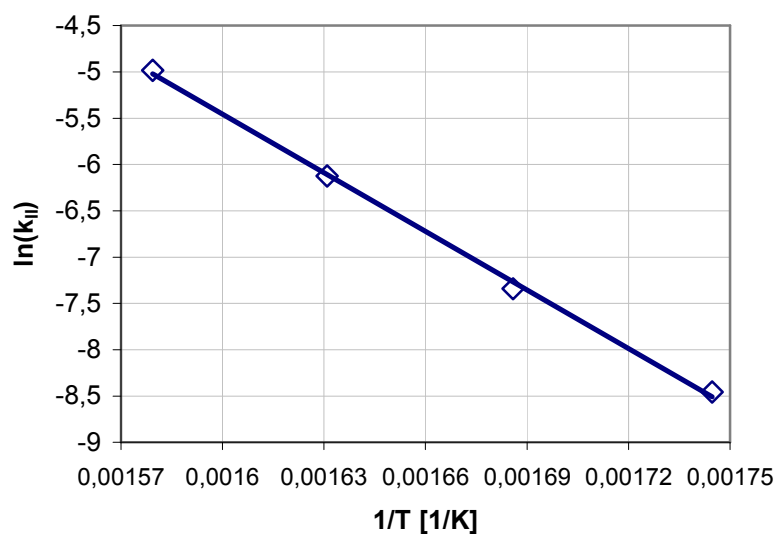


Figure 11. Arrhenius plot of  $k_{II}$  for the vinyl ester resin.



For 360°C a single rate constant was determined which was used with the  $k_{II}$  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  $k_{II}$  of the DCPD resin shown in figure 7.

## 6. THERMAL INDEX

The table below gives the rate constants determined and the thermal endurance of the resins investigated. TI is here the temperature giving 5% weight loss after 20000 hours.

	DCPD			Iso	VE
	a	$k_I$ [ $\text{min}^{-1}$ ]	$k_{II}$ [ $\text{min}^{-1}$ ]	k [ $\text{min}^{-1}$ ]	$k_{II}$ [ $\text{min}^{-1}$ ]
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.

Remarkably, higher thermal index is found for the DCPD resin even than the vinyl ester. Again this reflects that  $k_{II}$  values and temperature dependencies found are quite similar for DCPD and vinyl ester. 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  $k_{II}$  and a for which the Arrhenius plots, figure 7, showed poorer linearity.

## 7. CONCLUSIONS

Biphasic first order decompositions was found for the DCPD and vinyl ester resins tested. Isothermal experiments revealed this and provided 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 D-1641 For comparison with the other 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 outperforming the isophthalic resin.

The use of the ASTM D-1641 method to determine kinetic parameters for thermal decompositions of chosen DCPD and vinyl ester resin is 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".