Use of Differential Scanning Calorimetry Testing to Predict the Aging Behavior of Firestop Materials

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Introduction

Firestop materials need to be depended upon to perform as intended over a period of several decades. Different types of construction materials, such as concrete, cabling, fasteners, paints, and piping, have an assortment of methods to try to predict long-term service life of items. A review of test methods in Europe shows a similar diversity of methods in trying to predict "aging behavior". The goal of these assessment methods is to be able to predict the usefulness of the products after a given number of years, which requires an identification and evaluation of the type and severity of effects attributed to "aging". This of course leads to two wide open questions: first, what effects and environmental exposures are considered to represent "aging, and second, how many years should the assessment method aim to predict into the future.

This paper will examine the use of differential scanning calorimetry (DSC) as a method to provide some predictive information on the aging performance of firestop materials. The strengths and weaknesses of the method will be examined, comparing and contrasting to the strengths and weaknesses of some other methods, notably UL 1479, which is the only existing method used in the USA for assessment of firestop aging. Possible interpretation and use of DSC data will be discussed.

Present situation

Some environmental exposures that are typically considered in evaluations of aging are thermal load, humidity, radiation, and industrial exhaust gases. In the US, the benchmark for firestop aging evaluation is the battery of tests conducted by Underwriter's Laboratories (UL). They evaluate "aging" based on exposure to elevated temperature and humidity, each separately. Their accelerated aging tests involve exposing intumescent firestop materials to an elevated temperature of $70^{o}C$ for 9 months, and a separate test that exposes samples to 97-100% humidity at $35^{o}C$ for 6 months. They then test bench scale samples after the accelerated aging, looking for a minimum expansion pressure and expansion factor (foam height) that are at least 90% of their pre-aging values. If this criteria is not met either for the heated or humidified sample, then a full-scale installed firestop system must be subjected to the accelerated aging and then submitted to standardized (ASTM E814/UL1479) fire resistance testing. The installed firestop system must meet 75% of the F-rating (fire-resistance rating) compared to the listed fire-resistance rating.

The UL test has the major disadvantage of requiring a rather long time and substantial cost. This will be a significance hindrance to the prompt delivery to the market of new and innovative intumescent firestop products, given the built-in time lag due to the required age testing. So between time, cost, and hindrance to innovation, there is a definite incentive for the development of some alternate procedure(s) which could replace some or all of the UL testing. An additional major disadvantage of the UL methodology is the inability to predict how well the firestop material would perform after some specific number of years. In other words, there is

no disclosed correlation between the accelerated aging test and any specific number of years.

In researching this paper, request were made to UL technical staff to have them provide any available technical justification for the specific times and temperatures that they selected for the accelerated aging test. The only piece of information received from them was that they thought it might represent an exposure of approximately 20 years. An examination of that claim will lead us into the necessary discussion of reaction kinetics.

Chemical Reaction Kinetics

How fast a quantity of material will be transformed by chemical reaction to another form is dependant on the "rate constant" for the chemical reaction, all other conditions being equal (e.g. the concentration of reactants). The rate constant is not really a constant, as it depends on temperature. The Arrhenius Equation depicts the relationship between the rate constant and the temperature, as follows:

$$k = Ae^{(-E/RT)}$$

where k is the rate constant
A is a number which is practically constant
E is the molar activation energy for the reaction
R is the gas constant, 8.314 J per mol
T is the absolute temperature measured in degrees Kelvin
e is the base of natural logarithms, 2.71828…

A rule of thumb that is often quoted for the benefit of chemistry students is that the Arrhenius relationship results in roughly a doubling of the reaction rate for every 10 degree Kelvin (or Celsius) increase in temperature. In fact , the relationship is closer to a 50% increase in the reaction rate for every $10^{o}C$ increase, but the rule of thumb does provide a rough indication of the magnitude of the increase. It is on this principle of accelerated reaction with increasing temperature that accelerated aging tests using hot chambers are based. Applying the rule of thumb to UL's accelerated aging test for intumescents, we would conclude that the 9 months at $70^{o}C$ would be roughly equivalent to 17 years at $20^{o}C$.

Although it would be tempting to want to speed up the accelerated aging test by making the temperature even higher, two obstacles make an unlimited increase unwise. First, some intumescent materials will start to intumesce as low as the 100-110C range. The intumescence reaction must not be permitted to occur during the accelerated aging, since it is the preservation of the intumescence reaction over a number of years that the accelerated aging test aims to investigate. Some margin needs to be maintained between the highest aging chamber temperature, and the intumescence temperature. The fact that the intumescence reaction only starts to occur at some elevated temperature brings up another point, that using ever higher elevated temperatures for accelerated aging increases the risk of triggering some chemical reaction which simply would not have occurred over the normal lifetime of the product at ambient conditions. The "falsely" triggered reaction could then have an effect on the behavior of the aged sample, leading to a false conclusion regarding the behavior of the firestop material after aging.

A completely different approach is taken by the German authorities. Having studied "typical" construction materials over a long period of time, their studies have concluded that a cycling test more accurately and more quickly replicates the aged behavior of those materials. Without getting into the details, the test that is carried out in accordance with the "RILI SIB"[1] guidelines involves cycling the sample through wetting and drying, and through cold (-15C) and hot (60C), running 20 cycles over a period of 20 days. For firestop materials, the cycling test is conducted on a representative installed firestop system, and a fire test is run on the system to ascertain the fire-resistance rating of the aged sample. Based on their long term studies that have correlated actual long-term performance to their cycling test, they conclude that satisfactory performance of the product after being exposed to the 20-day cycling allows a prediction of acceptable product performance for 25-30 years, and even for 30+ years if there is no significant moisture load over the life of the installation.

The adoption of the German test by UL would certainly reduce the costs and time that are now being required. There have not been any reported cases of defective materials after years of service for materials that have been so tested, so the track record appears to be satisfactory. However, the desire to innovate is a natural human tendency, so a new approach will be here explored.

Differential scanning calorimetry

As mentioned earlier, the Arrhenius equation relationship between temperature and reaction rate provides the technical justification for any accelerated aging test that uses elevated temperature. So a natural question is whether we could predict the exact extent of any chemical reactions over any combination of time and temperature if only the rate constant, as defined by the Arrhenius equation, could be known. DSC testing allows that rate constant to be determined.

Without going into a detailed explanation of the DSC apparatus, the test involves heating up a milligram-sized sample of the material under investigation, and by detecting and measuring heat evolution or heat consumption by the sample, examining and quantifying the exothermic or endothermic reactions that occur while that sample is slowly heated up.

The time to run a DSC test and to interpret and analyze the output is less than a day. Running the DSC test will reveal at what temperature each reaction is initiated, which would allow a judgment of whether the reaction in question should even be considered when evaluating the aging of the material under anticipated extremes of environmental conditions. Additionally, the kinetic data obtained in combination with the thermodynamic data obtained can be used to calculate what percent of the material under investigation was converted by each specific detected reaction. In other words, what fraction of the total mass of the sample was chemically or physically changed to another form. Clearly, whether a detected reaction will act to change 1%, 10% or 90% of the sample will affect how important (i.e. worrisome) that reaction is deemed to be.

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[1] Guidelines for the redevelopment and renovation of construction parts, German Committee for Reinforced Concrete of the Federal Ministry of Transportation (DAfStb)

One possible use for DSC testing would be as a screening tool, to determine the need for more "traditional" age testing. In cases where DSC testing would indicate that some reaction occurs at a low enough temperature and results in a high enough conversion (percentage of material changed) the conclusion of whether or not the firestop performance would be acceptable can be determined through the more traditional accelerated aging tests that people seem to be comfortable with. On the other hand, where the thermal analysis shows that the material does not show any evidence of experiencing significant chemical or physical reactions, the accelerated aging test should be seen as largely unnecessary. Hoping and expecting many firestop materials to be chemically and physically stable over the long term, this screening test has the potential to eliminate the cost and time of unnecessary and redundant accelerated aging tests.

Test program

To explore the possibility and reveal any difficulties in using DSC testing to evaluate firestop aging, Hilti products CPXX1 intumescent firestop and CPXX2 non intumescent firestop were examined in a test series using differential scanning calorimetry (DSC). The samples were heated in the DSC from ambient temperature to 400 °C registering endothermic and exothermic effects. For each product, DSC testing was performed with samples exposed, during separate tests, to three different types of gas flow:
1) pure air
2) pure air saturated with water
3) pure air enriched with SO_2 .

Sample size was about 20 – 25 mg.

Evaluation of the DSC results (data curves) was carried out according to ASTM E 2041 – 01: "Standard Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchart and Daniels Method". The procedure will not be explained in any detail here, as it is essentially a standard procedure for chemical investigation using DSC equipment around the world.

As a brief summary, the data evaluation involves the following steps:

a) Plotting of a linear baseline (linear or proportional to conversion) from a point on the baseline before the exothermic reaction to a point on the baseline after the reaction
b) Calculation of total released Energy
c) Calculation of conversion as a function of time / temperature
d) Optionally, one or more revised baselines can be plotted in an iterative fashion based on the information gathered in a) through c) above
e) Determination of reaction order
f) Determination of Activation energy and frequency factor

For the purposes of the evaluation described in this paper, the data described above is then used to accomplish two additional steps.

g) Calculation of the reaction rate at 70°C
h) Calculation of extent of conversion within 270 days

i)   Optional: Calculation of the reaction rate at 50°C
j)   Optional: Calculation of the extent of conversion within 30 years (10950 days)

Note that for items i) and j), which are not done for this paper, such an extreme extrapolation is usually unadvised by experts in the field of kinetic data interpretation. However, a practitioner may be curious to know how the extent of conversion for 270 days would extrapolate if the temperature was a more realistic maximum of 50°C over a real-life time period of 30 years.

Test Results

The DSC test results are presented in Table 1. The application of the kinetic data is presented in Table 2. The data curves from the DSC apparatus and the interpreted "baselines" are shown in Figures 1 through 6, located at the end of this paper.

Table 1: Kinetic parameters determined from DSC data

Sample ID & Atmosphere	Peak-Onset, Range / °C	Energy / J / g	Activation Energy / kJ/mol	Frequency factor 1/min
CPXX1 Air	220 – 300	- 47	126	7,7E9
CPXX1 Air plus H_2O	180 – 270	- 334	99 168	3,9 E7 6 E14
CPXX1 Air plus SO_2 linear baseline	210 - 280	-193	359	3,4 E34
CPXX1 Air plus SO_2 revised baseline after first conversion calculation	120 - 220	-382	64	8 E3
CPXX2 Air	No exothermal effects			
CPXX2 Air plus H_2O	190 - 280	-197	287	2 E27
CPXX2 Air plus SO_2		- 103	372	7E34

Table 2: Calculation of reaction rate and predicted material conversion at 70°C

Sample ID & Atmosphere /	Reaction rate at 70°C / 1/min	Conversion within 270 days at 70 °C / %
CPXX1 Air	5,7 E-10	**0,02**
CPXX1 Air plus H_2O	3,3E-08 1st stage 1E-11 2nd stage	**1,3** **0**
CPXX1 Air plus SO_2 linear baseline	6,6 E-21	**0**
CPXX1 Air plus SO_2 revised baseline after first conversion calculation	2,2 E-6	**77**
CPXX2	No exothermal effects	
CPXX2 Air plus H_2O	3,4 E-17	**0**
CPXX2 Air plus SO_2	1,5 E-22	**0**

Results analysis and interpretation

From kinetic data a determination was done of reaction rates for reactions beginning at temperatures lower than the reaction peak appears. When calculating the predicted extent of conversion over 270 days at 70C (i.e. the UL accelerated aging temperature and duration and the UL heat aging temperature), the low reaction rate resulted in only a minuscule predicted conversion. This would tend to indicate that if these materials were actually tested in the UL test, they would have post-aging properties that should be almost unchanged from the pre-aging samples.

Although the exact data cannot be released for proprietary reasons, accelerated aging tests conducted by UL on CPXX1 resulted in expansion pressure and expansion factor results that were found to be acceptable in some cases, and statistically inconclusive (due to wide scatter in the data) in other cases. The DSC-predicted conversion of 0.2% (heat aging) and 1.3% (moisture aging) is consistent with the positive result obtained by UL. It is also notable that the data scatter produced only questionable results for some of the UL age testing conditions (expansion pressure after humidity aging, expansion factor after heat aging). Although some may view DSC testing as not providing results that would be useful and trustworthy every time, the existing accepted methodology, the UL test, apparently does not produce consistently usable results either. As an additional data point, it should be mentioned that this product was also deemed to be have successfully passed the German accelerated aging (cycling) test.

As CPXX2 is a non-intumescent firestop material, it does not require UL age testing, and so no UL test results are available for comparison.

As a potentially interesting side note, in the case where a conversion of about 1.3 % was calculated for 270 days at 70°C, there was actually a contribution of two distinct reactions within nearly the same temperature range. One can detect this on different slopes in the ln dx/dt plots. Higher conversion is due to the reaction with lower activation energy.

The potential difficulties of DSC data interpretation also revealed themselves in this limited test exercise. For CPXX1 tested with air + SO$_2$, when the baseline curve was redrawn after an iterative evaluation, the new kinetic data resulted in a predicted conversion of 77% over 270 days at 70°C. Clearly, if the material actually did change to this extent, it would not be an acceptable material. In this case, the DSC testing cannot indicate that the material would age acceptably. However, it also should not be *concluded* that the material would age unacceptably. The best interpretation of this result would be to indicate the need for further testing using the traditional, broadly accepted methods. In case one might be wondering which of the two baseline curves and conversion results is correct, the answer is that neither of them should be considered as correct. When the data curve is so ambiguous as to result in the possibility of widely differing interpretations, the best that can be said of that data curve is that it cannot be reliably interpreted to produce any results or conclusions.

Discussion and Conclusions

Thermal analysis, using the DSC method in this case, is generally suitable to qualitatively examine the issue of chemical and physical reactions that can occur with aging, by determining whether any possible reactions are detected. DSC testing and subsequent data analysis can be used to conclude that a product will be thermally stable and thus will age acceptably if clearly, no reactions are detected. In such a case, the method could replace a more complex subsequent investigation.

Where some conversion is calculated for 270 days at 70°C that is above an acceptable level, additional testing should be done using traditional methods to establish a firm conclusion that most people will feel confident with. The decision of what is an acceptable level of conversion, thus not requiring further testing, is thus far unanswered. One possible value to consider is a conversion of 5% or less as being acceptably small. This number is proposed based on the fact that UL aging tests allow a 10% decrease in post-aging expansion behaviour, with 5% being half of that value as a safety factor. However, a different acceptable % conversion may come to light after some additional data is available, on a broader range of samples, comparing DSC predictions to UL age testing results.

One issue that needs to be kept in mind is the homogeneity of any material tested. If the material is inhomogeneous, then it is possible that the tiny milligram-sized sample submitted to DSC testing may not yield a truly representative result. With inhomogeneous materials, either sample preparation should be done to ensure a truly representative single sample, or sufficient repeat tests should be conducted on multiple separate samples to ensure that the range of possible results is discovered.

An extrapolation of conversion values for substantially longer time periods (e.g. 30 years) is computationally easily feasible. However, it needs to be recognized that small variations in the DSC data interpretation can result in very large differences when extrapolated to such long time periods. The boundaries of acceptable Arrhenius plot extrapolation are not defined. This problem is unfortunately not resolved if one uses methods more sensitive than DSC testing, such as adiabatic testing, for determining the Arrhenius rate constant. What would still be lacking is an accurate relationship between the extent of predicted chemical conversion, and the actual decline over time in intumescent pressure and/or expansion factor. Despite these cautionary words regarding the extrapolation of laboratory data to a much longer time period, one needs to remember that the existing accepted methods (e.g. UL 1479) also do not have any technical basis to support an extrapolation of the test results to a number of decades. So perhaps an extrapolation of Arrhenius data obtained from DSC testing, which at least has solid chemistry fundamentals behind it and provides a "microscopic" look at all of the individual chemical reactions that go on in the sample, might actually be more trustworthy than what we are presently relying on.

Much experience and expert knowledge is required for the evaluation and interpretation of DSC measurements. Despite prefect conformance with ASTM E2041 in interpreting the data, the complexity of the evaluation can lead to the possibility of significantly different results when some ambiguous data sets are analyzed by different people. Knowing this fact can result in decreased confidence with this approach altogether. To prevent such a loss of confidence, it would be important for any lab analyzing and presenting the data to at least indicate in some way how easy or difficult (ambiguous) the DSC output was to analyze.

In some cases, the extent of conversion predicted by the DSC data could overstate the extent of decrease in performance with aging. One example of such a case would be if the measured and computed conversion was for the depolymerization of a polymer matrix. Although such a reaction could result in the surface of the material becoming brittle, it cannot be concluded that this would have any deleterious effect on the intumescent qualities of the material. This brings up the larger issue that it is not possible to distinguish those measured chemical conversions which will decrease the fire-resistance performance of the material from those that would not have any negative effect. Fortunately, this could only lead to conclusions being made on the conservative side, if it was assumed that any conversion of material could potentially decrease the desirable properties which provide the required fire resistance.

Future work

Further testing and investigation can help to provide additional confidence in the use of the proposed thermal analysis method and its specific strengths and weaknesses.

One issue that can warrant further study is whether the milligram-sized samples that are used for DSC testing can be considered to be representative of the bulk of the material under study. Because such a small sample is taken, any spatial chemical formulation variations within the product could result in inconsistent results. Some exploratory testing that would be useful would be to take repeat samples from one single product package, as well as repeat samples from among several packages, and do this for several classes of products. This issue is not so much one of investigating DSC test results, but rather investigation of the homogeneity of the materials under examination, by whatever methods. This issue could be lying undiscovered for the currently accepted methodologies as well.

An alternative approach to the DSC testing that would possibly be more directly indicative of fire performance for a firestop material after aging would be to test the pure form of whatever active/reactive material gives it its fire-resistive properties. These substances can be analyzed by DSC and assessed with respect to their individual stability. The systems can be reasonably expected to perform as when new if these active products are stable over time and do not somehow migrate out of the bulk of the material. There is already an abundance of test data and historical data for the carrier materials, such as foams, silicon sealants and acrylic sealants. A good forecast of firestop material performance could surely be made based on the available data about the carrier, combined with stability testing of the active ingredient(s) using DSC analysis. In the case of intumescent materials, that active material would be blowing graphite in the vast majority of cases. For non-intumescent firestop materials, it could be an amine, ablative or other family of chemicals. Of course, sometimes the entire bulk of the material provides the fire resistance, such as with firestop mortars, and no specific "active" material within the formulation can be isolated for testing.

It would obviously be quite desirable to be able to compare the predictions of material conversion determined from DSC testing to changes in intumescent behavior after actual or accelerated aging of the same materials. A collection of data on accelerated

aging tests will exist at Underwriters Laboratories after they complete their age testing of presently Listed intumescent materials. If funding could be obtained to test these same materials using DSC, and the % conversion predictions compared to and UL measured decreases in intumescence, the usefulness of DSC testing as a predictor of aging could be either strengthened or eliminated as a possibility. It is fully understood that UL age test results are proprietary, so the only apparently workable option would be for UL to assemble the comparison, keeping the accelerated age testing results anonymous.

Once a broad compilation of DSC test results and resulting kinetic data become available, the Arrhenius relationship between time and temperature will be known for the types of material under study. One determination that could then be done with that information would be to establish by how much an exposure chamber temperature would have to be increased in order to get the same amount of "aging" within a shorter amount of time. This could possibly be used as the basis for decreasing the time required for the established aging test, the UL accelerated aging test, to less than the 270 days and 180 days currently required. If desired, one could already simply use the existing rules of thumb, discussed earlier, to estimate the required temperature increase to accelerate the aging reactions to some shorter time. However, having the kinetic data from the DSC tests will allow this relationship between time and temperature to be known more accurately, therefore allowing reductions in accelerated aging time to be made with greater confidence and accuracy. DSC test results would also reveal whether any other chemical reactions would be initiated in the range between $70^{o}C$ and the temperature at which the intumescence reaction begins. Knowing about such reactions would forewarn the user that trying to shorten the accelerated aging test by raising the temperature above $70^{o}C$ could trigger some additional reactions that would otherwise not occur during a material's true-life aging, thus falsely worsening the results of the accelerated aging test, and thus making the higher temperature shortened test inadvisable in some cases.

This paper has presented a concept that has not been used to date to evaluate aging of firestop materials. However, since all that accelerated aging tests aim to do is to uncover the chemical reactions that could make a material lose its required performance over time, it is natural to look for other ways to discover those same chemical reactions. DSC testing is a well established means of examining the chemical reactions that will occur within a material, and its exploration for this purpose is well overdue, and will hopefully be further investigated.
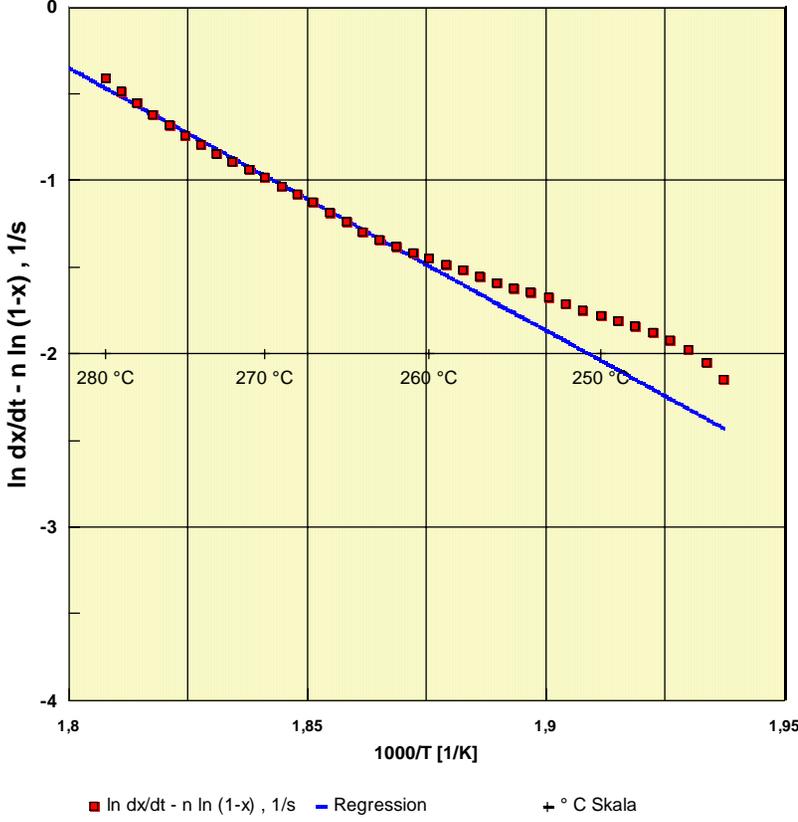
Fig. 1a: DSC output for CPXX1 w/Air Flow

Notes: No exotherm below 220°C. Exothermic reaction can be identified between 220°C and 300°C. At higher temperatures burning of organic material.
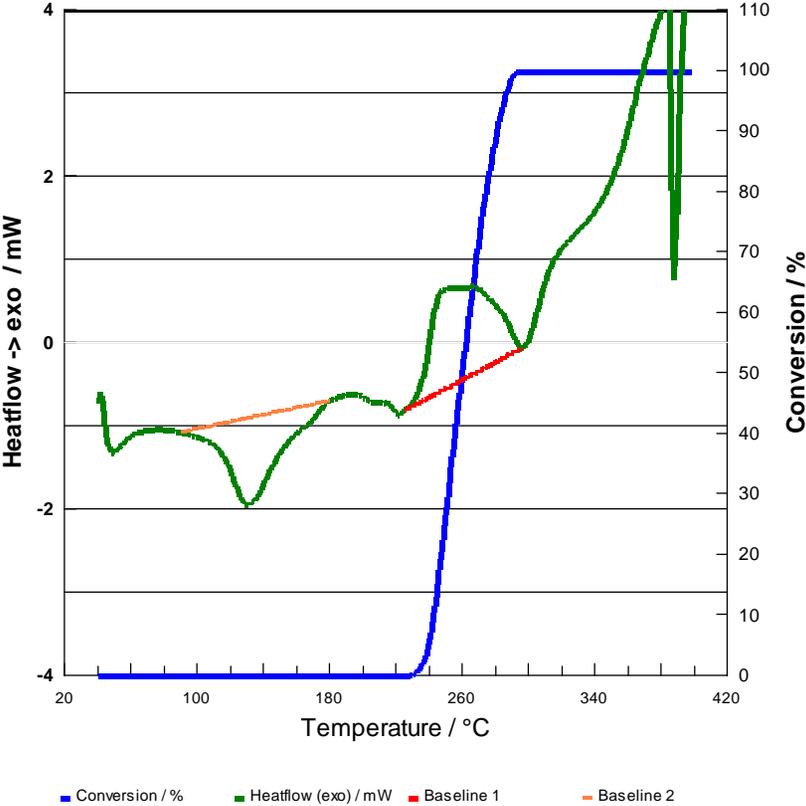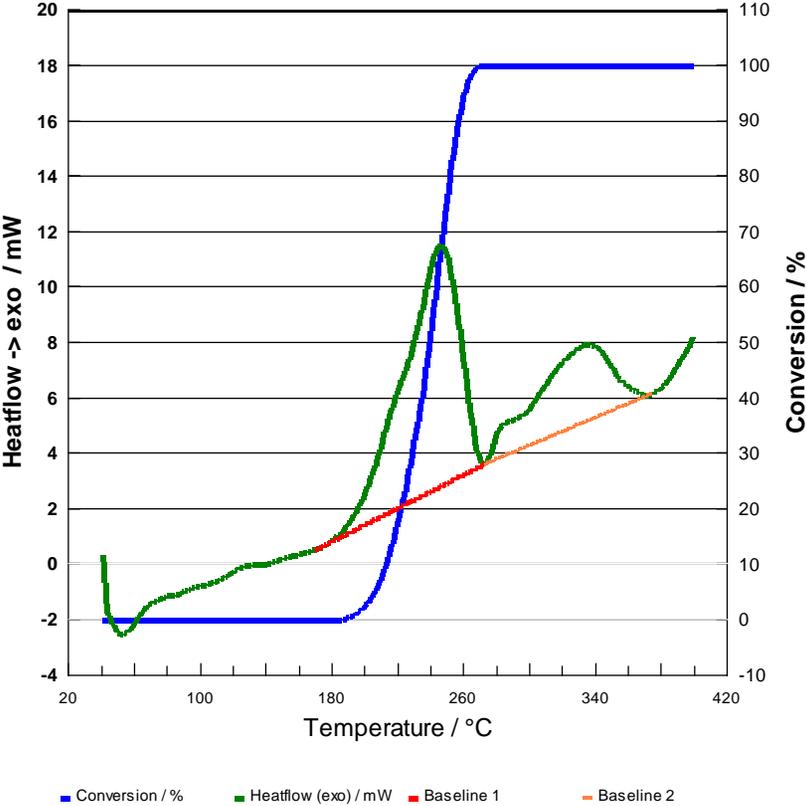
Fig 1b.: Regression between 260 and 280°C.
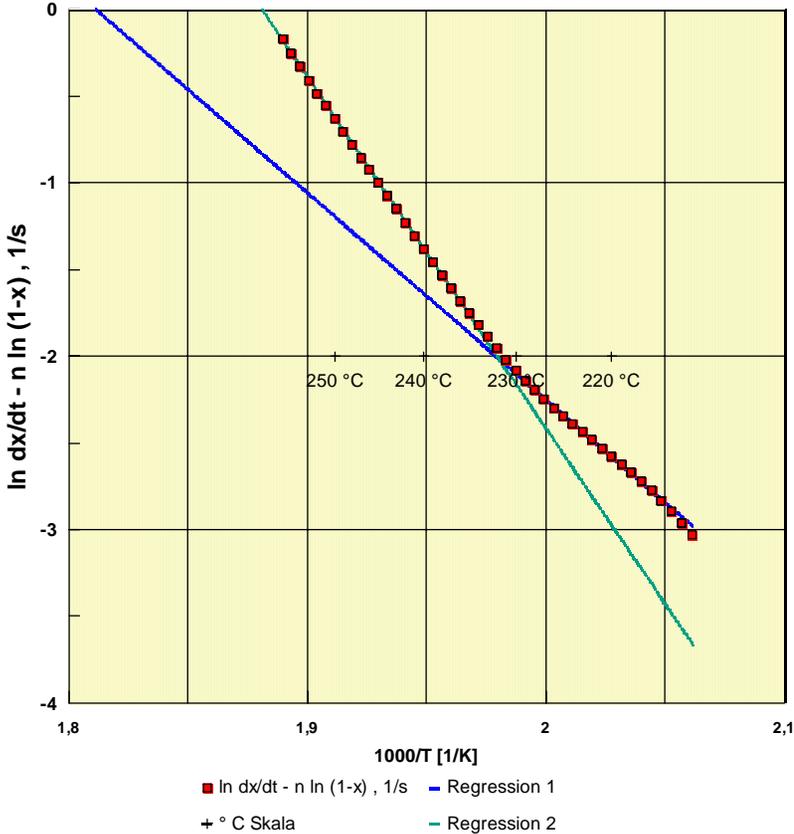
Reaction Order N = 1

Fig. 2a: DSC Output for CPXX1, Water-saturated Air

Notes: Two step reaction identified. First Peak evaluated. Possible Reaction is the hydrolysis of a polymer matrix
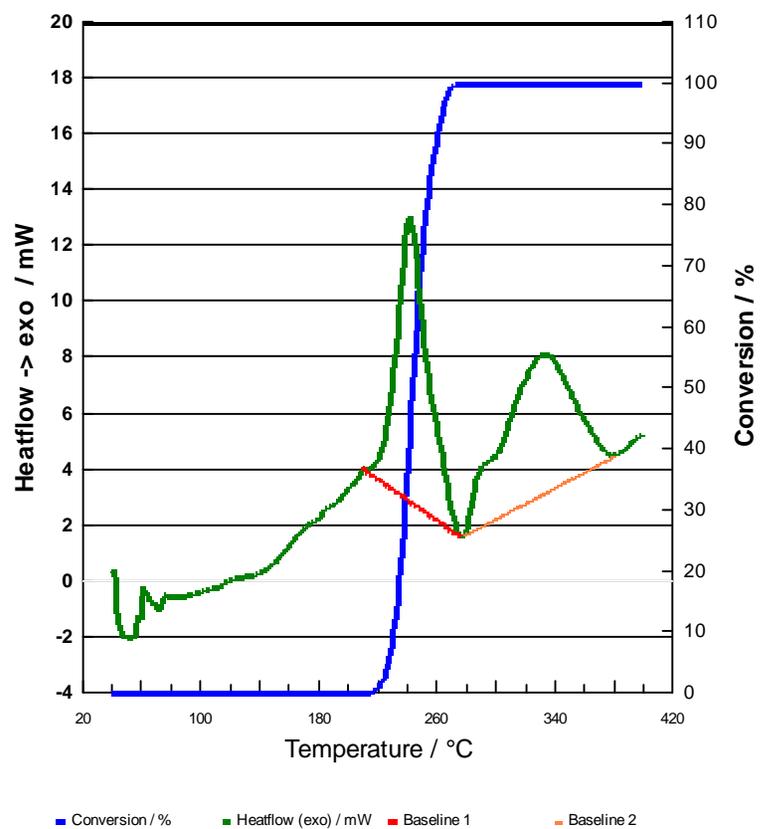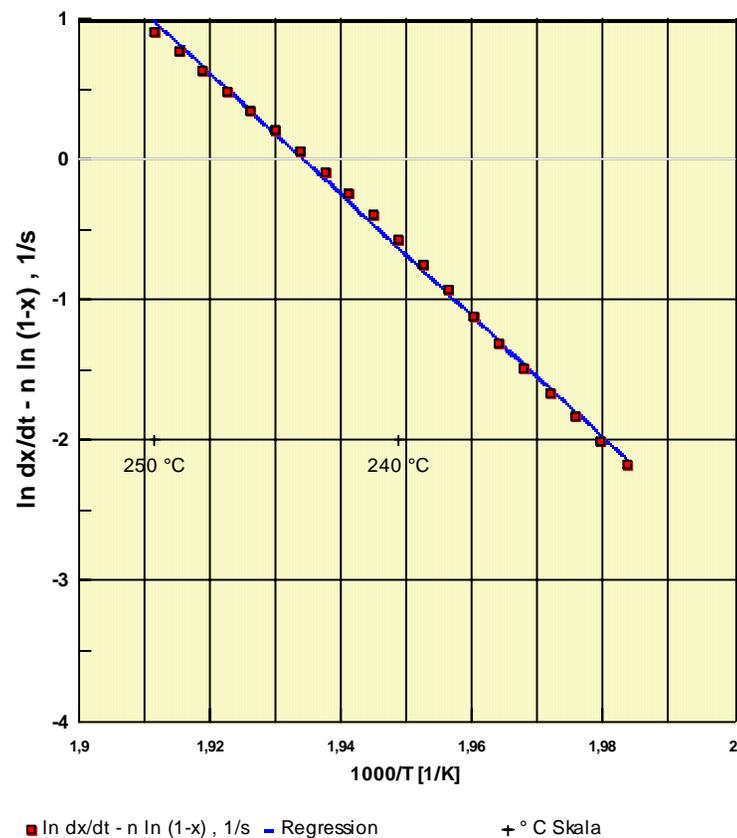
Fig. 2b: Data regressions

N = 1; Curve indicates a two stage reaction with different activation energies

Fig.3a: DSC Output for CPXX1, Air plus SO_2,
a linear baseline was applied for first reaction step

Fig 3b Data regression   n = 2

Fig.3c: DSC Output for CPXX1, Air plus SO$_2$, a baseline proportional to conversion was applied for the first reaction step (beginning at 120°C)
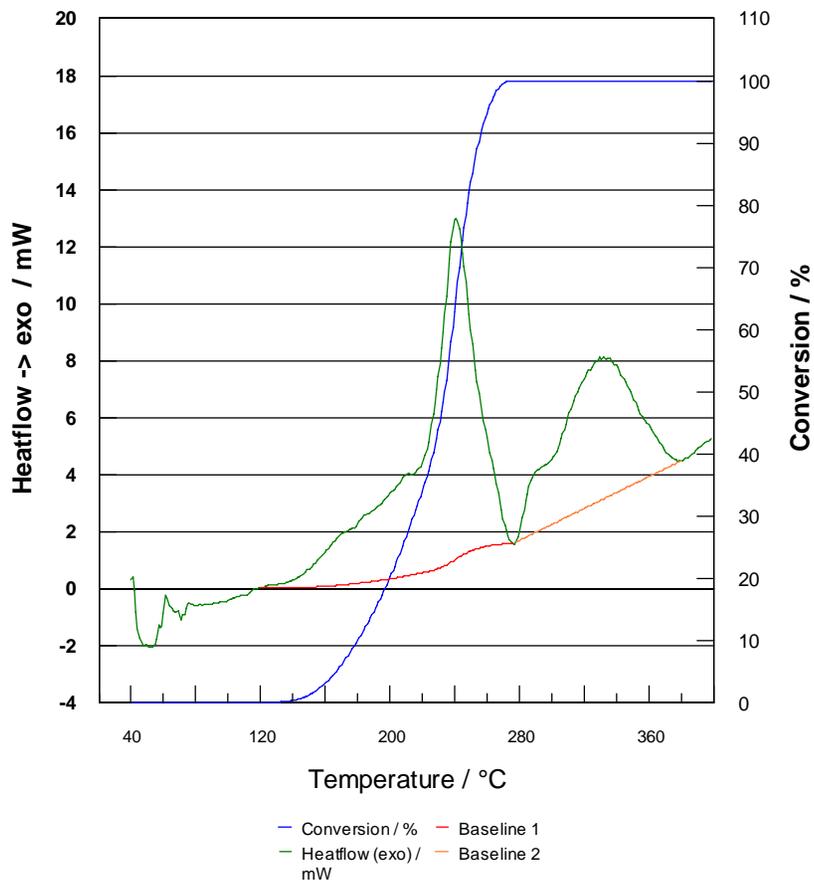
Fig 3d Data regression   n = 2,5
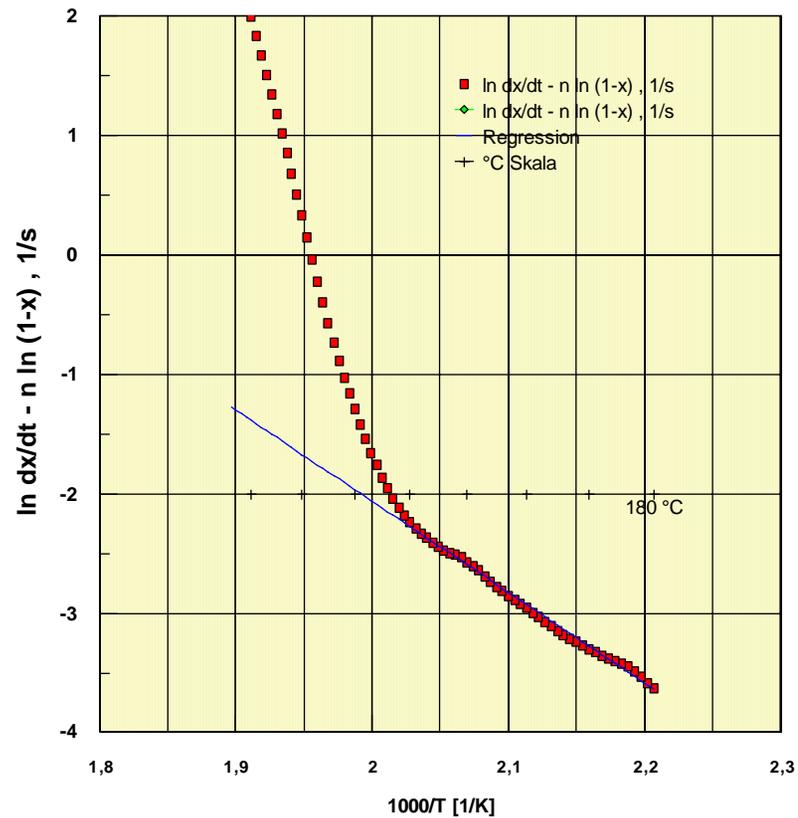
Fig.4: DSC data for CPXX2, w/air flow

Notes: only endothermic effects, water evaporation around 100°C
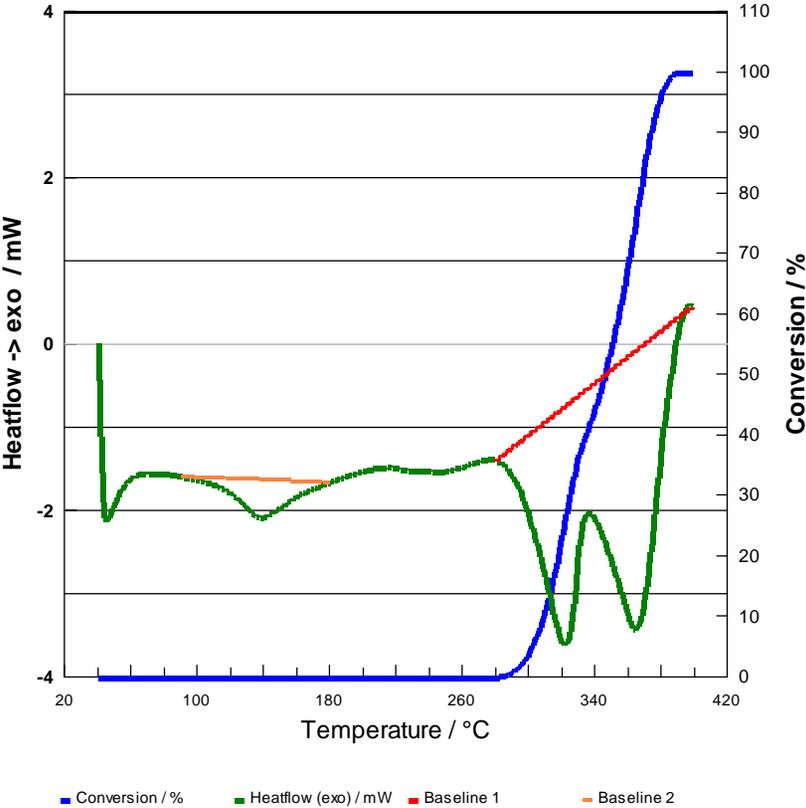
Fig. 5a : DSC data for CPXX2, water-saturated air
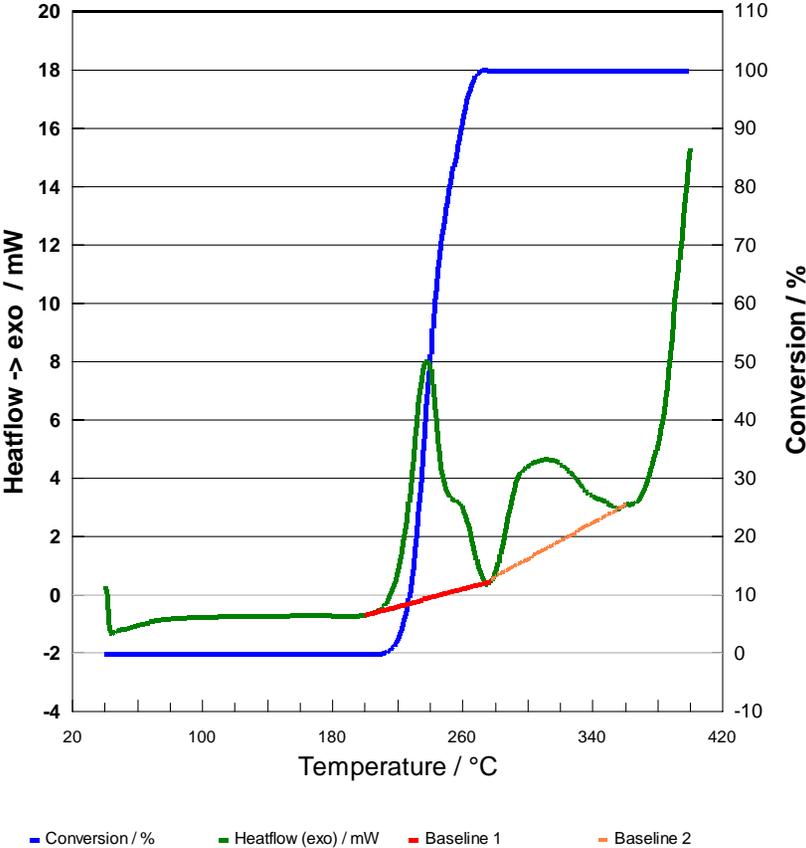
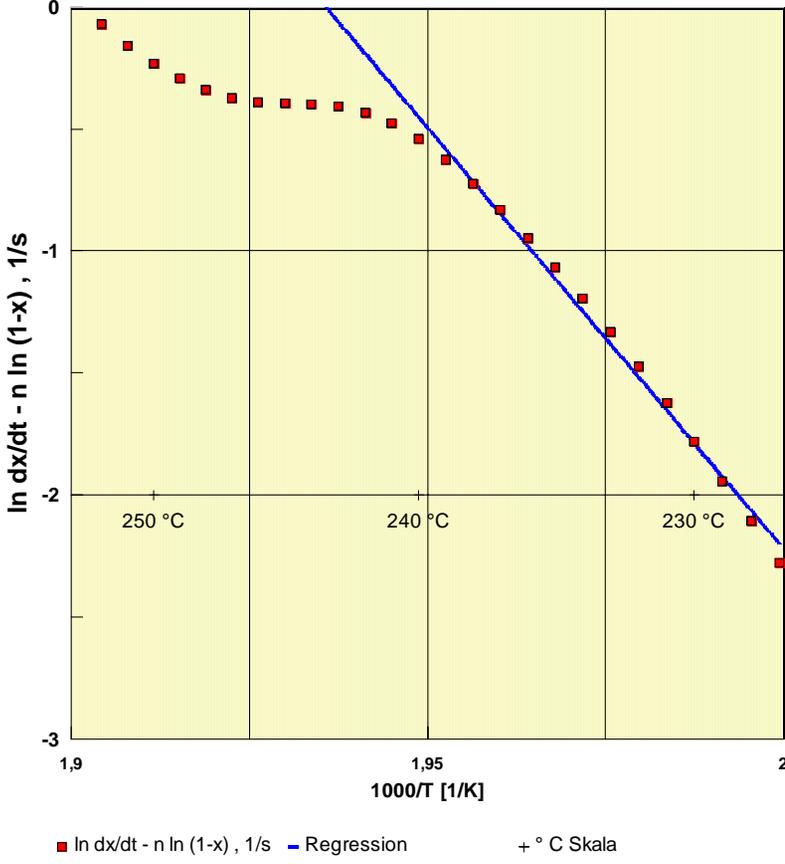**Fig. 5b**: Data regression

N = 1,5

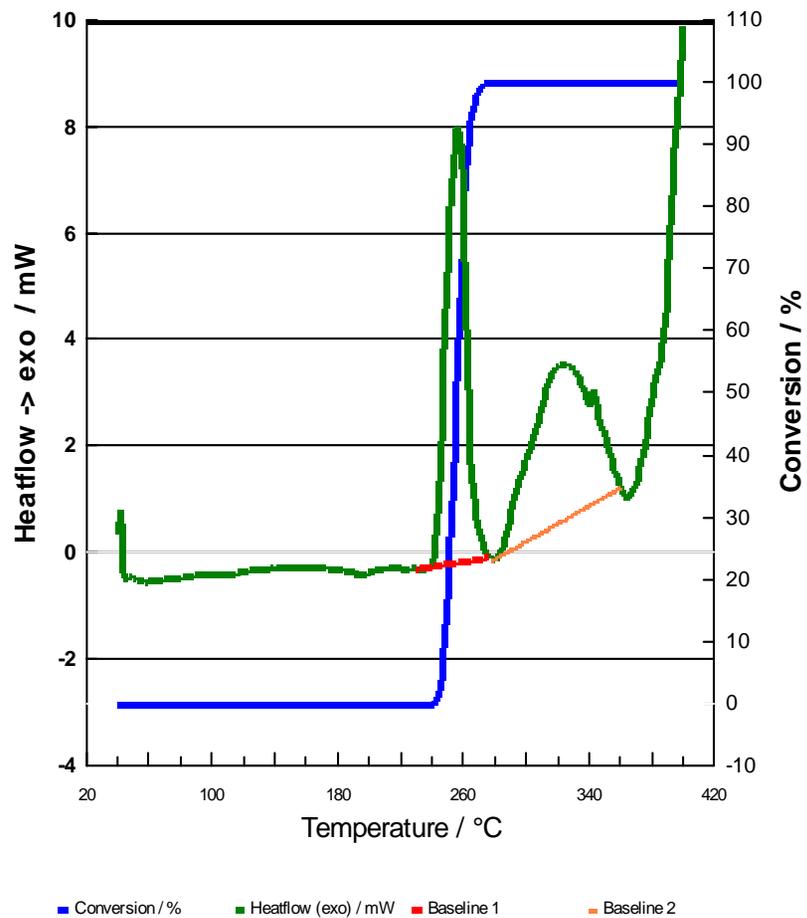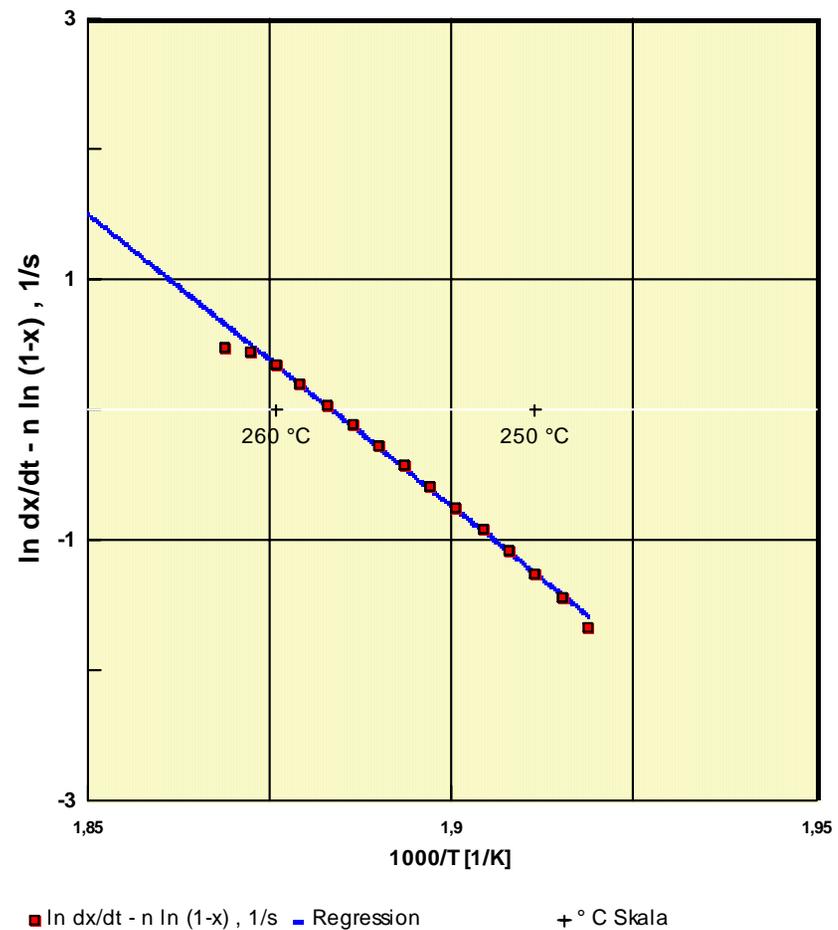**Fig. 6a :** DSC data for CP XX2, Air plus SO$_2$

Fig 6b: Data regression

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