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Evaluation of Reaction Kinetics and Properties of Epoxy Resin with Two Hardeners

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Abstract: ***Differential scanning calorimetry (DSC) is a useful tool used to measure the heat flow into or out of a sample, when the sample is exposed to a controlled thermal profile. DSC offers both quantitative and qualitative data about material transitions like crystallization, glass transition, melting, curing and decomposition. In this study the curing of one resin with two hardeners were being studied using DSC. The activation energy and rate of reaction were evaluated. The conversion time at different temperatures were evaluated and compared.***

Keywords: Epoxy resin, hardener, rate of reaction, half life, rate constant, kinetic study

1. Introduction

Epoxy resins are being used in industries because of its good bonding to various surfaces and high chemical and thermal resistance [1], [2]. Since these materials can protect metals against corrosion, they have been used for coating of internal and external surfaces of metal products such as pipes [3]. Epoxy resin is mixed with its hardener (curing agent) and curing takes place in proper conditions to achieve the desired properties. Knowing the kinetics of the curing reaction of epoxy resin can improve its coating quality. There are different techniques to study the curing kinetic of thermosetting resins like epoxy resin. Differential scanning calorimetry (DSC) is one of the most common and most accurate methods [4-6]. In the kinetic analysis of a chemical reaction such as resin curing, a mathematical equation between the conversion, conversion rate, and temperature is established [7].

Differential scanning calorimetry (DSC) is a useful tool to measure the heat flow into or out of a sample, when the sample is exposed to a controlled thermal profile. DSC offers both quantitative and qualitative data about material transitions like crystallization, glass transition, melting, curing and decomposition. For some of these transitions, DSC can, not only provide the temperature at which transition takes place and the amount of heat involved, but also significant data about the kinetics or rate of the reaction. The software packages provided for kinetic studies are Borchardt and Daniels, ASTM E-698 Thermal Stability and Isothermal Kinetics The kinetic packages provides rapid automatic calculation of reaction order (n and/or m), activation energy (Ea), pre-exponential factor (Z), and rate constant (k). Each also provides the ability to use the kinetics parameters obtained to generate predictive thermal curves which can be used to assess the transition in terms of percent conversion, time, and temperature.

2. Experimental

Epoxy resin used was ARALDITE AY 103 (A) (Huntsman Advanced Materials, UK). The resin was cured using Aradur® 76 (B) and Lapox K 6 (C) hardeners.

The cure kinetics of epoxy resin with the two hardeners were performed using differential scanning calorimetry, DSC (TA instruments, Q20). About 10 mg of the epoxy hardener mixture (1: X) is hermetically sealed in DSC aluminium pans. The samples were heated from room temperature to 200° C at a heating rate of 10 °C/min in nitrogen atmosphere. The data obtained from the study was used for the determination of cure kinetics of resin using the instrument software. The kinetics of the reaction was studied using Borchardt and Daniels (B/D) approach which is used for the determination of activation energy, heat of reaction, order of reaction, percentage conversion and rate constant from DSC scan.

Using DSC, the curing kinetics of the samples can be characterized by measuring heat signal generated during the curing reaction as a function of temperature and time The area under the curves is proportional to the conversion and it is defined by using the given equation

$$\alpha = \frac{H_t}{H_u}$$

The heat evolved during the reaction is recorded by DSC and is assumed to be proportional to the extent of consumption of the reactive groups. The curing rate for the process, could be described using the following equation

$$\frac{d\alpha}{dt} = \left(\frac{1}{H_u}\right)\frac{dH}{dt}$$

Where α is the extent of curing reaction, $d\alpha/dt$ is the curing rate, H_t is the reaction heat formed within time t, dH/dt is the heat flow rate, and H_u is the total heat of reaction.

Most curing kinetics can be described by the equation given below

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)f(\alpha)$$

where $d\alpha/dt$ is the rate of conversion, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is the absolute temperature and the function representing the kinetic model. The non-isothermal kinetic model can identify two types of reaction: n-th order or autocatalytic model. Autocatalytic model (Sesták–Berggren) assumes that the reaction obeys the equation given below

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)\alpha^m(1-\alpha)^n$$

Fig 1 shows the FTIR spectra of the resin and the two hardeners. The resin is Araldite 103 is a reaction product of Bispenol A – Epichlorohydrin and hardener Aradur 76 is a formulated polyether polyamine and LapoxK 6 is an unmodified aliphatic polyamine

3. Results and Discussion

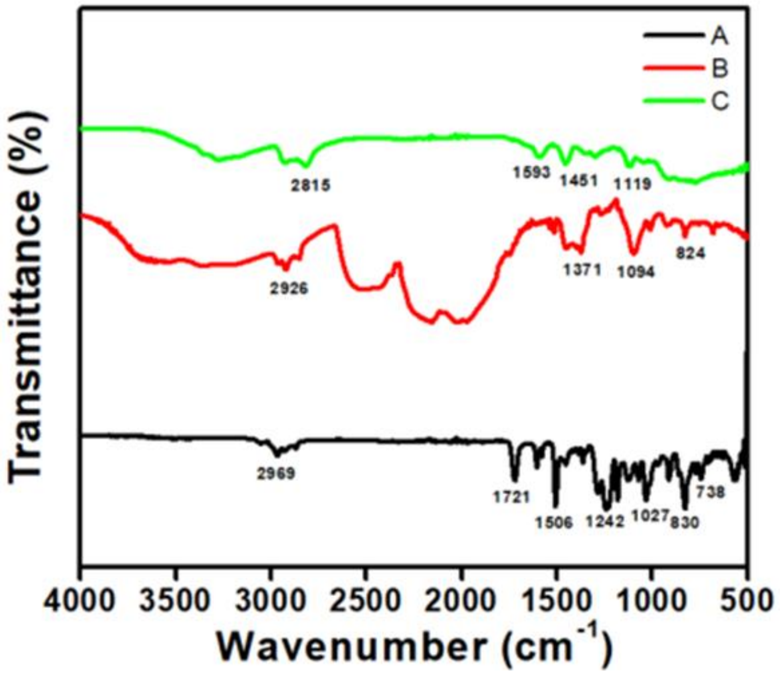

Figure 1: FT IR spectra of Resin A and the two hardeners B &C

The important peaks are marked in the spectrum

Determination of kinetics by DSC is based on two assumptions - (1) the heat flow relative to the instrument baseline is proportional to reaction rate and (2) the temperature gradients through the sample as well as the temperature difference between the sample and reference are small. Those assumptions are generally reasonable provided small sample sizes less than 20 mg is used

Borchardt and Daniels (B/D) kinetics approach is used for the determination of activation energy (Ea), pre exponential factor (Z), heat of reaction (DH), reaction order (n), and rate constant (k) from a single DSC scan. Originally this approach was explained by Borchardt and Daniels for solutions later it was fine tuned for solids.

dα/dt = k αm (1-α)n (7)

k = Z e-Ea/RT (8)

where dα/dt = reaction rate (1/sec)

k = rate constant (1/sec)

α = fractional conversion

m,n = reaction orders

According to the Borchardt and Daniels approach, the reaction follows nth order kinetics Sponsored by TA Instruments Jul 28 2015 Reviewing and Comparing of DSC Kinetics Methods Saved from URL: https://www.azom.com/article.aspx?ArticleID=12105 P /18 1 and follows the general rate equation:

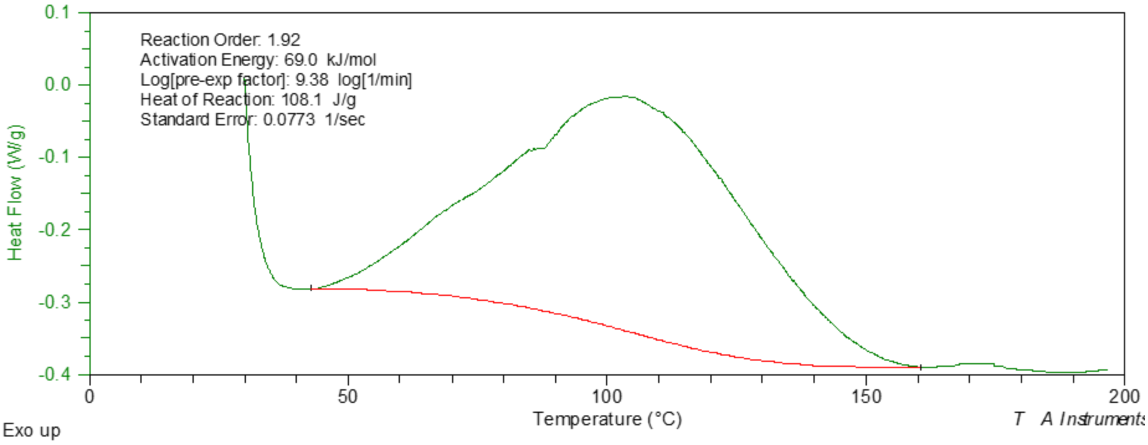

Figure 2: Shows the heat flow with temperature for epoxy resin A and hardener B

Figs 2 shows the heat flow with temperature for samples (sample resin A with hardener B. The order of reactions is 1.92 and activation energy 69.0kJ/mol

If the second assumption is valid, a plot of ln[k(T)] versus 1/T (Arrhenius plot) from this data must be a straight line (see Figure 2). The pre exponential factor (Z) and the activation energy (Ea) are obtained from the intercept and slope of this plot

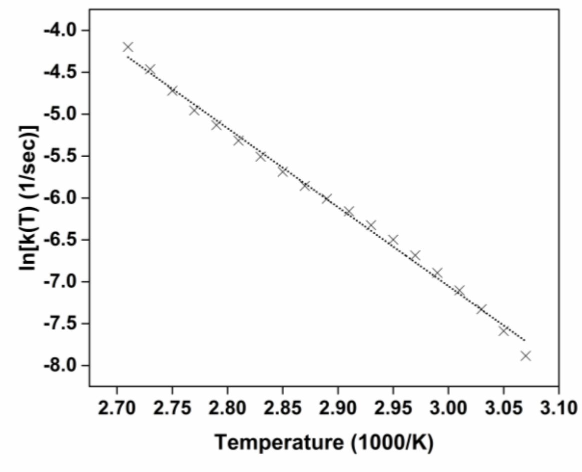

Figure 3: Plot of ln[k(T)] versus 1/T for epoxy resin A and hardener B

From the B/D kinetic modeling, two predictive curves are derived: Isothermal plots (Figure 3) – These provide the time and temperature conditions for a particular isothermal level. AI so conversion plots (Figure 4) – These offer time and temperature conditions for a particular conversion level.

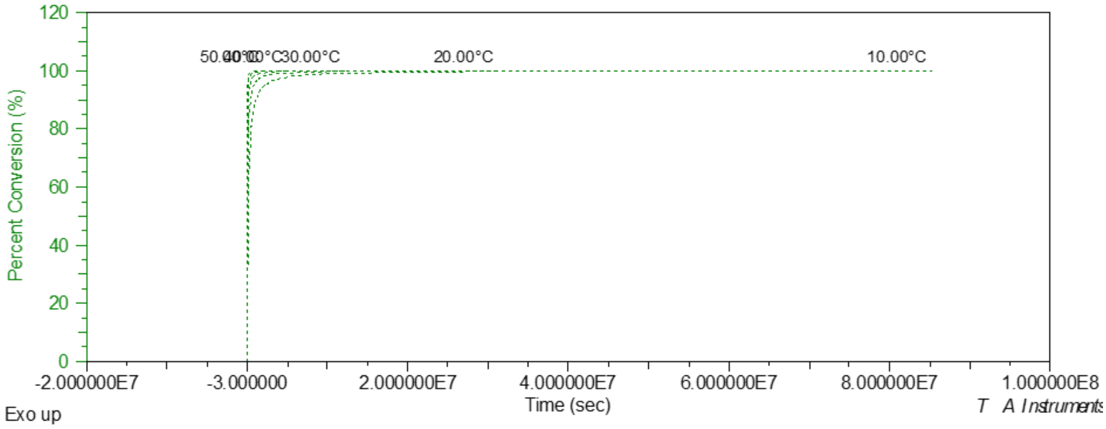

Figure 4: Percentage conversion versus time for epoxy resin A and hardener B

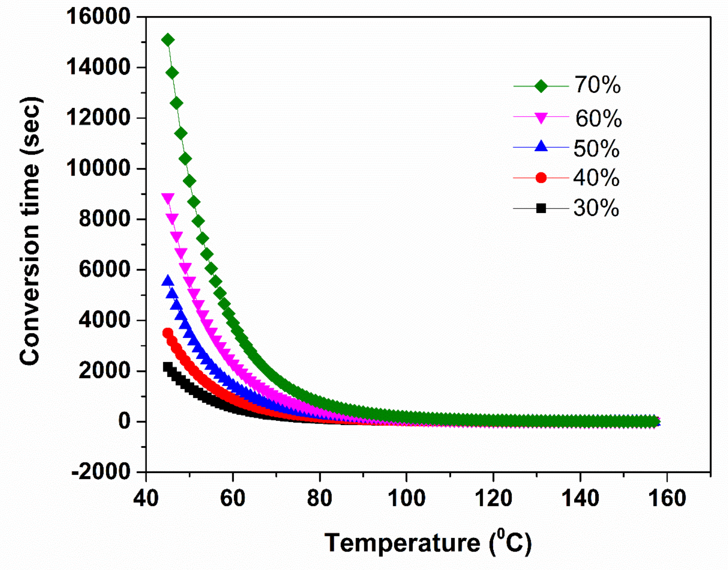

Figure 5: Percentage conversion time versus temperature for epoxy resin A and hardener B

The same resin A was mixed with a different hardener (C) and the kinetic study was repeated.

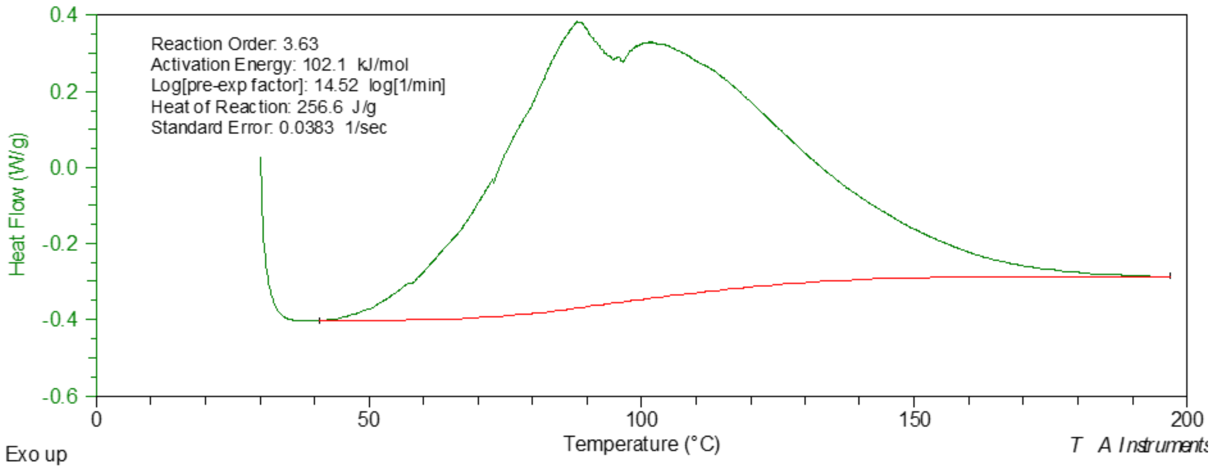

Figure 6: Shows the heat flow with temperature for epoxy resin A and hardener C

The order of reaction is found to be 3.63 and the activation energy is found to be 102.1 kJ/mol

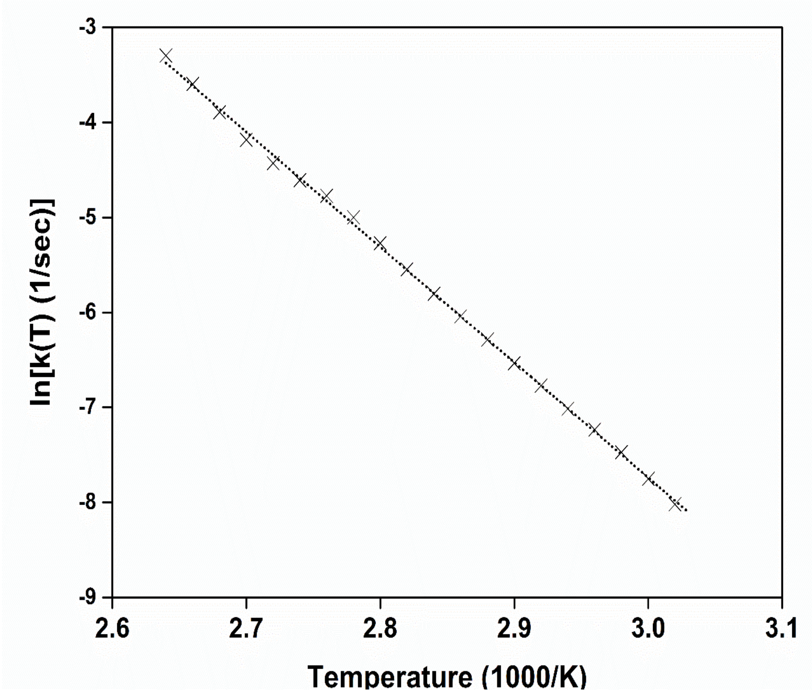

Figure 7: Plot of ln[k(T)] versus 1/T for epoxy resin A and hardener C

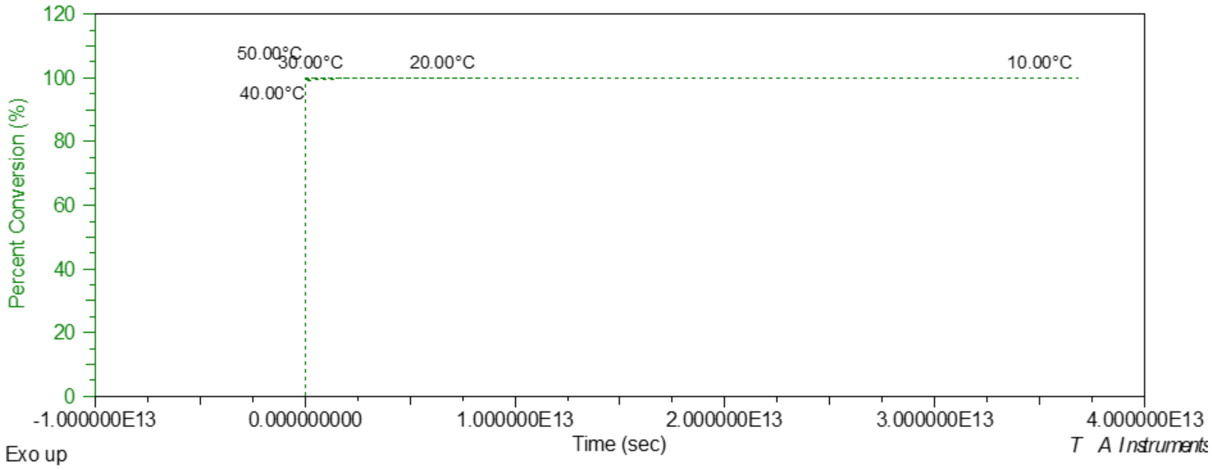

Figure 8: Percentage conversion versus time for epoxy resin A and hardener C

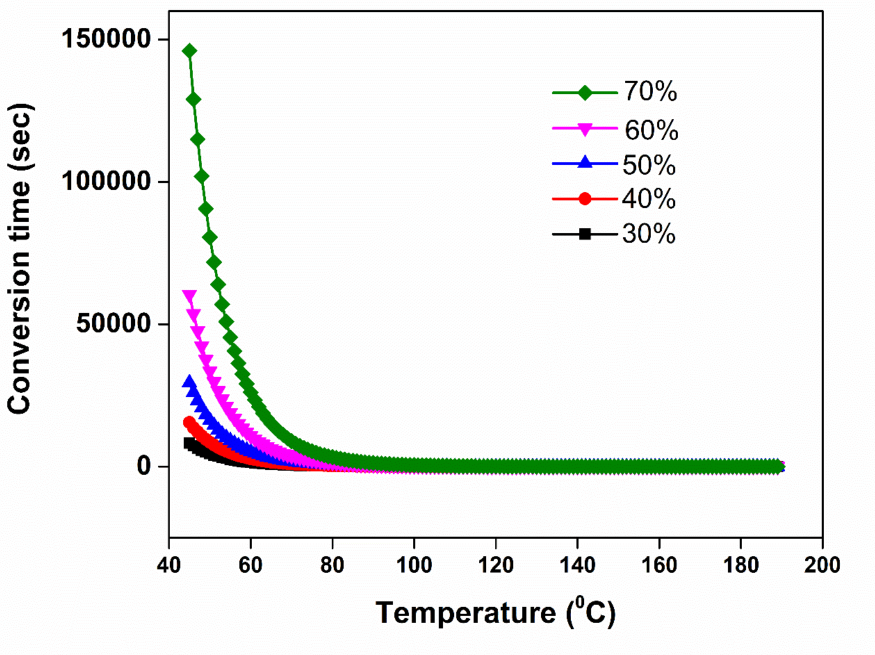

Figure 9: Percentage conversion time versus temperature for epoxy resin A and hardener C

From these data half life in seconds for the same resin with two hardeners were measured and plotted vs temperature Percentage conversion time versus temperature for epoxy resin A and hardener B

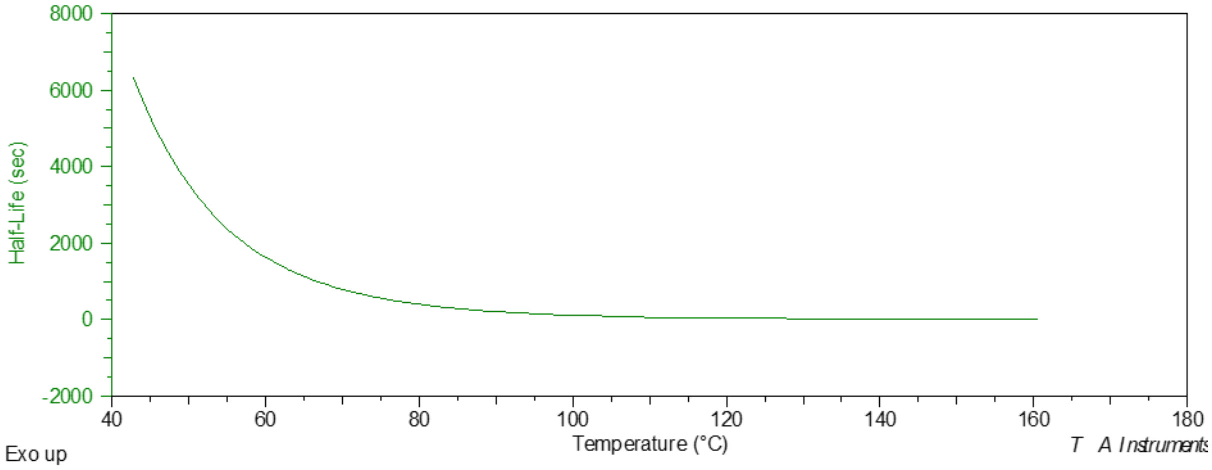

Figure 10: Plot of half life of the epoxy resin and hardener B with temperature

The half life the epoxyresin and the hardener B shows that half life decreases initially upto 80^0C and then levels off. For the same resin with hardener C the half life decreases and levels off at a lower temperature

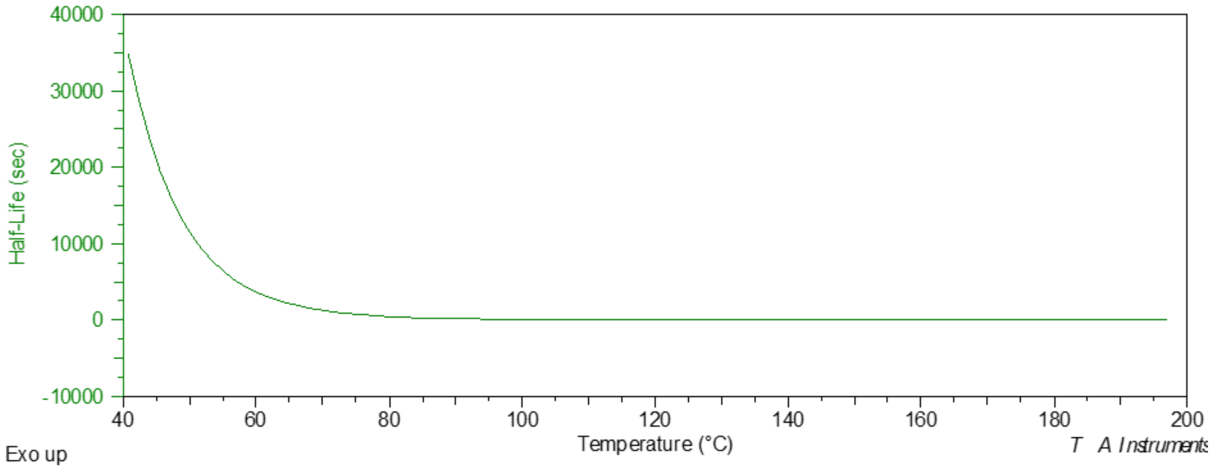

Figure 11: Plot of half- life of the epoxy resin and hardener C with temperature

The rate constant also was plotted versus temperature

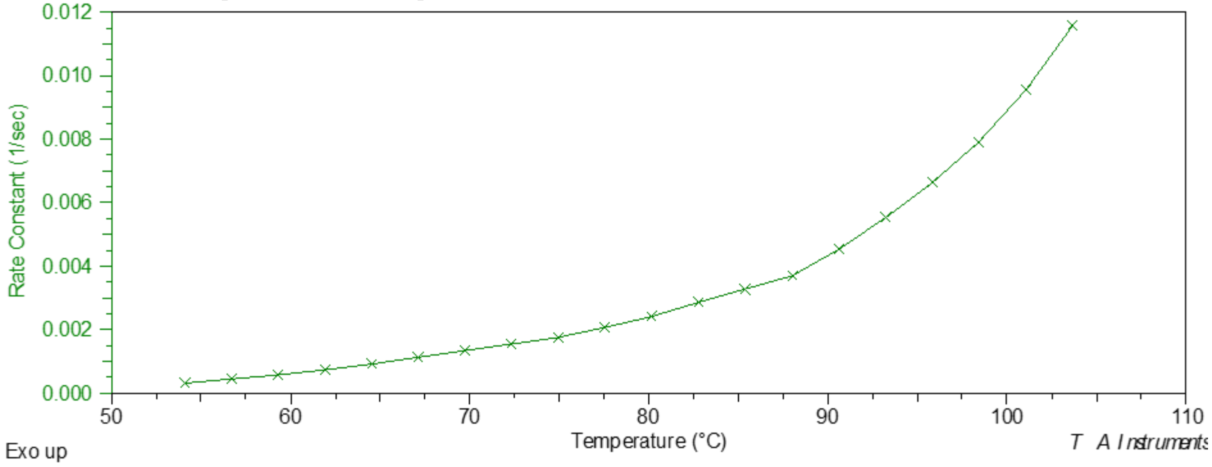

Figure 12: Plot of rate constant of the epoxy resin and hardener B with temperature

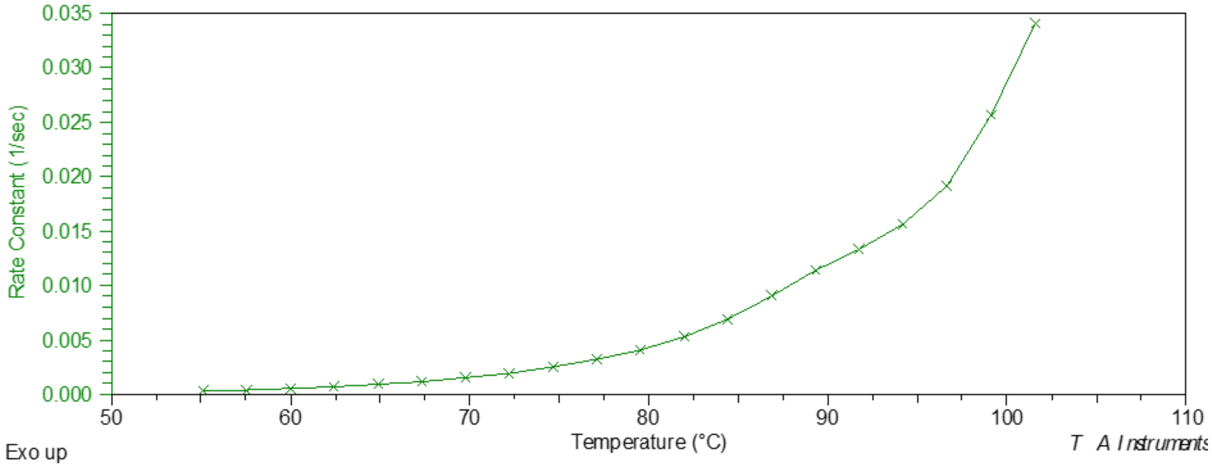

Figure 13: Plot of rate constant of the epoxy resin and hardener C with temperature

The rate constant increases with temperature as expected. The rate constant is found to be high for the resin A and hardener c compared to hardener B

4. Conclusions

The kinetic study reveals that the rate of curing reaction for resin A and hardener C is found to be much faster than that of resin A and hardener B. Activation energy is also found to be much higher for resin A and hardener C compared to resin A and hardener B.Rate constant is found to be higher for resin A and hardener C compared to resin A and hardener B. Half life of the reaction product is much lower for resin A hardener B compared to resin A hardener C.

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