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# Studies on thermal stability and life estimation of epoxy adhesive by thermogravimetric analysis for high-temperature applications

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**Abstract.** Structural epoxy adhesive was investigated for its thermal stability and degradation behaviour in a thermo-oxidative environment by thermogravimetry analysis (TGA). Non-isothermal TGA was performed at temperatures between 30 and 600°C utilizing different heating rates. The ageing characteristics of material were determined by an accelerated ageing study using isothermal TGA at different temperatures for 5% threshold conversion. The activation energies from both non-isothermal TGA and isothermal TGA were estimated and the activation energy values for 5% degradation from both the methods were in good agreement. The epoxy adhesive with titanium dioxide as filler showed a shelf life exceeding 13 years at ambient conditions (27°C). Additionally, the lap shear strength of the adhesive joint was also tested after treating the samples at 70°C with 90% relative humidity to evaluate the hydrothermal effect on adhesive joint.

**Keywords.** TGA; isothermal; non-isothermal; activation energy; Arrhenius equation.

## 1. Introduction

Epoxy resins are commonly used as adhesives and come under the high-performance adhesive category because of their excellent bonding ability to various materials, which include metals, composites, ceramic, plastics and rubbers. Along with strength, electrical insulation, flame retardance, oil and chemical resistance, with little modifications in the structural formulation, they offer high-temperature stability also. Epoxy adhesives are an important class of adhesives, being utilized in aerospace for various applications [1,2]. It is important to evaluate the long-term thermal stability of these adhesives for high-temperature applications, and prediction of adhesive's life in order to limit their usage at high temperatures. Ageing of materials is a crucial phenomenon from the point of view of reliability and cost. Thus, estimation of shelf life and thermal stability is an essential requirement for materials employed in aerospace structural applications. It is advocated to use accelerated ageing of material at elevated temperatures and then evaluating shelf life at desired storage or working temperatures rather than predicting shelf life by keeping the material at storage conditions for a long time and analysing the performance parameter at a regular time interval to ascertain their actual shelf life. Thermogravimetric analysis (TGA) has been in use for a long time to characterize thermal degradation phenomenon and predict working service life of materials. It is an alternate to oven ageing and a quicker method among all the accelerated ageing methods [3]. In a typical TGA, weight loss is analysed as a function of time or temperature to determine material degradation kinetic parameters under accelerated thermal ageing. Reviews by Sergey Vyazovkin [4,5] throw insight into various model free and model fitted methods to predict kinetic parameters and then thermal life of solid materials without knowing the reaction mechanism.

## 2. The Arrhenius model

The rate of reaction of a decay process is inversely related to the lifetime of materials. Arrhenius equation is a classical and popular method and it gives an exponential correlation for a reaction rate constant of chemical reactions. It also describes the relationship between storage temperature and

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degradation rate. Arrhenius extrapolations assume that a chemical degradation process is controlled by a reaction rate equation:

$$K(T) = Ae^{-E_a/RT} \tag{1}$$

where $K(T)$ is the reaction rate constant ($min^{-1}$); $E_a$ is the Arrhenius activation energy (J $mol^{-1}$); $R$ is the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$); $T$ is the absolute temperature (K) and $A$ is the pre-exponential factor ($min^{-1}$).

In case of TGA, the rate of degradation or conversion ($\alpha$) can be determined with time and when substituted into Arrhenius equation, the rate of reaction can be expressed as in equation (2):

$$\frac{d\alpha}{dt} = K(T)f(\alpha) = Af(\alpha)\exp\left(\frac{-E_a}{RT}\right). \tag{2}$$

Integrating the rate equation (2), under isothermal conditions gives equation (3), where $\ln[g(\alpha)/A]$ is constant at a conversion:

$$\ln t = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E_a}{RT}, \tag{3}$$

where $g(\alpha)$ is the integral conversion function defined as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}. \tag{4}$$

A plot of ln $t$ *vs.* $1/T$ gives a straight line with slope $E_a/R$. Extrapolating this line to the temperature of interest can indicate predicted life at that temperature.

The aim of this study was the determination of life at working condition and extent of degradation with time and temperature in the epoxy adhesive employed in structural applications for aerospace.

Experiments were conducted isothermally at four different temperatures ranging from 180 to 240°C in air atmosphere. The working life of an adhesive at different temperatures was predicted using Arrhenius equation. Wherein, the thermal behaviour up to 80% degradation in material was studied from the non-isothermal tests performed in the temperature range of 30–600°C under air atmosphere utilizing four different heating rates of 5, 10, 20 and 30°C $min^{-1}$, respectively. The activation energy was also calculated from non-isothermal tests by Flynn–Wall–Ozawa (FWO) method as per ASTM E 1641 as well as from isothermal data from equation (3). Lap shear strength of metal to metal joint was also tested after hydrothermal ageing for 1000 h.

## 3. Experimental

### 3.1 *Material*

A three-component structural epoxy adhesive (named KE-300) obtained from M/s Subond Adhesive Industries, Odhav, Ahmedabad was investigated in this study. The operational temperature is −20°C to +250°C. The mixing ratios of resins with filler in parts by weight are given in table 1. The properties of KE-300 adhesive are given in table 2.

### 3.2 *Sample preparation*

A measure of 10 g of adhesive part A was taken in a mixing bowl and to that 3 g of filler was added. It was mixed thoroughly by hand for 6–8 min. Then 4 g of hardener part B was added and mixed thoroughly to make a uniform paste. The sample was allowed to cure at room temperature (~27°C) for 24 h. When the sample was completely cured, it was cut into small pieces of around 1–2 g of weight for further TGA analysis.

The sample preparation for testing of lap shear strength was done by mixing all the three components in a similar way as mentioned above and then the adhesive was applied on the sample plates of aluminium to make a lap joint for measuring the lap shear strength as per ASTM D 1002. Figure 1 illustrates the drawing of the adhesive.

Both plates were pressed together at the adhesive area to make a lap shear joint as shown in figure 2. The joint was clamped to give pressure ~1 kg and kept for 24 h for curing.

### 3.3 *Instrumentation*

The TGA experiments were conducted using a TA model TGA–SDT Q600, thermogravimetric analyser. A finely powdered sample weighing 10 ± 2 mg was kept in a small alumina crucible for each run under air atmosphere with a

**Table 1.** Mixing ratio of components of KE-300 in parts by weight.

| Chemical constituents | Parts by weight (g) |
|---|---|
| Epoxy resin part A | 100 |
| Hardener part B | 40 |
| Titanium dioxide (filler) part C | 30 |

**Table 2.** Properties of KE-300.

| Parameter | Values |
|---|---|
| Mass fraction of dry residue | 90.0–92.50% |
| Lap shear strength for steel to steel (after 24 h cure at room temperature) | 205–215 kg $cm^{-2}$ |
| Density | 1.18–1.2 g $cm^{-3}$ |

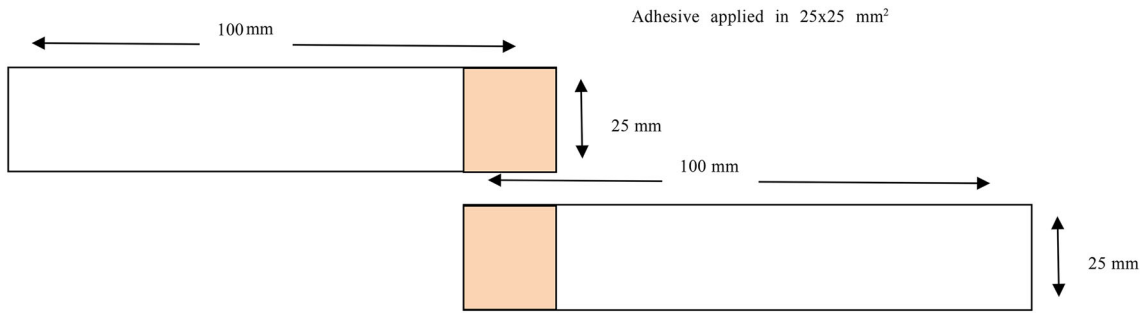


**Figure 1.** Diagram showing plates with adhesive.

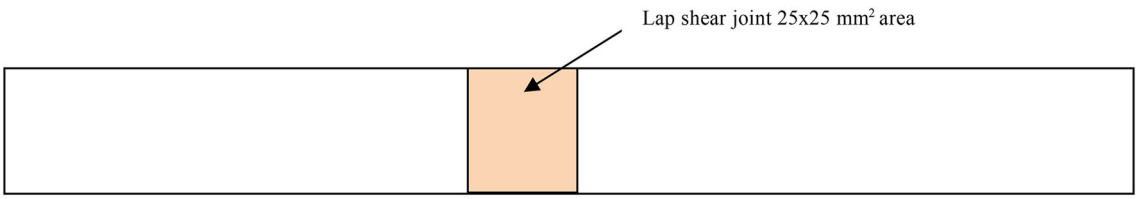


**Figure 2.** Diagram showing lap shear joints.

flow rate of 100 ml $min^{-1}$. The variation of weight loss in the material with respect to the time and temperature was recorded automatically by the instrument and determined through the TA universal analysis software. The experiments were repeated three times by taking the same weight ($10 \pm 2$ mg) under similar experimental conditions to check the reproducibility of the results. The lap shear strength was tested in a UTM machine with a load cell of 10 kN. The samples were also placed in a climatic chamber at a temperature of 70°C (considering maximum storage temperature) and 90% relative humidity (RH) to analyse the effect of humidity and temperature at various time intervals on lap shear strength.

3.3a *Non-isothermal TGA:* Thermal stability in material was studied with respect to its thermal degradation behaviour as a function of time and temperature. Non-isothermal tests were performed on the adhesive sample in the temperature range of 30–600°C with four heating rates at 5, 10, 20 and 30°C $min^{-1}$. The degradation behaviour of a material depends mainly on the temperature, heating rate, residence time and sample size in each test [3]. The FWO method as per ASTM E 1641 was used to obtain activation energy ($E_a$) from a plot of natural logarithm of heating rates, ln $\beta$ *vs.* $1/T$, which gives the linear relationship for a given value of conversion at different heating rates. It is expressed as:

$$\ln(\beta) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_a}{RT}, \quad (5)$$

where $g(\alpha)$ is constant at a given value of conversion. The activation energy was calculated from the slope of $-1.052E_a/R$.

3.3b *Isothermal TGA:* The basic assumption of the experimental design to estimate the storage lifetime method is that the reaction mechanism at constant conversion does not vary with temperature. The samples were analysed in thermo-oxidative environment at four different temperatures ranging from 180 to 240°C. The maximum ageing time was chosen as 140 min approximately. Since the objective was to predict the shelf life of epoxy adhesive at storage temperature ($\sim$27°C) from ageing data taken at higher temperature, the temperature selection was an important parameter. The working life of the cured adhesive in storage condition was predicted by using equation (4) for 5% conversion of material.

3.3c *Lap shear strength analysis:* The samples of lap joint ($n = 55$) were kept in climatic chamber at temperature 70°C and 90% RH to analyse the effect of humidity and temperature on lap shear strength at various time intervals. These conditions were taken by considering the possible maximum storage temperature and humidity. Five samples were taken out at every 100 h time duration to test the lap shear strength.

## 4. Results and discussion

### 4.1 *Thermal stability*

Thermal stability of a material is the main criteria for determining the limit of working temperature of material and the environmental conditions for safer use. It is related to the thermal decomposition temperature of material and the decomposition rate. Figure 3 shows plots of the TG decomposition data of the investigated material obtained at four different heating rates in the presence of air.

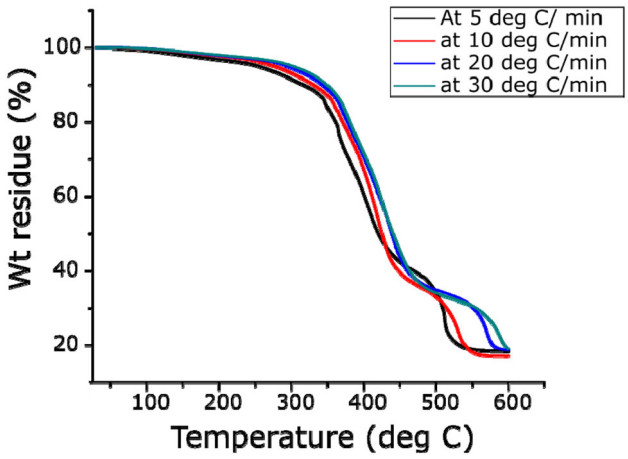


**Figure 3.** Non-isothermal degradation at different heating rates.

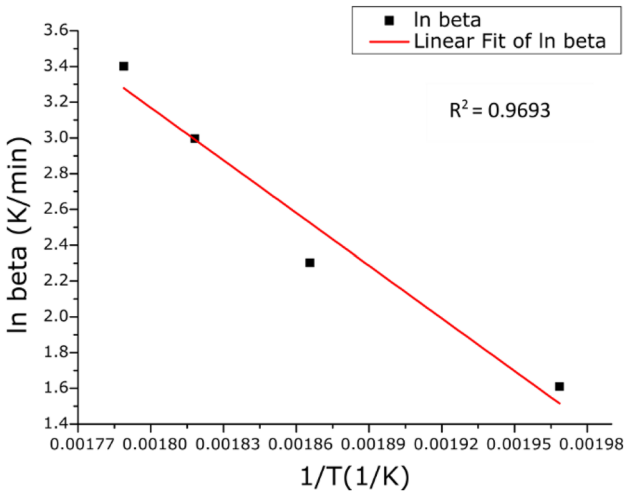


**Figure 4.** FWO plot for 5% of conversion of KE-300.

**Table 3.** $T_{5\%\ \text{wt loss}}$ and $T_{\text{half }50\%\ \text{wt loss}}$ of KE-300.

| Heating rate (°C min$^{-1}$) | $T_{5\%\ \text{wt loss}}$ (°C) | $T_{\text{half }50\%\ \text{wt loss}}$ (°C) |
|---|---|---|
| 5 | 235.4 | 421.2 |
| 10 | 263.0 | 425.7 |
| 20 | 277.2 | 438.0 |
| 30 | 286.1 | 440.0 |

The first region from below 120°C shows the extraction of moisture and volatiles in the adhesive sample, because of which the weight loss in the sample starts. The main degradation process starts in a range of 210–230°C temperature and ends at 450–480°C. This may be assigned as the first rapid degradation stage and ends with a small hump in the curve. The temperature for 5 and 50% decomposition of material ($T_{5\%}$ and $T_{\text{half}}$, respectively) are shown in table 3.

In the next stage of degradation, 80% thermal decomposition took place up to 600°C temperature. The residual mass represents the presence of filler titanium dioxide which degrades at very high temperature [6]. The increase in heating rate shifts the degradation towards the higher side of the temperature, but the curve pattern was the same at all heat rates. This shows that the kinetics is affected by the heating rates, but the compounds formed in the degradation process are the same. The obtained results agree well with literature reports for thermo-oxidative ageing of an epoxy adhesive [3,7]. A plateau in the second stage of degradation towards the end indicates that some oxidized products have formed, which are entirely different from the product of the main stage of degradation [8].

The activation energy was evaluated using the model-free FWO method for 5% of conversion, which allows the activation energy without knowledge of the reaction mechanism [9–12]. The FWO plot of ln $\beta$ *vs.* 1/$T$ for 5% of conversion is shown in figure 4. The slope of the linear fit of the plot yields the activation energy value as 77.57 kJ mol$^{-1}$ K$^{-1}$ at 5% of conversion.

Similar results for activation energy of thermo-oxidative degradation of glass-reinforced epoxy system have been obtained by Budrugeac using FWO and other model-free methods [13].

In the model fitted method, the auto catalytic reaction model has been successfully applied by many researchers for thermal degradation of epoxy systems [9,14–16]. Here, the maximum rate of reaction occurs in the later stage of the reaction usually after 20% of degradation whereas in the *n*th order of reaction the maximum rate of reaction will be attained at the initial stage of the reaction itself.

### 4.2 *Lifetime prediction for storage temperature*

Isothermal TGA was conducted at temperatures 180, 200, 220 and 240°C. From the non-isothermal test results, it is clear that 5% decomposition of KE-300 occurs above 230°C for all the heating rates. Therefore, if the temperatures are chosen below 180°C, the time taken for the 5% decomposition was more than 3 h. Isothermal TGA at various temperatures is shown in figure 5.

A plot of ln $t$ *vs.* 1/$T$ was drawn for 5% conversion of isothermal TGA (figure 6). The slope of the linear fit of plot gave the activation energy value of 79.003 kJ mol$^{-1}$ K$^{-1}$ at 5% conversion. The plot has been extrapolated to get the lifetime at 27°C, which is equal to 13.5 years for 5% conversion.

Similarly, the shelf life of KE-300 adhesive in cured condition was calculated for 5% conversion in the temperature range of 30–70°C. It covers normal to extreme temperature of the weather. The results are summarized in table 4 and will be helpful to specify the storage temperature of articles, wherever KE-300 adhesive is being used.

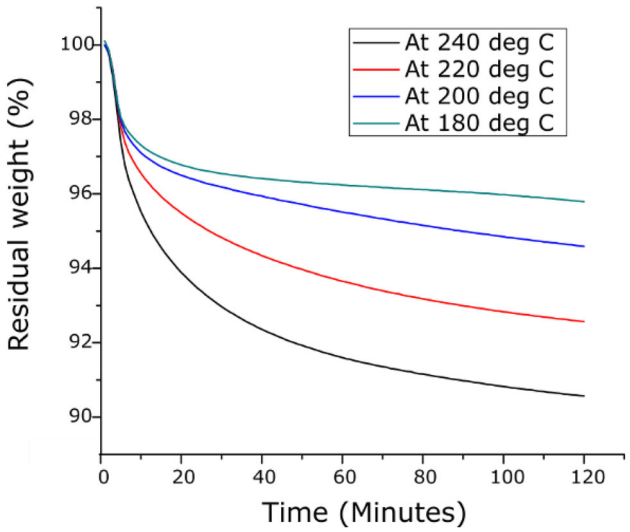


**Figure 5.** Isothermal TGA of KE-300 at various temperatures.

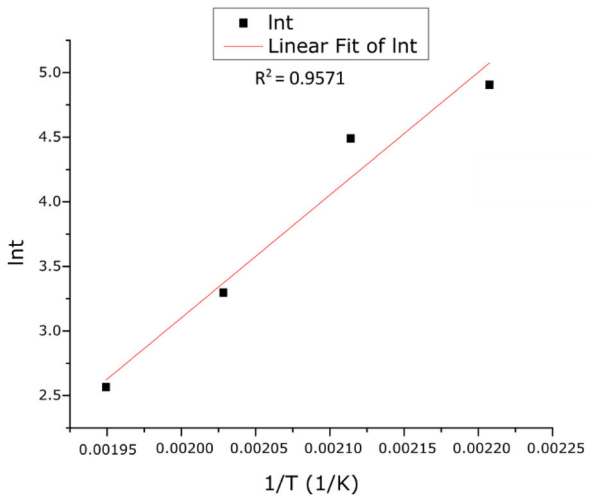


**Figure 6.** Life time *vs.* temperature plot for 5% of conversion of KE-300.

**Table 4.** Shelf life of KE-300 at various temperatures.

| Temperature (°C) | Time (years) |
|---|---|
| 30 | 9.832608 |
| 40 | 3.611432 |
| 50 | 1.410867 |
| 60 | 0.583159 |
| 70 | 0.253803 |

### 4.3 *Lap shear strength at various time intervals*

At 100 h intervals, five of the samples each were taken out from the chamber to test the lap shear strength. The results are summarized in table 5.

There was no substantial change in the lap shear strength even after keeping the samples at 70°C and maximum humidity of 90%, which shows that the impact of humidity is negligible up to 1000 h. The slight increase in values of lap shear strength at some time intervals may be attributed to change in cross-linking of polymer matrix. The lap shear strength depends on the adhesion of the material. The breaking of bonds during thermal degradation reduces the adhesion of material to the substrate [14]. Thus, the results indicate no changes in chemical structure of epoxy system even after 1000 h hydrothermal treatment. Dao and coworkers showed that small changes occur in epoxy system only after 7500 h at 70°C temperature [17,18].

**Table 5.** Lap shear strength of K-300-61(IND) at various time intervals.

| Time (h) | Lap shear strength, average of 5 samples (kgf $cm^{-2}$) |
|---|---|
| Before keeping in chamber | 210 |
| 100 | 220 |
| 200 | 215 |
| 300 | 224 |
| 400 | 229 |
| 500 | 225 |
| 600 | 220 |
| 700 | 226 |
| 800 | 228 |
| 900 | 225 |
| 1000 | 228 |

## 5. Conclusion

An experimental study on thermal degradation and life prediction on high-temperature titanium dioxide-based epoxy adhesive by TGA analysis was conducted. Thermal stability of material at 5% conversion of total mass was obtained from 235.4 to 286.1°C, which describes the working thermal limit of the material. Half-life was obtained from 421.2 to 440°C. The activation energies calculated by FWO method of non-isothermal TGA and isothermal TGA were nearly the same. The results indicate that adhesive KE-300 has a lifetime ~13.5 years at a storage temperature of 27°C. There is a negligible effect of storage temperature and humidity on the shear strength of the adhesive joint. The TGA results also show that at 70°C the material degradation is less than 5%. This study did not estimate the life of the adhesive and influence of various environmental parameters, such as humidity, UV light, microorganisms, ozone and so on.

## Acknowledgements

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