Degradation of GFReenforced Polymer Rebars

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Abstract

Glass Fiber Reinforced Polymers find new applications every year. They are of special interest to ***SAUDI ARABIA*** for two reasons; harsh environments in most of the country ($T_{ambient}$ range –5 to 55 ^{o}C), and the rapid development of the Saudi Polymer industry. The thermo oxidative degradation behavior of Glass Fiber Reinforced Polymer Rebars (GFRP) was studied by thermo gravimetric analysis (TG), differential thermal analysis (DTA), and Differential Scanning Calorimetry in order to obtain some thermodynamic properties and elucidate the decomposition process. The study resulted in the following average values: specific heat of .27 cal/g K; transition temperatures of 287 C, and 342 under N_2 atmosphere; heats of fusion - 3070 mJ/mg, and –6mW under N_2 atmosphere (50ml/min); and heats of transition, 3200 mJ/mg and 65 mW under N_2 atmosphere (50ml/min)

Keywords: Thermo gravimetric studies of polymers; Activation energy; Rate finding methods, Differential method, integral method, Kinetic Models; Thermo oxidative behavior, polymer degradation and stability , composites, glass fiber enforcement.

1. Introduction

Glass Fiber Reinforced Polymers (GFRP) is a relatively new class of material. They find newer applications every year. From engine gears to huge pipes, they proved to have high thermal and mechanical resistance .They are of special interest to ***SAUDI ARABIA*** for two reasons; harsh environments in most of the country ($T_{ambient}$ range –5 to 55 ^{o}C), and the rapid development of the Saudi Polymer industry. However, local standards, specs, and codes do not permit their use as a substitute for metal or steel bars due to the absence of fire ratings for continuous fiber reinforced polymer composites, which use combustible materials as polymer matrix materials or binders[1]. Therefore, if thermal stability and durability of such material were to be evaluated properly with respect to suitability for use in various sectors, it is necessary to perform an experimental study to evaluate the thermo oxidative degradation behavior and thermodynamic properties of the GFRP materials [2, 3, and 4]. The study of the thermal degradation of a polymer is of major interest since it can, in many cases; determine the upper temperature limit of use for a material. It is also significant to permit their introduction in the process industry as infra structure material for pipes, .supports, tunnels, or vessels

Thermal Gravimetric Analysis (TGA) gives the percent weight loss of a test sample while the sample is being heated at a uniform pre-set temperature program (rate) in an appropriate environment. The loss in weight over specific temperature ranges provides an indication of the decomposition behavior of the sample, including: fibers, volatiles, polymer matrix, active and inert fillers. Thermo gravimetric analysis has been also used to provide evidence of some dependence of thermal stability and molecular interactions with compatibility. As with many reactive processes, the rate and rate constants of the reaction are significant of all parameters.

2. Thermodynamic properties

Thermodynamics denotes the motion of energy on all levels. Thermodynamic properties control the rate of energy exchange and absorbance from an energy source. Properties such as specific heat and latent heats of phase change are essential parameters in the study of thermal behavior and stability of polymer composites. The TG/DTA Thermal analyzer used in this study gives a DSC signal as well. **DSC**; Differential Scanning Calorimetry shows the rate and magnitude of energy changes experienced by the sample. From the DSC curve, properties such as specific heat and latent heats of phase change or transition, and temperature of transition can be obtained directly.

3. Thermo oxidative process

Study of polymer degradation under gradually elevated temperature provides an indication of its stability and its response to variation under different physical conditions. Such studies can be obtained using was performed using thermal gravimetric analysis (TGA) [5-13]. TGA study shows the change of weight with temperature of a test sample. It also shows the amount of energy needed to components and to break down the polymer .chains to completely oxidize the polymer

Thermal analysis was performed in a Perkin Elmer TG/DTA thermal analyzer. The instrument was first calibrated using iridium and then checked using calcium oxalate. The samples were first weighed in mettler scale than placed in a platinum mini pan which was then placed in the instrument. Analysis in the first set took

place in air atmosphere to study the thermo oxidation process. The second sets of analysis were performed in nitrogen atmosphere (50 ml/min). Results of thermal analysis are shown in Figures 1-6 showing thermo grams under both nitrogen and .air atmosphere

4. Experimental

The GFRP samples were obtained from an earlier generation glass fiber reinforced polymer bars (seabar) 10 mm diameter GFRP. Before being introduced in a cylindrical frame for thermo gravimetric analysis, the samples were selected to accommodate the TG/DTA apparatus pan dimensions, and to conform to the weight requirement of the set up. The polymer composite pieces or powders (less than 15 mg) were first weighed separately in a Mettler balance and placed in the instrument. The instrument was calibrated using indium and calcium oxalate standards prior to the start of the analysis. The temperature range for the study spanned from room temperature through 800 °C in a TGA/DTA Differential Thermal Analyzer from Perkin Elmer controlled by a computer and PYRIS MUSE THERMAL ANALYSIS software, and equipped with a microbalance. This microbalance was calibrated using an indium standard sample.

The system was operated in the dynamic mode at different heating rates: 5, 10, and 15 °C/min. All the experiments were non-isothermal and were carried out under air atmosphere. The THERMAL ANALYSIS software can output analysis results in TG, DTA, and DSC modes enabling the extraction of numerical values for the thermodynamic properties desired.

5. Results and Discussion

Results of the analysis are shown in Figures 1 through 6. These figures show the TG thermo gram of GFRP samples.

Figure 1 DDTA, DSC, and TG thermograms of GFRP samples under air atmosphere, heating rate 5 º C/min

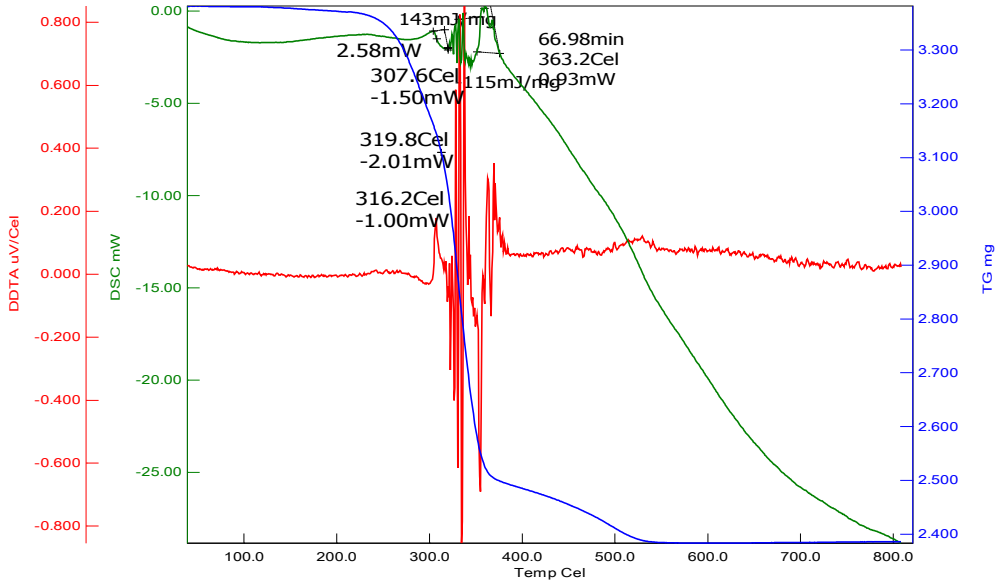


Figure 2 DDTA, DSC, and TG thermograms of GFRP samples under air atmosphere, heating rate 10 ° C/min

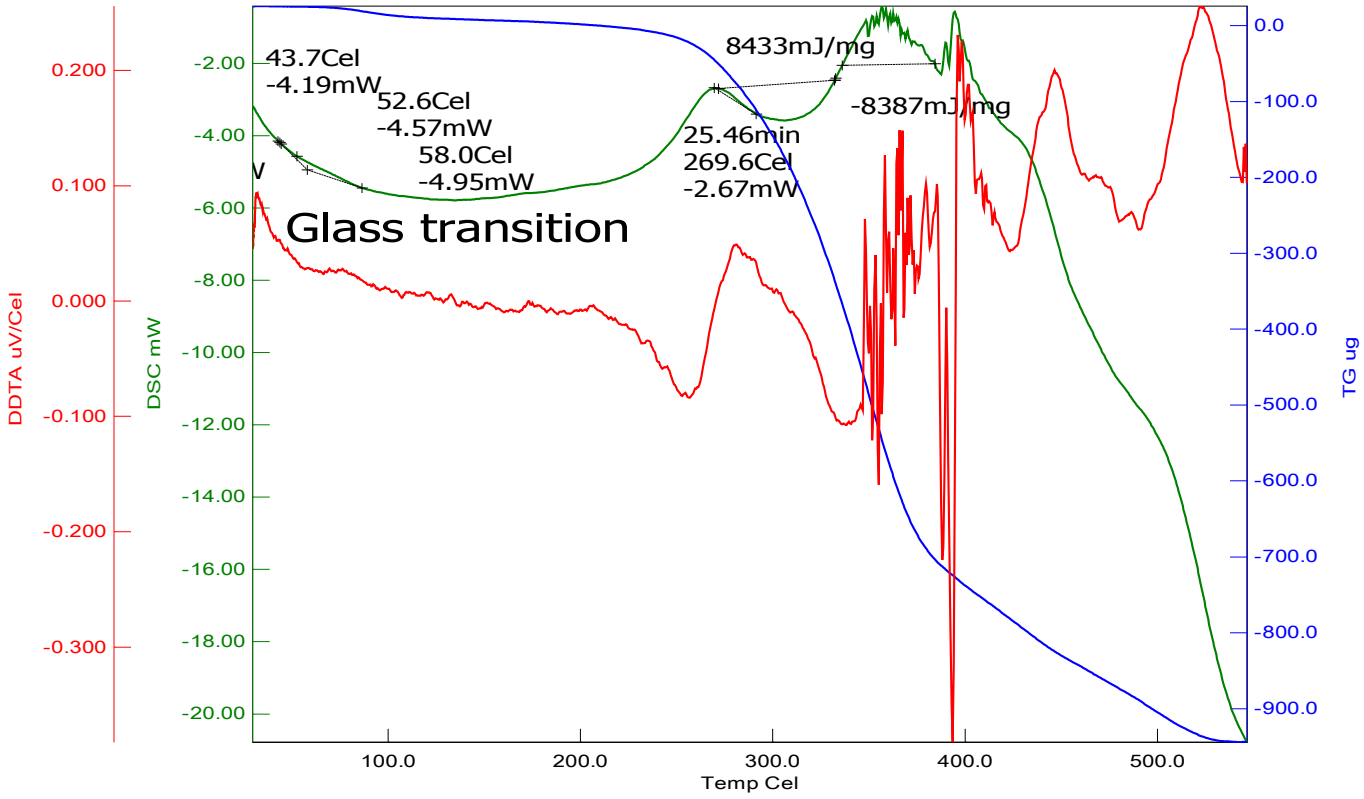


Figure 3 DDTA, DSC, and TG thermograms of GFRP samples under air atmosphere, heating rate 15 ° C/min

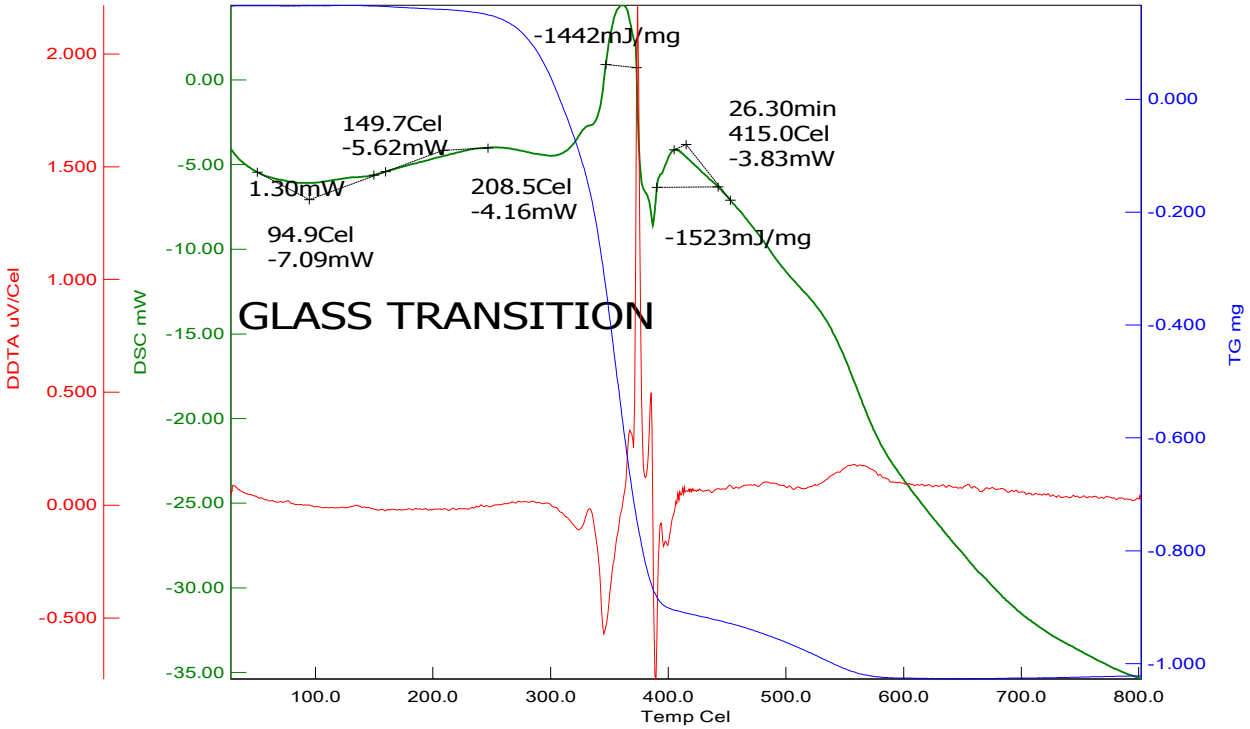


Figure 4 DDTA, DSC, and TG thermograms of GFRP samples under N_2 atmosphere, heating rate 5 ° C/min

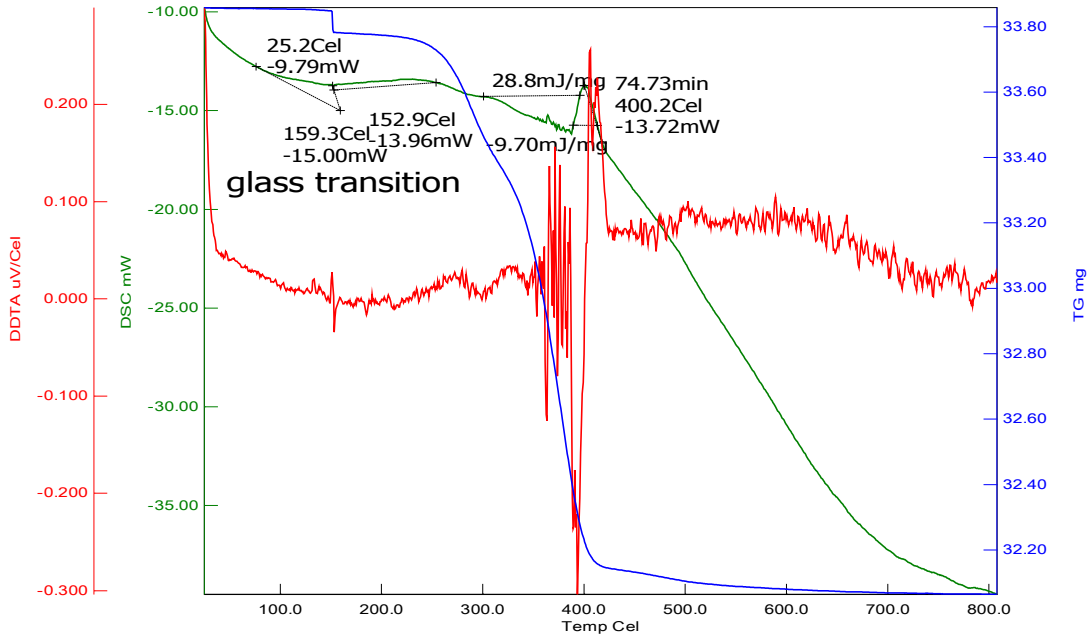


Figure 5 DDTA, DSC, and TG thermograms of GFRP samples under N_2 atmosphere,heating rate 10 ° C/min

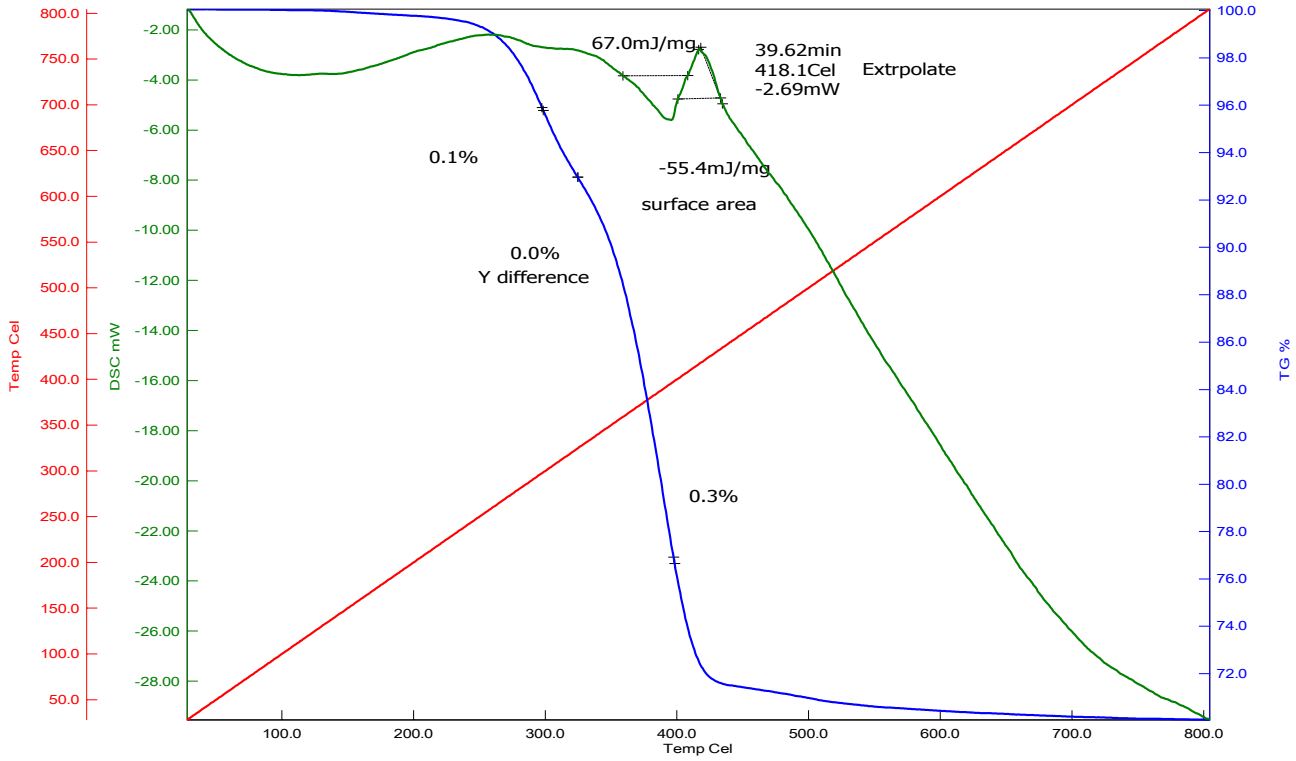


Figure 6 DDTA, DSC, and TG thermograms of GFRP samples under N_2 atmosphere, heating rate 15 ° C/min

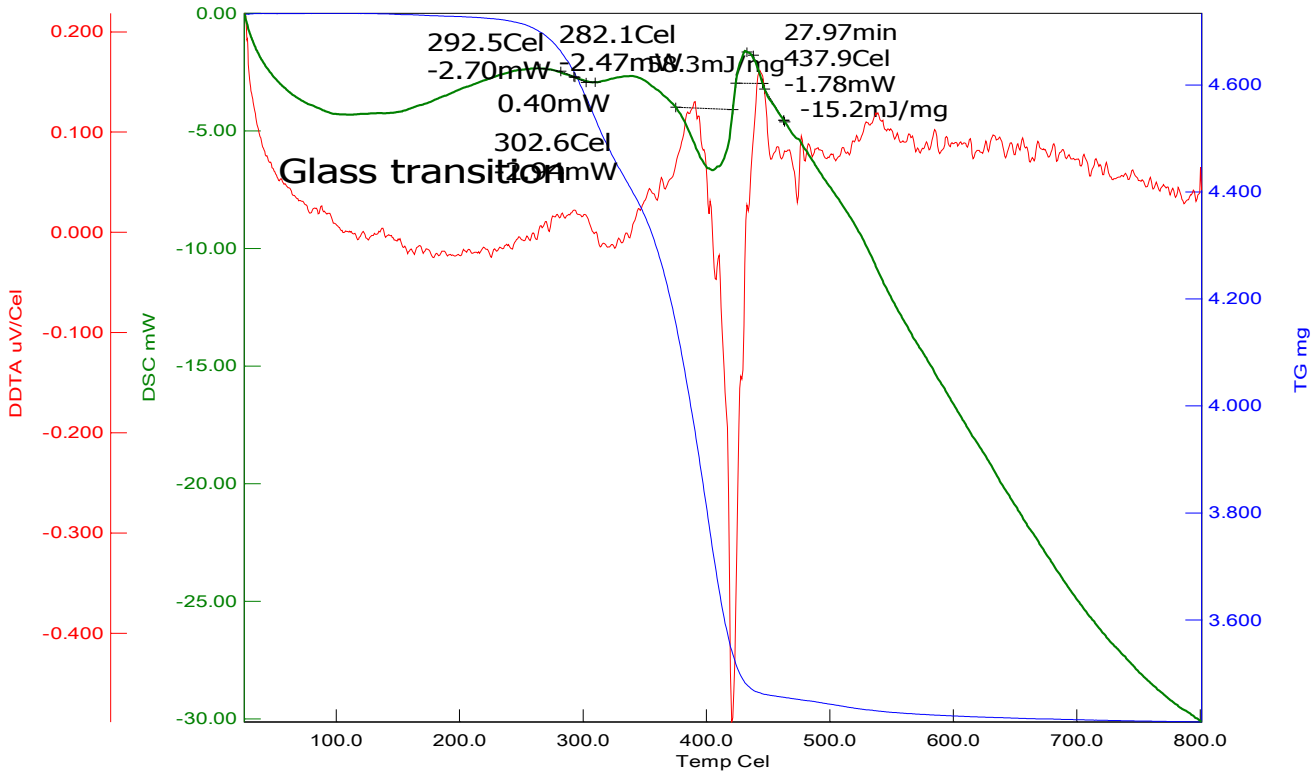


Figure 7: Kissinger Plot for Thermo Oxidative degradation of

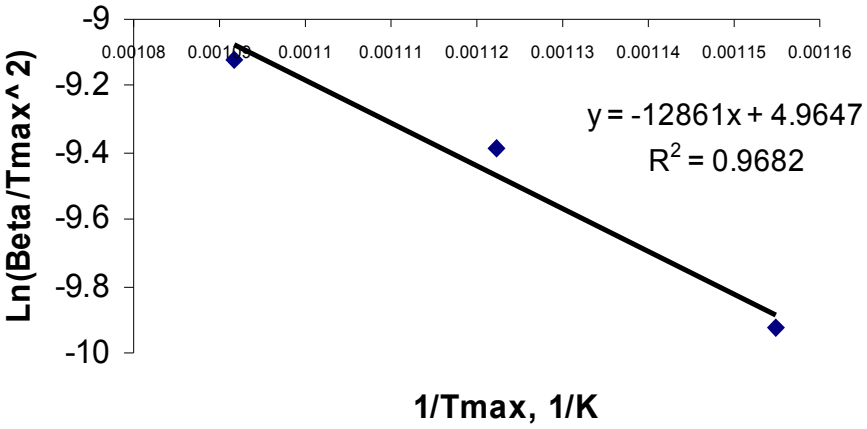
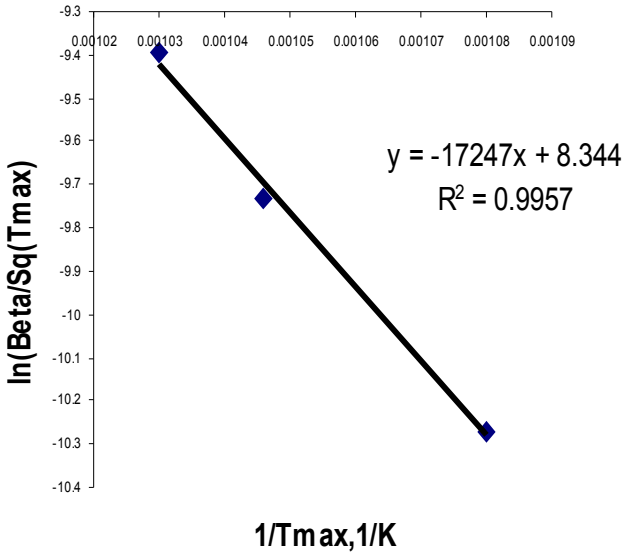


Figure 8: Kissinger Plot for Thermal Degradation of GFRP under N2 Environment.



The weight loss with temperature is recorded. Significant losses are indicative of the chemical composition of the composite. The first major drop in the weight reflect the degradation of urethane modified Vinyl ester, as about 15 % loss is experienced by the sample. The following losses take place in the magnitude of about 10% of the sample weight. This reflects the loss of the unstated polyesters. The material that did not thermally decompose even when the temperature was as high as 600 $^{\circ}$ C is 10.5 mg. The total % of glass and ceramic enforcement is 73.5 % for this sample this corresponds to 10.29 mg. These values show the thermal/weight behavior of the sample, which is attributed to the chemical composition of the sample, Table 1 below.

CONSTITUENT	**Composition%**
E-Glass	**70**
Urethane modified vinyl ester	**15**
Unstated polyester	**10**
Ceramic Reinforcement	**3.5**
Corrosion inhibitors	**1.5**

Table 1 Chemical Composition of GFRP Polymer Composites used in this study

Taking a look at the DSC curves of , average values on the curve are $\Delta H_{softening}$ =8.4 mW, $\Delta H_{transition}$= 20.6 mW, $T_{softening}$= 280 $^{\circ}C$, transition temperatures of 287 C, and 342 under N_2 atmosphere; heats of fusion - 3070 mJ/mg, and –6mW under N_2 atmosphere (50ml/min); and heats of transition, 3200 mJ/mg and 65 mW under N_2 atmosphere (50ml/min), $\Delta H_{\deg radation} = -181$ J/mg. From the DSC output, the initial deflection is proportional to the specific heat, $C_{p,}$ of the sample. Using the calibrated values for the instrument an average value of C_p= 0.27 cal/gm K is obtained. Kinetic evaluation resulted in values of 1542 kJ/mol for thermo oxidative process and 2095 kJ/mol under N_2 environment (50 ml/min).

Phenomena shown by the thermo grams and discussed above are indications of the flame retardancy -role of the E-glass fibers in the polymer composites [14]

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