

Kinetics of Thermo Oxidative Degradation of GFR Polymer Composites

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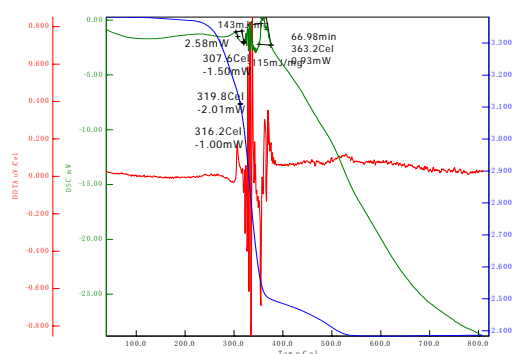
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Glass Fiber Reinforced Polymers find newer applications every year. They are of special interest to SAUDI ARABIA for two reasons; harsh environments and the rapid development of the Saudi Polymer industry. The thermo oxidative degradation behavior of Glass Fiber Reinforced Polymer Rebars (GFRP) was studied by thermo gravimetric analysis (TGA), differential thermal analysis (DTA), and Differential Scanning Calorimetry (DSC) 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, heat of fusion - 3070 mJ/mg, and heat of transition, 3200 mJ/mg .

Thermo Oxidative Process & Experiments

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) [1–5]. 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. Analysis took place in air atmosphere to study the thermo oxidation process. Results of kinetics of thermal degradation according to The Kissinger Method (A Differential Kinetic Method) are shown in Figures below.

The GFRP samples were obtained from an earlier generation GFRP. The samples(less than 15 mg) were first weighed separately in a Mettler balance and placed in in a platinum mini pan which was then placed in the instrument. The instrument was calibrated using standards prior to analysis. The temperature range for the study was 25 °C to 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. 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.

Results and Discussion

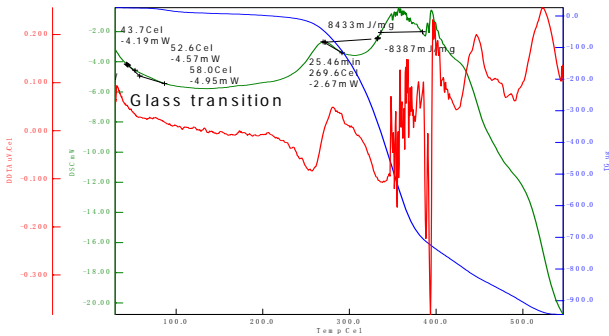
Results of the thermal analysis under air (Thermo Oxidative Degradation Process) are shown in Figures 1 through 3 below.

Figure 1 DDTA, DSC, and TG thermograms of GFRP samples

under air atmosphere, heating rate 5 ° C/min

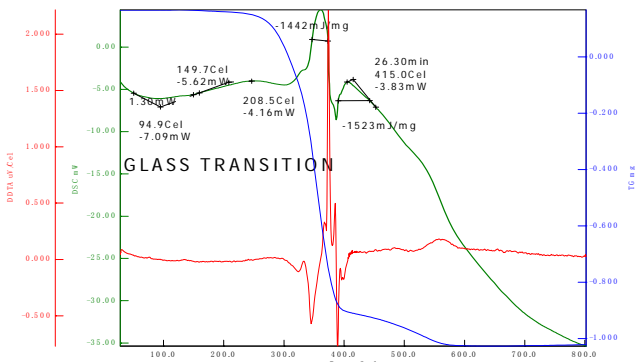
As the weight loss with temperature is recorded., significant losses are indicative of the chemical composition of the composite. The first major drop in the weight reflect the degradation of urethane modified Vinyl ester, as about 15 %

loss is experienced by the sample. The losses to follow 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 °C is 10.5 mg. The total % of glass and ceramic enforcement is 73.5 % for this sample this corresponds to 10.29 mg. Taking a look at the DSC curves,



average values on the curve are $\Delta H_{softening} = 8.4 \text{ mW}$, $\Delta H_{transition} = 20.6 \text{ mW}$, $T_{softening} = 280 \text{ }^\circ\text{C}$, transition temperatures of 287 C;

heat of fusion - 3070 mJ/mg, and heat of transition, 3200 mJ/mg, $\Delta H_{deg\ radation} = -181 \text{ J/mg}$. From the DSC output,



the initial deflection is proportional to the

Figure 2 DDTA, DSC, and TG thermograms of GFRP samples

under air atmosphere, heating rate 10 ° C/min

specific heat, C_p , of the sample. Using the calibrated values for the instrument an average value of $C_p = 0.27 \text{ cal/gm K}$ is obtained.

Figure 3 DDTA, DSC, and TG thermograms of GFRP samples

under air atmosphere, heating rate 15 ° C/min

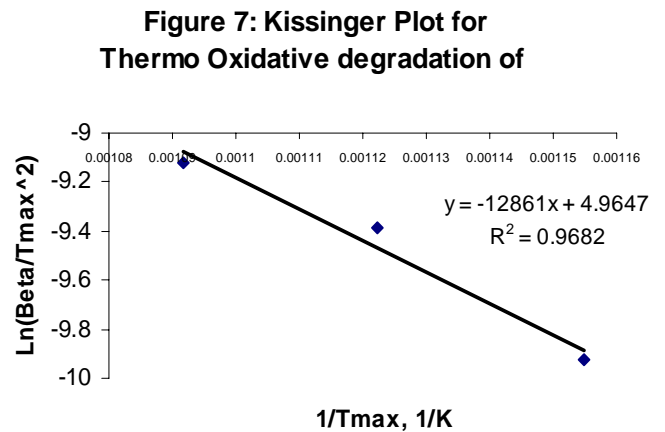
Kinetic information can be extracted from dynamic experiments by means of various methods. Relevant kinetic studies assume that the isothermal rate of conversion, da/dt , is a linear function of a temperature-dependent rate constant, k , and a temperature-independent function of the conversion, a . Kissinger method (6) (a differential rate determining method) has been used in the literature to determine the activation energy of thermal degradation of polymers and composites. The activation energy can be determined by Kissinger method without a precise knowledge of the reaction mechanism, using the following equations

$$E_a \beta (RT_p^2) = A e^{-E_a/RT_p}$$

where A is the frequency/ Pre exponential factor of The Arrhenius Equation and β is the heating rate, which is expressed as $\beta = dT/dt \text{ (C/min)}$. Taking the logarithm of the above equation, we obtain

$$-\ln(\beta T_p^2) = -\ln\left(\frac{AR}{E_a}\right) + \left(\frac{1}{T_p}\right)\left(\frac{E_a}{R}\right)$$

Activation energy, E_a can be obtained by plotting $\ln(\beta T_{max}^2)$ as function $1/T_{max}$, where T_{peak} or T_{max} is the maximum temperature. The plot produces a straight line the slope of which is E_a



Kinetic evaluation resulted in value activation energy of 1542 kJ/mol for the thermo oxidative degradation reaction/process.

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