

Investigation on the Thermal Stability of PMR Polyimide Resin and Its Carbon Fiber Composite

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The in situ polymerization of monomer reactants (PMR) has been demonstrated to be a powerful approach for solving many of the processing difficulties associated with the use of high temperature resistant polymers as matrix resins in high performance composites. KH-304, the PMR polyimide discovered in the early seventies, provide the best overall balance of processing characteristics and elevated temperature properties. Because its outstanding specific strengths, specific stiffnesses and thermal oxidative stability, KH-304 composites are currently being used to produce a variety of high quality structural components for use at temperature up to 316°C, Increased use of these materials is anticipated in the future^[1,2].

Thermal stability is one of the most important factors in determining the useful life of high performance composites. Investigation on their thermal decomposition kinetic process will be important for predicting their thermal stability. In this paper, we studied the thermal decomposition process of KH-304 resin and its carbon fiber composite by thermogravimetry (TG) in different atmosphere. Some basic data is provided for the realistic assessment of the use of KH-304 resin and its carbon fiber composite.

EXPERIMENTAL

1. Preparation of KH-304 Resin

The PMR consists of monomers which are polymerized in situ. The monomers used to prepare the PMR solutions are 5-norbornene-2,3-dicarboxylic acid monoethylester (NE), 3,3',4,4'-benzophenonetetracarboxylic acid diethylester (BTDE), and 4,4'-methylenedianiline (MDA). The mole ration of reactants NE:BTDE:MDA used for KH-304 is 2:2:3, which yields

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theoretically an oligomer whose formula weight is 1500. The reaction sequence for KH-304 resin is shown in Figure 1.

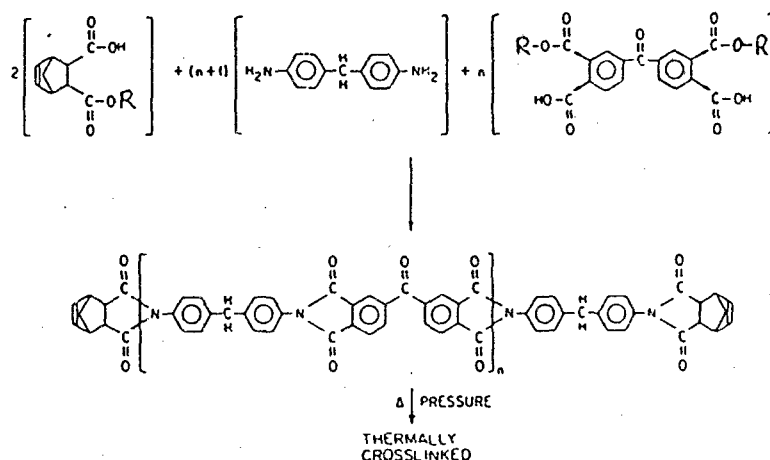


Figure 1. Reaction sequence for KH-304 resin

2. Composite Fabrication

The carbon fiber used in this study was Thornel 300 obtained commercially from Union Carbide Corp. The prepreg was prepared by drum winding the T300 yarn followed by brush application of a quantity of a 50 weight percent ethanol solution of resin components. The tapes were dried on the rotating drum at room temperature for some time, then removed from the drum, cut into small pieces and stacked unidirectionally for twelve plies. After these handling, they were inserted into autoclave and molded into laminate according to procedure discussed above.

3. Measurements of the Samples

The decomposition behaviours of KH-304 resin and the T300/KH-304 composite under different heating conditions were investigated separately in nitrogen and in air by using a Perkin-Elmer Thermogravimetric Analyzer TGS-2. The temperature range was specified in the range 40-950°C and the heating rates were 5, 10, 20, 40°C/min. All the samples were dehydrated in a vacuum oven at 120°C for 10 hours and were cut into small pieces for measurements.

RESULTS AND DISCUSSION

1. Thermal Decomposition Characteristics of KH-304 Resin and T300/KH-304 Composite

Composite

The thermogravimetric curves of KH-304 resin and the composite at a heating rate of 20°C/min in nitrogen and air are shown in Figure 2. Some of the thermal stability parameters of the two samples are listed in Table 1. Their thermal decomposition characteristics can be summarized as follows:

Both the KH-304 resin and the composite show no obvious weight loss at temperatures below 400°C, which indicate that both of them have very high thermal stability. However, for each sample, the thermal stability in nitrogen is better than that in air. On the other hand, it is very clear that in either nitrogen or air the composite begins to decompose at a higher temperature compared with pure resin under the same conditions. For example, in air, the temperature of 5% weight loss for the composite is 542°C, 85°C higher than that of pure resin.

There is also distinct difference in the temperatures at which the weight losses on the samples approach the maxima. In the air, the temperature of 100% weight loss for the resin is 776°C, while it is 946°C for the composite. However, in nitrogen, the weight loss at 950°C for the resin is 53%, while the weight loss at 950°C for the composite is only 15%.

Table 1. Comparison of thermal stability parameters of the two samples by TG

Samples	Atmosphere	5%Wt. loss(°C)	10% Wt. loss(°C)	Temp. at Max. wt. loss(°C)	Max. Wt. loss(%)	E (KJ/mol)
KH-304	N ₂	475	514	950	53	209
KH-304	Air	457	508	776	100	174
Composite	N ₂	563	638	950	15	234
Composite	Air	542	607	946	100	184

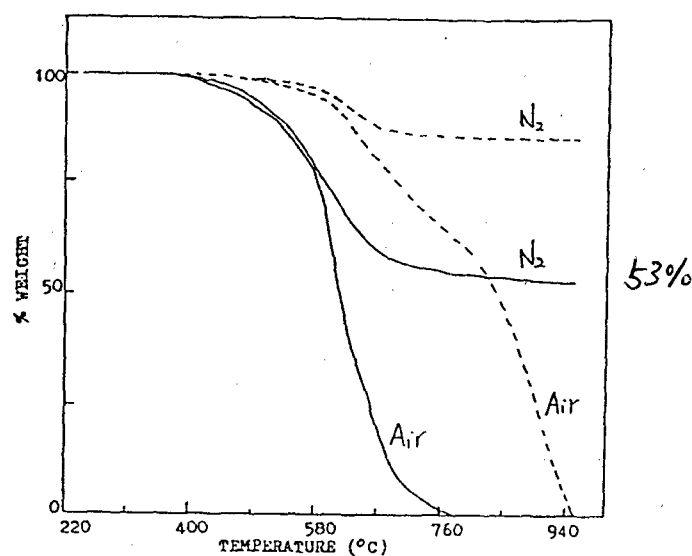


Figure 2. TG curves of KH-304 resin and T300/KH-304 composite at a heating rate of 20°C/min : — data for resin , ---- data for composite

2. Kinetics of Thermal decomposition

A mathematical calculation method for non-isothermal kinetics analysis, proposed by Ozawa, Flynn and Wall, and Doyle, was used to carry out the kinetics analysis from the experimental TG results^[3,4]. It has been observed that the following equation can be well fitted for the initial thermal decomposition process:

$$\text{Log}[\log(1-\alpha^{1/2})^{-1}] = \log(AE/2.3R\beta) - 2.315 - 0.457E/RT \quad (1)$$

Where E is the activation energy of decomposition, A is pre-exponential factors, R is the gas constant (8.314 Jmole⁻¹K⁻¹), T is the corresponding temperature at a constant weight loss, and β is the heating rate.

In this study, we took the data of temperature T at a constant weight loss from TG curves at different heating rates. According to the above equation, it was possible to plot $\log\beta$ against 1/T at several weight losses, thus the activation energy E can be calculated from the slope of the line. Figure 3 to Figure 7 show the Plot of $\log\beta$ Vs. 1/T for the two samples in different

atmosphere. For the four weight losses 2.5%, 5%, 10%, and 15%, each figure show a group of line nearly parallel to each other. The Values obtained from these figures are also given in Table 1. In nitrogen , the apparent activation energies of the PMR-15 resin and the composite are 209KJ/mol and 234KJ/mol respectively, While in air, they are 174KJ/mol and 184 KJ/mol correspondingly. The results obtained from kinetic analysis once again indicate that the thermal stabilities of either PMR -15 resin or T300/PMR-15 composite in nitrogen are better than those in air, and the thermal stability of the composite is better than that of the resin under the same experimental conditions.

ACKNOWLEDGEMENT

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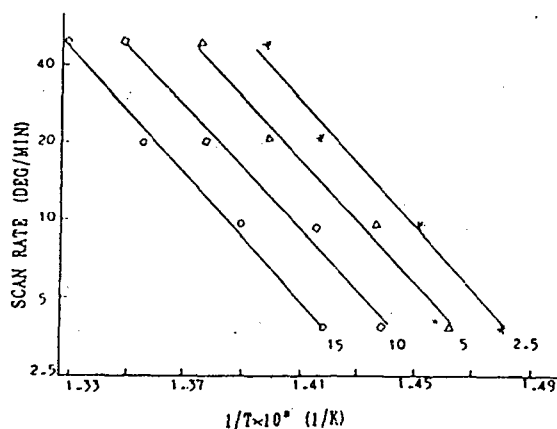


Figure3. Plot of $\log\beta$ vs. $1/T$ for resin in N_2

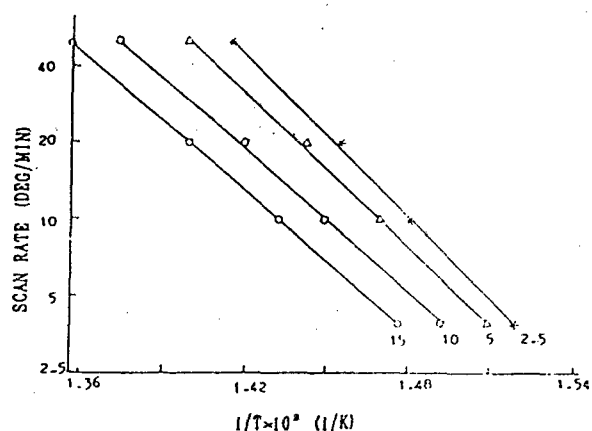


Figure 4. Polt of $\log\beta$ vs. $1/T$ for resin in air

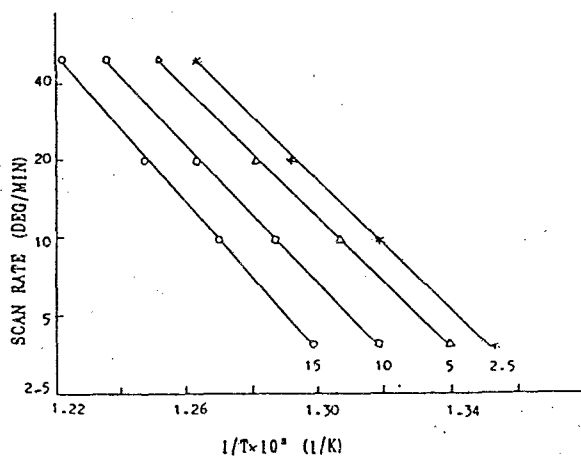


Figure 5. Plot of $\log \beta$ vs. $1/T$ for composite in N_2

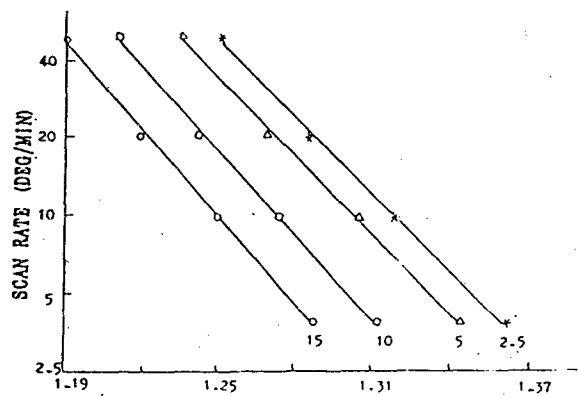


Figure 6. Plot of $\log \beta$ vs. $1/T$ for composite in air