

A KINETIC MODEL FOR THE CARBONIZATION OF PBO FIBER

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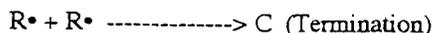
Introduction

Poly p-phenylenebenzobisoxazole (PBO), pictured in Figure 1, is the high-performance rigid-rod polymeric fiber produced by the Dow Chemical Company. Despite the exceptional tensile properties of the polymer, its use in composite reinforcement is limited by its comparatively poor compressive strength.

Carbon fibers offer an alternative to high-performance polymers. Commercial carbon fibers often possess an improved balance of properties, but the high cost of production limits their use. Much of this production expense is incurred during the stabilization process that converts the precursor fiber into a thermally stable form. Previous studies (1) have shown that PBO can be converted directly to carbon fiber without stabilization. However, for PBO to become a commercially viable precursor material, it is essential to develop an understanding of the conversion process.

Theoretical

In the current study, the free-radical reactions associated with the carbonization of PBO were modeled as a series of three reactions:



where P is a PBO molecule, $R\cdot$ is a free-radical containing molecular fragment, and C is a carbonized molecule.

The initiation reaction is induced by the thermal energy associated with carbonization temperatures. This energy strains the bonds between the atoms comprising the PBO molecule. The only bonds in the entire polymer backbone that are not stabilized by π -bonding are the carbon-oxygen and the carbon-nitrogen bonds between the bisoxazole rings and the phenylene carbons. The carbon-nitrogen σ -bond is the weaker of these bonds. In addition to the adjacent benzene ring which helps stabilize the free-radical formed by the breakage of this bond, the nitrogen is double bonded to the carbon in the oxazole ring. This also provides greater stability for the initial free-radical.

Determining the appropriate kinetic constants for the proposed initiation reaction is relatively straightforward. Because no external initiator is needed and the monomer pool is essentially infinite, the initiation reaction can be

assumed to be of zero-order. Thus,

$$v_I = k_I, \quad (1)$$

where v_I is the rate of the initiation reaction and k_I is the zero-order rate constant. Application of the Arrhenius equation allows equation (1) to be written as

$$v_I = k_{I0} \exp\left(-\frac{E_A}{RT}\right), \quad (2)$$

where k_{I0} is the pre-exponential Arrhenius constant, E_A is the activation energy of the initiation reaction, R is the gas constant and T is absolute temperature. The termination reaction can be represented by

$$v_T = k_T [R\cdot]^2. \quad (3)$$

An overall free-radical balance provides

$$\frac{d[R\cdot]}{dt} = k_{I0} \exp\left(-\frac{E_A}{RT}\right) - k_T [R\cdot]^2. \quad (4)$$

The unstable nature of free-radicals makes the activation energy for termination very small and, in fact, the energy is generally assumed to be zero (2). Thus, the termination rate constant has no temperature dependence.

The transient nature of free-radicals prevents $[R\cdot]$ from being measured directly. However, some boundary approximations can be made. At the onset of initiation, the concentration of free-radicals is small, so it can be assumed that the rate of initiation is much greater than the termination rate. Thus, a plot of $\frac{d[R\cdot]}{dt}$ versus T^{-1} would provide both the activation energy and the pre-exponential Arrhenius constant. The model assumes that the initiation rate of free-radicals is directly proportional to the observed mass loss during heating. If free-radical reactions serve as the primary mechanism of mass release, it is reasonable to assume that an increase in free-radicals would lead to a proportional increase in mass loss. Therefore, at initial times, equation (4) could be approximated by

$$K \frac{dM}{dt} = k_{I0} \exp\left(-\frac{E_A}{RT}\right), \quad (5)$$

where M is the sample mass, and K is a proportionality

constant. Initial mass loss data may be obtained from isothermal TGA trials at different temperatures.

If the termination reaction remained insignificant, the Arrhenius relationship would hold throughout the entire region of mass loss. However, as temperature increases and more free-radicals form, the termination reaction becomes increasingly significant, and the complete form of equation (4) applies.

$$\frac{dM}{dt} \approx \frac{1}{K} \frac{d[R^*]}{dt} = \frac{k_{i0}}{K} \exp\left(-\frac{E_A}{RT}\right) - \frac{k_T}{K} [R^*]^2 \quad (6)$$

or, alternatively,

$$v_T = \frac{k_{i0} \exp\left(-\frac{E_A}{RT}\right) - \frac{dM}{dt}}{K} \quad (7)$$

If equation (7) is valid, then the behavior of a ramped TGA trial can be predicted from the data obtained in the isothermal trials. In the early stages of mass loss, the initiation reaction should dominate, thus the termination rate should be very small. As temperature increases, the free radical concentration must increase and the termination reaction should become increasingly significant. Also, because temperature is a linear function of time in the ramped trial, the dt in equation (7) can be replaced by $\frac{1}{\alpha} dT$, where α is the linear heating rate. Thus, the right side of equation (7) can be written as a function of temperature only.

Experimental

TGA trials were performed in two different modes, ramped and isothermal. In the ramped mode, approximately two milligrams of PBO fibers were placed in the platinum balance pan of a Dupont model 951 TGA system. The fiber samples were heated under industrial grade argon at a linear rate from ambient temperature to 800°C. Temperature, time, and mass data were recorded at 0.1 second intervals by a TA2100 data compilation system.

In the isothermal mode, the TGA system was heated to the desired temperature before the fibers were placed in the heated zone. Once the system reached the set-point temperature, the balance pan was slid into the hot zone. Within seconds, the temperature of the fibers reached the hot zone temperature. The system maintained a constant temperature for the remainder of the experiment.

Results and Discussion

Figure 2 shows the results of the Arrhenius regression of the isothermal TGA data. The regression determined an activation energy of 76 kcal/mol for the free-radical initiation. Figure 3 shows the termination rate as a function of temperature. As expected, the termination rate was

insignificant at low temperatures, but became increasingly important as temperature increased. This supports the fundamental assumption of this model. Figure 3 also indicates that data obtained from isothermal trials can be applied to ramped trials. Ultimately, this technique demonstrated that the carbonization of PBO fibers can be modeled as a free-radical polymerization. Additionally, insight into the nature of the chemical changes occurring in PBO fibers during carbonization can be gained.

References

1. Newell, J. A., D. K. Rogers, D. D. Edie, and C. C. Fain, *Carbon* 32(4), 651 (1994).
2. Kochi, J. K., *Free Radicals*, Wiley and Sons, NY (1973).

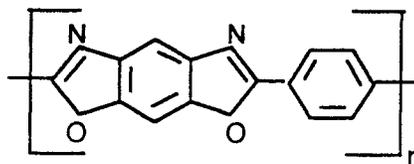


Figure 1. The Repeat Unit of PBO

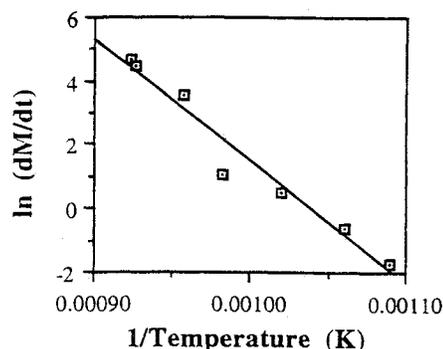


Figure 2. Arrhenius Regression of TGA Data

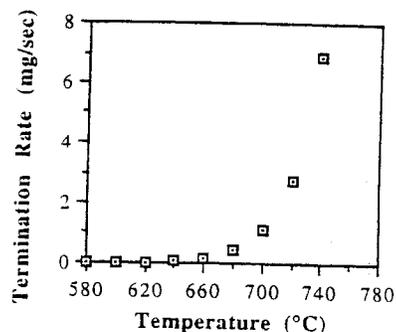


Figure 3. Temperature Dependence of Termination Reaction Rate