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The Kinetics of Oxidation Curing of Polycarbosilane Fibers

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Abstract−For the oxidation curing of polycarbosilane (PCS) fibers in air, a first-order reaction based on the weight gain w (in percentage) was approached with the kinetic equation $dw/dt=k(w_m-w)$. The maximum weight gain w_m was observed to be 16% under normal oxidation conditions and the activation energy E to be 79.27 kJ/mol. The numeric integration based on the kinetics provides a precise prediction of the curing degree of PCS fibers under various heating programs and conditions.

Key words: Polycarbosilane Fiber, Oxidation Curing, Kinetics

INTRODUCTION

Oxidation at elevated temperature is a common reaction in organic polymers. Most of the reaction leads to a deterioration of the properties of the polymer materials. But the reactions for some polymers are expected, for example, in the preparations of carbon fiber and silicon carbide fibers from preceramic polymers such as polyacrylonitrile [Grassie and Moguchan, 1972; Bahl and Manocha, 1975] and polycarbosilanes (PCS) [Yajima et al., 1976; Ishikawa et al., 1998], respectively. In these cases, the oxidation reaction is the critical step of curing or crosslinking that ensures the fibers are infusible under pyrolysis as the next step. Actually, the oxidation curing is a widely used method for many preceramic polymers to enhance the ceramic yield not only for making fibers [Kang and Yang, 1998].

As an example, curing of the PCS fiber in air at 150-250 °C enables the fibers to retain the shape and restrains the loss of small organic volatiles during pyrolysis [Yajima et al., 1976]. The curing, or oxidation reaction, takes place mostly in the Si-H bond as well as some of the C-H bonds in PCS and results in crosslinking of the polymer chains from the surface to the very inner part of the fibers. In the curing process for preparation of continuous SiC fibers, controlling the exact mount of oxygen in fiber and shortening the curing time are very important. At this point, attention was given to the curing kinetics and the theoretical prediction of the curing degree of PCS fiber.

Herman et al. [1991] studied the curing kinetics of PCS fiber focused on the thermal behavior using DSC and TG analysis. Shimoo et al. [1992] and Filipuzzi and Naslain [1992] investigated the oxidation kinetics of SiC fibers at high temperature based on fibers' weight gain. Since the weight gain is, for PCS fibers, the most useful and measurable data characteristic of the reaction degree, the amount of oxygen and the crosslinking structure, the kinetics based on weight gain, instead of the thermal behavior, was studied in this work by employing a standing style furnace designed our own. The resulted kinetics was tested in various curing facilities and conditions.

EXPERIMENTAL DETAILS

1. Preparation of PCS Fiber

The PCS fibers used in this study were prepared generally according to Yajima's route (i.e., by thermal decomposition and rearrangement of polydimethylsilane at high temperature [Yajima et al., 1976], followed by melt spinning). In all the experiments here, three kinds of PCS fibers, labeled F1, F2 and F3, were used. The number-average molecular weights of PCS of F1, F2 and F3 are 1697, 1290 and 1120 (GPC Waters-244) and the melting points are 210 °C, 195 °C and 180 °C, respectively.

2. Isothermal Curing [Wang et al., 2003]

Certain amount of F1 was hung in a quartz tube with a constant air flow; a standing style furnace (Fig. 1) with a pre-set temperature was lifted to the right place by hydraulic pressure lifter to ensure the fibers cured at a constant temperature through all the process (150 min). The mass change was recorded on-line with the precise scale (precision: 0.001 g) on the top.

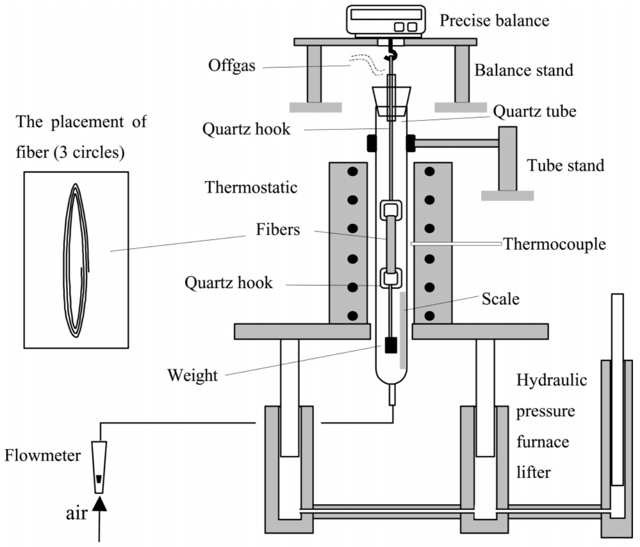

Fig. 1. The equipment measuring the weight changes of PCS fibers in curing process.

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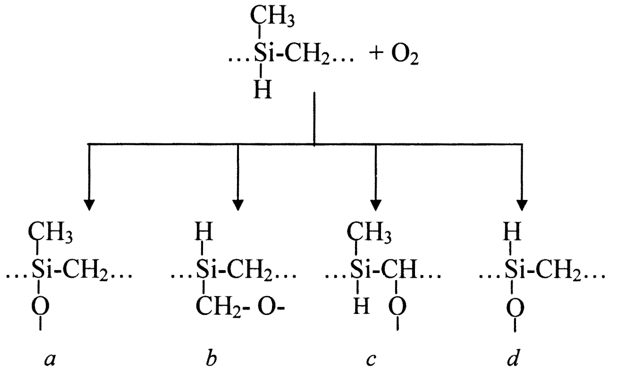
3. Curing with Various Heating Programs

F1, F2 and F3 were treated with different heating programs in three different furnaces. F1 was cured in the furnace of Fig. 1 and weight gain was recorded on-line with the precise scale. F2 and F3 were cured in a normal oven and a horizontal tube furnace, respectively, and the weight gains were measured by weighing the input and output fibers.

RESULTS AND DISCUSSION

Curing in air at elevated temperature is a gas-solid reaction, which can take place at various groups of PCS and can result into four oxidized groups (*a*, *b*, *c*, *d*) as shown by the following scheme.



The oxidation product can then be the combination of any two oxidized groups with -Si-O-Si-, -Si-C-O-Si- or -Si-C-O-Si-O-C-Si- structures, which are generally accordant identical with the NMR results reported by Taki et al. [1991] and Hasegawa [1989]. Since Si-H is the most reactive group, the combination *a*-*a* is the main product with Si-O-Si structure. It is well known that the repeat structure of PCS is somewhat far from the ideal formula [CH_3SiH-CH_2] and the true amount of Si-H is much lower than the expected value [Livage et al., 1998]. However, even according to the ideal PCS formula and all the Si-H bonds in fibers oxidized, the expected weight gain is only 12%, significantly lower than the experimental values (see below). Therefore, the reactions *b* and *c* should be counted even if they are less important. The reaction *d* is the replacing of a methyl to an oxygen and is not significant for weight gain. As evidence, the infrared spectra demonstrate, in Fig. 2, that of the number of groups of Si-CH_3 (1,250 cm^{-1}) and Si-CH_2-Si- (1,400 cm^{-1}) in PCS fibers decrease accompanied with the sharp shrinkage of that of Si-H (2,100 cm^{-1}) after oxidation. According to the many experimental results of this research (Fig. 3, Fig. 5, Fig. 6, Fig. 7, Fig. 8) and the data reported by Herman et al. [1991], the maximum weight gain w_m of PCS fiber is 16% under normal curing conditions (in air at moderate temperature).

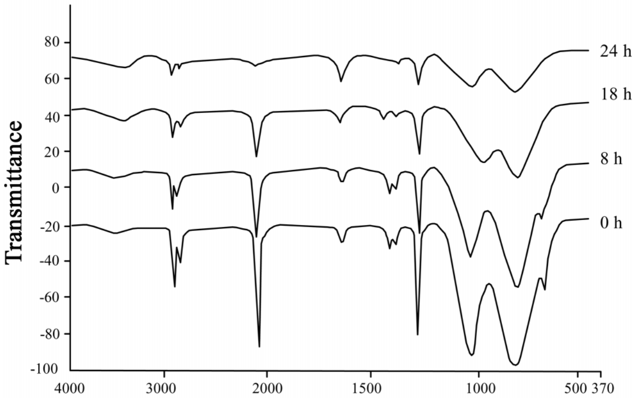


Fig. 2. IR spectrum of F1 cured for different time from 100 °C to 200 °C with a constant heating rate.

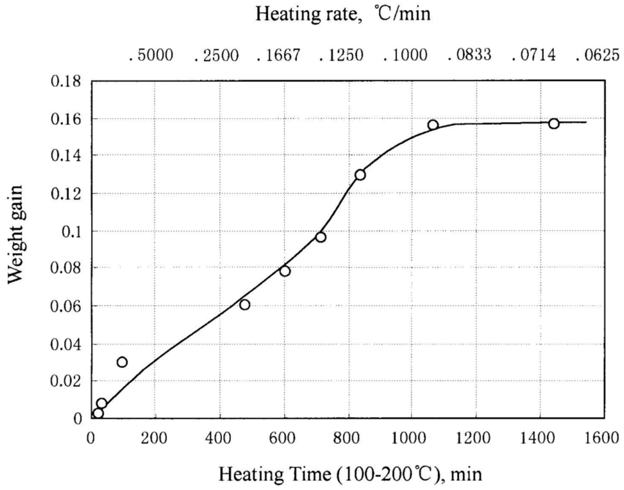


Fig. 3. The relationship between the weight gain and heating time for F1 (curing starts at 100 °C and ends at 200 °C with a constant heating rate).

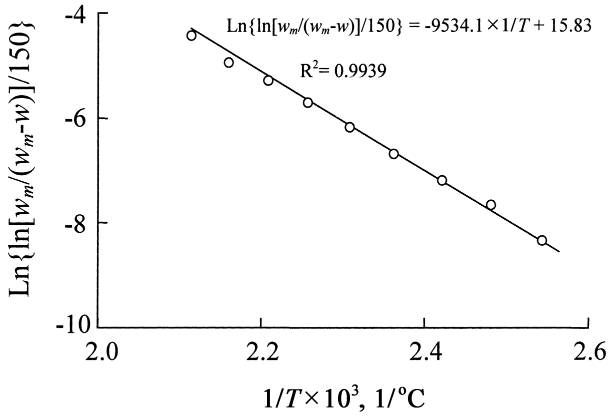


Fig. 4. The relationship between ln{ln[w_m/(w_m−w)]/150} and 1/*T* under isothermal curing of F1.

In order to find the kinetic model as a function of weight gain (*w*) versus temperature (*T*) and curing time (*t*), the other factors, such as air flow, the amount of fiber were fixed. A first-order reaction kinetics, Eq. (1), was established, which is basically similar to the simple form of a general conversion-dependence kinetics [Nam and Seferis, 1992].

$$dw/dt=k\cdot(w_m-w) \qquad (1)$$

Where *w* is weight gain in percentage of PCS fiber after curing time *t*, w_m is the maximum weight gain after infinite curing time and *k* is apparent reaction rate constant.

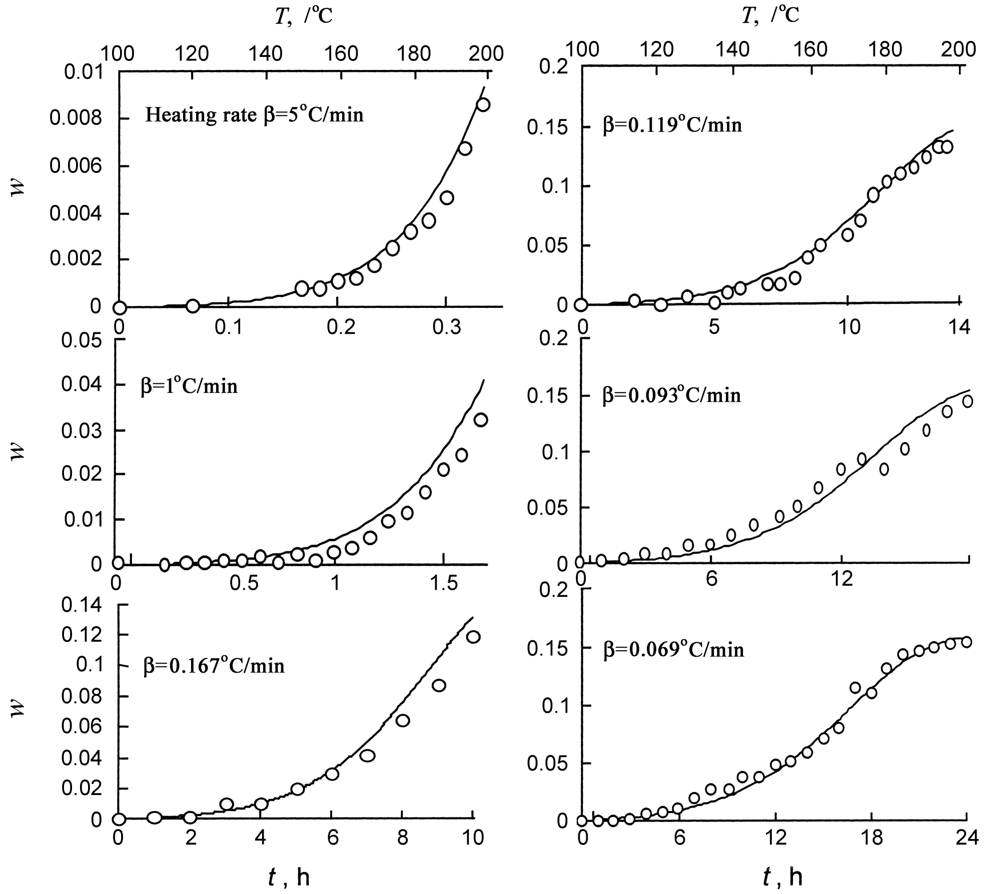


Fig. 5. The simulated (line) and observed (dot) weight gain of F1 cured under constant heating rates, *β*, from 100 to 200 °C.

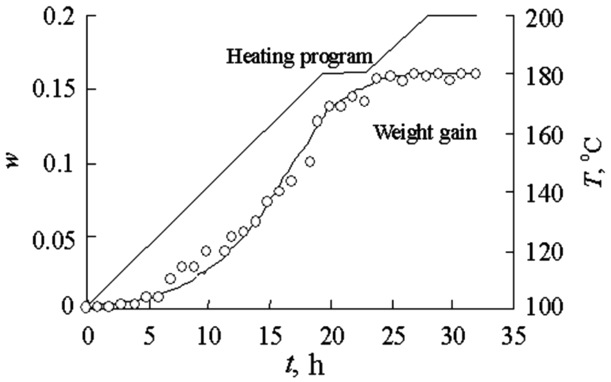


Fig. 6. The simulated (line) and observed (dot) weight gain of F1 cured through a heating program.

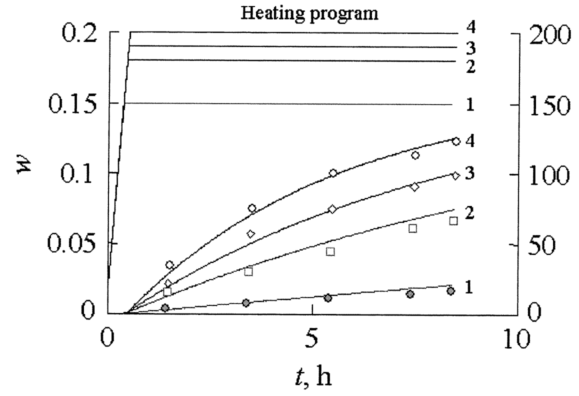


Fig. 7. The simulated (line) and observed (dot) weight gain of F2 cured through four heating programs.

Since the practical curing process is generally carried out from room temperature to about 200 °C with a preset heating program, *k* must be expressed as an Arrhenius equation. Thus a general form of the integrated kinetic equation is obtained:

$$w = w_m \cdot \{1 - \exp[-\int_0^t A \cdot \exp[-E/(R \cdot T(t))]dt]\} \qquad (2)$$

The right side of Eq. (2) contains an integral that generally cannot be integrable except for the isothermal process; numeric integration has to be adopted. In this process, one divided the curing time into small intervals. In the time range $t_i \sim t_i + \Delta t$, the corresponding temperature T_i is approximately written as the average of $T(t_i)$ and $T(t_i + \Delta t)$. Thus the weight gain can be calculated by Eq. (3) with Δt small enough.

$$w = w_m \cdot \left\{1 - \exp\left[-A \cdot \lim_{\Delta t \to 0} \Delta t \cdot \sum_{i=1}^{n} \exp(-E/(R \cdot T_i))\right]\right\} \qquad (3)$$

1. Isothermal Curing

To establish the activation energy, *E*, and the pre-exponential fac-

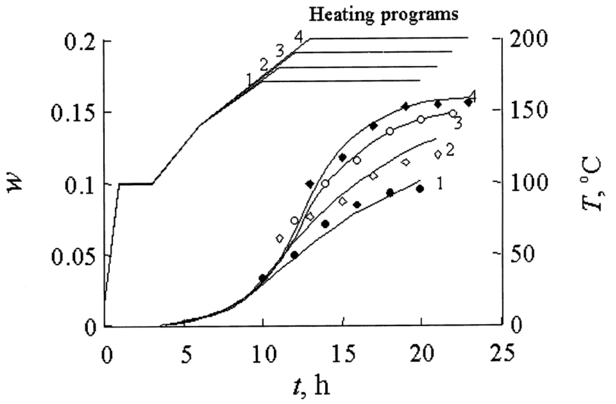


Fig. 8. The simulated (line) and observed (dot) weight gain of F3 cured through four multi-stage heating programs.

tor, A, isothermal curing of F1 was carried out with the equipment shown in Fig. 1 with fixed curing time (t=150 min). The process of fiber weight gain at different temperatures was treated by Eq. (4), which is the integrated form of Eq. (2) in which the function $T(t)$ is a constant.

$$\ln\frac{\ln\frac{w_m}{w_m-w}}{t}=\ln A-\frac{E}{RT} \tag{4}$$

The straight line is shown on Fig. 4, from which E and A of this condition were found to be 79.27 kJ/mol and 7.50×10^6, respectively. The E should always be a constant for the particular oxidation reaction, while A is strongly dependent on various conditions and environments, such as air flow, the amount of fibers and so on.

2. Curing with Various Heating Programs

2-1. Curing Process with Fixed Heating Rates

These processes were also carried out with the equipment shown in Fig. 1 and F1 was used. The fibers' weight gain processes at different heating rates were simulated with Eq. (3) with E and A values as obtained above. The results are shown in Fig. 5, from which one found that the simulation curves fit the observed results quite well.

2-2. Actual Curing Process

Three different furnaces were used for F1, F2 and F3. Air flow and amount of fibers are also different from each other. The simulations were performed by using Eq. (3) with E=79.27 kJ/mol as mentioned above, and different A values: 7.50×10^6, 1.80×10^6, and 3.00×10^6 for F1, F2 and F3, respectively. These A values were determined by simulation fitting.

The comparisons of observed and predicted weight gains from the multi-stage temperature programs are shown in Fig. 6, Fig. 7 and Fig. 8. The results of fitting imply the credibility of the kinetic model for any different curing conditions.

CONCLUSIONS

In this study, the synthesized PCS precursors with different molecular weight were melting spun to PCS fibers by Yajima route. The oxidation mechanism of the achieved PCS fibers was performed in air, and the Si-H, Si-CH_3 and Si-CH_2 bonds contributed to the weight gain of the PCS fiber's during oxidation curing. It was found that the maximum weight gain, w_m, was 16% under experimental conditions and the PCS fiber's oxidation curing in air is a first-order reaction related with the weight gain w. The kinetic equation of the oxidation curing, $dw/dt=k(w_m-w)$, with the active energy of about 79.27 kJ/mol, can be satisfactorily applied to actual curing process for the prediction of PCS fibers' curing degree under different heating programs.

ACKNOWLEDGMENT

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