Short- and long-term degradation of polymer-based composites [1]

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Abstract

The thermal stability of high-performance thermoplastic matrix composites is studied by thermogravimetric analysis. The study is focused on the degradation behavior, under different environments, of continuous carbon-fiber-reinforced composites with poly(ether-ether ketone) (PEEK) matrix. The experimental results are analyzed by two different methods. In one method a phenomenological kinetic model is developed and compared with the degradation behavior measured in isothermal and constant heating conditions. In the second method, a simple correlation is presented to describe the onset of the degradation at long times and under normal service conditions. Both approaches give similar results and confirm the good thermal stability of PEEK matrix/carbon fiber composites at high service temperatures.

INTRODUCTION

Because of their good thermal stability, polymer matrix composites are considered as possible materials for supersonic aeronautic applications in which the normal service temperatures are relatively high. This new application requires a reliable prediction of the long-term behavior of such materials. In particular the interest of the designer is focused on the performances of the material after long periods at elevated temperatures.

The characterization of the behavior of a composite that is utilized under critical temperature conditions, implies a knowledge of the exact degradation kinetics of the matrix which is related either to irreversible morphology changes or to chemical decomposition reactions. The degradation of polymeric composites has been studied mainly with respect to the reprocessability of thermoplastics after several cycles [1–3]. For example,

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poly(ether-ether ketone) (PEEK) changes its attitude to crystallization if it is repeatedly heated up to 400°C, indicating physical degradation. The weight loss occurring in a polymer that is kept at high temperatures for a certain period of time is considered another index of degradation. Such a weight loss can be attributed to evaporation of solvents and/or plasticizers or to chain decomposition. Moreover [4–6], the mechanisms of the degradation are functions of the polymer structure and can follow different steps because of the complexity of the polymeric chains. Functional group transfer, chain unzipping with elimination of volatiles, and formation of intermediate compounds, are the main decomposition mechanisms that complicate the development of a mechanistic kinetic model of the polymer degradation process. In particular, reported data on PEEK degradation have indicated benzoquinone as the first gaseous product of the chain-breaking reaction, followed by the rearranging of the polymer chain [6, 7].

The effect of the environment is very important in polymer degradation. Thermal oxidation, for example, is one of the major causes of polymer degradation. The presence of oxygen as reactant, combined with heat, causes very rapid degradation processes in polymeric chains. Therefore, it is very important to fix the environmental conditions when decomposition kinetics were studied.

In the particular case of polymer-based composite degradations, the presence of the carbon fibers has also to be taken into account. Carbon fibers can affect the degradation process and themselves degrade in the presence of oxygen. Furthermore, in the presence of degradation reactions where diffusion in the bulk is the controlling step, the presence of carbon fibers can significantly affect the overall process.

Thermogravimetry (TG) is commonly used to study the degradation of polymeric materials [8]. With this technique, the weight loss is measured as a function of time and temperature. In this way, the degradation kinetics can be studied by correlating the weight loss with the degree of reaction [9, 10]. Although TG data on degradation kinetics can be misinterpreted, because of the complexity of the degradation process, important information about the behavior of a polymer can be gained from TG experiments [4, 11, 12].

When long-term data are needed, the main experimental problem is the duration of the test. Then, accelerated degradation at high temperatures can be performed and the long-term behavior at lower temperatures can be extrapolated from the observed short-term behavior. This procedure can be applied, under particular restrictions, by assuming a simplified degradation process [9].

In this work, the results of several TG tests are used to develop two different methods to extrapolate the degradation behavior of PEEK matrix/carbon fiber composites for long-term application. In the first

method, an "autocatalytic" model is developed, and in the second, a simple correlation between the isothermal degradation temperature and the time to reach a small weight loss (<2%) is constructed. The study includes the effect of two different environments: nitrogen and air.

EXPERIMENTS AND MATERIALS

Degradation tests were performed on APC2 (ICI) thermoplastic matrix composites reinforced with AS4 carbon fibers. The polymeric matrix (poly(ether-ether ketone) (PEEK)) is a semicrystalline thermoplastic polymer that has been specially developed for high-performance composites [13]. It has a T_g of 147°C and a processing temperature of 400°C.

TG experiments were performed using a Du Pont 911 thermogravimetric analyzer; the test were performed in isothermal and dynamic modes at different temperatures and heating rates in order to cover a wide range of thermal conditions. Data obtained from TG experiments were dumped in ASCII format and analyzed using a computer program. TG tests were performed in both air and nitrogen.

RESULTS AND DISCUSSION

The results of several thermogravimetric tests performed on the PEEK matrix composite at different constant heating rates, in air and nitrogen environments, are reported in Figs. 1 and 2 respectively, in terms of the percentage weight loss as a function of time. The effect of the heating rate on the degradation kinetics is manifested in the shift of the curves of Fig. 2: higher heating-rate curves are shifted to higher degradation temperatures. This effect is mainly dependent on the activation energy of the degradation
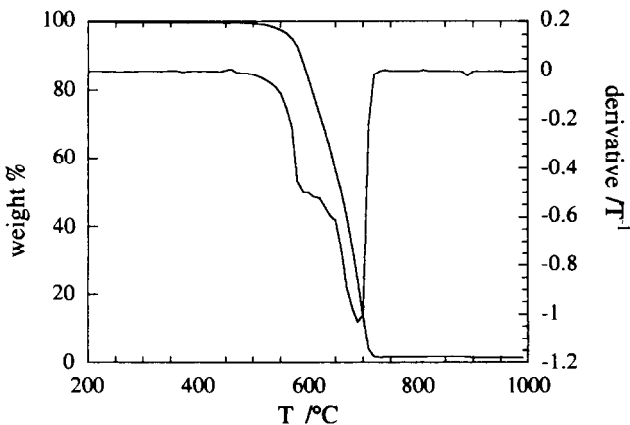

Fig. 1. Weight loss and its derivative as a function of temperature for a dynamic test in air at 10°C min^{-1}.
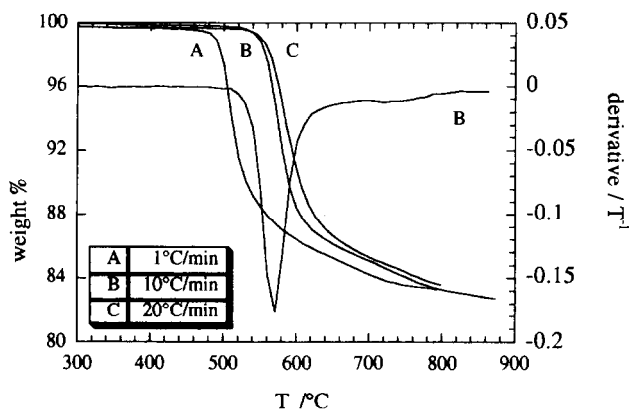
Fig. 2. Weight loss as a function of temperature for dynamic tests in nitrogen at different heating rates. The derivative is also reported for the test at 10°C min^{-1}.

process, as explained below. The second observation regards the evident difference between tests performed in nitrogen and air. A complete degradation of the material is achieved in air while only the matrix is degraded in a carbonization process when working in nitrogen. This difference is also manifested in the derivative curves, also shown in Figs. 1 and 2. A single peak characterizes the degradation reaction under nitrogen, but a double peak is associated with the process in oxygen. In the second case, the first peak is located in the same temperature range and with the same weight loss as that observed in nitrogen, and can be attributed to the matrix degradation, but the second peak is readily attributed to the oxidation of the carbon fibers and the carbon structure of the degraded matrix. Apart from this, no other differences are observed when working in different environments. A similar weight loss and temperature degradation interval characterizes the degradation of the matrix in both cases, suggesting that the degradation of the matrix is mainly by thermally controlled dehydrogenation, without a significant influence of the oxidation processes on the reaction yield. However, the similarities between matrix degradation in nitrogen and air are only qualitative, and a careful kinetic analysis should be performed to characterize fully the degradation behavior. The analysis will be facilitated when performed on the single peak reaction obtained for nitrogen environment tests.

While the dynamic test results shown in Figs. 1 and 2 give useful information on the temperature interval and total weight loss associated with the degradation reactions, isothermal test results are needed for kinetic analysis in order to decouple the contribution of temperature. These results are shown in Figs. 3 and 4 for different test temperatures. By simple inspection of the weight loss results it is now evident that the degradation process in air (Fig. 3) is faster than in nitrogen (Fig. 4). The derivatives of the thermogravimetric results are reported in Figs. 5 and 6 respectively.
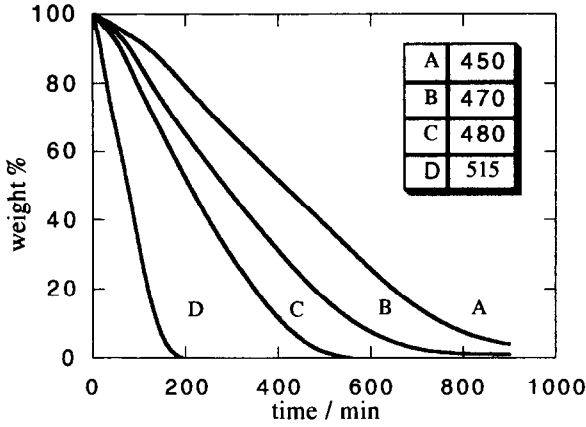
Fig. 3. Weight loss as a function of time during isothermal tests in air at different temperatures.
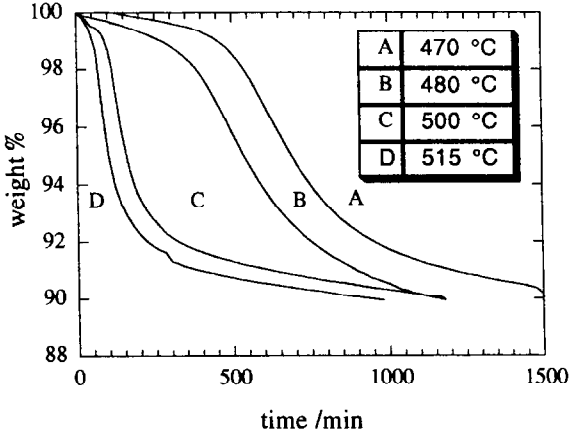

Fig. 4. Weight loss as a function of time during isothermal tests in nitrogen at different temperatures.
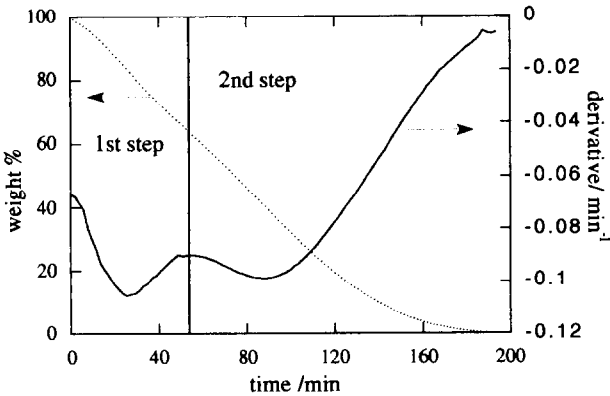

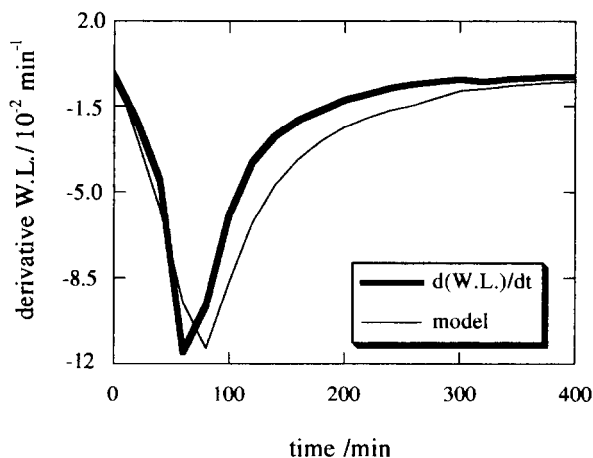Fig. 5. Reaction steps during an isothermal test in air at 515°C.

Fig. 6. Comparison between the model and experimental data for the derivative of the weight loss in an isothermal test at 515°C in nitrogen.

Again, a double peak is shown in the thermogram obtained in air (Fig. 5), confirming the presence of two different degradation processes, while only peak characterizes the thermogram obtained in nitrogen (Fig. 6).

The high thermal stability of the PEEK matrix composite is reflected in the long period of time required to complete the degradation in nitrogen atmosphere. A typical experiment performed near 500°C lasts for about 24 h; thus, it is practically impossible to perform experiments under controlled conditions in the region of interest (10–250°C). Therefore, other procedures must be followed in order to predict the long-term behavior of these materials under service conditions. The first approach analyzed in this research, was the development of a kinetic model to predict the weight loss as a function of exposure time and temperature. In order to correlate the TG experimental data with a kinetic expression, the degree of conversion can be defined as

$$\alpha = (M_0 - M)/(M_0 - M_f) \tag{1}$$

where M, M_0 and M_f are the actual, initial and final sample weights, respectively. A kinetic model can be commonly expressed [4] in the general form

$$d\alpha/dt = K(T)f(\alpha) \tag{2}$$

where the temperature dependence of the kinetic constant can be expressed with an Arrhenius expression

$$K = K_0 \exp(-E/RT) \tag{3}$$

where E is the activation energy. The form of the function $f(\alpha)$ depends on the form of the isothermal TG thermogram. Several kinetic models could

fit the form of the derivative curves of Figs. 5 and 6 [14], including a polynomial expression. However, following the results obtained on the kinetics of thermoset polymerization in isothermal and dynamic conditions [15], the autocatalytic model is proposed here to analyze the degradation process of PEEK

$$d\alpha/dt = K(T)\alpha^m(1 - \alpha)^n \tag{4}$$

where m and n are reaction orders. In agreement with the experimental results of Fig. 6, eqn. (4) predicts zero reaction rate at both ends of the process ($\alpha = 0$ and $\alpha = 1$). Several methods are reported in the literature to calculate the kinetic parameters of eqns. (3) and (4) [16–18]. In this work, a multiple non-linear regression analysis of the isothermal and dynamic results was performed using a statistical software package (Systat). The values of the model parameters obtained are: $\ln(K_0) = 34.53 \ln(min^{-1})$; $E = 241.106 \, kJ \, mol^{-1}$; $m = 0.8$; $n = 1.8$. A general agreement between predictions of the developed model and experimental results is observed in Figs. 6, 7 and 8. The comparison shown in Fig. 6 corresponds to the derivative of the isothermal TG thermogram, which is directly proportional to the reaction rate, while the results of Fig. 7 are expressed in terms of the degree of degradation α as a function of time for the different temperatures tested. Finally, the comparison of model and experimental results for two dynamic tests performed at different heating rates is shown in Fig. 9. Although a general agreement was obtained, in particular for the onset and for the first part of the degradation process, some discrepancies are observed in the last part. These differences can be attributed to complex degradation mechanisms that are oversimplified when represented by a simple model such as eqn. (4). However, for durability studies over long periods of time and at lower temperatures, the model developed is useful for determining the onset of degradation.
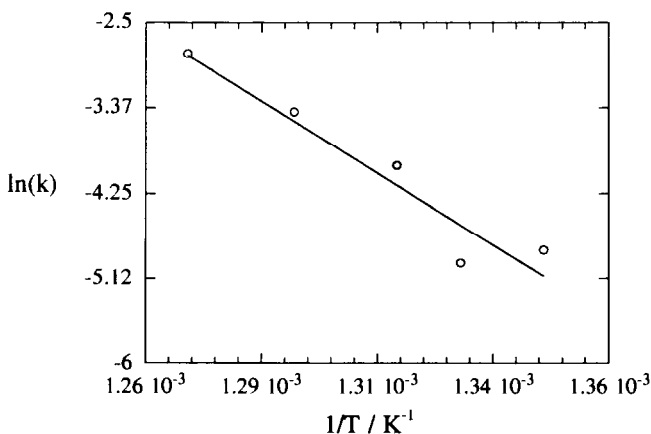

Fig. 7. Reaction rate as a function of the isothermal test temperature.
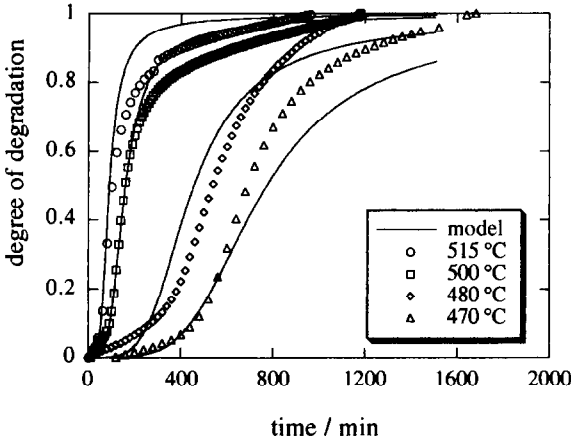
Fig. 8. Comparison between model results and experimental data for isothermal degradation at several test temperatures.

A second and faster engineering approach to the study of the long-term degradability of these materials is now described. In practice, a weight loss of 1% or 2% is considered a limit for the good functioning of the material. Therefore, it is not necessary to consider the whole degradation process. According to this assumption, a correlation between the time required to reach a weight loss of 1% or 2% and the temperature at which the test is performed must be developed. If such a correlation is valid, the time necessary to reach the limit of 2% weight loss in the polymer at any temperature can be extrapolated. Considering only a small weight loss, it can be proved that, following the eqn. (4) model, the time to reach a fixed
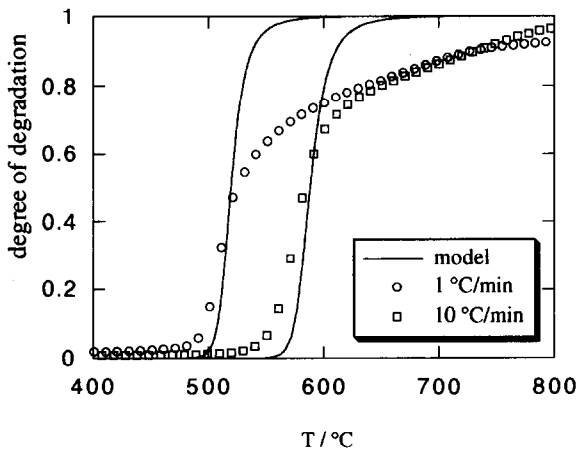

Fig. 9. Comparison between model results and experimental data for dynamic degradation at two different heating rates.
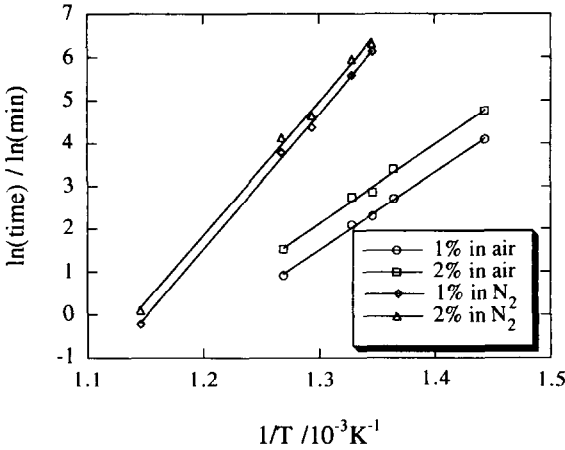
Fig. 10. Time required to achieve 1% and 2% of material degradation as a function of test temperature in air and in nitrogen.

weight loss at constant temperature is given by

$$t = \alpha^{(1-m)}/(1 - m) \exp(E/RT) \qquad (5)$$

Then, plotting $\ln(t)$ against $1/T$, the temperature values must lie on a straight line as shown in Fig. 9 for both levels of weight loss (1% and 2%) and for degradation in air and nitrogen. It can be seen that the experimental data for the two different weight losses lie on parallel lines. Indeed, the lines obtained in Fig. 10 by simple linear regression of experimental data are coincident with the linear behavior obtained by application of the eqn. (5) model. Therefore, by applying the hypothesis of small weight loss, it is possible to extrapolate to long-term behavior at lower temperatures from short-term data, as shown in Fig. 11. It has to be pointed out that this kind
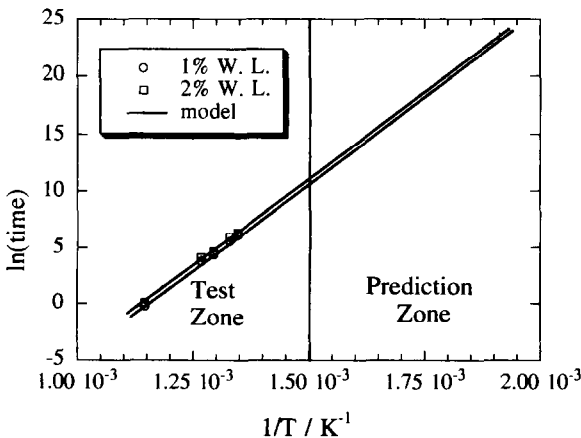

Fig. 11. Extrapolation of the long-term degradation results to service temperatures.

of analysis is an engineering approximation; therefore it will be more reliable the closer to the test temperature the prediction is made. The values obtained for PEEK in both air and nitrogen confirmed the good thermal stability of PEEK: at temperatures around the T_g the PEEK, the time necessary to reach a weight loss of 1% or 2% is almost infinite.

CONCLUSIONS

The thermal degradation of PEEK has been investigated using thermogravimetric analysis. A phenomenological kinetic model was developed to study the degradation kinetics of PEEK composites. The model was able to represent well the first part of the degradation process, while some discrepancies between the model and the experimental data were observed during the final part of the degradation. A simplified method to extrapolate long-term behavior at service temperatures gave reasonable results and was in agreement with the kinetic model. PEEK-based composites confirmed their good thermal stability in both air and nitrogen atmospheres.

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