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Kinetics of the thermal degradation of poly(phenylene sulfide) [1]

M. Day and D.R. Budgell [2]

Institute for Environmental Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Ontario K1A 0R6 (Canada)

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Abstract

The thermal degradation behaviour of two commercial samples of poly(phenylene sulfide) (PPS), Ryton P-4 and Fortron 0205B4, has been examined by both dynamic and isothermal thermogravimetric analysis. The kinetic parameters, i.e. the pre-exponential term, $\log A$, and the apparent activation energy E have been determined by applying the Kissinger and Ozawa–Flynn methods to the dynamic heating rate data, together with the values derived from the isothermal experiments using initial reaction rate data and using the whole data analysed by reduced-time-plots. The E values determined for the Ryton sample using these analyses were found to be 162, 183, 166 and 179 kJ mol^{-1} respectively. The Fortron sample gave the values 178, 169, 145 and 147 kJ mol^{-1}. Application of lifetime estimates to the kinetic data yields 10-year maximum temperature values of between 198 and 235°C and between 180 and 222°C for the Ryton and Fortron samples respectively. Lower values were obtained from the isothermal data which may reflect a thermal lag effect upon introduction of the samples.

INTRODUCTION

The increasing use of thermoplastic materials has necessitated a knowledge of their behaviour in the environments that they might encounter during processing and application. Unless the kinetics of the degradation mechanism for a material are known, overly severe conditions might be applied which reduce the integrity of the matrix and lead to premature failure.

Correspondence to: M. Day, Institute for Environmental Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Ontario K1A 0R6, Canada.

Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

[1] Issued as NRCC #32960.

[2] Present address: Enka AG, Werk Obernburg, D-8753 Obernburg, Germany.

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Previous work on the crystallization behaviour of poly(phenylene sulfide) (PPS) suggested that when PPS is held only a few degrees above its equilibrium melt temperature (the melting temperature of a perfect, infinite crystal), thermally induced degradation might affect its ability to crystallize [1]. A more extensive examination of the thermal stability of PPS is therefore of interest. This study deals with an assessment of the thermal stability and degradation kinetics of PPS in a nitrogen atmosphere by the use of thermogravimetry (TG) employing both isothermal and non-isothermal techniques.

In the TG experiments, the rate of weight loss ($d\alpha/dt$) is described by the equation

$$d\alpha/dt = kf(\alpha) \tag{1}$$

where $f(\alpha)$ is the conversional factor and k is the rate constant.

While TG provides information on only the global kinetics of $d\alpha/dt$, valuable information can be obtained from this method, particularly when both isothermal and dynamic methodologies are employed.

EXPERIMENTAL

The PPS samples employed were Ryton P-4 (Philips Petroleum) and Fortron 0205B4 (Hoechst-Celanese). The Fortron sample is believed to possess less chain-branching than the Ryton sample [2,3]: this belief is supported by crystallization studies of the two products [1].

TG measurements were made on a DuPont Model 951 TG connected to a DuPont 2100 Thermal Analyzer. The sample holder was an open-pan arrangement; to minimize sample size effects, sample masses were all 14.45 ± 0.1 mg. The nitrogen flow rate was 50 ml min^{-1}.

For dynamic TG experiments, heating rates from 0.03 to 50°C min^{-1} were employed. For the isothermal experiments, programmed temperatures between 370 and 425°C were used.

RESULTS AND DISCUSSION

Typical curves for dynamic TG and derivative thermogravimetry (DTG) are shown in Fig. 1 for both the Ryton and Fortron samples heated at 1°C min^{-1}. The presence of a single peak in the DTG curves suggests that weight loss occurs in a single stage. Weight loss begins at approximately 380°C and has its maximum rate at 492°C; above 550°C there is only a gradual reduction in mass. When other heating rates were used, it was found that the temperature at which the maximum rate of weight loss occurred was sensitive to this parameter. Figure 2 shows the DTG curves for samples of Fortron at varying heating rates from 0.03 to 5.0°C min^{-1}. As the heating rate is increased, the peak maximum decreases in intensity

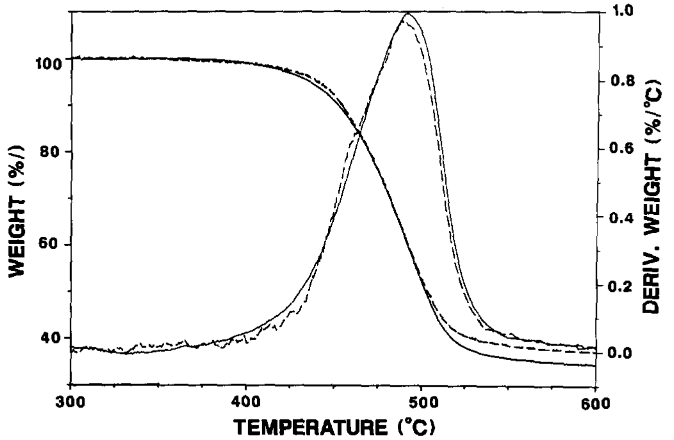

Fig. 1. Weight loss and derivative weight losses for Fortron (-) and Ryton (– – –) samples heated at 1.0°C min^{-1}.

but moves to higher temperature. The DTG curves are plotted with respect to temperature ($d\alpha/dT$) rather than with respect to time ($d\alpha/dt$) because the heating rate acts as a normalization factor and allows a comparison to be made with the theoretical curves developed by Flynn [4]; the curves are found to correspond to those predicted for a first-order weight loss mechanism.

Although a variety of methodologies have been developed and debated to analyse the kinetic degradation behaviour [5–12], two have found common usage for kinetic analysis: the Kissinger method [9] and the Ozawa–Flynn–Wall method [10,11].

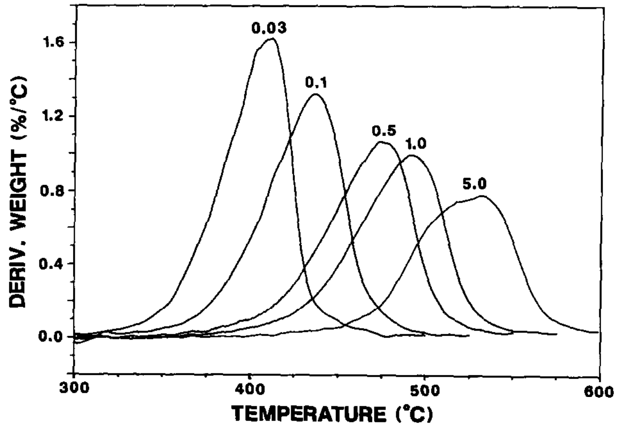

Fig. 2. DTG curves for Fortron samples heated at rates from 0.03°C min^{-1} to 5°C min^{-1}.

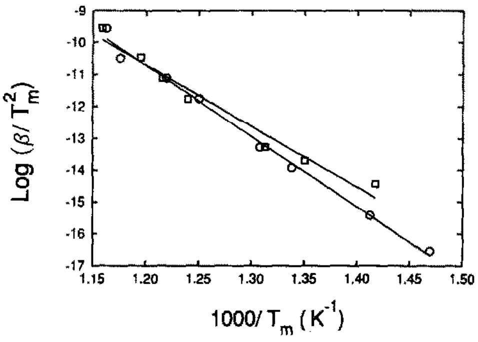

Fig. 3. Kissinger plots of Fortron (○) and Ryton (□) samples.

The Kissinger method bases the calculation of the apparent activation energy E on the temperature at which the maximum rate of weight loss, T_m occurs in the DTG curve at several rates. The Kissinger equation is

$$\ln(\beta/T_m^2) = \ln\left[An(1-\alpha)_m^{n-1}\right] - (E/RT_m) \tag{2}$$

where β is the heating rate, A is the pre-exponential factor, n is the order of the reaction and R is the universal gas constant. A plot of $\ln(\beta/T_m^2)$ versus $(1/T_m)$ (Fig. 3) then gives E from the slope of the line. The calculated E values of Ryton and Fortron are 162 ± 33 and 178 ± 14 kJ mol^{-1}, respectively. A difficulty with the Kissinger method is that it requires the value of T_m to be known accurately, but temperature imprecision is probably the greatest source of error in thermal analysis [13]. The reliability of the T_m values is also suspect because endotherms and exotherms associated with the weight loss process can affect the data, especially in the region of T_m [14].

An alternative to the Kissinger model is the Ozawa–Flynn–Wall method, proposed independently by Ozawa [10] and by Flynn and Wall [11]. This method is based on the representation of the degradation reaction by power law kinetics and the determination of the rate constant k by the Arrhenius equation [15]

$$k = A\exp(-E/RT) \tag{3}$$

This method uses the approximation of Doyle [16] to evaluate the integrated form of the rate equation and yields eqn. (4) as an approximate solution, assuming $E/RT > 20$:

$$\log F(\alpha) = \log(EA/R) - \log(\beta) - 2.315 - 0.4567E/RT \tag{4}$$

where $F(\alpha)$ represents the weight loss function. E is obtained from a plot of log β versus $1/T$ for fixed degrees of conversion (Fig. 4) and the slope of the line is given by $-0.4567E/R$. An advantage of this technique is that the calculated activation energy is independent of the order of the reaction.

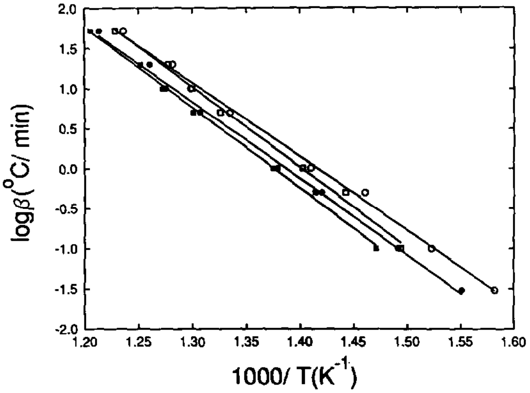

Fig. 4. Isoconversional plots of Fortron for α values of 0.05 (○) and 0.10 (●) and Ryton for α values of 0.05 (□) and 0.10 (■).

This method has been found to be the most reliable of the various kinetic models for evaluating the degradation behaviour of poly(ethylene terephthalate) samples [8,17]. Table 1 shows the calculated E values for Ryton and Fortron.

Table 1 shows that over the conversion range of $\alpha = 0.02$–0.15, the values of E for Ryton are effectively constant while those for Fortron show a slight increase with increasing degree of conversion. Both sets of values compare reasonably well with those obtained by the Kissinger method. These values are also in line with those found by Port and Still [18] for non-commercial PPS samples as calculated by the method of Atkinson and MacCallum [12].

An examination of the kinetics as determined by isothermal degradation is also of interest. The weight losses of PPS for several temperatures between 366 and 419°C were measured and some of these data are shown in Fig. 5 for the Ryton samples. Calculation of E is accomplished by plotting the fractional weight-loss rate at each temperature versus $1/T$ (Fig. 6). The weight loss range employed for these calculations is from

TABLE 1

Kinetic parameters for PPS degradation as determined by the isoconversional method of Ozawa, Flynn and Wall

Degree of conversion	Ryton		Fortron	
	log A (min^{-1})	E (kJ mol^{-1})	log A (min^{-1})	E (kJ mol^{-1})
0.02	14.1 ± 1.4	177 ± 18	12.7 ± 1.4	157 ± 17
0.05	14.1 ± 0.9	183 ± 12	13.2 ± 0.8	169 ± 10
0.10	13.9 ± 0.7	184 ± 11	13.3 ± 0.7	174 ± 9
0.15	13.6 ± 0.9	182 ± 13	13.3 ± 0.7	176 ± 9

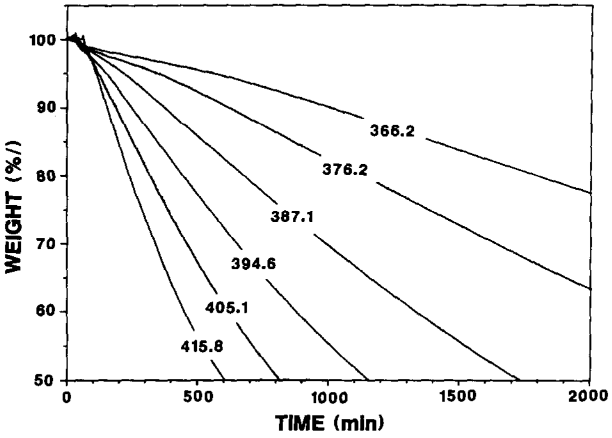

Fig. 5. Weight loss curves of Ryton under isothermal heating conditions at various temperatures.

$\alpha = 0.05$ to $\alpha = 0.2$, because within this range the rate of the weight loss is effectively constant. Unfortunately, data in the range of $\alpha = 0$–0.05 is unreliable because there is a thermal lag when the sample chamber is introduced into the preheated oven. The apparent activation energy values for Ryton and Fortron were found to be 166 ± 8 and 145 ± 8 kJ mol^{-1} respectively, while the log A values were 10.4 ± 1.8 and 8.7 ± 2.1 respectively. These values agree reasonably well with those found by the dynamic techniques. The values may be affected, however, by applying a kinetic analysis to a situation where phase-boundary-controlled and/or diffusion-controlled reactions occur [19].

In view of the nature of the isothermal weight loss curves it was possible to assess the final mass loss from a plot of percentage mass loss against reciprocal time. Once this final mass has been determined it is possible to transpose the isothermal weight loss data into reduced-time plots. These results are shown in Figs. 7 and 8 for the Fortron and Ryton samples

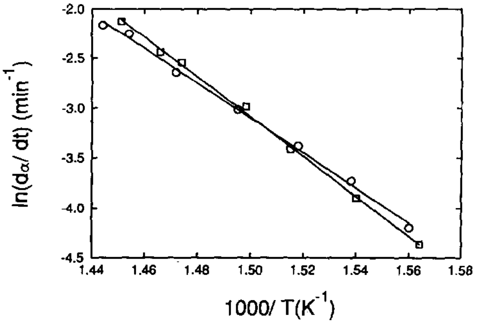

Fig. 6. Arrhenius plot for weight-loss rates for Fortron (○) and Ryton (□) samples.

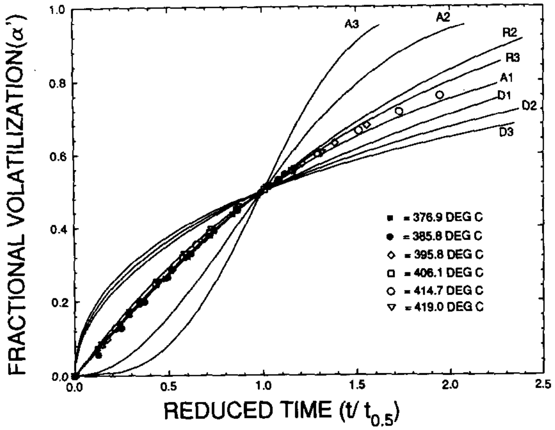

Fig. 7. Reduced-time plot for Fortron and the theoretical relationships between α' and $t/t_{0.5}$ for different g (α) functions.

respectively in which the fraction volatilized (α') is plotted against the reduced time $(t/t_{0.5})$ where $t_{0.5}$ is the time for 50% volatilization. Also presented in Figs. 7 and 8 are the obtained decomposition curves calculated using some of the more commonly used $g(\alpha)$ functions [20] which are tabulated in Table 2.

Visual examination of these two figures indicates that in the case of the Fortron sample, the R3 mechanism provides the best fit of the experimental and theoretical data, while for the Ryton sample the best fit is obtained with an R2 mechanism. This procedure enabled the degradation kinetic law to be identified for both the Fortron and Ryton samples and the specific reaction rate to be determined for each isothermal temperature.

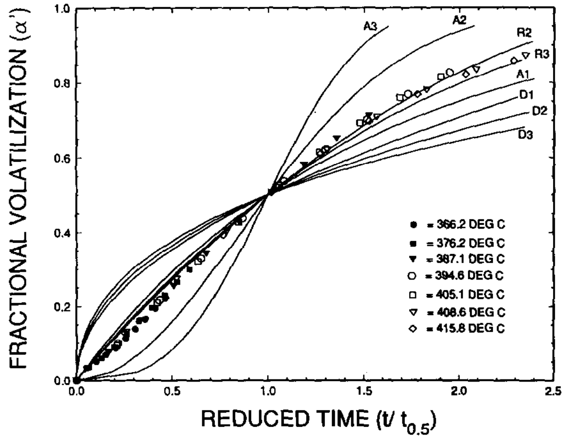

Fig. 8. Reduced-time plot for Ryton and the theoretical relationships between α' and $t/t_{0.5}$ for different g (α) functions.

TABLE 2

Kinetic equations used for the construction of the simulated decomposition curves

Mechanism	$g(\alpha)$	Kinetic model
D1	α^2	One-dimensional diffusion (plane symmetry)
D2	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two-dimensional diffusion (cylindrical symmetry)
D3	$[1\text{-}(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (spherical symmetry)
R2	$1\text{-}(1-\alpha)^{1/2}$	Two-dimensional phase boundary (shrinking cylinder)
R3	$1\text{-}(1-\alpha)^{1/3}$	Three-dimensional phase boundary (shrinking sphere)
A1	$-\ln(1-\alpha)$	Random nucleation or unimolecular decay
A2	$[-\ln(1-\alpha)]^{1/2}$	Two-dimensional nucleation according to Avrami–Erofeev
A3	$[-\ln(1-\alpha)]^{1/3}$	Three-dimensional nucleation according to Avrami–Erofeev

The Arrhenius parameters were then obtained by plotting ln k against the reciprocal temperature (see Fig. 9). The apparent activation energies obtained using this approach for Ryton and Fortron were found to be 180 and 148 kJ mol^{-1} respectively while the log A values were found to be 10.6 and 7.8 respectively.

A frequent application of TG kinetic data is to the estimation of material lifetimes. The limitation of this analysis method is that many materials can suffer a loss of physical properties prior to, or with only minimal, weight loss. The application of a weight loss technique to the prediction of lifetimes must therefore be treated with caution unless actual lifetime experiments are used to supplement the predictions. However, at

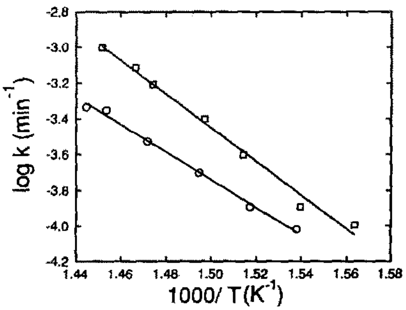

Fig. 9. Arrhenius plot of the isothermal decomposition of Fortron (○) and Ryton (□) based upon the reduced-time plot data.

TABLE 3

Summary of kinetic parameters and lifetime predictions

	log *A* (min^{-1})	*E* (kJ mol^{-1})	Lifetime at 350°C (h)	10-year lifetime maximum temperature (°C)
Dynamic				
Kissinger Method				
Ryton	–	162	–	–
Fortron	–	178	–	–
Isoconversional for $\alpha = 0.05$				
Ryton	14.1	183	30.4	235
Forton	13.2	169	19.7	222
Isothermal				
Reaction rate plot				
Ryton	10.4	166	2.8	198
Fortron	8.7	145	2.4	180
Reduced-time plot				
Ryton	10.7	180	11.5	222
Forton	7.8	148	10.0	200

an absolute minimum the method provides a means of assessing the relative thermal stability of materials.

Application of the kinetic parameters found here by the various degradation theories yields the predicted lifetimes shown in Table 3. For the isoconversional technique, it can be seen from Table 3 that the kinetic data yield a 10-year lifetime temperature maximum of 235 and 222°C for Ryton and Fortron respectively, assuming the lifetime limit is reached when $\alpha = 0.05$. The use of the isothermal rate data gives values of 198 and 180°C, respectively, for Ryton and Fortron over the range of $\alpha = 0.02$–0.15. These values are lower than those obtained by the isoconversional technique but this is probably the result of the thermal lag that is associated with the sample introduction as well as the assumption of a first-order mechanism for the degradation process. However, using the more sophisticated analysis of the data by the more formal mechanistic analysis of the data via the reduced-time plot analysis, 10-year lifetime maximum temperatures of 222 and 200°C are obtained for the Ryton and Fortron samples respectively. These data would further suggest that thermal lag could be a problem with the isothermal analysis. This arises because the whole pyrolysis chamber must be slid into the heating chamber and its large mass means that the initial sample degradation must be ignored. Unfortunately, it is precisely these data which are most relevant for the prediction of the lifetimes.

The lifetime estimates obtained for a temperature of 350°C would suggest that even in the worst case, PPS would be stable for reasonable periods, yet crystallization studies with melt temperatures in this range show that there is a loss of crystallizable material with melt residence times considerably shorter than those predicted here to be safe [1]. This illustrates the need for caution when predicting material lifetimes based on weight loss data and the need for complementary experiments.

CONCLUSION

The thermal degradation parameters of two commercial PPS samples have been measured by TG. The degradation kinetics have been analysed by the Kissinger method, the Ozawa–Flynn–Wall isoconversional method and by two isothermal methods. The dynamic Kissinger and Ozawa–Flynn–Wall methods were found to produce comparable results for estimations of the kinetic parameters while those obtained by the isothermal method were slightly lower. Lifetime estimates based on the kinetic data were also calculated. The values obtained suggest that PPS is a durable thermoplastic material.

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