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HIGH-TEMPERATURE PYROLYSIS OF POLYMERS

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The experimental results on the pyrolysis of thermoplastic polymers under high-temperature heating and burning conditions are discussed. The reaction of polymer degradation in this case proceeds in the same way as in a low-temperature region.

In this paper we discuss polymeric materials and their widespread application, in connection with the increase in their production. Attention is focused on their resistance to external exposure, and in particular to heating exposures of various intensities. Such exposure of a polymer surface results in heating of the polymer and leads to thermal degradation. The latter process is of paramount importance from different points of view.

Questions concerning various aspects of the isothermal degradation of polymers and of theories of thermal degradation have been discussed in detail by a number of investigators; attempts have also been made to establish the dependence of the decomposition mechanisms of polymers on their structures. Comprehensive monographs on these subjects have been written by Jellinek [1], Grassie [2], Madorsky [3] and others [4, 5].

Extrapolation of the "isothermal" bulk degradation kinetics data to the range of pyrolysis rates usually encountered in surface pyrolysis and burning is considered invalid [6].

The simplest case is the thermal degradation and pyrolysis of thermoplastics, i.e. when a polymer is gasified completely. In this connection, it becomes possible to study high-temperature degradation and pyrolysis under quasi-stationary conditions. In the case of polymers of the second and third types, a char residue accumulates on the condensed phase surface; this leads to a continuous change in the conditions of heat transfer in the interface between the gas and condensed phases. The present work is devoted to an analysis of experimental data on the pyrolyses of thermoplastic polymers.

A number of techniques have been developed for study of the kinetic characteristics of pyrolysis. These cannot be studied by classical isothermal methods because the pyrolysis rates and temperatures are in ranges inaccessible to

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such techniques. In contrast to the methods for studying polymer thermal degradation in the low-temperature region up to 300–400°, based both on mass-loss rate measurements and on the analysis of volatile products [3], all methods for studying high-temperature pyrolysis at environmental temperatures above 300–400° are based on mass-loss rate measurements only. The important problem here is the recording of the environmental temperature, the pyrolyzing polymer surface temperature and the thermal flux to the sample surface.

For study of the high-temperature pyrolysis of polymers, a technique permitting recording of the mass loss, the polymer surface temperature and the gas flow temperature was suggested in [7].

The data for polymer degradation kinetics are usually correlated with an Arrhenius-type expression for the reaction rates. If kinetic data are described by this dependence, one can predict the polymer behaviour in different temperature ranges from the data obtained for one temperature region.

Hansel [6] points out that a successful correlation is limited, as one has to know such quantities as T_s and the thermodynamic properties of a given polymer. If experiments are carried out in the low-temperature region (up to 300°), when the degradation process occurs in the "kinetic region", i.e. when the sample heating time is far shorter than the chemical reaction time, then the polymer temperature is equal to the temperature of the reaction vessel or to the environmental temperature. Shteinberg [15] examined the physics of endothermic volume regression (gasification) of a sphere of a substance. Taking into consideration the characteristic times, viz. the heating time of the sphere, $\tau_h = r^2/a$, and the substance regression time at T_s, $\tau_r = [K_0 \exp(-E/RT_s)]^{-1}$, he estimated the reactive thickness Δ of the reaction layer.

At comparatively low T_s values, $\tau_h \ll \tau_r$ and the whole of the substance is heated up to the temperature $T \approx T_s$ (the temperature gradient over the sample thickness is practically equal to zero) long before a certain appreciable portion of it has regressed; in this case, $\Delta = r$. With increasing T_s, the regression time τ_r becomes comparable with the heating time τ_h, and $\Delta < r$. When $\tau_h/\tau_r \gg 1$, the reaction layer thickness is far smaller than the material thickness $\left(\frac{\Delta}{r} \ll 1\right)$ and the regression occurs near the hot surface, which moves quasi-permanently together with the heating wave. The temperature profile in the condensed phase is determined by the relationship between the heating wave velocity and the thermophysical properties of the polymer sample according to Mikhelson's equation [9]. When a degradation reaction occurs during pyrolysis, measurement of the temperature is a matter of some difficulty.

A systematic study of the effect of the environmental temperature on the surface

Table 1 T_s values during pyrolysis of thermoplastics in hot gas flows

Polymer	T_s, °C, at temperature T_∞					
	500	600	700	800	900	1000
PMMA	410	440	460	470	480	485
POM	450	490	515	530	535	540
PS	465	500	525	545	555	565
PE	485	535	570	595	610	620
PP	480	525	560	585	600	610

temperatures of thermoplastic polymers undergoing pyrolysis in hot gas flows has been carried out (see [7] and Table 1).

The pyrolysis process usually proceeds under "quasi-stationary" conditions, when the heat consumed by the degradation reaction is equal to the heat delivered to the polymer. To find, within the framework of formal kinetics, the precise dependence of the mass degradation rate on the external conditions, it is necessary to solve the non-stationary heat-conduction equation in each particular case. Knowing the temperature distribution $T(x, t)$, inside the sample, one can define the mass degradaton rate as

$$\frac{\mathrm{d}m(x, t)}{\mathrm{d}t} = \varrho K_0 \int_V \exp\left[-E/RT(x, t)\right] \mathrm{d}V \qquad (1)$$

where ϱ is the material density, K_0 is the preexponential, E is the activation energy of degradation and R is the universal gas constant.

It is rather a difficult problem to find a solution of high accuracy for the non-stationary heat equation, even for the case of spherical symmetry of bulk thermal degradation in a polymer melt and with variable heat flux to the sphere surface. This problem can be successfully solved only in particular cases.

However, the heat balance equation may sometimes be quite helpful for many pyrolysis problems:

$$q_1 + q_2 + q_3 = \frac{\mathrm{d}m}{\mathrm{d}t} L + q_4 \qquad (2)$$

where q_1 is the radiation heat flux, q_2 is the convective or conductive heat flux, q_3 is the heat flux delivered via the sample holder, $\frac{\mathrm{d}m}{\mathrm{d}t}$, L is the heat consumed by chemical reaction (L denotes the heat of gasification), and q_4 is the heat required for heating the sample. Then, for q_4 we have $q_4 = C\varrho U(T_s - T_0)$ or $q_4 = \frac{\mathrm{d}m}{\mathrm{d}t} \cdot c \cdot (T_s - T_0)$.

If q_4 is combined with $L\cdot\frac{dm}{dt}$, and if $q_3 = 0$:

$$q_1+q_2+q_3 = \frac{dm}{dt}[L + c(T_s - T_0)] = \frac{dm}{dt}\cdot L_{\text{eff}} \tag{3}$$

Therefore, different effective heats of gasification correspond to different radii of the sphere, viz. from ca. 200 cal/g [10] for uniformly heated PMMA samples (diameter up to 1–2 mm) to ca. 400 cal/g [11, 12] for PMMA linear pyrolysis (large diameters).

If the temperature of the sample is constant throughout its volume, then the pyrolysis rate is proportional to the mass of the sample:

$$\frac{dm}{dt} = mK_0e^{-E/RT_s} \tag{4}$$

If convection and radiation are taken into account, the heat balance equation may be represented as

$$\begin{aligned}\frac{dm}{dt} &= mK_0e^{-E/RT_s} = \frac{1}{L_{\text{eff}}}\sum_i q_i = \\ &= \frac{1}{L_{\text{eff}}}\left[\varepsilon\sigma(T_1^4 - T_s^4)S + \frac{\lambda_f Nu}{d}(T_2 - T_s)S\right]\end{aligned} \tag{5}$$

Figure 1 shows the graphical solution of Eq. (5). Curve 1 characterizes the rate of heat consumption by the chemical reaction, and curves 2 and 3 the radiative and convective heat transfer, respectively. The dashed curve 4 represents the total heat supply to the polymer sample. The point of intersection of curves 1 and 4 gives the unknown "quasi-equilibrium" temperature of the sample during its pyrolysis. It is evident that an increase of the heat flux to the polymer at the fixed diameter results in a rise of the sample temperature. At very high heat fluxes, it is observed that T_s seems to tend to a certain limit [16].

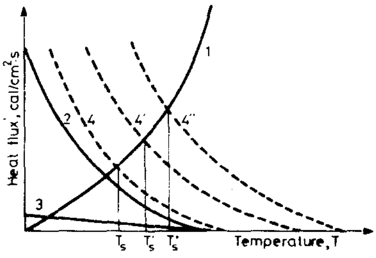

Fig. 1 Graphical solution of Eq. (5)

The above conclusions are confirmed by the data for some thermoplastics by the dependence of T_s on the heating exposure rate or on the gas flow and radiator temperatures [7, 17–20].

Kinetic parameters have been obtained graphically for the pyrolysis of some polymers using the mass pyrolysis rate and temperature data reported in [7] (see Table 2).

Table 2 Activation energy for PMMA, PE and PS degradation

Polymer	E, kcal/mol present work	E, kcal/mol others	References
PMMA	38	30	[3]
		31	[1]
		29, 6	[4]
		74	[12]
		40–43	[13/14]
PE	35	45	[16]
		46–66	[1]
		63	[5]
		26–63	[3]
PS	46	55	[5]
		45–55	[3]
		25–95	[15]

Much attention has been given to the linear pyrolysis of thermoplastics [8, 13, 21–27]. In this case the temperature distribution in the condensed phase is defined by Mikhelson's equation [9]. This is confirmed by the data [28] obtained by Kishorė from a study of the heat transfer during polymer burning. The linear pyrolysis rate is determined by the relation [29]:

$$U_{l.p.}^2 = aK_0 e^{-E/RT_s}\left[\frac{RT_s^2}{E\left(T_s - T_0 - \frac{1}{2}\frac{Q}{C_p}\right)}\right] \tag{6}$$

This equation is valid for the model of linear pyrolysis of a semi-infinite continuum. The effective activation energy is equal to half the actual activation energy.

It should be noted that, in the case of the pyrolysis of thermoplastics, the temperature distribution in the condensed phase will be described by Mikhelson's equation and will represent a flat curve if the thermal diffusivity is assumed to be constant. However, as shown in a number of works, there exist a heated layer, a molten layer and a "boiling" layer in a polymer during its linear pyrolysis. As stated above, intense heat transfer takes place in the latter layer and its density is far lower

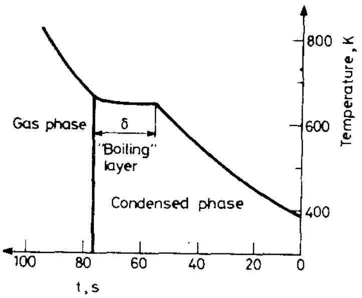

Fig. 2 General temperature profile at pyrolysis [31]

than that of the non-heated portion. Kishore [28] has found that the thicknesses of the heated and melt layers of polystyrene are in inverse proportion to the pyrolysis rate.

The "boiling" layer thickness is also inversely proportional to the pyrolysis rate $U_{l.p}$ [30], i.e. the temperature distribution due to intense heat transfer in this layer is the same as shown in Fig. 2 [31].

If the linear pyrolysis rate tends to zero, the reaction layer thickness will tend to infinity. Under these assumptions, the linear pyrolysis rate may be represented as

$$U_{l.p} = K_0 \int_0^\infty e^{-E/RT(x)} \varrho \, dx = K_0 \int_0^\delta \varrho e^{-E/RT(x)} dx + K_0 \varrho \int_\delta^\infty e^{-E/RT(x)} dx \qquad (7)$$

Under conditions of intense heat transfer in the "boiling" layer, $T(x) \approx$ const. in the range $0 \leqslant x \leqslant \delta$.

If a noticeable reaction rate is assumed in the layer δ, the second integral in Eq. (7) may be neglected and the linear pyrolysis rate will be

$$U_{l.p.} = K_0 e^{-E/RT_s} \int_0^\delta dx = K_0 \cdot \delta \cdot e^{-E/RT_s} \qquad (8)$$

Under the condition $\delta \sim \frac{1}{u_{l.p.}}$, we have $U_{l.p.}^2 \sim K_0 e^{-E/RT_s}$, i.e. the same dependence of the linear pyrolysis rate on reciprocal temperature as in formula (6).

The characteristics of PMMA degradation kinetics K_0 and E obtained for high-temperature pyrolysis agree with the K_0 and E values for "bulk isothermal" degradation reported in [1, 3]. This agreement indicates that the degradation mechanism is apparently much the same for low- and high-temperature regions. Either the inaccuracy of surface temperature measurement during pyrolysis or the neglect of the complicated macrokinetics in each particular case (a complex temperature profile varying with time and environmental variations) may influence the conclusions arrived at by various authors about the change of mechanism. The final conclusion concerning the degradation mechanism requires new investigations with due regard to all factors involved.

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Zusammenfassung — Die experimentellen Ergebnisse der Pyrolyse von thermoplastischen Polymeren unter Erhitzungs- und Brennbedingungen hoher Temperatur werden besprochen. Die Reaktion der Polymerzersetzung verläuft in diesem Falle genau so wie in der Niedrigtemperaturzone ab.

Резюме — Обсуждены экспериментальные результаты пиролиза термопластических полимеров при их высокотемпературном нагреве и горении. Реакция распада полимеров в таких условиях протекает аналогично тому, как и при низкотемпературном режиме.