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IGNITABILITY OF POLYMERS RELATED TO POLYMER PROPERTIES AND DIFFERENT STEADY STATES OF COMBUSTION

Theoretical approach

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Abstract

A mathematical model of ignition and burning of organic polymers was used for evaluation and quantification of the tendency of polymers to ignition. The model permits investigation of the influence of one parameter of the polymer on the others. It was found that the model could be used for the verification of the ignitability method developed by Miller *et al.* [1].

Different steady states of combustion were found when using the model proposed. There is a characteristic steady state for normal flaming combustion, another for non-flaming combustion, and there are also unstable steady states that have no real physical meaning.

Keywords: ignition, polymer combustion modelling, stability, steady state

Introduction

Ignition of organic polymers requires an energy input, which induces the decomposition of polymer to yield volatile and combustible gases to a certain critical level. If the heating rate of the polymer is less than some critical value, the decomposition of the polymer occurs without ignition and burning. This critical heating rate depends on the chemical properties of the sample and on the physical conditions of the experiment. If the physical parameters of the system are kept constant, the ignition becomes the function of only the chemical nature of the sample.

A number of ignition tests have been developed, based usually on an empirical approach. An attempt has been made by Miller *et al.* to quantify the tendency of materials towards ignition based on two parameters [1]. The first parameter is the critical decomposition temperature of the polymer at its surface while the second is the critical heating rate of the polymer surface. Miller *et al.* [1] postulated that these two parameters could be used for the characterization of polymer ignitability. The critical decomposition temperature and heating rate of the poly-

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mer are affected by the heat flux at the given surface. This heat flux depends on the temperature of the surrounding medium, i.e. temperature of the furnace.

The decomposition temperature and heating rate were detemined at the critical temperature, defined as the maximum furnace temperature at which the sample was not ignited. This value seemed to be size independent and characteristic of the given material [1].

Miller *et al.* [1] determined the ignitability characteristics in the following way: the polymer sample was inserted into the TG oven at the critical furnace temperature. The mass of the sample and its temperatures were followed as functions of the time. At the moment of declining of the TG curve from its baseline, the surface temperature of the polymer and its first derivative with respect to time were recorded as critical decomposition temperature and critical heating rate of the polymer, respectively. Each polymer was represented by one point on the plot of critical decomposition temperature *vs.* critical heating rate. The distance of the point from the origin determined the ignitability of the sample. The closer the point to the origin of the system of coordinates, the greater the tendency of the given material to self-ignition [1].

Results and discussion

The model of polymer ignition and burning is based on Semenov's [2] model, derived for the burning of gaseous fuels:

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{1}{C}\sum_{\mathrm{i}} q_i v_i-\frac{\alpha S}{CV}(T-T_0) \tag{1}$$

Semenov's model uses space-averaged [2] variables and parameters; T – temperature, T_0 – temperature of the surrounding medium, C – heat capacity of unit volume, S/V surface/volume ratio, α – heat transfer coefficient, q_i – reaction heat of the i^{th} reaction, v_i – rate of the i^{th} reaction.

The model of polymer ignition and burning consists of four ordinary differential equations describing the balance of heat and mass on the polymer surface and in the gasesous phase [3].

$$\begin{aligned}
\frac{\mathrm{d}T}{\mathrm{d}t}&=M_1k_1w[\mathrm{O_2}]-M_2k_2w-N_2(T-T_0)-N_1(T-T_\mathrm{p})\\
\frac{\mathrm{d}T_\mathrm{p}}{\mathrm{d}t}&=-M_0k_0+N_1(T-T_\mathrm{p})\\
\frac{\mathrm{d}w}{\mathrm{d}t}&=k_0-k_1w[\mathrm{O_2}]-Lw\\
\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t}&=-\mathrm{k}_1w[\mathrm{O_2}]+\mathrm{k}_3([\mathrm{O_2}]_0-[\mathrm{O_2}])
\end{aligned} \tag{2}$$

The differences of (1) and (2) are due to the greater complexity of polymer burning. The first equation of (2) corresponds to Semenov's model extended by the heat transfer between the polymer surface and flame. The gaseous fuel is fed to the flame from the solid phase as a product of degradation of the polymer (third equation of 2). This degradation is forced by the heat transfer from the gaseous phase. The important role of the solid phase in the process makes necessary to take into account its temperature (second equation of 2). The fourth equation is the time dependence of the oxygen concentration in the flame.

The rate coefficients k_i are defined via Arrhenius equations ($k_i=A_i e^{-Ei/RT}$). The unit of k_i is s^{-1}. The model parameters M_i correspond to the ratio q_i/C of (1), proportional to the heat (q_i) of the given process (M_0 – volatilization, M_1 – combustion and M_2 – endothermic processes in the flame). The unit of M_i is K (substituting units for instance kJ m^{-3} for q_i and kJ Km^{-3} for C). m^{-3} is present in these units due to the use of space-averaged values [2]. N_1 and N_2 are the heat transfer parameters between the flame and the polymer surface and between the flame and surrounding medium, respectively. The physical meaning and definition of heat transfer coefficients N_i can be derived from comparison of (1) and (2); $N_i = \alpha S / CV$ ($CV/\alpha S$ can be identified with the thermal relaxation time [2]). The unit of N_i is s^{-1}. L denotes the ventilation coefficient (in s^{-1}) of the fuel to the surrounding medium, T_0 (in K) is the temperature of the reactor and $[O_2]_0$ (in rel. units) is the concentration of oxygen in the surrounding medium. The model permits theoretical determination of combustion and ignition charactersitics, such as limiting oxygen index, heat release rate, mass loss rate, time to ignition, etc. [3–5].

The basic set of parameters used in the model calculations is presented in Table 1. In the calculation of the stable and unstable steady states M_1=40.000 K and M_2=0.4 K. The values of the parameters were taken partly from the literature, (A_0, E_0, A_1, E_1, A_2, E_2 [6]) and partly fitted to have limiting oxygen index in the range 17–40 [3], which is valid for a number of commonly used polymers. The main purpose of this modelling was to reveal the net influence of different properties of the polymer on the combustion characteristics, not affected by the others. This aim is hardly possible to achieve experimentally, because the use of different polymers or additives in the experiments causes changes in more than one parameter.

The system of equations (2) was solved using different methods. By integrating (2) obtained the time dependence of system variable. The second way was setting the left hand side of (2) zero and solving the right hand side as a system of non-linear equations. The results of this method were the steady states of (2). For the calculations we used FORTRAN subroutines from IMSL or SLATEC program libraries. The calculations were carried out with a numerical precision of 10^{-6} of the calculated variables. The steady state results obtained by the two different methods were the same within the above mentioned precision.

Table 1 The basic set of parameters of model (2)

Parameter	Value	Unit	Process
M_0	400	K	degradation of polymer
A_0	2.958×10^6	s^{-1}	and volatilization
E_0	87900	J mol^{-1}	of products
M_1	10000	K	oxidation of
A_1	1.983×10^6	s^{-1}	the fuel
E_1	107800	J mol^{-1}	in the flame
M_2	0.1	K	endothermic
A_2	4.3×10^{16}	s^{-1}	reaction in
E_2	242800	J mol^{-1}	the flame
A_3	2.958×10^6	s^{-1}	diffusion of oxygen
E_3	138000	J mol^{-1}	from the surrounding medium
N_1	2	s^{-1}	heat transfer from the flame to the polymer surface
N_2	1	s^{-1}	heat transfer from the flame to the surrounding medium
L	4	s^{-1}	escape of the fuel from the flame without oxidation to the surrounding medium
T_0	723	K	temperature and
$[O_2]_0$	1	rel. u.	concentration of oxygen in the surrounding medium

The basic idea of Miller *et al.* [1] was to correlate the degradation of a polymer at a temperature, which is characteristic of the given material, with its ignitability. For this purpose, they chose a characteristic point of the polymer decomposition, and they used to describe the polymer ignitability the polymer surface temperature and its rate of increase in that special point. In the present paper we have changed the approach of Miller *et al.* This change concerned the choice of the characteristic point in the curve of polymer decomposition or in our case in the corresponding curve of the release of gaseous products (w). At the beginning, the concentration w (the mass loss) in the TG experiments of Miller *et al.* was zero, on the other hand it was not zero in the computer experiment. It is understandable, because the Arrhenius rate constant ($k_0=A_0\exp(-E_0/RT_p)$) of polymer degradation differs from zero if the temperature is higher than 0 K. In addition no sudden change or other special point can be observed in the time dependence curve of a fuel ($w=f(t)$). As a characteristic point the first maximum of the curvature of the fuel production appeared to be useful, where the acceleration of the formation of gaseous products was the highest.

This phenomenon is quite commonly used in differential geometry, but not in chemistry. The curvature of an arbitrary function can be calculated using the following equation:

$$\varphi = \frac{y''}{(1+y'^2)^{3/2}} \tag{3}$$

φ – curvature of the given function, y' and y'' are the first and second derivatives of the given function, respectively. The physical meaning of this phenomenon is the measure of the change of the tangent of the function divided by the length of the curve arc. $1/\varphi$ is equal to the radius of a circle with curvature φ.

The avoid the possible effect of different scales of the axes (time and concentration of gaseous products of degradation) on the curve length, we have rescaled them to the mutually comparable scale, when the curvature was calculated. Integrating (2) at the critical furnace temperature, the curvature of the fuel production ($w=f(t)$) was calculated simultaneously, and in the moment of its first maximum the polymer surface temperature (T_p) and its time derivative (dT_p/dt) were recorded as critical surface temperature and critical heating rate, respectively.

To determine the correlation between the system parameters (the properties of the polymer or experimental conditions) and ignitability characteristics, a number of calculations were carried out for different values of the chosen parameter, while the others were kept constant.

The ignition plot of M_0 indicates that the higher the value of the paramter M_0, the more difficult is to ignite the polymer (Fig. 1). With increasing value of M_1, the ignition of the polymer is easier (Fig. 2).

The ignitability plot of E_0 exhibits unexpected behaviour in the region of low values (Fig. 3). From E_0=80 up to 95–100 kJ mol^{-1} a decrease occurs in the criti-

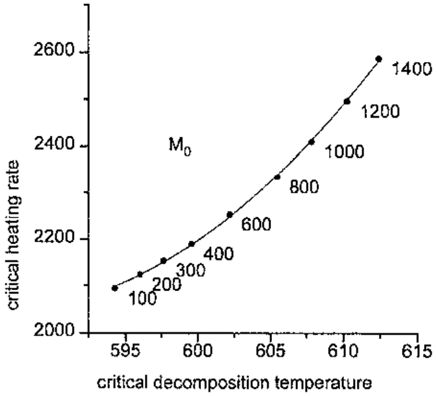

Fig. 1 Critical heating rate (in K min^{-1}) plotted *vs.* decomposition temperature (in K) for different values of M_0

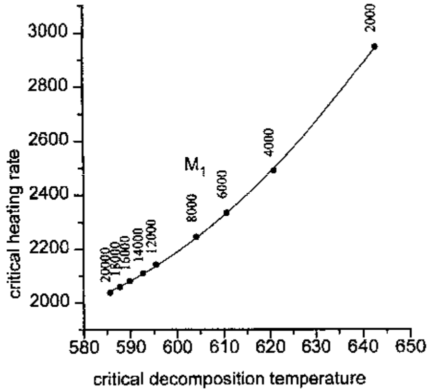

Fig. 2 Critical heating rate (in K min^{-1}) plotted *vs.* decomposition temperature (in K) for different values of M_1

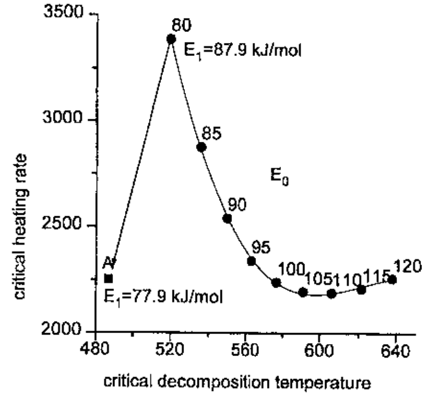

Fig. 3 Critical heating rate (in K min^{-1}) plotted *vs.* decomposition temperature (in K) for different values of E_0

cal heating rate. Above 100 kJ mol^{-1} it remains approximately constant. On the other hand, above 100 kJ mol–1 the critical decomposition temperature increases. Thus, the ignitability, defined by the method of Miller *et al.*, decreases with increasing E_0 only for E_0>95 kJ mol^{-1}. In the region from 80 kJ mol^{-1}<E_0<95 kJ mol^{-1} the ignitability increases with increasing E_0.

This can be explained as follows: if the rate of polymer decomposition depending on E_0 is too high in comparison with the rate of gas reaction determined by E_1, the decomposition of the polymer to volatiles occurs without ignition. The position of the point A in Fig. 3, which is out of the curve, indicates the close connection between the ignitability and the E_0/E_1 ratio. Here, the value of E_1 is by 10 kJ mol^{-1} lower, which causes a significant shift of the point towards the origin of the axes, and to an increase in the ignitability of the polymer.

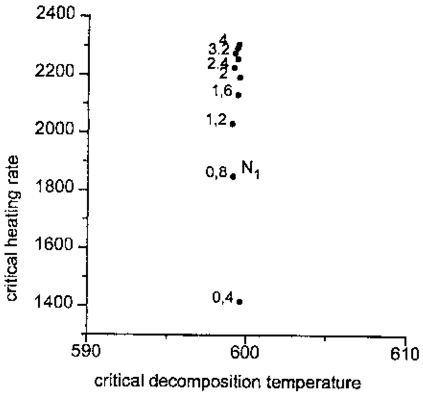

Fig. 4 Critical heating rate (in K min^{-1}) plotted *vs.* decomposition temperature (in K) for different values of N_1

The ignitability plot for N_1 is interesting (Fig. 4). The plot is approximately parallel with the critical heating rate axis. The variation of this parameter does not change the critical decomposition temperature and only affects the critical heating rate. An increasing value of N_1 leads to an increase in the critical heating rate. According to the approach by Miller *et al.* [1], the sample should be more difficult to ignite. However, the critical furnace temperature ($(T_\infty)_c$) and the time (t) (Table 2), which is necessary to achieve the critical decomposition temperature (~599 K for all values of N_1) decrease with increasing N_1. Among the ignitability values experimentally measured by Miller *et al.* [1] that of wool is the lowest, i.e. wool seems to be the most difficult to ignite (Table 3) despite the fact, that is critical furnace temperature is considerably lower than that of PBI, Kermel®

Table 2 Theoretical ignitability characteristics for different values of N_1 $(T_\infty)_c$ – critical furnace temperature, t – time to achieve the critical values $(\Delta T/\Delta t)_c$ – critical heating rate of the polymer surface $(T_d)_c$ – critical decomposition temperature of the polymer surface

N_1(s^{-1})	$(T_\infty)_c$/K	t/s	$(\Delta T/\Delta t)_c$/K min^{-1}	$(T_d)_c$/K
0.4	692.	6.357	1416	599.6
0.8	686.5	4.712	1848	599.1
1.2	684.5	4.169	2030	599.1
1.6	684	3.900	2130	599.6
2.0	683.5	3.741	2190	599.4
2.4	682.5	3.638	2224	599.2
2.8	682.5	3.563	2254	599.4
3.2	682.	3.509	2273	599.3
3.6	682.	3.466	2291	599.4
4.0	682.	3.432	2305	599.5

and Nomex®, which are thermostable polymers, having lower flammability than wool. The high value of heating rate of wool and its low ignitability are worth noticing. Probably, the heat transfer should be expressed in the case of wool by the high value of N_1 in the mathematical model (Table 2).

Table 3 Experimental ignitability characteristics of chosen polymers published by Miller *et al.* [1]. $(\Delta T/\Delta t)_c$ – critical heating rate of the polymer surface, $(T_\infty)_c$ – critical furnace temperature, $(T_d)_c$ – critical decomposition tmeperature of the polymer surface, $[I]$ – ignitability of the polymer expressed by Miller's [1] equation: $[I]=100/\{[(\Delta T/\Delta t)_c/3379]^2+[((T_d)_c-25)/619]^2\}^{1/2}$

Polymer	$(\Delta T/\Delta t)_c$/K min^{-1}	$(T_\infty)_c$/°C	$(T_d)_c$/°C	$[I]$
Nomex®	734	600	545	115
Kermel®	1709	625	525	105
PBI	522	700	644	99
Wool	3379	590	357	88

Let us consider the ignitability of the polymer as the ease with which the system is transferred from its non-burning steady state to flaming combustion at critical conditions for flaming combustion. With this in mind, we perturbed the system by introducing a temperature fluctuation on the polymer surface which caused that the system with lower value of heat transfer coefficient (N_1=0.4) was ignited, while that with higher value (N_1=4) remained in the non-burning state (Fig. 5). The temperature perturbation was 0.1% of the critical decomposition temperature for 0.01 s from the instant of the critical conditions. It means that systems with higher N_1 are less sensitive to small fluctuations, which are more easily damped. The dependence of the ignitability of polymers on the heat trans-

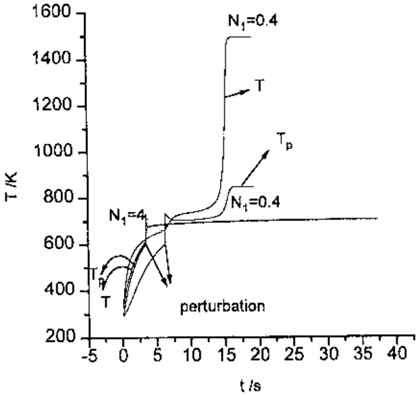

Fig. 5 The time evolution of gas phase (flame) and polymer surface temperature for N_1=0.4 and N_1=4 at critical conditions. The fluctuations of the surface temperature are introduced at the moment indicated

fer coefficient in the sense of the method of Miller *et al.* correlates with the sensitivity of the model to temperature fluctuations.

Different steady states of burning

The steady state values of the system variables (gaseous phase temperature, polymer surface temperature, concentration of flammable gases – fuel – in the flame, concentration of oxygen in the flame) depend on system parameters. In most cases one steady state of burning characterized by one set of system variables is expected.

As shown in Table 4, sometimes more than one steady state follows from the above system of equations. E.g. for $[O_2]_0$=0.36–0.45 three different steady states can be found. The first steady state with the highest gas phase temperature represents normal flaming combustion. This type of combustion is characterized by

Table 4 Values of system variables at different oxygen concentrations in the surrounding atmosphere. The units of concentrations are relative units, the temperature is in K
$^aT_0$=723 K, $^bT_0$=293 K

	Stable flaming			Stable non-flaming			Unstable steady state		
$[O_2]_0$	T	w	$[O_2]$	T	w	$[O_2]$	T	w	$[O_2]$
1.[a]	1506.8	0.0017	0.9415				813.8	0.0426	0.0209
1.[b]	1506.3	0.0017	0.9413				878.7	0.0799	0.0192
0.9	1492.4	0.0020	0.8363				884.5	0.0840	0.0172
0.8	1476.0	0.0024	0.7299				891.2	0.0888	0.0153
0.7	1457.4	0.0030	0.6217				898.9	0.0944	0.0133
0.6	1435.2	0.0039	0.5102				908.2	0.1014	0.0114
0.5	1406.7	0.0056	0.3925				919.8	0.1145	0.0091
0.45	1389.0	0.0071	0.3314	1157.0	0.1503	0.0232	926.6	0.1156	0.0085
0.4	1363.0	0.0100	0.2568	1116.0	0.1956	0.0134	934.9	0.1221	0.0076
0.38	1348.8	0.0121	0.2225	1106.9	0.2023	0.0117	938.6	0.1250	0.0072
0.36	1327.0	0.0164	0.1774	1098.0	0.2068	0.0104	944.9	0.1301	0.0067
0.34				1089.4	0.2097	0.0093	947.2	0.1319	0.0065
0.32				1080.8	0.2110	0.0084	952.2	0.1360	0.0061
0.3				1071.9	0.2109	0.0075	958.0	0.1406	0.0058
0.28				1062.2	0.2092	0.0067	964.8	0.1461	0.0054
0.26				1051.2	0.2057	0.0060	973.2	0.1529	0.0051
0.24				1037	0.1989	0.0053	984.9	0.1622	0.0048
0.23				1026.5	0.1927	0.0049	994.3	0.1696	0.0046
0.22				293.0	0.000	0.2200	293.0	0.0000	0.2200

relatively high flame temperature, low fuel concentration and relatively high oxygen concentration in the flame. The other two steady states have lower flame and polymer surface temperature, higher fuel and lower oxygen concentration in the flame. The second steady state probably represents glowing. The fuel-rich regime of burning leads to incomplete burning with lower heat production.

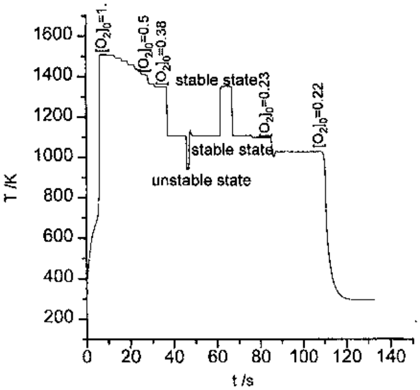

Fig. 6 Flame temperature *vs.* time curve for different concentrations of oxygen in the environment. The time lags between respective changes of parameters are arbitrary

In these calculations the steady states of the model were found by solving a system of algebraic equations, obtained from differential equations setting the time derivatives of the system variables to zero. This is a very efficient and fast method, but it yields not only the roots, which are stable steady states, but the unstable steady states, too. It is easy to check, whether the given steady state is stable or not. The solution of the system of ordinary differential equations using the step by step integration method terminates always at one of the stable steady states. In this way we found that one of the steady states is unstable (Fig. 6).

Another method to prove the stability or instability of a steady state is the calculation of Ljapunov's exponents of the system in a linear approach [7]. In this method the behaviour of the system is investigated in the close vicinity of the steady state. Each of the system variables (gaseous phase and polymer surface

Table 5 Characteristic values of the Jacobi matrix of a stable steady state and an unstable steady state. The characteristic values belong to the state at $[O_2]_0$=0.4 of non-flaming combustion and unstable steady state (Table 3)

Stable state		Unstable state	
Real part	Imaginary part	Real part	Imaginary part
–2.3625	0.0	0.0592	0.0
–0.0871	0.0	–0.0514	0.0
$-0.1310\cdot10^{-4}$	0.0	$-0.9065\cdot10^{-5}$	0.0
$-0.1351\cdot10^{-5}$	0.0	$-0.1873\cdot10^{-6}$	0.0

temperatures, fuel and oxygen concentration in the flame) is perturbed and a Jacobi matrix is created from the time derivatives of variables in the point of perturbation. If the steady state is stable, the real parts of the characteristic values (sometimes called eigenvalues) of the Jacobi matrix are less than zero. The steady state is unstable when at least one of the characteristic values is positive (real part of the complex values) [7] (Table 5).

In Fig. 7 are shown the results of calculations, where the system variables vary as functions of the oxygen concentration in the atmosphere ($[O_2]_0$). The two branches of the steady states join in a critical point – corresponding to the limiting oxygen index. If the oxygen concentration increases from zero, a steady state appears at LOI, which is split into a stable (glowing, non-flaming combustion) and an unstable branch. At $[O_2]_0$=0.36 a new stable steady state appears which, according to the flame temperature, and fuel/oxygen concentration ratio corresponds to flaming combustion. Above $[O_2]_0$=0.45 the steady state of non-flaming

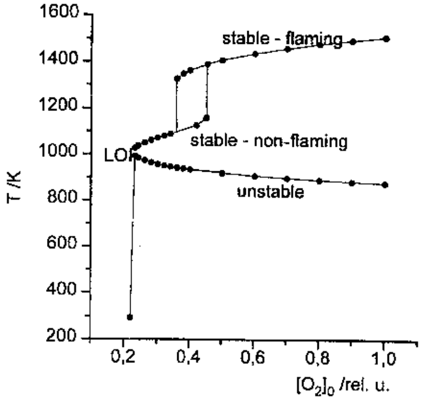

Fig. 7 Dependence of steady state flame temperatures on concentration of oxygen in the environment

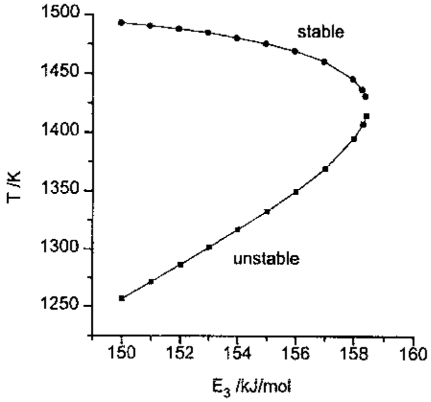

Fig. 8 Stable and unstable branch of flame temperature depending on E_3

combustion disappears and the only possible way of polymer combustion is a normal flame.

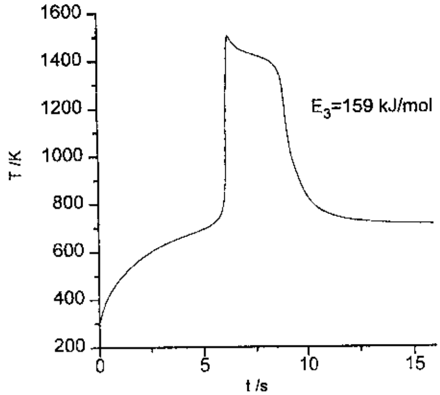

Fig. 9 Gaseous phase temperature *vs.* time curve for E_3>critical values (159 kJ mol^{-1})

Quite similar behaviour was observed for the parameter E_3, which is the temperature coefficient of oxygen diffusion from the surrounding medium to the flame. Below its critical value both the stable and ustable steady states exist (Fig. 8). Above this value a temperature peak appears in the gaseous phase temperature *vs.* time curve, but it is unstable and after a certain time relaxes to the temperature of the surrounding medium (Fig. 9).

Conclusions

The method developed by Miller *et al.* [1] which was tested on different polymers to quantify their ignitability appeared to be useful for computer experiments, when combined with some suitable model of polymer ignition. The results show that the ignition of the polymer is difficult not only if the polymer is too stable, but also if it is too unstable, and decomposes at a very low temperature. At that temperature the rate of oxidation in the gaseous phase is not high enough to generate the required amount of heat to maintain the steady state burning of the polymer. The dependence of ignitability on the coefficient of heat transfer to the polymer surface shows peculiar behaviour confirmed also in the systems of materials tested experimentally by Miller *et al.* [1].

Using the model proposed earlier [3] it is possible to find different steady states of polymer burning. These steady states represent either normal flaming combustion or non-flaming combustion (glowing). Under certain conditions, these steady states can exist simultaneously. Important phenomena of polymer combustion, as for example limiting oxygen index or transition between flaming and non-flaming combustion etc., are often connected with changes in the stability of the burning system.

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