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A SIMPLE MODEL FOR PREDICTING POLYMER IGNITION IN A THERMOGRAVIMETRIC ANALYZER

Y.-H. HUANG and M.A. SERAGELDIN

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, MI 49931 (U.S.A.)

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ABSTRACT

Ignition of three polymers (PP, PS and PVA) in air was studied using a DuPont 951 thermogravimetric analyzer (TGA). Time to ignition and ignition temperature were reported as a function of furnace temperature which varied between 550–700°C. The suitability of a simplified model to predict time to ignition was tested. The predicted value of time to ignition was heavily dependent on the assumed sample layer thickness (D). For example, when the average particle diameter, d_p, was ~ 0.5 mm, assigning D a value of $D = 2\ d_p$ (i.e. two layers of particles in sample pan) produced a good estimate of the time to ignition. However for $d_p \sim 1$ mm, a good estimate was obtained when D was chosen equal to d_p. The results indicated a deviation from experimental values of less than 15% at 700°C.

INTRODUCTION

Polymers are being used increasingly as components in many applications. These materials, which are composed mainly of carbon and hydrogen, will burn when the conditions of oxidant and temperature promote the formation of oxidizable products [1,2]. It is the flammability of these decomposition products which will define the ease of ignition of a polymer. The importance of ignition is that it is the first step leading to a fire [3,4].

In this work a simplified model to predict time to ignition is formulated. The model is tested against values obtained experimentally in a DuPont 951 thermogravimetric analyzer (TGA). This technique involves rapidly inserting a sample into a hot zone and recording the change in temperature and mass-loss with time [5,6]. The inflection point on the temperature–time curve, occurring after the sample loses mass, defines the ignition point as shown in Fig. 1.

EXPERIMENTAL

Materials and procedure (quartz tube not attached to sample housing unit)

Three polymers were tested: polypropylene (PP), polystyrene (PS) from Scientific Polymer Product, Inc., and polyvinyl alcohol (PVA) 99% hydro-

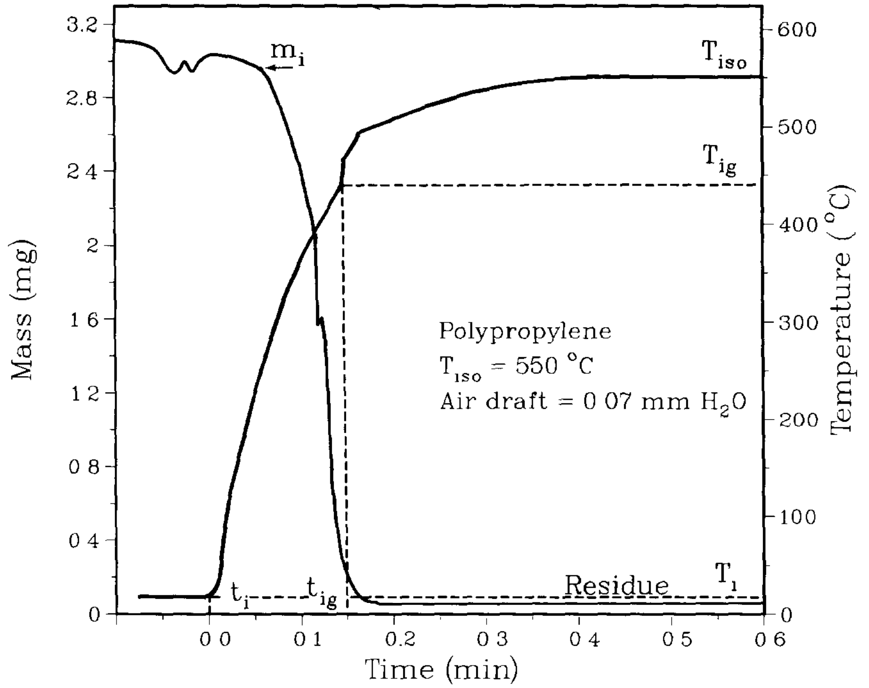


Fig. 1. Thermogram showing sample mass loss and temperature curves for polypropylene in air (draft: 0.075 mm H_2O).

lyzed from Matheson, Inc. These materials were commercially available and did not contain additives (e.g. fillers, plasticizers). The properties and structure are given in Table 1.

About 3–4 mg of finely divided polymer material were added to the platinum pan of a DuPont 951 thermogravimetric analyzer (TGA). The system was set up so that the apparatus recorded the change in mass-loss

TABLE 1

Structure and properties of polymers

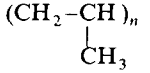
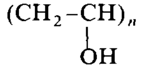
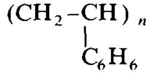
Polymer	m (mg)	d_p (mm)	C_p (kJ kg^{-1} K^{-1})	ρ_{solid} (kg m^{-3})	Repeating unit
PP	~ 3.1	0.3 ~ 0.5	2.79, (120 °C) [10]	900 [13]	 $(CH_2\text{-}\underset{CH_3}{\underset{\vert}{CH}})_n$
PVA	~ 3.7	0.5 ~ 0.7	1.50, (30 °C) [11]	1290 [11]	 $(CH_2\text{-}\underset{OH}{\underset{\vert}{CH}})_n$
PS	~ 3.1	0.8 ~ 1.0	2.01, (150 °C) [12]	1110 [12]	 $(CH_2\text{-}\underset{C_6H_6}{\underset{\vert}{CH}})_n$

TABLE 2

Regression equations [a]

Polymer	$T_{iso} = a + b/t_{ig}$		r^2	$T_{iso} = a' + b'/T_{ig}$		r^2
	a	b		a'	b'	
PP	458	774	0.976	1383	−1.96	0.971
PVA	403	748	0.933	1213	−2.13	0.834
PS	470	624	0.999	974	−1.06	0.906

[a] r^2 = the square of the correlation coefficient.

(TG) and sample temperature with time (0–500 s). The air flow was fixed by maintaining the draft of about 0.075 mm of water in a 10 cm diameter exhaust pipe positioned at the downstream end of the TGA. The draft was measured using a Bacharach draft gauge.

The TGA quartz tube was left in the furnace during the heating up stage. The sample housing was rapidly introduced into the hot zone after 300 s from the time the furnace reached the set isothermal temperature (T_{iso}). During the heating up period the sample was shielded with a glass flask to protect it from external drafts.

The time to ignition (t_{ig}) was recorded at several isothermal temperatures (T_{iso}) at which the sample ignited; the ignition point was defined at the second inflection of the temperature time curve, which occurred after the sample decomposed. The values used to obtain the regression equations reported in Table 2 were read off thermograms similar to that shown in Fig. 1. The regression equations were used to generate at each T_{iso} the corresponding smoothed experimental values of t_{ig} that were compared with those predicted by the model.

IGNITION MODEL

The mathematical description of the ignition process will vary in degree of complexity depending on the simplifying assumptions that can be made. However these will depend on the experimental situation. For the ignition of polymer powders with a constant furnace temperature the energy balance can be written as:

$$\frac{d(mH)}{dt} = Ah_c(T_{air} - T_s) + A\mathscr{F}\sigma(T_{iso}^4 - T_s^4) - r\,\Delta H_r \tag{1}$$

where m = sample mass; H = enthalpy per unit mass; A = effective surface area of sample for heat transfer; h_c = convective heat transfer coefficient; T_{air} = temperature of the air; T_{iso} = temperature of the furnace; T_s = temperature of the sample; $\mathscr{F}$= a factor for radiation which reduces to ϵ the emissivity of the sample for the case of a small body in a large enclosure [7];

σ = the Boltzmann constant; r = the rate of reaction; ΔH_r = the heat of reaction.

The first term in eqn. (1) represents the enthalpy change of the system with time while the next two terms represent the energy absorbed by the sample from the surrounding air by convection and from the furnace by radiation. The last term represents the contribution due to reaction. Here one should note that eqn. (1) is only applicable for the case where the temperature is uniform throughout the sample. For the ignition of a small amount of polymer powder the assumption of uniform sample temperature is justified, since the characteristic thickness of the sample is so small that the internal heat resistance can be neglected.

If the rate of reaction, $r(-\mathrm{d}m/\mathrm{d}t)$, during the heating period is negligible, then the first term in eqn. (1) can be simplified:

$$\frac{\mathrm{d}(mH)}{\mathrm{d}t} = m\frac{\mathrm{d}H}{\mathrm{d}t} + H\frac{\mathrm{d}m}{\mathrm{d}t} \approx m\frac{\mathrm{d}H}{\mathrm{d}t} \tag{2}$$

Furthermore, when the mass loss is negligible, the enthalpy change is solely due to the change of sensible heat, i.e.,

$$m\frac{\mathrm{d}H}{\mathrm{d}t} = m\frac{\mathrm{d}(C_\mathrm{p}T_\mathrm{s})}{\mathrm{d}t} \tag{3}$$

where C_p is the heat capacity of the sample. Substituting eqns. (2) and (3) into eqn. (1) and assuming $T_\mathrm{air} = T_\mathrm{iso}$, $r \to 0$ and $\mathscr{F} \to \epsilon$, we obtain:

$$m\frac{\mathrm{d}(C_\mathrm{p}T_\mathrm{s})}{\mathrm{d}t} = Ah_\mathrm{c}(T_\mathrm{iso} - T_\mathrm{s}) + A\epsilon\sigma(T_\mathrm{iso}^4 - T_\mathrm{s}^4) \tag{4}$$

One can also combine the convection and radiation effects by introducing a radiation heat transfer coefficient h_r which is defined in this case as:

$$\epsilon\sigma(T_\mathrm{iso}^4 - T_\mathrm{s}^4) = h_\mathrm{r}(T_\mathrm{iso} - T_\mathrm{s}) \tag{5}$$

where

$$h_\mathrm{r} = \epsilon\sigma(T_\mathrm{iso}^3 + T_\mathrm{iso}^2T_\mathrm{s} + T_\mathrm{iso}T_\mathrm{s}^2 + T_\mathrm{s}^3) \tag{6}$$

Equation (4) then becomes

$$m\frac{\mathrm{d}(C_\mathrm{p}T_\mathrm{s})}{\mathrm{d}t} = A(h_\mathrm{c} + h_\mathrm{r})(T_\mathrm{iso} - T_\mathrm{s}) \tag{7}$$

A numerical solution of eqn. (7) is only possible if the values of C_p, h_c and h_r are known throughout the temperature range of interest. However, by assuming that these parameters are only slightly dependent of temperature, one can integrate the equation between the initial temperature T_in and the ignition temperature T_ig to obtain the following equation:

$$t_\mathrm{ig} = \left(\frac{m}{A}\right)\left(\frac{C_\mathrm{p}}{h_\mathrm{c} + h_\mathrm{r}}\right)\ln\left(\frac{T_\mathrm{iso} - T_\mathrm{in}}{T_\mathrm{iso} - T_\mathrm{ig}}\right) \tag{8}$$

where the values of C_p, h_c and h_r are determined at the average sample temperature (T_{av}), defined as $(T_{in} + T_{ig})/2$.

RESULTS AND DISCUSSION

Figure 1 shows the temperature and mass-loss curves for an ignition run for PP when the furnace temperature was set at 550°C. It took about 9 s for ignition to occur under the conditions of this experiment. The zero time was located at the point where the temperature–time curve began to deflect from the base line, which represents room temperature. From Fig. 1 one can see that a large part of the time to ignition is due to the heating-up stage which ends when the material begins to decompose. In Fig. 1 this period is defined by t_d (i.e. time to decomposition). The difference between t_{ig} and t_d is the time it takes for the material to decompose, move away into the oxidant stream, mix with it and ignite. For PP at 550°C this stage was terminated within 4.1 s and the mass-loss to ignition was $\sim 38\%$. The mass loss to ignition, time to ignition, and so on varied with T_{iso} and polymer type.

The temperature at which ignition occurred (T_{ig}) was also read off the curves. Its value was always less than T_{iso} and was visibly correlated with it (Table 2)—a feature of this set-up. In previous studies on polymer ignition the quartz tube was attached to the sample housing unit [6,7]. Such a trend with temperature was not observed—the relationship was haphazard. The time lag before the quartz tube reaches the isothermal temperature will depend on its wall thickness and on the value of T_{iso} used. Details regarding the experimental aspect of this work will be the subject of a separate publication.

Test of model

The following equation was used to calculate t_{ig}:

$$t_{ig} = \left(\frac{m}{A}\right)\left(\frac{C_p}{h_c + h_r}\right) \ln\left(\frac{T_{iso} - T_{in}}{T_{iso} - T_{ig}}\right) \tag{8}$$

The parameters in eqn. (1) have been defined in the previous section. The sample mass (m) was varied around 3.0 mg in the cases of PP and PVA and was closer to 4 mg in the case of PS. The actual sample mass for each run was used to calculate t_{ig}. The values of C_p in Table 1 were assumed to be sufficiently close to those of the tested material. To estimate the free convection heat transfer coefficient (h_c) the following equation was used which is applicable when the product of the Prandtl number (Pr) and the Grashoff number (Gr) falls between 10^{-2} and 10^2 [8].

$$N_u = \frac{h_c D}{k} = 1.02(Pr \times Gr)^{0.148} \tag{9}$$

The physical properties of air were calculated at the average film temperature, i.e. $(T_{av} + T_{iso})/2$.

In the calculation of h_r an effective emissivity of 0.3 was assumed. This value was arrived at by calculating the geometric mean value of the polymer emissivity (~ 0.81) and the emissivity of the platinum pan (~ 0.11) [9]. The assumption is reasonable considering that the lower part of the sample was covered by the platinum pan.

To calculate the characteristic dimension, D, in eqn. (9), it was first assumed that $D = d_p$, the average particle diameter which was 0.4 mm in the case of PP (Table 1). This implies that when the material was added onto the TGA sample pan, it spread out a length L such that only one layer formed. The value of L shown in Table 3 was calculated by dividing the sample volume by the cross sectional area of a cylinder of diameter equal to D. The sample volume was calculated by dividing the sample mass by the densities in Table 1.

Table 3 shows the predicted values of T_{iso} at 550°C up to 700°C in the case of PP for different assumed values of D. Assigning a value of $D = 2d_p$, i.e. 0.8 mm, provides a good estimate of t_{ig} with an error of about 15%. From Fig. 2 one can deduce that D is somewhat less than $2d_p$, i.e., we do not really have two perfect layers, one on top of the other. The same conclusions can be made regarding PVA (Fig. 3). However, in the case of PS (Fig. 4) there is good agreement with the experimental results when D is assigned a value equal to $d_p = 0.9$ mm. These results lead one to conclude that better predictions may be obtained when particles having a $d_p \approx 1$ mm are used, since the particles can be carefully spread onto the sample pan in one layer.

The assumption that mass loss, hence rate of reaction prior to ignition, is small is basically correct when $T_{iso} \geq 600$°C, as shown in Table 4. However, there was still good agreement between the experimental and the predicted

TABLE 3

Parameters for calculating t_{ig} at different t_{iso} for PP

T_{iso} (°C)	T_{ig} [a] (°C)	D (mm)	L (mm)	A/m ($m^2\ kg^{-1}$)	h_c ($W\ m^{-2}\ K^{-1}$)	h_r ($W\ m^{-2}\ K^{-1}$)	$(t_{ig})_{cal}$ (s)	$(t_{ig})_{exp}$ (s)
550	425	0.4	27.3	11.1	84.0	22.3	3.4	8.4
		0.8	6.8	5.5	57.3	22.3	9.1	
600	399	0.4	27.3	11.1	86.7	24.4	2.4	5.5
		0.8	6.8	5.5	58.9	24.4	6.4	
650	374	0.4	27.3	11.1	88.6	26.7	1.8	4.0
		0.8	6.8	5.5	60.2	26.7	4.8	
700	348	0.4	27.3	11.1	90.8	29.2	1.4	3.2
		0.8	6.8	5.5	61.8	29.2	3.6	

[a] T_{ig} was calculated from the regression equation in Table 2.

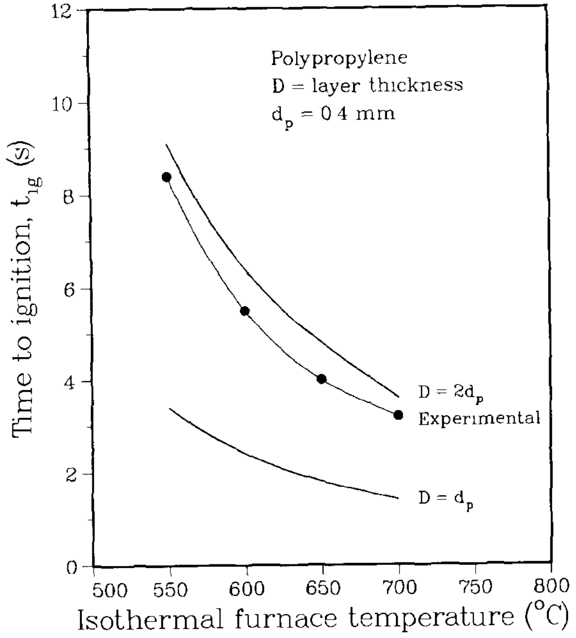


Fig. 2. Comparison between experimental and predicted time to ignition for polypropylene.

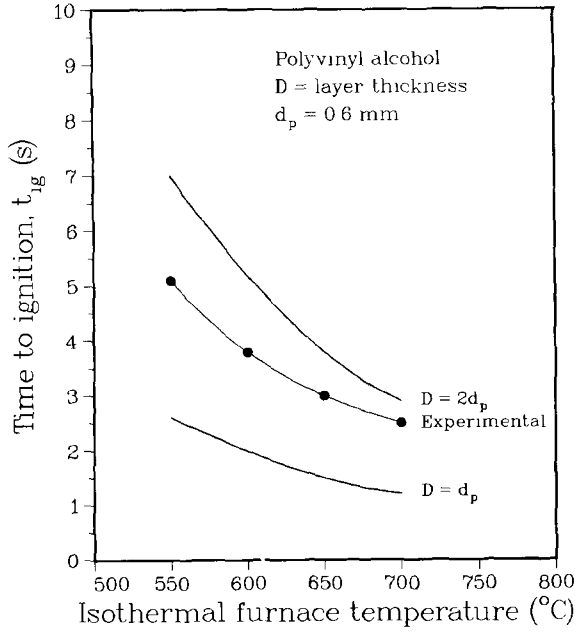


Fig. 3. Comparison between experimental and predicted time to ignition for poly(vinyl) alcohol.

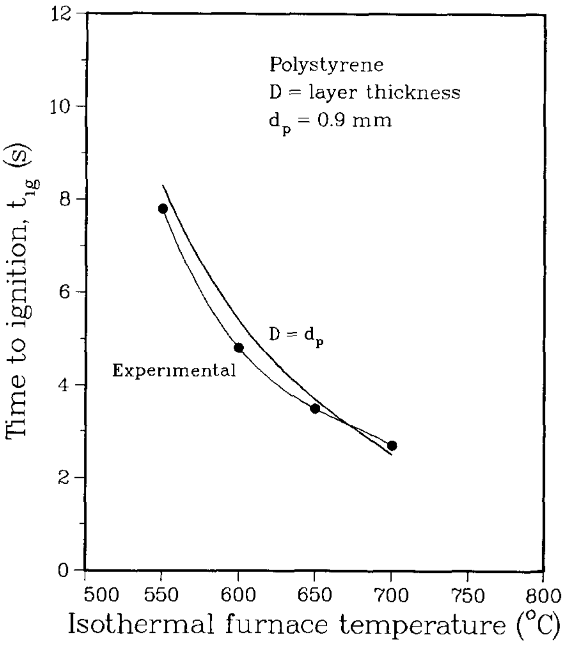


Fig. 4. Comparison between experimental and predicted time to ignition for polystyrene.

value of t_{ig} when the mass loss was ~ 38%, e.g. PP at 550°C. This implies that:

$$\left(m\frac{\mathrm{d}H}{\mathrm{d}t} + H\frac{\mathrm{d}m}{\mathrm{d}t} + r\Delta H_{\mathrm{r}}\right) \approx \left(m_{\mathrm{i}}\frac{\mathrm{d}H}{\mathrm{d}t}\right) \tag{10}$$

where m_{i} is the initial mass, and the parameters to the left and right hand side of the equation are, respectively, in the presence and absence of decomposition.

TABLE 4

Decomposition parameters for PP

T_{iso} (°C)	t_{ig} (s)	t_{d} (s)	% mass loss to ignition	$\Delta m/\Delta t$ [a] (mg s^{-1})
550	8.6	4.5	38	0.29
600	6.1	3.7	10	0.13
650	3.6	3.1	2.5	0.15
700	3.1	2.8	2.0	0.25

[a] $\Delta t = t_{ig} - t_{d}$.

CONCLUSIONS

The results obtained in this work show that it is possible to predict with reasonable accuracy time to ignition of polymers in a TGA using the simplified model which neglects the effect of heat due to chemical reaction.

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