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Comments

LIFETIME PREDICTION FOR POLYMERS VIA THE TEMPERATURE OF INITIAL DECOMPOSITION*

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In the paper [1], the authors proposed a thermogravimetric non-isothermal procedure to predict the thermal lifetime of polymeric materials by using the temperature of initial decomposition, T_{id}, as a failure criterion. This procedure was applied in order to predict the thermal lifetime of seven polymeric materials.

Some critical remarks in connection with: (1) the relationship for thermal lifetime prediction and (2) the method of the kinetic parameters evaluation from non-isothermal data, will be made below.

The relationship for thermal lifetime prediction

In order to evaluate the thermal lifetime of the polymeric materials, Dobkowski and Rudnik [1] have used the relationship:

$$t_f = \frac{f(P)}{A}\exp\left(\frac{E}{RT}\right) \tag{1}$$

where t_f is the time to failure of the selected polymer property, P is the relative property, $f(P)$ is the function of the polymer property change, A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

This equation was derived by Dakin [2, 3] who proposed an approach to thermal degradation of the polymeric materials based on chemical rate theory. Dakin [2, 3] considered that the rate of the thermal degradation of the property is given by the relationship:

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[*] Comments on the paper by Z. Dobkowski and E. Rudnik, J. Thermal Anal. 48 (1997) 1393.

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$$-\frac{\mathrm{d}P}{\mathrm{d}t}=g(P)A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where $g(P)$ is the differential function of the property degradation.

Through integration of this equation, one obtains:

$$t_\mathrm{f}=\frac{f(P)}{A}\exp\left(\frac{E}{RT}\right) \tag{3}$$

where:

$$f(P)=-\int_1^P\frac{\mathrm{d}P}{g(P)} \tag{4}$$

$f(P)$ is the integral function of the property degradation.

Dobkowski and Rudnik [1] have assumed the mass loss as a specific polymer property and, consequently, P is equal with the degree of conversion of the thermal degradation (α). Also, it was assumed that the thermal degradation of the polymeric material is kinetically described by reaction order model:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A(1-\alpha)^\mathrm{n}\exp\left(-\frac{E}{RT}\right)\equiv f(\alpha)A\exp\left(-\frac{E}{RT}\right) \tag{5}$$

where n is the reaction order.

Finally, these authors have considered:

$$f(\alpha)\equiv f(P) \tag{6}$$

In connection with these hypotheses, we note:

a) for the property = mass loss, $P=1-\alpha$, because, only so for $t=0$, $\alpha=0$ and $P=1$;

b) the relationship (6) is not valid because the relationship (2) turns into relationship (5) only for $P=1-\alpha$ and

$$g(P)\equiv g(\alpha)=(1-\alpha)^\mathrm{n} \tag{7}$$

In the reaction order model:

$$f(\alpha)=-\int_0^\alpha\frac{\mathrm{d}(1-\alpha)}{(1-\alpha)^\mathrm{n}}=\begin{cases}-\ln(1-\alpha) & \text{for } n=1\\ \dfrac{1-(1-\alpha)^{1-\mathrm{n}}}{1-n} & \text{for } n\neq1\end{cases} \tag{8}$$

The confusion between $f(P)$ and $g(P)$ which was made by Dobkowski and Rudnik [1] led to the wrong result: $f(\alpha=0)=1$ ($\alpha=0$ corresponds to the temperature of the initial decomposition, T_id). This is in disagreement with the relationship (8) from which results $f(\alpha=0)=0$. Dobkowski and Rudnik [1] used the wrong relationship $f(\alpha=0)=1$ and have derived the following relationship:

$$t_f = \frac{1}{A_{id}} \exp\left(\frac{E_{id}}{RT_{id}}\right) \quad (9)$$

where the index *id* corresponds to $\alpha = 0$.

This relationship is in disagreement with the theory of the thermal lifetime prediction [4, 5] in which the thermal lifetime is evaluated for a certain endpoint criterion, i.e. in our case, for an imposed α value different of zero and lower than 1.

The method of the kinetic parameter evaluation from non-isothermal data

In order to evaluate A_{id} and E_{id}, Dobkowski and Rudnik [1] have used the Kissinger method [6] applied to the initial temperatures of the thermal decomposition, evaluated from the thermogravimetric curves plotted at some heating rates. We consider that this method is not adequate because the Kissinger relationship for evaluation of the activation parameters is applicable only for the maximum rate conditions. Therefore, linearity of the plots $\log(\beta/T_{id}^2)$ *vs.* $1/T_{id}$ (β is the heating rate), obtained for 3–5 values of the heating rate is fortuitous. Moreover, the poor precision of T_{id} evaluation from TG curve should be noted. On the other hand, A_{id} and E_{id} can be evaluated from the parameters of the Flynn–Wall–Ozawa straight lines [7, 8] ($\log\beta$ *vs.* $1/T_{id}$). These straight lines are shown in Fig. 1 from [1]. Table 1 contains comparatively the values of the activation energy evaluated by Flynn–Wall–Ozawa method for α=0 and those evaluated by Dobkowski and Rudnik [1]. Also, the relative deviations of E_K from E_{FWO} (d%) have been listed. It can be noted that in some cases $|d\%|>10\%$. The differences between E_{FWO} and E_K should be attributed to the evaluation of E_K by an inadequate method and to inherent errors in the evaluation of T_{id} values.

Table 1 Activation energy of initial decomposition

Material	E_K/kJ mol^{-1}	E_{FWO}/kJ mol^{-1}	d%
PC-A (st)	81.4	88.3	–7.8
PC-A (nst)	88.9	83.4	6.6
PBT	79.6	88.7	–10.3
PET	81.0	91.4	–11.4
PPO	85.3	94.7	–9.9
PVC (e)	69.7	79.1	11.9
PVC (c)	76.5	83.0	–7.8

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