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Note

LIFETIME PREDICTION FOR POLYMERS VIA THE TEMPERATURE OF INITIAL DECOMPOSITION
PART 2

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Introduction

Several years ago, in the paper entitled as above, considered here as Part 1 [1], we have proposed the temperature of initial decomposition T_{id} determined from TG and DTG curves of mass loss as a parameter applied for the characterisation of the ultimate thermal behaviour of polymer materials. Thus, the thermal stabilities of polymers can be simply compared using the linear plots of $1/T_{id}$ *vs.* $\log\beta$, where β is the heating rate in deg min^{-1}, Fig. 1 in [1]. Therefore, an influence of additives to polymer materials, and/or of applied processing techniques, on the thermal resistance and stability of polymers can simply be evaluated. Moreover, the time – temperature characteristics in the form of the chart where the time to failure t_f in min obtained from the T_{id} data is plotted *vs.* reciprocal T in K^{-1} have been proposed for lifetime prediction, Fig. 2 in [1]. Similar plots of β and t_f against reciprocal absolute temperature, where the time to failure t_f was determined in various ways, can be found in literature [2–11]. Using T_{id} for assessing failure criteria has an essential advantage over the Kissinger's temperature of decomposition at the maximum decomposition rate T_{dmax}, namely an investigated material at T_{id} still exists as a polymer and it can be characterized by its E_{ai} at T_{id}. At T_{dmax}, usually a mass of unidentified decomposition products have to be taken into account and such decomposed material, usually not being a polymer any more, is characterised by calculated values of E_{amax}. It has also been mentioned in literature that 'it may be hazardous to use other characteristics than the initial temperatures of decomposition T_i to specify the thermal stability of materials. For example $E_{a\,max}$ may coincide even if T_i are quite different' [4]. We are aware that the precision of T_{id} determination can be low in some cases (e.g. if volatile components are evolved), however, the determination of T_{dmax} can also be imprecise and inaccurate in many cases, cf. [9].

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The use of T_{id} has been checked for 7 types of polymers, i.e. bisphenol A polycarbonate, stabilized and unstabilized, poly(butylene terephthalate) and poly(ethylene terephthalate), polyphenylene oxide, and poly(vinyl chloride), extruded and calendered material, and it has been found convenient for comparison of thermal stability and prediction of lifetime of polymer materials [1].

Recently, the proposed procedure using T_{id} [1], called the Dobkowski and Rudnik (D&R) method, has been applied for the E_a and t_f determinations and for the lifetime prediction in the studies of thermal degradation of biomedical polyurethanes [12]. D&R method has been assessed as 'easy to use' comparing to the Salin and Seferis method [13].

Also recently, critical remarks on the D&R method have been published by Budrugeac [14], nb. using our title [1]. We firmly deny Budrugeac's statements that we 'used the wrong relationship' which 'led to the wrong result'. Therefore, we are ready to discuss details.

Discussion

1. Budrugeac: 'Dobkowski and Rudnik [1] have used the Kissinger method ..... and this method is not adequate'.

D&R. For calculations of E_{id} and A_{id} we used the Kissinger's approach only, starting with the kinetic relationship [15, 16]

$$-(1/V)\mathrm{d}x/\mathrm{d}t = (x/V)\, nA\exp[-E_a/RT] \tag{1}$$

where V is the volume, x is the number of particles of a material, n is the reaction order.

Eq. (1) was differentiated and compared to zero, since for T_{id} we have $\mathrm{d}/\mathrm{d}t(\mathrm{d}x/\mathrm{d}t) = 0$ (any value of TG function at $t = 0$ is still constant and $\mathrm{d}x/\mathrm{d}t$ at $t=0$ is constant), and at T_{id} we have

$$(E_a\beta)/R\,T_{id}^2 = n(x/V)_{id}^{n-1}A_{id}\exp[-E_a/RT_{id}] \tag{2}$$

Then, it has been assumed that the polymer decomposition process can be described as a quasi-first-order reaction, cf. [17], i.e. $n = 1$. Thus, the term $n(x/V)_{id}^{n-1} = 1$, and hence

$$\beta/R\,T_{id}^2 = \{A_{id}\,R/E_a\}\exp[-E_a/RT_{id}] \tag{3}$$

Thus, Eq. (3) has been derived using the sound theoretical basis. Equation (3) for T_{id} was applied for calculations of E_{id} and A_{id} (in a similar way as the Kissinger's equation for T_{dmax}), and then for calculations of time to failure t_f and for the lifetime prediction from the time – temperature plots.

2. Budrugeac: 'linearity of the plots $\log(\beta/T_{id}^2)$ *vs.* $1/T_{id}$ ... obtained for 3–5 values ... is fortuitous'.

D&R. It is usually a disadvantage of any method for E_a calculations that the experimental temperature range is often very narrow and a few experimental points are usually available. Therefore, even 3 experimental points are often used to obtain linear relationships, e.g. for the Ozawa-Flynn-Wall approach [18], or even suggested as a recommendation, cf. Fig. 1 and Fig. 2 in the ISO standard [10]. Of course, the number of experimental points should be as high as possible.

3. Budrugeac: 'poor precision of T_{id} evaluation'

D&R. We are aware of this obvious disadvantage concerning precision, if T_{id} is used, as it has been pointed out above in Introduction. Nevertheless, the determination of T_{id} from TG and/or DTG is possible with a satisfactory precision and accuracy. However, similar disadvantage was also observed for the determination of T_{dmax}.

4. Budrugeac: 'in order to evaluate the thermal lifetime of the polymeric materials, Dobkowski and Rudnik [1] have used the relationship: $t_f = \{f(P)/\mathrm{A}\}\exp(E/RT)$ ... (1) ... This equation was derived by Dakin ... one obtains : $t_f = \{f(P)/A\}\exp(E/RT)$ ... (3)'

D&R. Thus, Budrugeac confirmed that the relationship for t_f used by D&R is theoretically adequate and it agrees with the equation given in literature. Therefore, for T_{id} we can write

$$t_f = \{f(P)_{id}/A_{id}\}\exp(E_{id}/RT_{id}) \tag{4}$$

Eq. (4) can be derived from the Arrhenius plot $k(T) = A\exp(-E/RT)$ and the state of chemical reaction $F_a(t_i) = k_i\,(T_i)\,t_i$ cf. [10].

The identical equation was given also by Montanari and Lebok [5] for the lifetime L of electrical insulating materials

$$L = \{F(p_n)/k_t\}\exp(B/T) \tag{5}$$

where $F(p_n)$ is a function of a property p at the end-point, while k_t and B are parameters of the Arrhenius equation.

5. Budrugeac: 'Dobkowski & Rudnik used the wrong relationship $f(\alpha=0) = 1$ and have derived the following relationship: $t_f = \{1/A_{id}\}\exp(E_{id}/RT_{id})$ ...(9) .... This relationship is in disagreement with the theory of the thermal lifetime prediction [4, 5] {as quoted by Budrugeac in [14]} in which the thermal lifetime is evaluated for a certain endpoint criterion'.

D&R. Equation (4) is adequate in general, as it has been proved above in item 4. Now it should be noted that any polymer property $f(P)$, considered for the determination of time-to-failure during polymer degradation is treated as a relative one. Also in Eq. (5) a property p 'is expressed relative to an initial value' [5–7]. Therefore, any initial value of relative property function $f(P)_{id}$ (i.e. at $t = 0$ and $\alpha = 0$) is equal to 100 % (in percentage), or it is equal to 1 (if fractions are taken into account). Then

$$t_f = \{1/A_{id}\}\exp(E_{id}/RT_{id}) \tag{6}$$

should be valid.

Thus, we have found that the relative property value at t=0 and α=0 is $f(P)_{\mathrm{id}}=1$ which gives Eq. (6) from Eq. (4).

Moreover, if time-to-failure can be measured directly, e.g. as the oxidation induction time (OIT), [8, 19, 20] we have

$$t_{\mathrm{f}}(\mathrm{OIT}) = C\exp(E_{\mathrm{a}}/RT) \tag{7}$$

where time OIT is the initial time-point of the oxidation curve (onset on the curve) and simultaneously end-point-criterion for the endurance of a material observed during thermooxidative degradation process of a polymer. Then, the lifetime can be predicted from the time-temperature plot, cf. [8, 20].

Therefore, there is not any disagreement with the theory of the lifetime prediction and references quoted by Budrugeac [14] do not contain any evidence against the D&R method using T_{id}. It should be noted, however, that Budrugeac quoted in [14] the old 2nd edition of the IEC Standard 216 (1974) which was long ago withdrawn, [21], and the lifetime theory is not given in the actual 5th edition of the IEC Standard 216 [21]. Actually, the temperature index (TI) is only recommended for the endurance of electric materials [21]. The value of TI in °C is obtained from the plot of time to failure in hours *vs.* temperature in °C by linear extrapolation from 2 points for 10 000 and 20 000 h (2.3 years).

6. Budrugeac: ‘the thermal lifetime is evaluated for a certain endpoint criterion’.

D&R. The procedure for the thermal endurance of electrical insulating materials [5–7] should be started from: (1) selecting a property for investigations, and (2) choosing a certain endpoint criterion specific for a selected property. For example, Montenari [7] recommended electrical strength (*ES*), tensile strength (*TS*), and mass or mass loss (*W*) as properties that should be selected for investigations of electrical insulating materials. In the case of *W*, which is the subject of our interest, the thermal endurance graphs were obtained by mass end point 3%. Similarly, 0% mass loss at the initial decomposition temperature can be considered as the end-point criterion. Thus, the first sign of deterioration (i.e. the initial mass loss) is taken as the end-point criterion similarly as in the case of OIT.

7. Budrugeac: ‘Table 1 ... the activation energy evaluated by Flynn-Wall-Ozawa method for α=0 and those evaluated by Dobkowski and Rudnik [1] ... the relative deviations of E_{K} {i.e. D&R data} from E_{FWO} (d%) {i.e. Flynn-Wall-Ozawa method} have been listed ... in some cases $d\% > 10\%$ ... the differences can be attributed to the evaluation of E_{K} by an inadequate method’.

D&R. As it has been proved in items 1 and 4–6, our method is theoretically adequate, and Budrugeac’s calculations of d% revealed that our method is also experimentally reliable. It is evident that the differences d% are statistically dispersed within the limits of ±12% with the mean value of –4% and SD = 8.6%, calculated only for 7 types of polymers. Such statistical dispersion can be attributed to errors of both FWO and D&R methods, including errors in determination of T_{id} values.

Thus, Budrugeac [14] proved the validity of the D&R method by comparison with the FWO method and found that both methods are consistent within the limits of ±12 %.

Conclusions

The Dobkowski and Rudnik method for lifetime prediction for polymers via the temperature of initial decomposition T_{id} is based on recognised theoretical backgrounds, given in literature. The method has already been applied by others and it has experimentally been proved as 'easy to use' and more convenient than the Salin and Seferis method. Moreover, it has been proved by Budrugeac that the Dobkowski and Rudnik method for calculating the activation energy of initial decomposition is consistent with the Flynn-Wall-Ozawa method within the limits of ±12 %.

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