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LIFETIME PREDICTION FOR POLYMERS VIA THE TEMPERATURE OF INITIAL DECOMPOSITION

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Abstract

The temperature of initial decomposition T_{id} was determined from TG and DTG curves of mass loss during thermooxidative polymer decomposition in an environmental air atmosphere. The values of T_{id} were applied for comparison of the thermal stabilities of several polymers, e.g. PC-A, PBT, PET, PPO and PVC. Both the activation energies of initial decomposition E_{id} and the preexponential terms A_{id} of the Arrhenius equation were calculated by using the Kissinger approach. The initial mass loss is proposed as a criterion for calculation of the time to failure t_f from the known values of E_{id} and A_{id}, and hence for a prediction of the lifetime of polymer materials.

The following thermal stability sequence was found for the investigated polymer materials: PC-A (st) >PC-A (nst) >PBT>PET>PPO>PVC (e) >PVC (c). The activation energy of initial decomposition had a mean value of $E_{id}=83$ kJ mol^{-1} for PC-A, PBT, PET and PPO, and $E_{id}=73$ kJ mol^{-1} for the PVC samples.

The calculated time to failure, t_f, for PC-A, PET and PVC under specified conditions was in reasonable agreement with published experimental data.

The proposed parameters of thermal decomposition T_{id}, E_{id} and t_f, can be applied for the characterization and comparison of various polymer materials, and for a prediction of their lifetime.

Keywords: activation energy of initial decomposition, comparison of thermal stability, lifetime prediction, temperature of initial decomposition, thermal analysis of polymers

Introduction

Prediction of the lifetime of polymers, or the time to failure of specified properties during long-term service, is of great commercial importance. Thus, the highest permissible service temperature and/or the recommended time of service under specified conditions can be estimated to assess the scope of application of polymeric materials, and in particular engineering thermoplastics [1, 2]. Moreover, time – temperature characteristics are also important as concerns the relatively short-time behaviour of polymers, e.g. during processing [3]. Several methods applied for these purposes involve common aging procedures for measurement of a chosen property P, which is a crucial one for a given application, e.g. specified mechanical or electrical properties. Selected failure criteria, e.g. maintenance of 50% of the initial flexural strength [1] or of ultimate elongation [4, 5], a 2% increase in density

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[4] or a 2% mass loss [4], and forms of the Arrhenius equation are used. Methods of thermal analysis, and in particular thermogravimetric procedures, have also been applied for the prediction of the life-time of polymers, e.g. with a 5% mass loss as a failure criterion [2, 6, 7], and have been recommended for standard estimation of the thermal life of polymeric materials [8].

The present paper describes a thermogravimetric non-isothermal procedure for investigation of the time – temperature characteristics of polymers. The lifetime of polymeric materials has been estimated by using the temperature of initial decomposition, T_{id}, as a failure criterion.

Theory

It is usually assumed that the rate of change of a measured polymer property P is related to the rate constant of polymer decomposition [1], and

$$f(P) = t_f k(T) \tag{1}$$

where $f(P)$ is the function of the polymer property change, t_f is the time to failure of the selected polymer property, and $k(T)$ is the rate constant at temperature T, described by the Arrhenius equation:

$$k(T) = A \exp(-E/RT) \tag{2}$$

where A is the preexponential term, in reciprocal time units, E is the activation energy, in J mol^{-1}, R=8.31441 J mol^{-1} K^{-1} is the gas constant, and T is the temperature, in K. By combining Eq. (1) and (2), we have

$$t_f = \{f(P)/A\} \exp(E/RT) \tag{3}$$

For the complex kinetics of decomposition of polymeric materials, the following equation is usually applied [6, 9] (cf. also [3, 10]):

$$\mathrm{d}\alpha/\mathrm{d}t = A(1-\alpha)^n \exp(-E/RT) \tag{4}$$

where α is the fractional conversion (or conversion degree) evaluated from the mass loss, and n is the order of reaction. It is usually assumed that the polymer decomposition process can be described as a quasi-first-order reaction [11].

Thus, it has been assumed for Eq. (4) that the conversion α is proportional to the amount of non-decomposed material, i.e. $f(\alpha) = 1-\alpha)^n$, and the polymer decomposition process can be described by the Arrhenius equation [2].

Equation (4) has been solved by Kissinger [12]. He applied the maximum decomposition rate conditions to Eq. (4), i.e. $\mathrm{d}(\mathrm{d}\alpha/\mathrm{d}t)\mathrm{d}t=0$ for $\mathrm{d}\alpha/\mathrm{d}t=\max$, and after differentiation found

$$\beta/T_{md}^2 = (A_{md}R)/E_{md} \exp(-E_{md}/RT_{md}) \tag{5}$$

where $\beta = dT/dt$ is the heating rate, and the subscript *md* denotes values at the maximum decomposition rate.

The same conditions of differentiation of Eq. (4) are also satisfied for $\alpha = 0$ corresponding to the temperature of initial decomposition T_{id}, and T_{id} can be applied in Eq. (4) instead of T_{md}. Thus, the following equation, similar to Eq. (5), is obtained [3]:

$$\beta/T_{id}^2 = (A_{id}R)/E_{id} \exp(-E_{id}/RT_{id}) \tag{6}$$

Hence, the plot of $\ln\beta/T_{id}^2$ *vs.* $1/T_{id}$ gives the values of E_{id} and A_{id}.

We assumed that the mass loss during non-isothermal decomposition can be taken as a specific polymer property, i.e. $f(P) = f(\alpha)$, and the first change of this property is observed at temperature T_{id}. At T_{id} we have $\alpha = 0$, and hence $f(\alpha) = 1$. Taking these into account in Eq. (3), we found [3]

$$t_f = (1/A_{id}) \exp(E_{id}/RT_{id}) \tag{7}$$

Thus, Eq. (7) is identical in form with that proposed later by Langlois *et al.* [4] for crosslinked linear PE.

Experimental

Materials

The following polymer samples were investigated:

- PC-A (st) – bisphenol A polycarbonate, stabilized pellets of commercial Makrolon LS3100, Bayer AG;
- PC-A (nst) – bisphenol A polycarbonate, non-stabilized powder Bistan AF, pilot plant product of 'Zachem' Chemical Works, Bydgoszcz, Poland;
- PBT – poly(butylene terephthalate), commercial polymer Crastin SK 605, Ciba Geigy;
- PET – poly(ethylene terephthalate), an injection moulded grade for polymer blends, 'Elana' Chemical Works, Toruń, Poland;
- PPO – poly(2,6-dimethylphenylene oxide), a pilot plant product of ICRI, Warsaw, Poland, in the form of non-stabilized powder;
- PVC (e) – poly(vinyl chloride), extruded material; and
- PVC (c) – poly(vinyl chloride), calendered material.

Both polymer materials PVC (e) and PVC (c) were obtained from the polymer processing works 'Cefol-Erg', Wojciechów, Poland.

Instrument and procedure

A Q 1500D derivatograph (MOM, Budapest) was used. Polymer samples of about 40 mg were heated from 30 to 1000°C at various heating rates in the range from 1.25 to 20°C min^{-1}. All experiments were performed in an environmental air atmosphere without induced circulation. The temperature of initial decomposition,

T_{id}, for different heating rates was determined from the TG and DTG curves as the point of deviation from linearity corresponding to the mass loss due to polymer degradation (cf. [3, 10, 13]).

Results and discussion

Comparison of thermal resistances of polymer materials

The experimental results on the temperature of initial decomposition T_{id} are shown in Fig. 1 as the dependence $1/T_{id}$ *vs.* $\log\beta$. It was found that the plots of $1/T_{id}$ *vs.* β are linear for the different polymers, and the positions of the plots correspond to the thermal resistances of the commercial polymer materials. The following thermal stability sequence was found for the investigated polymer materials:

$$\text{PC–A(st)} > \text{PC–A(nst)} > \text{PBT} > \text{PET} > \text{PPO} > \text{PVC (e)} > \text{PVC (c)}$$

It was proposed that a single value of T_{id}, i.e. the conventional value of T_{id} at $\beta = 1°\text{C min}^{-1}$, $T_{id(1)}$, can be applied for comparison of the thermal resistances of the investigated polymers. The value of $T_{id(1)}$ was calculated from (Table 1).

$$1/T_{id} = 1/T_{id(1)} - m(\log\beta) \qquad (8)$$

Table 1 Temperature of initial decomposition T_{id}

Parameters	Polymers						
	PC-A(st)	PC-A(nst)	PBT	PET	PPO	PVC(e)	PVC(c)
$T_{id(1)}$/°C at $\beta = 1°\text{C min}^{-1}$	326	297	265	231	224	195	182
Correlation coeff. r^2	1.00	0.98	0.96	0.94	0.94	0.94	0.97
Slope, $m \times 10^4$	-2.06	-2.18	-2.05	-1.99	-1.92	-2.30	-2.19

It was found that the slope of dependence (8) is approximately constant for all the investigated polymers. However, two groups of results can be distinguished:

(1) for PC-A, PBT, PET and PPO, where the mean value of the slope is $m = -2.04 \times 10^{-4}$ with a variation coefficient of 4.2%, and

(2) for PVC material, where the mean slope is $m = -2.25 \times 10^{-4} \pm 2.4\%$.

It seems that the conventional value of $T_{id(1)}$, and also the plots in Fig. 1, can be applied not only for

– comparison of the thermal resistances of different polymer materials (in this case in air atmosphere), but also for

– assessment of the effects of thermal stabilizers on the thermal resistances of polymers (cf. PC-A (st) and PC-A (nst): PC-A (st) obviously exhibits better thermal resistance than PC-A (nst), and

– assessment of the influence of a processing technique on the thermal resistances of polymers (cf. PVC (e) and PVC (c), where the calendered material deterioriated during processing as compared with the extruded PVC).

The values of T_{id} were applied to calculate the activation energy of the initial decomposition, E_{id}, according to Eq. (6), and the time to failure according to Eq. (7).

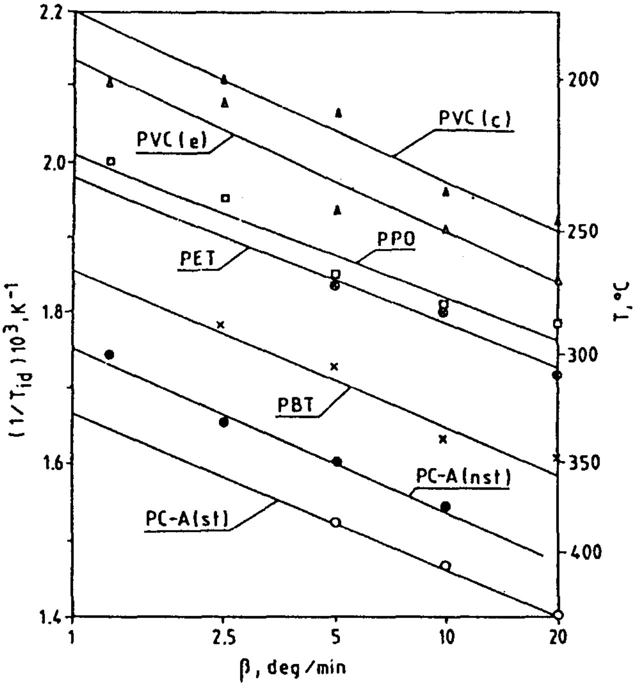

Fig. 1 Comparison of polymer materials using the plot of $1/T_{id}$ *vs.* logβ

Activation energy of initial decomposition

The activation energy of initial decomposition, E_{id}, and the corresponding preexponential term, A_{id}, can be calculated from the Kissinger-type dependence written for T_{id} as Eq. (6). The results of the calculations are given in Table 2.

Table 2 Activation energy of initial decomposition

	Polymers						
	PC-A(st)	PC-A(nst)	PBT	PET	PPO	PVC(e)	PVC(c)
E_{id}/kJ mol^{-1}	81.4	88.9	79.6	81.0	85.3	69.7	76.5
A_{id}/10^{-6} min^{-1}	0.36	4.34	1.94	10.85	43.23	2.54	28.98
Number of data	3	5	4	3	5	5	4
Correlation coeff. r^2	1.00	0.95	0.95	0.92	0.93	0.93	0.96

The value of E_{id} can be regarded as the activation energy of the initial decomposition process monitored by the mass loss. It was observed in general that the values of E_{id} are approximately constant, at abut 80 kJ mol^{-1}, with a variation coefficient of 7.1%. However, two groups of polymer materials can be distinguished, similarly as for T_{id}:

(1) PC-A, PBT, PET and PPO, i.e. three polyesters and a poly(aromatic oxide), where the decomposition process involves chain-breaking at the weakest bonds of the macromolecules, and the mean value of E_{id} is 83 kJ mol^{-1} with a variation coefficient of 4.1%, and

(2) PVC samples with a mean value of E_{id}=73 kJ mol^{-1} and a variation coefficient of 4.7%, where the mechanism of decomposition is rather complex; it involves the initial breaking of C–Cl bonds to form Cl radicals, which are responsible for HCl evolution and polyene formation during the decomposition.

The results on E_{id} seem reasonable, since for group (1) the decomposition is initiated by splitting of the ester C–O linkage, as well as aromatic oxide C–O bonds.In the case of PVC, group (2), the mean value of E_{id} is lower by about 10 kJ mol^{-1}. This suggests that the complex decomposition of PVC is energetically more facile than the splitting of C–O bonds.

The preexponential term A in the Arrhenius-type equations represents a number of acts of the process, according to the Eyring theory for chemical reactions. Hence, a lower A_{id} was found for the stabilized PC-A (st) sample as compared with the nonstabilized PC-A (nst). Similarly, A_{id} for extruded PVC (e) of higher thermal resistance was lower than that for calendered PVC (c) (Table 2).

Lifetime prediction

The mass loss during polymer degradation under environmental air conditions was applied as a criterion for the prediction of the lifetime of the polymer materials. Thus, the time to failure t_f can be calculated from Eq. (7) if the values of E_{id} and A_{id} are known. Typical plots of $\log t_f$ *vs.* $1/T$ for PC-A, PET and PVC are shown in Fig. 2. The calculated values of t_f for selected temperatures are shown in Table 3.

In spite of several uncertainties involved in the calculation of E_{id} and A_{id}, as well as in the extrapolation of time to long term, and/or of temperature from high values

Table 3 Lifetime prediction from the time to failure t_f (examples for 127 and 227°C)

	Polymers						
	PC-A(st)	PC-A(nst)	PBT	PET	PPO	PVC(e)	PVC(c)
$\log t_f$/min, at 127°C	5.073	4.972	4.107	3.542	3.503	2.697	2.528
t_f	82 d	65 d	9 d	2.4 d	2.2 d	8.5 h	5.6 h
$\log t_f$/min, at 227°C	2.947	2.650	2.028	1.426	1.275	0.877	0.530
t_f	14.8 h	7.4 h	1.8 h	27 m	19 m	7.5 m	3.4 m

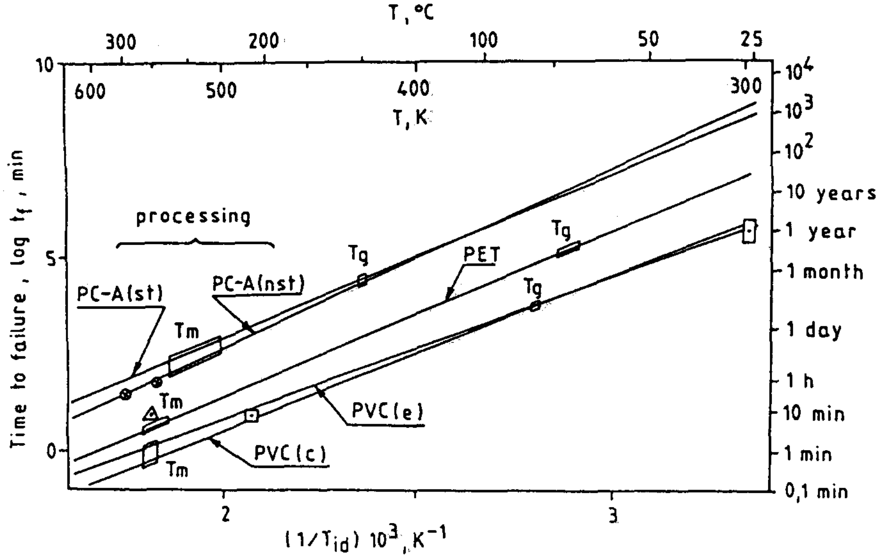

Fig. 2 Chart for life time prediction. Experimental data for PC-A: ⊗ [14], for PET Δ [14], for PVC □ [15]

to room temperature, the obtained results seem reasonable and agree with available experimental data (cf. Fig. 2). Thus, the melt viscosity of PC-A at processing temperatures of 548 and 573 K is stable during 55 and 30 min, respectively [14], and close to the values of t_f obtained from the plot of log t_f *vs.* $1/T$ for P-CA (Fig. 2). Similarly, colour failure is observed within 10 min at 553 K for PET [14]. The UV induction period test for PVC at 483 K indicates the 10 min processing time [15], while outdoor-exposed PVC samples retained the tensile impact properties during a 6 to 24 month exposure, depending on the modifier and stabilizer system [15].

It may be expected that some errors will be involved in the time – temperature extrapolation method if the mechanism of degradation is changed in the extrapolated range. This should be taken into account in particular in the case of PVC, where the mechanism of decomposition is complex and still not completely understood [16]. Nevertheless, the literature data for PVC [15], shown in Fig. 2, are in agreement with the calculated time – temperature line.

Concluding remarks

It has been found that the initial decomposition parameters, such as T_{id} and/or E_{id}, can be applied as conventional and well-defined parameters characterizing the thermal stabilities of polymers. It may be assumed that such parameters correspond to the first moment of breaking of the weakest bonds of the macromolecule, responsible for further decomposition.

The normalized value of $T_{id(1)}$, i.e. T_{id} at a heating rate of $\beta = 1°C\ min^{-1}$, can be used for comparison of the thermal stabilities of different polymer materials. For the same material, the effects of stabilizers and/or the influence of processing techniques on the thermal stabilities of polymers can be investigated.

It has also been found that the activation energy of initial decomposition E_{id} is equal to 83 kJ mol^{-1} for the investigated polyesters and 73 kJ mol^{-1} for PVC.

The time to failure t_f can be calculated, and then the polymer lifetime predicted, from the values of E_{id} and A_{id}. It has been found that the predicted lifetime values of PC-A, PET and PVC are in reasonable agreement with published experimental data, in spite of several uncertainties involved in the time– temperature extrapolation method.

It can be concluded that the proposed parameters of thermal decomposition, i.e. T_{id}, E_{id} and t_f, can be applied for the characterization and comparison of various polymer materials, and for the prediction of their lifetimes.

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