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THERMOANALYSIS STUDY OF THE LIFETIME OF AN AUXILIARY FOR CHEMICAL FIBRE

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ABSTRACT

This paper describes the kinetic study of an organic auxiliary for chemical fibre using thermal analysis. The thermal decomposition reaction order ($n = 0.94$) and activation energy were calculated using the Kissinger and Ozawa methods ($E_K = 144.6$ kJ mol^{-1}, $E_O = 144.0$ kJ mol^{-1}, respectively). The 10% weight-loss lifetime was measured by constant temperature TG and the lifetime equation was deduced as

$$\lg \tau = 7.624 \times 10^3 \frac{1}{T} - 13.172$$

The activation energy calculated in this way was $E_L = 145.98$ kJ mol^{-1}. The 10% weight-loss lifetime of the auxiliary under different temperature regimes was also calculated using this lifetime formula.

INTRODUCTION

There are many methods of measuring the thermal stability of materials. The simplest method is to take the temperature of the extrapolated onset on the TG curve or the peak temperature of the thermal decomposition peak on the DTA curve as the "thermal decomposition temperature". However, this method has been found to be too approximate. In this paper, the determination of thermal stability using the lifetime method and the 10% weight-loss lifetime formula is improved.

EXPERIMENTAL

Kissinger's method [1]

The TG–DTA curves for an auxiliary for chemical fibre were determined using a simultaneous TG–DTA apparatus (Rigaku, Japan). Sample weights used were 5–7 mg and the heating rates (ϕ) were 20, 10, 5 and 2.5 K min^{-1}. The TG–DTA curves are illustrated in Fig. 1.

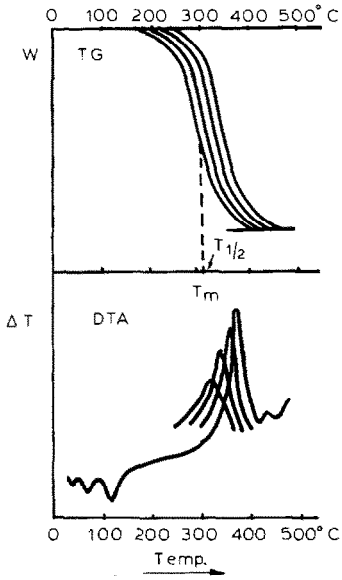

Fig. 1. TG and DTA curves for the auxiliary at different heating rates.

As shown in Fig. 1, the initial weight-loss temperature on the TG curves and the exothermic peak temperature on the DTA curves decrease with decreasing heating rate. These data are given in Table 1 where t_m and T_m are the peak temperatures of the DTA curves in degrees centigrade and Kelvin,

TABLE 1

The kinetic data of the auxiliary by the Kissinger and Ozawa methods

ϕ (K min^{-1})	t_m (°C)	T_m (K)	$1/T_m \times 10^3$	$\ln(\phi/T_m^2)$	$t_{0.5}$ (°C)	$T_{0.5}$ (K)	$1/T_{0.5} \times 10^3$	lg ϕ
20	372	645	1.5504	−9.9427	351	624	1.6026	1.3010
10	351	624	1.6026	−10.5697	337	610	1.6373	1.0000
5	342	615	1.6260	−11.2338	326	599	1.6694	0.6990
2.5	328	601	1.6639	−11.8809	309	582	1.7182	0.3979

TABLE 2

The lifetime tests on the auxiliary using constant temperature TG

No.	Sample (mg)	10% (mg)	Constant temperature		Time (min)	Weight loss (mg)	Lifetime (min)
			t (°C)	T (K)			
1	4.8	0.48	215 ± 1	488 ± 1	100	0.17	282.4
2	6.3	0.63	236 ± 1	509 ± 1	64	0.63	64

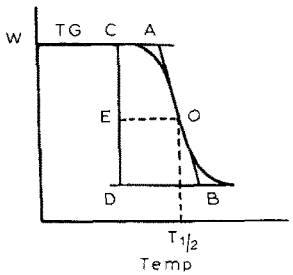

Fig. 2. Illustration of the TG median point.

respectively, and $t_{0.5}$ and $T_{0.5}$ are the temperatures of the half weight-loss point of the TG curves in centigrade and Kelvin, respectively, as in Fig. 2.

According to Kissinger's method, the shape index I of the DTA peak in Fig. 3 is 0.56 and the reaction order n is 0.94. The data of the relationship $\ln(\phi/T_m^2)$ versus $1/T_m$ can be calculated by one-place linear regression on a programmable calculator and the following results were obtained: correlative coefficient $r = 0.9876$; regression coefficients $a = 17.1108117$, $b = -17.39439$; and $E_K = 17.39439 \times 8.314$ J mol^{-1} = 144.61 kJ mol^{-1} (34.71 kcal mol^{-1}).

Ozawa's median point method [2]

Ozawa's equation is

$$\frac{d(\lg\phi)}{d(1/T_{0.5})} = -0.4567\frac{E_O}{R} \tag{1}$$

The measurement of $T_{0.5}$ using the $\lg\phi$ and $1/T_{0.5}$ values listed in Table 1 is illustrated in Fig. 2 and E_O can be calculated by one-place linear regression. The results are $r = 0.9952$, $a = 13.96038$, $b = -7.9106476$, and hence, $E_O = 7.9106476 \times 8.314/0.4567 = 144.0$ kJ mol^{-1} (34.56 kcal mol^{-1}).

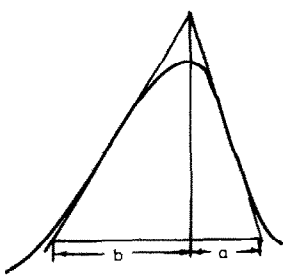

Fig. 3. The DTA shape index of decomposition of the auxiliary.

Thermal ageing test by constant temperature TG measurement

The service lifetime of a material is usually very important and depends on three interrelated factors. The first is a performance index which is determined from specific properties of the different materials. In this paper, the life-span index of the auxiliary was determined by the 10% weight-loss method. The second factor is the operating temperature and the third is time of service, i.e. the lifetime value.

Dakin [3] has suggested that electrical insulation deterioration may be treated as a chemical rate phenomenon and has deduced a lifetime equation. This formula was used by Toob [4] and by Jiang Shicheng et al. [5] as follows. With a residual weight at the end of the life span, i.e. the time of 10% weight loss in this paper, of W_L, the Arrhenius formula becomes

$$-\mathrm{d}W/\mathrm{d}t = A[\exp(-E/RT)]W^n \tag{2}$$

where t is time, W is the residual weight at time t, E is the apparent activation energy, A is the pre-exponential factor, n is the reaction order, R is the gas constant and T is the temperature (K). Rearranging and integrating of eqn. (2) yields

$$\int_1^{W_L} -\mathrm{d}W/W^n = A\exp(-E/RT)\int_0^{\tau}\mathrm{d}t \tag{3}$$

where τ is the lifetime. When $n = 1$, eqn. (3) can be integrated to give

$$\lg \tau = \frac{E}{2.303R}\frac{1}{T} + \lg\left(\ln\frac{1}{W_L}\right) - \lg A \tag{4}$$

When $n \neq 1$, eqn. (3) can be integrated to give

$$\lg \tau = \frac{E}{2.303R}\frac{1}{T} + \lg\left[\frac{1}{1-n}(1 - W^{1-n})\right] - \lg A \tag{5}$$

A general lifetime formula can thus be obtained

$$\lg \tau = a\frac{1}{T} + b \tag{6}$$

where τ is the lifetime at temperature T, a is a constant ($a = E/2.303R$) and is related only to the activation energy E, b is a constant related to the reaction order n and to the pre-exponential factor A, etc. In this study, the weight-loss lifetime was measured by constant temperature TG of the auxiliary at 215 and 236 °C; the 10% weight-loss lifetimes were 282.4 and 64 min, respectively. The first result was calculated from a short reaction time (100 min) because the reaction was approximately first-order ($n = 0.94$). These data are listed in Table 2.

TABLE 3

Lifetime values of 10% weight loss of the auxiliary at different temperatures

t (°C)	T (K)	τ (min)	τ [a]
25	298	2.58×10^{12}	4.9×10^{6} yr
100	373	1.85×10^{7}	35.2 yr
200	473	883.9	14.7 h
215	488	282.4 [b]	4.7 h
220	493	196.0	3.3 h
236	509	64.0 [b]	
240	513	48.9	
250	523	25.4	
260	533	13.5	
280	553	4.12	
300	573	1.36	

[a] yr, Years; h, hours.

[b] Results determined from lifetime tests.

Substituting the data from Table 2 into the lifetime formula, eqn. (6), the following simultaneous equations can be obtained

$$\lg 64 = a\frac{1}{509} + b \tag{7}$$

$$\lg 282.4 = a\frac{1}{488} + b \tag{8}$$

The solution for the equations is $a = 7.624 \times 10^3$ and $b = -13.172$. Hence, the lifetime formula is

$$\lg \tau = 7.624 \times 10^3 \frac{1}{T} - 13.172 \tag{9}$$

From this, the lifetime values listed in Table 3 can be obtained.

The activation energy E_{Life} can be calculated from $a = E_{\text{L}}/2.303R$, i.e. $E_{\text{L}} = 2.303aR = 145.98$ kJ mol^{-1} (34.88 kcal mol^{-1}). The result obtained by the above method agrees with those using Kissinger's method ($E_{\text{K}} = 144.98$ kJ mol^{-1}) and Ozawa's method ($E_{\text{O}} = 144.0$ kJ mol^{-1}).

RESULTS AND DISCUSSION

In this paper, kinetic studies were carried out for an organic auxiliary for chemical fibres. The thermal decomposition reaction order n was found to be 0.94. The apparent activation energies calculated using three different methods, namely, Kissinger's, Ozawa's and a new formulation of the lifetime method were 144.6, 144.0 and 145.98 kJ mol^{-1}, respectively, the average value being 144.86 ± 1.2 kJ mol^{-1}, with an observed relative error of about 1%.

The 10% weight-loss lifetime was measured by constant temperature TG tests. The method used here has two differences from the point-and-slope method in which a thermal ageing test is carried out at a higher temperature (the point) and the apparent activation energy E is calculated from the decomposition reaction by thermal analysis (the slope, $b = -E/R$). In this case, the lifetime can be calculated at any service temperature as long as the decomposition reaction mechanism remains unchanged. The first difference is that no real thermal ageing test is required, only two constant temperature TG curves being needed. Secondly, the TG tests were carried out with the auxiliary alone, not mixed with the polymer, making the test very convenient to perform.

The maximum applicable temperature of 240 °C (see Table 3) for the auxiliary was approved by the producer and user.

REFERENCES

1 E.H. Kissinger, Anal. Chem., 29 (1957) 1702.
2 T. Ozawa, J. Therm. Anal., 2 (1970) 301.
3 T.W. Dakin, AIEE Trans., 67 (1) (1948) 113.
4 T.D. Toob, IEEE Trans., EI-6 (1971) 2.
5 Jiang Shicheng, Shang Baoxu and Cao Yuanchun, Huaxue Tongbao, (1980) 401.