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Thermal analysis in the evaluation of the thermal lifetime of solid polymeric materials

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Abstract

The results of a derivatographic investigation of some polymeric materials are presented. The application of these results in the planning of thermally accelerated ageing experiments, and for a rapid evaluation of the thermal lifetime of these materials, is discussed.

INTRODUCTION

In order to design equipment with components made from polymeric materials, it is necessary to know their lifetime with respect to their conditions of use (environmental, mechanical and electrical stresses). An estimate of the lifetime can be made using the method of accelerated ageing based on the change with time of the mechanical properties (fracture, elongation at break, compression, traction resistance, residual deformation under constant deflection, etc.) as well as of the electrical properties (dielectric strength, resistivity, etc.); and fast analytical methods (thermal analysis, chemiluminiscence, etc.).

This work studies the estimation of thermal lifetimes. To obtain these data, the material must be subjected to thermally accelerated ageing and the isotherms showing the change with time of the property of interest recorded. By statistical analysis of the results obtained, the lifetime in the use conditions can be obtained [1]. The accelerating factor of the thermal ageing has to be correctly chosen such that it can be extrapolated for the use conditions of the materials. Thus, the heating curves (TG, DTG,

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DTA or DSC) which yield the temperature range of chemical stability of the material, as well as the temperatures of the phase changes, are very useful. The first part of this paper deals with the application of thermal analysis in the evaluation of the temperatures of accelerated ageing of some polymeric materials.

The estimate of thermal lifetime using the method of accelerated ageing requires some eight months of experiments. Hence, the necessity of devising more rapid techniques, described as analytical methods. These are not yet generally accepted. In the second part of the paper, the possibility of using TG, DTG and DTA curves to estimate the thermal lifetime of polymeric materials will be discussed.

The use of thermal analysis in the selection of the temperatures of thermal ageing

A suitable temperature for thermal ageing must be chosen [2]. An ageing temperature that yields predictive information in less than 100 h is considered to be too high. The use of a minimal ageing temperature which allows the highest amount of information to be obtained in a maximum of 500 h is recommended.

The minimal and maximal temperatures of accelerated ageing should belong to the so-called range of chemical stability of the material, i.e. the temperature range in which for the relatively short time of several hours, no chemical changes are detected in the material. It is obvious that one has to account for the phase changes (softening and glass transition). The range of chemical stability, as well as the temperatures corresponding to the phase transitions, can be determined from the TG, DTG and DTA curves. The curves were recorded using a Q-1500 D MOM Budapest-type Paulik–Paulik–Erdey derivatograph, in static air atmosphere in the temperature, range 20–500°C; with a heating rate β of 2.5 K min^{-1}.

Table 1 lists the temperature ranges of chemical stability for some polymeric materials whose lifetimes were determined, together with the temperatures of the phase transitions (when these are lower than the temperatures of decomposition or thermooxidation) and the temperatures at which the accelerated ageing measurements were performed. With the exceptions of polyethylene and the EVA compound, the table shows that the materials, when heated in air, undergo an initial thermal decomposition or thermooxidation. They exhibit lower thermal ageing temperatures than the upper limit of the thermal stability range obtained in non-isothermal conditions. There are some polymeric materials for which the temperatures of accelerated ageing should not be lower than the softening temperature, such as EVA compound or some sorts of crosslinked polyethylenes which can be softened without flowing.

The results obtained using the TG, DTG and DTA heating curves are influenced, to some extent, by the heating rate. Because the heat transfer

TABLE 1

The characteristic temperatures (°C) obtained by thermal analysis and the temperatures of the accelerated thermal ageing

Material	T_g [a]	T_t [b]	ΔT_{st} [c]	T_a [d]
Polyethylene	–	105	20–240	80, 85, 90, 100
PVC	80	–	20–170	85, 100, 115, 125
Polycarbonate	135	–	20–315	100, 120, 130
EVA compound	–	80 [e]	20–230	130, 145, 180
Polychloroprene rubber	–	–	20–235	70, 80, 90, 100
Nitrile-butadiene rubber	–	–	20–200	80, 90, 105
Ethylene-propylene rubber	–	–	20–230	100, 115, 125, 135
Glass-reinforced epoxy resin	–	–	20–190	145, 160, 180, 190
Teflon	–	320	20–350	265, 280, 295

[a] T_g, temperature of glass transition. [b] T_t, softening temperature. [c] ΔT_{st}, range of chemical stability. [d] T_a, temperature of accelerated ageing. [e] At 80°C, the EVA compound undergoes softening without flow.

is not instantaneous, the temperatures of changes determined by thermal analysis tend to be higher than the true values. Therefore it is recommended that the maximum temperature of accelerated ageing should be at least 20 K lower than the minimum temperature corresponding to the chemical change or softening with flow of the polymer.

A rather difficult problem arises with polymeric materials that exhibit a glass transition. At the temperature T_g corresponding to this transition (in fact, there is a range of temperatures), the mechanical and electrical properties of materials undergo a sharp change. In such conditions it is difficult, if not impossible, to extrapolate the results obtained at temperatures higher than T_g to temperatures lower than T_g. The values of the mechanical and electrical properties of the aged materials at temperatures corresponding to the glass transition exhibit a significant statistical scattering. Such results have been obtained with the accelerated thermal ageing of polycarbonate at 120 and 130°C, temperatures which are close to the glass transition temperature ($T_g = 135$°C).

Thermal analysis and the rapid evaluation of the thermal lifetime of polymeric materials

The rapid analytical methods that can be applied to determine thermal lifetimes are based on Dakin's kinetic equation [3, 4]

$$-\frac{dP}{dt} = Af(P)\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

where P is the mechanical or electrical property of interest, which depends on the degree of degradation and $f(P)$ is the differential function of degradation; the other symbols have their normal meanings.

Integrating eqn. (1), one obtains

$$F(P) = t \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where the integral function of degradation $F(P)$ is given by

$$F(P) = -\frac{1}{A}\int_{P_0}^{P} \frac{\mathrm{d}P}{f(P)}$$

The logarithmic form of eqn. (2) is

$$\ln t = \frac{E}{RT} + \ln F(P) \tag{3}$$

For P = constant, the activation energy E can be obtained from the slope of the straight line ($\ln t$ versus $1/T$). For P = constant, it is also possible to use the following formula in order to calculate the lifetime of the polymeric material

$$\ln t_u = \ln t_a + \frac{E}{R}\left(\frac{1}{T_u} - \frac{1}{T_a}\right) \tag{4}$$

where the subscripts "u" and "a" correspond to ageing at the temperature of use and at the temperature of accelerated ageing, respectively.

Thus in order to determine the thermal lifetime t_u, t_a and E should be known. The rapid analytical method to determine t_u consists of the determination of the activation energy from thermal analysis data and the plotting of only one isotherm of accelerated ageing, corresponding to the maximum admitted temperature for accelerated ageing (≈300 h of thermal ageing). This method is based on the assumption [5, 6] that the value of the activation energy of the degradation of the property equals the value of activation energy of the first degradation step observed on the derivatogram (thermogram). In order to check this assumption, we determined the activation energy values for the isothermal and non-isothermal degradation of some polymeric materials in air (thermooxidative degradation). The results are listed in Table 2, which shows that, except for the ethylene–propylene rubber, the two values of the activation energy are rather close. For glass-reinforced epoxy resin which exhibits only one step of thermooxidative degradation, the non-isothermal activation energy was determined using the following five methods: Coats–Redfern [7], modified Coats–Redfern [8], Flynn–Wall for constant heating rate [9], Kissinger [10] (from the temperatures of the DTA peaks

TABLE 2

Comparison between the isothermal and non-isothermal values of the activation energy

Material	Isothermal		Non-isothermal	
	Property	*E* (kcal mol^{-1})	*E* (kcal mol^{-1})	Method[a]
Glass reinforced	Flexural strength		12.6–14.7	C–R [7]
				Mod. C–R [8]
		16.6		F–W (β const.) [9]
			14.5	Kissinger [10]
			16.3–17.5	F–W(iso). [11]
NBR (I)[b]	Elongation at break	20.5	21.1	Kissinger [10]
NBR (II)	DRC[c]	16.1	21.5	Kissinger [10]
NBR (III)	DRC	17.1	17.8	Kissinger [10]
NBR (IV)	DRC	22.6	18.9	Kissinger [10]
Compound EVA	Elongation at break	25.0	21.0	Piloyan et al. [12]
Polychloroprene rubber	DRC	17.0–27.3[d]	11.0–27.0[d]	F–W (iso). [11]
Ethylene-propylene rubber	Elongation at break	12.6	25.3	Kissinger [10]

[a] C–R, the Coats–Redfern method; mod. C–R, the modified Coats–Refern method; F–W (β constant), the Flynn–Wall method for constant heating rate; F–W(iso.), the Flynn–Wall method for isoconversion. [b] NBR(I), NBR(II), NBR(III) and NBR(IV) are various sorts of nitrile butadiene rubber. [c] DRC, residual deformation under constant deflection. [d] *E* varies with the degradation degree.

obtained for various heating rates) and Flynn–Wall for isoconversion [11]. The closest non-isothermal value of the activation energy with respect to the isothermal value is that obtained by the Flynn–Wall method for isoconversion. Because this method does not require a knowledge of the integral conversion function, and also because it indicates the changes in the activation energy with the conversion, we recommend its use.

As shown in Table 2, the change in activation energy value with conversion was observed for the polychloroprene rubber. The thermal lifetime of this material cannot be evaluated using relationship (4) which assumes that the activation energy does not depend on the conversion. Therefore a new method for the evaluation of t_u based on the assumption of a linear variation of E with conversion was derived [13].

For the ethylene–propylene rubber, there is a discrepancy between the two values of the activation energy (12.6 kcal mol^{-1} and 25.3 kcal mol^{-1}). This can be accounted for by taking into account that the isothermal degradation is limited by the diffusion of oxygen in the polymer, for which activation energy values in the range 8–13 kcal mol^{-1} have been independently determined [14]. It should be noted that the rate of degradation of the ethylene–propylene rubber increases with increasing oxygen pressure [15].

According to Flynn and Dickens [16], an accurate evaluation of thermal lifetime requires accurate values of the activation energy (the maximal deviation of its value should not exceed 0.2 kcal mol^{-1}). As shown in Table 2, the differences between the isothermal and non-isothermal values of the activation energy are higher. Hence, methods of thermal analysis are less precise in the determination of thermal lifetimes than the method of isothermal accelerated ageing. But, in some favourable cases, methods of thermal analysis can be used for the rapid determination of the thermal lifetime of polymeric materials.

CONCLUSIONS

It has been shown that thermal analysis curves (TG, DTG and DTA) can be used for planning thermally accelerated ageing experiments on polymers, as well as for the rapid evaluation of their thermal lifetimes. Some results concerning isothermal and non-isothermal ageing of polymeric materials have been presented and discussed. It has been shown that, in some cases, thermal analysis methods can be used for the rapid determination of thermal lifetimes.

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