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THERMOGRAVIMETRIC ANALYSIS OF POLYMERS FOR ASSESSING THERMAL DEGRADATION *

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ABSTRACT

Experimental techniques and theoretical analyses of thermogravimetry as applied to the thermal decomposition of polymers are reviewed. It is concluded that little useful mechanistic information can be derived simply by measuring weight loss during heating. Stability assessments can be based on apparent A and E values determined by isothermal analysis. However, such parameters will apply only within the temperature range defined by the conditions of data collection.

INTRODUCTION

With increasing use of polymers in high-temperature applications, either alone or as components of mixtures, a test procedure to assess and predict the performance of the material under investigation is needed. Different aspects of performance may be important in a required application and a procedure of this kind should measure, or at least relate to, the particular property of the material relevant to its use. Thus, weight-loss measurements, i.e., thermogravimetry, would only be worth taking if, for example, integrity of shape were necessary in whatever use the polymer was applied, or if physical properties, such as the mechanical strength required in use, could be related to loss-of-weight behaviour.

In this paper, I shall briefly review the principles of thermogravimetry in polymer applications and attempt to assess how good a procedure this technique is for measuring thermal stability. Ideally, one would make kinetic measurements using thermogravimetry, apply the results to evolve a mechanism and then extrapolate the kinetic rate expressions to predict performance in other conditions.

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EXPERIMENTAL TECHNIQUE

In essence, the technique is quite simple. A sample must be heated and weighed in a controlled atmosphere and from the ensuing data appropriate conclusions may be drawn. A number of balance systems are available commercially and I shall not take up space dealing with such apparatus. I shall comment on a number of points about experimental procedures which bear on the validity of measured results.

Sample preparation

A number of factors affect the apparent performance of a given material.

Size

It is important that the starting weight of a sample does not alter the weight-loss characteristics. This can happen for a variety of reasons. For very small samples of material containing additives, which can be examined on the sensitive equipment now available, the sample under investigation may not be representative of the whole, in that inhomogeneity of mix can occur. A not uncommon occurrence for large samples is internal hold-up of volatile products causing secondary reactions; the very fact that thermogravimetry is being used assumes such products. In this event, sample size and geometry affect the build-up of products and their consequent effect on apparent weight-loss behaviour. Sample history and preparation must be taken into account and reported. Catalyst residues and molecular weight are two of the less obvious parameters which have a bearing on weight loss. The former can be treated as an impurity and, under this general classification, any such substance may profoundly change performance.

Atmosphere

It is customary to perform thermogravimetry in a vacuum or an inert atmosphere. Such conditions are not really relevant to normal usage when oxygen would be available, at least to the surface, of a polymer in use at elevated temperatures. On the basis, I suspect, that things are bad enough in non-interacting conditions, experiments are rarely performed with oxygen present and, therefore, great care must be exercised when applying results obtained in an inert atmosphere to performance prediction in air.

An interesting artefact can occur in reduced-pressure experiments. As volatiles are produced and evolve from the sample, it is possible to build up pressure differentials around the weighing platform [1]. Such differentials change with the pumping characteristics of the apparatus and the rate of evolution of volatiles. However, since the weighing platform is very sensitive to applied forces, normally the weight of substance, pressure differences are recorded as mass differences, with consequent distortion of the observed rate of change of weight.

Temperature control

Continuous weighing of a sample complicates the measurement of its temperature. In many sets of apparatus, temperature measurement and control are performed by the same device. Heat transfer into and within the sample may set up such severe thermal gradients that the recorded temperature is significantly different from the "average" for the whole sample. Another real possibility is a time-lag between temperature recorded and actual temperature experienced: this can cause problems in samples undergoing temperature cycling as part of the experimental procedure.

I believe the most serious difficulty arises from the development of temperature gradients. This effect is more significant with larger samples undergoing rapid chemical change. Heat transfer is an analogous problem to bulk transfer of reactants and products.

KINETIC ANALYSIS

Having highlighted one or two of the problems associated with experimental techniques, it is now appropriate to consider how we analyse the data obtained.

Adopting the approach of analysis of simple homogeneous reactions, the mathematical statement of the rate is taken to be of the form

$$(-\mathrm{d}N_\mathrm{R}/\mathrm{d}t)_\mathrm{T} = k(N_\mathrm{R})^n/(V)^{n-1} \qquad (1)$$

where N_R is the number of moles of reactant at time t, and k the rate constant for the process of order of reaction n, taking place in a volume V. The reason for stating the rate expression in this form is that translation to the thermogravimetry of polymers can be achieved by consideration of the constituent terms.

A few points should be made about this form of the rate expression. If indeed it is a simple reaction, then by using eqn. (1) we assume that this reaction is the only one occurring during the heating cycle. Alternatively, eqn. (1) may be argued to be the rate expression for some chain reaction which involves a number of steps resulting in the production of a range of chemical products, none of which interferes with the decomposition reaction. It is evident that both assumptions are really quite restrictive. With regard to the former, it would be reasonable to propose restricted temperature regimes for such a proposal and the following alternative is possible

$$-(\mathrm{d}N_\mathrm{R}/\mathrm{d}t)_\mathrm{T} = (N_\mathrm{R})^n/V^{(n-1)}(k_1 + k_2) \qquad (2)$$

in which k_1 and k_2 are rate constants for two parallel decomposition reactions and the same reaction order. The point to note is that when eqn. (2) applies, the apparent rate constant is in reality the sum of two rate constants. Turning to the latter situation, gas kineticists who are very experienced in the study of chain reactions assure me that eqn. (1) is almost a naive statement for the rate of a chain reaction. Matters become somewhat complex when a residue remains: rate expressions have been derived for this condition [2].

Returning to eqn. (1), the inclusion of V, the volume of the sample, is necessary because in the thermogravimetry of a sample of polymer this parameter changes throughout the reaction. Since the overall weight of the sample is what is determined experimentally, then volume must be converted to weight, resulting in

$$(-\mathrm{d}W_R/\mathrm{d}t)_T = k^1 W_R \tag{3}$$

in which $k^1 = k(d/m)^{n-1}$ with d the density of the sample and m the molar mass of the reactant. It is apparent that for an experiment measuring only change of weight, W_R, then the reaction will be apparently first order, whereas in fact the reaction is nth order. This very elementary treatment of the kinetics of a hypothetically simple process illustrates the difficulties inherent in this type of measurement for obtaining the order of a reaction—a parameter which is very relevant to determining the mechanism of a particular process. When the reaction is complex, that is, a multi-step chain or a series of concurrent decompositions, then the position with regard to the order of individual processes is virtually hopeless and not worth further investigation at this stage.

I now turn to k, the rate constant. This is the parameter we could adapt to assess or index stability. The approach universally adopted in analysis of data obtained during thermogravimetry of a polymer is to use the Arrhenius equation to replace k.

$$k = A \exp(-E/RT) \tag{4}$$

A is the pre-exponential constant and E the activation energy. This step immediately leads us to one of the great controversies of thermogravimetry, since we can now replace the temperature-dependent rate constant with a function allowing derivation of real indices of thermal behaviour, A and E. The correct procedure for expressing the rate of a reaction for the condition of varying temperature has been a topic of debate for over ten years [3,4]. A proof of what can be described as the two-term rate expression has recently been published [5]. To date, no reasoned rebuttal of that proof has appeared. In a review paper, it is not relevant to enter into the debate: however, the basic point of significant difference is worth discussing. In thermogravimetry conducted under isothermal conditions, it is necessary to define accurately the time at which the sample attains test temperature. Frequently, this is rather difficult to do since rapid heat transfer may result in overshoot, and slower heat transfer causes significant decomposition in the pre-heat period. On the other hand, the outstanding benefit of programmed thermogravimetry was the fact that apparently it was not necessary to define or even guess the onset temperature for decomposition. The fact that one set of measurements required what can be described as an initial boundary condition whereas the other did not, was my prime reason for investigating the theoretical justification.

It is now necessary to see how meaningful parameters can be extracted from the thermogravimetry of polymers. From experience, it is apparent that something equivalent to a "rate constant" should be evaluated, if possible. We can write, by analogy with eqn. (1)

$$(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{T}} = k(1-\alpha)^{a} \tag{5}$$

in which α is the weight fractional conversion, a an index, and k is an apparent rate constant best described as a constant of convenience, since it has the dimensions of a first-order rate constant in normal kinetic connotation, though in my view the concept of order of reaction is of no value in thermogravimetry. It certainly has no mechanistic significance. We can now assume that k obeys the Arrhenius equation (4) and allows evaluation of A and E, the calculated values being again without mechanistic significance. Since what is measured experimentally is α, it is the integrated equivalent of eqn. (5) which should be tested.

Now the question is: "isothermal or programmed thermogravimetry?" My answer is unequivocally "isothermal". The implicit assumption in this method is that we can measure A and E values which can be used to index thermal stability. The measured values will only apply in the temperature range in which they are determined: the temptation to extrapolate to higher temperatures should be avoided. Apart from the theoretical difficulties mentioned above, the drawback with programmed thermogravimetry is that it is quite possible to traverse the temperature range of single-reaction dominance and move into another range in which mixed reactions of the form of eqn. (2) become operative. Thus

$$k_{(\mathrm{apparent})} = k_1 + k_2 \tag{6}$$

and then

$$k_{(\mathrm{apparent})} = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT)$$

with the obvious conclusion that the dependence of $k_{(\mathrm{apparent})}$ on temperature is not of the Arrhenius form. With experiments performed isothermally, A and E can be obtained for narrow temperature regimes and the temperature limitations for evaluated parameters can be defined. In eqn. (5) the value of a has no significance whatsoever.

APPLICATIONS

The difficulties inherent in thermogravimetry as a means for assessing thermal stability are best illustrated by considering two widely used poly-

TABLE 1

Range of activation energies obtained experimentally

Polymer	Activation energy, E (kJ mol^{-1})	Reference
Polytetrafluoroethylene	309	6
	297	7
	327–190	8
	332	9
Polystyrene	252	10
	244	11
	210	12

mers, polystyrene and polytetrafluorethylene. Table 1 shows the range of values published for E, the apparent activation energy for thermal decomposition of these materials. The method of analysis of weight loss data varied as, of course, did the polymer sample, from laboratory to laboratory. Nevertheless, the spread of values obtained indicates the problems associated with this technique.

CONCLUSION

It would be reasonable to assume that thermogravimetry should make the assessment of thermal stability possible. I believe some success in quantifying this parameter has been achieved, but it must be said that simple weight loss measurements of what is frequently a mixture of products yielding varying amounts of residue cannot be expected to be a sensitive means for determining thermal stability. I believe that past attempts to evolve rate expressions have been dominated by the approach used for homogeneous, constant-volume systems. A simpler, pragmatic approach would, in my opinion, serve just as well, hence my suggestions given above. I would also add a word of caution insofar as data collection and analysis can now be performed using dedicated computers. If the basic technique has its limitations, so also have the conclusions, no matter how sophisticated the kinetic analysis.

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