NOTE

Initiators Used in Reactive Extrusion: Novel Parameters for Thermal Decomposition Process

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INTRODUCTION

Reactive extrusion is an important process for the secondary modification of mass polymers (e.g., polyolefines). Extrusion conducted in the presence of monomers with appropriate reactivity results in transformation of the original polymer by graft copolymerization or substitution by single monomeric units. The resulting modified polymers have specific properties, depending on the chemical structure of the monomer used. The field of application of such modified polymers is growing steadily.

The chemical processes of the above modifications are radical reactions and they generally need radical initiators to take place at a sufficient rate and with good efficiency. The initiators used are peroxide compounds in the vast majority of cases. The selection of the initiator for a given reactive extrusion process in not an easy task however. The radicals (or secondary radicals) formed in the decomposition process and the following radical isomerization reactions must have an appropriate reactivity. The minimum requirement is that they must be able to abstract hydrogen atoms from the polymer and form radical centers that can react with the monomer molecules. In addition, the thermal decomposition kinetics of the initiator must harmonize with the technological characteristics of the extrusion process. This second requirement is not emphasized sufficiently in the articles and reports published on reactive extrusion.

During the extrusion process the materials transported along the device are heated from ambient temperature to 200°C and higher in a relatively short time (some minutes in most of the cases). Thus, the initiat-ing process, which is the thermal decomposition of the initiator, is a nonisothermal process that must be nearly completed before the exit of the polymer from the extruder. An earlier study investigated the kinetics of the nonisothermal unimolecular decomposition process.[1] Because the temperature course during the transport of materials may be exceedingly different for various technological parameters, the simplest treatment assuming a hyperbolical temperature increase [i.e., $d(1/T)/dt$ = const.] as proposed originally by Zsakó was used.[2] The results of my theoretical considerations were applied for small-scale laboratory extrusion modification with good results.[3,4]

However, the data published in the literature on the temperature dependent decomposition of initiators[5,6] was found to not be very suitable for selecting an initiator for a given reactive extrusion process. The published data are either half-life temperature values (often for very long half-life times, such as 10 h), which are clearly useless for the rapid nonisothermal process, or Arrhenius parameters not directly related to the temperature and heating rate values of the extrusion process investigated. In the following a different way to characterize the nonisothermal decomposition properties of initiators is proposed.

PARAMETER TRANSFORMATION AND CONCLUSION

As deduced in a previous study,[1] the temperature of the maximum decomposition rate in a nonisothermal process can be given as follows:

$$T_m = \frac{B}{\log A - \log B - \log C} \tag{1}$$

where $B = E_a/R$ (K), A is the preexponential factor with the same dimension as the unimolecular rate constant k_d (min^{-1}), and $C = -d(1/T)/dt$ is the rate of hyperbolic temperature change (K^{-1} min^{-1}). Consequently, $A/(BC)$, the logarithm of which is the denominator in expression (1), is dimensionless. (Natural logarithms are used through this article.)

If we can define a characteristic value for the rate of temperature change, this will also determine a characteristic value, T_c, for the temperature of maximum decomposition (initiation) rate. The simplest and most effective way to do this is equating the numerical value of C to the reciprocal of B. This results in the following simplest expression (2) for the characteristic decomposition temperature:

$$T_c = \frac{B}{\log A} \tag{2}$$

Rearranging and taking exponents we have

$$A = \exp(B/T_c) \tag{3}$$

and from this follows that the characteristic value of the decomposition rate constant at T_c is

$$k_d(T_c) = A \exp\left(-\frac{E_a}{RT_c}\right) = 1 \text{ min}^{-1} \tag{4}$$

In other words, the characteristic decomposition temperature is that at which the value of the decomposition rate constant equals one.

Now we look at the value of the heating rate resulting in a peak decomposition temperature, T_c. In the vicinity of the peak one can clearly calculate with a linear heating rate $w = dT/dt$ (K min^{-1}), so we can write

$$C = \frac{1}{B} = -\frac{d(1/T)}{dt} = \frac{1}{T^2}\frac{dT}{dt} \tag{5}$$

For the characteristic linear heating rate, w_c, we obtain the following similarly simple result by the use of expression (2):

$$w_c = \frac{B}{(\log A)^2} \tag{6}$$

The T_c and w_c are equivalent to the Arrhenius parameters. These latter ones can be expressed by the above derived characteristic decomposition values

$$\log A = \frac{T_c}{w_c} \tag{7a}$$

$$\frac{E_a}{R} = \frac{T_c^2}{w_c} \tag{7b}$$

We suppose that the newly introduced parameters, T_c and w_c, are much more easily perceivable for the people working in the field of reactive extrusion than the abstract Arrhenius parameters that only indirectly characterize the temperature course of the initiation rate constant. To illustrate this, we take the generally used initiator dicumyl peroxide (DCUP) as an example. The Arrhenius parameters of the unimolecular decomposition process of this compound have the following values as recalculated from the data of Kharasch and coworkers,[7]: $A = 6.544.10^{16}$ min^{-1}, $\log A = 38.72$, $E_a = 147.06$ kJ mol^{-1}, and $B = 17,680$ K. From these $T_c = 456.61$ K (=183.45°C) and $w_c = 11.79$ K min^{-1}.

It is remarkable that the dependence of the maximum initiation rate temperature on the linear heating rate is also obtainable by similarly simple calculations. If the rate of hyperbolic temperature change is expressed by $C = z/B$, the peak temperature and the corresponding linear heating rate can be formulated as follows:

$$T_m = \frac{B}{\log A - \log z} \tag{8a}$$

$$w = \frac{zB}{(\log A - \log z)^2} \tag{8b}$$

However, eq. (8) is a system of two parametric equations. Elimination of parameter z yields the heating rate as a function of peak temperature. If eq. (8b) is divided by the square of eq. (8a), the result is

$$\frac{z}{B} = \frac{w}{T_m^2}, \quad (\text{i.e.,} \quad \log z = \log B + \log w - 2 \log T_m) \tag{9}$$

Substituting eq. (9) into (8a), and rearranging we have

$$\log w = \log A - \log B + 2 \log T_m - B/T_m \tag{10}$$

Expression (10) contains the Arrhenius parameters. We can formulate the above dependence by using the equivalent parameters T_c and w_c, too. Substituting these into (10) for T_m and w and subtracting the resulting equation from (10), we obtain the following relationship:

$$\log\left(\frac{w}{w_c}\right) = \log\left(\frac{T_m^2}{T_c^2}\right) + \frac{T_c}{w_c}\frac{T_m - T_c}{T_m} \tag{11}$$

With the aid of the relatively simple eqs. (10) or (11) the linear heating rate values are easily calculable for any peak decomposition temperature. One must bear in mind, however, that these heating rates are valid only locally. Nevertheless, the equations may extremely useful in the optimization of technological parameters of any reactive extrusion process. For example, if we

wish to assure a maximum initiation rate at an 195°C melt temperature in a section of the extruder, the temperature increase of the material (calculable from the melt transport rate and the temperature gradient at this place) should be about 32 K min^{-1} for the DCUP initiator. If it is technologically infeasible, another initiator must be chosen. For the best efficiency the maximum decomposition rate of the initiator and the heating rate of the material in the extruder must be fitted.

A compilation of T_c and w_c values calculated for various radical initiators from literature data and my experimental results is under preparation.

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