KINETIC COMPENSATION EFFECT IN THE THERMAL DEGRADATION OF POLYMERS

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Abstract

The kinetic study of thermal degradation takes into account the validity of the Arrhenius equation. From TG data, the activation energy, E_a and pre-exponential factor, A, are evaluated. These results are interpreted by using the 'kinetic compensation effect' as basis. A linear correlation between $\ln(A)$ and E_a is obtained in all cases studied. However, in a plot of the logarithm of the rate constant as a function of reciprocal temperature for the same series of reactions, the thermal oxidative degradations of Nylon-6 and PVC display a point of concurrence and one isokinetic temperature, whereas those of HIPS and PC do not. Therefore, in the thermal oxidative degradations of Nylon-6 and PVC a 'true' compensation effect occurs, which could be related to the bulk properties of metal oxides, such as different valence states, whereas for other polymers it displays only an 'apparent' compensation effect. This means that degradation is largely independent of the bulk properties of oxides, but may be related to the distribution of different kinds of active links in the polymer surface having different activation energies.

Keywords: kinetics, thermal degradation

Introduction

The thermal degradation of a polymer is a complex solid–gas reaction and its mechanism remains largely unclear, since it may take place via radical chain depolymerization, disproportionation of the chain end or chain scission reactions [1]. It may be affected by the diffusion of gaseous products and heat transfer through the layers of polymer, which are generally non-conductive. This kind of reaction may also be influenced by the shape and size of the sample and the sample holder. An unequivocal kinetic explanation of the thermal degradation of polymers has been described for well-defined stationary states or under isothermal conditions. However, non-isothermal kinetic explanations based on kinetic parameters are not unequivocal, because they depend on the conversion and the heating rate in addition to other factors [2, 3].

Kinetic discussions concerning the thermal degradation of polymers generally deal with the simplest mechanism, which means elementary reaction steps,

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and especially the depolymerization reaction [4]. However, even in this case the analysis is restricted to stationary states of radical concentration, depending on the nature of the initiation (random chain scission or chain end scission), kinetic chain length and termination (recombination or disproportionation), and the activation energy is determined [5, 6].

In non-isothermal TG, the overall kinetic parameters show a conversion dependence, even if the reaction mechanism does not change because of the temperature increase during the conversion. Thus, for the evaluation of the kinetic parameters, methods have to be used which allow demonstration of the conversion dependence [7]. A major theme in the literature on polymer degradation is how to understand the mechanism and the pattern of the behavior of the various types of polymer when these are subjected to heat under isothermal and non-isothermal conditions. In many cases of polymer degradation, it is still not very clear how many distinct mechanisms are being sought or whether the mechanism is significantly different when additives are added. Studies on the additives have revealed that the surface area and intrinsic properties of the additives may influence the thermal degradation of the polymer [8–12]. The effects of additives or catalysts on certain solid-gas reactions have been studied by many workers by evaluating the kinetic parameters by means of the Arrhenius equation. They have found compensation behavior in these additive-catalysed reactions [13–17]. Compensation phenomena have been found to influence the interphase/interface elastic process in polymer matrix composites [18].

The kinetic parameters (A and E_a) vary with the experimental conditions even if the degradation mechanism does not change. This has led to the elucidation of a precise mechanism of thermal degradation of polymers in the presence of additives. The major theme of the work is the search for patterns of behavior of the kinetics of thermal degradation of polymers in the presence of added metal oxides. In this communication, we consider the kinetic compensation as a basis for interpretation of the thermal degradation behavior of some polymers. The polymers chosen for the purpose of these studies were Nylon-6 (NY6), polycarbonate bisphenol A (PC), high-impact polystyrene (HIPS) and poly(vinyl chloride) (PVC).

Methods

Sample preparation

The PC (Lexan, GE, USA), HIPS (Polychem, India) and PVC (Sri Ram Vinyl, India) samples were prepared from a solution of the respective polymer, dissolved in a suitable solvent, to which metal oxide was added to give a polymer to oxide ratio of 5:1. After stirring for about half an hour, the solvent was

removed by evaporation. The residue was metal oxide coated with polymer [19]. NY6 (Garware Nylons, India) samples were prepared by mixing Nylon-6 and metal oxide powder to give a polymer to oxide ratio of 5:1 (5 parts of NY6 and 1 part of metal oxide by mass). After mixing, the mixture was ground in an electrical vibrator. The resulting intimate mixture was used as sample. The sources and the physical properties of the metal oxides are listed elsewhere [11].

The TG curves of PC, HIPS, PVC and the polymer-coated oxides were recorded in nitrogen atmosphere on a Thermal Analyzer System, Perkin-Elmer TGS2, TADS1700 at a heating rate of 10 K min^{-1} at the Regional Sophisticated Instrumentation Center, Nagpur, while those of NY6 and the polymer oxides were recorded in static air on a laboratory-assembled instrument at a heating rate of 4 K min^{-1} [11].

Evaluation of kinetic parameters

It is generally accepted that the temperature dependence of the rate of thermal degradation of a polymer obeys the Arrhenius rate equation and gives not absolute, but relative rate constants. The apparent kinetic parameters of the thermal oxidative degradation of NY6 were estimated by the Sharp-Wenthworth method, assuming a reaction order of one. The Sharp-Wenthworth equation is

$$\ln\left\{\frac{d\alpha / dT}{(1-\alpha)}\right\} = \ln\left\{\frac{A}{\beta}\right\} - \left\{\frac{E_a}{RT}\right\} \tag{1}$$

where α is the fraction decomposed and A, β and E_a have the usual meanings. Kinetic parameters obtained by using Eq. (1), were evaluated graphically.

The kinetic parameters for PC, HIPS and PVC were evaluated by using the inflection point method developed by Gupta and Viswanath [12, 20]. The rate equation is written as

$$\frac{d\alpha}{dT} = (1-\alpha)^n \left\{\frac{A}{\beta}\right\} \exp\left\{-\frac{E_a}{RT}\right\} \tag{2}$$

where n is the reaction order. $d\alpha/dT$ is maximum at the inflection point and $d^2\alpha/dT^2 = 0$. Hence Eq. (2) is transformed into

$$\ln\left\{\frac{d\alpha}{dT}\right\} = n\left\{\ln(1-\alpha) - \frac{\Theta_s}{T}\right\} + \ln\left\{\frac{A}{\beta}\right\} \tag{3}$$

where Θ_s is given as

$$\Theta_s = \left\{\frac{T_s}{(1-\alpha_s)}\right\}\left\{\frac{d\alpha}{dT}\right\}_s \quad \text{at an inflection point and}$$

$$\frac{E_a}{R} = \left\{\frac{nT_s^2}{(1-\alpha_s)}\right\}\left\{\frac{d\alpha}{dT}\right\}_s = n\Theta_s \qquad (4)$$

Thus, with the use of Eqs (3) and (4), n, E_a and A were evaluated graphically.

Results and discussion

It is observed that E_a and A vary both with the oxide used as additive and with the pure polymer. It is most unusual to find two closely similar heterogeneous reactions which obey the Arrhenius rate equation, but with different activation energies and the same pre-exponential factor, A. The variations of E_a and A, however, are nearly always in the same sense. Plots of $\ln(A)$ against E_a (kJ mol^{-1}) for all the systems studied are shown in Fig. 1(a–d). It is observed that the data yield a good fit to a straight line with a positive slope, of the form

$$\ln(A) = \ln(k_o) + E_a/RT_o \qquad (5)$$

where k_o and T_o are the isokinetic rate constant and isokinetic temperature, respectively. The linear relations deduced from Fig. 1(a–b) are given below:
This behavior shown by a large group of heterogeneous reactions is called the kinetic compensation effect (CE) [13, 14]. Such a plot does show, however, in

(i)	$\ln(A) = 0.142\,E_a - 2.65$	(NY6)
(ii)	$\ln(A) = 0.171\,E_a - 3.84$	(PC)
(iii)	$\ln(A) = 0.179\,E_a - 5.29$	(HIPS)
(iv)	$\ln(A) = 0.221\,E_a - 7.17$	(PVC)

a reasonable way, that E_a and A generally vary in the same sense fox the heterogeneous reaction in a given group. T_o indicates the approximate magnitude of the isokinetic temperature for any group of reactions with significantly different activation energies. The isokinetic temperatures, T_o, and the isokinetic rate constants, k_o, are listed in Table 1.

Evidence of such compensation behavior is reported in numerous studies and several theories predict such linear compensation behavior [13–18, 21]. These theories suggest that the CE is probably due to entropy-enthalpy compensation, the tunneling effect, the simultaneous occurrence of reaction on the surface centers involving different activation energies, and the existence of interrelated kinetic behavior within a group of rate processes. The isokinetic temperature has been regarded either as the temperature at which relative rates within a group roup of reactions undergo inversion, or as the temperature at which the rate constants of all the reactions in the series have the same value [17].
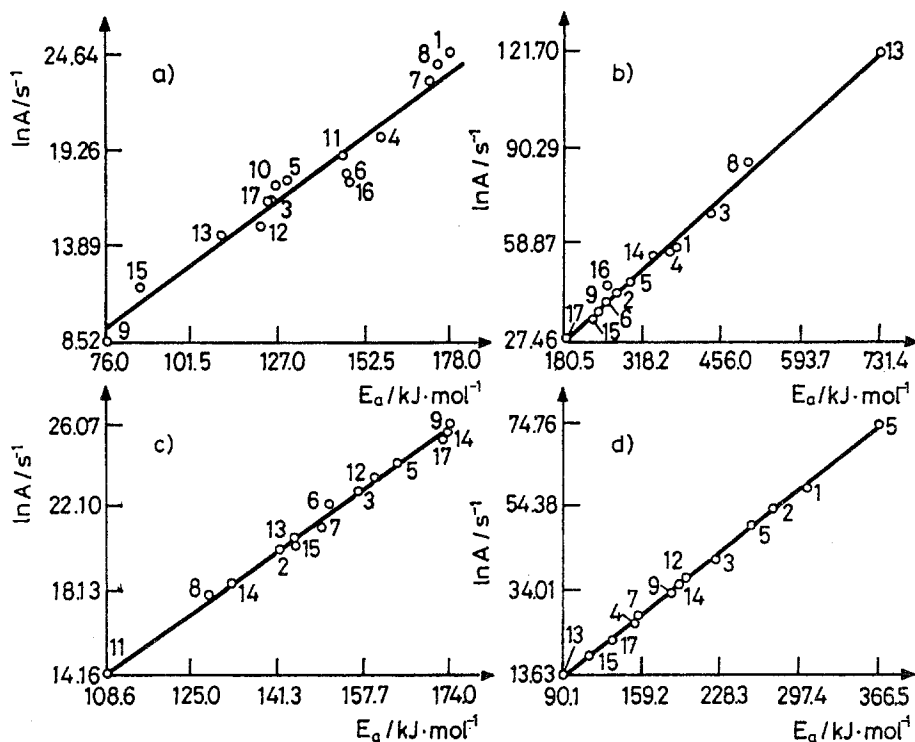
Fig. 1 Arrhenius plots of $\ln(A)$ vs. E_a for the thermal decomposition of polymers in the presence of metal oxides. (a) NY6, (b) PC, (c) HIPS, (d) PVC. (1) Polymer, (2) Al_2O_3, (3) CeO_2, (4) Cr_2O_3, (5) Cu_2O, (6) CuO, (7) Fe_2O_3, (8) MnO_2, (9) MoO_3, (10) NiO, (11) PbO, (12) Sb_2O_3, (13) SnO_2, (14) TiO_2, (15) V_2O_5, (16) ZnO, (17) ZrO_2

Table 1 Isokinetic parameters for polymers with different additives

Polymer	Isokinetic temperature/ K	Isokinetic rate constant (k_o)/ s^{-1}
NY6	841.0	7.06×10^{-2}
PC	703.0	2.15×10^{-2}
HIPS	672.0	5.04×10^{-3}
PVC	543.0	8.0×10^{-4}

However, Agrawal [22] suggested an alternate method for detecting true compensation behavior via an Arrhenius plot of $\ln(k)$ vs. $(1/T)$ for a series of related reactions. Accordingly, true compensation behavior is displayed when the Arrhenius plots show a point of concurrence. If the Arrhenius plots do not display a point of concurrence and a plot of $\ln(A)$ vs. E_a is a straight line, only then

is it assumed to be an apparent compensation effect. Such Arrhenius plots of $\ln(k)$ *vs.* $1/T$ for all the systems under study are shown in Fig. 2(a–d). It is worth noting from Figs 2(a, d) that, for most of the reactions, the thermal degradations of NY6 and PVC in the presence of metal oxides do display a point of concurrence. In contrast, HIPS and PC do not exhibit such behavior, even though the plots of $\ln(A)$ *vs.* E_a are straight lines for all four systems. Thus, for PVC and NY6, the temperature corresponding to the point of concurrence is the temperature at which the rate constants of all the reactions in the series have the same value, whereas for HIPS and PC, the apparent compensation behavior may mean some kind of inversion in the rate process.
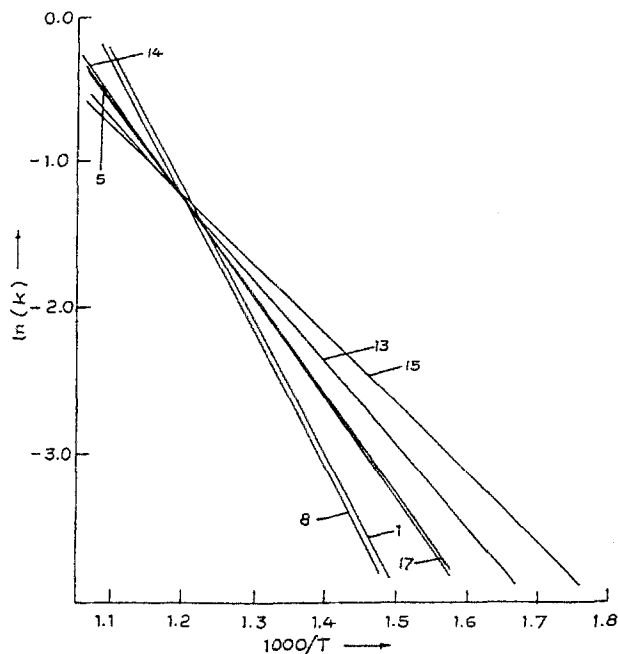

Fig. 2a Kinetic compensation in the thermal degradation of Nylon-6 in the presence of metal oxides. For meanings of numbers, see Fig. 1

The occurrence of a point of concurrence was first observed by Feats *et al.* [14] in a kinetic study of the catalyzed oxidation of carbon. It was concluded that if a number of reactions obeying the Arrhenius rate law can occur simultaneously on a single sample, for which the kinetic parameters are linked by compensation behavior ($\ln(A)$ *vs.* E_a), then the reactions occur on surfaces with different activation energies. Two kinds of reactions are possible: one in which E_a(additive)$>E_a$ (pure component), and the point of concurrence (the isokinetic temperature) is located a few degrees higher than in the reaction without additives, and one in which E_a (additive)$<E_a$(pure component), and the point of

concurrence is located a few degrees below. From Fig. 2(a), it is observed that the point of concurrence for NY6 is located at a higher temperature (841 K, where the lines converge), whereas for PVC it is located at a lower temperature (533 K, where the lines diverge after this point). The results for NY6 and PVC show that the point of concurrence is observed only in the case of transition metal oxides. Non-transition metal oxides, such those as of Al, Zn, Sn and Pb, do not exhibit such behavior.

It was further pointed out by Feates *et al.* [14] that when a reaction is changed from chemical-controlled to diffusion-controlled, and the active centers on the surface of the reactant may act as sites for simultaneous reactions with different activation energies, then the Arrhenius plots do not display a point of concurrence, even though the plots of $\ln(A)$ *vs.* E_a show compensation behavior. For HIPS and PC, there is no point of concurrence, as observed from Fig. 2(b, c). Ranganathan *et al.* [23] also investigated the importance of the compensation effect in heterogeneous reactions, assuming the catalysts as additives. It was suggested that additives or catalysts having different bulk properties have different k_o (isokinetic rate constant) values, whereas those with similar bulk properties, but different surface properties, have identical k_o values. This means that the polymers exhibit different decomposition behavior with different metal oxides. In NY6 and PVC, the metal oxides exhibit different surface behavior, but the same bulk behavior, whereas in HIPS and PC, only the bulk properties of the oxides play an important role in the surface reaction.
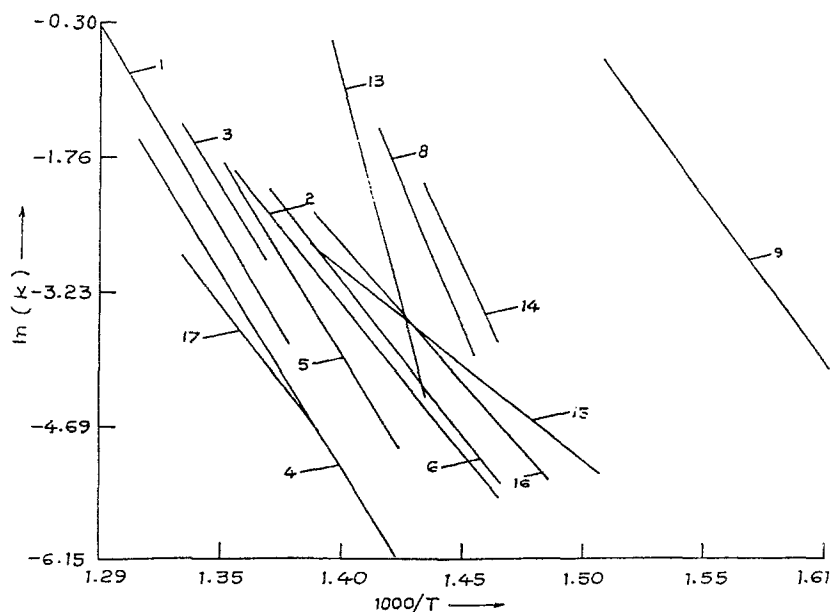

Fig. 2b Kinetic compensation in the thermal degradation of polycarbonate bisphenol *A* in the presence of metal oxides. For meanings of numbers, see Fig. 1
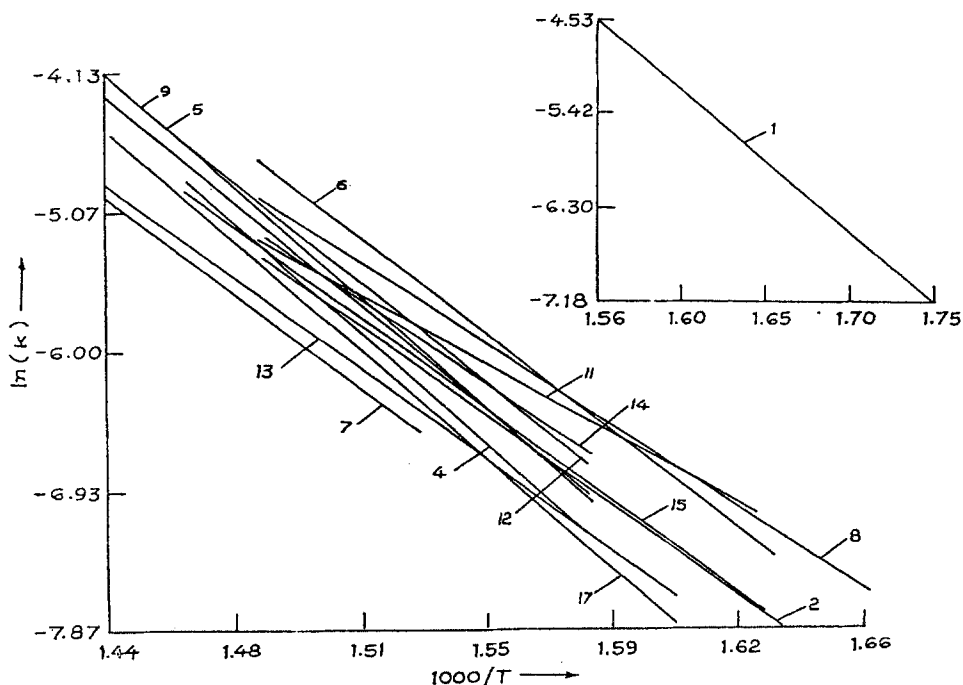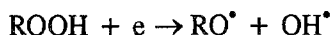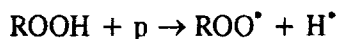
Fig. 2c Kinetic compensation in the thermal degradation of high-impact polystyrene in the presence of metal oxides. For meanings of numbers, see Fig. 1

Nylon-6 (NY6)

The Arrhenius plot of $\ln(k)$ vs. $1/T$, as shown in Fig. 2(a), exhibits a point of concurrence at 843 K (546°C) and the isokinetic rate constant, k_o, is 6.31×10^{-2} s^{-1} for transition metal oxides. T_o and k_o agree very well with the values given in Table 1 obtained from the $\ln(A)$ vs. E_a plot. It may be noted by comparing Fig. 1(a) and Fig. 2(a) that those metal oxides which do not intersect the point of concurrence in Fig. 2(a) do not fall on the straight line in Fig. 1(a) either. The faster reaction has the higher activation energy above T_o, whereas below T_o it has the lower activation energy. T_o is therefore a transition temperature for a group of interrelated reactions (transition metal oxides).

The point of concurrence in Fig. 2(a) for samples containing transition metal oxides indicates that the thermal oxidative degradation of NY6 is correlated with the bulk properties of the metal oxides such as variable valence states of the oxides. The degradation may therefore be described via an electron transfer mechanism (redox) as [11]

$$ROOH + e \rightarrow RO^{\bullet} + OH^{\bullet}$$

$$ROOH + p \rightarrow ROO^{\bullet} + H^{\bullet}$$

where the peroxides are formed by the reaction of oxygen from the air at elevated temperature. As the temperature increases, the rate of decomposition increases.
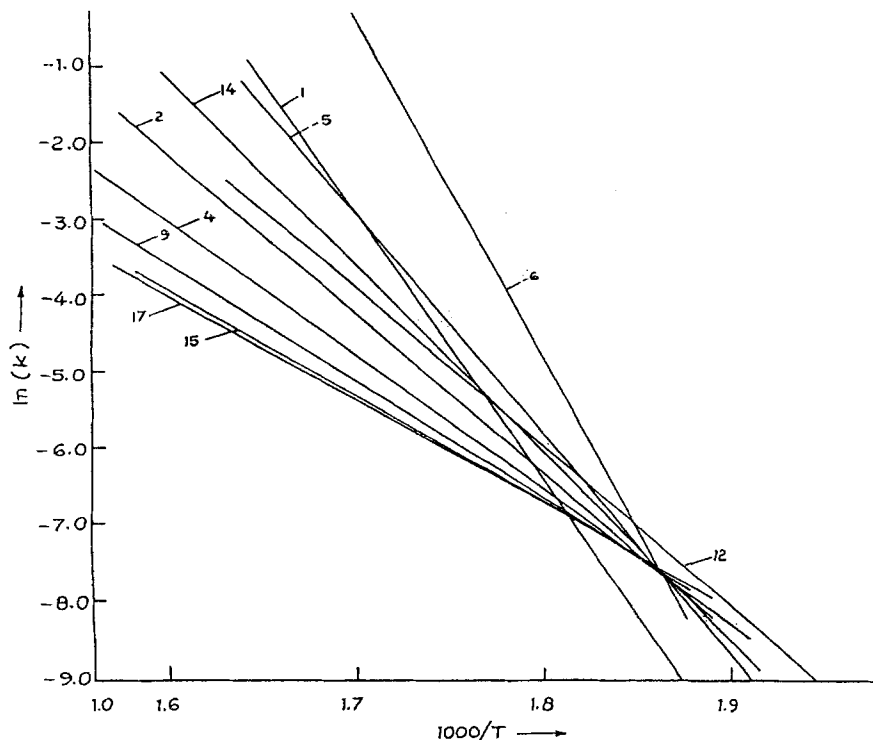

Fig. 2d Kinetic compensation in the thermal degradation of polyvinyl chloride in the presence of metal oxides. For meanings of numbers, see Fig. 1

Cremer [13] suggested that electron transfer in metal ions with variable oxidation states is due to a 'tunnel effect'. If the electron rather than an atom or a hole tunnels in a reaction, then the transition probability for an electron to tunnel is much higher than for a hole or an atom, due to its smaller mass. If a 'tunnel effect' occurs, then according to Erying, the rate constant is given by

$$k = \frac{k_b T}{h} \tau \exp\left\{\frac{\Delta S^{\#}}{R}\right\} \exp\left\{-\frac{\Delta H^{\#}}{RT}\right\} \tag{6}$$

in which the transition coefficient, τ, is correlated with the excess energy of the electron, W ($\approx E_a$) by

$$\tau = \exp\left\{-\frac{8\pi R}{3h}[2m(V - W)]^{1/2}\right\} \tag{7}$$

where V is the height of the barrier and R is the width of the barrier. This shows that the higher the value of W, the larger the probability of tunneling and the larger A. Therefore, there is a compensation in $\ln(A)$ and E_a.

Polycarbonate bisphenol A (PC)

The plots of $\ln(k)$ vs. $1/T$ do not exhibit a single point of concurrence and the activation energy is lower than that for the degradation of PC. It also results in a single straight line for $\ln(A)$ vs. E_a. Thus, the thermal degradation may be a surface-induced reaction which is diffusion-controlled. Accordingly, weak links in the polymer chain produce macroradicals which interact with the metal oxide surface [12]. Formation of this metal oxide macroradical adduct is the rate-controlling step in the thermal degradation. Since the mechanism of the thermal degradation is the same, the plot of $\ln(A)$ vs. E_a gives a straight line which exhibits compensation behavior, but not a point of concurrence in the respective Arrhenius plot.

High-impact polystyrene (HIPS)

The Arrhenius plots of $\ln(k)$ vs. $1/T$ do not exhibit a point of concurrence and the lines are almost parallel to each other, but $\ln(A)$ vs. E_a does give a straight line. The activation energy of the thermal degradation in the presence of metal oxides is higher than for pure HIPS. This indicates that the thermal degradation is a surface-induced reaction in which active centers are produced at the surface and act simultaneously as reaction sites [24]. The number of such reaction sites (weak links) may vary with the metal oxide. The thermal degradation of HIPS without additive may follow a different reaction mechanism, but in the presence of metal oxides the reaction follows the same mechanism; hence, the plot of $\ln(A)$ vs. E_a shows reaction rate compensation.

Poly(vinyl chloride) (PVC)

This exhibits, for transition metal oxides, a point of concurrence when $\ln(k)$ is plotted vs. $1/T$. The point of concurrence is at low temperature ($T_o = 533$ K and $k_o = 8.0 \times 10^{-4} s^{-1}$), which is close to the softening temperature of PVC. The lines diverge at higher temperature. The reaction is faster at higher temperature. Therefore, as in the case of NY6, the thermal degradation of PVC can be correlated with the bulk properties of the transition metal oxides. It is well known that PVC degrades by the evolution of HCl at temperatures close to softening temperature [25]. This decomposition of PVC takes place via the formation of HCl, which reacts with the metal oxides; the rate will be higher at elevated temperature, and thus the activation energy will be lower than for pure PVC. The metal chlorides may vaporize at higher temperature.

Conclusions

The compensation behavior of polymer degradation in the presence of metal oxides provides an insight into the mechanism of the degradation. The fact that a plot of $\ln(A)$ vs. E_a is a straight line indicates only that the reaction follows the same mechanism, while any deviation from the straight line indicates a different mechanism. However, concurrent $\ln(k)$ vs. $1/T$ plots for a group of reactions indicate by the presence or absence of an isokinetic temperature, T_o (point of concurrence), whether the compensation is due to reaction at the additive surface or to the bulk property of the additive.

Thus, the kinetic behavior of the thermal degradation of a polymer in the presence of metal oxides can be correlated with the compensation phenomena. The linear relation between $\ln(k)$ and E_a reveals compensation due to various factors. The Arrhenius plot of $\ln(k)$ vs. $1/T$ reveals the nature of the similar reaction mechanism which leads to compensation.

References

1 H. H. G. Jellinek, in Aspects of Degradation and Stabilization of Polymers (Ed. H. H. G. Jellinek), Elsevier, Amsterdam, 1983, Chapter-1.
2 H. A. Schneider, J. Thermal Anal., 40 (1993) 687.
3 S. L. Madrosky, Thermal Degradation of Organic Polymers, Interscience, New York 1964.
4 R. Simha and L. A. Wall, in Encyclopedia of Polymers, Vol. IV, (Ed. H. H. G. Jellinek), Interscience, New York 1962.
5 R. H. Boyd, J. Polym. Sci., 49 (1961) 81.
6 A. Audebert and C. Aubeneau, Europ. Polym. J., 6 (1970) 165.
7 H. A. Schneider, Survey and Critique of Thermal Methods and Results in Degradation and Stabilization of Polymers (Ed. H. H. G. Jellinek), Elsevier, Amsterdam 1983, Chapter-10.
8 C. F. Cullis and H. S. Laver, Europ. Polym. J., 14 (1978) 575.
9 R. H. Hansen, C. A. Russell, T. de Banedictus, W. M. Martin and J. V. Pascale, J. Polym. Sci., Part A-2, 2 (1964) 587.
10 J. K. Dixon and J. E. Longfield, in Catalysis, Vol. 7, (Ed. P. H. Emmett) Reinhold, New York 1960.
11 M. C. Gupta and A. T. Jais, Thermochim. Acta, 230 (1993) 155.
12 M. C. Gupta and S. G. Viswanath, J. Thermal Anal., 45 (1995).
13 E. Cremer, Adv. Catal., 7 (1956) 75.
14 F. S. Feates and P. S. Harris, J. C. S. Trans. Faraday I, 70 (1974) 2011.
15 C. Fairbridge, R. A. Ross and P. Spooner, Wood Sci. Technol., 9 (1975) 257.
16 Z. Adonyi and G. Körösi, Thermochim. Acta, 60 (1983) 23.
17 J. A. Azizi, D. Dollimore, P. J. Dollimore, G. R. Heat, P. Manley, W. A. Kneller and W. Jim Yong, J. Thermal Anal., 40 (1993) 831.
18 C Lavergne, A. Dufresne, D. Chatain and C. Lacabanne, J. Thermal Anal., 40 (1993) 705.
19 A. T. Jais, Ph. D. Dissertation, 'Effect of Metal Oxides on Thermal Degradation of Polymers', Nagpur University, 1993.
20 S. G. Viswanath and M. C. Gupta, Thermochim. Acta, (Commun.) 1995.
21 A. K. Galway, Adv. Catal., 26 (1977) 247.
22 R. K. Agrawal, J. Thermal Anal., 31 (1986) 73, 34 (1988) 1141.
23 R. Ranganathan, N. N. Bakshi and J. F. Mathews, Can. J. Chem. Eng., 55 (1977) 544.
24 M. C. Gupta and S. G. Viswanath, J. Thermal Anal. (Commun.) 1995.
25 W. L. Hawkins, in Polymer Degradation and Stablization, Springer-Verlag, Berlin 1984, p. 68–71.