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EFFECT OF METAL OXIDES ON THE THERMAL DEGRADATION OF HIGH IMPACT POLYSTYRENE

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Abstract

The kinetic parameters for the thermal degradation of high impact polystyrene (HIPS) in presence of some metal oxides exhibit reaction rate compensation effect. In thermal degradation of HIPS in presence of transition metal oxides different active centers act simultaneously as reaction sites and macroradicals are formed through random chain scission, disproportionation or cyclization. Some oxides retard the polymer degradation through crosslinking and cyclization by the interaction of macroradicals with the double bond in butadiene.

Keywords: catalysts, effect of additives, high impact polystyrene, kinetic parameters, thermal degradation

Introduction

There are a few kinetic interpretations of thermal degradation of polymers in the literature and the apparent activation energy and pre-exponential factor from the TG studies by various methods have been reported [1–4]. In these, the Arrhenius equation is widely accepted as a useful tool for predicting a variation in the reaction rate constant as a function of temperature. Using this equation, apparent activation energy, E_a and pre-exponential factor, A, have been calculated. For a series of related reactions, $\ln(A)$ *vs.* E_a sometimes exhibit a linear relationship, which has been reported as a 'compensation effect' or 'isokinetic effect' [5–8]. However these kinetic parameters vary with experimental condition such as heating rate even if the decomposition mechanism, particle size sample distribution, mass transfer phenomena [9, 10], method of calculation of kinetic parameters and kinetic rate law assumed for TG analysis in heterogeneous reaction do not change [11].

As a part of comprehensive study of thermal degradation of polymers, in this communication the thermal degradation of high impact polystyrene (HIPS) alone and in the presence of metal oxides has been investigated.

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Experimental

Materials

HIPS, a copolymer of styrene and butadiene which contains 10–20% butadiene is a general purpose molding grade product manufactured by Polychem (India), Bombay [12]. This commercial HIPS sample was purified by repeated dissolution in benzene and precipitated by a non-solvent, methanol at room temperature. Dried HIPS is used for sample preparation. Various metal oxides were used as additives to HIPS for studying thermal degradation. Their physical properties and source are tabulated elsewhere [13].

Sample preparation and procedure

HIPS was coated onto metal oxides by the method similar to one described by Cullis *et al.* [14]. It was dissolved in dichloromethane and a weighed amount of metal oxide, to get polymer to oxide ratio 5:1 by mass, was added to solution. The mixture was then stirred for half an hour and then solvent was removed by evaporation leaving metal oxide particles coated with a thick film of HIPS.

TG curves were recorded out on a Perkin-Elmer TG Thermal System TGS2 in a flow of nitrogen gas at a heating rate of 10 K min^{-1} using 5–10 mg sample in an aluminum crucible at Regional Sophisticated Instrumentation Center, Nagpur.

Theoretical method of calculation of kinetic parameters

In the pyrolysis of polymers volatile products are formed and end product is generally carbon char. In presence of additives (oxides) the end product is a mixture of oxide and carbon char. Hence the reaction rate equation used to study heterogeneous reaction involving gaseous products and solid residue has been used. The non-isothermal parameters for these compounds were calculated by inflection point method [15], similar to the method used for thermal decomposition of bisphenol A polycarbonate alone and in presence of oxides [16].

Results and discussion

Representative TG curve for thermal degradation of HIPS with and without metal oxide are shown in Fig. 1. The figure shows that the temperature of onset of degradation in presence of additives is higher than that of pure HIPS, showing the stabilization of HIPS by metal oxides in the initial stage. The kinetic parameters computed by using these data are shown in Table 1. A plot of $\ln(A)$ against E_a is shown in Fig. 2 to correlate these values of E_a and A. Figure 2 shows that a linear a relationship exists between $\ln(A)$ and E_a for the thermal degradation of HIPS in presence of metal oxides, in an inert atmosphere. Such linear relation

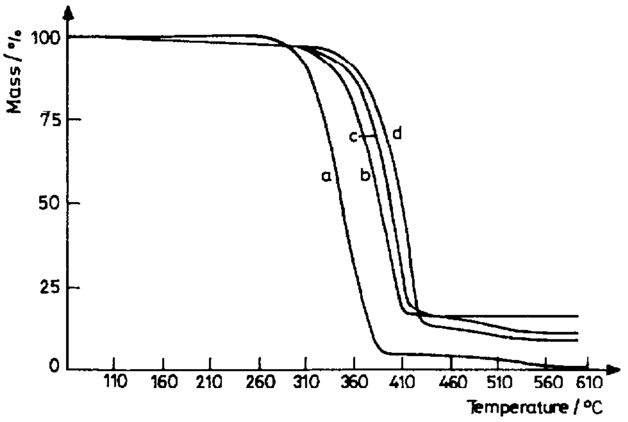

Fig. 1 Representative TG thermograms of HIPS and metal oxides coated with HIPS.
a) HIPS, b) MnO_2, c) V_2O_5 and d) SnO_2

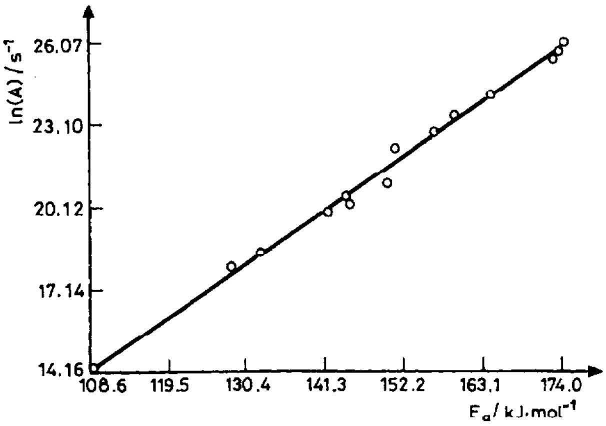

Fig. 2 Kinetic compensation in the thermal degradation of HIPS in presence of metal oxides

can be expected from Arrhenius equation which is expressed in logarithmic forms as,

$$\ln(A)=\ln(k_{\mathrm{iso}})+(E_a/RT_{\mathrm{iso}}) \qquad (1)$$

where k_{iso} and T_{iso} is the isokinetic reaction rate constant and the isokinetic temperature respectively. These are 'isokinetic parameters' and the relationship is 'isokinetic effect' or 'compensation effect' (C.E.). Such a reaction rate compensation effect is normally associated with the variation of heterogeneous reaction rate in different solids [13, 17]. The results in Fig. 2 may be expressed by Eq. (2) as,

$$\ln(A)=0.179\,E_a-5.29 \tag{2}$$

The isokinetic temperature and isokinetic reaction rate constant are 671.0 K and $5.0\cdot10^{-3}$ respectively. At this temperature, reaction rate at different degradation sites may be same.

Several theories [18] that predict such linear compensation behaviour have been reported. Amongst the various causes, these theories suggest that the relation such as in Eq. (2) is probably due to enthalpy-entropy relationship and simultaneous occurrence of reactions on surface centers involving different interrelated kinetic behaviour within the group of rate processes. The isokinetic temperature, T_{iso} has been suggested to characterize the temperature of onset of reaction, to signify a temperature at which relative reaction rates within the group of related reactions undergo an inversion or represent the temperature at which the reaction rate constant of all reactions of the series have same value. Feates *et al.* [5] have considered the form of kinetics in which reactions obeying Arrhenius rate law can occur simultaneously on a single sample and exhibit linear relation as Eq. (2).

Table 1 Kinetic parameters for the thermal degradation of HIPS in presence of metal oxides

S.No.	Additive (Metal Oxide)	Order of reaction/ n	Activation energy (E_a) kJ mol^{-1}	Pre-exponential factor (A)/ s^{-1}
1	NIL	1.0	116	$2.9\cdot10^{7}$
2	PbO	0.4	109	$1.4\cdot10^{6}$
3	MnO_2	0.7	128	$6.4\cdot10^{7}$
4	TiO_2	0.5	132	$1.0\cdot10^{8}$
5	Al_2O_3	0.5	141	$4.7\cdot10^{8}$
6	V_2O_5	0.6	144	$8.0\cdot10^{8}$
7	SnO_2	0.6	145	$6.2\cdot10^{8}$
8	Fe_2O_3	0.2	150	$1.3\cdot10^{9}$
9	CuO	0.8	151	$4.6\cdot10^{9}$
10	CeO_2	0.4	156	$8.1\cdot10^{9}$
11	Sb_2O_3	0.8	159	$1.6\cdot10^{10}$
12	Cu_2O	0.7	164	$6.2\cdot10^{10}$
13	ZrO_2	0.6	172	$1.1\cdot10^{11}$
14	Cr_2O_3	0.6	174	$1.5\cdot10^{11}$
15	MoO_3	0.8	174	$2.1\cdot10^{11}$

Analysis of data shows that the thermal degradation of HIPS without additive is first order process whereas in presence of metal oxides it is fractional order.

Jellineck [19] has dealt the thermal degradation of polymers by considering different mechanisms and showed that thermal degradation via random chain scission by free radical formation is first order, degradation via chain end initiation leading to depolymerization is zero order and in case both processes occur simultaneously or through free radical formation and disproportionation is fractional order rate process. Thus the present data show that in the degradation of HIPS in presence of metal oxides different active centers may act simultaneously as reaction sites and the number of these reaction sites may alter during reaction, leading to different mechanisms which exhibit isokinetic behaviour. HIPS in presence of transition metal oxides undergo degradation leading to macroradical formation through random chain scission, disproportionation or cyclization. The macroradicals are formed via chain scission, as,

$$R—R \rightarrow 2R^{\cdot}$$

These macroradicals could take part in hydrogen abstraction, free radical chain scission, crosslinking or cyclization.

Higher activation energy of thermal degradation of HIPS, when the order of reaction is fractional or first order indicates stabilization of HIPS through crosslinking and cyclization which would occur due to interaction of free macroradicals with the double bonds in HIPS because of the presence of butadiene as proposed by Cullis *et al.* [20] in their studies on carboxy terminated polybutadiene.

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