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ACTIVATION ENERGY FOR THE OXIDATIVE THERMAL DEGRADATION OF PLASTICS

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SUMMARY

For the purpose of measuring kinetic data for the oxidative thermal degradation reaction, Kissinger's relation was applied to 10 commercial thermoplastic resins. When these contain hydrogen as a constituent, in general, they give rise to an exothermic oxidation reaction and begin to decompose, in the presence of oxygen, at a temperature slightly less than 200°C. Their E values were mostly from 10 to 20 kcal/mole. A compensation effect was observed in which ln A increased with an increase in E. Evidently, an oxidation reaction occurs at the surface of molten plastics prior to the thermal degradation. The coexistence of trace amounts of water with plastics was found to play a part in lowering the activation energy of this reaction. It was concluded that the activation energy of the oxidative thermal degradation could express well the relationship between the molecular structure and its behavior when heated, and could be used as a guide in the search for heat-resistant plastics.

INTRODUCTION

Since the oxidative thermal degradation refers to a chemical reaction between a substance and oxygen, the probability of the reaction depends on the chemical structure of the substance. Accordingly, the activation energy for the oxidative thermal degradation of plastics is closely connected with this sort of reaction. However, systematically measured data seem to be unavailable, leaving only those reported fragmentally.

Rudin *et al.*[1] obtained 23.5–33 kcal/mole for the activation energies of the induction period in the oxidation of polyethylene. Hawkins *et al.*[2] found 21.6 kcal/mole for the oxygen uptake reaction of a thin-molded slab of polyethylene. In oxygen uptake studies on polyethylene, Wilson[3] obtained 25 kcal/mole for the activation energy of the reaction during the induction period. Myers[4] measured an activation energy of 16 kcal/mole for carbonyl formation in polyethylene.

In this study, applying Kissinger's relation[5] [shown in Eqns. (1) or (2)] and the Arrhenius Eqn. (3) to the exothermic thermal degradation reactions, kinetic data such as activation energy, frequency factor and specific reaction rate were determined on 10 commercial thermoplastic resins (all made in Japan) in oxygen and air under

atmospheric pressure. In addition, the values for the degradation in nitrogen were determined for comparison under the same condition.

$$E/RT_m^2 = A\exp(-E/RT_m) \quad (1)$$

$$d(\ln\varphi/T_m^2)/d(1/T_m) = -E/R \quad (2)$$

$$k = A\exp(-E/RT) \quad (3)$$

Though confirmative[6] and critical[7] reviews on the validity of this relation exist, Kissinger's equation is thought to be sufficiently valid, judging from the performance throughout this study.

EXPERIMENTAL

Instrument

The Rigaku Denki Thermoflex type 8021, a differential thermogravimetric analyser, was used throughout this study. Both the standard DTA cell and procedures were used[8].

Materials

The ten commercial plastics used are listed in Table I. If pure plastics containing only monomers were available, the values for those could be obtained. It is well-known, however, that synthetic plastics inevitably contain not only the monomer, but also the other additives like catalysts, antioxidants or sometimes emulsifiers. Relating to this point, the presence of a phenolic-type antioxidant has been known to

TABLE I

LIST OF SAMPLES

Plastic	*Manufacturer*	*Features*
Polyethylene	Furukawa chemical industries	Film, 0.02 mm thick. trade name: Staflene E-640.
Polypropylene	Mitsubishi oil chemical industries	Powder. Melt index = 24.
Polyisobutylene	Furukawa chemical industries	Viscous liquid. trade name: Furukawa polybutene HV-1900.
Polyacrylonitrile	Mitsui-Toatsu	Powder.
Polystyrene	Mitsui-Toatsu	Sheet, 0.5 mm thick. m.w. = 150,000. trade name: Topolexsheet.
Polyethyleneglycol-terephthalate	Toray	Sheet. trade name: Tetoron.
Polyamide Nylon 6	Toray	Sheet.
Cellulose triacetate	Fuji photofilm	Film, 0.117 mm thick. trade name: Fujitac "Matt".
Polycarbonate	Teijin	Film. trade name: Panlite.
Polytetrafluoro-ethylene	Nippon vulca industries	Film, 0.05 mm thick. trade name: Vulflontape 7900.

prolong the induction period, but has no effect on the uptake rate itself[3]. A similar result was obtained by Biggs[9] with an amine-type antioxidant. In this study it was considered important to obtain these data on samples at present in the market.

Techniques

The temperature of the sample holder was measured at the side of the reference. Platinum *vs.* platinum–10% rhodium thermocouples were used to withstand oxidative atmospheres. Three heating rates (~30, ~15, and ~6°C/min) were employed. All samples were kept, before measurements were taken, for more than two weeks in a desiccator in which a saturated solution of potassium carbonate was present, providing a relative humidity of *ca.* 40% at room temperature. A significant influence on the value of E was observed unless the humidity hysteresis of a sample was kept constant. Samples were not mixed with the reference material, but only laid on it. Sample amounts were ~2–4 mg in air or oxygen, and ~10–15 mg in nitrogen. A dynamic gas flow system was maintained during determinations, air, oxygen or nitrogen, being passed over the sample at a constant rate of 0.5 l/min under atmospheric pressure. α-Alumina was used as the reference material, ignited for 30 min in a crucible before each run. Each measurement was repeatedly carried out until its reproducibility was assured. The resolution of peak temperatures was within ±2°C.

RESULTS

The kinetic parameters measured are summarized in Table II, in which E, ln A and k refer to activation energy, logarithm of frequency factor, and specific rate of the reaction, respectively. Plastics containing hydrogen as a constituent, in general, gave rise to an exothermic oxidation reaction and began to decompose, in the presence of oxygen, at temperatures a little less than 200°C. Their E values in oxidative atmospheres were mostly from 10 to 20 kcal/mole, except for polycarbonate and polytetrafluoroethylene. The value of E, however, generally increased with an increase in T_m. It should be noted that a higher value of E corresponded to a Kissinger's plot of a steeper slope, and, hence, is liable to be incorrect.

Fisher *et al.*[14] obtained an ignition point of 250°C for polyethylene in oxygen. Schwenker and Beck[10] reported an exothermic temperature of 340°C for nylon 66 in air. The melting point of polyacrylonitrile (PAN) was obscure, consistent with Dunn and Ennis' report[11] that the melting of PAN is nearly obscured when the heating rate is 40°C/min or lower. They also obtained 44 kcal/mole for the activation energy of the thermal degradation of PAN in nitrogen, while Hay[12] obtained 30 kcal/mole for the same material and conditions. Rather higher E values in the case of polycarbonate seemed to be obtained, probably due to the evolution of carbon dioxide accompanying the thermal degradation, with the suppression of diffusion of oxygen onto the surface of the plastics.

With regard to the ease of the thermal degradation in the presence of oxygen, it is generally well-known that the formation of hydroperoxide is the initial stage of

TABLE II

KINETIC RESULTS FOR OXIDATIVE AND NON-OXIDATIVE THERMAL DEGRADATION OF SEVERAL PLASTICS BY THE DTA METHOD

Plastic	*m.p.* (°C)	*in air*				*in oxygen*				*in nitrogen*			
		T_m	E	ln A	k	T_m	E	ln A	k	T_m	E	ln A	k
Polyethylene	120	248	14.7	12.6	0.20	226	17.1	15.9	0.20	473	53.6	34.8	0.30
Polypropylene	143	226	13.6	12.1	0.15	193	14.0	13.7	0.25	456	35.8	22.8	0.27
Polyisobutylene		221	12.4	11.1	0.21	199	22.7	25.2	0.41	389	41.8	30.8	0.37
Polyacrylonitrile	obscure									369	32.1	23.8	0.25
Polystyrene		302	20.8	16.7	0.22	279	20.8	17.5	0.25	422	62.0	44.3	0.74
Polyethyleneglycol-terephthalate	229	337	20.6	15.3	0.19	313	21.7	17.2	0.25	435	42.8	29.2	0.30
Polyamide PA 6	215	387	14.8	9.14	0.12	329	13.1	8.82	0.12	447	42.0	28.6	0.30
Cellulose triacetate	270	353	22.8	16.7	0.20	317	18.7	14.3	0.18				
Polycarbonate	220	477	34.6	21.4	0.17	452	37.0	24.3	0.25				
Polytetrafluoro-ethylene	325	551	73.0	43.4	0.30	544	124.0	75.4	0.37				

T_m = peak temperature (°C) at a heating rate of 6°C/min; E = activation energy (kcal/mole); ln A = logarithm of the frequency factor; k = specific reaction rate (min^{-1}) at T_m. Any vacancies refer to the cases in which confident results were not obtained.

the oxidation reaction in the case of organic substances containing hydrogen[13]. The initial step of the thermal degradation of most plastics is also expected to go through this stage. Accordingly, it might be seen that these plastics have almost identical E values, even if there is little difference between the strengths of the bonds between the hydrogen atom and the main chain, this depending on the kind of plastic under consideration.

A so-called compensation effect is observed, in which ln A increases with an increase in E. Consequently, it could be concluded, mainly from this effect, that specific reaction rates of most plastics are nearly equal at the temperature of the first exothermic peak as evident from Table II. The fact that the values of k at the peak temperatures are almost the same, independent of the type of plastic, means first of all that the peak temperature of the thermal degradation is generally a temperature at which the specific rate of the degradation reaction of a plastic attains a certain value common to each plastic. At the same time, this fact might be considered to constitute sole proof that the value of E and A obtained are reasonable. An E value, therefore, accompanied by a considerably higher k value, is less reliable. In any event it would seem likely that k can have a similar value for a compensating combination of A, E and T_m.

DISCUSSION

Surface oxidation reaction and ignition mechanism of plastics

Though a discussion of the ignition process is beyond the purpose of this paper, some suggestions on the process obtained through this study are put forward. It

seems to be obvious that in the initial stage of the ignition of high-molecular weight substances, such as plastics, having very low vapor pressures, at temperatures of a few hundred degrees, an initiation of the oxidation reaction and self-heating phenomena on the surface of the plastics play an important part, prior to the evolution of flammable gases.

Fisher and Gerstein[14] stated in their paper on the combustibility of polyethylene that a surface or near-surface oxidation reaction occurred prior to ignition. In experiments[15] in which samples of polyethylene or polyvinylchloride were heated in an oxygen atmosphere in a furnace, the temperature of the sample was observed to rise as much as 100 °F above the furnace temperature just prior to ignition, indicating the occurrence of an oxidation reaction taking place in the solid sample. Biggs and Hawkins[9] also reported a tendency for an oxygen uptake rate of polyethylene to be proportional to the sample surface area rather than the mass. They found that the oxygen reacts with the surface before it can diffuse into the center of the polyethylene film, unless the film is very thin.

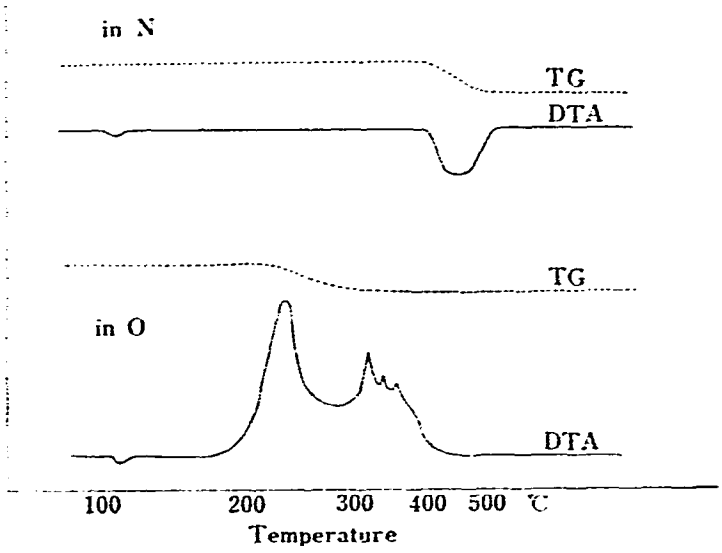

Fig. 1. DTA and TG curves for polyethylene in nitrogen and oxygen.

According to the general concept of the ignition process which proceeds through the thermal degradation—evolution of flammable gases—ignition, the evolution of gas which is equal to a perceptible weight-loss should be observed prior to any exothermic reaction. With polyethylene, as illustrated in Fig. 1, it is not until *ca.* 400 °C that the weight-loss begins in nitrogen, whereas in oxygen an exothermic reaction starts at *ca.* 180 °C and the weight-loss commences together with the first exothermic peak of *ca.* 230 °C. These facts appear to imply that the exothermic reaction does not occur suddenly at a time after the gas-evolution phenomena, but in the presence of oxygen an oxidation reaction on the surface of the plastic constitutes a significant step of the ignition process, with the attainment of a limiting concentration of flammable gas[16].

Effect of oxygen partial pressure on activation energy

It is already known that the phenomenological combustion velocity, even in a heterogeneous system, is usually proportional to the partial pressure of oxygen[17]. It was thought that it might be of interest to know whether or not any effect of oxygen partial pressure on the activation energy was observed.

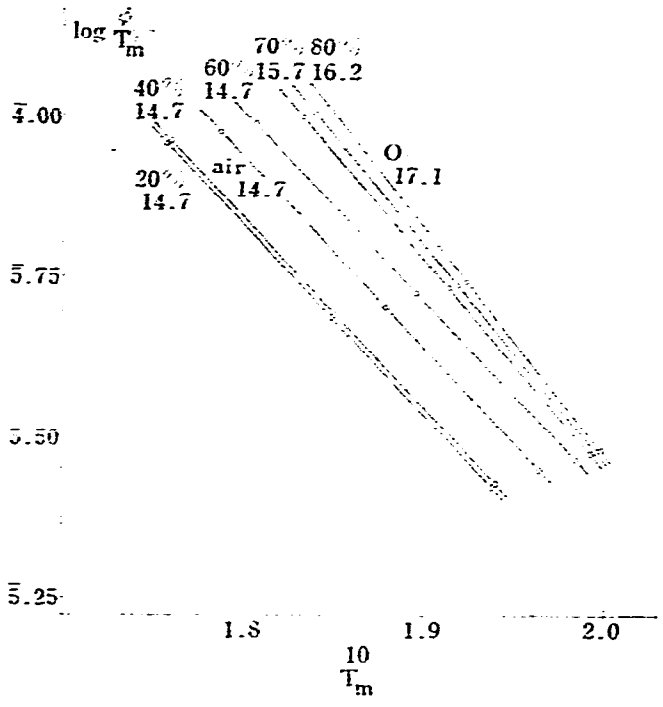

Fig. 2. Effect of oxygen partial pressure on the activation energy of polyethylene.

This effect was investigated on polyethylene between oxygen and air, in terms of oxygen % in nitrogen. It is shown in Fig. 2 that up to about 60% of oxygen concentration the same slope as the one in air was obtained, but above this concentration, the slopes became increasingly steeper. According to the DTA and TG curves in Fig. 3, in oxygen, a weight-loss begins near the temperature of the first large peak and almost all the sample decomposes near this peak. On the other hand, in air, the first exothermic peak is small, the weight-loss is hardly observed throughout this peak region, and a clear-cut weight-loss takes place together with the beginning of the second peak.

From the facts observed above it would be considered that in air, at first only an oxidation reaction of hydrogen occurs, while in oxygen such a process is expected, because, even if an oxidation of hydrogen occurs initially, the oxidative decomposition of the carbon skeleton is induced almost simultaneously because of a large velocity of generation and accumulation of heat. It would accordingly be assumed that even in oxygen, the E values mainly reflect the reaction between the oxygen and hydrogen of the plastics. Therefore, E values in air are presumed to be more intrinsic.

At any rate it would be clear that with a certain substance, the specific rate of the oxidative thermal decomposition reaction is independent of the oxygen partial pressure under the conditions of this study.

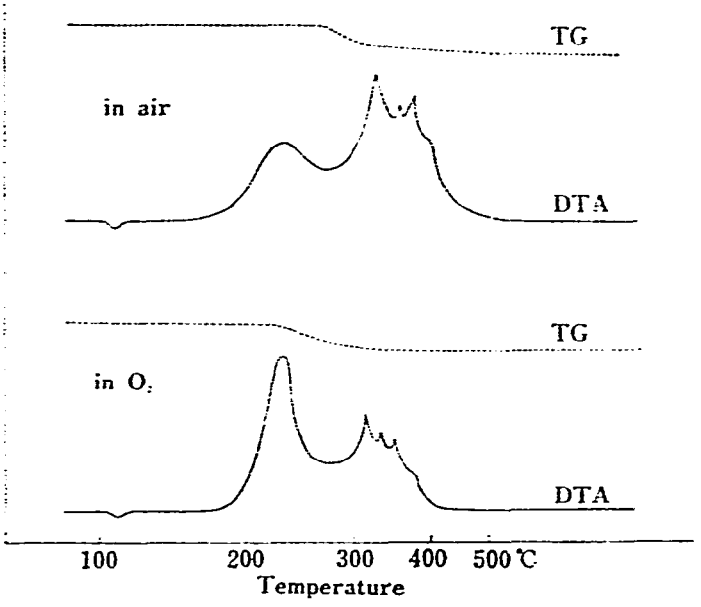

Fig. 3. DTA and TG curves for polyethylene in air and oxygen.

Effect of relative humidity on activation energy

With polyethylene, this effect was measured in air after the sample had been kept for more than two weeks in atmospheres of several relative humidities at room temperature.

It was observed (Table III) that coexistence of trace amounts of water, contrary to the usual sense, was able to play a part in lowering the activation energy for the oxidative thermal degradation reaction. There also seems to be a slight tendency toward lower exothermic peak temperatures with higher humidities. Specific reaction rate, however, is evidently larger with drier than with wetter samples.

TABLE III

EFFECT OF RELATIVE HUMIDITY ON THE OXIDATIVE THERMAL DEGRADATION OF POLYETHYLENE

Saturated aqueous solution of salts (at room temp.)	*Relative humidity (%)*	*Peak temp. (°C) (at 6 °C/min)*	*Activation energy (kcal/mole)*	*ln A*	*k (min^{-1})*
	100	241	10.9	8.8	0.16
NH_4Cl	80	245	12.6	10.5	0.18
$K_2CO_3 \cdot 2\,H_2O$	43	250	14.7	12.7	0.21
CH_3COOK	20	252	19.3	16.8	0.25

It is curious that even at temperatures of a few hundred degrees, an effect of relative humidity on the activation energy is still observed. However, this fact could be better interpreted by considering a sort of chemisorption of water onto the surface of the sample, rather than a simple physical adsorption.

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