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THERMOANALYTICAL STUDIES OF THE PYROLYSIS OF ORGANIC POLYMERS

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Some applications of thermoanalytical techniques (TG and DTA) to the study of organic polymer pyrolysis are described. It is shown that in order to obtain meaningful kinetic parameters strict control of environmental conditions is required. Experimental results are given for selected ethylene-propylene co- and ter-polymers, for halogenated polymers including polyvinyl chloride and neoprene in admixture with ferric oxide, and for other materials.

This paper reviews some of the work carried out at the National College of Rubber Technology on the pyrolysis of raw organic polymers and certain polymer-additive mixtures of technological importance.

The ultimate thermal stability of a polymer, the mode of degradation and the influence of certain additives is of prime interest both to the polymer chemist preparing new polymers and to the technologist seeking to use a compounded polymer at elevated temperatures. The studies reported here use thermogravimetry (TG) and differential thermal analysis (DTA) to characterize polymer degradation processes and it is shown that careful control of experimental conditions enables a satisfactory correlation of data from these techniques.

Materials and preparation methods

The raw polymers used were as follows:

Polyvinyl chloride: Geon 101, British Geon Ltd. Styrene-butadiene rubber: Krylene NS, Polymer Corporation. Ethylene-propylene rubbers: ECP900, Shell Chemical Co.; Dutral S, Montecatini—Shell Corporation; Enjay 404, Enjay Rubber Co.; Royalene 201, U.S. Rubber Co. Polychloroprene, Neoprene W; chlorosulphonated polyethylene, Hypalon 20; vinylidene fluoride—hexafluoropropylene copolymer, Viton A: DuPont Co.

Additive materials

Ferric oxide, zinc oxide: Analar reagents; sulphur, stearic acid: GP reagents, ex Hopkin and Williams Ltd. 2-mercaptobenzthiazole (Vulcafor MBT), dibenzthiazyldisulphide (Vulcafor MBTS), tetramethyl thiuram disulphide (Vulcafor TMT): industrial grades, ex ICI Ltd. Dicumyl peroxide (Perkadox BC-40; 40% active material on inert base): ex Novadel Ltd.

Earlier work [1] had shown certain EP polymers to contain small amounts of low-molecular-weight extractable oils; these were removed by extracting with an azeotrope of acetone/methanol/chloroform 350/274/291 vol/vol and the polymers dried to constant weight at 40° under vacuum.

Preparation and characterization of compounds

The polymer-additive mixtures were compounded on a cooled 15 × 30 cm two-roll laboratory mill. The vulcanization experiment compounds were tested on the Shawbury curometer at 160°; optimum cure was calculated by Juve's method [2].

Techniques

Thermogravimetric technique

The TG equipment consisted of a Stanton TR1/1 mg sensitivity thermogravimetric balance [3], fitted with a choice of linear heating rates. This had been modified [4] for use under "inert gas" conditions and sample temperatures were sensed by a Pt/Pt-13% Rh thermocouple with the junction in contact with the base of the sample support and its output fed to a high quality, multi-range potentiometric recorder [5]. The balance was operated under a controlled dynamic atmosphere of inert gas (oxygen-free nitrogen).

Differential thermal analysis

The DTA equipment consisted of a DuPont 900 Differential Thermal Analyser [6] and a calorimeter cell designed for quantitative differential thermal analysis. (*Q*-DTA), based on the design principles of Boersma [7]. This was calibrated in the usual manner by melting standard pure metal samples. The cell was evacuated and purged three times with oxygen-free nitrogen, the pyrolysis being carried out in flowing nitrogen.

Quantitative TA techniques

The thermal degradation of a polymer involves rupture of chemical bonds. In the absence of environmental reactions such as oxidation this requires energy and the overall pyrolytic process is endothermic. The energy absorbed per unit mass degraded would appear to be a useful characterization parameter. Estimates of this energy may be made directly using *Q*-DTA to obtain values of the heat of decomposition ΔH_{dec} [8, 9]. The method of Borchardt and Daniels [10] has been applied to the *Q*-DTA data to obtain overall activation energies $(E_p)_H$ for the degradation process.

The weight-loss vs. temperature (TG) measurements have been used to calculate an overall activation energy $(E_p)_G$ with respect to weight-loss. Overall first-order kinetics with respect to weight-loss were assumed according to the method of Newkirk [11] and modified [12] to apply to each separate pyrolysis stage.

Control of environmental variables

In order to obtain meaningful kinetic parameters using these techniques, the environmental conditions require to be closely controlled. The effects on pyrolysis of the major variables are now discussed:

Thermogravimetry

(a) *Dynamic gas flow and buoyancy effects:* Thermal degradation of organic polymers generally follows a different course in vacuo or inert atmosphere from that in air or oxygen. A modification to the atmosphere control equipment for the TG balance [4] has been found to eliminate buoyancy effects regardless of crucible geometry, crucible and sample weight, or heating rate up to at least 600° [13]; at 950°, even for light crucibles, the weight gain is small.

(b) *Sample support (design and material):* The design of sample support has received considerable attention [14, 15]. Use of a flat, shallow dish avoids diffusion control during pyrolysis.

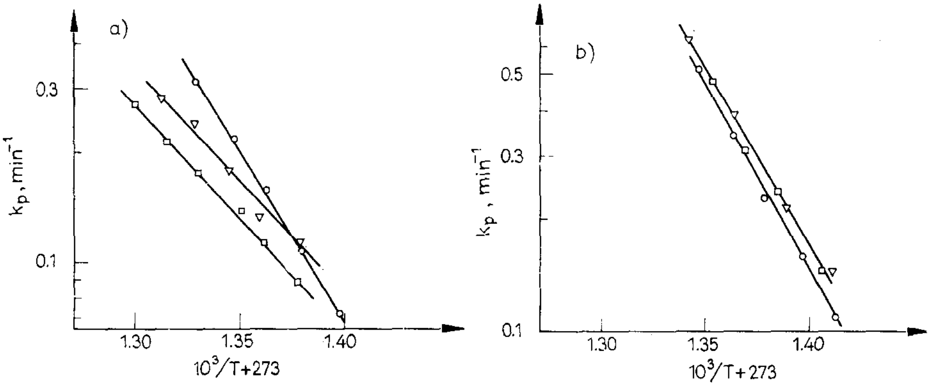

Fig. 1. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature for the final stage pyrolysis using different sample supports: nickel (○); platinum (▽); silica (□); *a)* for PVC, *b)* for SBR. Data from ref. [13]

Figure 1 shows Arrhenius plots for the main-chain degradation of PVC and SBR using platinum, nickel and silica crucibles. The pyrolysis of the relatively saturated SBR is not influenced by choice of sample support material, although nickel appears to exhibit a small catalytic effect on the degradation of the supposedly highly unsaturated residual PVC backbone structure.

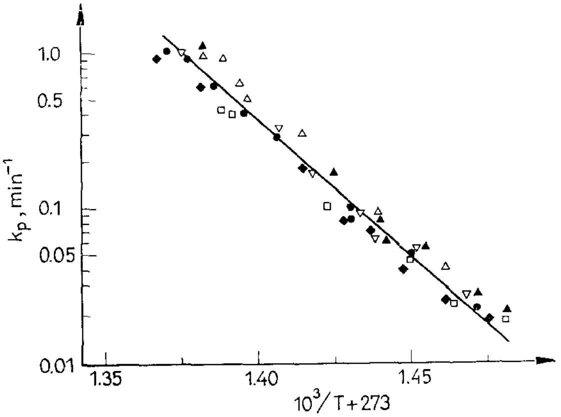

Fig. 2. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature for raw EPT pyrolysis with variation of sample mass and heating rate: 20 mg, 6.0 °C min^{-1} (●); 20 mg, 9.0 °C min^{-1} (▽); 50 mg, 6.0 °C min^{-1} (▲); 50 mg, 9.0 °C min^{-1} (△); 100 mg, 6.0 °C min^{-1} (◆); 300 mg, 9.0 °C min^{-1} (□). Data from ref. [13]

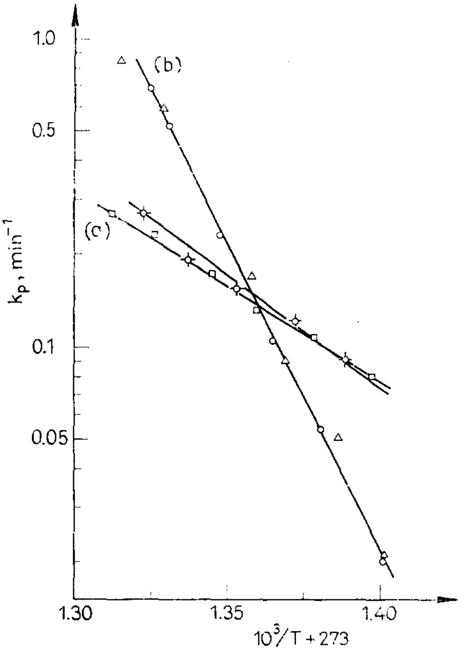

Fig. 3. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature. Curves *a)* for the final stage pyrolysis of PVC in different atmospheres: in 'oxygen-free' nitrogen (□); in catalytically-treated nitrogen/hydrogen (99 : 1) mixture (-○-). Curve *b)* for EPT decomposition: in 'oxygen-free' nitrogen (△); in catalytically-treated nitrogen/hydrogen (99 : 1) mixture (○). Data from ref. [13]

(c) *Sample mass; degree of comminution; heating rate:* These related variables are grouped together in the context of "diffusion control" of reaction rate, it being assumed that the rate of loss of volatiles from a massive sample subject to rapid heating will be determined by the barriers to migration of these volatiles from the interior of the polymer to the free surface, the actual evolution falling behind the chemical rate for free decomposition. Fig. 2 shows that for EPT within the range of sample sizes and heating rates evaluated, and using a "free-diffusion" support, the pyrolysis is not diffusion-controlled. These studies of pyrolysis kinetics of amorphous, essentially linear polymers, suggest that sample masses up to 300 mg together with heating rates up to 9° $\min^{-1}$ give acceptable data.

(d) *Composition of "inert" atmosphere:* The effect of a trace quantity of oxygen was examined by comparing the kinetic results of pyrolyses carried out using a 99/1 nitrogen/hydrogen gas mixture passed through a "De-Oxo" unit with results obtained using commercial "oxygen-free" nitrogen known to contain some 200 ppm O_2. The "inertness" of each gas system was determined using the method of Gilbert et al. [16] by measurement of the oxidation rate of carbon black. Fig. 3 shows some results for PVC and EPT pyrolyses; the more "inert" system influences the main-chain degradation of PVC, whilst EPT appears uninfluenced.

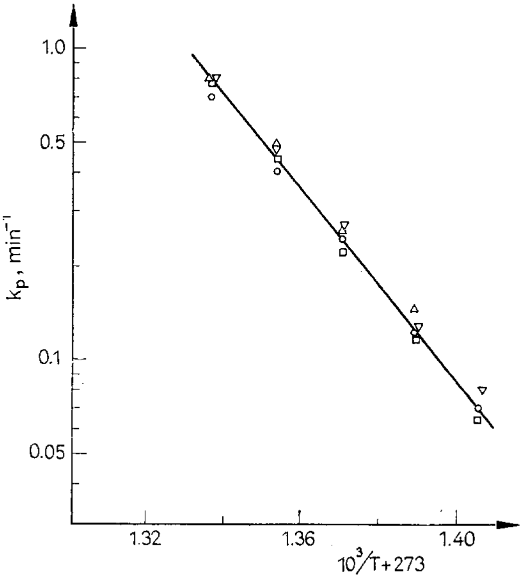

Fig. 4. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature (after Borchardt and Daniels) for Q-DTA. Sample size data: 1.75 mg (△); 2.56 mg (▽); 3.20 mg (□); 4.97 mg (○). Data from ref. [9]

Differential thermal analysis

(a) *Sample size:* Table 1 and Fig. 4 show data for the pyrolysis of ECP 900 polymer at a heating rate of 10°C min^{-1}. Within the range 2.0 to 7.3 mg, sample size has no effect on ΔH_{dec} or the Arrhenius plots.

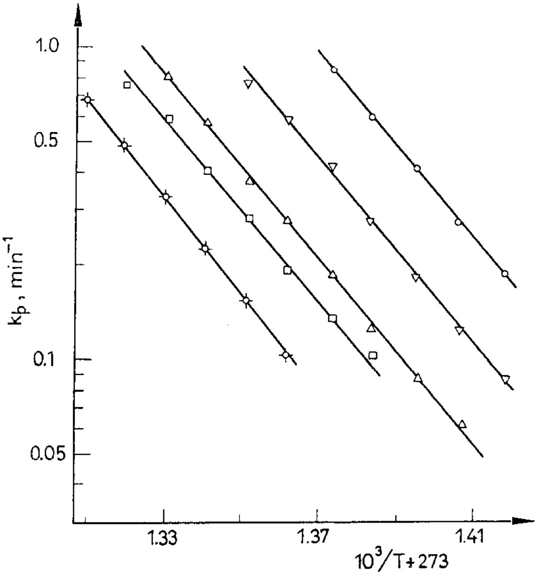

Fig. 5. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature (after Borchardt and Daniels) for Q-DTA. Heating rate data: 2.5° min^{-1} (○); 5.0° min^{-1} (▽); 10.0 °C min^{-1} (△); 15.0 °C min^{-1} (□); 20.0 °C min^{-1} (◇). Data from ref. [9]

Table 1

Q-DTA: Influence of sample size on pyrolysis of EPT (ECP 900). Data from ref. [9]

Mass mg	Area in^2	ΔH_{dec} cal g^{-1}
1.99	2.13	128.0
2.43	2.65	131.0
2.55	2.68	126.0
3.20	3.38	122.0
5.08	5.13	127.0
7.29	8.05	129.0

(b) *Heating rate:* The data for a fixed sample size (3.0 mg) of ECP 900 are shown in Table 2 and Fig. 5. The ΔH_{dec} and $(E_p)_H$ values appear to be unaffected by increasing the heating rate but the peak decomposition temperatures are increased; the Arrhenius plots are parallel and displaced towards regions of higher temperature. This results in an apparent shift of the Arrhenius pre-exponential (A or Z) factor.

Table 2

Q-DTA: Influence of heating rate on pyrolysis of EPT (ECP 900). Data from ref. [9]

Heating rate °C min^{-1}	Peak temperature °C	ΔH_{dec} cal g^{-1}
2.5	451	124.0
5.0	459	131.0
10.0	473	127.0
15.0	480	121.0
20.0	486	135.0

Characterization of the thermal degradation of uncompounded polymers

(a) *Ethylene-propylene co- and ter-polymers:* Fig. 6 and Table 3 show pyrolysis data for three EP polymers. Fig. 7 shows the pyrolysis to be a single-stage pyrolysis process, the temperature of maximum decomposition

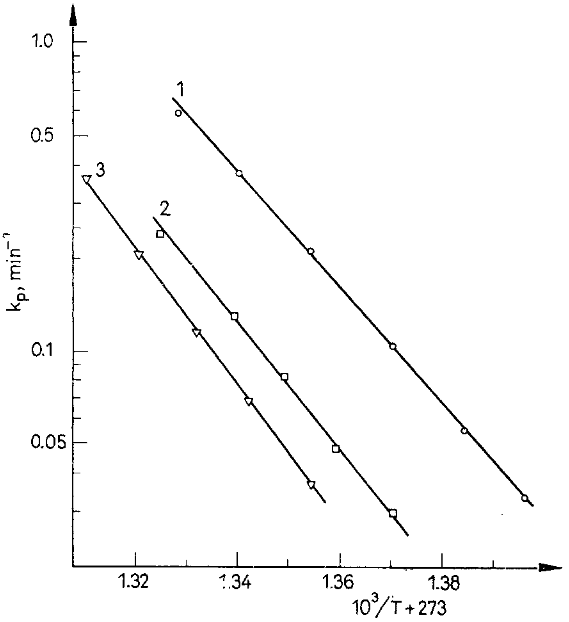

Fig. 6. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature for the pyrolysis of EP polymers: 1. Enjay 404 (○); 2. ECP 900 (□); 3. Dutral S (▽);

being around 470°. Pyrolysis-gas chromatography studies [17] have shown that the observed degradation products originate from scission processes similar to those which occur during linear ethylene and propylene homopolymer degradation [18].

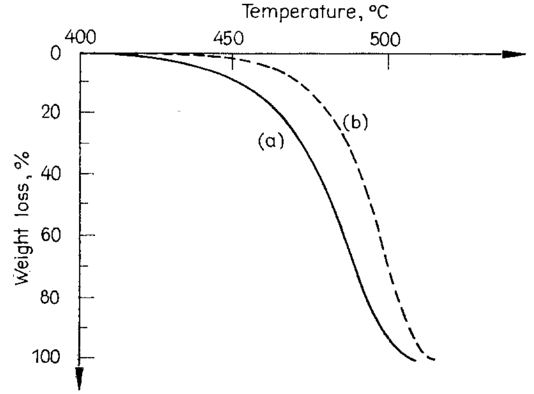

Fig. 7. A plot of % weight loss *vs* temperature for the EP polymers *a)* Enjay 404; *b)* Dutral S at a heating rate of 9 °C min^{-1}. Data from ref. [9]

Table 3

TA data for EP Co- and ter-polymers			TG data at 9°C min^{-1}		*Q*-DTA data at 10°C min^{-1}		
Polymer	E/P Ratio	FEV	$(E_p)_G$ Kcal mole^{-1}	A factor sec^{-1}	Peak temperature °C	ΔH_{dec} cal g^{-1}	$(E_p)_H$ Kcal mole^{-1}
Enjay 404 (co-)	—	0.99	86.7	1.6×10^{21}	465	135.0	66.7
ECP 900 (ter-)	65/35	1.0	92.9	1.1×10^{25}	471.5	139.9	86.2
Dutral S (ter-)	60/40	0.99	102.1	3.4×10^{30}	474	139.8	69.8

The ΔH_{dec} values for these polymers are in the range 130—140 cal g^{-1}, the $(E_p)_H$ values are close to 70 Kcal mole^{-1}, except for Dutral S (86.0 Kcal mole^{-1}). The EP copolymer (Enjay 404) exhibits slightly different degradation characteristics, indicated by the slightly lower decomposition temperature and $(E_p)_G$ value. The $(E_p)_G$ values range from 86.7 to 102.1 Kcal mole^{-1}; the A factors also reflect increasing polymer stability going from Enjay 404 to Dutral S.

(b) *Halopolymers:* PVC and polychloroprene (Fig. 8) exhibit a two-stage weight-loss pyrolysis the initial weight-loss being associated with dehydrochlorination, the second with decomposition of the main chain. Hypalon 20 undergoes an additional small weight-loss at about 200° [19] associated with the loss of chlorosulphonate groups, followed by dehydrochlorination and main chain degradation.

(c) *General polymer comparison:* Table 4 and Fig. 9 show TG data for Viton A (vinylidene fluoride—hexafluoropropylene copolymer), Krylene NS (SBR), PVC and Hypalon 20 (chlorosulphonated polyethylene) respectively. The Arrhenius

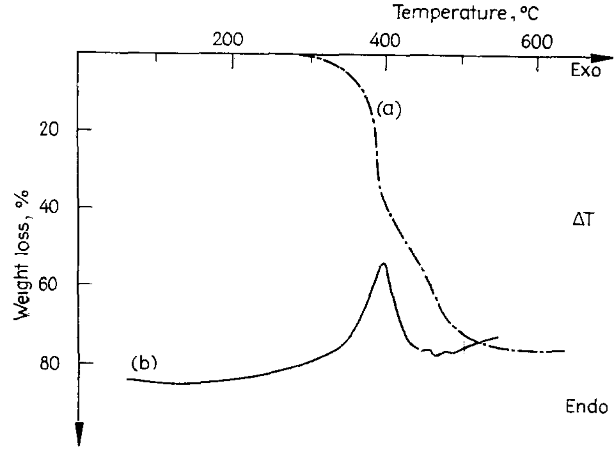

Fig. 8. A plot of *a)* % weight-loss *b)* DTA curve *vs* temperature °C for Neoprene W. Data from ref. [22]

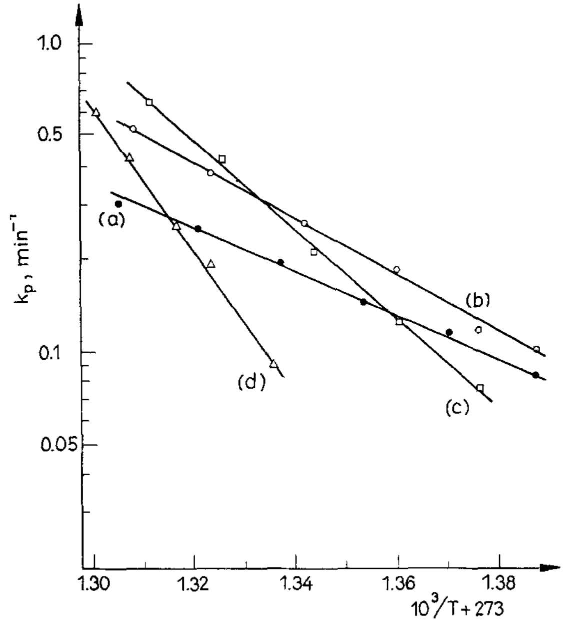

Fig. 9. Arrhenius plots of specific rate (on a logarithmic scale) as a function of reciprocal absolute temperature for the main chain pyrolysis of *a)* PVC (●); *b)* Krylene NS (○); *c)* Hypalon 20 (□) *d)* Viton A (△)

plot together with the calculated $(E_p)_G$ and A factor values provide a generalised assessment of polymer thermal stability. The data shown here apply to the main chain degradation.

Table 4

TG data at 9°C min^{-1}		
Polymer	$(E_p)_G$ Kcal mole^{-1}	A factor sec^{-1}
Geon 101	33.7	1.59×10^{9}
Krylene NS	44.1	1.09×10^{10}
Hypalon 40	64.0	1.84×10^{15}
Viton A	98.8	1.16×10^{21}

Characterization of polymer-additive interaction

(a) *Reactions of halogenated polymers with metal oxides:* The addition of a common inorganic pigment, ferric oxide, alters drastically the thermal degradation of halopolymers, inducing premature exothermic degradation; Fig. 10 shows DTA curves for neoprene/ferric oxide mixtures [21]. Isothermal DTA studies for CSPE (ΔT vs time) have shown this exothermic reaction to be extremely rapid following an induction period; reciprocal values of the induction period, treated as first-order rate coefficients, obey the Arrhenius law (Fig. 11). A series of concentrations of the oxide, from 0.2 to 25% w/w, yielded a series of parallel lines corresponding to an activation energy of 32 Kcal mole^{-1} (Fig. 12).

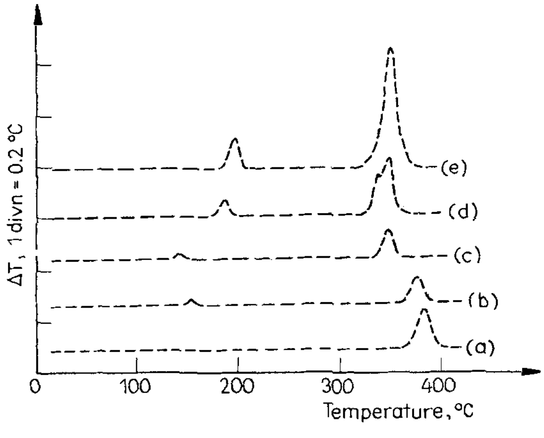

Fig. 10. DTA curves for Neoprene/ferric oxide mixtures: *a)* 0.0% Fe_2O_3; *b)* 0.1% Fe_2O_3; *c)* 1.0% Fe_2O_3; *d)* 5.0% Fe_2O_3; *e)* 10.0% Fe_2O_3. Data from ref. [21]

The problem of lowest oxide concentrations resulting in lowest stability was resolved by postulating formation of the active Lewis acid, ferric chloride in place of the inactive ferrous chloride formed at higher stoicheiometric ratios of iron to available chlorine [20]. Similar data have been obtained for mixtures of

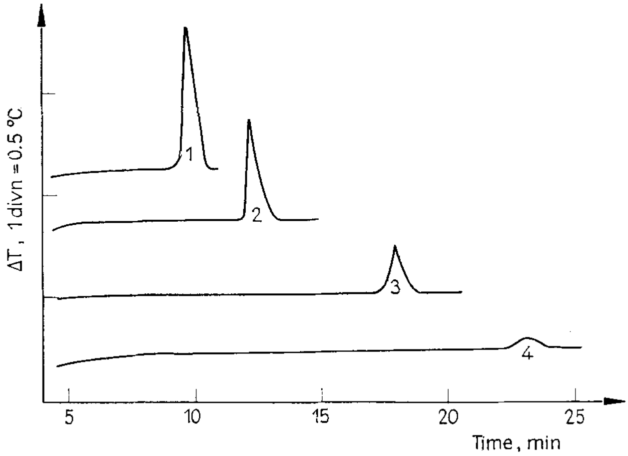

Fig. 11. Typical ΔT *vs* time (isothermal) curves for glass-diluted CSPE/10% Fe_2O_3 mixtures (8 mg) at four different temperatures: curve 1, 164°; curve 2, 159°; curve 3, 155°; curve 4, 150°. Data from ref. [20]

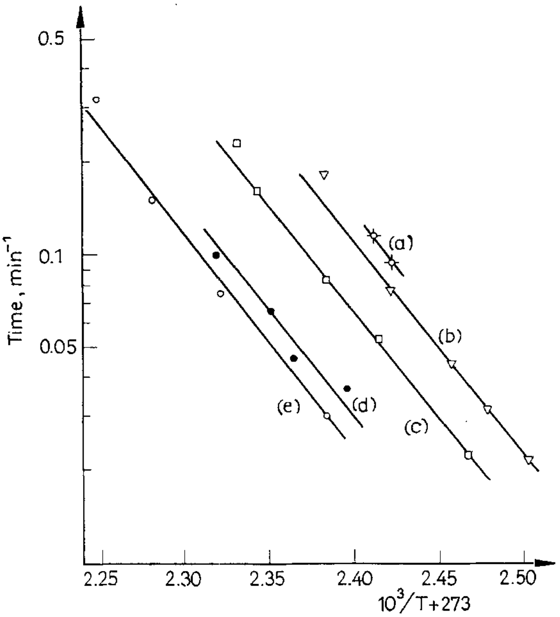

Fig. 12. Arrhenius plots of log $(t_0)^{-1}$ *vs* $(T^\circ \text{ abs})^{-1}$ for different CSPE/Fe_2O_3 mixtures: % Fe_2O_3. Curve *a)* 0.2%; curve *b)* 1.0%; curve *c)* 5.0%; curve *d)* 10%; curve *e)* 25%. Data from ref. [20]

ferric oxide with PVC and with neoprene [21]. The latter polymer has also been investigated with zinc oxide, preliminary results being also of a similar form [22]. It seems likely that the majority of commercial grades of chloro-polymers contain structurally imperfect segments containing labile (probably allylic or tertiary) chloride.

(b) *Vulcanization of EPT:* In high temperature (oxidative) conditions of service, it is frequently beneficial to vulcanize rubbers with "heat-resistant" curing systems. It was not known whether such systems were beneficial under anaerobic conditions. To investigate this the four vulcanisation systems in Table 5 were examined by TG. Fig. 13 shows that for sulphur vulcanization $(E_p)_G$ increases with degree of cure whilst for peroxide vulcanization, $(E_p)_G$ passes through a maximum.

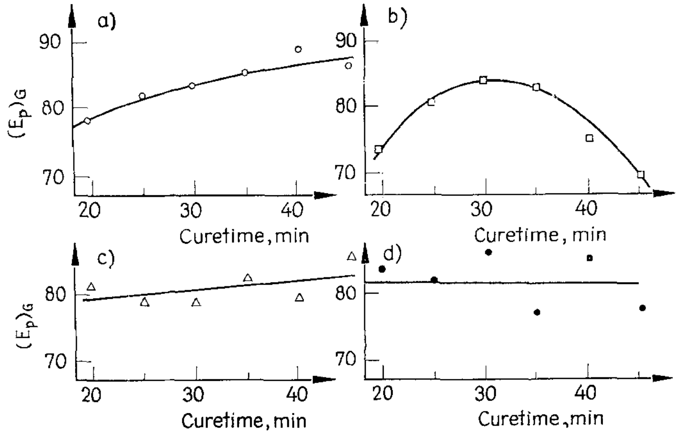

Fig. 13. $(E_p)_G$ values *vs* cure time for four vulcanizates: *a)* sulphur (○); *b)* peroxide (□); *c)* peroxide/sulphur (△); *d)* P.Q.D.O. (●). Data from ref. [9]

Table 5

EPT vulcanization systems

Ingredients	Sulphur	Peroxide	Peroxide/ sulphur	P.Q.D.O.
Royalene 201	100.0	100.0	100.0	100.0
Zinc oxide	3.0	—	—	—
Tetramethylthiuram disulphide	1.5	—	—	—
Mercaptobenzthiazole	0.75	—	—	—
Sulphur	1.5	—	0.3	—
Dicumyl peroxide		6.0	2.6	—
p-quinone dioxime				4.0
Lead dioxide				7.0
Benzthiazyldisulphide				1.0

The $(E_p)_G$ value might be expected to increase with degree of cure since an increase in the crosslinking means that there are more bonds per unit mass of polymer which must be broken and hence more energy is required to degrade a given mass of polymer to form volatile products. The decrease in $(E_p)_G$ for peroxide vulcanizates at longer vulcanization times may be explained in terms of two competing reactions occurring during the vulcanization process: (a) crosslinking (b) chain scission. In the early stages of vulcanization, many sites are available for crosslinking and reaction (a) predominates; hence $(E_p)_G$ increases. At higher extents of reaction, the rate of crosslinking falls and chain scission predominates; hence $(E_p)_G$ falls.

The results in Fig. 13 suggest that under nonoxidative conditions, technological "heat resistant" formulations offer little or no advantage over conventional vulcanization systems in EPT.

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Résumé — On décrit l'application des techniques thermo-analytiques à l'étude de la dégradation des polymères organiques. Le contrôle rigoureux des conditions expérimentales est d'une extrême importance pour l'obtention de paramètres cinétiques acceptables. On donne les résultats pour les co- et tripolymères d'éthylène-propylène, pour les polymères halogénés, et parmi ceux-ci, pour le polychlorure de vinyle, et le néoprène en mélange avec l'oxyde de fer (III) ainsi que pour d'autres substances.

ZUSAMMENFASSUNG — Es wurden über verschiedene Anwendungen der thermoanalytischen Methoden zur Untersuchung des Abbaus von organischen Polymeren berichtet. Verläßliche kinetische Parameter erhält man nur bei strenger Kontrolle der Versuchsverhältnisse. Ergebnisse für ausgewählte Äthylen-Propylen Co- und Terpolymere, für halogenierte Polymere, darunter Polyvinylchlorid und Neopren in Mischung mit Eisen(III)oxyd und für andere Stoffe konnten erhalten werden.

Резюме — Описано применение термического метода (ТГ, ДТА) к исследованию распада органических полимеров. Установлено, что для получения имеющих физических смысл кинетических параметров необходим строгий контроль условий окружающей среды. Исследовались этилен — пропиленовые кополимеры, полимеры, содержащие галогены, в том числе поливинилхлорид, и неопрен в смеси окиси железа(3) и других материалов.