Thermal & Oxidative Degradation of Cross-linked Styrene-Polyester Copolymers

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Thermal (in the presence of air) and oxidative degradation (at different flow rates of oxygen) of four styrene-polyester copolymers have been studied isothermally by TGA. Two different rate constants are found to be present for the thermal degradation whereas a single rate constant is found to be present for the oxidative degradation. An explanation has been offered for the thermal and oxidative degradation of these polymers.

DURING the investigation of heterogeneous combustion of cross-linked polymers[1,2] it was felt that a more thorough study of degradation behaviour is needed in order to predict the mass regression rate from kinetic parameters. Although considerable work has been published[3-5] on the degradation of polymers, especially polymers derived from vinyl monomers, the data are scanty on the degradation of cross-linked polymers. For the present study styrene-polyester copolymer has been selected.

Materials and Methods

The linear polymer was prepared by the process described earlier[1]. The fractionally distilled styrene was used in the cross-linking of linear polyester. The polymers prepared with varying degree of cross-linking are designated in terms of molar ratios of maleic anhydride, phthalic anhydride, styrene as M:P:S.

Degradation studies — The apparatus used for the thermal and oxidative degradation comprised the following units: (i) furnace with its accessories; (ii) temperature control unit; and (iii) weighing unit.

A vertical muffle furnace containing a long silica glass tube was used. The bottom of the silica glass tube was closed with a rubber bung having two holes, one of which was meant for a hard glass tube for introducing gases and the other was meant to introduce the pyrometer wires.

The crucible for holding the test sample was made up of platinum with a cylindrical shape of 2 cm in length and 1 cm in diameter. It was freely suspended by a platinum wire into the tube furnace, so that the tip of the pyrometer was exactly midway of the crucible height. The other end of the wire was attached to the bottom of the balance pan.

The pyrometer was made up of chromel alumel and the two wires were separated by porcelain beads; the pyrometer ends were connected to the thermoregulator (Industrial Pyrometer Co., Birmingham, England). To maintain constant temperature within

± 2·0° an Okay control kit (Industrial Pyrometer Co, Birmingham) was used.

A sensitive balance with air-damping arrangement was taken to have quick and accurate measurement for adding or withdrawing the weights. Arrangement for a lamp and scale was provided for reading very minute weights. The smallest weight that could be read on this balance was 0·0001 g.

The apparatus was duly calibrated (Fig. 1) from the melting point of standard chemical substances.

For the thermal degradation study small rectangular slices (70-100 mg) of different polymers were taken. At first the furnace was heated slowly to reach the desired temperature. The piece of polymer was taken in the platinum crucible which was then introduced into the furnace by platinum wire from a hook attached to the left arm of the balance pan. A stop watch was started simultaneously to record the time of degradation.
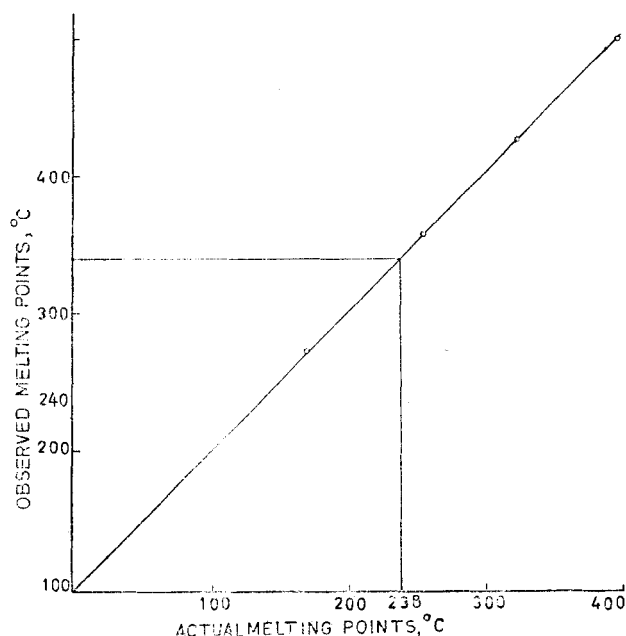

Fig. 1 — Calibration plot for the apparatus

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TABLE 1 — THERMAL RATE CONSTANT VALUES AT DIFFERENT TEMPERATURES FOR DIFFERENT COPOLYMERS

200°		250°		300°		350°		400°		450°	
$k_1 \times 10^6$ sec^{-1}	$k_1 \times 10^6$ sec^{1-}	$k^1 \times 10^6$ sec^{-1}	$k_1 \times 10^6$ sec^{1-}	$k_2 \times 10^6$ sec^{-1}	$k_1 \times 10^6$ sec^{-1}	$k_1 \times 10^6$ sec^{-1}	$k_2 \times 10^6$ sec^{-1}	$k_1 \times 10^6$ sec^{-1}	$k_2 \times 10^6$ sec^{-1}	$k_1 \times 10^6$ sec^{-1}	$k_2 \times 10^6$ sec^{-1}
M:P:S::0·4:0·6:0·4											
82	17	165	48	798	133	4796	250	12793	401	25588	825
M:P:S::0·5:0·5:0·5											
32	73	163	44	279	62	1566	266	10966	100	19191	521
M:P:S::0·6:0·4:0·6											
33	11	94	33	366	92	3838	109	19191	4·6	51166	1866
M:P:S::0·5:0·5:1·0											
119	18	169	43	1150	100	426	195	11810	246	19191	511

For the oxidative degradation study a slow stream of oxygen was passed over the surface of the polymer in order to stimulate the degradation condition of heterogeneous combustion. Weight loss data were obtained at different flow rates, measured by means of a gas flow meter.

Results and Discussion

By applying Wilhelmy's equation (a type of first order rate equation), $w_t = w_0 e^{-kt}$ where w_t is the weight of the polymer at time t and w_0 is the initial weight of the polymer and plotting log w_t/w_0 versus time, two distinct linear plots are obtained (Fig. 2) under isothermal conditions at all temperatures, viz. 200°, 250°, 300°, 350°, 400° and 450° in the presence of air. This indicates that two first order reactions are present for this type of polymer under the above condition. This trend has been confirmed by repeating several experiments. The rate constants k_1 and k_2 have been calculated from the slopes and are given in Table 1. It can be safely assumed that up to a certain point the polymer degrades with say k_1 and thereafter with another k_2. But in the presence of oxygen at all flow rates there is no change in the slope of the plot, i.e. the polymer degrades at constant rate (Fig. 3).

The Avrami-Erobeev equation $[-\ln (1-\alpha)]^{\frac{1}{4}} = kt$ where $\alpha = w_i - w_t / w_i - w_f$ has also been applied for this polymer. But the plots are not quite good.

The degradation can be explained if the concept of Grassie and coworkers[7-9], that degradation is due to the breaking of weak links followed by end initiation and unzipping is modified to suit the structure of polymer. As the structure is highly strained due to cross-linking between chains hence first the strained bonds and cross-links are ruptured followed by random scission of linear chain or end initiation and unzipping process. But the possibility of random breaking of free linear chains is greater because there is wide variety of bonds in the backbone and not —C—C— bonds as in vinyl polymers. These will continue to break randomly till the critical size of vaporizing is formed. This is defined as fragment size vaporizing (FSV) by Kumar and Stickler[10].

It seems that in the presence of oxygen the rate of breaking of strained bonds and cross-links is almost equal to the rate of formation of fragment size vaporizing by random scission of free chains; so that degradation satisfies the first-order rate law. The typical plot of oxidative degradation data is shown in Fig. 3.

The value of activation energy was calculated from the equation, $k = Ae^{-E/RT}$ where R is the gas constant and T is the absolute temperature. The Arrhenius plots are linear and the values of activation for thermal and oxidative degradations are given in Tables 2 and 3 respectively.
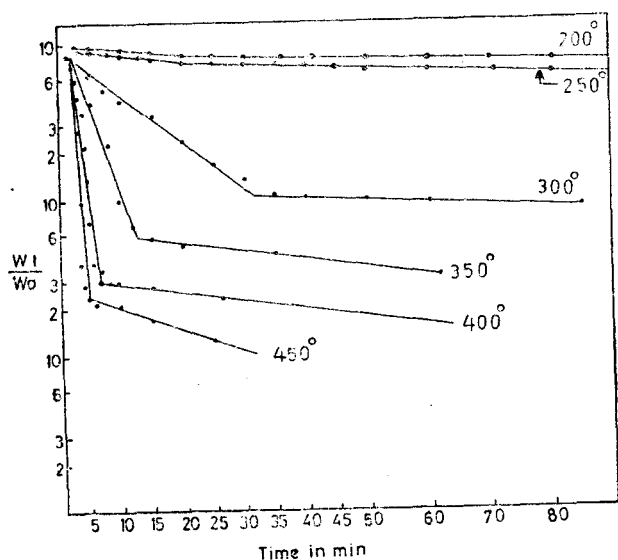

Fig. 2 — Typical plots of fraction vaporized versus time (thermal degradation)

TABLE 2 — E AND A VALUES FOR RATES k_1 AND k_2

Polymer composition M:P:S	E_1 kcal/mol	$A_1 \times 10^{-3}$ sec^{-1}	E_2 kcal/mol	$A_2 \times 10^{-3}$ sec^{-1}
0·4:0·6:0·4	15·19	0·50	14·24	0·0078
0·5:0·5:0·5	17·09	0·41	11·99	0·0057
0·6:0·4:0·6	18·23	0·87	11·39	0·0070
0·5:0·5:1·0	14·70	0·37	0·49	0·0033

TABLE 3 — E AND A VALUES AT DIFFERENT FLOW RATES OF OXYGEN

Polymer composition (M: P: S)	2 litres/min		4 litres/min		6 litres/min		8 litres/min	
	E kcal/mol	$A \times 10^{-3}$ sec^{-1}	E kcal/mol	$A \times 10^{-3}$ sec^{-1}	E kcal/mol	$A \times 10^{-3}$ sec^{-1}	E kcal/mol	$A \times 10^{-3}$ sec^{-1}
0·4 : 0·6 : 0·4	13·95	0·0660	10·12	0·0330	9·62	0·0066	3·42	0·0050
0·5 : 0·5 : 0·5	16·78	0·3330	11·40	0·0130	5·92	0·0015	2·50	0·0011
0·6 : 0·4 : 0·6	14·77	0·4000	11·17	0·0058	7·25	0·0069	2·28	0·0013
0·5 : 0·5 : 1·0	11·49	0·1330	10·23	0·0666	9·71	0·0541	6·41	0·0173
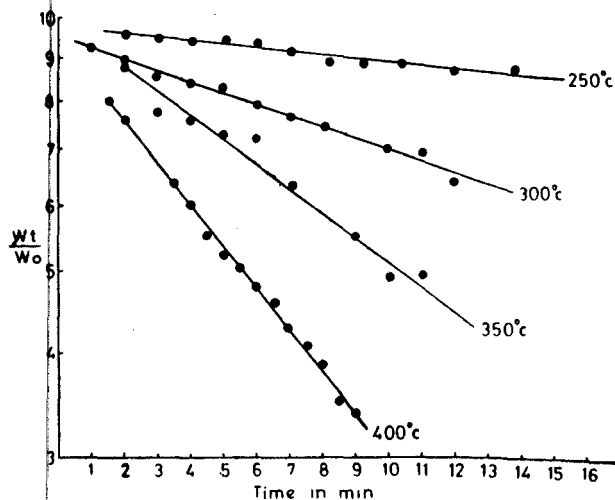
Fig. 3 — Typical plots of fraction vaporized versus time (oxidative degradation)

(I) * crosslinks

while k_2 on the rate of critical size vaporizing. In order to confirm the above views the volatile components are being analysed.

Acknowledgement

It is observed that there is a considerable difference between the values obtained from thermal and oxidative data. This was also checked by repeated experiments to ensure the trend. In fact there is no definite trend in E and k values when the degree of cross-linking is increased but as expected the polymer degrades faster at higher concentration of oxygen.

Regarding the mechanism of degradation, let us first assume the probable structure (I) for the polymer.

It is now fair to assume that process of depolymerization, i.e. (i) end initiation and unzipping and (ii) random initiation and unzipping, is not feasible as proposed by Rabinovitch[6] in order to explain degradation of polystyrene.

In thermal degradation k_1 may largely depend on rate of breaking of weak bonds and cross-links

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