Thermochimica Acta, 186 (1991) 259–263
Elsevier Science Publishers B.V., Amsterdam

Thermal degradation of HET-acid based unsaturated polyester resins: a kinetic analysis of thermogravimetric data

C.T. Vijayakumar and Sarasvathy Vijayakumar

Institut für Chemie der Kunststoffe, Montanuniversität Leoben, A-8700 Leoben (Austria)

P. Sivasamy

Postgraduate Department of Chemistry, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi-626 124 (India)

(Received 21 December 1990)

Abstract

The dynamic TG analysis of HET-acid based polyesters cured with styrene is presented. The Coats–Redfern analysis is applied.

INTRODUCTION

In the synthesis of unsaturated polyesters, HET-acid (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid) is used as a reactive co-monomer in order to impart flame retardancy. A family of unsaturated polyesters containing varying amounts of HET-acid was synthesized, and extensive studies on the mechanism of the flame retarding action of HET-acid have been reported [1,2]. In this note the dynamic thermogravimetric (TG) analysis of HET-acid based polyesters cured with styrene is presented. Employing the method of Coats and Redfern [3], the TG curves are analysed and the energies of activation for the different stages of degradation are calculated and discussed.

EXPERIMENTAL

All the unsaturated polyesters employed in the present study were synthesized by azeotropic condensation using toluene. Details of the synthetic procedure were described elsewhere [1]. The measured acid number and the components used for the unsaturated polyester synthesis are given in Table 1. The unsaturated polyester (0.7 part) and styrene (0.3 part) were mixed and cured at 90 °C for 1 h by adding 1% (w/w) of benzoyl peroxide.

0040-6031/91/$03.50

TABLE 1

Composition of unsaturated polyesters

Sample code	Feed composition (mol) of various components				Acid number of polyester (mg KOH g^{-1})
	(1)	(2)	(3)	(4)	
UPA	1	0.0	1.0	2.2	42.77
UPB	1	0.2	0.8	2.2	47.69
UPD	1	0.6	0.4	2.2	48.54
UPE	1	0.8	0.2	2.2	51.36
UPF	1	1.0	0.0	2.2	55.21

[a] Components: (1) fumaric acid; (2) phthalic anhydride; (3) HET-acid (1,4,5,6,7,7-hexachloro-5-norbonene-2,3-dicarboxylic acid); (4) 1,4-butanediol.

Post-curing for 3 h at 120 °C was carried out. In order to distinguish the styrene cured resins from the uncured polyester, the letter "S" (Styrene) is added to the code of the respective uncured polyester sample.

The thermogravimetric analysis was performed in a Stanton Redcroft TG-750 instrument under a static air atmosphere at a heating rate of 10 °C min^{-1}. The samples were heated from 50 to 600 °C and the sample size was 5 to 7 mg.

Theory

According to Coats and Redfern [3], for the reaction $x\text{X(s)} \rightarrow y\text{Y(s)} + z\text{Z(g)}$ it can be shown that

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{aE}\left[1 - \frac{2RT}{E}\right] e^{-E/RT} \tag{1}$$

where α is the fraction of X decomposed at time t, n = the order of the reaction, A = frequency factor, a = linear heating rate in deg min^{-1}, E = activation energy and R = gas constant.

After taking logarithms, eqn. (1) becomes

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\frac{AR}{aE}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.3RT} \quad \text{for } n \neq 1 \tag{2}$$

and

$$\log_{10}\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right] = \log_{10}\frac{AR}{aE}\left[1 - \frac{2RT}{E}\right] - \frac{B}{2.3RT} \quad \text{for } n = 1 \tag{3}$$

Thus plots of $-\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ against $1/T$ for $n \neq 1$ and $-\log_{10}[-\log_{10}(1-\alpha)/T^2]$ against $1/T$ for $n = 1$ should result in a straight line of slope $-E/2.3R$ for the correctly chosen values of n.

RESULTS AND DISCUSSION

The thermograms recorded for the five polyester samples cured with styrene are presented in Fig. 1. Assuming the order of the degradation of the cured polyester samples to be 1, the plots between $-\log_{10}[-\log_{10}(1-\alpha)/T^2]$ and $1/T$ reveal that the samples undergo two stages of degradation. The temperature range of the degradation stages, the fractional weight loss (α) occurring in each stage and the corresponding activation energy (E) are given in Table 2.

The data reveal that the activation energies for the first stage of the degradation of the polyester samples decrease with the decrease in HET moiety content in the polyester backbone (Fig. 2A, curve a), whereas in the second stage of degradation the activation energy is found to increase (Fig. 2A, curve b). The activation energies for the first stage of degradation of the four-component polyesters (UPBS, UPDS and UPES) show a linear relationship with respect to the molar concentration of HET-acid in the monomer feed. The three-component polyesters (UPAS and UPFS) deviate from this linearity. The HET moiety incorporated in the polyester backbone has a direct influence on the primary stage of degradation. For the second stage of degradation, the activation energies show an exponential decrease with the increase in molar concentration of HET-acid, which may be ascribed to the complexity of the different degradation routes that are possible in this higher temperature region.

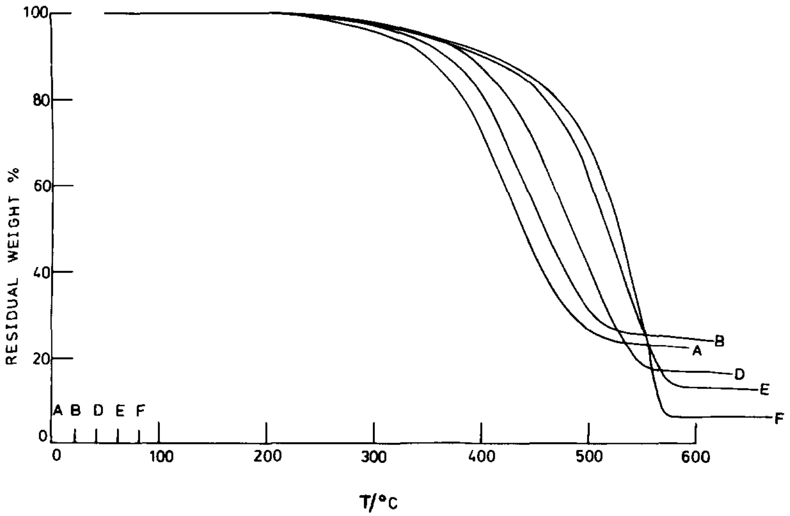

Fig. 1. Thermograms of the cured polyester resins UPAS (A), UPBS (B), UPDS (D), UPES (E) and UPFS (F). The curves B, D, E and F are shifted along the abscissa by distances AB, AD, AE and AF respectively.

TABLE 2

Calculated first-order activation energies (kcal mol^{-1}) for the different stages of degradation of polyesters according to the Coats–Redfern method [3]

Sample	T (K)	Fractional weight loss (α)	E (kcal mol^{-1})
Stage I			
UPAS	631–709	0.12–0.48	16.2
UPBS	631–709	0.12–0.48	17.3
UPDS	632–714	0.12–0.48	15.8
UPES	657–710	0.16–0.36	14.1
UPFS	643–714	0.16–0.44	14.1
Stage II			
UPAS	716–751	0.52–0.68	10.7
UPBS	717–751	0.52–0.68	11.4
UPDS	721–757	0.52–0.72	14.0
UPES	716–766	0.40–0.76	19.2
UPFS	719–747	0.48–0.76	25.8

The percentage char residues observed for the cured polyester resins UPAS, UPBS, UPDS, UPES and UPFS are 23, 25, 17, 13 and 6 respectively. The plot of percentage residue at 600 °C against the molar concentration of HET-acid is shown in Fig. 2B. The type of linearity observed for the activation energies of the first stage of degradation is also noted here.

Van. D. Kreveleven [4] proposed the following expression to calculate the oxygen index of a material from the char residue obtained by thermogravimetric methods in static air or nitrogen atmosphere by employing a heating rate of 10 or 20 °C min^{-1}

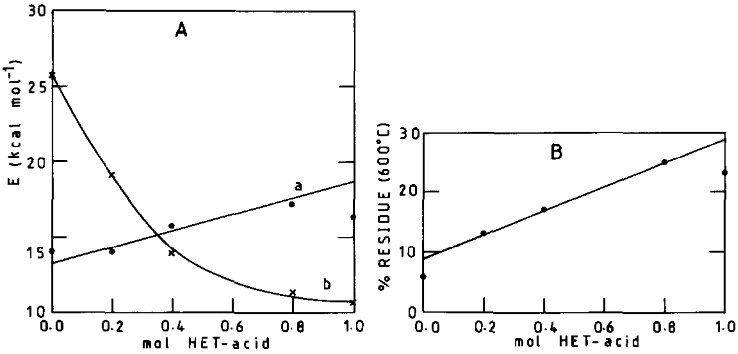

Fig. 2. A. Variation of the activation energies for degradation with respect to the molar concentration of HET-acid in the monomer feed for different cured polyester resins: a, first stage of degradation; b, second stage of degradation (See Table 2). B. Variation of the percentage char residue (at 600 °C) for cured polyester resins having different HET-acid contents.

Oxygen index (O.I.) × 100 = 17.5 + 0.4 (% char residue at 850 °C)

When the O.I. is $\leq 26\%$ the material is classified as flammable, whereas if the O.I. is $> 26\%$, the material is considered not flammable. It is observed that in all the thermograms of the polyester resins (Fig. 1) the weight loss above 600 °C is insignificant. Taking the percentage char residue at 600 °C instead of at 850 °C, the O.I. values for the polyester resins have been calculated to be UPAS 26.7%, UPBS 27.5%, UPDS 24.3%, UPES 22.7%, and UPFS 19.9%. The resin with zero HET content is highly flammable, whereas those resins with higher contents (0.8 and 1.0 mol) of HET-acid are not flammable.

ACKNOWLEDGEMENTS

Authors C.T.V. and S.V. thank the Austrian Ministry and Afro-Asiatisches Institut, Graz, Austria respectively for providing a fellowship. The help rendered by Prof. Dr. K. Kishore, IISc, Bangalore, India is gratefully acknowledged. Author P.S. thanks the management and the principal of ANJA College, Sivakasi, India for their constant encouragement. The authors are indebted to Dr. J.K. Fink, Montanuniversität, Austria for his valuable suggestions and encouragement.

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