Thermal Stability and Degradation Studies of Polyester Resins

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Synopsis

Thermal behavior and degradation mechanisms of three polyester resins, namely bisphenol A based, isophthalic acid based, and general purpose were studied. These resins were cured with styrene in the presence of benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKP) as initiators. The cured resins were studied by thermogravimetric analysis and mass spectrometry. From the thermogravimetric data it was observed that the cured bisphenol-A-based polyester resin was thermally more stable than the cured isophthalic acid-based and general purpose polyester resins. It was also observed that polyester resins cured with MEKP are thermally more stable than benzoyl peroxide-cured products. Thermogravimetric analysis data shows that there are two first-order degradation reactions during thermal degradation in nitrogen atmosphere. The first degradation step involves the scission of cross-links/weak links with the liberation of free linear chains. The second step involves a random scission of the free linear chains into smaller fragments. The fragmentation patterns of the polyester resins were identified by mass spectrometery. Possible mechanisms for the degradation of the cured polyesters accounting for the experimental observations are discussed.

INTRODUCTION

A great deal of research work has been undertaken on the thermal stability of polymers.[1-3] The unsaturated polyester resins, however, have not been studied thoroughly. These materials have found wide applications in practically all major industries such as paints, varnishes, and textile fibers. The thermal behavior of polyester resins and their cured products over a wide temperature range is an important aspect which determines their potential utility. Thermal gravimetric analysis (TGA) methods have been used not only for the evaluation of stability but also for the elucidation of information about the oxidation reactions and chemical composition. These techniques are based on the continuous and automatic measurements of changes in certain physical and chemical properties of materials as a function of temperature. In this article, we report the results of a comparative study on the thermal stability of isophthalic acid based polyester resin, bisphenol A-based polyester resin and general purpose polyester resin, cured with styrene in the presence of benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKP) as initiators. We have also proposed a degradation mechanism of the cured isophthalic acid-based and bisphenol A-based polyester resins supported by mass spectrometric analysis.

EXPERIMENTAL

Preparation

Preparation of isophthalic acid-based polyester resin (A): This polyester resin was prepared according to the procedure noted elsewhere.[4]

Preparation of bisphenol A-based polyester resin (B): This polyester was prepared according to the instructions given by Feuer and Torres.[4]

Preparation of general purpose polyester resin (C): This polyester resin was prepared as described earlier.[5]

These polyester resins were characterized by evaluating the following properties:

Gardener color index (A, 2; B, 2.3; C, 1); viscosity (A, 650 Cps; B, 700 Cps; C, 100 Cps); specific gravity (A, 1.11; B, 1.05; C, 1.15); molecular weight (A, 2,337; B, 4,007; C, 2,157).

Curing

The resins were cured with styrene[6] according to the following conditions: Using 1% benzoyl peroxide as initiator and cured:

1. At 85°C for 4 h and the samples are labeled as A_1, B_1, C_1.
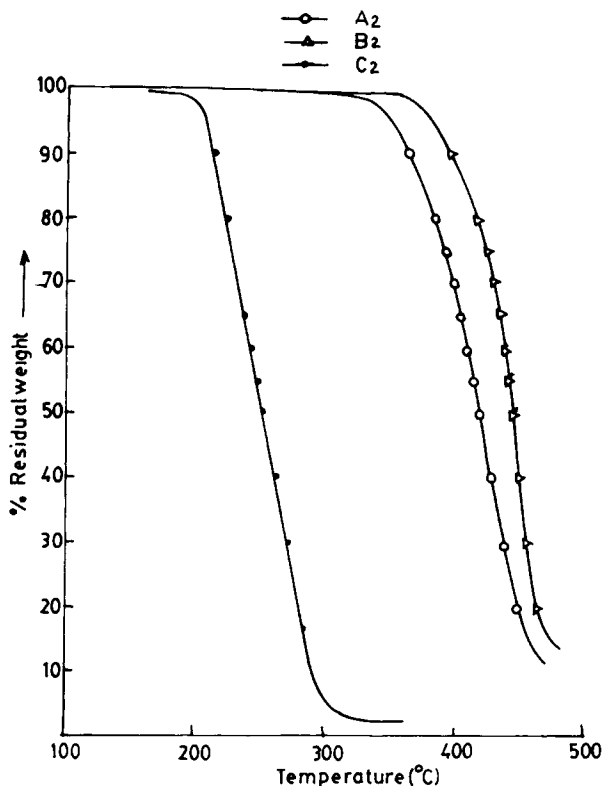2. At 120°C for half an hour and the samples are designated as A_2, B_2, C_2.

Fig. 1.   Typical thermograms of polyester resins A_2 (—○—), B_2 (—△--), C_2 (—●—).

TABLE I
Decomposition Temperature of Cured Polyester Resins

Cured resin	Initiator	IDT (°C)	Temperature (°C) of weight loss (%)						
			10	20	30	40	50	60	70
A_1	BPO	305	348	358	372	387	404	416	424
B_1	BPO	352	400	416	425	432	435	442	446
C_1	BPO	202	235	240	252	260	268	273	280
A_2	BPO	327	360	378	390	408	420	430	439
B_2	BPO	353	390	415	425	430	440	450	455
C_2	BPO	203	210	221	230	245	250	261	270
A_3	MEKP	360	365	375	398	412	431	438	449
B_3	MEKP	362	373	401	420	448	461	488	500
C_3	MEKP	225	228	230	240	249	259	266	272

Using 1% methyl ethyl ketone peroxide as initiator and cured: By keeping for 24 h at room temperature followed by heating at 85°C for 3 h. These samples are labeled as A_3, B_3, C_3.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed with a TG 780 Stanton thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of 10°C/min up to the temperature required for complete degradation.

Mass Spectra

Mass spectra of all the polyester resins were scanned using JEOL spectrophotometer at 70 EV.

RESULTS AND DISCUSSION

Thermal properties of the polyester resins cured with styrene in the presence of initiators like benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKP) have been examined by studying their primary thermograms. The latter being obtained from TGA traces by plotting the percentage

TABLE II
Kinetic Parameters of Polyester Resins and Cured
Products from TGA Data

Resin	Initiator	T_s (°C)	E (kJ/mol)	(s^{A_1})
A_1	BPO	404	13.60	6.02
B_1	BPO	424	28.40	6.55×10^2
C_1	BPO	243	8.24	10.55
A_2	BPO	412	15.13	9.34
B_2	BPO	425	29.52	8.33×10^2
C_2	BPO	247	8.65	12.20
A_3	MEKP	434	19.20	26.57
B_3	MEKP	453	35.98	3.21×10^3
C_3	MEKP	254	10.44	28.87

residual weight against temperature (Fig. 1). Initial decomposition tempera-
tures (IDT) for all these cured resins were recorded (Table I). It is evident
that the stability parallels the increase in IDT.

The activation energies for the thermal degradation (TD) were calculated
using the familiar Dharwadker Kharkhandwala[7] modified equation.

The observation that the cured bisphenol A-based polyester resin is more
stable than the cured isophthalic acid-based polyester resin, which in turn, is
more stable than the general purpose polyester resin has been supported by
the kinetic data shown in Table II.

The properties of the cured polyesters are largely determined, among other
factors, by the curing conditions. For curing of polyester resins A, B, and C
with BPO, two temperatures, namely 85 and 120°C were tried. It was found
that the resins cured at 120°C were slightly more stable than those cured at
85°C. This also resulted in a cure time reduction from 4 h (85°C) to 30 min
(120°C). For MEKP, conditions for complete curing were employed.

Thermal stability of the cured polyester resins was also studied by the
thermogravimetric methods. The cured polyester resins obeyed first-order
kinetics and yielded a reasonably straight line plot between $\ln(\ln(1 - \alpha)^{-1})$
versus Q. The first few points (initial 10–15%) did not fall in the line until it
was a hard solid, known not to obey first-order kinetics in initial stages, while
the last few points also (after 80–85%) did not fall on the line due to
secondary reactions.[8]

The TGA traces (Fig. 3) of the cured polyester resins showed two decompo-
sition steps for the overall degradation of the polymers during thermal
degradation. From this, it is anticipated that the degradation of cured
polyester resins takes place in two consecutive steps. Grassie and co-workers[9–11]
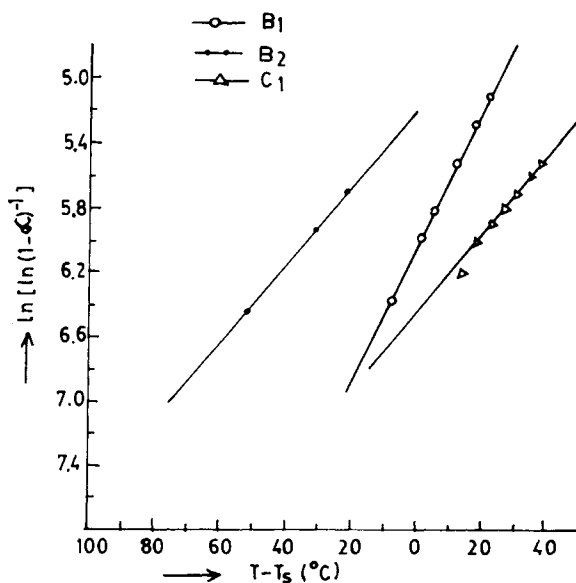have invoked the concept of scission of weak links first, followed by end

Fig. 2. Plots of $\ln(\ln(1 - \alpha)^{-1})$ vs. $(T - T_s)$ for resins B_1 (—○—), B_2 (—●—),
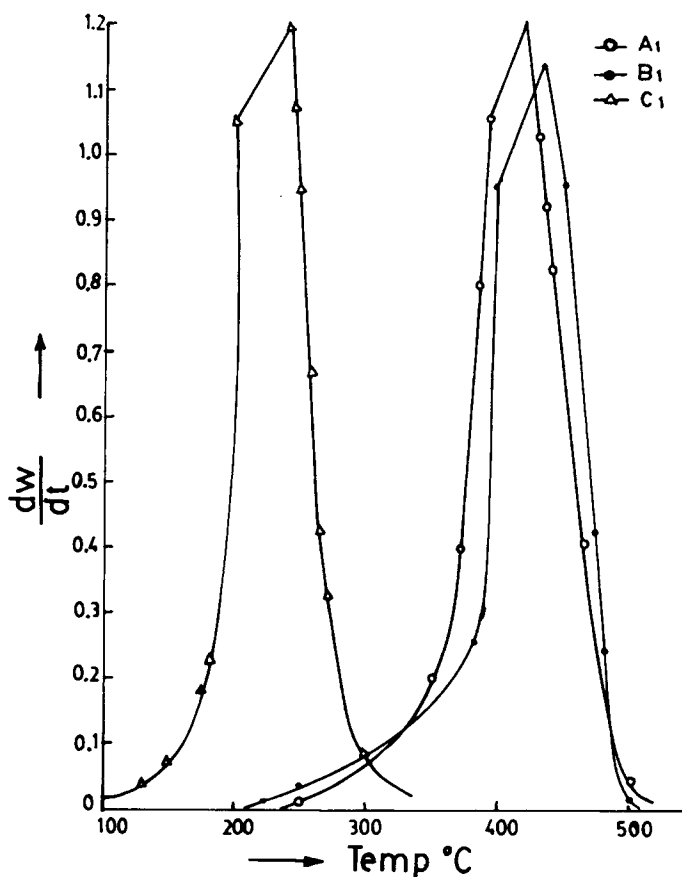C_3 (—△—).

Fig. 3. Plots of decomposition rate vs. temperature for resins A₁ (—○—), B₁ (—●—), C₁ (—△—).

initiation and unzipping of polymer chains to explain the degradation of various polymers. In highly crosslinked polymer, one can expect first the scission of highly strained cross-links as well as weak links in polymer chains. Thus a random scission of linear chains will continue until a critical size of vaporizing is formed. This is defined as frequent size vaporizing (FSV) by Kumar and Stickler.[12] The scission of weak links was confirmed by infrared (IR) spectroscopy.[13] So the first step is mainly due to scission of cross-links as well as weak links present in the linear chains. The second step represents the random scission of the free linear chains formed during the first degradation step into still smaller fragements.[14] The following Scheme I for the thermal degradation of cured bisphenol A-based polyester resin based on mass spectra (Figs. 4, 5) has been postulated. In bisphenol A-based polyester resin the first step involves scission at the cross-link and formation of styrene (a) and the linear polyester (b) which subsequently breaks randomly. Peaks at m/Z 329 were registered as the base peak. Other peaks at m/Z 344, 213, 230, 163, 104, 91, and 76 were obtained and are explained in Scheme I. For the isophthalic acid-based polyester resin also, a parallel scheme can be suggested. In this resin, peak at m/Z 87 was registered as the base peak, which is attributed to

m/e 91

(a)

(b)

m/e 344

$CH_3 +$ ... m/e 329

m/e 213

m/e 76

m/e 330

m/e 77 m/e 163
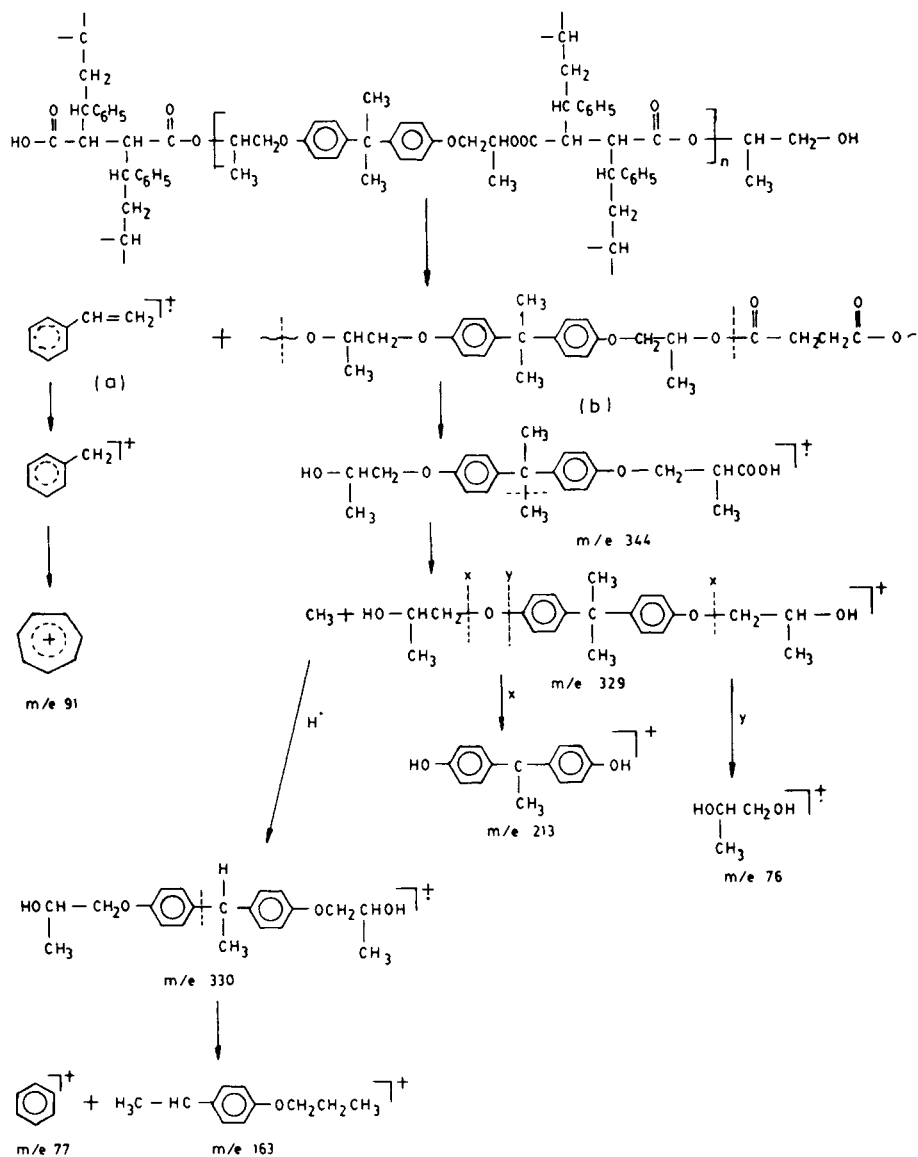
Scheme I.

$[CH_2-CA-CH_2-CH_3]^+$. Peaks at m/Z 279, 237, 193, 163, 149, 150, and 148 were also obtained.

where the CA bears a $C{=}O$ (shown as $\overset{O}{\underset{\parallel}{C}}$).

CONCLUSIONS

The following conclusions were derived:

1. Cured bisphenol A-based polyester resin is more stable than the cured isophthalic acid-based and cured general purpose polyester resins.
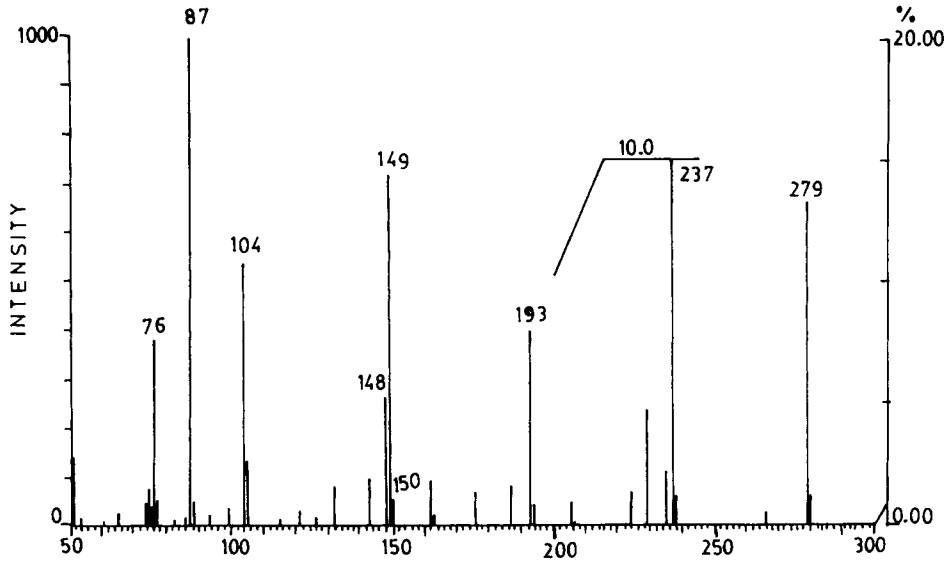
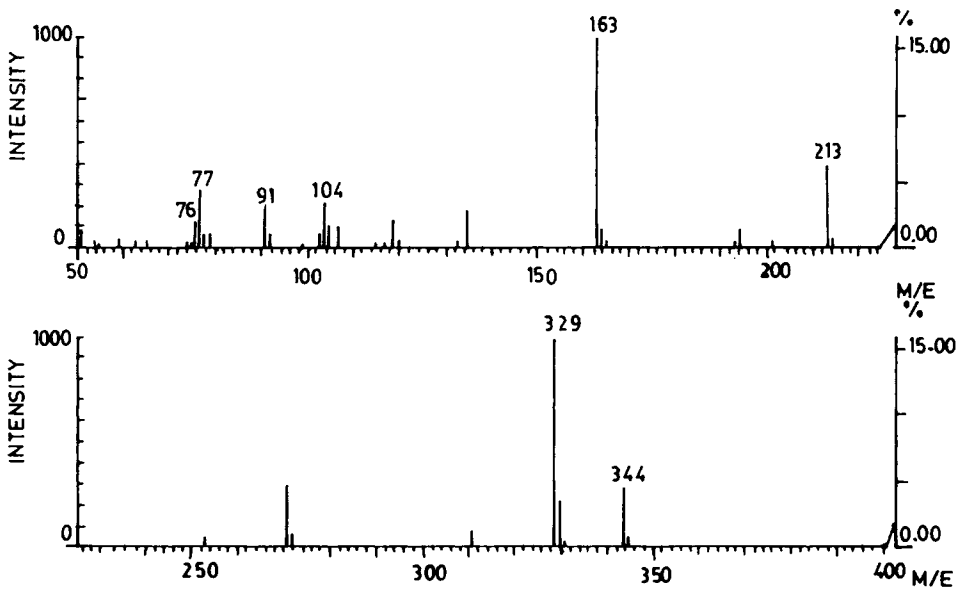Fig. 4. Mass spectra of isophthalic acid-based polyester resin (A$_3$).

Fig. 5. Mass spectra of bisphenol A-based polyester resin (B$_3$).

2. Polyester resins cured with MEKP are more stable than those cured with BPO.
3. Polyester resins cured with BPO at 120°C are found to be slightly more stable than those cured at 80°C.
4. In TGA, two steps of degradation were observed in nitrogen atmosphere. The first is due to the bond scission cross-links/weak links forming linear

chains. The second step is due to the random scission of the linear chain into smaller fragments.

5. On the basis of mass spectral analysis, the thermal degradation of cured isophthalic acid-based and cured bisphenol A-based polyester resins are postulated. Peaks at m/Z 87 and 329 are registered as base peaks of isophthalic acid-based and bisphenol A-based polyester resins, respectively. Other peaks have been well accounted for from the mass spectra of these two polyesters.

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