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The thermal degradation of polyester resins II. The effects of cure and of fillers on degradation.

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Abstract

The effects of altering the composition, the cure regime and of incorporating different fillers and fibres on the degradation of polyester resins have been studied by thermal analysis and other methods. Results are presented comparing the degradation behaviour of each type of structure, cure, filler and fibre and conclusions are drawn summarising the changes which occur in the thermal stability and in the stages of decomposition of the resins.

Keywords: Fillers; Polyester resins; Polymer cure; Thermal degradation; Thermogravimetry

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1. Introduction

Polymer matrix composites account for more than 75% of the total volume of composite materials currently in use. Polyester resins cross-linked by reaction with vinyl monomers form a large part of this volume, especially when reinforced with fibres or with other fillers. However, their use is limited by their thermal instability and flammability [1–4].

As part of a continuing study of the effects of additives on the thermal behaviour and degradation of polyester resins under both oxidative and non-oxidative conditions [1–6], the effects of the method used for curing the unsaturated polyester-styrene mixture into a three-dimensional, cross-linked network were investigated in this work. Styrene is the most widely used cross-linking monomer because of its compatibility, ease of use, and cost. The cross-linking involves the reaction of the unsaturated sites in the polymer chain with the vinyl group of the styrene.

The reaction is invariably a free-radical reaction. Two types of free-radical initiators are commonly used, which are effective *either* at elevated temperatures *or* at room temperature. Benzoyl peroxide typifies an initator which is readily decomposed into radicals when heated. The polyester resin and styrene are reasonably stable in the presence of benzoyl peroxide at room temperature, but rapidly cross-link when heated beyond ~70°C. If room temperature cure is required, the initiator normally consists of a peroxy compound, such as methyl ethyl ketone peroxide (MEKP) with an accelerator which is a salt of a transition metal; usually this is a cobalt compound such as the octanoate or naphthenate. The effects of

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different initiators have been reported by Bansal et al. [7], who conclude that structural effects are important and that resins cured with MEKP are more thermally stable than the benzoyl peroxide cured products. Cross-linking may also be induced by high-energy radiation [8]. This would eliminate any effects due to residual products of peroxide cure.

The cross-linked polyester resin is a relatively brittle material with a low tensile modulus. For many end-uses, it is necessary to add other components to the resin mix in order to improve its properties. In general these may be classified as:

reinforcing agents	such as glass or carbon fibres or silica or carbon black fillers;
inert fillers or pigments	which may not change final properties but may be important in processing;
fire retardant fillers	such as Sb_2O_3, MoO_3 or hydrated alumina which alter the thermal degradation to produce less flammable materials; and
other additives	such as antioxidants and lubricants.

Since the behaviour of the polymer system is affected by the interaction of the surface groups on the additive with the residual structure of the resin or of the intermediate products of thermal degradation, it is important to investigate the changes in degradation which result from the inclusion of both inert and active fillers and reinforcing materials [9].

2. Experimental

2.1. Preparation of the polyester resins

The full details of the preparation of the three series of resins studied are given in an earlier paper [6]. The resins were prepared from glycols, both straight-chain and branched-chain, by reacting with maleic anhydride and either phthalic anhydride, isophthalic acid or terephthalic acid as the aromatic diacid reagent. To prevent the unsaturated sites in the maleic anhydride units cross-linking, 100 ppm of *m*-tertiary butyl hydroquinone (MTBH) were added. For the phthalic anhydride, the reaction was carried out as a one-stage process, heating the reactants under nitrogen and removing water in a Dean and Stark trap until the acid number reached 30–40.

For the iso- and terephthalic acids, the different reactivities required a two-stage process, first reacting the glycol and aromatic acid and then adding maleic anhydride and continuing the reaction to an acid number of 30–40.

After cooling with stirring to below 60°C, styrene was added to give 35% styrene by weight.

2.1.1. Cure regimes

To investigate the effects of any residual catalysts or metal salts on the degradation, different cure regimes were studied.

2.1.1.1. Normal cure regime. The resins were normally cured by the addition of ~2% cobalt naphthenate accelerator (as a 6% solution in styrene) and ~4% MEKP catalyst. The resin was then cast either as a thin sheet between Melinex films, or as small blocks in silicone rubber moulds and cured for 24 h at room temperature, followed by 3 h in an oven at 80°*C.*

2.1.1.2. High-temperature post-cure regime. The 'normal' resin (2.1.1.1, aforementioned) was post cured at 150°*C for 3 h.*

2.1.1.3. Peroxide only system. Benzoyl peroxide (1% by weight) was added to the polyester resin. This was then warmed for 5 min at 80°*C to dissolve the benzoyl peroxide. After stirring the mixture, samples were prepared in the usual way and cured at 100°C for 2 h.*

2.1.1.4. Electron bombardment. Two resins were cured by high-energy electron bombardment. A 5 g sample of resin was sandwiched between Melinex sheets and irradiated to a surface dose of 20–60 kGy (kilo Gray). The dose rate was 2 kGy s^{-1}, for which the range was 0.68 g cm^{-1}.

The beam was generated by a Van de Graaff generator, which was a 1.5 MeV source and gave a 200 μA and a 15 cm scan.

2.2. Fillers and fibres

Fillers such as silica or calcium carbonate were stirred into the polyester before the catalyst and accelerator had been added. The amount of filler added often depended on the viscosity of the resin. Once mixed, samples were cast in silicone rubber moulds or between Melinex sheets as described earlier.

To prepare the glass-reinforced resin, a mat of glass fibres (GF) was roved on top of a Melinex sheet. A small quantity of resin was then poured onto the fibres, making sure that all the fibres were properly wetted with the polyester.

2.3. Thermal analysis

2.3.1. Thermogravimetry (TG)

Samples of ~10 mg were heated in a platinum crucible on a Stanton Redcroft TG 770 thermobalance at 15°C min^{-1} in a gas flow of air or nitrogen of 3 cm^3 min^{-1}. The derivative thermogravimetric (DTG) curve was calculated electronically and the curves for temperature, weight and DTG recorded on a Linseis 3-pen recorder. Results were generally averaged over five replicates.

2.3.2. Differential thermal analysis (DTA)

This was carried out using samples of 10–30 mg diluted with alumina and contained in a platinum crucible. The reference material was also alumina and both sample and reference were heated in a Stanton Redcroft DTA 673 at 15°C min^{-1} in a gas flow of air or nitrogen of 100 cm^3 min^{-1}.

2.3.3. Differential scanning calorimetry (DSC)

This was carried out on a Perkin–Elmer DSC 2C with samples of 5–10 mg in open aluminium pans run at 10 °C min^{-1} in flowing nitrogen. The results were collected, stored and analysed using the P–E Data Station.

2.3.4. Pyrolysis–gas chromatography. (Py–GC)

Samples as small flakes were pyrolysed using a Chemical Data Systems ribbon pyroprobe. Pyrolysis was performed for 20 s at 600°C with a heating rate of 20°C ms^{-1}. The products were analysed on a Perkin–Elmer 8320 capillary GC using a 25 m BP1 column and an FID detector. The temperature programme was held at 35°C for 2 min, followed by heating at a rate of 7°C min^{-1} to 165°C, holding for 3 min, heating at 12°C min^{-1} to 295°C and finally holding for 10 min. Some components were identified using Py–GC coupled to an AEI MS30 mass spectrometer, and this work is reported fully elsewhere [10].

3. Results and discussion

3.1. Cure regimes

In order to make comparisons with a real system, the commercial resin Crystic 196, which is prepared from a mixture of 1,2-ethanediol and 1,2-propanediol, maleic anhydride and phthalic anhydride, was used in each cure regime. The results are compared in Table 1 together with those for some other resins.

In each of the following tables, the onset temperature represents the loss of the first 1% of the original mass. The temperatures quoted for each stage are the peak maximum temperatures from the DTG curves and the values are given for both air (Fig. 1–upper) and nitrogen (Fig. 1–lower). The quantity in brackets is the percentage mass loss in that stage.

For Crystic 196, the changes observed are not very marked, and the three stages of degradation are present in all cases. Post curing at a temperature as high as 150°C seems to reduce the stability in air and make the sample more sensitive to oxidation, while both the benzoyl peroxide ('catalyst only') and the resins cured by radiation show higher temperatures for the main degradation step and the final char oxidation step. It seems possible that a more compact char structure could be produced using these cure regimes.

These effects are also observed with the other resins, when prepared either with phthalic anhydride or with terephthalic acid. The temperatures of the main and oxidation steps are higher when the peroxide only or electron bombardment cure regimes are followed.

The most significant effects were observed when the post-cure cycle was varied. Too low a temperature, or too short a time, for post-cure left the surface

Table 1
Thermogravimetric results showing the effect of cure regime on the degradation of the resins. Note: in all tables, results for *air* above, results for N_2 below

Cure	Onset	Temperature/°C (Loss%)		
		Stage 1	Stage 2	Stage 3
A: Crystic 196				
Normal cure	206 (air)	233 (5.6)	387 (87.2)	540 (7.2)
	203 (N_2)	236 (5.0)	393 (93.1)	1.9% residue
High T postcure	169	220 (4.0)	377 (88.7)	533 (7.4)
	185	238 (3.8)	404 (93.4)	2.6%
Peroxide only	182	230 (6.0)	399 (89.0)	547 (7.1)
	211	231 (4.2)	402 (93.4)	2.4%
Electron bombardment 20 kGy	159	225 (7.5)	385 (83.5)	560 (7.2)
	150	229 (5.6)	386 (88.2)	2.7%
Electron bombardment 60 kGy	222	235 (4.1)	390 (88.3)	558 (7.1)
	230	240 (3.8)	398 (94.2)	2.0%
B: Propylene glycol-maleic anhydride-phthalic anhydride				
Normal cure	175	215 (4.6)	353 (85.0)	557 (8.9)
	172	214 (5.3)	370 (90.8)	3.5%
Electron bombardment 20 kGy	151		385 (90.5)	555 (7.1)
	226	236 (4.2)	383 (93.2)	2.6%
Electron bombardment 60 kGy	210		378 (93.5)	549 (5.4)
	231		393 (97.2)	2.1%
C: Propylene glycol-maleic anhydride-terephthalic acid				
Normal cure	216		387 (89.7)	542 (10.3)
	328		393 (95.6)	4.4%
Peroxide only	281		395 (90.4)	564 (9.3)
	283		398 (97.0)	3.0%

'tacky', while too high a temperature made the resin more susceptible to oxidative degradation.

The technique of radiation curing using electron bombardment was not very successful. The resins cured by this method were found still to be very soft and required the usual thermal post-curing at 80°C for 3 h, although no additional initiator or accelerator was required. Estimates of the residual cure from DSC experiments [11] showed that the 20 kGy samples were very much undercured, while the 60 kGy sample was similar to the chemically cured resin.

The Py–GC of resins such as Crystic or P2MP (Table 2) cured according to the 'normal regime' generally showed a great many peaks, the most prominent of which were shown to represent styrene, styrene dimer and trimer and degradation products from styrene such as benzaldehyde, toluene, ethyl benzene, and phenylacetaldehyde, together with phthalic anhydride, dimethyl phthalate plus a large number of minor products [10]. The resins cured by other regimes showed only minor changes in the proportions of products and no evidence of the for-

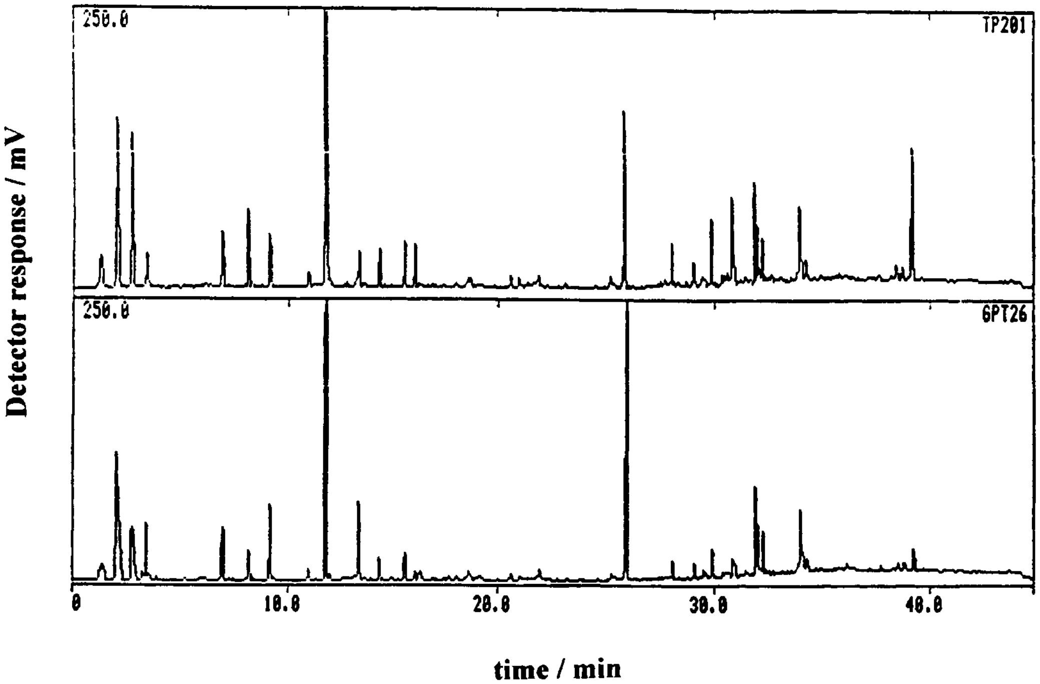

Fig. 1. Pyrolysis–gas chromatography traces for P2MT resin without glass fibre (top) and with 71.7% glass fibre reinforcement (bottom).

mation of any new products. An exception was the absence of the dimethyl phthalate peak from the resins cured with no catalyst. Since the catalyst was added as a 50% solution in dimethyl phthalate, this was probably due to the catalyst solvent and not to any degradation pathway of the resins.

3.2. Glass fibre reinforced polyesters

The polyester resins were loaded with ~60% of E-type GF as described earlier. The percentage mass losses are corrected for the GF content by subtracting the amount of filler or GF, calculated from the complete degradation in air, from the amount remaining at each stage. As the filler or fibre was not distributed perfectly uniformly, this led to calculated losses greater than 100% in a few cases. The results may be compared directly to the unfilled polymer.

The resins studied are classified in three series, showing the structural effects of glycol chain length, of chain branching and of the isomeric nature of the aromatic diacid (Tables 2 and 3).

Table 2
Resins studied

Series A.1: Straight chain glycols/maleic/phthalic	Polyester Code
1,3-Propanediol	PMP
1,4-Butanediol	BMP
1,6-Hexanediol	HMP
Series A.2: Branched chain glycols/maleic/phthalic	
1,2-Propanediol	P2MP
Series B: Propylene glycol/maleic/iso- and terephthalic acids	
1,2-Propanediol/maleic/isophthalic	P2MI
1,2-Propanediol/maleic/terephthalic	P2MT

For the A.1 series with straight-chain glycols, the temperatures of the first stage both in air and in nitrogen are generally decreased, by ~5°C in air and by ~15°C in nitrogen. For the second stage they are decreased on average by ~12°C in both atmospheres and the third stage is decreased by ~15°C in air in the presence of GF.

The A.2 series with branched-chain glycols shows a more complex pattern. While the first stage maximum

Table 3
Thermogravimetric results showing the effects of glass fibre on degradation of resins

Code	Temperature/°C (Loss%)		
	Stage 1	Stage 2	Stage 3
A.1 Series			
PMP	246 (9.2)	402 (85.8)	544 (5.0)
	251 (9.2)	416 (88.4)	2.4%
PMP/GF (47.3% GF)	236 (10.5)	395 (80.4)	524 (9.5)
	225 (9.0)	402 (80.2)	10.8%
BMP	238 (6.8)	413 (87.5)	542 (5.7)
	241 (6.8)	420 (90.9)	2.3%
BMP/GF (55.3% GF)	229 (6.7)	391 (84.9)	529 (8.4)
	228 (7.4)	413 (84.9)	7.7%
HMP	234 (8.7)	417 (85.5)	542 (5.8)
	240 (9.2)	425 (89.8)	1.2%
HMP/GF (55.8% GF)	238 (10.0)	398 (82.0)	524 (8.4)
	233 (9.3)	417 (90.7)	0%
A.2 Series			
P2MP	215 (4.6)	353 (85.0)	557 (8.9)
	214 (5.3)	370 (90.8)	3.5%
P2MP/GF (59.4% GF)	222 (4.4)	363 (87.2)	532 (8.1)
	221 (5.4)	374 (88.2)	6.4%
B. Series			
P2MI		388 (91.7)	532 (8.3)
		392 (97.1)	2.9%
P2MI/GF (64.3% GF)	170 (4.5)	380 (82.1)	523 (13.3)
	168 (5.8)	386 (82.0)	12.2%
P2MT		387 (89.7)	542 (10.3)
		393 (95.6)	4.4%
P2MT/GF (71.7% GF)	167 (4.5)	378 (81.0)	524 (14.0)
	165 (5.3)	385 (90.5)	4.2%

is raised by 8–26°C, the second stage shows an *increase* ~10°C for the P2MP. The third stage oxidation temperature is *increased* by ~10°C because of the presence of GF.

For the B series, the first stage present with P2MP is absent when the aromatic acid is changed to iso- or terephthalic acids. This is thought to be due to the decreased tendency to eliminate the acid derivatives. GF introduces a weight loss at a much lower temperature, suggesting that a different mechanism operates here. The temperatures of the second and third stages are lowered by ~8°C in the presence of GF.

3.3. *The effects of other fillers*

To test whether any of the effects observed with GF could be due to the chemical nature of the fibre especially on its surface, alternative fillers were studied using the commercial Crystic 196 resin system. The E-type GF used earlier was coated with a sizing at ~1.5% by weight and was also compared with de-sized fibres as well as with fibres sized with an epoxy coating. Additionally, the degradation of resins containing silica and calcium carbonate powders as fillers were investigated. This work is reported in Table 4.

All of these fillers and fibres lower the temperatures of the degradation stages. The smallest effects are observed with the de-sized fibres, but even they

Table 4
Thermogravimetric results showing the effects of various fillers on the degradation of Crystic 196

Filler	Temperature/°C (Loss%)		
	Stage 1	Stage 2	Stage 3
None	233 (5.6)	387 (87.2)	540 (7.2)
	236 (5.0)	393 (93.1)	1.9%
Glass fibre (sized, 49.3%)	223 (8.5)	370 (85.0)	533 (7.9)
	226 (8.1)	385 (90.9)	1.0%
Glass fibre (epoxy sized, 58.7%)	218 (8.0)	362 (82.6)	522 (0.4)
	226 (7.5)	388 (83.6)	8.9%
Glass fibre (de-sized, 33.5%)	234 (7.7)	378 (84.5)	524 (7.8)
	233 (7.4)	385 (96.4)	0%
Silica (25.5%)		361 (86.6)	515 (8.6)
	219 (5.1)	372 (94.1)	0.8%
Calcium carbonate (57.9%)	220 (4.5)	348 (84.6)	466 (9.7)
	220 (5.0)	361 (89.3)	5.7%

reduce the char-oxidation step temperature by 16°C. The two high area powder fillers, which show no thermal changes in this temperature range, exert the largest effects, lowering the temperatures of all the stages. The 'missing' Stage 1 with silica in air may be due to the greater overlap with Stage 2. The type of sizing used seems to have little effect since all the stages occur within a few degrees for either type. The epoxy sizing has a larger effect on the final stage.

Comparison of the Py–GC traces for the various polyesters revealed few differences due to GF reinforcement. There were minor changes in the proportions of products, but no new peaks were observed, although they might be expected from sized GF. The relative amount of styrene trimer was considerably reduced with some of the reinforced resins, especially HMP and P2MI.

4. Conclusions

From the TG and DTA results it is possible to make the following general comparisons. The resins start to degrade at ~200°C, but the major weight loss occurs at ~400°C. Considering the effects of cure and of fillers, it is evident that:

1. The method used for cure does affect the stability although only to a small extent.
2. The addition of fillers or GF reinforcement reduces the stability of the resins and reduces the temperature of char oxidation. Again, these are relatively minor changes in the stability of the polymer system.
3. The degradation products are unchanged by altering the curing regime or by adding reinforcing GF, although the proportions of products may be altered.

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