

NOTES

The Effect of Needle Coke Graphite on the Curing and the Strength of a Polyester Resin

INTRODUCTION

The reinforcement of rubber by fine particles of carbon has been attributed to a free-radical mechanism,¹ and carbon black is known to inhibit free-radical reactions. It was therefore decided to investigate the effect of a carbon filler on the cure and properties of an unsaturated styrene-polyester resin. Dielectric heating was investigated as a means of accelerating the reaction.

The effect of varying particle size and concentration of carbon on the crossbreaking strength (under three-point loading) and impact strength of polyester castings containing carbon was studied.

The effect of induction time was also investigated in an attempt to determine the extent of interaction between the carbon particles and the growing polymer chains produced by the addition reaction.

EXPERIMENTAL

The specimens for crossbreaking and impact measurements (B.S. 2782, Pt. 3, 1957) were cured in an oven at 120°C for 16 hr because of the difficulty in using the large metal mold in the dielectric heater (Radyne Ltd. M6/D).

The curing reactions were followed by measuring the exotherm with a pair of opposed thermocouples, one in the specimen of polyester plus initiator and the other in a sample of polyester alone. The polyester was a general-purpose propylene glycol-phthalate-fumarate containing 35% styrene (R660 Berger Chemicals Ltd). The carbon used was Needle Coke Graphite (Anglo Great Lakes, Newcastle upon Tyne) Type DC2, which is manufactured from petroleum coke and coal tar pitch, graphitized at ca. 2800°C, crushed, and sieved.

The carbon was separated into four fractions by means of B.S. sieves: the arithmetic means of the two extreme sizes was taken as the particular size of the fraction. The proportions of carbon employed were 0, 5, 10, 15, 20 and 25 phr (parts by weight per hundred parts of resin): 1 phr of benzoyl peroxide was used as initiator.

Mineral-insulated thermocouples (NiCr-NiAl) were necessary owing to the excessive noise induced in normal thermocouples by the electric field of the heater. This was greatly reduced by earthing the sheaths of the mineral-insulated thermocouples. The mixtures were placed in 25.4-mm-diameter polypropylene dishes by means of a 2-ml syringe. Various settings of the electrodes of the dielectric heater were used.

The results of the crossbreaking tests are given in Figure 1. It can be seen that for each concentration of carbon, the crossbreaking strength varies in an approximately linear manner with changes in the particle size of the carbon. Similar results are found for impact strength (Fig. 2). In both cases, but particularly for the impact results, there are departures from linearity at higher concentrations.

From the results of the investigation of the effect of carbon on induction time, the following empirical relationships were found for carbon concentrations greater than zero:

(a) Variation of induction time with electrode separation:

$$I_t = H + 0.661S$$

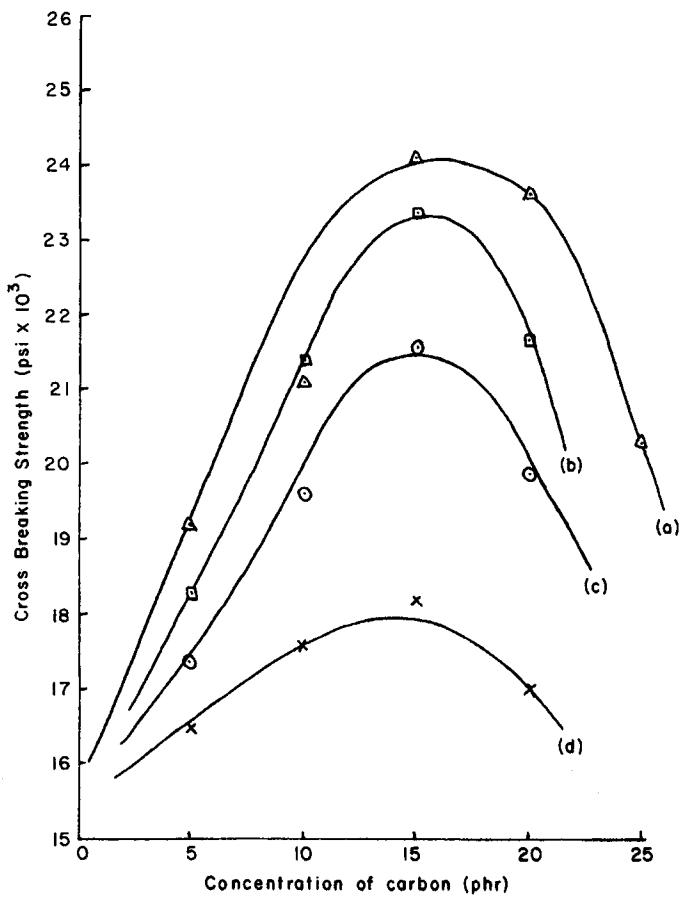


Fig. 1. Variation of crossbreaking strength of polyester/carbon black castings with concentration of carbon black; (Δ) 64-micron carbon; (\square) 113-micron carbon; (\circ) 185-micron carbon; (\times) 320-micron carbon.

where I_t = induction time in min, S = electrode separation in mm, H = factor varying with particle size and concentration of carbon.

(b) Variation of induction time with particle size of carbon:

$$I_t = L - 1.4 \times 10^{-2}P$$

where P = particle size of carbon in microns, and L = factor varying with electrode separation and concentration of carbon.

(c) Variation of induction time with concentration of carbon:

$$I_t = M + 0.2C$$

where C = concentration of carbon in phr, and M = factor varying with electrode separation and particle size of carbon.

SUMMARY

The crossbreaking and impact strengths of the polyester filled with carbon increase with increasing concentration of filler up to 15 phr, unlike the action of fine silica² in

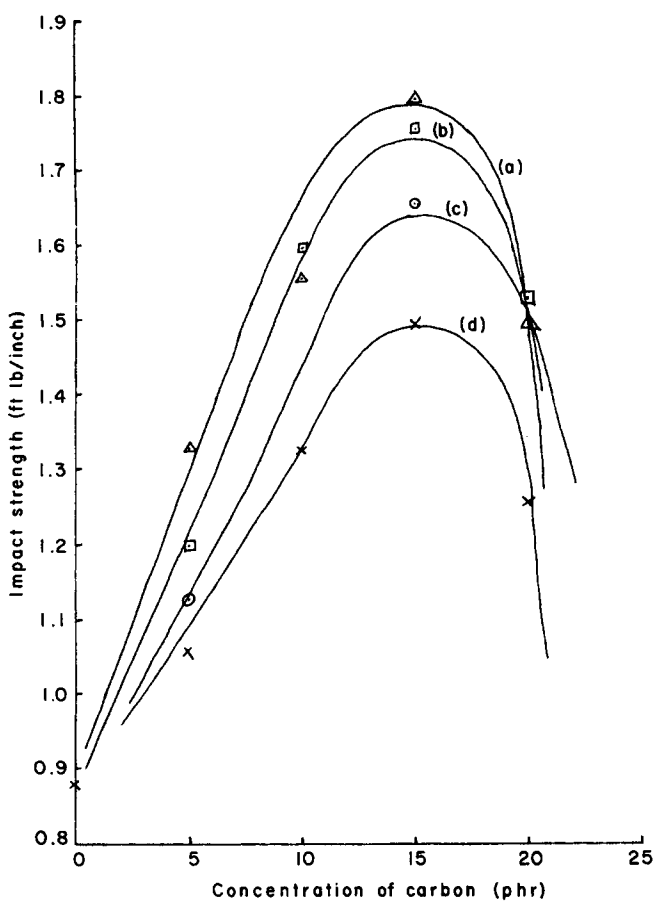


Fig. 2. Variation of impact strength of polyester/carbon black castings with concentration of carbon black; (Δ) 64-micron carbon; (\square) 113-micron carbon; (\circ) 185-micron carbon; (\times) 320-micron carbon.

TABLE I
Values of L Versus Electrode Separation and Concentration (phr) of Carbon

Electrode separation, mm	L , min				
	5 phr	10 phr	15 phr	20 phr	25 phr
33.8	16.55	17.55	19.10	19.40	20.20
31.8	15.10	16.20	17.20	18.10	19.00
29.7	13.65	14.30	15.80	16.70	17.80
27.6	12.20	13.20	14.20	15.10	16.70
25.5	10.75	11.90	13.00	13.80	15.40

which the flexural modulus decreased with increasing concentration. This indicates that reinforcement of the polyester similar in nature to that produced in rubber is taking place, i.e., that the active sites on the surface of the carbon particles form primary bonds with growing styrene linkages and become an integral part of the polymer matrix. This

TABLE II
Values of H Versus Particle Size and Concentration (phr) of Carbon

Particle size, μm	H , min.				
	5 phr	10 phr	15 phr	30 phr	25 phr
320	-10.10	-9.00	-7.75	-6.70	-5.75
185	-8.45	-7.30	-6.25	-5.25	-4.25
113	-7.35	-6.30	-5.20	-4.25	-3.40
64	-6.60	-5.30	-4.35	-3.45	-2.60

TABLE III
Values of M Versus Electrode Separation and Particle Size (μm) of Carbon

Electrode separation, mm	M , min			
	320 μm	185 μm	113 μm	64 μm
33.8	11.3	12.2	14.2	14.9
31.8	9.5	10.6	12.5	13.4
29.7	8.5	9.6	11.5	12.0
27.6	6.8	8.4	10.1	10.2
25.5	5.4	6.8	8.5	8.9

TABLE IV
Induction Time of Polyester Alone Versus Electrode Separation

Electrode separation, mm	Induction time, min
33.8	5.75
31.8	4.75
29.7	3.75
27.6	2.60

would account for the rapid decline in the mechanical properties of the castings with more than 15 phr of carbon when the excess filler would bring about the normal decrease in mechanical properties produced by an inert filler.

The inhibition produced appears to be related to the total surface area of the carbon. For thermally polymerized styrene, the inhibition period is directly related to the presence of combined oxygen in the carbon black.³ We made no measurements of combined oxygen, on the assumption that it would be the same throughout the single batch of carbon used. Our results agree with those of Donnet³ in that increasing inhibition was found with the smaller particles that are expected to contain more oxygen. An acceleration in the rate of reaction following the inhibition period that was also related to the surface area of the carbon black and hence particle size³ could not be confirmed in the present apparatus, since errors induced in the thermocouple signal by the dielectric heater are such that small changes in the rate of reaction cannot be distinguished. This acceleration subsequent to the retardation has been observed in room temperature-cured polyester resins filled with carbon.⁴

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References

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