

NOTE

Carbonate-Modified Unsaturated Polyesters

The preparation of linear saturated polyester-polycarbonates by reaction between dibasic acids, dihydroxy compounds, and carbonyl halides in amine solution has been reported.¹ This note describes the synthesis of carbonate-modified unsaturated polyesters and their copolymerization with styrene. All products were prepared with isophthalic acid, maleic anhydride, and propylene glycol, with the carbonate groups being incorporated by *trans*-esterification with diphenyl carbonate. Several formulations were examined, but severe gelation problems during processing caused only a limited number of products to be successfully prepared and evaluated.

Best results were obtained when 1 mole each of isophthalic acid and maleic anhydride were first esterified with 3 moles of propylene glycol to an acid number less than 5. This product was then *trans*-esterified with 1 mole of diphenyl carbonate. Both esterification and *trans*-esterification were run at 200°C. in a four-necked flask equipped with stirrer, nitrogen inlet, and thermocouple for recording temperature. In the first step, water of esterification was removed through a steam-jacketed condenser; in the second, by-product phenol was removed through a straight, heated take-off tube. *Trans*-esterification proceeded smoothly in the absence of a catalyst, and products were generally processed to a molecular weight of about 5000 (endgroup analysis). Resin solids were dissolved in styrene, heat cured between 1/8-inch casting frames, and tested by standard ASTM methods.² Table I lists properties of two products. Product 1, which was washed with dilute base to remove residual phenol, developed higher Barcol hardness and flexural properties, possibly because the inhibiting effect of phenol was removed. Product 2, which was tested at both 30 and 40% styrene, had slightly better flexural strength and modulus at the higher styrene level.

TABLE I
Properties of Cured 1/1/3/1 Isophthalic/Maleic/Propylene Glycol/Diphenyl Carbonate Polyesters^a

Product No.	1 ^f	2	
Per cent styrene	30	30	40
Viscosity, ^b poise	6.27	34.0	5.50
Barcol hardness	40	30	32
Deflection temp., under load, ^c °C.	54	54	54
Flexural strength, ^d psi	14,000	10,000	12,000
Flexural modulus, ^e psi × 10 ⁻⁵	4.0	3.1	3.5
Impact strength, ^e ft-lb./in.	2.6	2.7	3.0

^aCatalyzed with 0.5% benzoyl peroxide (1% Lupercos ATC), 0.33% MEK peroxide (0.55% Lupersol DDM), and 0.15% cobalt naphthenate. Cured for 4 hr. at 38°C. and 1 hr. each at 60, 80, and 135°C.

^bDetermined with Gardner-Holdt standards at 25°C.

^cASTM D 648-56.

^dASTM 790-59T; average of 5 samples.

^eIzod unnotched, ASTM D 256-56; average of 10 samples.

^fStyrene solution washed with cold 5% NaOH.

Clear castings were prepared of a product having a mole ratio of 1/1/4/2 isophthalic/maleic/propylene glycol/diphenylcarbonate (viscosity 2.50 poises at 70% resin solids in styrene), but they were too brittle for cutting into test specimens. Attempts to process to higher viscosities resulted in gelation.

Formulations in which gelation could not be prevented were (mole ratios) 2/2/5/1 isophthalic/maleic/propylene glycol/diphenyl carbonate and 1/2/1 maleic/propylene glycol/diphenyl carbonate. In both cases gelation occurred even when inhibited with up to 500 ppm of diphenylquinone. It was characterized by an extremely rapid viscosity increase (about 0.5 poise to gel in 5-10 mins.) that was independent of inhibitor level.

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References

1. Goldberg, E. P., U. S. Pat. 3,030,331 (to General Electric Company), 1962.
2. *ASTM Standards on Plastics*, Am. Soc. Testing Materials, Philadelphia, 1961.

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