

Preparation and Properties of a Diaryl Sulfone-Containing Unsaturated Polyester

J. C. SPITSBERGEN, P. LOEWRIKKEIT, Y. K. KIM, and W. L. LAUZÉ, *Witco Chemical Corporation, Technical Center, Oakland, New Jersey 07436*

Synopsis

Thermoset poly(dipropoxylated bisphenol S-fumarate) showed an increase in heat deformation resistance over thermoset poly(dipropoxylated bisphenol A-fumarate). However, the poly(dipropoxylated bisphenol S-fumarate) required the incorporation of about 20 mole-% of dipropoxylated bisphenol A into the polyester molecule to be styrene compatible. Condensation polymerization of various ratios of the dipropoxylated bisphenols with fumaric acid was employed to prepare the polyesters. The polyesters were then thermoset by crosslinking with styrene using a peroxide initiator. The thermoset of a poly(dipropoxylated bisphenol S-fumarate), into which 20 mole-% of the dipropoxylated bisphenol A had been incorporated, had a heat distortion temperature 13°C higher than the poly(dipropoxylated bisphenol A-fumarate) thermoset.

INTRODUCTION

The value of the diaryl sulfone group for increasing heat deformation resistance of thermoplastics has been well established with aromatic polysulfones.¹⁻³

Increases have also been indicated for thermosets containing this sulfone group. In the case of epoxy resins,^{4,5} the increase in heat deformation resistance was substantial. For phenolic resins,⁶ increased heat aging has also been shown. The sulfone group was usually incorporated into the thermoset by using bisphenol S, an isomer mixture of 4,4'- and 2,4'-dihydroxydiphenyl sulfone, the 2,4'-isomer being a minor component (0 to 20%).

It can now be shown that the sulfone group imparts increased heat deformation resistance to thermosets based on unsaturated polyesters. For this purpose, a bisphenol S unsaturated polyester, poly(dipropoxylated bisphenol S-fumarate), has been compared with a bisphenol A unsaturated polyester, poly(dipropoxylated bisphenol A-fumarate).

EXPERIMENTAL

The incorporation of a bisphenol into a polyester is facilitated by using an alkoxyated bisphenol.^{7,8} Therefore, the bisphenol S unsaturated poly-

ester was prepared by condensing dipropoxylated bisphenol S with fumaric acid. The method of Kass⁸ was used. A bisphenol A unsaturated polyester (A-F) was similarly prepared.

The bisphenol S polyester or blends of this polyester and A-F, however, were incompatible with styrene at the 30–50% styrene content desired for solutions. Compatibility was obtained by replacing a portion of the dipropoxylated bisphenol S in the polyester with dipropoxylated bisphenol A. (The amount needed to be replaced is dependent on the 2,4'-isomer content of the bisphenol S, the molecular weight of the resulting polyester, and the desired styrene content of the solution.) For this comparison, styrene-compatible bisphenol S (13% 2,4'-isomer) unsaturated polyesters were prepared by replacing 20 to 50 mole-% of the dipropoxylated bisphenol S with dipropoxylated bisphenol A. Resin properties are shown in Table I.

TABLE I
Resin Properties

	A-F	50S/50A-F*	70S/30A-F*	80S/20A-F*
Acid no.	17.1	29	20	18.9
Durrans softening point	111	116	132	154

* Designates the mole ratio of dipropoxylated bisphenol-S to dipropoxylated bisphenol-A in the polyester.

Thermosets of these polyesters were prepared by casting a solution of the polyester (40% styrene content), containing 1.5 phr MEK peroxide and 0.5 phr cobalt naphthenate, in a glass mold. A rigid thermoset was obtained after about 16 hr. Crosslinking was further increased by heating at 100°C for 4 hr.

RESULTS AND DISCUSSION

A comparison of the thermoset polyesters shows increased heat deformation resistance, as indicated by increased heat distortion temperature, as the sulfone content is increased. This can be seen in Figure 1. Since in most cases the acid numbers indicate similar molecular weight, this effect must be due to the replacement of the isopropylidene group present in bisphenol A with the sulfone group present in bisphenol S.

The presence of the sulfone group also appears to slightly increase rigidity, as indicated by increased flexural modulus, and heat aging resistance, as shown by the lower weight loss after 24 hr at 260°C, for the 80S/20A-F polyester in Table II. An increase in nonpolar solvent resistance is also indicated by the higher retention of rigidity after immersion in toluene. However, although high chemical resistance after immersion in nitric acid or sodium hydroxide is also indicated in Table II, retention of rigidity is lower than with A-F. Although the greater rigidity of the 80S/20A-F poly-

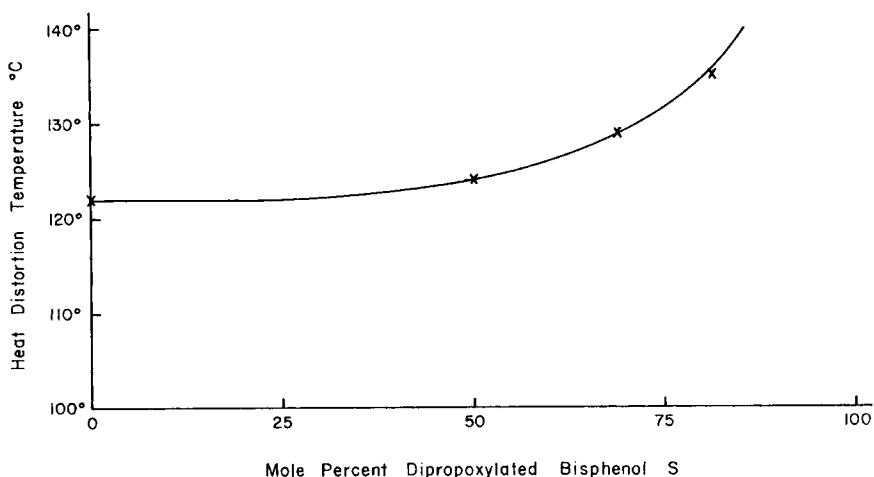


Fig. 1. Effect of bisphenol S on heat deformation resistance.

ester should enhance chemical resistance, the polarity or hydrophilicity due to the sulfone group counteracts this somewhat in aqueous systems.

TABLE II
Properties of Thermoset Bisphenol-S Unsaturated Polyester

	A-F	80S/20A-F
Flexural strength (ASTM D-790) psi	11,900	10,700
Flexural modulus (ASTM D-790), psi	413,000	453,000
HDT (ASTM D-648), °C	122	135
Barcol hardness	23	29
Weight loss after 24 hr at 260°C, %	7.5	6.4
Flexural modulus retained after		
18 hr at 92°C in toluene, %	68	86
4 days at 96°C in 10% NaOH, %	104	91
4 days at 96°C in 10% HNO ₃ , %	99	97

The incorporation of dipropoxylated bisphenol A into the bisphenol S polyester to obtain styrene compatibility probably prevents maximum enhancement of properties. However, methods that involve incorporation of a rather flexible group to obtain styrene compatibility have a more drastic effect. For example, a styrene-compatible bisphenol S unsaturated polyester was prepared by using a polypropoxylated bisphenol S having a 3.7-to-1 mole ratio of propylene oxide to bisphenol S (instead of using the 2-to-1-ratio dipropoxylated bisphenol S and bisphenol A). The resulting polyester had an acid number of 13.4 and a Durrans softening point of 114°C. Although rigidity and resistance to toluene of the thermoset compared to A-F were increased, heat deformation resistance was not. Further, chemical resistance to sodium hydroxide and nitric acid at 96°C was greatly re-

duced. This is in part due to the presence of a long dialkyl ether link which contributes a flexibilizing effect.

Another method for obtaining a styrene-compatible polyester involves replacing 25 wt-% of the fumaric acid with phthalic anhydride (instead of replacing dipropoxylated bisphenol S with dipropoxylated bisphenol A). Preliminary results indicate that a two-step, one-pot reaction is required. The phthalic anhydride must be reacted with the dipropoxylated bisphenol S before the fumaric acid is added. An acid number of 17.7 and a Durrans softening point of 139 were obtained.

References

1. R. N. Johnson, A. G. Farnhan, R. A. Clendinning, W. F. Hale, and C. N. Merrian, *J. Polym. Sci. A-1*, **5**, 2375 (1967).
2. M. E. A. Cudby, R. G. Feasey, B. E. Jennings, M. E. B. Jones, and J. B. Rose, *Polymer*, **6** (11), 589 (1965).
3. H. A. Vogel, *ACS Polymer Preprints*, **10** (1), 160 (1969).
4. J. E. Singley and A. Christiansen, U.S. Pat. 3,044,983 (1962).
5. J. C. Spitsbergen, P. Loewrigkeit, C. Bluestein, J. Sugarman, and W. L. Lauzé, 26th Annual Tech. Conf., SPI Reinf. Plastics/Composites Div. 19-C, 1971.
6. J. Harding and W. C. Coleclough, Jr., U.S. Pat. 3,256,361 (1966).
7. J. R. Caldwell, U.S. Pat. 2,593,411 (1952).
8. P. Kass, U.S. Pat. 2,634,251 (1953).

Received April 13, 1970

Revised April 25, 1971