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Properties of Fluorenone Polyesters

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ABSTRACT

Several high-glass-transition-temperature (T_g) bisphenol fluorenone polyesters and copolyesters, suitable for conversion into film and fiber, were found to have very good thermal and flame resistance and produced medium char yields in the 30-60% range. The fact that the polyester structure does not contain nitrogen is a potential advantage in fire-resistant fiber applications, since there is no likelihood of HCN generation during burning.

INTRODUCTION

Fluorenone polyesters made from isophthalic acid or terephthalic acid/isophthalic acid and bisphenol fluorenone have many outstanding characteristics, especially heat resistance. A typical molecular formula is as shown on the following page.

Preparation of linear aromatic polyesters from diphenols and dibasic acids has been reported in some early patents [1-3]. More recently, Morgan [4] synthesized aromatic polyesters by interfacial and solution methods from aromatic diacid chlorides and bisphenols

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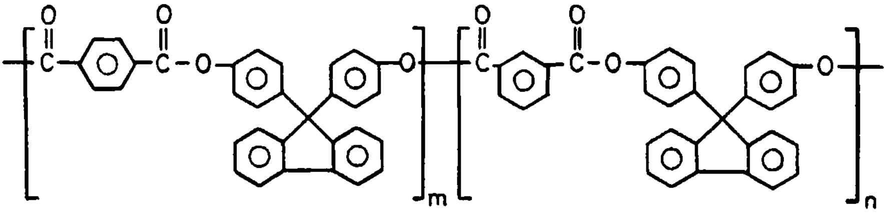

that have essentially planar, doubly attached groups on the methylene units between the phenylene rings. Bier [5] reviewed the literature on polyesters made from aromatic dicarboxylic acids and bisphenols and described the preparation of some bisphenol monomers and polyesters made therefrom by various methods, e.g., interfacial condensation, solution condensation, melt condensation, and reesterification reaction paths.

A wide range of polyesters can be made by varying the ratio of acids (terephthalic and isophthalic) and bisphenols (bisphenol fluorenone and bisphenol A) and by regulating the molecular weight. The characteristics of this important new family of resins have been only partially reported in the past. This paper describes the properties of several high glass transition temperature bisphenol fluorenone polyesters and copolyesters that were found to be suitable for conversion into film and fiber.

EXPERIMENTAL

Fluorenone Polyesters

The following fluorenone polyesters, obtained from Isovolta, Austria, were characterized and their potential applications were evaluated:

FPE-1	Bisphenol A/bisphenol fluorenone (90/10) polyterephthalate
FPE-2	Bisphenol fluorenone polyisophthalate
FPE-3	Bisphenol A/bisphenol fluorenone (20/80) polyisophthalate
FPE-4	Bisphenol fluorenone copolyester of terephthalic and isophthalic acids (50/50)

Properties Studied

The polyester characterizations included fire resistance determination, solution viscosities, thermal analyses, dynamic mechanical analysis, Clash-Berg moduli determination, and evaluation of mechanical properties. The materials were molded, cast as films, spun as fibers from solution, and blended with an ethylene terpolymer.

Characterization Methods

Thermomechanical Analysis (TMA). TMA scans were recorded on a DuPont thermal analyzer, Model 943 TMA fitted with a penetrating tip probe, at 2 g load and 10°C/min temperature rise. Vertical displacement and the first derivative of that displacement with respect to time were recorded as a function of temperature.

Dynamic Mechanical Analysis (DMA). These data were obtained with a DuPont 981 DMA instrument.

Tensile Properties. These were determined using a 10,000-lb Instron tester at a strain rate of 0.5 in./min on a 1-in. test specimen by ASTM Method D-882.

RESULTS AND DISCUSSION

Fire Resistance Study

Fluorenone polyester films were tested for fire resistance and compared against a polycarbonate control. The testing was qualitative and was done with a propane torch in a hood. Films, 2 in. × 2 in., were mounted and torched for 20 s. The burning was then observed.

Films of FPE-2, -3, and -4 had good flame resistance. They did not support combustion, did not drip, and were nearly self-extinguishing. When they burned, black soot was given off. Films of FPE-1 were slightly inferior to the other films in flame resistance. The control polycarbonate burned with excessive dripping and considerable black soot. Thus the fluorenone polyesters have potentially outstanding fire resistance properties.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) on the four polyesters were performed in air and helium. The TGA curves are shown in Figs. 1 (FPE-1 and -4) and 2 (FPE-2 and -3); all scans were taken at a rate of 10°C/min temperature rise. The data for FPE-4 are rather typical, showing weight loss starting at 430°C with pyrolysis continuing up to 600°C. The advanced stages of weight loss in air involved char "burnoff" as indicated by the differences between the helium and air traces in Fig. 1 and the second stage decomposition inflections in Fig. 2. From the TGA thermograms, char formation levels are seen to be in the 30-60% range.

Solubility and Intrinsic Viscosity

Fluorenone polyesters are readily soluble in methylene chloride, dimethylformamide, dimethylacetamide, and tetrahydrofuran.

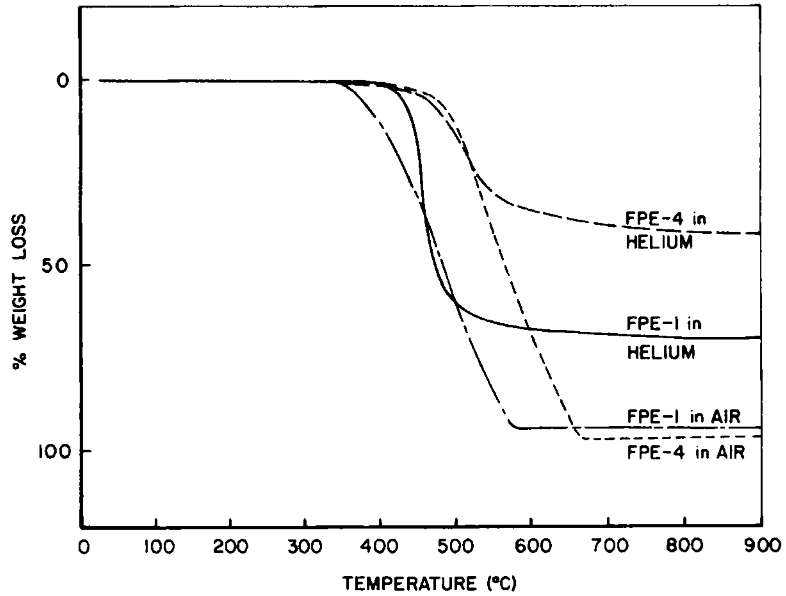

FIG. 1. TGA of Samples FPE-1 and -4.

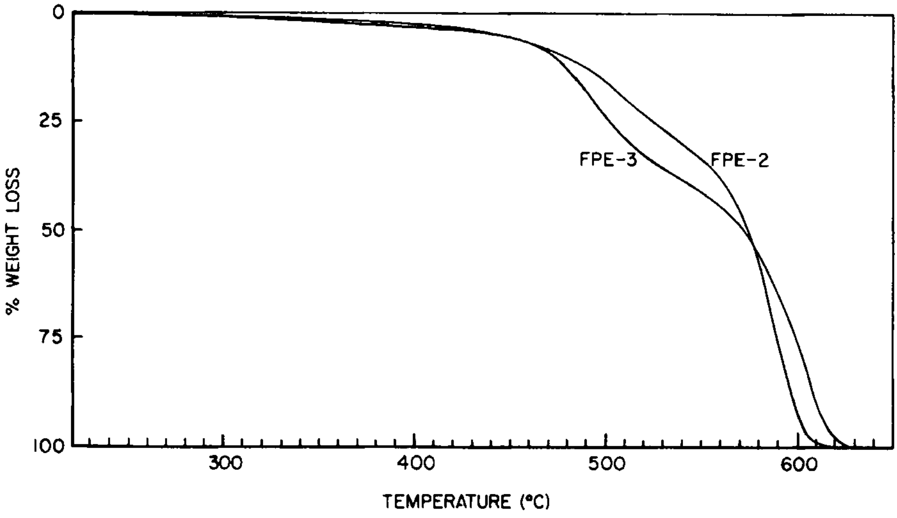

FIG. 2. TGA of Samples FPE-2 and -3.

TABLE 1. Intrinsic Viscosities of Fluorenone Polyesters in Methylene Chloride

Sample	$[\eta]$
FPE-1	0.720
FPE-2	0.501
FPE-3	0.537
FPE-4	0.351

Intrinsic velocities $[\eta]$ in methylene chloride were determined at 25°C (see Table 1).

Preparation of Films and Fibers from Solution

Films can be cast and fibers can be spun (wet or dry) from 10% polymer solution in methylene chloride or tetrahydrofuran (THF). An advantage of THF is that it is a good solvent for the ethylene terpolymer as well, which we used to modify the fluorenone polyesters. The fluorenone polyester films formed were transparent. The polyesters can be blended with 10% ethylene terpolymer and form slightly cloudy films. Blending in this case was carried out with FPE-4 in an attempt to toughen the polymer. However, the cloudy appearance of the films indicates that some phase separation occurs and toughening is not likely to occur.

Thermomechanical Analysis

The TMA scan on a molded FPE-1 film is shown in Fig. 3. A glass transition temperature (T_g) of 180°C was observed. FPE-4 did not mold well so TMA was run on a sintered sample of FPE-4. A T_g of 270°C was observed (Fig. 3). The TMA of FPE-4 blended with 10% ethylene terpolymer is also included in Fig. 3. Reduction in T_g to 238°C was noted for the polyblend. The polyblend should exhibit two distinct glass transition temperatures. The ethylene terpolymer can engage in transesterification and cross-linking reactions with fluorenone polyesters under elevated temperature during TMA runs. The cross-linking reactions are responsible for a single T_g.

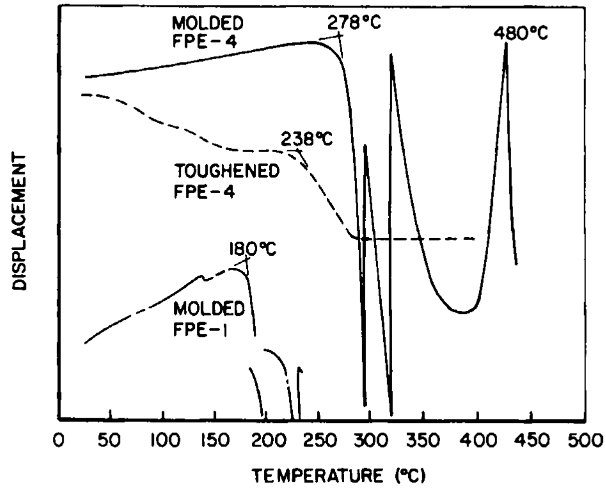

FIG. 3. TMA Scan of molded FPE-1, molded FPE-4, and FPE-4 plus ethylene terpolymer 90/10 blend.

Dynamic Mechanical Analysis

The modulus loss tangent data for FPE-2 and -3 are shown in Figs. 4 and 5. The data for FPE-2 were obtained from a compression molded film and those for FPE-3 were obtained from a film cast from methylene chloride.

The glass transitions of FPE-2 and -3 (as indicated by loss modulus maxima, not shown) are 270 and 280° C, respectively. There are also various sub-T_g transitions apparent for each polymer. The peak damping value (tan $\delta > 1.0$) observed for FPE-3 is comparable to that for polymers which exhibit a sharp transition from glassy to rubbery behavior.

Modulus-Temperature Data (Clash-Berg)

The Clash-Berg moduli obtained for FPE-1 and -4 over a temperature range of 0 to 280° C are shown in Fig. 6. The Clash-Berg T_f, the temperature where the rigidity modulus equals 45,000 psi, gives a measure of the low temperature limit of application. Below this temperature, the polymer will be glassy. T_{675} is the temperature where the rigidity modulus falls to 675 psi.

FPE-1, the bisphenol A/bisphenol fluorenone copolyester, had a T_f (indicative of glass transition) at 177° C. Polymer FPE-4 could

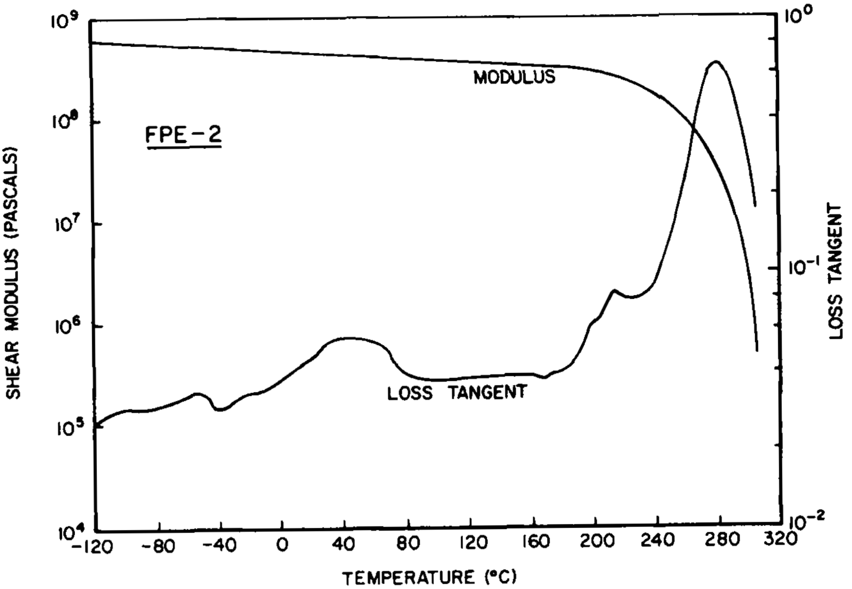

FIG. 4. DMA of Sample FPE-2.

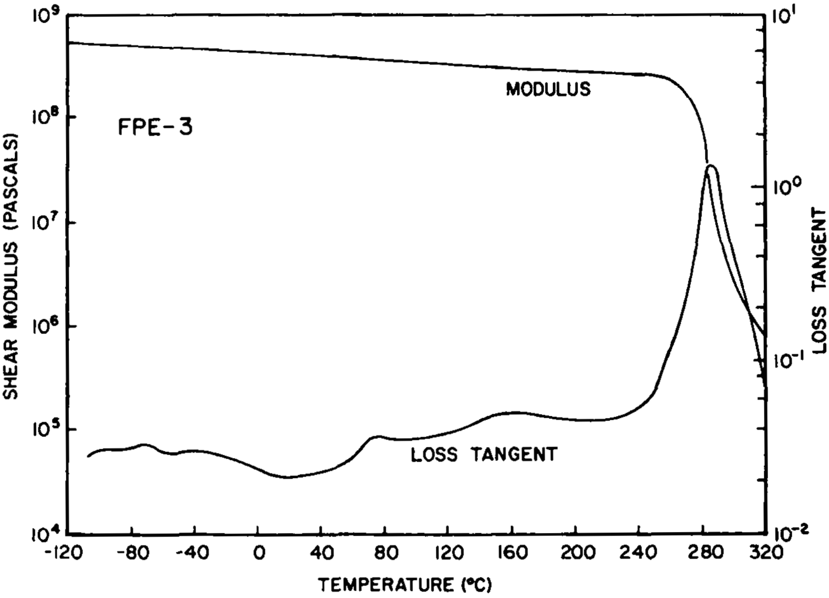

FIG. 5. DMA of Sample FPE-3.

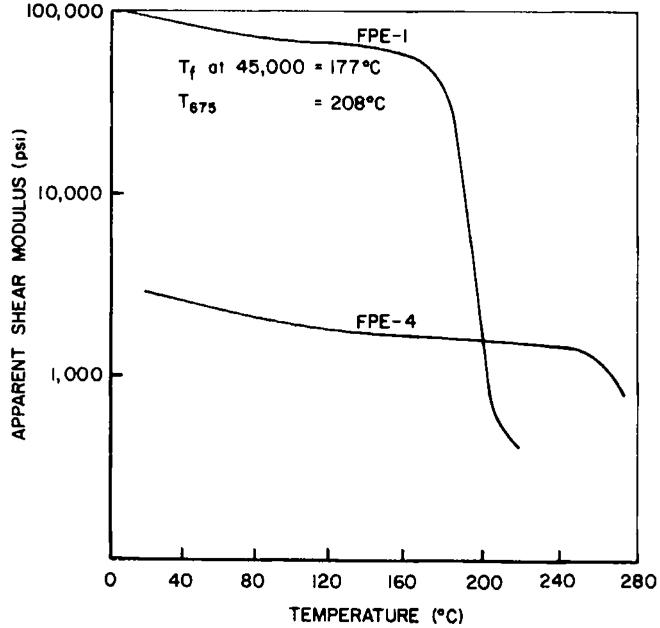

FIG. 6. Clash-Berg modulus curves of FPE-1 and -4.

TABLE 2. Tensile Data on Fluorenone Polyester Films and Ethylene Terpolymer Modified Polyesters[a]

	FPE-1	FPE-4	Sample FPE-1 plus terpolymer (90/10)	Sample FPE-4 plus terpolymer (90/10)
Tensile strength, psi	4,450 ± 750	8,500	3,940 ± 330	6,500
Tensile modulus, psi	146,000 ± 29,000	250,000	124,000 ± 12,000	110,000
Elongation, yield %	4.6	8.0	6.7	-
Ultimate elongation, %	26.0	11.5	-	9.6

[a] By ASTM D882 at a strain rate of 0.5 in./min.

not be molded into a Clash-Berg specimen. Therefore, a filter paper was coated by THF solution of sample FPE-4 and dried. Eight strips were compiled and made into one test specimen and the Clash-Berg test was run. A T_g of 270° C is indicated (Fig. 6). This is the same value as that determined by thermal mechanical analysis.

Tensile Properties

Table 2 gives the tensile properties of two fluorenone polyesters and their blends with ethylene terpolymer. The addition of terpolymer caused a considerable reduction in tensile properties.

CONCLUSIONS

The fluorenone polyesters have very good thermal and flame resistance and produce medium char yields in the 30-60% range. They do not drip at high temperatures and will not ignite under sustained external flame exposure. Films can be cast and fibers can be spun from solutions of these polymers (wet or dry). They can be blended with 10% ethylene terpolymer without much loss in heat resistance properties.

The fact that the polyester structure does not contain nitrogen is a potential advantage in fire-resistant fiber applications, since there is no likelihood of HCN generation during burning. Because of high glass transition temperature of fluorenone polyesters, these polymers can be used as heat-resistant films and fibers. Bisphenol A/bisphenol fluorenone (90/10) polyterephthalate (FPE-1) will retain its desirable mechanical properties at temperatures up to 177° C. This temperature is ~40° C higher than for bisphenol A polycarbonate and provides a real plus in performance applications requiring added heat resistance.

By virtue of not containing any nitrogen, polymers made from bisphenol fluorenone will be free of any hydrogen cyanide emission during burning. Thus this feature and the unique structure of bisphenol fluorenone should be utilized to make high performance polymers, e.g., acetylene-terminated fluorenone polymers, bisphenol fluorenone/formaldehyde, and bisphenol fluorenone ester carbonates.

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