Aging Behavior of Polyarylsulfone Films

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Synopsis

The aging behavior of two experimental polyarylsulfone films is discussed. The mechanical and electrical properties of the films were measured as a function of time at temperatures of 300°, 275°, and 250°C. The effect of "reprocessing" the material is also reported. DTA and TGA analysis, coupled with other aging test results, point out the excellent thermal stability of the polyarylsulfones. However, some peculiar behavior is exhibited by the unrefined polymer. Free film aging of this material showed no signs of discoloration or deterioration in properties after 1000 hr at 300°C. Film aged wrapped on metal and glass rods discolors badly, is subject to stress cracking, and embrittles. The reprocessed" film is superior to its predecessor and exhibits none of the disadvantages that characterize the unrefined polymer. Solubility studies, coupled with the other aging tests, provided some insight into the degradation phenomenon of this polymer. Resistance to ultraviolet light is extremely poor. Reprocessing of the material provided for a much superior film material with a higher level of mechanical, electrical, optical, and thermal properties.

INTRODUCTION

Early in 1967, a new family of high-temperature resins was introduced by the 3M Company. These materials were disclosed as being polyarylsulfones, completely void of aliphatic linkages. This distinguishes them from the polysulfones containing the isopropylidene unit currently on the market.[1] These and similar materials have been reported on since the early sixties, as evidenced in the literature.[2-5]

Because of the absence of any aliphatic groups and the inherent stability of the phenyl ring, the polyarylsulfones are characterized as having exceptional thermal stability. The oxygen and sulfone bridges impart flexibility to the material, thus contributing to its film-forming properties. Several grades of polysulfones are available, but the materials under study in this report are experimental polymer films designated A and B, "unrefined" and "reprocessed" films, respectively. Recently, several papers have appeared in the literature[6,7] on the polyarylsulfones, but none has characterized the aging behavior of the film grade material.
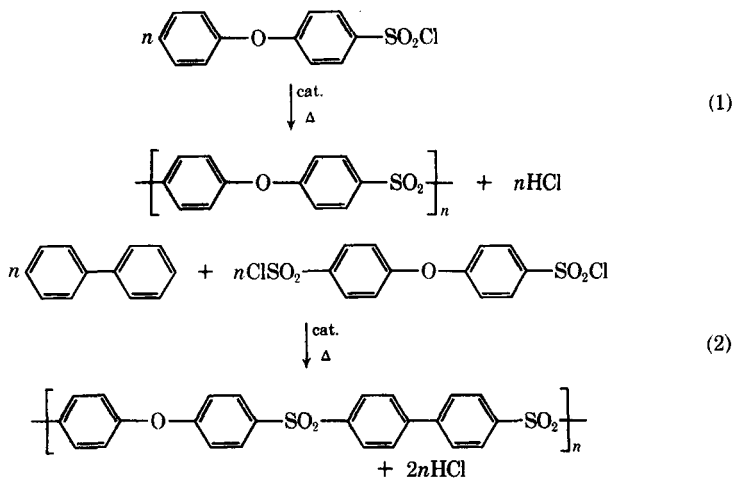
This paper reports the study of the aging behavior of these experimental polymer films and the effects of aging at elevated temperature on their mechanical, electrical, and chemical properties.

EXPERIMENTAL

Material

These materials are reported to be polyaryloxysulfone copolymers and were supplied by the 3M Company in film form 1.4 mil thick. The unrefined film had a light yellow tinge. Infrared analysis indicated that the polymer is 1,4-substituted and contains no aliphatic groups.

Elemental analysis gave the following results: found C, 64.31, 64.12%; H, 3.49, 3.65%; O, 17.87, 18.01%; and S, 13.97, 13.76%. These results, supplemented by those reported in the literature, indicate that the polymer is composed of about 60 mole-% biphenylene sulfone and 40 mole-% oxydiphenylene sulfone groups. The inherent viscosity of this polymer is reported[2] to be about 0.68 dl/g. The polymers can be prepared by the Friedel-Crafts condensation of aromatic sulfonyl chlorides with aromatic compounds. The general reaction scheme is illustrated in eqs. (1) and (2):

$$n \text{—SO}_2\text{Cl} \quad (1)$$

$$\left[\text{—O—} \text{—SO}_2 \right]_n + n\text{HCl}$$

$$n \text{—} + n\text{ClSO}_2\text{—} \text{—O—} \text{—SO}_2\text{Cl} \quad (2)$$

$$\left[\text{—O—} \text{—SO}_2\text{—} \text{—SO}_2 \right]_n$$
$$+ 2n\text{HCl}$$

The other film material is chemically the same as the "unrefined" one but has been "reprocessed" to give a cleaner film (almost colorless) with improved properties.

Test Methods

Mechanical properties were measured according to ASTM D882 (tensile, elongation, and modulus). Flexibility was determined by manually creasing the film 180 degrees and also by ASTM D2176 (MIT Folding Test under a 1-kg load).

Electrical properties, dielectric strength, dielectric constant, dissipation factor, and d.c. volume resistivity were measured according to ASTM D149 (60 Hz), ASTM D150 (1 KHz), and ASTM D257, respectively.

Infrared spectra were recorded on the Perkin Elmer Model 521 spectrophotometer and the Beckman IR-12.

Ultraviolet exposure tests were conducted by exposing the films in a Weather-O-Meter as per ASTM 1499. In addition, the films were also exposed in a unit containing fluorescent sunlamps and black lamps to simulate a dry UV environment in contrast to the Weather-O-Meter exposure.[8,9]

Aging Tests

The polymer film was examined using the du Pont 950 TGA and 900 DTA thermal analyzer at a heating rate of 10°C/min in an atmosphere of flowing air and nitrogen.

Several methods were used to evaluate the stability of the film material:

1. Dielectric strength life tests were conducted on the film. This test consists of wrapping a 1-in.-wide film with a $^1/_2$-in. overlap on round-edge aluminum test bars 0.024 × 0.625 in. Five electrodes are placed at spaced intervals along the test bar and the bars are aged at each test temperature. The bars are periodically removed, inspected, and tested for electr cal breakdown under voltage at the five points along the bar. A particular value of electric strength (usually 1000 V/mil in our tests) is chosen as the endpoint, and an Arrhenius plot is constructed to determine the life of the material. The test temperatures used were 300°, 275°, 250°, 225°, and 200°C.

2. One-inch wide strips of the film were wrapped with a $^1/_2$-in. overlap on aluminum, steel, galvanized iron, and glass rods of different diameters to determine if the film is sensitive to thermal stress cracking and/or a catalytic effect of the metal rod. Failure of the film was reached when the film was unable to be creased without cracking.

3. Films approximately 8 × 10 in. were clamped on metal frames and aged in a mechanical convection oven at 300°, 275°, and 250°C. Film samples were removed periodically and mechanical properties measured at room temperature.

Solubility Tests

The film samples aged on aluminum rods at 250°–275°–300°C were examined by their solubility behavior in dimethylacetamide (DMAC). In this way, at least a qualitative estimate of the degree of degradation or crosslinking was obtained.

RESULTS AND DISCUSSION

General Properties

A summary of the mechanical, electrical, and thermal properties of the "unrefined" and "reprocessed" materials is presented in Table I. The three most significant property differences between the two polymers are elongation, fold endurance, and heat shrinkage. However, there are other small differences, notably in color, dissipation factor, and dielectric strength.

TABLE I
Properties of Polyarylsulfones

Film	Tensile strength, psi $\times 10^3$	Tensile modulus, psi $\times 10^6$	Elongation, %	Tear strength, g/mil	Fold[a] endurance, cycles	Dissipation factor (at 24°C and 200°C)	Dielectric constant (at 24°C and 200°C)	DC volume resistivity (at 24°C and 200°C)	Dielectric strength (at 24°C and 200°C), kV/ml	Film brittle after aging Time, hr	Temp., °C
Unrefined A	11.4	0.30	8	467	1,000	0.0006	3.8	1×10^{11}	4.0	300	300
						0.010	3.5	1×10^{13}	4.9	2724	275
Reprocessed B	13.0	0.25	35	481	30,700	0.002	3.4	5×10^{11}	4.2	>400	300
						0.001	3.5	1×10^{12}	3.2	>3000	275
										>3518	250

[a] 1.4 mil thick, 1 kg load.

In polymer B, the elongation to break has been improved fourfold and the fold endurance has increased substantially. As a result, this polymer is considerably tougher than its predecessor. It would appear that the "reprocessing" treatment provided a significant orientation of the polymer film.

Significant differences appear in the thermal behavior of the two polymers. Polymer A discolors faster than B at all temperatures. In addition, the former is subject to thermal stress cracking, whereas no cracking was evident in the latter polymer.

Thermogravimetric Analysis

Figure 1 illustrates the TGA curves for polymer A film in air and in nitrogen. The decomposition temperatures are 490° and 460°C, respectively. The pure thermal degradation of the polymer appears to be a slow, one-stage process, as indicated by the shape of the TGA curves. This is verified by the differential plot which shows one marked inflection point. This point occurs in the region between 510° and 590°C, with a maximum rate of weight loss of 1 mg/10°C-min. In nitrogen, the film loses weight fairly rapidly up to 600°C, but then begins to level off, and at 1000°C the polymer has lost only 55% of its weight. In contrast, the film in an air atmosphere, although it has a slightly higher decomposition temperature, loses weight very rapidly in a multiple-stage process until it is exhausted at 670°C. There are several maxima indicated by the differential plots, the most striking being the one occurring at the final weight loss stage between 610° and 670°C. The change of slope beginning at about 580°C on the TGA curve, coupled with the solubility data, suggests the formation of a cross-linked network prior to the final weight loss.[10] Because of
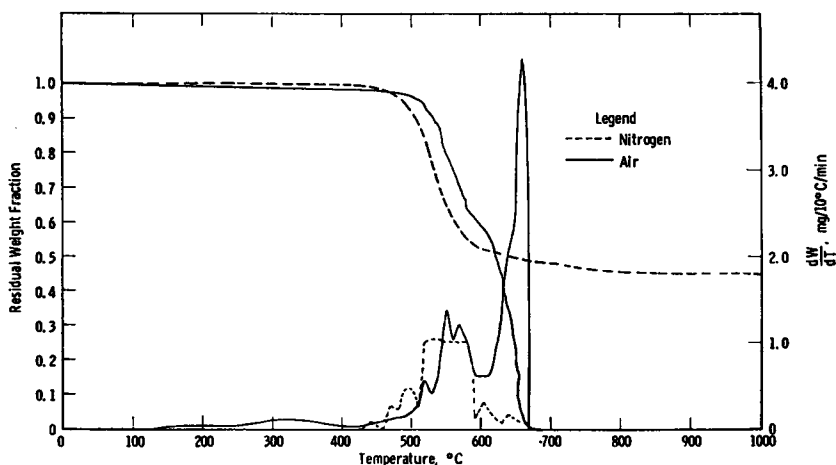

Fig. 1. TGA curves for polymer A film in air and nitrogen atmospheres at heating rate of 10°C/min.

the height of the final peak (4.2 mg/°C-min), it seems possible that a tight crosslinked structure was formed prior to this final weight loss and that this large and rapid weight loss was the final volatization of the polymer after the rupture of the crosslinked structure. The insolubility of the aged polymer lends support to a crosslinked structure.

Differential Thermal Analysis

The DTA curves are illustrated in Figure 2. In nitrogen, the poly-arylsulfone is relatively stable, exhibiting only a small but broad exotherm at 476°C. In air, the onset of degradation is shifted to a slightly higher temperature of 494°C and is accompanied by a rather large exotherm corresponding to a temperature rise of about 20°C.

These temperatures correspond very well with the data obtained from the TGA curves both in air and nitrogen. The fact that there is a drop
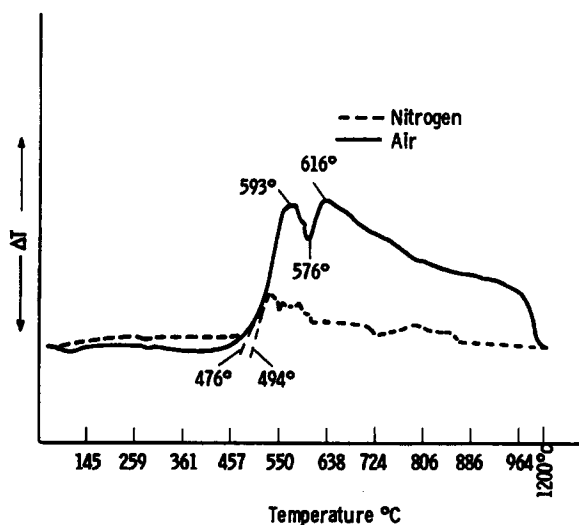

Fig. 2. DTA curves for polymer A in air and nitrogen at heating rate of 10°C/min

in peak height in air could be due to the formation of a crosslinked structure prior to its final decomposition. This inflection point seems to correspond to the inflection point on the TGA curve at about 580°C. If oxidative crosslinking were to occur, then a finite time interval would exist corresponding to the life of this crosslinked species prior to its final decomposition. A crosslinked structure is indicated from the solubility studies.

Aging of Film on Metal Rods

An initial screening test of aging the film wrapped on various diameter rods yielded some interesting results. Details of these results are shown in Table II. It should be noted that none of the polymer B samples crazed under any condition of testing.

TABLE II
Aging of Films on Metal Rods

Rod type	Diameter, in.	Time, hr	Temp., °C	Remarks
Steel	1	984	250	film OK; no crazing noted
		968	275	film OK; no crazing noted
luminum	$^1/_2$ & $^3/_{16}$	140	250	no crazing evident
	$^3/_{16}$	186	300	crazing in stressed areas only
	$^1/_4$	76	250	slight crazing but none at 275° and 300°C
	$^1/_4$	332	250	some yellowing at overlap sections
		332	275	some yellowing at overlap sections
		332	300	entire film dark and very brittle
Glass	1	186	300	very slight yellowing of film at overlap sections
Galvanized steel	1	2724	275	film yellow and brittle
		2740	250	not tightly wrapped; very slight yellowing
Rectangular aluminum Rod with a radius of 0.024 in.			300	all polymer A samples crazed at all
			275	temperatures within 400 hr of
			250	aging; none of the polymer B samples crazed even after 400 hr at 300°C and 12,000 hr at 225°C

Films wrapped on these metal and glass rods were subject to thermal stress cracking, and crazing of the polymer A film occurred on all of the metal substrates tested. This crazing was dependent upon the strain initially placed on the film during wrapping. Those films wrapped tightly crazed very readily at all temperatures, while those which were wrapped loosely did not craze, even at 300°C. The second interesting observation to be noted was a yellowing of the film aged on the rods. At first, this yellowing was confined to the overlap portions of the film, but as time progressed, the yellowing spread. This effect was most pronounced at 300°C and caused the film to become extremely brittle in the colored area.

Solubility tests on films wrapped on aluminum rods and aged 332 hr at 300°–275°–250°C indicated that crosslinking was taking place. These results are reported in Table III.

TABLE III
Solubility of Aged Film Samples in DMAC

Exposure time, hr	Results
332 (at 250°C)	soluble at room temperature
332 (at 275°C)	partially soluble with gel formation in hot solvent
332 (at 300°C)	insoluble in hot solvent

The nature of this yellowing is not completely understood, but it does not seem to be due to a catalytic effect of the metal, since discoloration of

the film was observed on glass, but to a lesser extent. A plausible explanation is that volatile products were trapped in the overlap sections and caused degradation of the film. These volatiles may be degradation products or traces of residual catalyst. It is believed that this last interpretation is the major contributor. This discoloration was evident on both film samples, although to a lesser extent on the "reprocessed" material. The time required to produce the first trace of yellowing was dependent on the temperature. At 275°C, 31 days (745 hr) elapsed before some yellow color was noticed. At 250°C, 150 days (3600 hr) was required. At 225°C, 425 days (10,200), and at 200°C, 500 days (12,000 hr) was required.

The results of emission spectroscopic analysis confirm the presence of a catalyst, namely, an indium salt. Traces of iron, chromium, and manganese were also present in higher concentration in sample B. But the indium was proportionately higher in concentration than the other metals. These other metals were probably incorporated into the resin either during synthesis of the resin or processing of the film. In addition, sodium was also found and appeared to be present in greater concentration in the "unrefined" sample.
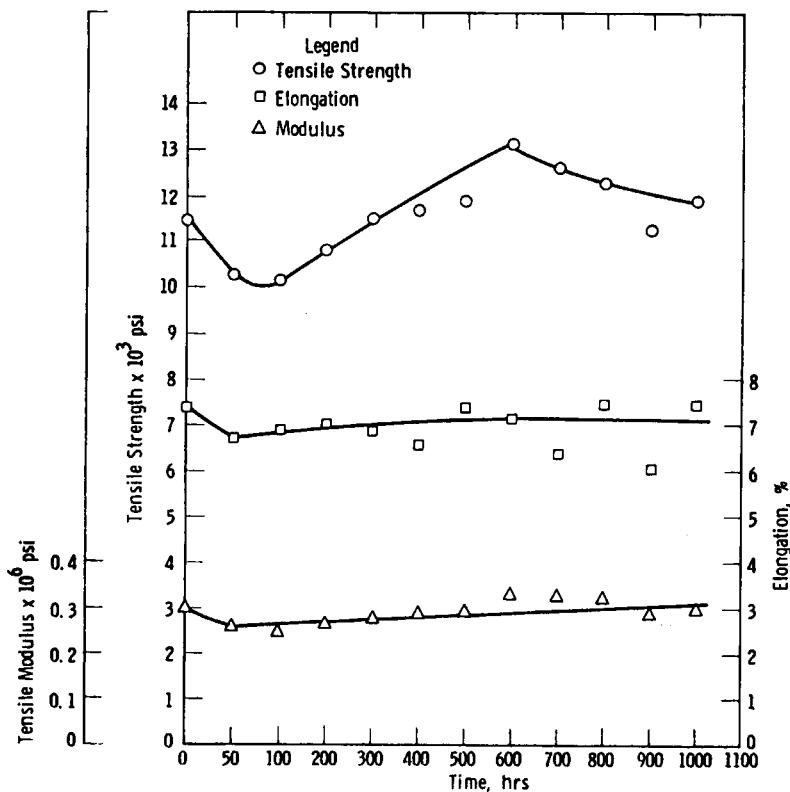

Fig. 3. Mechanical properties of polymer A film aged at 250°C on aluminum frames.

Mechanical Properties Versus Aging

Unlike the film samples wrapped on the rods, samples that were clamped on frames did not exhibit any color change whatsoever, even after 1000 hr at 300°C. The film material was still flexible and creasable and showed no signs of deterioration. Mechanical properties measured on the exposed films are reported in Figures 3 to 5. These results indicate that no significant deterioration of properties was apparent, even after 1000 hr at 300°C, when free films were aged.

A comparison of these results with the rapid deterioration of films wrapped on metal bars lends support to the interpretation that the yellowing and embrittlement are due to volatile entrapment. Since no color change was observed on the free films at the point of contact with the aluminum frame, metal catalysis seems to be ruled out. Mechanical stress, however, may still be a factor contributing to the deterioration of the wrapped films.
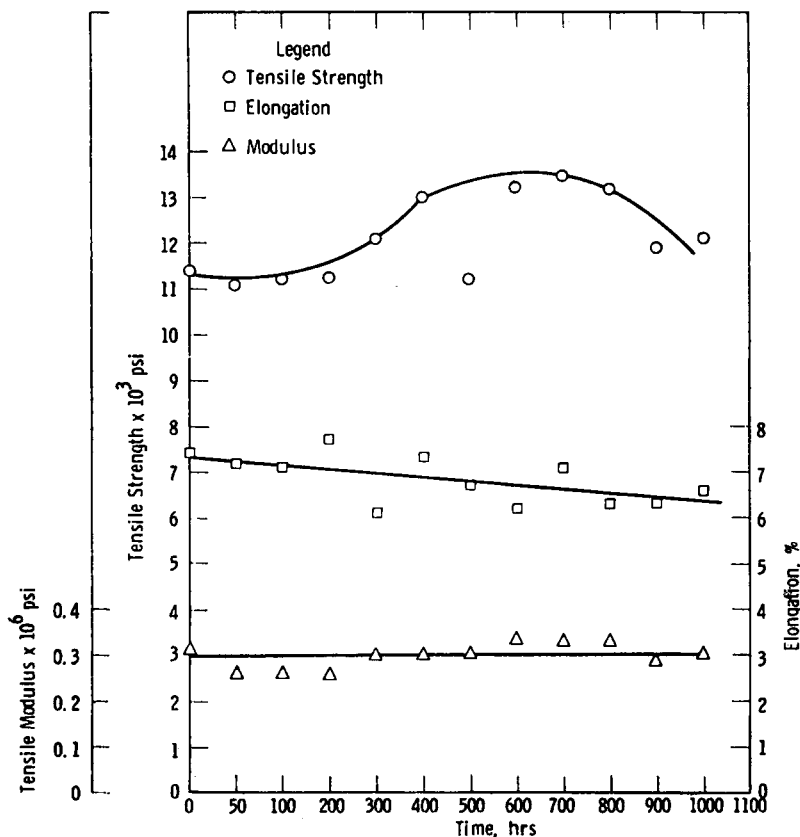

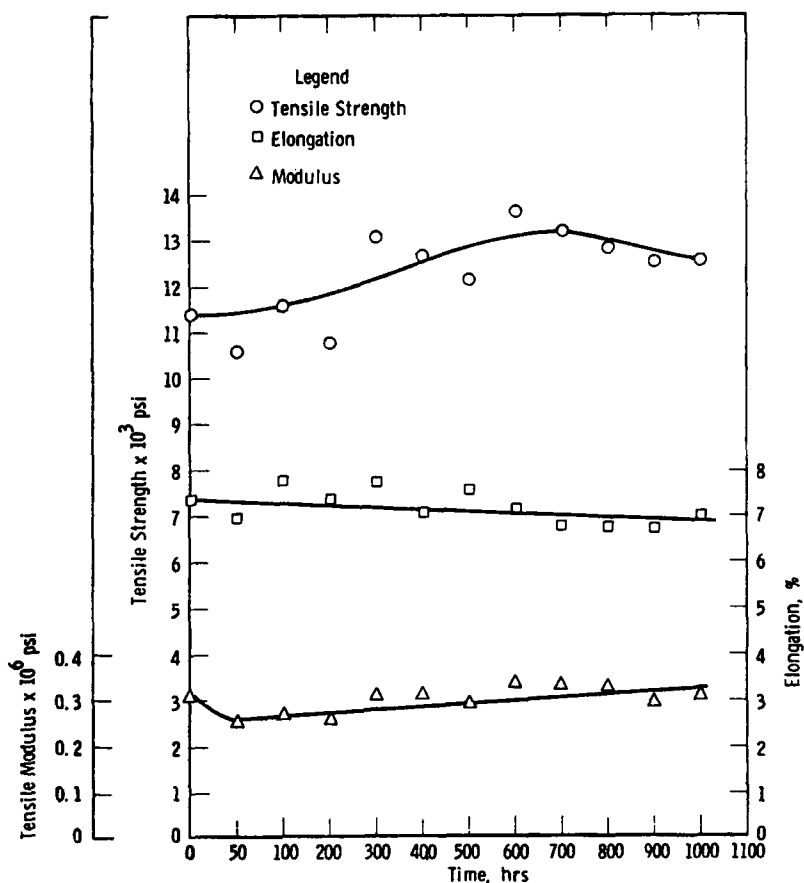Fig. 4. Mechanical properties of polymer A film aged at 275°C on aluminum frames.

Fig. 5. Mechanical properties of polymer A film aged at 300°C on aluminum frames.

Infrared Analysis

In order to explain some of the anomalous behavior of the "unrefined" polymer film, infrared spectra were recorded on films aged 332 hr at 300° and 275°C wrapped on aluminum bars on both the light- and dark-colored portions. These spectra are shown in Figure 6. The most striking characteristic observed in the dark portion of the films aged at 300° and 275°C is the formation of a band at 3400 cm^{-1} which is characteristic of polymeric hydroxyl groups.[11] In addition, the changing pattern in the regions between 2000–1800 cm^{-1} and 1000–800 cm^{-1} suggests a conversion from a disubstituted to a trisubstituted aromatic ring.[11] This conclusion seems plausible since crosslinking, as evidenced from the solubility data, would cause changing substitution patterns. In addition, there appear to be bands growing in the region between 1700 and 1650 cm^{-1} which are not present in the unaged film spectra. These are attributed to acid- and/or quinone-type[11] carbonyl stretching vibrations. Clearly, then, oxidation
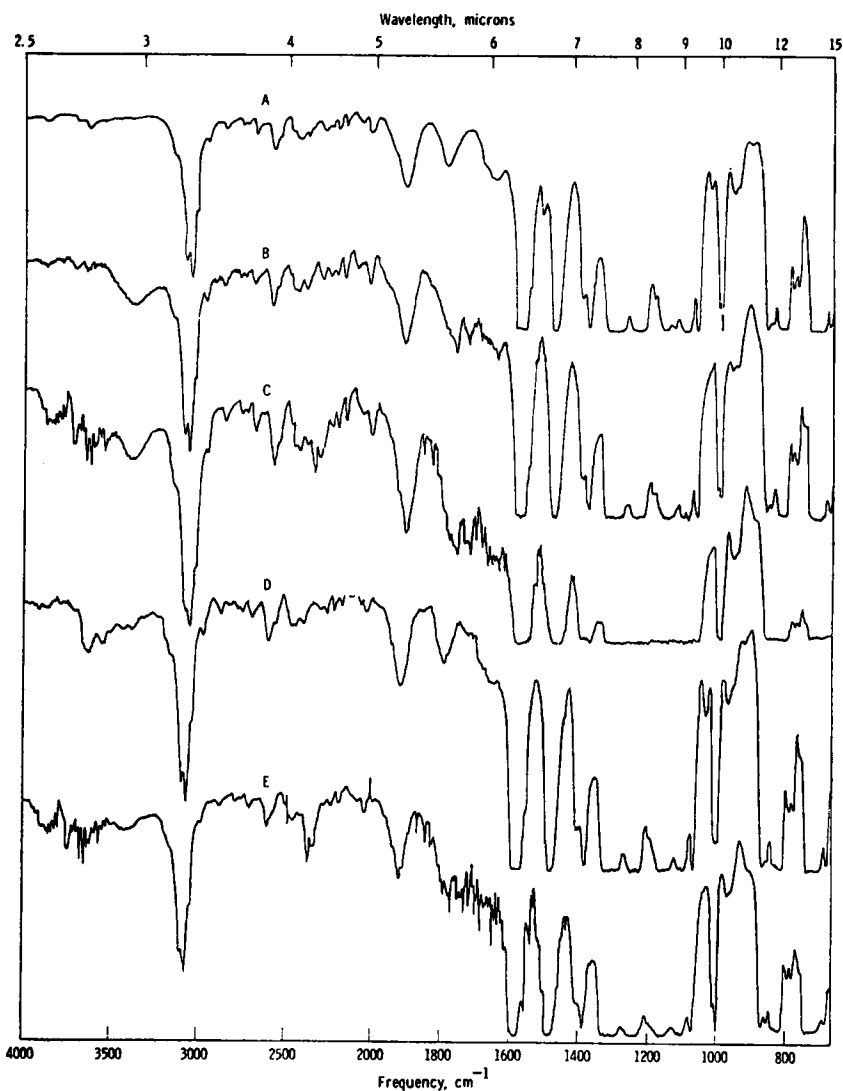
Fig. 6. Spectra of films after aging 332 hr at 300° and 375°C on aluminum rods: (A) control unaged film; (B) dark portion of film aged 332 hr at 275°C; (C) dark portion of film aged 332 hr at 300°C; (D) light portion of film aged 332 hr at 275°C; (E) light portion of film aged 332 hr at 300°C.

has taken place in the film.   However, negligible oxidation has taken place in the light portion of the films as indicated in spectra D and E of Figure 6, although the film aged at 300°C is beginning to show signs of oxidation.

Electrical Properties Versus Aging

Film samples of both polymers were wrapped on aluminum bars and aged at their respective temperatures as described in the experimental

TABLE IV
Dielectric Strength as a Function of Time at Temperature Wrapped Bar Tests[a]

Film	Original breakdown voltage, kV	300°C Breakdown voltage, kV	300°C Time, days	275°C Breakdown voltage, kV	275°C Time, days	250°C Breakdown voltage, kV	250°C Time, days	225°C Breakdown voltage, kV	225°C Time, days
A	6.7	crazed		4.6	13	1.9	22	1.2	22
				1.3	16				
B	5.8	3.0	4	4.9	8	3.9	45	2.0	374
		1.9	7	4.6	14	4.6	60		
		0.6	10	3.3	21	2.1	115		
				0.7	31				

[a] All aged samples took a 180° bend and crease without cracking.

section. The electric breakdown strength of the "unrefined" film under the conditions of this test deteriorated rapidly. The results of these tests are shown in Table IV. A subsequent microscopic examination of the sample disclosed the reason for the rapid breakdown of the film to be crazing and cracking of the film parallel to the length of the bar along its radius. These same craze lines could be reproduced by heating a wrapped bar directly to 275°C, maintaining it at that temperature for 1 hr, and returning the bar directly to room temperature. Clearly, this is an example of heat shock sensitivity. "Reprocessed" film, on the other hand, showed no signs of thermal stress cracking at any of the test temperatures, even after prolonged aging (12,000 hr at 225°C). Film samples of this polymer were aged 14 days at 300°C and were subject to short excursions to 330°C (about 3 days). Although they became deeply discolored (dark yellow), they did not exhibit any crazing or cracking. The breakdown voltage for
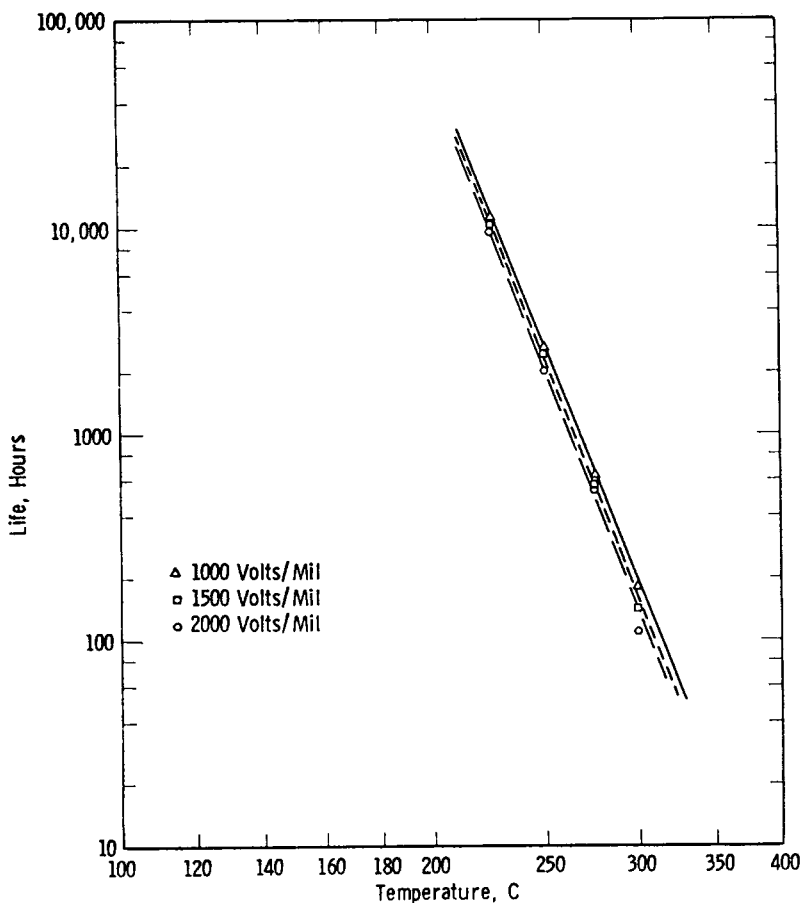

Fig. 7. Electric strength life of polymer B film wound half lapped on rectangular aluminum conductors.

the "reprocessed" material at several temperatures is also shown in Table IV. It is apparent that this latter film material is superior thermally to its predecessor. A log time–temperature curve was constructed for this polymer film by plotting the time to reach a specific breakdown strength versus temperature. This curve is shown in Figure 7 for breakdown strength at the 1.0, 1.5, and 2.0 kV levels. Extrapolation of the curve indicates that polymer B does have excellent high-temperature service capabilities. Because of the crazing sensitivity of the "unrefined" polymer, no meaningful life curve could be constructed for this film.

Ultraviolet Aging

Film samples of the "reprocessed" polymer exposed in the Weather-O-Meter became opaque and quite brittle after only 300 hr of aging. Samples exposed to a dry UV environment developed a surface bloom over the entire sample that was pasty in texture. This surface bloom was washed off with acetone. The film shriveled up and became quite brittle. Evidence from infrared spectra, although not conclusive, indicates the material to be di- or trisubstituted phenyl ether with acid or ester functional groups. It is obvious that this polyarylsulfone polymer is extremely unstable toward ultraviolet light. The spectrum of the surface bloom material is shown in Figure 8. The infrared spectrum of the film after the surface bloom was removed is shown in Figure 9. It is interesting to note the ingrowth of bands in the 1700–1800 cm^{-1} region, probably acid and/or ester groups. In addition, a broad band is well developed in the hydroxyl region beginning around 3800 cm^{-1}.

In addition to the pasty texture of the surface bloom material, a powdery substance was also washed from the surface of the film. The spectrum of this material is shown in Figure 10. Considerable oxidation has taken place
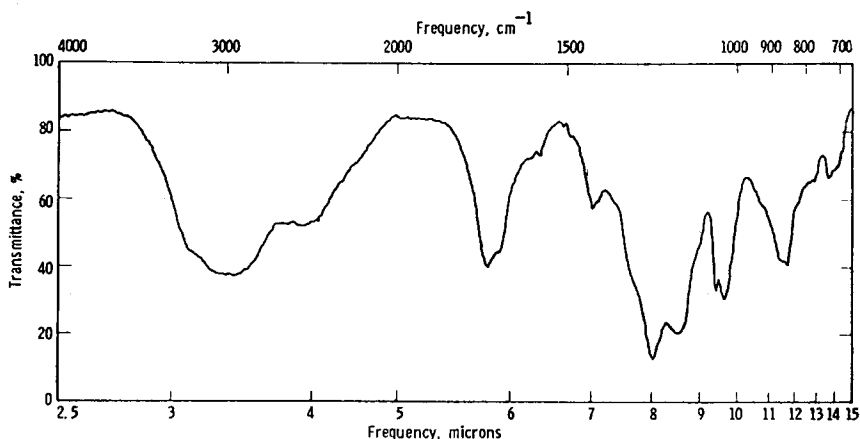
Fig. 8. Spectra of pasty surface bloom found on polymer B film after UV irradiation.

as evidenced by the ingrowth bands in the 1650–1750 cm⁻¹ region and also
from the broad OH absorption.   In comparing the spectrum with the
control (designated A in Fig. 6), there appears to be considerable change in
the ring substitution pattern (800–1000 cm⁻¹).   The spectrum illustrated
in Figure 10 shows that there is still some SO_2 and ϕ—O—ϕ linkages, so
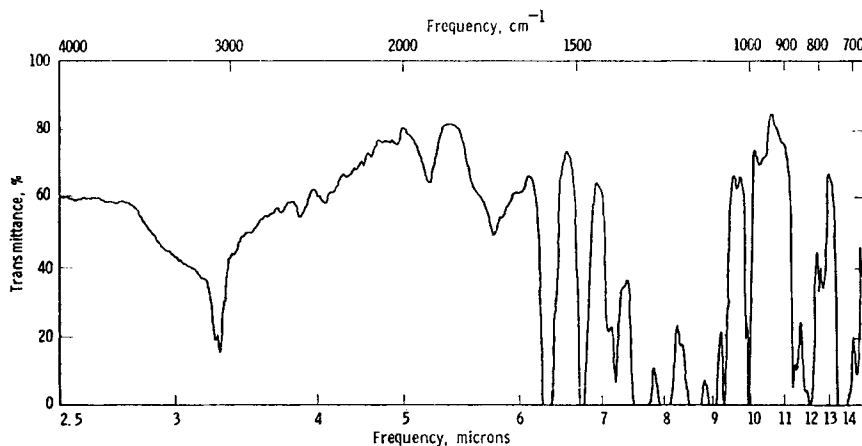
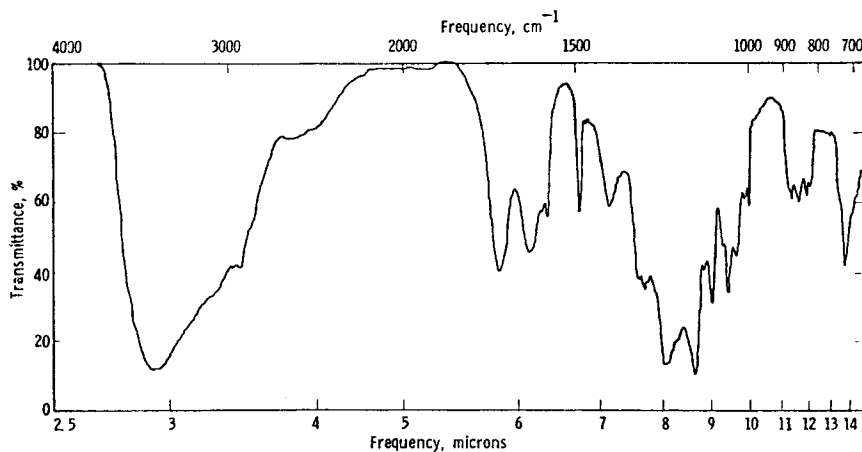Fig. 9. Spectra of polymer B film after UV irradiation.

Fig. 10. Spectra of powdery material washed from polymer B film after UV irradiation.

that this powdery material might possibly be low molecular weight polymer
with acid functionality resulting from chain scission.   Both the pasty and
powdery materials are soluble in 5% sodium hydroxide solution, and their
aqueous solutions are acid to litmus.   This information, coupled with that
from infrared, strongly indicates acid functionality.   Furthermore, Gesner
et al.[12] have studied the photo-oxidation of a polysulfone prepared from

2,2-bis(4-hydroxyphenyl)propane and 4,4-'dichlorodipenyl sulfone and have shown the formation of acidic and ester-type degradation products as well as the formation of sulfonic acids resulting from scission of aryl ether and arylsulfone bonds along the polymer chain. The evidence indicated in the present study does suggest the formation of degradation-type products similar to those found by Gesner et al. The film, after exposure to UV, is still soluble in dimethylacetamide (DMAC).

The film samples exposed in the Weather-O-Meter were so brittle and discolored that infrared analysis was not made on them.

CONCLUSIONS

The aging behavior of aromatic polysulfone polymers has been investigated. The results of this study show that the polymers exhibit peculiar behavior under varying conditions of oxidation. DTA and TGA indicate that the polymers have high decomposition temperatures. Aging of the polymers as free films produces no significant deterioration in mechanical properties, nor was there any discoloration of the film. On the other hand, aging of the film wrapped on itself produces discoloration of the film, the intensity of which varies with the time and temperature of exposure. Eventually, the film embrittles as the discoloration becomes more intense. In addition, the "unrefined" polymer A is very sensitive to thermal stress crazing which manifests itself in a rapid decline in dielectric strength. The "reprocessed" film B shows no tendency for the weaknesses of the former film and is, indeed, superior to it in all properties. The ability of the "reprocessed" polymer to retain its electrical properties is confirmed by the dielectric strength life tests.

Oxidative studies of the polymers indicate that the degradation proceeds through a crosslinked structure. In addition, the volatile materials liberated during aging seem to play a role in the degradation process. The exact nature of the volatile materials is not known at the present time, but it seems reasonable that catalyst residues could account for part of the observed phenomenon.

The ultraviolet exposure data point out the extreme instability of the polyarylsulfones toward UV light. Sufficient data have not been obtained to completely define the UV degradation process. Infrared spectral data indicate the formation of acid or ester functionality. This is supported by the solubility of some of the degradation products in dilute alkali. In addition, there is evidence to suggest changing ring substitution patterns.

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