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Thermal Properties of Poly[N,N′-(4,4′-Diphenyl Ether) 4-Amidophthalimide] Film

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Synopsis

The aging behavior of a polyamide–imide film was investigated. Film samples have been exposed to temperatures from 225° to 350°C for various times and the mechanical and electrical properties measured. This information was used to construct log life plots to gain an insight into the service life of this material. TGA and DTA results coupled with the information from the aging tests indicate that this film can be used at temperatures of 180° to 200°C for extended periods of time. Mechanical properties, especially elongation, of the film deteriorate faster than the electrical properties.

INTRODUCTION

For a number of years we have been investigating the properties of high-temperature polymers for use as dielectric materials. Our efforts have been directed toward those polymers that form tough, flexible films capable for use as a Class H insulation material. One particular polymer system has been found to possess an excellent combination of properties that make it suitable for operation at elevated temperature. Some of its chemistry and properties have been reported previously.[1] This paper reports our study of the thermo-oxidative behavior of this polyamide–imide film.

EXPERIMENTAL

The monomers, synthesis, and properties of film have been described in previous papers of this series.[2,3]

Test Methods

Tensile strength, elongation, and modulus were measured according to ASTM D882.

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 air and nitrogen atmospheres.

Other Tests

Several other methods were also 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 were 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 electrical breakdown under voltage at the five points along the bar. A particular value of electric strength (in our case 1500 and 2000 V/mil) is chosen as the endpoint and a log life-versus-reciprocal temperature plot is constructed to determine the electrical life of the material. The test temperatures used were 325°, 300°, 275°, 250°, and 225°C.

2. Brittle point failure was determined by wrapping 1-in.-wide film strips with a 1/2-in.-overlap on 1/2-in.-diameter aluminum rods. They were then aged at various temperatures from 225° to 350°C. Failure of the film was reached when it was unable to be bent 180 degrees without cracking. The time required for the film to become brittle was used as the criterion for failure, and a log life-versus-reciprocal temperature plot was constructed to determine the brittle life of the material.

3. Films approximately 8 × 10 in. were clamped on aluminum frames and aged in mechanical convection ovens at 225°, 250°, 275°, and 300°C. Films were removed periodically and the mechanical properties measured at room temperature. Log life plots were constructed using the time to reach 50%, 25%, and 15% of the original property values.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Figure 1 illustrates the TGA curves for the polymer film in air and nitrogen atmospheres. The initial decomposition temperatures are 420° and 460°C, respectively. In air, the film loses weight in a two-step process as indicated by the shape of the TGA curve. The initial period is characterized by a slow gradual weight loss from 420° to 570°C amounting to about 18%. This is followed by a very rapid weight decrease until the film has essentially lost all of its weight at about 700°C. The differential plot shows

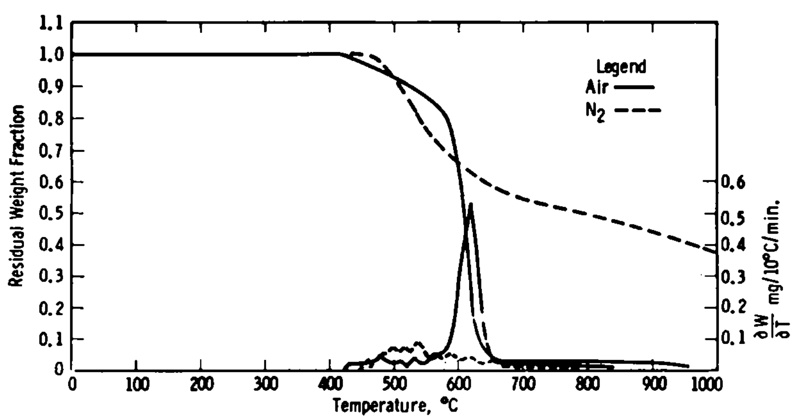

Fig. 1. TGA curves for poly[N,N′-(4,4′-diphenyl ether) 4-amidophthalimide] film.

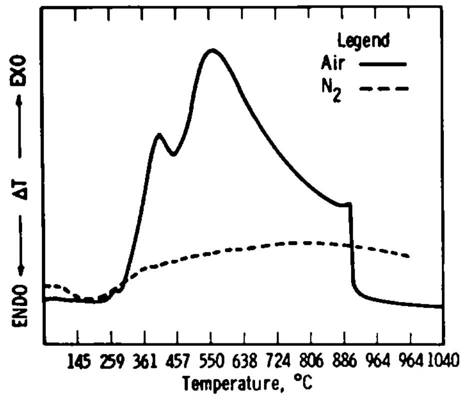

Fig. 2. DTA curves for poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide] film.

only one maximum indicating that the major weight loss region occurs between 580° and 650°C. In nitrogen, however, the initial decomposition temperature is about 40°C higher and the film has lost almost 30% of its weight at the same temperature (570°C) where the film in air has lost 18% of its weight. However, after this temperature, there is only a slow, gradual weight loss up to 950°C where 40% of the polymer still remains in contrast to almost complete weight loss of the film in air some 300°C below this temperature. The maximum rate of weight loss in nitrogen occurs at about 550°C.

Differential Thermal Analysis

The DTA curves are illustrated in Figure 2. In nitrogen, the polymer is relatively stable, exhibiting only a small but broad exotherm. In air, the degradation is accompanied by two large exothermic reactions corresponding to the two weight loss regions in the TGA curves. The maximum temperature rise associated with the highest exotherm peak is about 14°C.

Aging Studies of Film

There are many properties of a polymer film that affect its thermal life under a given set of operating conditions. It is important, therefore, to choose and measure the appropriate property under accelerated aging tests in order to gain some knowledge on the material's service life. Often the criteria of failure for one property will not coincide with that of another property. We have examined the aging behavior of poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide] film with respect to its electrical, mechanical, and flexibility properties. In Figure 3 is presented the thermal life curve for this amide–imide film using flexibility as determined by creasing the film 180 degrees as the criteria for failure. The point at 225°C represents 27,000 hr of testing and the film is still quite creasable. There is a considerable color change in the film going from light amber to almost black in color after aging at temperatures ≥275°C. Some shrinkage was evident on the wrapped films and was more apparent at temperatures ≥250°C.

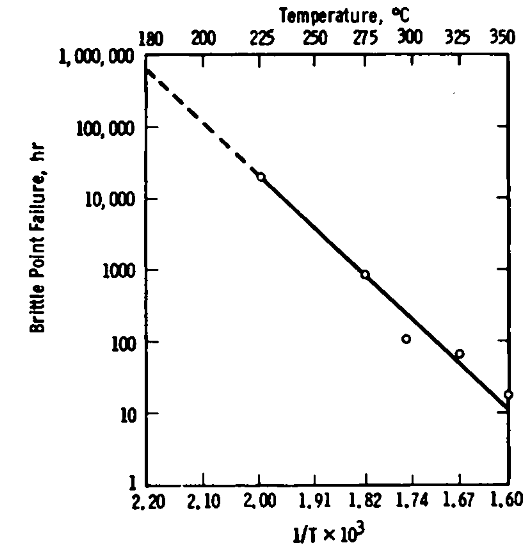

Fig. 3. Thermal life curve for poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide] film, 1.3 mils thick.

Mechanical Properties Versus Aging

The deterioration in film properties after each aging period is shown in Figures 4–7 as a semilog plot of per cent property retained versus aging

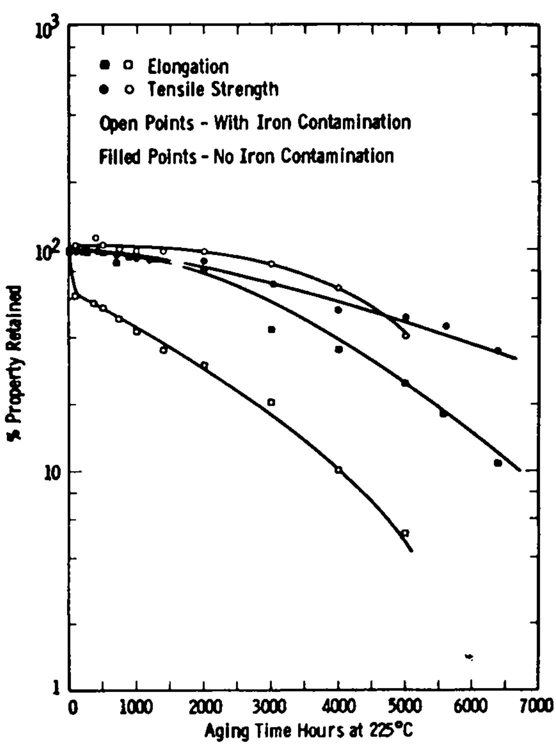

Fig. 4. Property retention vs. aging time for poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide film.

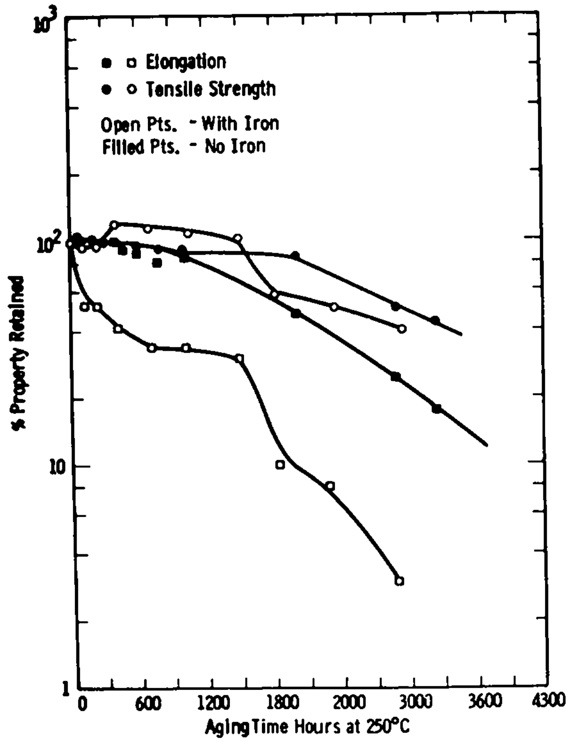

Fig. 5. Property retention vs. aging time for poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide] film.

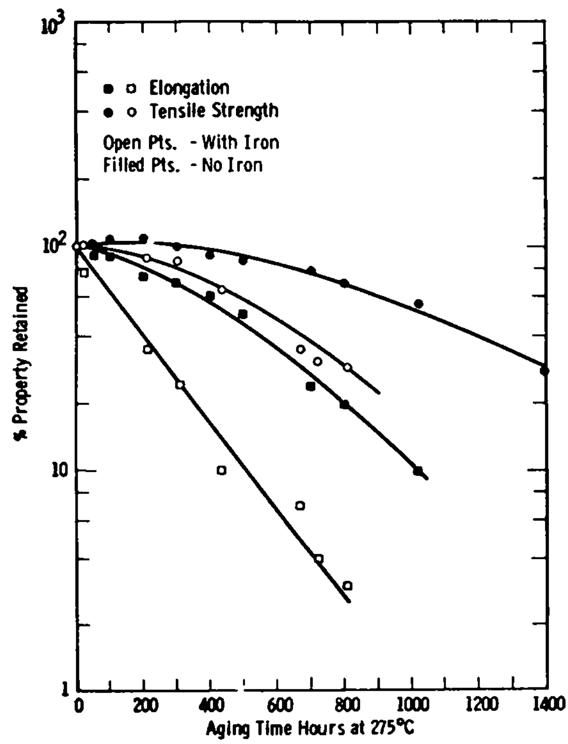

Fig. 6. Property retention vs. aging time for poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide] film.

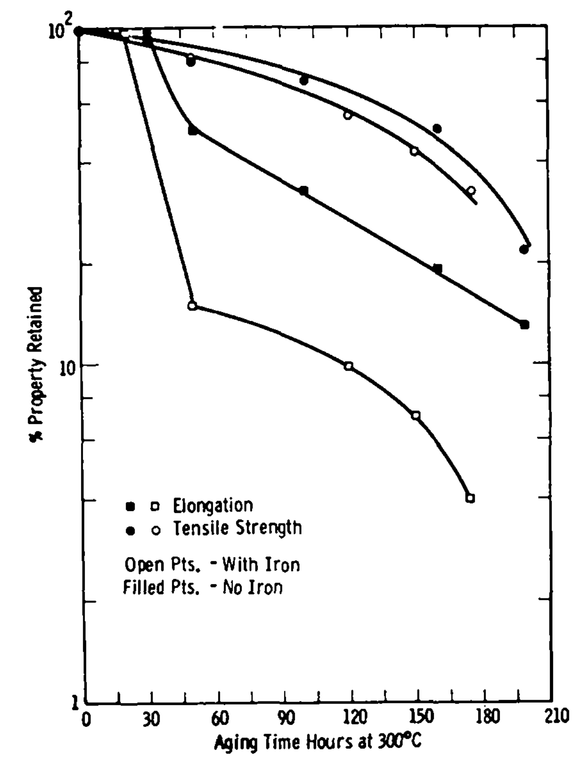

Fig. 7. Property retention vs. aging time for poly[N,N'-(4,4'-diphenyl ether) 4-amidophthalimide] film.

time. Emission spectroscopic analysis of one set of films indicated the presence of iron in the sample at a concentration of about 100 ppm. The source of this contamination was not established but the presence of iron in the film was quite damaging. Four curves are shown representing the tensile strength and elongation of films aged with and without an iron contamination. At 300°C, there is a rapid decline in all properties even after 20 hr of aging. Similarly, at temperatures $\leq 275°C$, the elongation decreases steadily from the outset but the tensile strength of the film increases before it begins to drop off. In fact, it appears that the tensile strength of the film containing iron increases more than the film without it suggesting that the iron may be contributing to this phenomenon. In all cases, the elongation deteriorates more rapidly than tensile strength and those films containing iron deteriorate faster than those without iron. Certainly, one could conclude that iron catalyzes the decomposition of this film. The data from these curves were used to construct the log time–temperature curves shown in Figures 8–11 in order to get an indication of the service life of this film in terms of its mechanical properties. The criterion chosen for these curves was the time to reach the 50%, 25%, and 15% retention levels of the original tensile strength and elongation. It is evident from these data that iron markedly reduces the service life of this amide–imide film. The exact nature of the role played by iron has not been explored; however, when iron as a solution of $FeCl_3$ is added to a solution of the polyamide acid precursor, the resin gels.

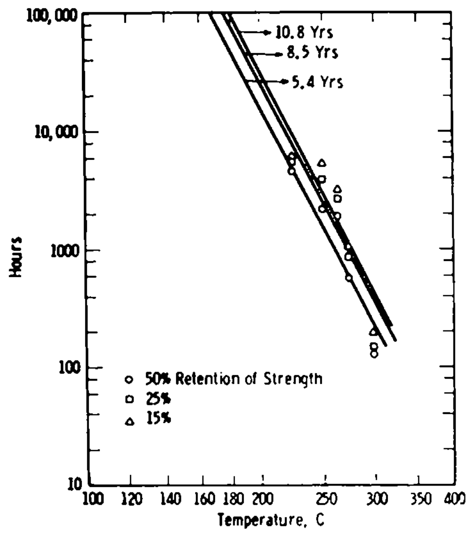

Fig. 8. Tensile strength life of polyamide–imide film with iron contamination.

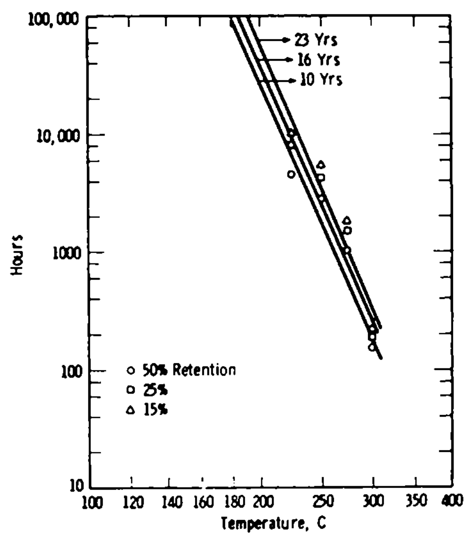

Fig. 9. Tensile strength life of polyamide–imide film without iron contamination.

Electrical Properties

A log time–temperature curve was constructed for this amide–imide film by plotting the time to reach a specific breakdown strength versus temperature. This curve is shown in Figure 12 for breakdown strength at the 1.5 and 2.0 kV/mil levels. Extrapolation of the curve indicates that this polymer has excellent high temperature service capabilities.

Comparison of Data

Each of the curves in this report present data using different property measurements on the extrapolated service life of the film. One can see that the mechanical properties (tensile strength and elongation) of the film

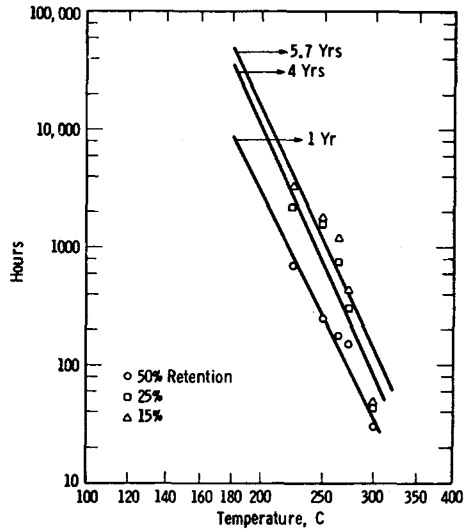

Fig. 10. Elongation life of polyamide–imide film with iron contamination.

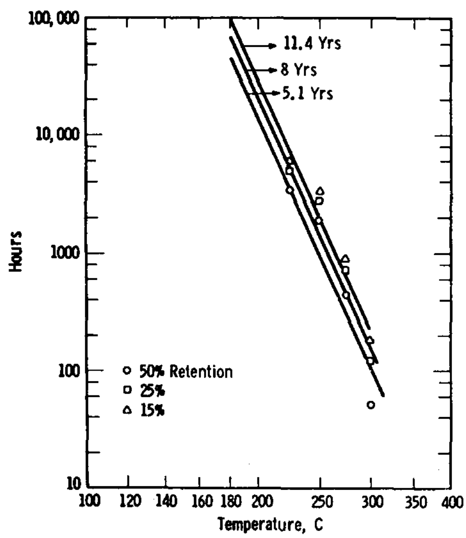

Fig. 11. Elongation life of polyamide–imide film without iron contamination.

deteriorate faster than the electrical strength. Film flexibility is maintained long after the mechanical properties have decreased to 75% of their original values. *On the basis of these data, the film will maintain its* electrical integrity much longer than it will its mechanical strength. However, all of the data indicate that the film can be used satisfactorily at elevated temperatures.

CONCLUSIONS

The results indicate that poly[N,N′-(4,4′-diphenyl ether) 4-amidophthalimide] film can be used satisfactorily as a Class H insulation material. DTA and TGA indicate that the polymer has a fairly high decomposition

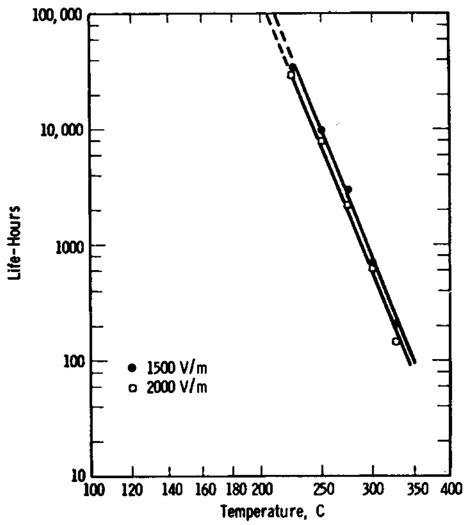

Fig. 12. Thermal life curves in terms of electric strength for polyamide–imide film.

temperature. The film will maintain its electrical integrity longer than it will its mechanical strength.

Elongation deteriorates faster than tensile strength under oxidative conditions.

The presence of iron contamination in the film enhances the deterioration of the film properties.

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