Ultraviolet Stability of Polyimides and Polyamide–Imides

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Synopsis

The ultraviolet stability of polyimides and polyamide–imides was determined in both a wet and dry environment. Films have been exposed to these environments for 3000 and 6000 hr, respectively. The polymers are not stable to UV radiation (2900–4000 Å); serious deterioration of the mechanical properties occurs under both wet and dry conditions with the former giving rise to greater damage. The polyamide–imide polymer is more unstable to UV radiation than the two polyimides evaluated; however, it is more resistant to hydrolysis as indicated from rate data obtained from a kinetic analysis of the mechanical property degradation curves. The electrical properties of the polymers are relatively unaffected in the dry environment but begin to deteriorate as the polymer becomes brittle. In the wet environment these properties begin to deteriorate more rapidly. Dissipation factor and dielectric strength are the properties most affected.

INTRODUCTION

The thermal and oxidative stability of polyimides has been well documented in the literature since their first appearance in the early sixties.[1–7]

The radiation stability of these materials is reported to be quite good.[8] However, very little information is available on their ultraviolet stability. The supplier's bulletin indicates that type H polyimide film possesses good resistance to UV light.[9] This conclusion was apparently based on data from experiments conducted under vacuum or in a dry environment. A reported study[10] indicates that the mechanical properties of the film deteriorate somewhat. Data on long exposure times of these films to UV light are not available.

It is the objective of this work to present the results of long-time exposure of selected polyimide films to ultraviolet irradiation in both a wet and dry environment. Toward this end the mechanical, electrical, and chemical properties of these films were measured after each exposure period. A further objective was to determine the effect of structure on their UV stability and finally to ascertain the contribution of the environment (wet or dry) in the presence of UV light.

EXPERIMENTAL

Materials

Three imide-type polymers were evaluated in this study. Each of these polymers contained the same diamine component but a different dianhydride. One of the polymers, designated C, was obtained commercially from E.I. du Pont de Nemours and Company. The other two were synthesized at the Westinghouse Research Laboratories.

Monomers

4-Chloroformylphthalic anhydride (TMAC), and 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) were obtained from Interchemical Corporation and Gulf Oil Corporation, Petrochemical Division, respectively, and used without further purification. 4,4′-Diaminodiphenyl ether (DAPE) was obtained from the Sumitomo Chemical Company, Osaka, Japan, and used as received. Dimethylacetamide (DMAC) was obtained from the Monsanto Chemical Company and used as received. Propylene oxide (PO) was obtained from Fisher Scientific and used as received.

Polymerization

Polymerizations were carried out in three-necked flasks in an N_2 atmosphere by adding the stoichiometric amount of dianhydride to a stirred DMAC solution of the diamine at room temperature. The polymerization reaction was allowed to continue while maintaining a temperature of 25–40°C until a maximum viscosity was reached. The resin solution was filtered and refrigerated until use.

An acid acceptor (PO) was added to the resin solution of the polymer from TMAC after a maximum viscosity value was reached.

Viscosity was measured at 25°C in DMAC.

Polymer Characterization

Polymer A. A polyimide prepared from BTDA and DAPE: solids content, 16%; Gardner viscosity Z1; inherent viscosity, 0.98 dl/g. Its structure is illustrated below
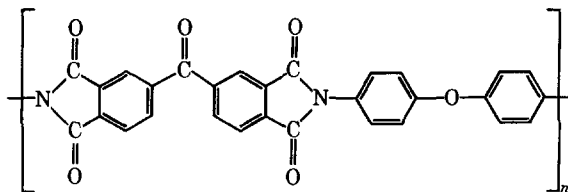
Polymer B. A polyamide–imide prepared from TMAC and DAPE. Solids content, 20%; Gardner viscosity, Z2; inherent viscosity, 0.78 dl/g. The following illustrates its structure:
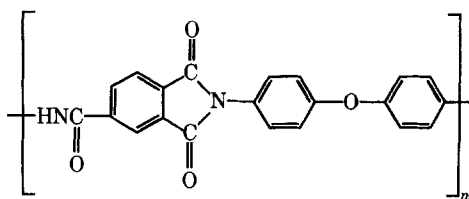
Polymer C. A sample of a commercially available polyimide polymer film was obtained from the du Pont Company. Its structure is reported to be as shown below:
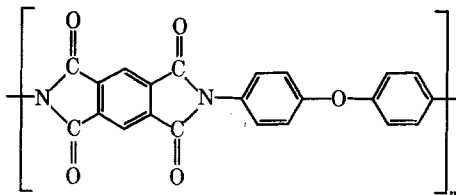
Sample Preparation

Film samples were prepared from the resin solution by casting onto a Pyrex glass plate and curing to 150°C, removing the film, and further curing it under restraint to 300°C.

The resulting film samples were amber colored and approximately 0.001 in. thick.

Test Methods

Mechanical Properties. Tensile strength and elongation were measured according to ASTM D882.

Electrical Properties. Dielectric constant (1 KHz), dissipation factor (1 KHz), dielectric strength (60 Hz), and dc volume resistivity were measured according to ASTM procedures D149, 150, and 257.

Infrared Spectra. Recorded on a Beckman IR 12 spectrophotometer.

Ultraviolet Exposure Tests

Because of the variability of climate conditions, accelerated exposure tests fall short in exactly reproducing outdoor exposure characteristics. An excellent review on weatherability was presented in 1967 at the National Bureau of Standards.[11] Many accelerated devices exist, however, and two have been chosen to simulate the UV exposure in a wet and dry environment. These are the Atlas Weather-O-Meter and another commercial instrument containing a series of fluorescent sunlamps/blacklamps (FS/BL) (American Ultraviolet Company, Summit, New Jersey). The latter unit has been used to evaluate the stability of other polymers (polyester, polyolefins, PVC, and ABS) and found to correlate well with sunlight data.[12] The ultraviolet spectral energy distribution curves for these two sources compared with sunlight are shown in Figure 1.

Atlas Weather-O-Meter

Film samples were exposed only on the top rack of the Weather-O-Meter using a sunshine carbon arc with Corex D filters. Sample distance from the light source was 9 in., and an exposure cycle (Cam No. 7) was used giving a cycle consisting of 102 min of light, 18 min of light and water. The temperature inside the unit was 45°C. This test was performed in accordance with ASTM 1499 and E42.

Fluorescent Sunlamp/Blacklamp Unit

In this unit, an equal number of fluorescent sunlamps (Westinghouse) 40WFS40) and blacklamps (Westinghouse 40BL) are alternately mounted inside the circular rotating drum upon which samples are placed. The energy output is maintained relatively constant by a staggered replacement of the lights. In this case, two lamps were changed every 100 hr. The sample distance from the light source was 4 in. and the temperature inside the unit was approximately 36°C. The major advantage of this unit is that it provides uniform illumination over the entire height of the sample rack compared to other devices in which the radiation emanates from a small central area of the light source. The wavelength range of this unit is 2800–4000 Å.

Samples were removed periodically from these weathering devices and were visually examined, and their mechanical and electrical properties were measured.

RESULTS AND DISCUSSION

Films Exposed in the FS/BL Unit

Mechanical Properties

The deterioration in properties for each of the films as measured after each exposure period is shown in Figure 2 as per cent property retained versus aging time. There is an immediate decrease in properties after only 100 hr of irradiation. A rather rapid decline of properties continues until about 1000 hr. This is followed by a levelling off prior to a more rapid decline at the longer exposure times. The elongation deteriorates more rapidly than the tensile strength for all films and shows a more rapid decrease in polymer B which contains an equal number of amide–imide groups.

The elongation seems to be more sensitive to the photolytic process of deterioration than the tensile strength. In all cases, the elongation begins to drop off immediately. This may mean that changes in the ultimate elongation are a reasonable measure of the damage done in the polymer by the radiation.

Polymers A and C, in that order, follow polymer B with respect to property deterioration. It is interesting to note that polymer A exhibits a
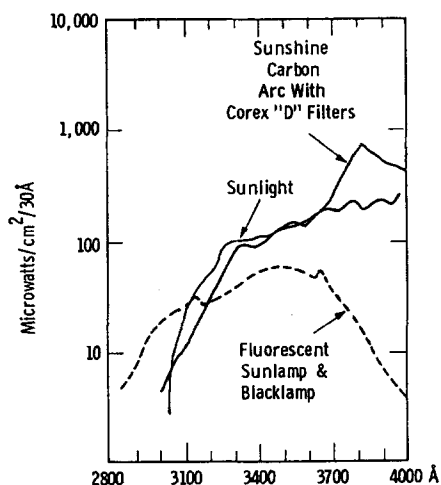
Fig. 1. Combination of Westinghouse fluorescent sunlamp, blacklamp, and carbon arc compared with sunlight.
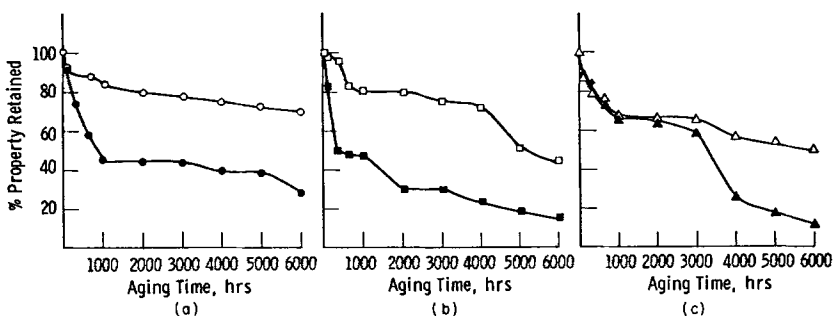

Fig. 2. Effect of UV light on the properties of imide and amide–imide films (polymers A, B, and C) aged in the FS/BL unit; open symbols: tensile strength; closed symbols: elongation.

slower decline in properties over the total exposure period. Its tensile strength and elongation have decreased 30% and 75% of its original value, respectively, after 6000 hr. After this exposure time, the values decreased to 60% and 85% of their original value for polymer B and 50% and 90% for polymer C. No visual change was observed on the films after the exposure period; however, films of polymers A and C were creasable, whereas polymer B broke when it was creased 180 degrees. These results indicate that the order of stability is: polymer A > C > B. Because the polyimides absorb strongly in the ultraviolet between 200 and 450 mμ, it is not surprising that UV radiation does deteriorate these polymers. However, it is interesting that polymer A is least affected. This polymer contains the benzophenone group, a known UV stabilizing molecule and could possibly impart some resistance in polymer A against UV radiation.

Electrical Properties

For the sake of brevity, the various electrical properties of polymer A are shown in Figure 3 after each exposure period. Although these values are not exactly the same for polymers B and C, they are typical of the imide-type polymers. The change in these properties as indicated for polymer A follows a very similar pattern for polymers B and C; notable changes are presented in the text without duplicating figures for B and C polymers. No significant deterioration of the electrical properties of polymers A and C was observed. However, in polymer B the dissipation factor begins to deteriorate rapidly after 4000 hr of exposure, going from 0.001 to 0.013. This property increases by a factor of 10 within the time interval from 3000 to 4000 hr. None of the other properties seemed to be affected, although the dielectric strength is beginning to show signs of deterioration. Its value drops from about 4.5 kV to 3.0 kV after 6000 hr of exposure. Apparently, these properties are not affected as drastically as the mechanical properties. Electrical deterioration may not manifest itself until the polymer has degraded to a point where it is brittle and physically weak. The point at which the dissipation factor for polymer B began rising corresponds to the observation that the polymer was brittle when creased. McMahon et al.[13] observed in the hydrolysis of polyesters that the film did not lose its dielectric strength until it became brittle. Again, as with the mechanical properties, the electrical property deterioration begins first with polymer B. Evidence thus far indicates that the amide–imide polymer is more unstable toward UV radiation than the imide polymers.

Films Exposed in the Weather-O-Meter

Mechanical Properties

The deterioration in properties for each of the films after each exposure is shown in Figure 4 as per cent property retained versus aging time. All polymers show an immediate and sharp decrease in properties after only
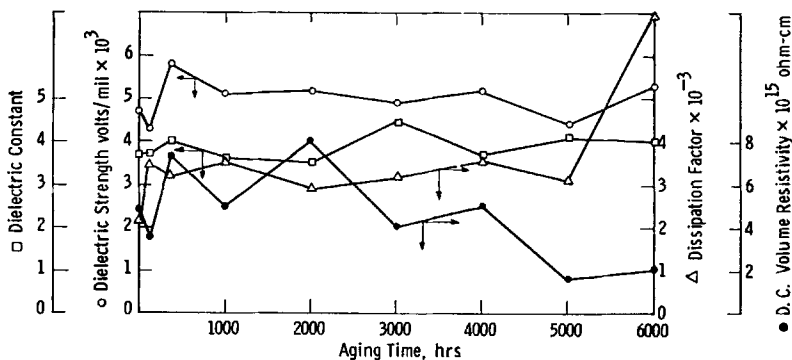

Fig. 3. Effect of UV light on the electrical properties of polymer A film aged in the FS/BL unit.
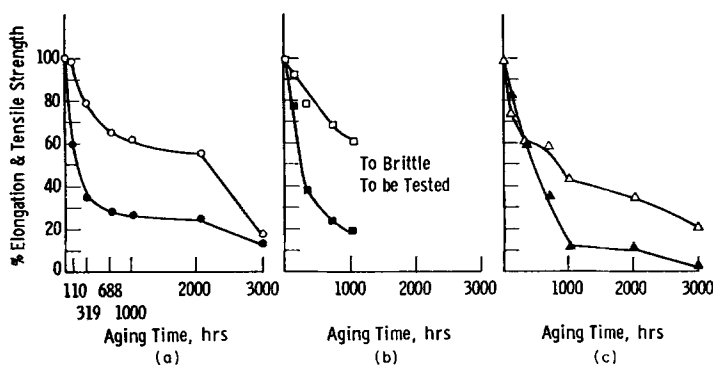
Fig. 4. Effect of Weather-O-Meter aging on the properties of imide and amide–imide films (polymers A, B, and C); open symbols: tensile strength; closed symbols: elongation.

100 hr of exposure. After the initial rapid decline, the property deterioration follows the same trend as was observed in the dry UV environment, except at a faster rate. Elongation deteriorates more rapidly than tensile strength for all films and shows a more rapid decrease in polymer A, a complete imide polymer followed by polymer C and B. This trend, at least in the early stages of exposure, is almost a complete reversal compared to the dry UV environment, indicating that the wet environment contributes to the degradation process. Although polymer B shows a slower decline in properties, it becomes extremely brittle after 1000 hr of exposure. It has lost 40% and 80% of tensile and elongation properties, respectively. Polymers A and C, although they exhibit more of a per cent decrease in properties, still retain sufficient strength to be handled. After 3000 hr of exposure, both polymers B and C are very brittle but polymer A is still barely creasable. The tear resistance of these films is extremely poor, and all of the films lost transparency but remained translucent after 2000 hr.

Electrical Properties

The change in electrical properties after Weather-O-Meter exposure is shown in Figure 5 for polymer A. Again, the values shown, although not
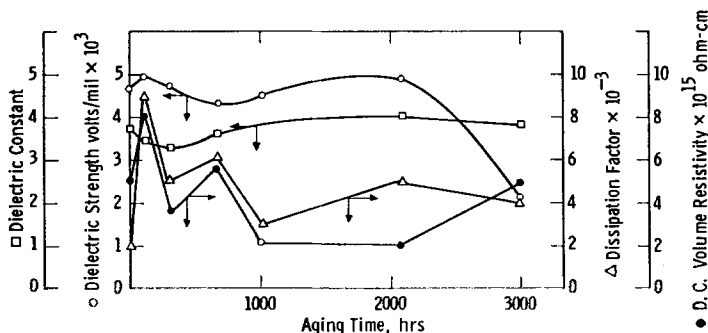

Fig. 5. Effect of Weather-O-Meter aging on the electrical properties of polymer A.

exactly the same for polymers B and C, are typical for this class of polymers. Notable changes in the property behavior of polymers B and C that do not follow the trend indicated in Figure 5 are mentioned in the text. For polymer A, no significant changes in the electrical properties occurred except in dielectric strength. After 3000 hr of aging, it dropped to 57% of its original value. On the other hand, for polymer C, the only significant change was an increase in dissipation factor which amounted to about 500%. Polymer B is seriously degraded. Dissipation factor increased from 0.001 to 0.013, a tenfold increase. Polymer B became extremely fragile after only 600 hr of exposure, and further electrical tests could not be made. Polymer C was brittle after 3000 hr, and polymer A was just barely creasable after the same time period.

Kinetic Treatment of Data

During the initial stages of the photolysis there appears to be a linear decrease in mechanical properties with time (Fig. 2 and 4). In order to determine if the effects of environment and structure on the photolytic stability of these polymers were significant, the data were analyzed using the appropriate rate equation. Methods for treating the rate constant k can be found in any treatise on physical chemistry.[14,15] In brief, the rate at which a reaction proceeds will be some function of the reaction property. In this case, the rate is related to the decrease in mechanical properties. In general, the rate may be expressed as

$$\int_{P_0}^{P} \frac{dP}{dt} = k \int_{t_0}^{t} p^n \tag{1}$$

where P is the property of the polymer and n is defined as the order of the reaction. On separation of the variables and integration when P_0(defined as the value P when $t = 0$), one obtains

$$-\int_{P_0}^{P} \frac{dP}{p^n} = k \int_{t_0}^{t} dt. \tag{2}$$

For a first-order reaction,

$$\ln (P_0/P) = kt$$

$$\ln C = \ln P_0 - kt \tag{3}$$

$$\log C = \frac{-kt}{2.303} + C.$$

Hence, for a first-order reaction, a plot of log property versus time should be linear, with a slope of $-k/2.303$, from which k may be evaluated. Expressions for the various other orders may by obtained by substituting the respective values of n. The reaction of interest here was found to be first order, at least during the initial stages of the reaction.

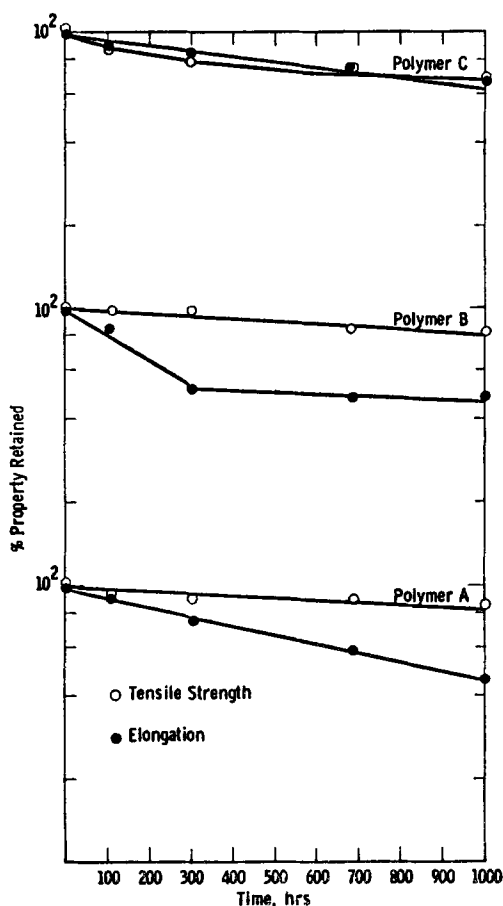The experimental results are summarized in Figures 6 and 7 in which the

Fig. 6. First-order plot of data from dry UV exposure.

logarithm of the per cent property retained is plotted against time in hours. The first-order rate constants have been calculated from these graphs according to eq. (3). Where deviations from linearity were experienced, the rate was determined over the initial linear portion of the curve. The experimentally obtained reaction rate constants are summarized in Table I.

TABLE I
Experimentally Determined Rate Constants k^a

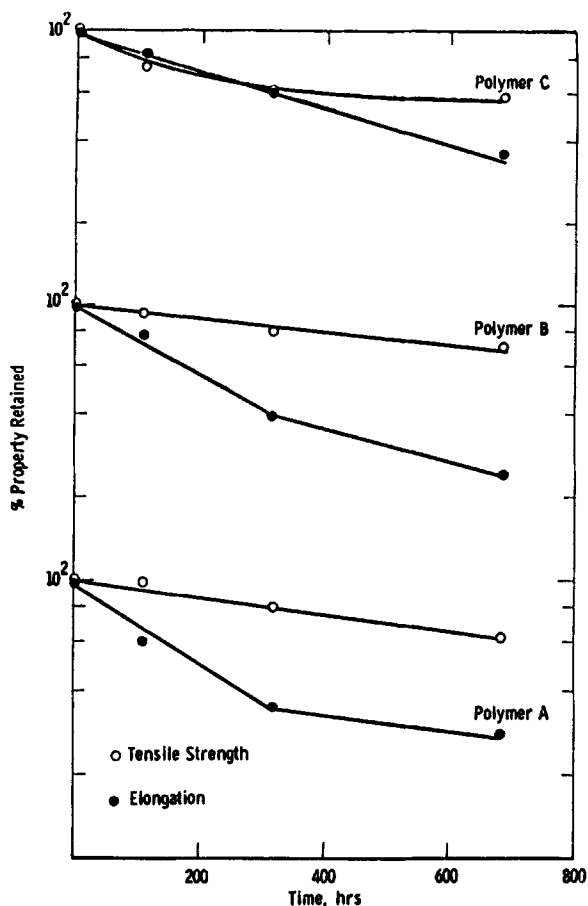|	Dry UV		Wet UV	
Polymer	Tensile strength	Elongation	Tensile strength	Elongation
A	2.3	9.3	7.4	34.0
B	2.4	22.0	5.8	27.0
C	9.3	5.5	26.0	16.0

[a] In units of hr.$^{-1}$

Fig. 7. First-order plot of data from wet UV exposure.

Environmental and Structural Effects

From Table I it is seen that there is a rather large increase in rate for both elongation and tensile strength in going from the dry to the wet environment. The order of magnitude of these changes is about the same for each of the properties. This change in elongation is most apparent with polymers A and C, exhibiting a 270% and 190% rate increase, respectively, while polymer B shows only a 22% increase. Tensile strength is similarly affected. Although the amide–imide polymer (B) exhibited the smallest rate constant increase, it became considerably more brittle than the other two polymers (A and C). It is clear from these data that the environment plays an important part in the degradation process. Hydrolysis of the polymers is undoubtedly responsible for this enhanced rate increase, in that once the hydrolytic products are formed, giving rise to an o-carboxy amide group, the rate is increased even further. Bender et al.[16] have shown that large rate increases are obtained in the hydrolysis of phthalamic acid due to

a catalytic influence exerted by the *o*-carboxy group. Furthermore, the data suggest that the amide–imide grouping in polymer B is not as hydrolytically sensitive as the imide group in polymers A and C. Frost et al.[17] have shown that the amide structure is considerably more resistant to hydrolysis than the imide structure. They immersed films of polyamide, polyimide, and polyamide–imide polymers in 5% sodium hydroxide for 20 hr at 25°C. The polyimide was completely dissolved while the polyamide was unaffected. The polyamide–imide showed only a fading of color.
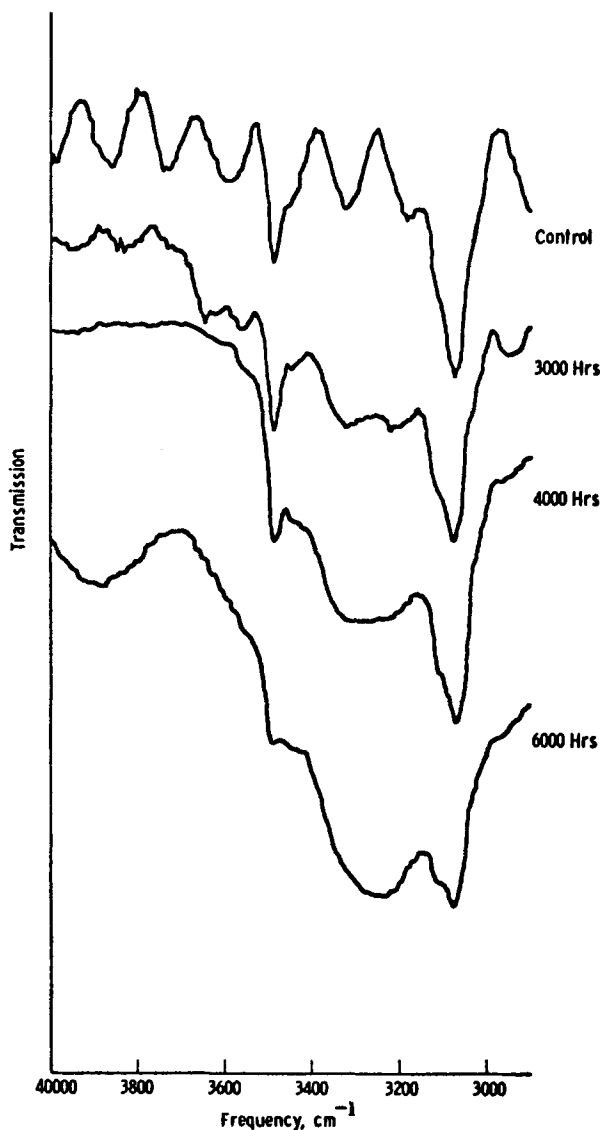
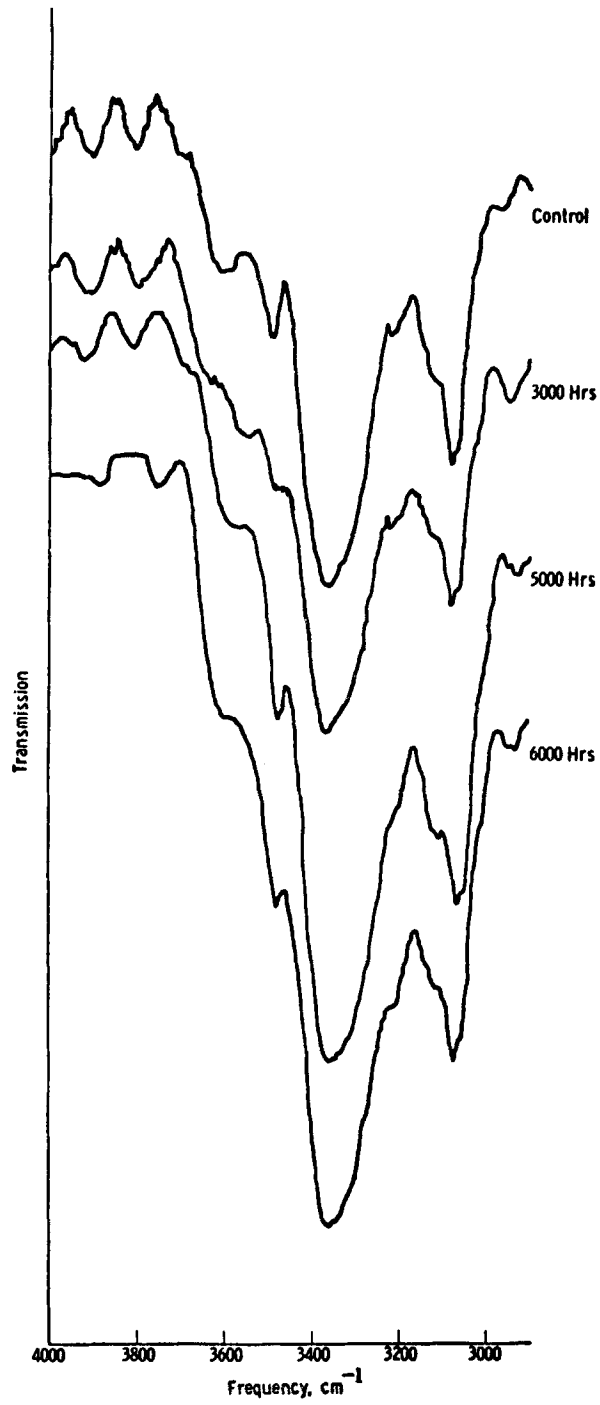Fig. 8. Infrared spectra of polymer A film after exposure in the FS/BL unit.

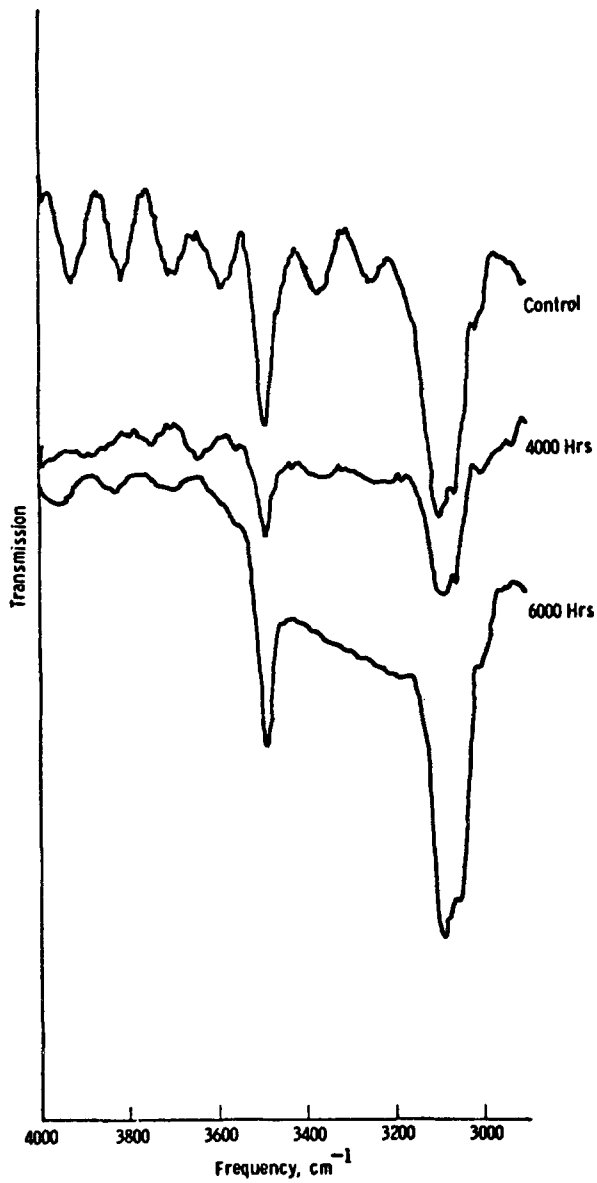Fig. 9. Infrared spectra of polymer B film after exposure to the FS/BL unit.

Fig. 10. Infrared spectra of polymer C film after exposure in FS/BL unit.

In ranking the polymers with regard to rate constant and property, the order of increasing rate for tensile strength in a dry atmosphere is polymer C > B > A; for elongation, B > A > C. In the wet environment for tensile strength, we have C > A > B, and for elongation it is A > B > C.

Infrared Analysis

There are physical changes in the films that influence their spectra, one of which is thickness.   Because of the thickness of the films and the intensity of the absorptions, meaningful data could not be obtained in the 5.0- to 6.0-
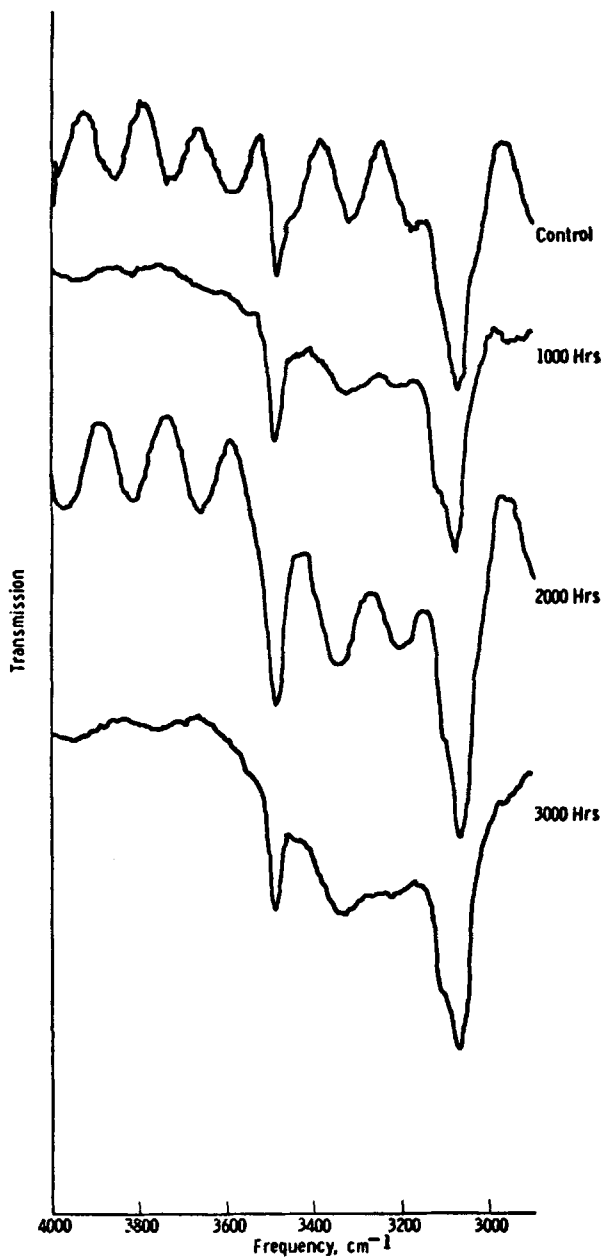

Fig. 11. Infrared spectra of polymer A film after exposure in the Weather-O-Meter.

micron region.   The film samples exposed to the radiation were subjected to infrared analysis after each exposure period.   Significant changes did occur in all polymers exposed to both environments and could be analyzed in the 2.5 to 3.5-micron region.   The spectral changes occurring in films A, B, and C after exposure in the dry environment are shown in Figures 8 to 10 and for the wet environment in Figures 11 to 13.   For polymer A, exposed in the dry environment, there is a broadening of the absorption bands in the 3700–2800 cm^{-1} region, probably due to carboxyl formation, with the OH frequency occurring about 3340 cm^{-1}.   The main band being formed is in the 3300–3200 cm^{-1} region.   This band is broad and gradually shifts to a lower frequency centered around 3250 cm^{-1} which corresponds to N—H absorption.   The broad N—H absorption could be due to bonded N—H, since in the free state the absorption is usually sharp.   The N—H could easily hydrogen bond with the carboxyl groups being formed.   In the wet environment, the changes in the 3300–3500 cm^{-1} region are indicative of bonded OH and NH absorptions.   There is broadening of the spectra in this region, again suggesting the formation of a carboxyl OH band.   This broadening is not as pronounced as in polymer B.   For the latter polymer there is again a large broadening in the 3700–2800 cm^{-1} region, suggesting the formation of strongly bonded OH groups in both wet and dry environments; however, it is broader in the former case.   The band at 3200 cm^{-1} appears to be increasing in intensity and could reflect an increase in the N-H content possibly in the form of NH$_2$ groups.   On the other hand, it could be due to strong hydrogen bonding arising from the formation of more C=O groups, thus causing a shift to lower energy.   Similar changes occur in polymer C; there is a large broadening of the spectra in the 3700–2800 cm^{-1} region and a gradual shift of frequency to shorter wavelengths.   This is attributed to the combined effect on OH and NH formation, with the latter appearing at about 3300 cm^{-1}.   In the dry environment, although much slower in formation, there is still the broadening effect characteristic of carboxyl formation.   The formation of N—H cannot be detected.

In general, the spectral changes do indicate the formation of hydroxyl and amide–amine groups in all polymers.   These species arise from the photolytic process and are enhanced by hydrolysis in the wet environment.

CONCLUSIONS

The results indicate that the polyimides and the polyamide–imides are sensitive to ultraviolet light.   This sensitivity is enhanced by the presence of moisture.   In general, the mechanical and electrical properties of the polyamide–imide deteriorates faster than those of the polyimides tested in both a wet and dry environment.   However, the rate of increase in deterioration from the dry to the wet environment is much greater for the polyimides, indicating that the amide–imide structure is more resistant to hydrolysis.

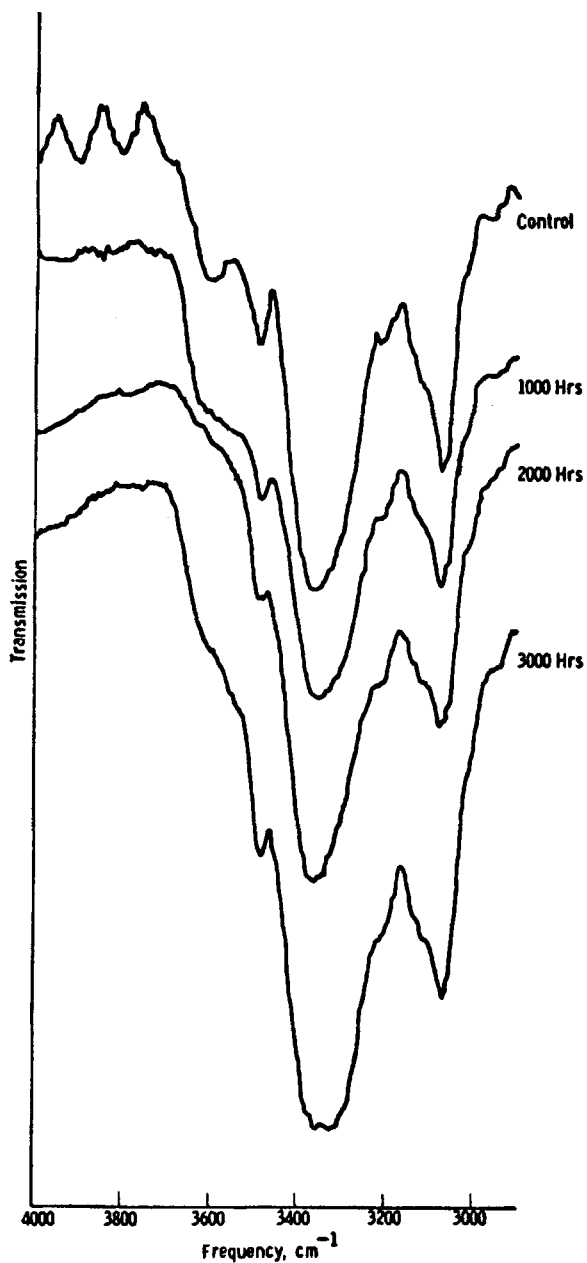There is an immediate decrease in tensile strength and elongation for all

Fig. 12. Infrared spectra of polymer B film after exposure in the Weather-O-Meter.

polymers in both the dry and wet environments, with the latter showing a more rapid decline in these properties. Change in elongation is more sensitive to the photolytic process than tensile strength. The films become quite brittle and opaque after exposure in the Weather-O-Meter. Polymer
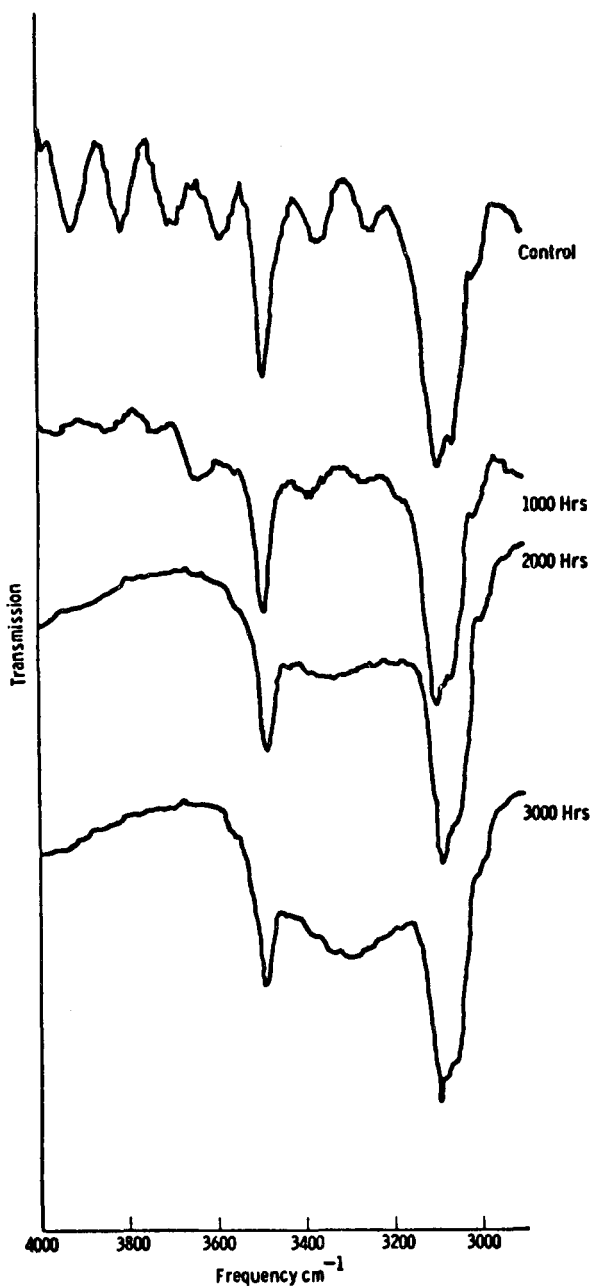
Fig. 13. Infrared spectra of polymer C film after exposure in the Weather-O-Meter.

A is slightly more resistant to UV in the dry environment. The presence of the benzophenone group in this polymer could account for this resistance.

The electrical properties of the polyimides are unaffected in the dry environment even after 6000 hr of aging. Those of the polyamide–imide

begin to deteriorate (dielectric constant and dissipation factor) after 4000 hr of exposure. In the wet environment, some of these properties eventually deteriorate for all polymers, but again the amide–imide polymer is most seriously degraded.

Infrared data confirm that degradation has taken place. All of the polymers show the formation of carboxyl OH and amide groups resulting from both irradiation and hydrolysis.

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