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**THE EFFECTS OF THE INTERACTION
OF POLYMERIC MATERIALS WITH THE SPACE ENVIRONMENT**

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Introduction

Polymeric materials in low earth orbit (LEO, 300 to 500 km) will be exposed to a harmful environment mainly due to atomic oxygen and ultraviolet radiation. In geosynchronous earth orbit (GEO, 36,000 km), the major hazards to such materials are energetic charged particles and ultraviolet radiation. We report here the progress of our studies on the effects of these hazards on three materials, a polyetherimide, a polyimide, and an epoxy adhesive.

Atomic oxygen (AO) is formed from the dissociation of molecular oxygen, O_2 , and ozone, O_3 , by ultraviolet radiation of short wavelength (< 200 nm). The AO concentration varies with the latitude, solar cycle, season of the year, and local solar time. It is the predominant chemical species at LEO altitudes, varying in concentration from $10^8 - 10^9$ atoms cm^{-3} at 300 km to $10^6 - 10^8$ atoms cm^{-3} at 500 km. The particle density is multiplied by the speed of a satellite to give the particle flux incident on the forward facing surfaces. A satellite in LEO with a typical speed of 8 km s^{-1} will undergo $10^{14} - 10^{15}$ collisions $cm^{-2} s^{-1}$ of AO with its forward facing surfaces. Atomic oxygen is known to cause surface erosion on polymeric materials.

Ultraviolet radiation in both LEO and GEO has an energy flux of 0.14 joules $cm^{-2} s^{-1}$. In GEO, an additional radiation environment is caused by energetic charged particles trapped by the earth's magnetic field. The radiation consists primarily of electrons and protons, each with a flux of 10^8 particles $cm^{-2} s^{-1}$. Polymeric materials subjected to ultraviolet

radiation and/or energetic charged particles are known to suffer a degradation of properties due to both chain scission and crosslinking.

Polyetherimide Studies

Films of a polyetherimide containing up to 25 percent by weight of bis-(triphenyltin) oxide (BTO) were prepared by evaporation of the solvent from a solution containing both materials as solutes. The repeat unit of the polyetherimide and the structural formula of BTO are shown in Figs. 1 and 2. The polymer was obtained commercially and is sold under the General Electric tradename of Ultem. The effects of atomic oxygen on these films were simulated in the oxygen atmosphere of a radio-frequency glow-discharge chamber. Typical results are shown in Fig. 3, where the degradation rates of polyetherimide films with and without 20% BTO are plotted as a function of exposure time. After about 90 minutes of exposure, a layer of tin oxide has formed on the surface of the film and after 200 minutes of exposure, the erosion rate drops to approximately two thirds that of the undoped polymer. (Fifty minutes in the discharge chamber corresponds to approximately 1 month in orbit at 500 km.)

Films of the polyetherimide containing 10% BTO were exposed to either 100 keV electrons or ultraviolet radiation. The difference in the infrared absorbance spectrum of a film taken before and after exposure is plotted in Fig. 4 as a function of wavenumber. Exposure to ultraviolet radiation for 170 hours at 1.5 suns produces no change in the infrared spectrum of the film. However, exposure to 5×10^9 rads of 100 keV electrons produces a noticeable change at 1750 wavenumbers corresponding to a decrease in the concentration of carbonyl groups (C=O) after exposure. Similar differences in the infrared spectra were obtained when films of the pure polyetherimide were exposed to energetic electrons or ultraviolet radiation. The uv/visible spectrum was also taken for films exposed to these radiations. Figures 5, 6, 7, and 8 show the spectra before and after irradiation. It is important to note that the transparency in the visible region (400 to 700

nm) is the same for the pure polyetherimide and films of the material doped with 10% BTO.

These results show that, when BTO is added to the polyetherimide, the rate of erosion with atomic oxygen is reduced significantly over a period of 10 hours. However, the BTO additive does not reduce the resistance of the polyetherimide to ultraviolet radiation, nor does it change the effects due to exposure to energetic electrons.

Since the polyetherimide is readily soluble in several common solvents, we studied the possibility of spraying a solution of the BTO doped material onto surfaces as an atomic-oxygen resistant film. A chloroform solution of the polyetherimide and BTO was placed in a small sprayer (Sure Shot Model C, Milwaukee Sprayer Mfg. Co.). The sprayer was pressurized to about 90 psi with compressed nitrogen gas, and a thin, uniform film was applied to a glass plate. The film was dried in an oven and removed from the plate with water. The film was very thin and fragile making it extremely difficult to study, however, one sample was exposed to ultraviolet radiation. The infrared and uv/visible spectra were taken before and after. The sprayed film showed the same resistance to ultraviolet radiation as the thicker films.

Polyimide Studies

Studies have been initiated on a polyimide formed by the reaction of pyromellitic dianhydride and di-(4-aminophenyl) ether and sold commercially with the duPont trade name Kapton.¹ Typical of most polyimides, Kapton is infusible and insoluble. Our purpose here was to introduce AO-resistant additives during the synthesis at a point where the additive is easily mixed with the soluble polyimide precursor. The same compounds tested with the polyetherimide were tested here. It was found that five compounds were soluble: octaphenylcyclotetrasiloxane (OPCTS), octamethylcyclotetrasiloxane

(OMCTS), decamethyltetrasiloxane (DMTS), diphenylmethylsilane (DPMS), and bis-(triphenyltin) oxide (BTO).

Films of the polyamic acid were formed on a clean glass plate with a doctor blade according to established procedure. The film was then thermally imidized with a temperature ramp given in the literature.² All films produced in this fashion were clear and of good quality. Films doped with BTO were made with concentrations of 5%, 3%, and 1% (w/w) BTO. It was found that the films containing 5% BTO were brittle and could not be pulled from the glass plate, however, films containing the lower concentrations were more flexible and could be separated easily from the plate. Two thicknesses of films were made, 0.5-1.0 mil and 2.5-3.0 mil. In addition, thin films (0.5-1.0 mil) containing 3% (w/w) OPCTS were also made

Some initial atomic oxygen exposures have been performed with the synthesized films both pure and doped with BTO. Exposure periods of ninety minutes were chosen so that comparisons with previous studies on the polyetherimide described above could be made. A polyimide film doped with 1% BTO completely disappeared during the first ninety minute period, while a pure polyimide film did not disappear until the second ninety minute period. In an exposure with the pure synthesized film and pure commercial film, it was found that the synthesized film eroded much faster. This result is similar to our findings in previous studies with polyetherimide and polysulfone films. We believe that the surface characteristics are different between our films drawn on a glass plate and the commercial films which are extruded.

Epoxy Adhesive Studies

Our work has focused on an epoxy adhesive manufactured by Dexter-Hysol and sold as EA934NA. Previous studies had shown that this material had very little resistance to ultraviolet radiation. Thus, it was a good material in

which to test various ultraviolet absorbers. Ironically, the material was much more resistant to atomic oxygen than any other epoxy material tested.

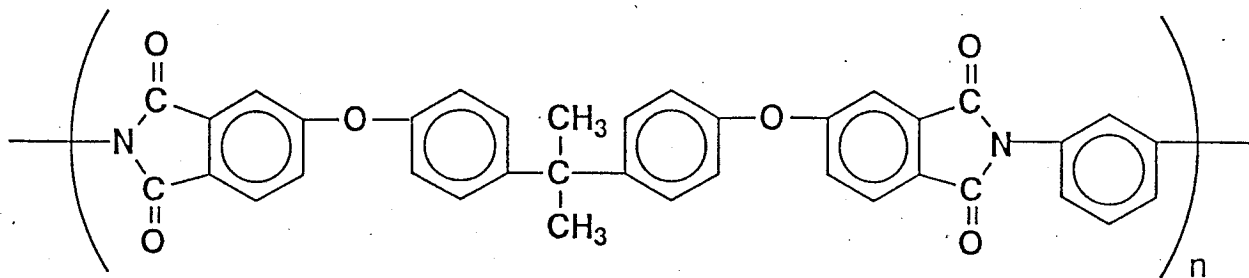
The ultraviolet radiation studies were carried out in a small vacuum chamber at the NASA Langley Research Center. The chamber can be evacuated to a pressure of 10^{-8} torr. An Inficon IQ 200 mass spectrometer is incorporated in the chamber so that volatile products can be monitored. Ultraviolet radiation enters the chamber through a quartz window and is supplied by an Oriel 6141 system with a 1000 watt xenon-arc lamp. The intensity of radiation at the surface of the sample is approximately 1.5 suns.

Samples of pure EA934NA immediately decomposed when exposed to ultraviolet radiation. So many volatile products were emitted that within 30 seconds the pressure in the vacuum chamber rose by two orders of magnitude. Large peaks appeared in the mass spectrum at mass numbers 18, 28, and 44. After about 10 minutes, the rate of emission of volatile products decreased and the pressure in the vacuum chamber went down. Since the composition of the material is proprietary information, no attempt was made to suggest any reaction mechanism.

Samples of the epoxy material were made incorporating two different ultraviolet absorbing compounds, benzophenone and nickel acetylacetonate. In both cases, 10% (w/w) samples were made. When exposed to ultraviolet radiation, these samples decomposed more rapidly than the pure material. In both cases, additional peaks appeared in the mass spectrum which could be correlated with decomposition products of the added compounds. Possibly, the added materials accumulated at the surface during the cure of the epoxy adhesive. These materials would probably degrade more quickly than the epoxy adhesive thus causing the increase in volatile products.

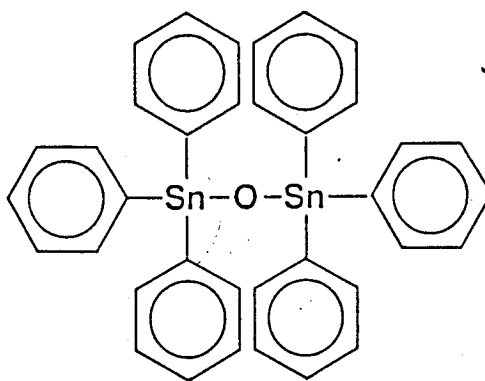
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2. F. W. Harris in Polyimides, eds. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, pp. 26-29, Chapman and Hall, Glasgow (1990).



REPEAT UNIT OF THE POLYETHERIMIDE

Figure 1. The repeat unit of the polyetherimide.



BTO

Figure 2. The structural formula of bis(triphenyl tin) oxide or BTO.

COMPARISON OF RATES OF EROSION IN ATOMIC OXYGEN

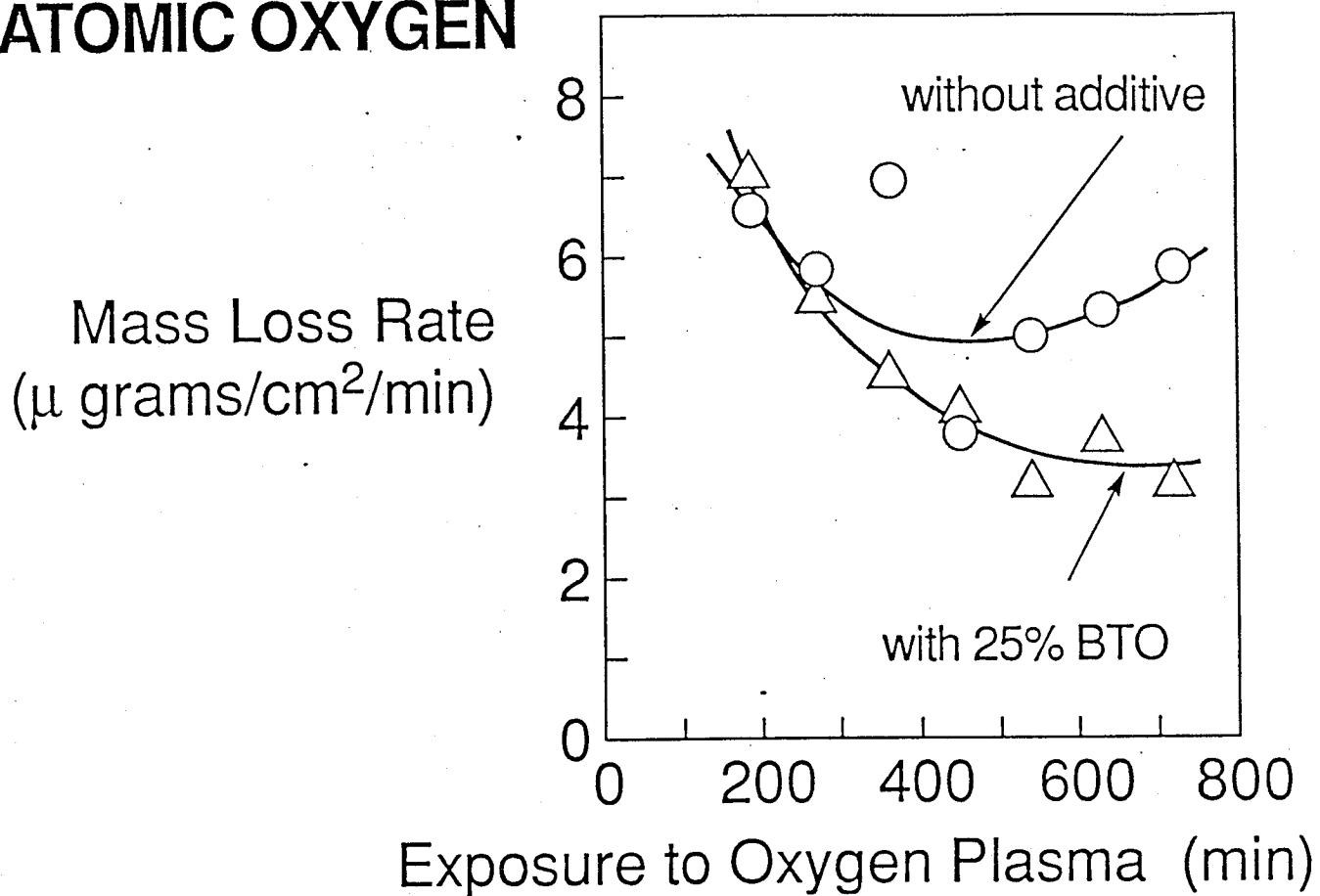


Figure 3. Erosion rates of films in atomic oxygen. A comparison of polyetherimide films pure and with 20% BTO.

EXPOSURES OF POLYETHERIMIDE / BTO FILMS (10% BTO)

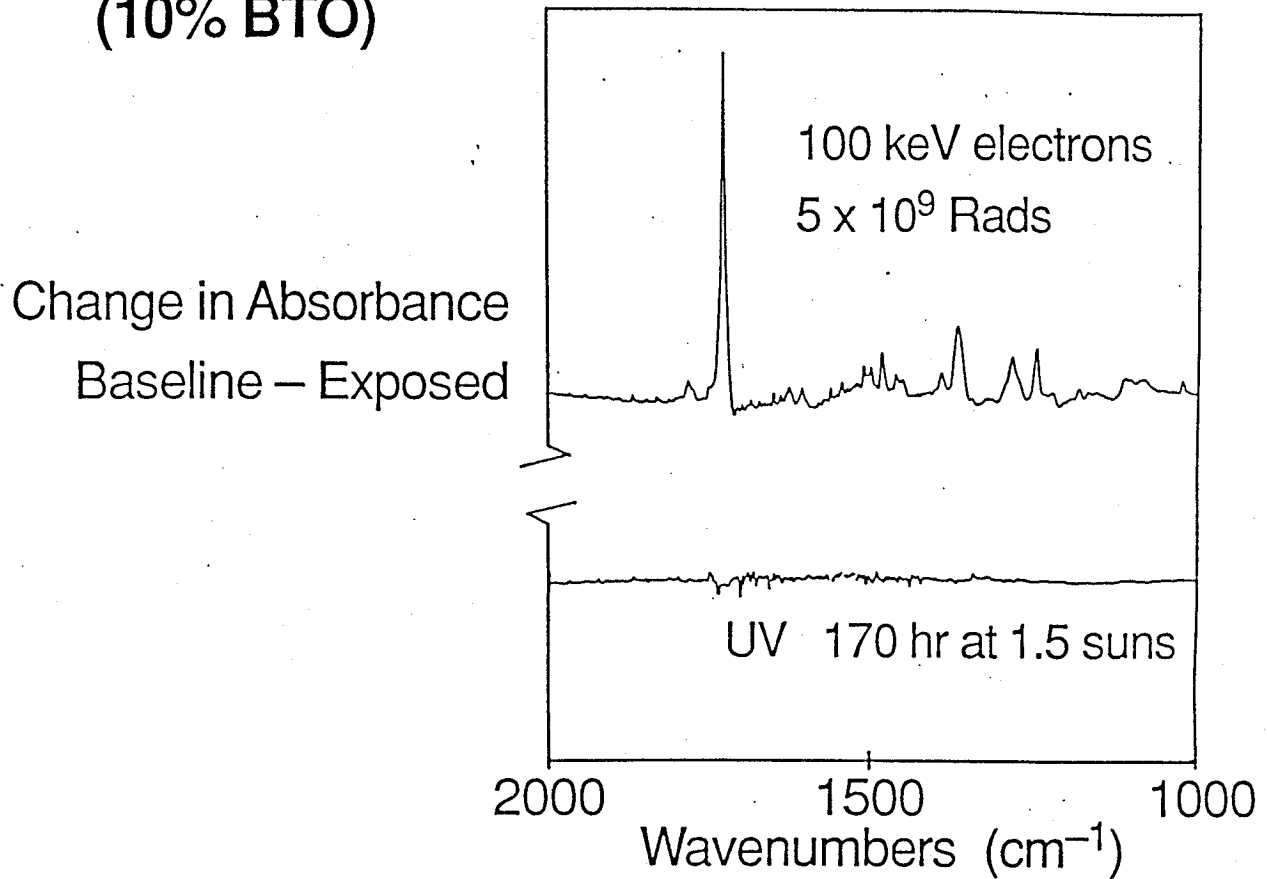


Figure 4. The difference in the infrared absorbance spectra of polyetherimide/10% BTO films taken before and after exposure to 100 keV electrons and ultraviolet radiation.

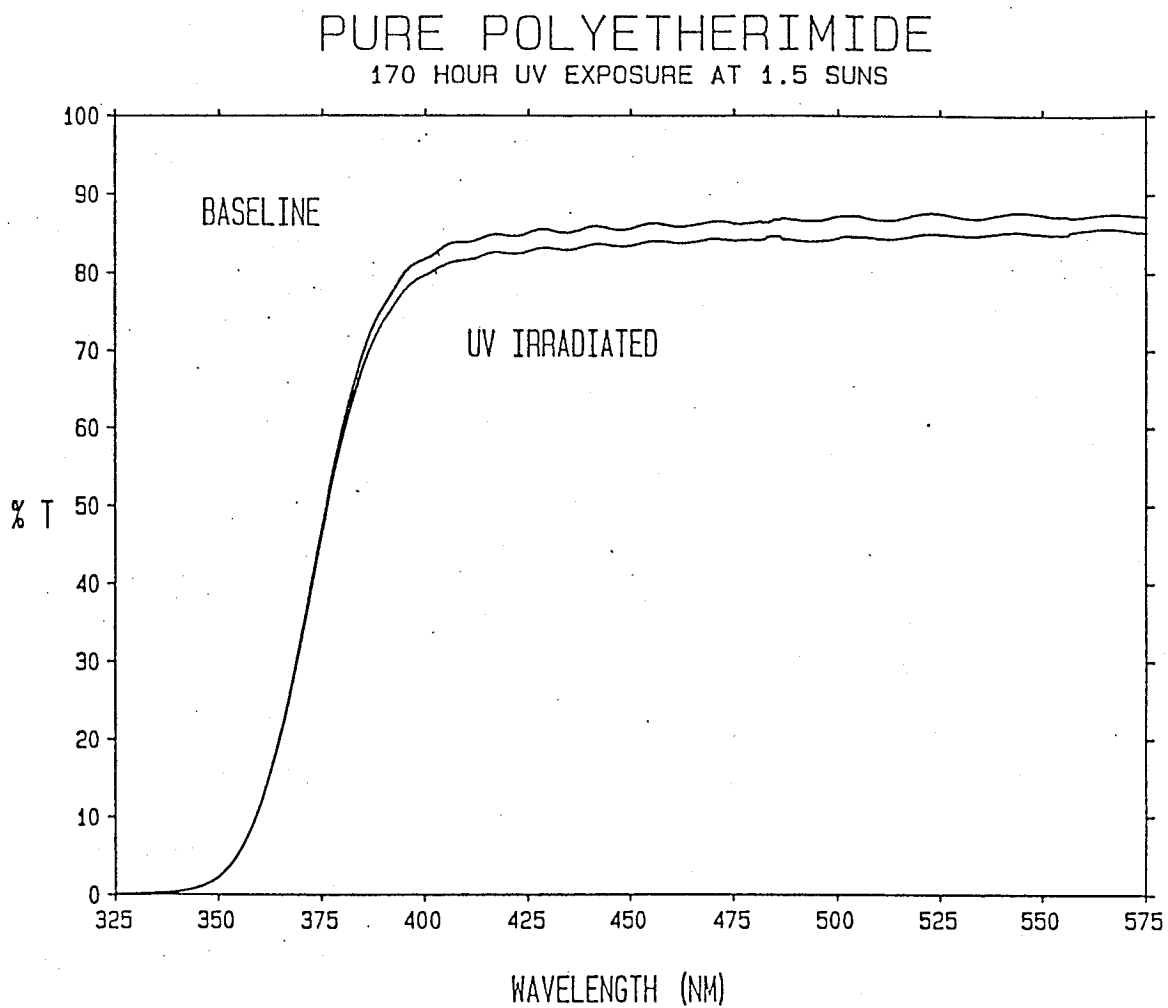


Figure 5. The uv/visible spectra of a pure polyetherimide film before and after exposure to ultraviolet radiation.

POLYETHERIMIDE WITH 10% BTO
170 HOUR UV EXPOSURE AT 1.5 SUNS

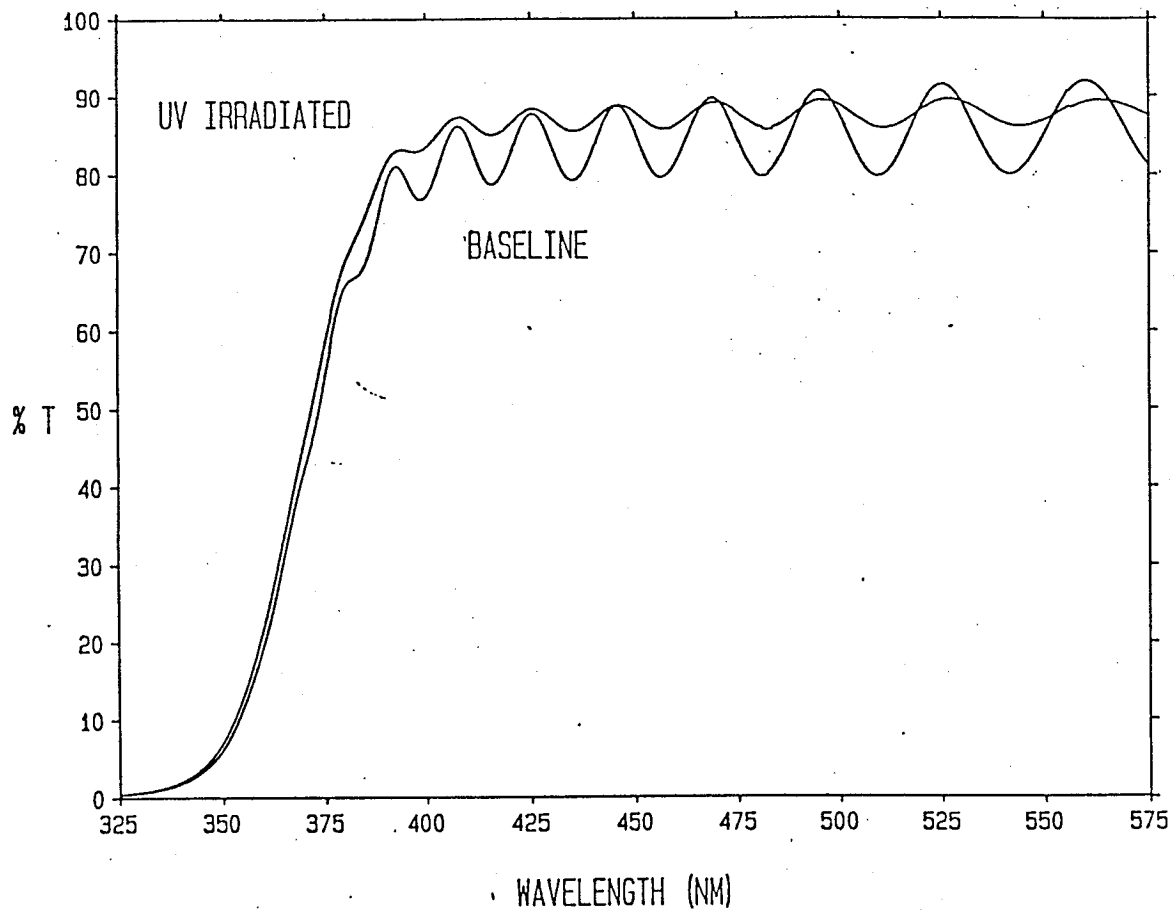


Figure 6. The uv/visible spectra of a polyetherimide film with 10% BTO before and after exposure to ultraviolet radiation.

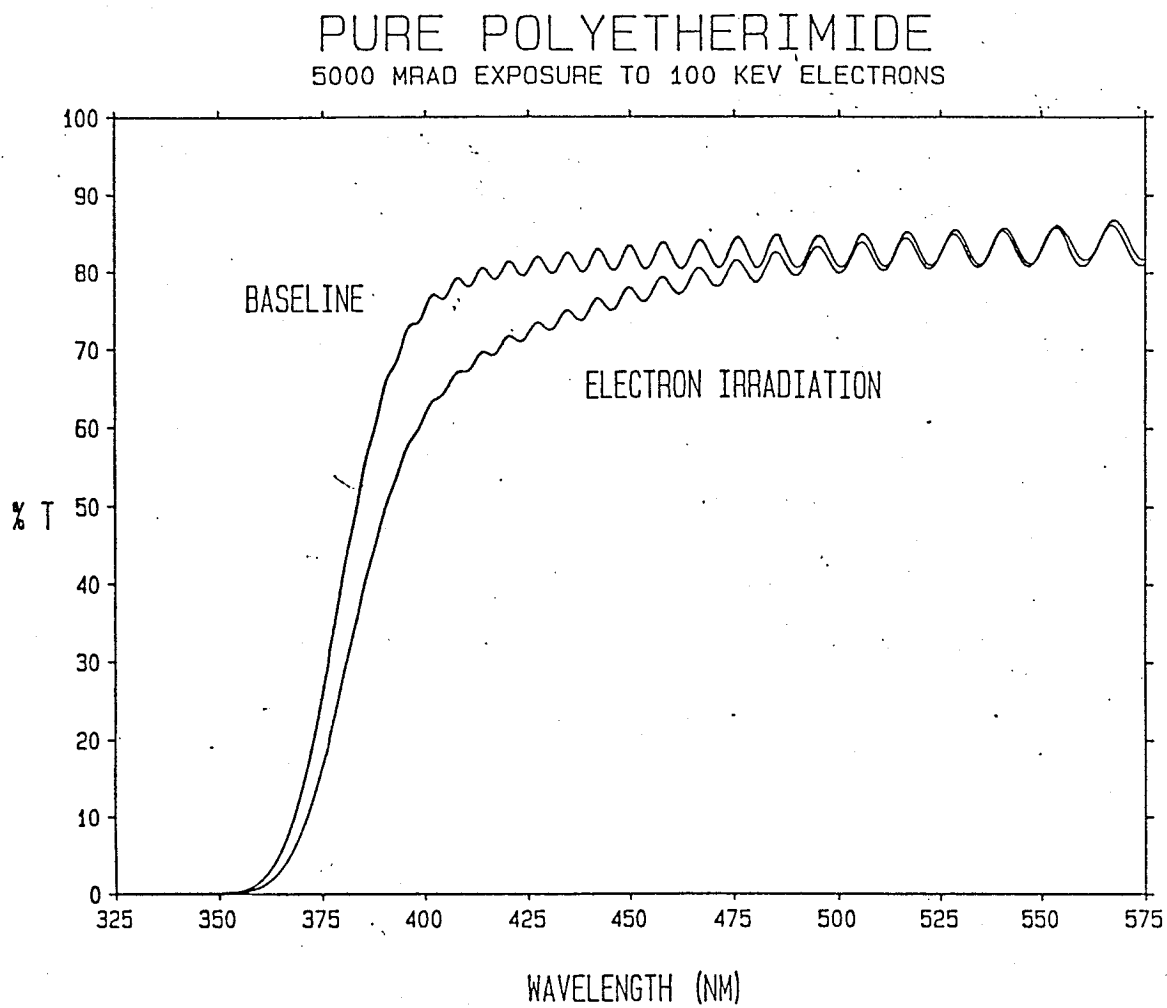


Figure 7. The uv/visible spectra of a pure polyetherimide film before and after exposure to 100 keV electrons.

POLYETHERIMIDE WITH 10% BTO
5000 MRAD EXPOSURE TO 100 KEV ELECTRONS

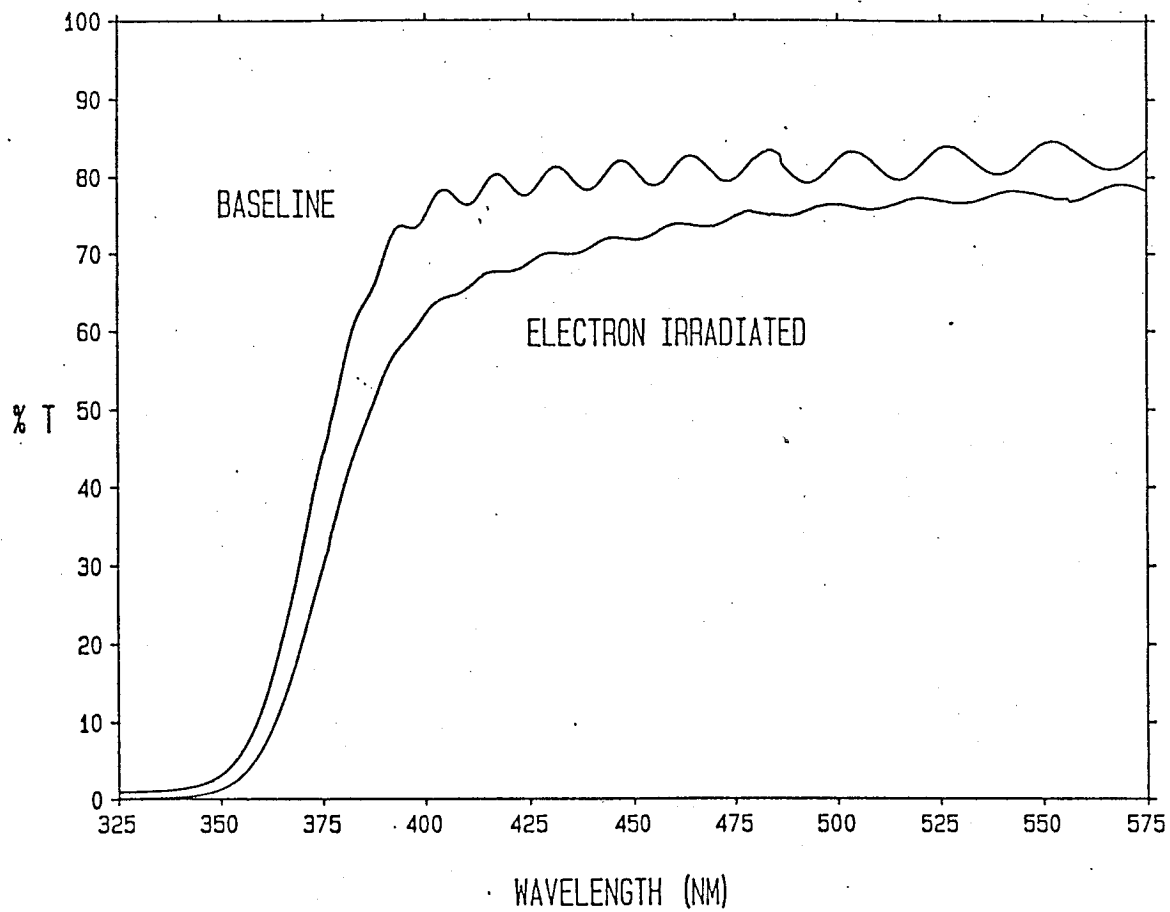


Figure 8. The uv/visible spectra of a polyetherimide film with 10% BTO before and after exposure to 100 keV electrons.