DETERIORATION OF FIBROUS MATERIALS BY ULTRAVIOLET LIGHT*

by

C. V. Stephenson
Southern Research Institute
Birmingham, Alabama

I. REVIEW OF PREVIOUS WORK

There is extensive literature on the effects of high-energy ionizing radiations on polymers. For a comprehensive bibliography of this work the reader is referred to the excellent books by Bovey,[1] Charlesby,[2] and Chapiro.[3] The effects of nonionizing radiation such as ultraviolet light has not been reported nearly as exhaustively as the effects of ionizing radiation. It is therefore appropriate to review some of our earlier work[4-6] concerning the ultraviolet degradation of polymeric materials, since many of the results and conclusions reached in those studies are relevant to the more recent studies of ultraviolet degradation of other polymers.

A. Materials and Methods

The materials were 1.0 mil films of nylon 66, high-density polyethylene (Marlex), and Teflon; 0.25 mil film of Mylar; and the following fibers: 3.3 denier Acrilan, 139 denier polyethylene (Royalene, high density), and 14.3 denier nylon 66. The materials contained no plasticizers and were as nearly pure as could be obtained without going to laboratory-prepared samples. Laboratory-prepared samples were not used during this early work because they were expected to be inferior to production samples in such pertinent characteristics as uniformity, crystallinity, and reproducibility. In our more recent work with experimental fibers, when laboratory samples were used, nonuniformity of the samples has been a major problem.

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The radiation sources were the General Electric A-H6 high-pressure mercury arc and G-30T8 germicidal lamp. The germicidal lamp emits about 90 percent of its energy at 253.7 mμ. The A-H6 emits a broad continuum with peaks in the ultraviolet region at 244 mμ, 314 mμ, and 369 mμ. Bands centered at these peaks have been selected with either a monochrometer or an interference filter. The intensity of the ultraviolet light at the position of the sample was checked periodically with a thermopile, and the output of the lamp was monitored constantly with a recording photocell hook-up.

Samples were irradiated at room temperature either in vacua of 10^{-3} mm or 10^{-6} mm or in nitrogen or oxygen at atmospheric pressure. Analysis of the nitrogen showed less than 0.01 percent oxygen and in a check experiment with specially purified nitrogen the difference in results was within experimental error.

B. Results for Polyethylene, Nylon, Mylar, and Acrilan

1. Changes in tensile properties

The same general trends were found for these four polymers with regard to the degradation of their tensile properties by ultraviolet light. Typical results are shown for polyethylene film in Figure 1 and Figure 2. Figure 1 shows the changes in tensile strength and ultimate elongation for polyethylene irradiated *in vacuo*, in nitrogen, and in oxygen. The physical property that seems to be most sensitive to the photolytic processes of deterioration is the elongation. Figure 2 shows the effects of ultraviolet light of different wavelengths. It is seen that the shorter wavelengths are more effective than the longer wavelengths in producing deterioration.

It is difficult to directly compare the changes in the tensile properties of films and fibers since fibers are more highly oriented than films. This higher degree of orientation gives the fiber a tensile strength that is an order of magnitude greater than the film and an elongation that is an order of magnitude lower. However, it has been observed that fibers of nylon and polyethylene deteriorate at essentially the same rate as the film. The effect of environment is generally the same for fiber as for film and, as is shown in Figure 3 for nylon fiber, wavelength effects are similar.

2. Gel formation in irradiated film

Crosslinking and chain scission are two effects of radiation that affect the tensile properties of polymers. A sufficient amount of crosslinking will cause a soluble polymer to exhibit an insoluble gel fraction. The theoretical aspects of radiation-induced crosslinking and scission as related to gel formation have been treated by several authors. We have analyzed our data by methods described by Charlesby[7] and Charlesby and Pinner.[8] The results of gel formation experiments for nylon irradiated in nitrogen and in vacuo are shown in Figure 4. In this figure the solid lines are theoretical curves for the scission-to-crosslinking ratios, β/α, shown. It is seen that the scission-to-crosslinking ratio is higher for irradiation in nitrogen than it is for vacuum irradiation. No gel was formed in nylon irradiated in oxygen. Similar results were found in the other hydrogen-containing polymers; however, it was necessary to introduce a five-day delay period between the finish of irradiation and gel determination for ultraviolet-irradiated polyethylene in order to allow the long-lived crosslinking radicals in this polymer to react.

C. Results for Teflon

The effect of varying the wavelength of the ultraviolet used to irradiate Teflon was similar to that found for other polymers; however, the effect of the atmospheric environment was different. Teflon deteriorated more rapidly in a vacuum than in either nitrogen or oxygen. The rate of deterioration in oxygen however is more rapid than in nitrogen. Figure 5 shows the change in tensile properties of Teflon film irradiated in oxygen and in vacuo. Teflon fiber has also been found to deteriorate at essentially the same rate as Teflon film. The fiber shows the same environmental effect in that it deteriorates more rapidly when irradiated in vacuo than when irradiated in either nitrogen or oxygen, but deterioration is more rapid in oxygen than in nitrogen.

II. CONTINUED PROGRAM ON FIBERS

During the past year we have continued the study of ultraviolet deterioration of fibrous materials. Two of these materials – fused silica and Fiberglas — were not detectably affected by ultraviolet and will not be discussed. Before presenting further results, though, it may be well to mention the experimental difficulty encountered in the tensile testing of irradiated fiber. It has been found – and this can be seen from the results of tests as well as by microscopic examination — that fibers are extremely nonuniform. This is true not only when comparing one fiber to another but also when comparing different segments of the same fiber. Nonuniformity is a particularly aggravating problem in laboratory-prepared samples of experimental polymers. Because of the nonuniformity of fibers, the following sampling technique has been employed. All the samples used for a particular irradiation experiment were taken from a single fiber. The fiber was cut into convenient lengths for testing and every other length was kept as a control sample. The tensile properties of each irradiated sample was then compared with the tensile properties of the control sample immediately adjacent to it. The properties of the irradiated sample were then expressed as a percentage value of the properties of the control sample. The values of the tensile properties given in this report are calculated by multiplying the average percentage value of all the samples at each irradiation time by the average value of the tensile properties of a large number of control samples.

A. Orientation in Polyethylene Fiber

Highly oriented polymeric fibers are birefringent and will thus produce an interference pattern when illuminated with polarized light incident at right angles to the axis of the fiber. The interference pattern can be used to determine the degree of orientation of the polymer in the fiber.[9] This method has been used to determine if ultraviolet irradiation caused an appreciable change in the orientation of polyethylene fibers. The interference patterns produced by polyethylene fibers are shown in Figure 6. The top picture is the pattern produced before irradiation, and the bottom picture is the pattern produced after irradiation with 3000 joules/cm^2 of the total spectrum of the A-H6 lamp. As can be seen, there is no detectable change in orientation.

B. Deterioration in Dacron Fibers

4.4 denier dacron fibers have been irradiated with ultraviolet light in the three wavelength bands at 244 mμ, 314 mμ, and 369 mμ. The results of tensile tests of the irradiated samples are given in Figure 7. These data show a wavelength dependence that is different from that found for most polymers in that there seems to be less deterioration of Dacron caused by the 244 mμ ultraviolet light than is caused by 314 mμ ultraviolet; although there is less deterioration in Dacron caused by 369 mμ ultraviolet than for either of the other two wavelengths. This wavelength dependence for Dacron is somewhat unusual in that a similar dependence was not noted for Mylar film; however, the observed difference probably has a ready explanation.

There is a sharp increase in ultraviolet absorption by Mylar at about 310 mμ in going from longer to shorter wavelengths. Thus it might be expected that Mylar would furnish its own protection in the short wavelength regions and that the deterioration caused by 244 mμ ultraviolet would be less than that at 314 mμ. The fact that this was not observed in Mylar is probably attributable to the thinness of the film tested — only 0.25 mil. The Dacron fibers, however, have a diameter a little greater than 1.0 mil, and the surface shielding at short wavelengths should be more noticeable. Thus, one might expect the smaller rate of deterioration that was noticed in Dacron at short wavelengths. This explanation would also explain another observation.

The rate of deterioration is essentially the same for both film and fiber for all those polymers for which film and fibers were both available except for the Mylar film-Dacron fiber combination. It was found that Dacron deteriorated less rapidly than Mylar when they were irradiated with the G30T8 lamps. Since the ultraviolet light from the G30T8 lamp is almost all short wavelength radiation (254. 7 mμ), this difference might well be expected.

The scission-to-crosslinking ratio seems to be a little higher in Dacron than it is in Mylar, as is seen in Figure 8. This is the same trend that has been noted in the comparisons of scission-to-crosslinking ratios in films and fibers of polyethylene and nylon also.

C. HT-1, Experimental Fiber

HT-1 is an experimental fiber noted for its high-temperature stability. Very little is known about the composition of this polymer except that it is described by the manufacturer, du Pont, as an aromatic polyamide. It has no known solvents that do not cause degradation.

The tensile properties of this material have been determined after various irradiations with 244 mμ, 314 mμ, 340 mμ, and 369 mμ ultraviolet light and with visible light at 437 mμ in an atmosphere of nitrogen at 750 mm pressure.

The data for the tensile strength and elongation are plotted in Figure 9. HT-1 deteriorates more rapidly when irradiated with 244 mμ ultraviolet than when irradiated at 314 mμ. However, unlike the other polymers, HT-1 deteriorates more rapidly when irradiated with 369 mμ ultraviolet light than it does at either of the other wavelengths. Because of this unusual wavelength dependence, the irradiations at 340 mμ and 437 mμ were made to further confirm and to clarify the effect. It is seen that the deterioration caused by 340 mμ ultraviolet light is essentially the same as that caused by 369 mμ ultraviolet light. The visible light is virtually ineffective, although some deterioration is seen at long irradiation times. The explanation for the unexpectedly high deterioration at 369 mμ is not known with certainty since the energy absorption characteristics of the polymer fibers as a function of wavelength are not known. There could be some protective effect at the shorter wavelengths in the aromatic rings that the polymer is said to contain. An intentionally added protective agent would not be out of the question, since no information is available on this point.

The rate of deterioration has been found, within experimental error, to be the same whether irradiated *in vacuo*, in nitrogen, or in oxygen.

D. Polybenzimidazole

Experimental samples of polybenzimidazole have been irradiated with ultraviolet light and tested. The results of environmental tests are shown in Figure 10.

The most obvious change in tensile properties was in those samples irradiated in oxygen. Irradiation in oxygen causes a rapid decrease of the ultimate elongation of polybenzimidazole. Although the tensile strength does not decrease as rapidly as the elongation, deterioration of the tensile strength of polybenzimidazole is more rapid in oxygen than it is *in vacuo* or in nitrogen. There was almost no deterioration of this polymer during vacuum-irradiation. Although there is considerable spread in the data, all values of the elongation found after irradiation *in vacuo* are above that of the unirradiated polymer. This fact would indicate that there is some crosslinking during vacuum-irradiation.

The conclusion that crosslinking occurs is verified by gel formation experiments. In these experiments the gel formed in the polymer was determined by dissolving the sample in dimethyl sulfoxide. It is to be noted that even the unirradiated polymer contains some gel. There is thus a considerable amount of crosslinking in the polymer even before irradiation. This initial crosslinking is presumably the result of crosslinking during polymerization. However, additional crosslinking by ultraviolet light is evidenced by an increase in the gel found in irradiated samples.

The effects of different wavelengths of ultraviolet light have also been determined. The tensile properties of polybenzimidazole irradiated in nitrogen at 244 mμ, 314 mμ, and 369 mμ have been determined for different amounts of incident radiation. These data are plotted in Figure 11. It is seen that the deterioration caused by 244 mμ ultraviolet light is essentially the same as that caused by 314 mμ ultraviolet; but the deterioration by 369 mμ ultraviolet is greater than at either of the other wavelengths. This is probably due to the self-protection afforded the polybenzimidazole fibers due to greater surface absorption at the lower wavelengths similar to the effects noted in HT-1 and Dacron.

III. CONCLUSIONS

The rate of deterioration of fibers of Dacron, HT-1, and polybenzimidazole by ultraviolet light has been determined. The environment of the polymer during irradiation plays an important part in the deterioration of Dacron and polybenzimidazole. Both of these polymers deteriorate rather rapidly in oxygen, not so rapidly in nitrogen, and least of all *in vacuo*. The environment seems to have little effect on the rate of deterioration of HT-1.

Unlike any of the polymers previously studied, these three materials have higher rates of deterioration at some of the longer wavelengths of ultraviolet than at the shorter wavelengths. This effect is probably the result of self-protection caused by absorption peaks in the low wavelength ultraviolet region.

IV. REFERENCES

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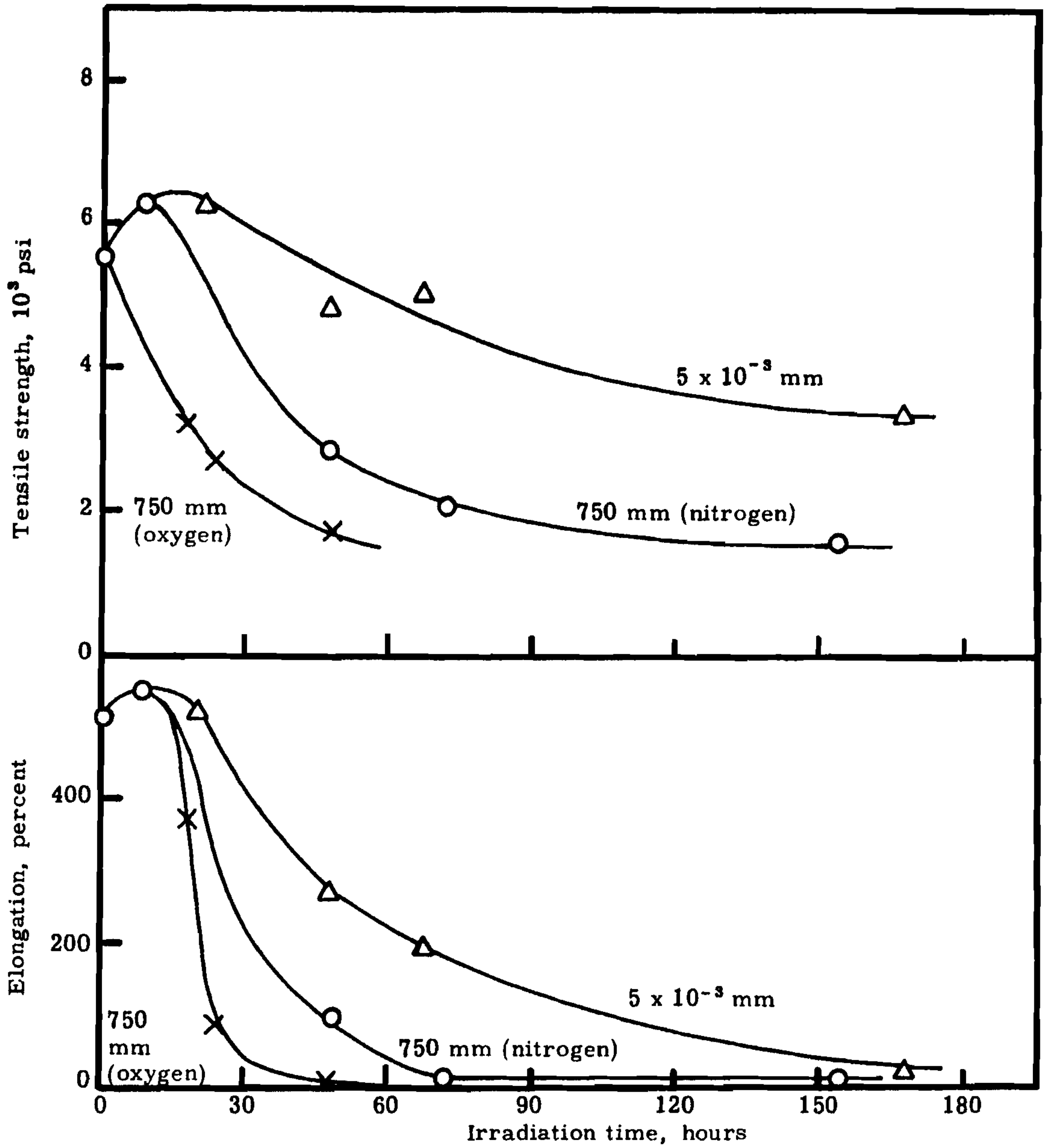


Figure 1. Variation of the tensile strength and ultimate elongation of polyethylene film irradiated with ultraviolet light in oxygen, nitrogen, and a vacuum of 5 x 10^{-3} mm.

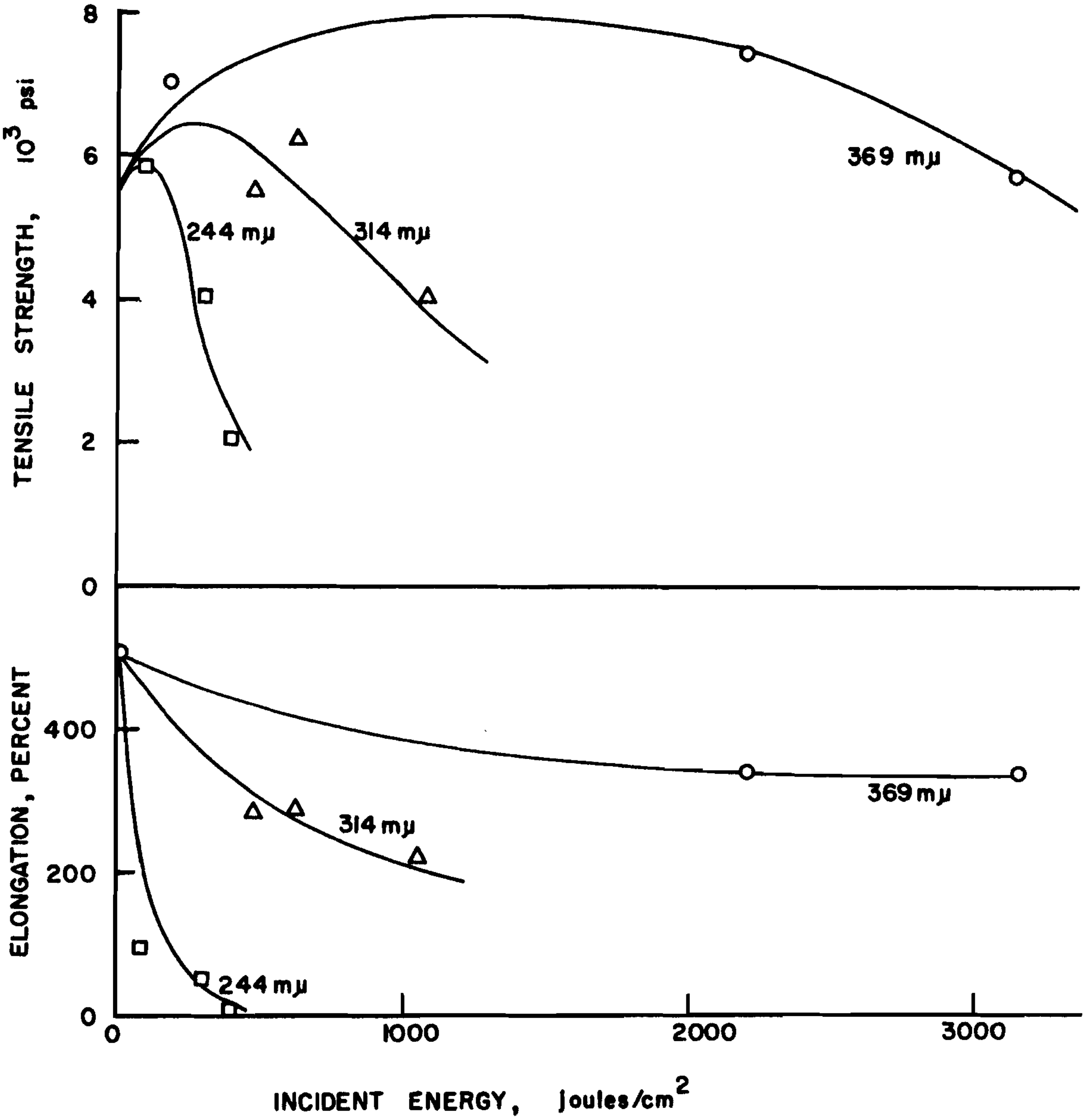


Figure 2. Variation of the tensile strength and ultimate elongation of polyethylene irradiated in nitrogen with bands of ultraviolet light centered at 244, 314, and 369 mμ.

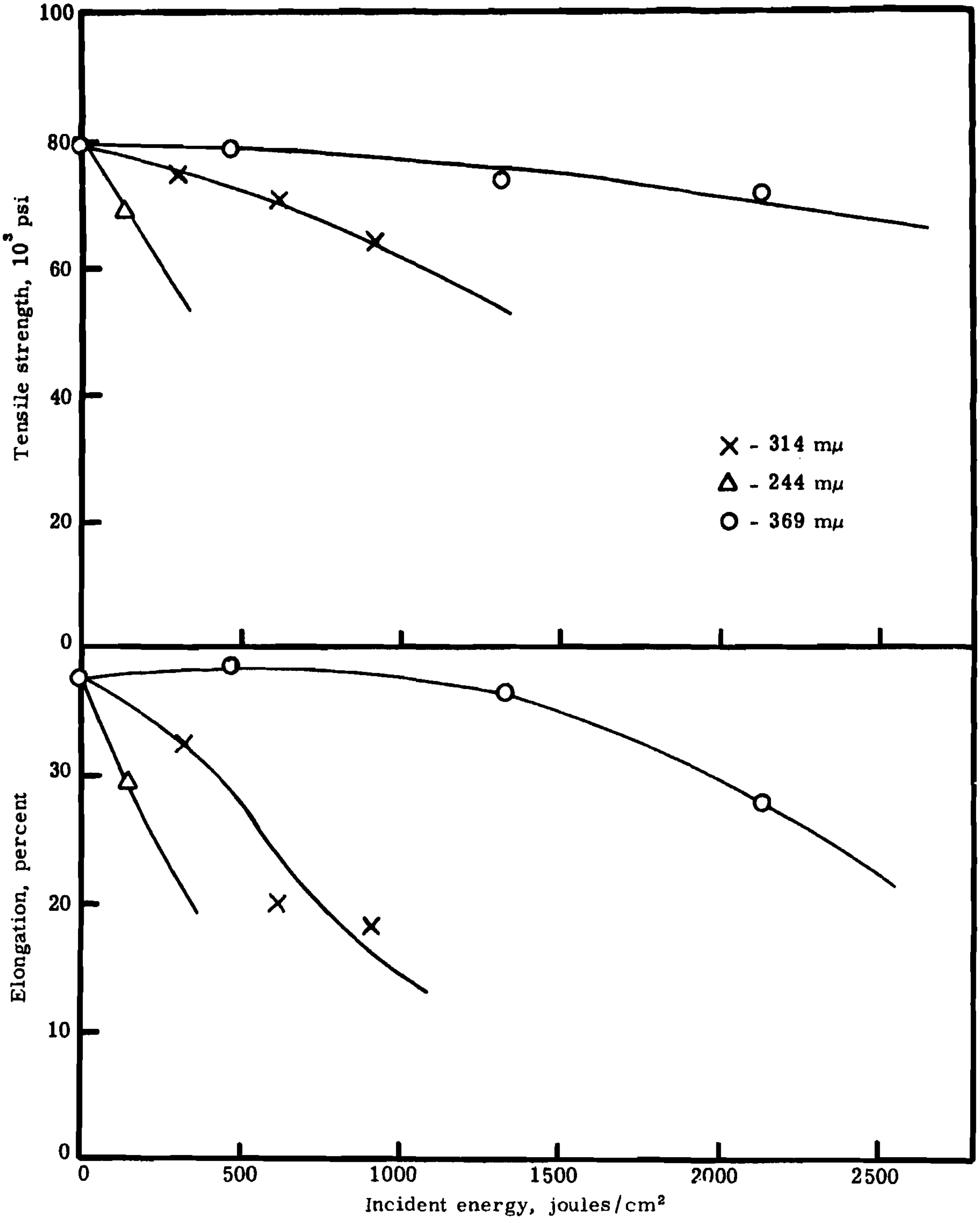


Figure 3. Variation of the tensile strength and elongation of nylon fibers irradiated in nitrogen at 244 mμ, 314 mμ, and 369 mμ.

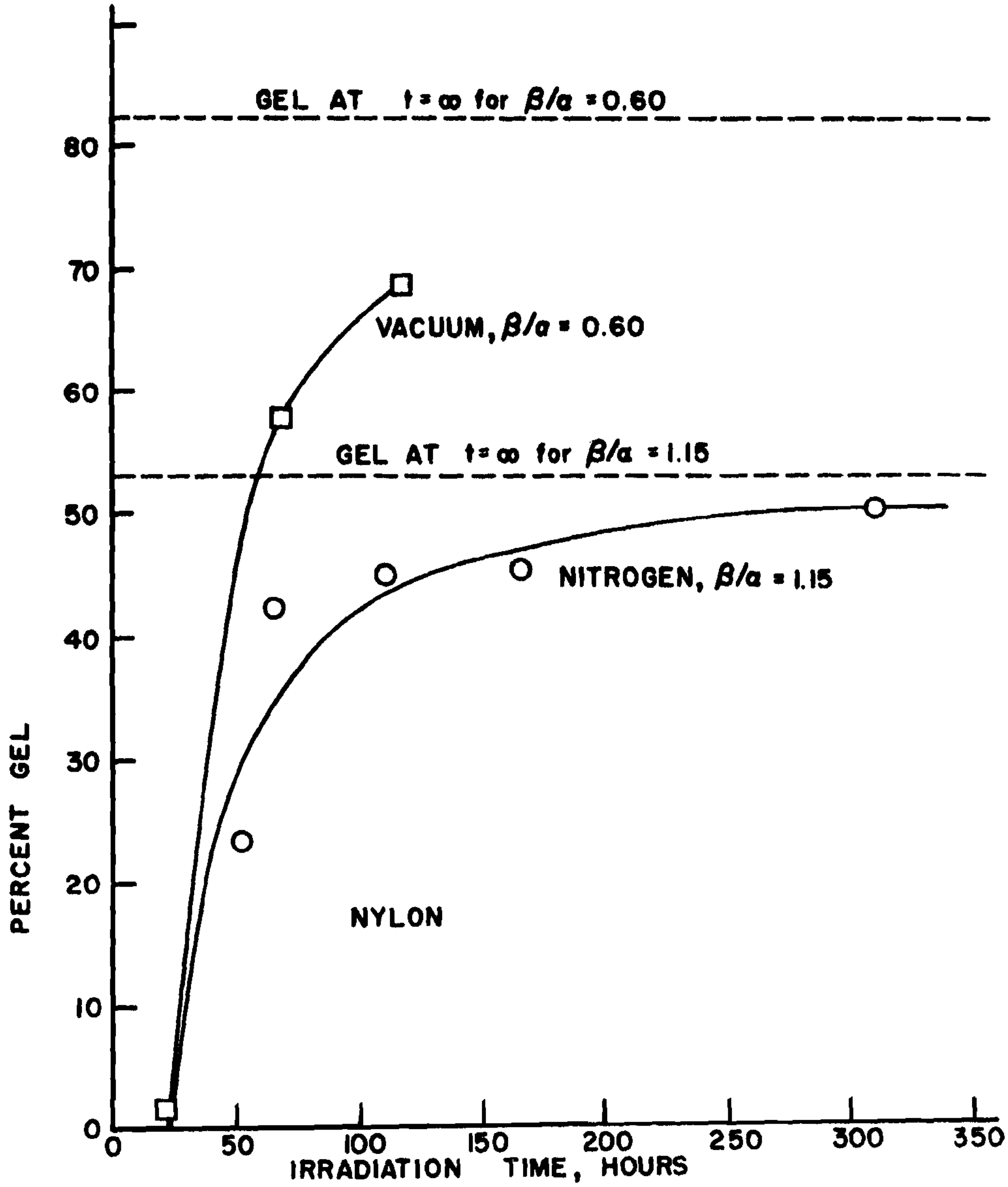


Figure 4. Gel formation in nylon irradiated in vacuo and in nitrogen with 253.7-mμ ultraviolet light.

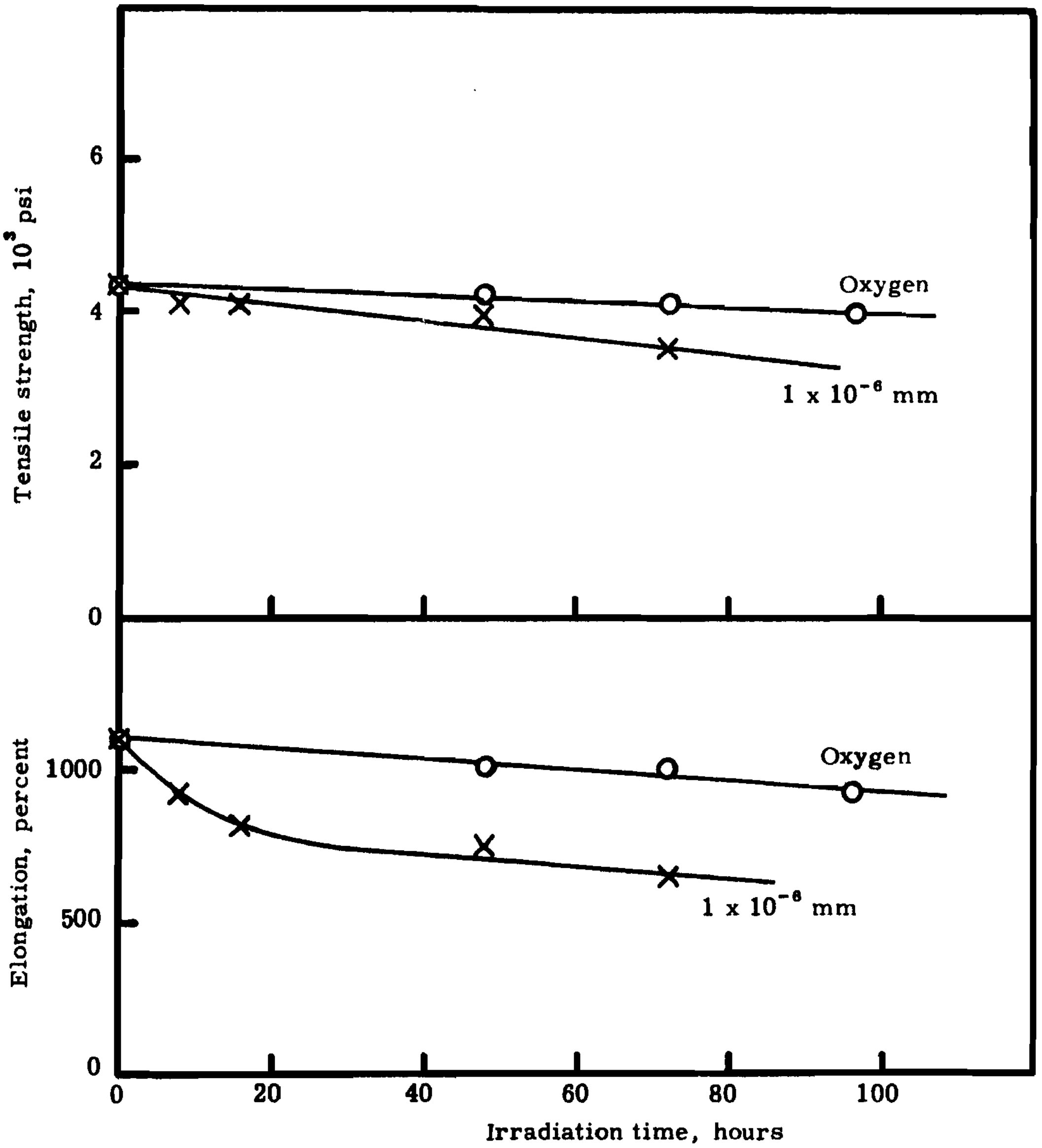
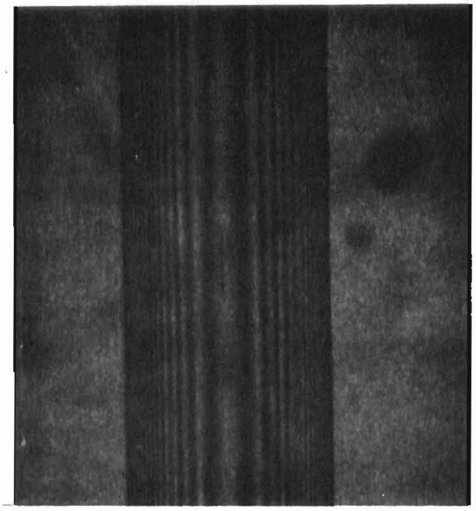
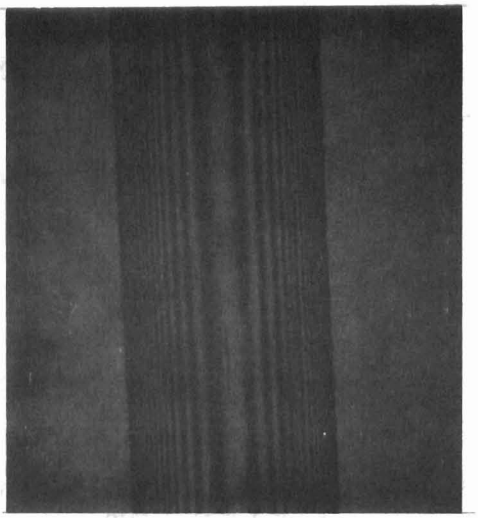


Figure 5. Tensile properties of Teflon film irradiated in oxygen and in a vacuum of 1 x 10^{-6} mm.



Before Irradiation



After Irradiation

Figure 6. Interference patterns produced by polyethylene fibers before and after irradiation.

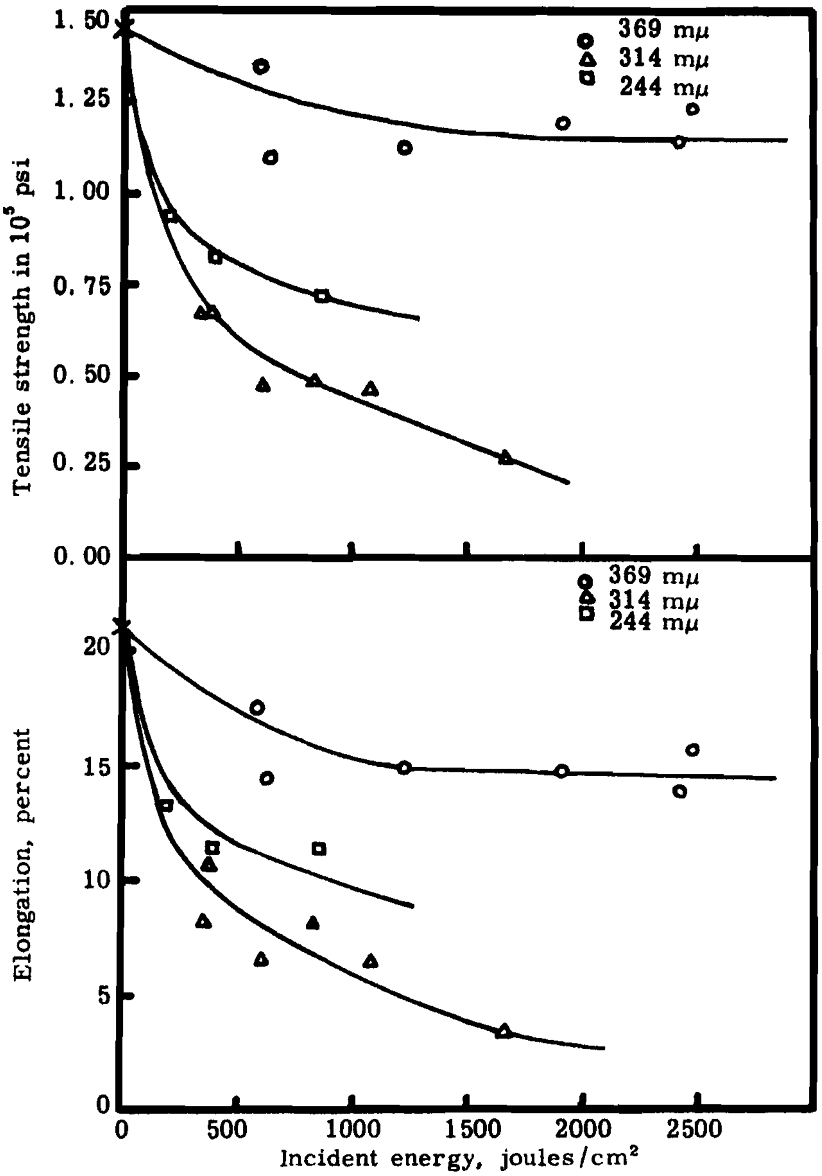


Figure 7. Variation of tensile properties with incident energy for Dacron irradiated in nitrogen with the A-H6 lamp.

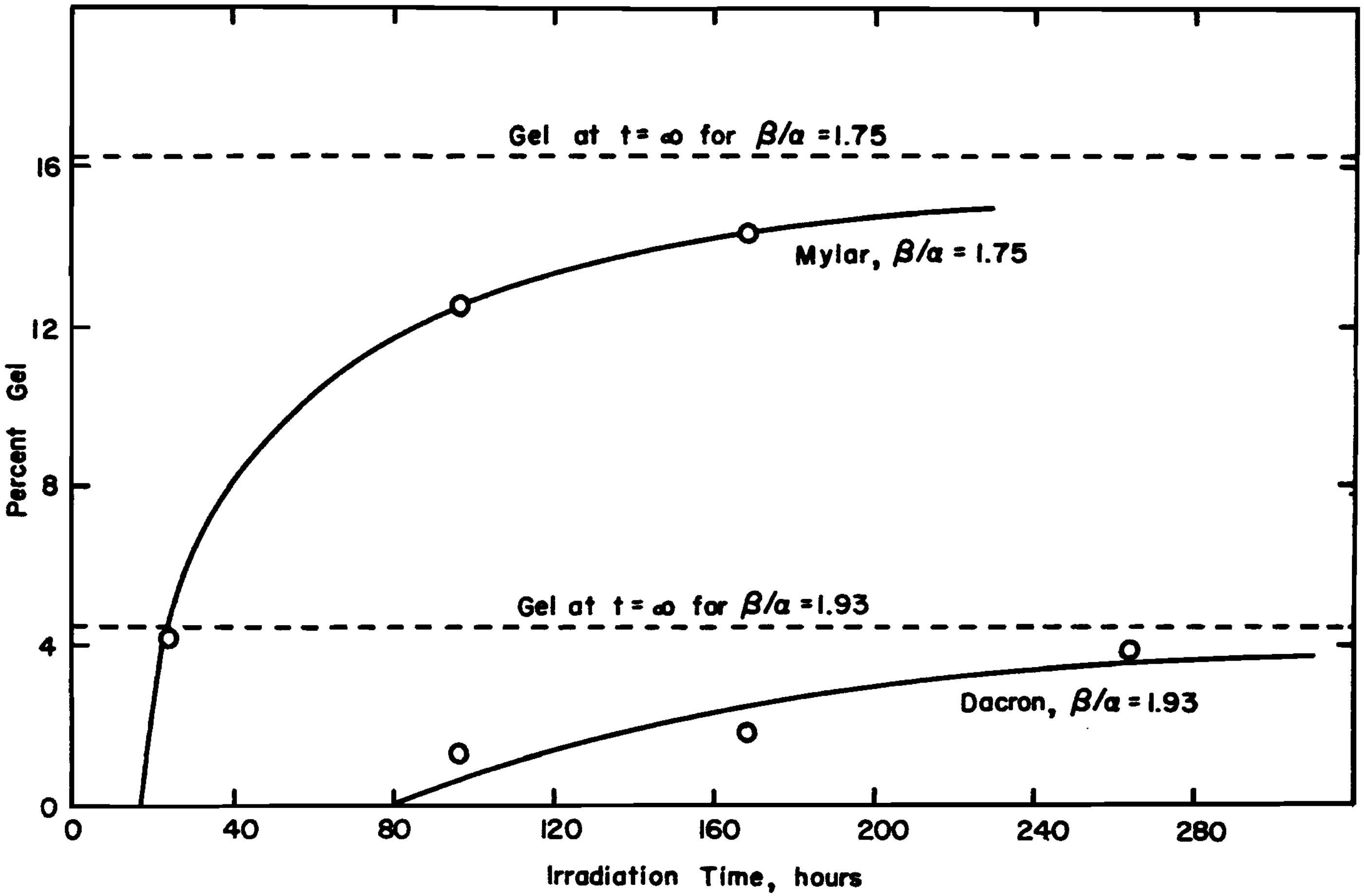


Figure 8. Gel formation in Mylar film and Dacron fibers irradiated with ultraviolet light in a vacuum of 5×10^{-2} mm.

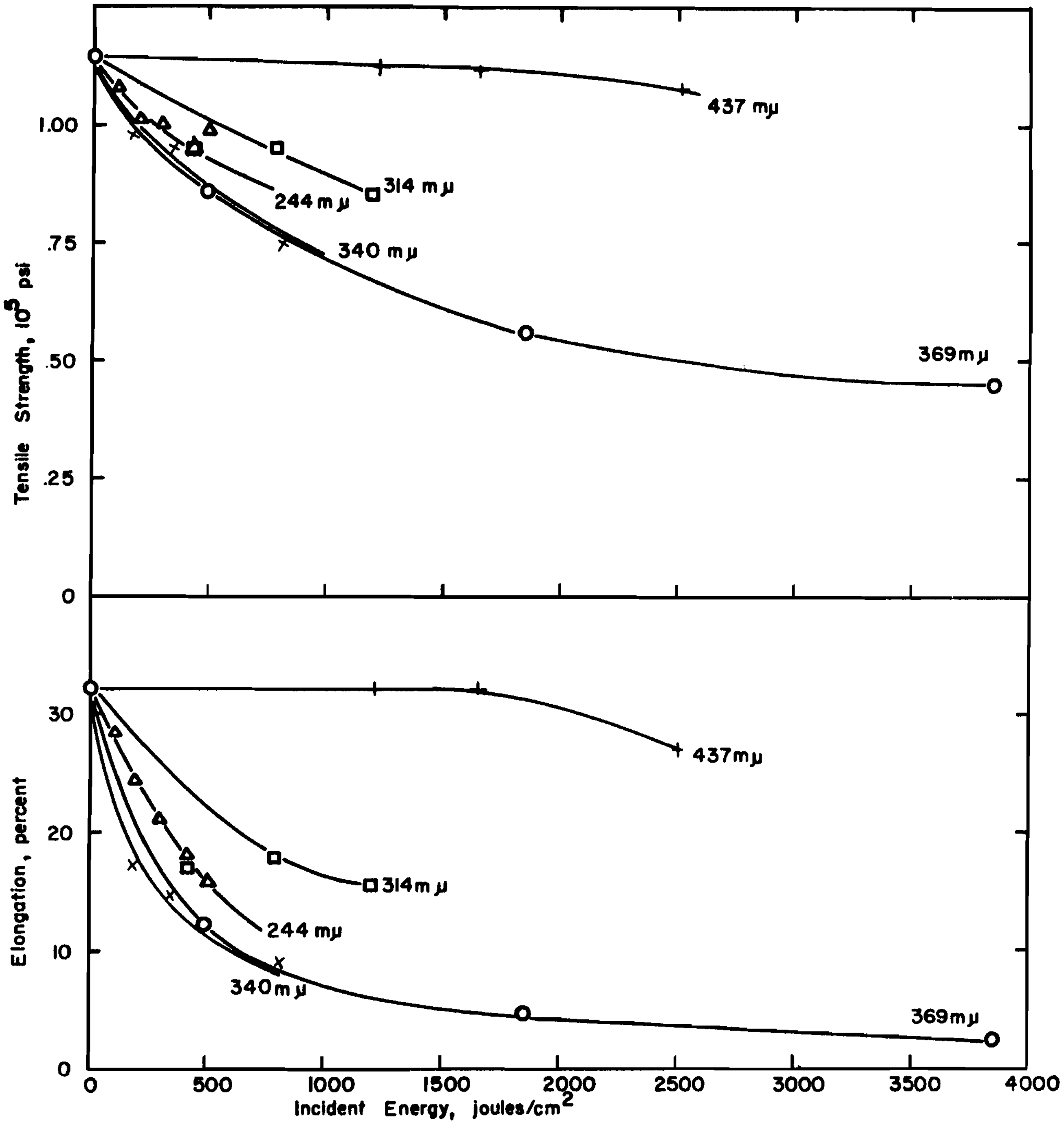


Figure 9. Variation of the tensile strength and ultimate elongation of HT-1 irradiated in nitrogen with ultraviolet light at 244 mμ, 314 mμ, 340 mμ, and 369 mμ, and with visible light at 437 mμ.

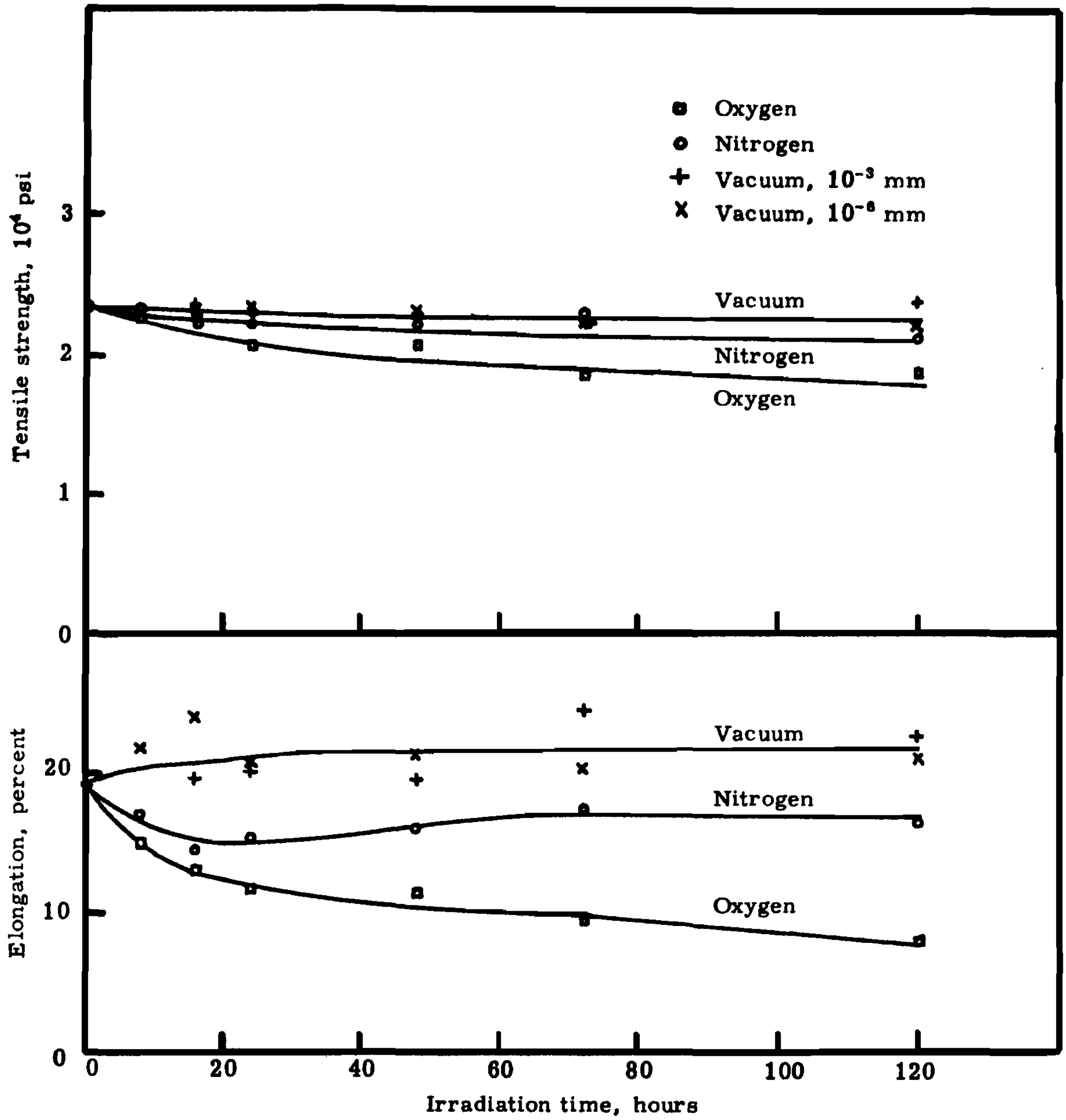


Figure 10. Variation of tensile strength and ultimate elongation of polybenzimidazole irradiated *in vacuo*, in oxygen, and in nitrogen with G30T8 lamps.

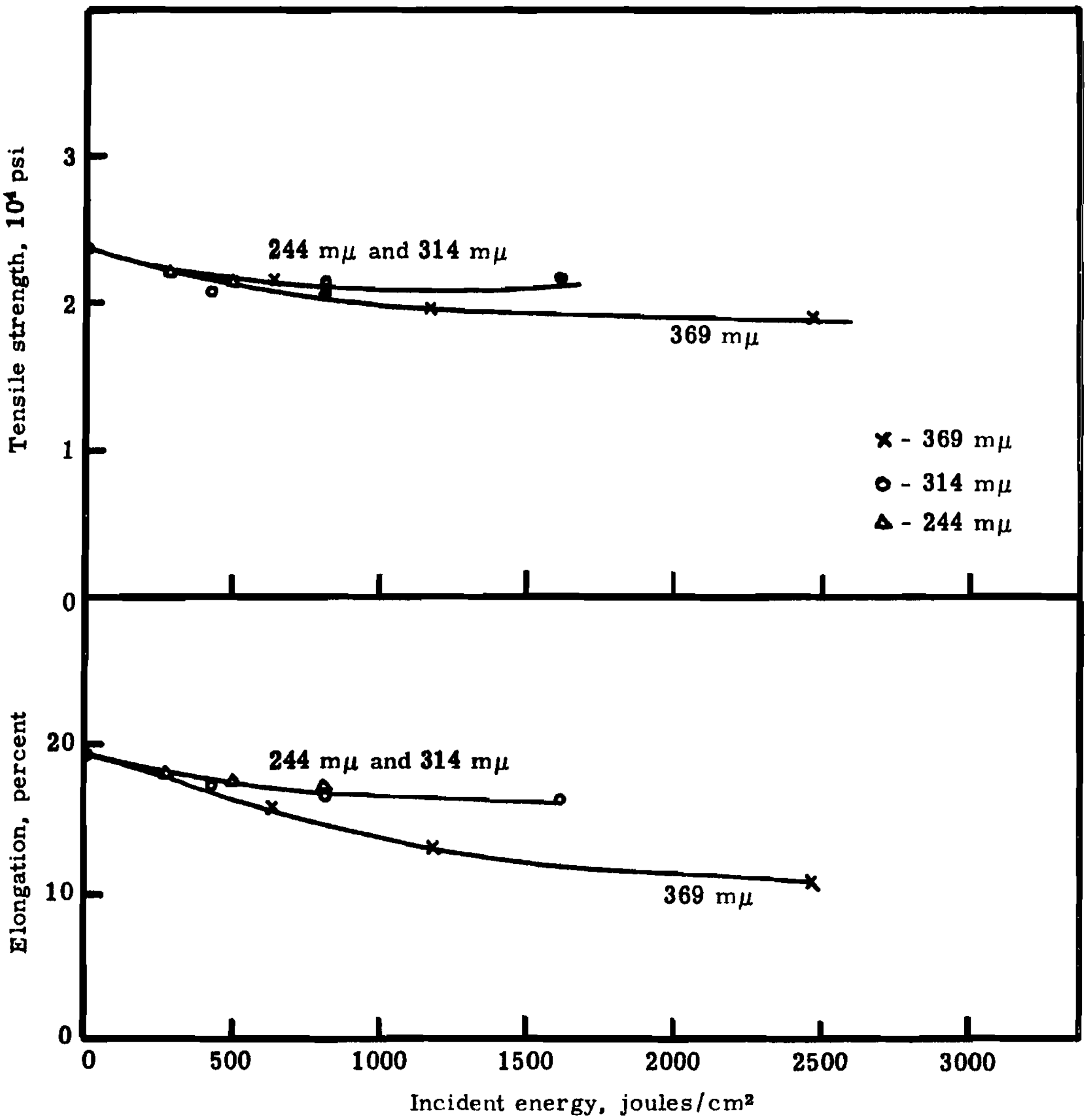


Figure 11. Variation of tensile strength and ultimate elongation of polybenzimidazole fibers irradiated with ultraviolet light at 244 mμ, 314 mμ, and 369 mμ in nitrogen.