

Comparison of Effects of Ultraviolet and ^{60}Co Gamma Ray Irradiation on Nylon 6 Mono-filaments

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Abstract: The effect of UV and ^{60}Co gamma radiations on the physical and mechanical properties of nylon 6 mono-filaments with different draw ratios has been studied. Specimens were exposed to either up to 25 Mrad of gamma or up to 168 hrs of intense UV irradiation. The results show that nylon mono-filaments exposed to gamma rays, with much higher quantum energy than UV, undergo a larger extent of molecular chain scission. Higher irradiation dose also results in the production of insoluble, macroscopic three-dimensional cross-linked network structure. The amorphous regions with a lower density of cohesive energy (lower molecular orientation) show a higher extent of cross linking reaction whereas amorphous regions with a higher density of cohesive energy (higher orientation) show higher extent of chain scission reaction, irrespective of UV ray or gamma ray irradiation.

Keywords: Nylon, UV radiation, Gamma radiation, Mechanical and physical properties

Introduction

Human beings have been continually enlarging their stage of living activities. Based on the successes thus far it may not be farfetched to envision that in the near future there will be exciting possibilities for the human beings to live in space colonies. In such cases, space clothing would be an important issue. While several specialty fibers are used in building the present space suit, nylon 6 fibers have been commonly used for the undergarment of the space suit. Nylon 6 fibers are also used in many other applications including ropes and commonly worn apparel that are exposed to significant amounts of sun light.

Materials used in space are exposed to several types of high energy ionizing radiations including gamma rays, electrons and UV; all of which are known to degrade mechanical properties of polymers. Even on earth the depletion of the ozone layer has significantly increased the amount of UV radiation reaching the ground, creating a dangerous environment for all human beings. This has prompted many researchers to study the effects of UV radiation on the properties of nylon 6 fibers used in day-to-day textiles. The present paper discusses the effects of high-energy radiations of UV and gamma rays, simulating the environment of the space activities as well as daily life, on physical and mechanical properties of nylon 6 mono-filaments.

It is well known that the high-energy irradiation of polymeric materials generally gives rise to molecular chain scission and/or cross-linking reactions, mainly in the amorphous regions of the specimens. The extent of these reactions depends on the type of polymer. Experimental evidence indicates that

equal amount of absorbed radiation energy by polymer causes equivalent changes in the polymer properties, independent of the radiation type [1]. In the case of UV irradiation of nylon 6 film, Yano and Murayama [2] have shown that the chain scission reaction proceeds first and the cross-linking reaction follows. Even after stopping the irradiation, the cross-linking reactions continue for a while as the radicals generated by chain scission, during irradiation, keep combining over a period of time. Recently, Katsuragi and Sakai [3] investigated the stress-strain behavior of nylon 6 mono-filaments exposed to UV radiation and showed that the chain scission effect predominantly occurs in the amorphous region with a higher density of cohesive energy than in the region with a lower density of cohesive energy. These results have been further supported by Ohtsuka and Sakai [4] through their observations in the changes of heat capacities of specimens before and after UV exposure as well as through the comparison of average molecular weights estimated by the viscosity method for nylon 6 mono-filament specimens drawn to different draw ratios. Further, it was suggested that the cross-linking effect predominantly occurred in the amorphous region with a lower density of cohesive energy. They stated that these interpretations should be consistent with the general understanding of the effect of gamma ray exposure on polymeric materials that the chain scission predominates when exposed to gamma radiation at temperatures below the glass transition temperature whereas cross-linking reactions predominate above the glass transition temperature [4]. This is simply because above the glass transition temperature there is sufficient segmental motion that can provide opportunities for the radicals to come close and combine.

In the present research we have compared the effects of UV and ^{60}Co gamma ray exposures on the physical and

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mechanical properties of nylon 6 mono-filaments drawn to two different draw ratios i.e., having two different molecular orientations.

Experimental

Nylon 6 mono-filaments used in this study were provided by SHOWA DENKO K. K. Specimens were formed at 260°C and the two draw ratios were 1) as spun (PA1) and 2) drawn to a draw ratio of 3 (PA3). These specimens were exposed to ^{60}Co gamma-radiation, with 5 Mrad, 10 Mrad and 25 Mrad doses, in air, at room temperature in the Ward Laboratory for Nuclear Studies at Cornell University. Some PA1 and PA3 specimens were also irradiated with UV light. The lamp used for UV treatment was an air-cooled, high-pressure mercury vapor lamp manufactured by TOSHIBA K. K., Type H400-P. The highest intensity of the spectrum was located around 365 nm. Intensity of UV light on the specimens was measured as $0.8 \pm 0.05 \text{ mW/cm}^2$. Exposure times were set at 24 hr, 48 hr and 168 hr.

Control (unirradiated) and irradiated nylon 6 mono-filaments were dissolved in 85 % formic acid, and the viscosity of the solution was measured using Ostwald viscometer. All viscosity data were obtained in formic acid at 25 °C. Weight average molecular weight (Mw) was calculated according to the following equation

$$[\eta] = 0.0226 \text{ Mw}^{0.82} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity [5].

Specimen density was measured using a density gradient column prepared using a mixture of carbon tetrachloride (1.594 g/cm^3) and xylene (0.863 g/cm^3). Specimens were cut to 3 mm long pieces and dropped in the density gradient column. When the mono-filament specimens got neutral buoyancy, the specific gravity of the mixture was measured using densimeter and recorded as the specimen density. The specimen crystallinity values were calculated using the measured density values and using the simple rule of mixture. For these calculations the density of 100 % nylon 6 crystal was assumed to be 1.220 g/cm^3 and the density of 100 % nylon 6 amorphous part was assumed to be 1.090 g/cm^3 [6].

Thermal analysis was performed using a Seiko electronic differential scanning calorimeter, DSC200-SCC5020, calibrated with Indium. Specimens were heated from -10 to 250°C at the heating rate of 10°C/min for the first run. After being held at 250°C for 2 min, the specimens were cooled down to -10°C at a cooling rate of 10°C/min . The specimens were reheated to 250°C at the same heating rate of 10°C/min for the 2nd run. Melting temperature, T_m , melting enthalpy, ΔH_m , and glass transition temperature, T_g , values were obtained from both heating runs. Crystallinity was calculated from ΔH_m value, assuming the heat of fusion for 100% nylon 6 crystal of 168 J/g [7]. Tensile properties of the filaments were

characterized using Instron (model 1122) tensile testing machine. The gauge length of 100 mm and a strain rate of 0.2 min^{-1} were used for all tensile tests.

Results and Discussion

Average Molecular Weight Measurement

The intrinsic viscosity values, average molecular weights and their standard deviations obtained for PA1 and PA3 nylon 6 specimens, before and after UV irradiation, are presented in Tables 1 and 2, respectively. These data clearly indicate that the average molecular weight of as-spun, PA1, specimen increases with increasing irradiation time i.e., increase in dose. In the case of PA3 specimens, however, the molecular weight decreases, initially, for the 24 hr irradiation period. After the initial 24 hr period, however, the molecular weight increases continuously with increasing irradiation period within the experimental time limit of 168 hr.

These results indicate the combined effects of chain scission and cross-linking. Considering the effect of molecular orientation on the cohesive energy density of the amorphous region, the observed fact may suggest that the amorphous region with the lower density of cohesive energy (PA1) tends to cross-link the structure more. On the contrary, the amorphous region with the higher density of cohesive energy (PA3) shows an initial tendency of molecular chain scission. Such chain scission process leads to relaxing of the constraint on the molecular mobility, as the T_g gets gradually lowered. Beyond this point i.e. after lowering the T_g , however, the cross-linking reaction begins to dominate resulting in an increase in average molecular weight, as the UV exposure continues. This is very much in agreement with the earlier results of Yano and Murayama [2].

Table 3 gives the intrinsic viscosity values and average molecular weights for PA3 specimens irradiated with gamma

Table 1. Effect of UV irradiation on the weight average molecular weight of PA1 specimens

	$[\eta] (\times 10^2)$	$\text{Mw} (\times 10^4)$	$\text{Mw } \sigma^* (\times 10^4)$
Control	1.00	2.80	0.35
UV 24 hr	1.16	3.02	0.37
UV 48 hr	1.18	3.21	0.34
UV 168 hr	1.21	3.54	0.36

* σ represents standard deviation.

Table 2. Effect of UV irradiation on the weight average molecular weight of PA3 specimens

	$[\eta] (\times 10^2)$	$\text{Mw} (\times 10^4)$	$\text{Mw } \sigma^* (\times 10^4)$
Control	1.15	3.31	0.22
UV 24 hr	0.59	1.47	0.27
UV 48 hr	0.65	1.64	0.06
UV 168 hr	1.19	3.46	0.18

* σ represents standard deviation.

Table 3. Effect of ^{60}Co irradiation on the weight average molecular weight of PA3 specimens

	$[\eta] (\times 10^2)$	Mw ($\times 10^4$)	Mw σ^* ($\times 10^4$)
Control	1.15	3.31	0.22
5 MRad	1.14	3.28	0.09
10 MRad	1.70	5.32	0.21
25 MRad	0.59	1.47	0.87

* σ represents standard deviation.

rays. No significant changes in intrinsic viscosity or molecular weight values, compared to control specimens, are seen for specimens irradiated with 5 Mrad dose. However, the average molecular weight increases significantly for specimens exposed to 10 Mrad dose. The specimens exposed to 25 Mrad dose dissolved only partially in formic acid and hence the intrinsic viscosity value reflects the dissolved part only. It is clear that the dissolved part shows significant chain scission. The part that did not dissolve was expected to be cross-linked. In the case of PA1, the specimen irradiated with even 5 Mrad dose did not dissolve in formic acid solution because of the cross-linking. Thus it was not possible to measure the average molecular weight for PA1 specimens.

These behaviors are somewhat similar to those observed for the specimen PA1 and PA3 irradiated by UV rays. Namely, it seems certain that the exposure to high-energy radiations such as UV or gamma ray, initially, gives rise to the cross-linking in specimens such as PA1 and polymer chain scission in those like PA3. The former, PA1, contains mostly relaxed amorphous region with lower cohesive energy whereas the latter, PA3, contains amorphous regions with much higher cohesive energy, in other words, highly oriented amorphous regions.

The higher molecular orientation obtained as a result of the drawing procedure brings molecules closer to each other. This facilitates the combining of radicals resulting in the inter-molecular cross-linking, provided the molecules become sufficiently mobile. In the initial period of irradiation, the molecular chain scission tends to occur in the highly ordered amorphous region lowering its T_g . Once the T_g is sufficiently lowered and the segmental mobility is increased, the cross-linking reaction begins. In the case of gamma irradiation, a drastic chain scission may take place with a smaller dose compared with UV irradiation, because of its high energy [1]. Such a drastic chain scission leads to a faster lowering of T_g and associated relaxation of molecular constraint. As a result, both chain scission and cross-linking reactions can proceed almost simultaneously and thus competitively. The PA3 specimens treated with 5 Mrads exposure showed little change in the average molecular weight, as a result of these competing effects.

Further, PA3, after exposing to a dose of 25 Mrad of gamma radiation, as mentioned earlier, did not completely dissolve in the formic acid solution and remained in the form of

residue. This indicates that it had developed a macroscopic three-dimensional network structure. The insoluble part (cross-linked network) was estimated, gravimetrically, to be approximately 37 % by weight. The average molecular weight of the soluble part was measured and is listed in Table 3. The calculated value of the molecular weight is less than half of that observed for control specimen. This also supports our earlier observation that drastic chain scission occurs in PA3 specimens when irradiated with gamma rays.

Mass Density Measurement

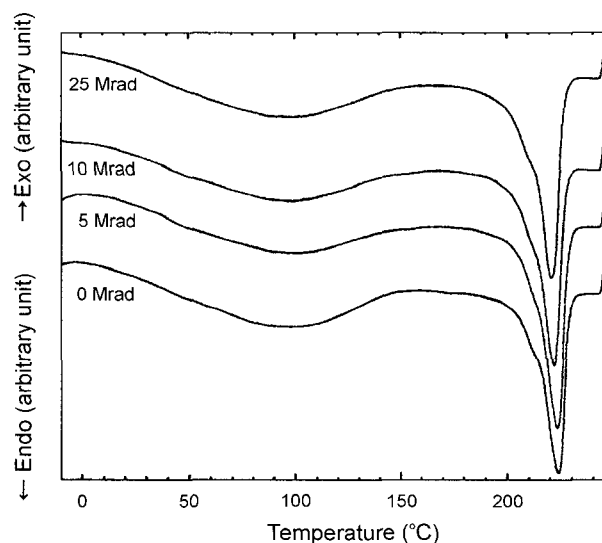
Densities of crystalline and amorphous regions as well as their volume contents for PA3 specimens, before and after gamma ray exposure, are listed in Table 4. As mentioned earlier, the crystallinity values were calculated by assuming the density of 100 % nylon 6 crystal to be 1.220 g/cm^3 [6]. It is clear from these data that both density and crystallinity values steadily increase with increase in irradiation dose confirming the cross-linking. As noted, the density of 1.150 g/cm^3 obtained for the specimen irradiated to 25 Mrad corresponds to the insoluble (cross-linked) part only.

Figure 1 shows typical DSC thermograms for control and irradiated specimens. In Figure 2 we have plotted the shoulder regions of the thermograms for easy comparison. The ther-

Table 4. Effect of ^{60}Co irradiation on the density of PA3 specimens

	Control	5 MRad	10 MRad	25 MRad	25 MRad*
Density	1.133	1.134	1.135	1.136	1.150
Volume ratio of crystal Vc	0.328	0.336	0.345	0.355	0.461

*Molecular weight of the soluble part only.

**Figure 1.** DSC thermograms (1st run) of PA3 specimens with various irradiation times.

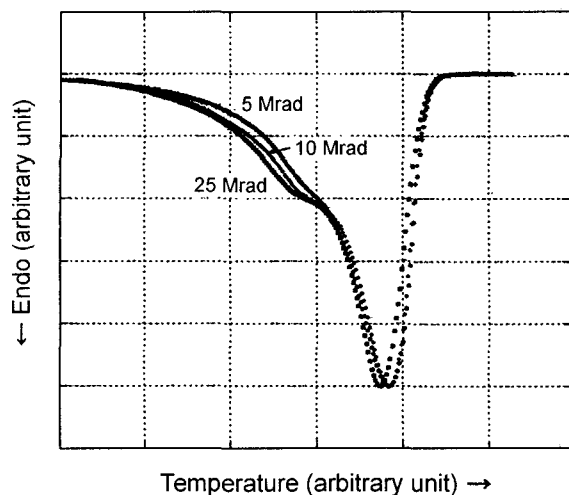


Figure 2. Expanded view of the DSC thermograms of PA3 specimens showing the shoulder regions around the endothermic peak at 223 °C.

Table 5. Effect of ^{60}Co irradiation on the thermal properties of PA3 specimens

Dose (MRad)	1st run		2nd run	
	Crystallinity (%)	T_m (°C)	Crystallinity (%)	T_m (°C)
0	37.7	223.5	32.3	220.3
5	39.5	222.5	31.2	221.8
10	43.1	221.2	34.1	221.2
25	45.9	219.6	32.9	220.4

mograms show a qualitative increase in the shoulder area preceding the endothermic peak, located around 223 °C, for the melting of the crystalline part, with radiation dose. This shoulder region is perhaps due to the crystallization of the short length molecular chains, created by the chain scission, as a result of the gamma irradiation.

Table 5 presents the crystallinity, melting temperatures, T_m , and glass transition temperatures, T_g , for various gamma irradiation conditions for PA3 specimens. The data show that the crystallinity increased with irradiation dose. However, the melting temperatures do not show any significant change as a function of radiation dose indicating that the crystal size remained unchanged after irradiation. As mentioned earlier, the density value of 1.15 g/cm³, indicated in Table 4 for PA3 specimen irradiated to 25 Mrad dose corresponds to the insoluble (cross-linked) part, directly obtained from an insoluble body. It is to be noted that this value is relatively higher than 1.090 g/cm³ commonly proposed for the amorphous region of nylon [6]. When nylon, or any polymeric material, undergoes cross-linking, the molecules are drawn closer by the links. As a result, the density of the cross-linked part is higher than the normal amorphous region. This is similar to the epoxy resins which are known to shrink 5-10 % after cross-linking,

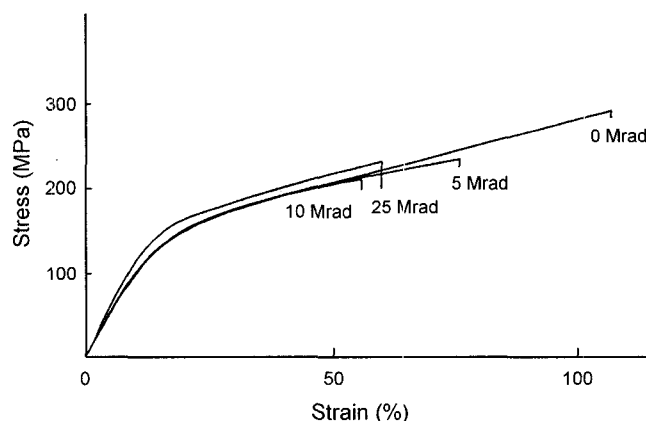


Figure 3. Stress-strain curves of PA3 specimens after various gamma irradiation times.

reducing their volume but not mass. This is another major factor contributing to the increase in density after irradiation.

Further, it is possible to deduce the density of the amorphous part soluble in formic acid, if one can assume the rule of mixture for the volume of crystalline region, and the volume of amorphous region consisting of soluble and insoluble parts. Estimated density, in this study of 1.000 g/cm³, less than that of the amorphous region, may suggest that the soluble amorphous part is made up of shorter (broken) molecular chains, with significant amount of free volume, a result of chain scission. On the other hand, the densities of the UV irradiated nylon 6 filaments did not change compared to the initial value of density until 32 hrs of exposure. While for very long irradiation periods of over 200 hrs, the specimens showed an increase in density, according to our earlier results [4].

The difference observed in the present study in the behavior of mass density between UV and gamma irradiation can be attributed to the big difference in the energy level at exposure. Compared to UV rays with wavelength of the order of 365 nm, gamma rays (order of 10⁻⁵ nm) have much higher quantum energy to be able to initiate drastic polymer chain scission.

Stress-strain Behavior

Figure 3 shows typical stress-strain plots for control and gamma irradiated PA3 specimens. The fracture stress decreased for all radiation doses compared to control. In addition, the fracture strains also were smaller than control for the irradiated specimens. A similar stress-strain behavior was reported for poly(hydroxybutyrate-co-hydroxyvalerate) irradiated with gamma rays [8]. Netravali and Manji [9] also observed similar decreases in mechanical properties with gamma radiation, for epoxy resins. Many other researchers have also shown UV irradiation to decrease the mechanical properties of several fibers including nylon and polyester [3,10].

Katsuragi and Sakai [3] analyzed such phenomena using nylon 6 filament yarn and presented the following scheme.

The amorphous regions with a higher density of cohesive energy may construct the tighter nodes in the network structure bearing a higher stress during tensile loading. Such amorphous regions show higher sensitivity toward the effect of molecular chain scission compared to the amorphous regions having a lower density of cohesive energy. That is, the chain scission reaction easily proceeds in the tighter nodal area connecting polymer chains to construct the network structure and the weakened nodal area by the chain scission causes shifting of break point toward the lower stress side. It must be noted that the fracture stress of fibers is a function of defect or flaw type and size. The chain scission locations in the amorphous region, resulting from irradiation, act as defects or weak points in the fiber structure, and reduce the ultimate fracture stress and strain.

The stress-strain curves for the irradiated specimens closely track the curve for the control specimen. However, on close observation of the curves, a shift towards higher modulus as well as a higher necking stress is indicated. This change might be attributed to the development of cross-linked structure induced by the gamma irradiation, and confirm the conclusions from the average molecular weight and mass density measurements.

Conclusions

In this paper, we compare the effects of UV and gamma radiation on the physical and mechanical properties of nylon 6 mono-filaments with different draw ratios. The results obtained are as follows:

1) Since gamma rays have much higher quantum energy than UV, nylon monofilaments exposed to gamma radiation

undergo a larger extent of molecular chain scission. Higher irradiation dose also accelerates the creation of a macroscopic three-dimensional cross-linked structure.

2) Amorphous regions with a lower density of cohesive energy show a higher extent of chain scission reaction whereas amorphous regions with a higher density of cohesive energy show higher extent of cross-linking reaction, irrespective of UV ray or gamma ray irradiation.

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