The Weatherability of Polypropylene Monofilaments. Effects of Fiber Production Conditions

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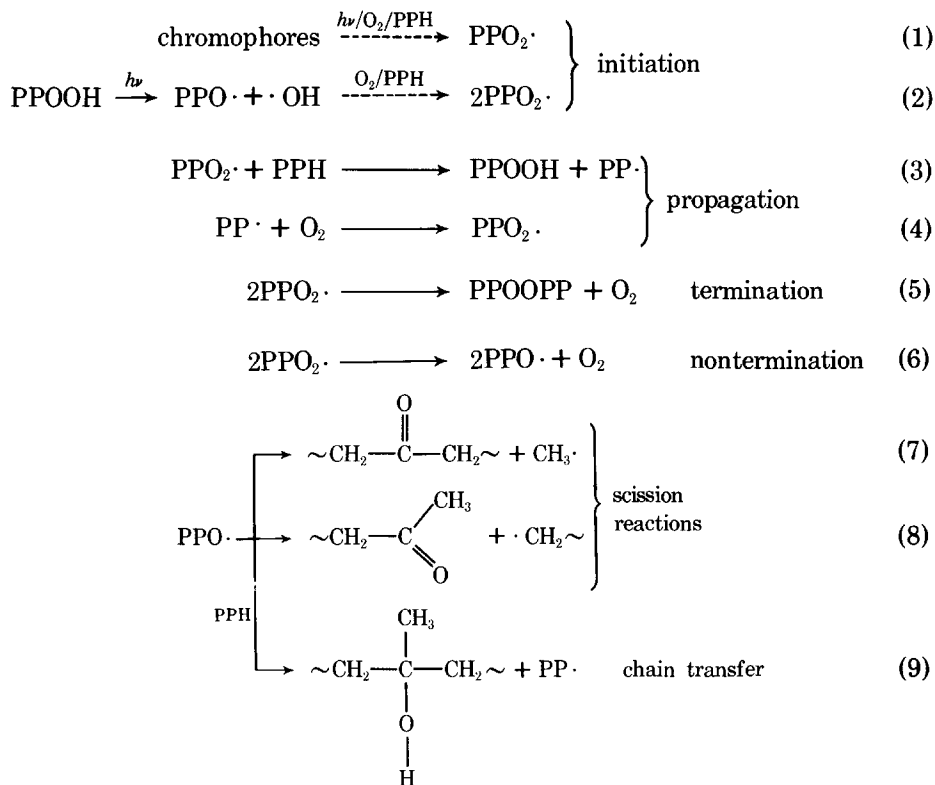
Synopsis

From a comparison of the photo- and γ-irradiation-initiated oxidations of monofilaments and films, polypropylene oxidation rates and product ratios were found to be independent of sample morphology and orientation. Filament sensitivity to photo-oxidation was, however, drastically affected by extrusion and draw conditions, photosensitivity increasing with increasing draw speed and decreasing draw temperature. Draw effects were minimized by the exclusion of oxygen, indicating that free radicals produced by backbone cleavage during draw react with oxygen to give chromophoric oxidation products. The most important product detectable after drawing was probably the polypropylene hydroperoxide. A phenolic antioxidant reduced hydroperoxide formation, although sufficient hydroperoxide was still produced to accelerate photodegradation as compared with a similarly stabilized undrawn filament. Melt oxidation within the extruder was concluded to be much more important than thermal oxidation of the extruded filament as it cooled on the spinline.

INTRODUCTION

Unstabilized polypropylene (PPH) fibers are known to be very susceptible to sunlight-initiated deterioration.[1] A catastrophic drop in elongation to break, together with a buildup of hydroperoxide and carbonyl oxidation products, has been reported after less than 100 hr of accelerated weathering by xenon arc irradiation in air.[2] Appreciable morphological and structural changes accompany photo-oxidation, with the fibrillar zones being apparently more resistant to photo-oxidative scission than the surrounding nonfibrillar matrix.[3]

The photo-oxidation of PPH films has received extensive study[4] and is believed to be described by reactions (1)–(9). During the early stages of photo-oxidation, initiation to give peroxy radicals $PPO_2\cdot$, reaction (1), is thought to be caused by traces of UV-absorbing impurities (chromophores) such as catalyst residues or oxidation products introduced during processing.[4,5] The nature and concentration of any oxidation products arising from processing must be a major factor in the weatherability of the resulting filament. The major product of photo-oxidation is the tertiary hydroperoxide (PPOOH) which is itself readily photolyzed to give free radicals that can propagate further oxidative chains, reaction (2);

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$$\text{chromophores} \xrightarrow{h\nu/O_2/PPH} PPO_2\cdot \left.\right\} \quad (1)$$

$$PPOOH \xrightarrow{h\nu} PPO\cdot + \cdot OH \xrightarrow{O_2/PPH} 2PPO_2\cdot \left.\right\} \text{initiation} \quad (2)$$

$$PPO_2\cdot + PPH \longrightarrow PPOOH + PP\cdot \left.\right\} \quad (3)$$

$$PP\cdot + O_2 \longrightarrow PPO_2\cdot \left.\right\} \text{propagation} \quad (4)$$

$$2PPO_2\cdot \longrightarrow PPOOPP + O_2 \quad \text{termination} \quad (5)$$

$$2PPO_2\cdot \longrightarrow 2PPO\cdot + O_2 \quad \text{nontermination} \quad (6)$$

$$PPO\cdot \begin{cases} \to \sim CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\sim + CH_3\cdot & (7) \\ \to \sim CH_2-C\overset{CH_3}{\underset{O}{\diagdown}} + \cdot CH_2\sim & (8) \\ \xrightarrow{PPH} \sim CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\overset{|}{O}\!\!\underset{|}{H}}{C}}-CH_2\sim + PP\cdot & (9) \end{cases}$$

scission reactions

chain transfer

The hydroperoxide produced during propagation, reaction (3), soon becomes the dominant source of free radicals for further initiation by process (2), and the photo-oxidation accelerates rapidly.[5] Production of free peroxy radicals from any initiator in PPH is, however, a relatively inefficient process because many radical–radical terminations, such as reaction (5), occur within the surrounding polymer cage. In fact, only about one in eight radicals escapes cage combination to take part in propagation reactions.[6] Initially, chain lengths for propagation of free $PPO_2\cdot$ may be 100 or more,[5,6] but this value decreases at higher oxidation levels where high radical concentrations make the termination reaction (5) proportionately more important.

The carbonyl and hydroxyl products result from reactions (7)–(9), involving the macro-alkoxy radicals from reaction (6). These reactions will become more important as photo-oxidation proceeds but do not generally account for more than 15 mole % of the oxidation products and unstabilized PPH films have a fivefold molar excess of PPOOH over $>C=O$ at brittle failure.[4,7] A commercial PPH monofilament has, however, been reported to photo-oxidize to predominantly carbonyl products.[2] It is unclear whether this anomaly results from morphological differences between fibers and films or from the presence of the phenolic stabilizer in the commercial fiber sample.[2]

An objective of the present work was then the clarification of the possible effects of sample morphology on the photo-oxidation mechanism of a series of additive-free, laboratory-extruded PPH monofilaments. A further objective was the determination of the stages of fiber production which are responsible for the photoinitiating oxidation products introduced by the thermal and me-

chanical processes involved in extrusion and orientation. This was achieved by the systematic variation of the extrusion and drawing conditions.

Industrial practice usually involves the inclusion of a phenolic antioxidant in the molten PPH to minimize melt degradation. The work discussed here was largely carried out without melt antioxidants because these additives cannot be extracted completely from the oriented filaments.[2] However, the usefulness of antioxidants in reducing the oxidation during the various steps of the production processes is also discussed.

EXPERIMENTAL

Monofilament Preparation

Unprocessed, commercial, additive-free, isotactic PPH (Monomer Polymer Labs) was used. Its intrinsic viscosity in decalin at 135°C was found to be 3.2 dl/g, indicating a molecular weight of about 400,000 (Mark–Houwink constants[8] $k = 1.0 \times 10^{-4}$, $a = 0.80$). Extrusion at 220°C with N_2 blanketing of the hopper (see below) was found to cause a 10% drop in intrinsic viscosity for an antioxidant-free melt. The titanium content of the polymer was found by x-ray fluorescence to be 79 ppm. Other PPH samples examined included the commercial 150-μm monofilament used previously (Amtech Inc. Ti content 10 ppm) which contained 0.24 wt-% of octadecyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionate[2] and a commercial film (Enjay, 25 μm, Ti content 80 ppm). Both were Soxhlet extracted with acetone for 48 hr and vacuum dried; this procedure gave an additive free film, but did not remove the phenol from the fiber.[2] Samples of the Amtech filament and the unprocessed additive-free polymer were also pressed into films in a nitrogen atmosphere.[7] UV spectroscopy confirmed that the stabilizer in the Amtech polymer could then be removed by acetone Soxhlet extraction. In one sample, 0.1 wt-% 2,4-di-*tert*-butylphenyl(4′-hydroxy-3′5′-di-*tert*-butylbenzoate) (Ciba-Geigy) was compounded with the additive-free polymer before extrusion to investigate its effectiveness as an antioxidant during filament production and as a UV stabilizer after various processing steps.

PPH monofilaments ranging from 50 to 200 μm in diameter were produced using a Maxwell-type screwless extruder (Fig. 1). A commercial laboratory-scale extruder (Custom Scientific Instruments) was used, although the barrel and header were redesigned to improve melt flow and minimize holdup in the barrel. A throughput of about 2 g/min was attained using a 0.125-cm-diameter, single-hole spinneret. Filaments were extruded into air (or nitrogen) and collected at known windup speeds of up to 40 m/min. Spinline tensions (0–5 g) were measured using a damped, top-loading balance (Sartorius 1106) equipped with suitable guides. The hopper used for storage of the polymer was water cooled and could be purged with a continuous flow of nitrogen to minimize degradation. When required, nitrogen blanketing of the spinline was achieved by extruding the filament directly through a narrow cylindrical manifold 60 cm long by 5 cm in diameter in contact with the spinneret face (Fig. 1). A continuous nitrogen flow maintained an atmosphere of <1.5% oxygen as measured by a paramagnetic oxygen analyzer (Taylor Servomex Ltd.). Solidification and cooling then took place virtually entirely in a nitrogen atmosphere. When investigating the effect of the absence of spinline N_2 blanketing, the enhanced cooling of the filament
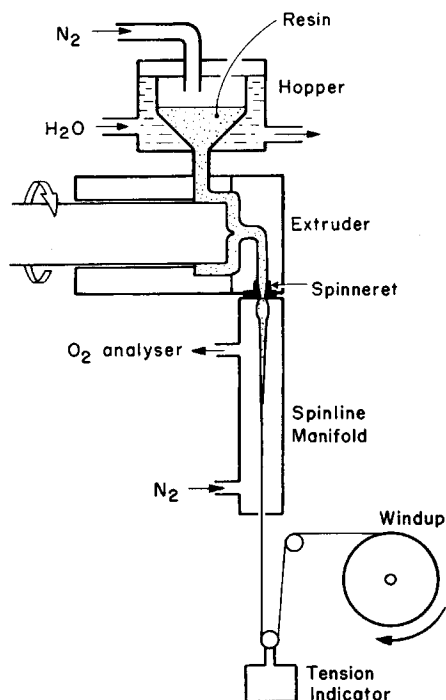
Fig. 1. Laboratory extrusion system. Modified Maxwell extruder, polymer holdup ~4 g.

produced by this continuous nitrogen flow was duplicated by a similar flow of air through the narrow manifold.

Off-line hot drawing normally took place by passage through an air oven at 180°C (30 cm in length), the draw ratio being determined by the relative speeds of the feed and take-up spools. Short lengths of filament (7 cm) were also drawn at known rates on an Instron mechanical tester (Model TTC) at 25°C. Similar samples were drawn under water at temperatures from 25° to 95°C on a Suter horizontal tensile tester, with a fixed draw speed of 12 in./min. Short lengths of filament were also drawn rapidly (~20 in./min) under high vacuum in attempts to eliminate the small amounts of oxidation that appeared to take place on drawing in air.

Photo-oxidation

Single short lengths of filament (4 cm) rigidly mounted on cardboard formers were irradiated in air in an Atlas Weather-Ometer, Model 6000 WR, fitted with a 6000-watt xenon arc lamp and borosilicate inner and outer filters. The Weather-Ometer was run at a constant 30% humidity and a 34°C silver panel temperature.

γ-Initiated Oxidations

Parallel arrays of selected monofilaments, mounted on cardboard frames[2] together with film samples for comaprison purposes, were irradiated in Gammacell 220 (Atomic Energy of Canada Ltd.) cobalt 60 sources at dose rates of 300 and 1000 rads/min. These dose rates are only nominal values because of vari-

ations with sample position in the cell. However, within any series at a given dose rate, that dose rate was constant. In the high dose rate cell, the sample compartment reached a temperature of 35°–40°C.

Monofilament Characterization

(i) Infrared (IR) spectra of monofilaments may be obtained by techniques described earlier.[9] Apart from γ-irradiated samples, all spectra reported here were obtained using the "single fiber" technique.[9] Each single monofilament sample was mounted securely on a small cardboard "picture frame" former during irradiation so that IR analysis at each irradiation time could be performed on precisely the same length of the filament. Only a 1-cm length of photo-oxidized fiber is examined by this procedure. The changes in the IR spectrum of PPH on photo-oxidation are well known.[4,7,10] An extinction coefficient of $70M^{-1}cm^{-1}$ was assigned to the 3400 cm^{-1} absorption band, which is largely due to hydroperoxide groups.[10] An average value of $300M^{-1}cm^{-1}$ was assigned to the composite carbonyl absorption centered at 1715 cm^{-1}.[10] Effective sample thicknesses were calculated from the C—H absorption at 2720 cm^{-1} which had been calibrated with a series of film and filament samples of known thickness.

(ii) X-Ray diffraction analysis of rotated single-fiber samples was carried out using Ni-filtered Cu$K\alpha$ radiation from a Philips x-ray source and a modified power camera.[3] The fiber lengths were rotated in a plane at 90° to the incoming x-ray beam to give a diffractogram which depended only on the crystalline/amorphous content of each fiber. The diffractograms were scanned with a Spex microdensitometer and digitized to permit subsequent data processing.

(iii) The tensile properties of the monofilaments were determined both to characterize the unoxidized filaments and to study the mechanical deterioration produced by photo- and γ-initiated oxidations. The Instron tensile testing machine was used to draw filaments in air at 25°C.

(iv) The total hydroperoxide content of the filaments was determined by a sensitive iodometric method.[5] Filament samples, up to 100 mg, were dissolved in peroxide-free decalin under vacuum by heating briefly (<1 min) to about 140°C and cooling rapidly. The resultant finely divided precipitate was accessible to the reducing medium of sodium iodide in acetic acid/isopropanol, enabling the hydroperoxide content of the whole fiber to be determined. After 5 min of refluxing, the reaction mixture was filtered through a coarse cellulose acetate filter to remove suspended polymer, and the liberated I_3^- determined spectrophotometrically at 360 nm. Separate experiments showed that the filtration process did not change the I_3^- concentration. To determine the extent of photo-oxidation that had occurred on a thin surface layer, whole (undissolved) samples were refluxed in the same manner. The access of the reagents into the hydrophobic monofilament is expected to be restricted to a surface layer a few microns in thickness.[2]

RESULTS

A Comparison of Fiber and Film Oxidative Behavior

Photo-oxidation has been shown to proceed at a rate dependent on the concentrations of UV-absorbing impurities present in the sample.[5] These con-
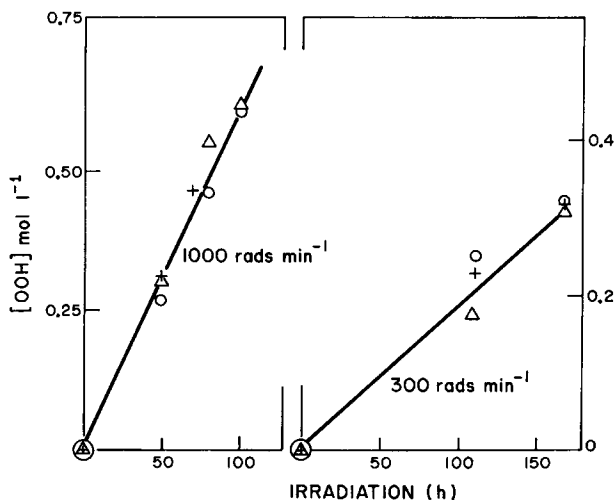
Fig. 2. γ-Initiated oxidation of PPH: (O) undrawn monofilament B4; (+) hot-drawn monofilament B1A; (Δ) film (Enjay).

centrations may vary appreciably with the processing conditions and so mask any effects of differing morphologies for a series of samples prepared under different processing conditions. Initiation of PPH oxidation by γ-radiation, however, occurs at random throughout the sample because of indiscriminate bond breaking. Propagation and termination reactions are thought to proceed in the same manner in both γ- and UV-initiated oxidations.[4,11]

Figure 2 shows that the γ-initiated oxidative behavior of two additive-free laboratory-extruded filaments (B1A and B4) and the commercial 25-μm film at dose rates of 300 and 1000 rads/min is independent of the nature of the sample. Only the hydroperoxide buildup is shown, but it was found that the carbonyl buildup was similarly independent of the nature of the sample. The yield of carbonyl products was always about 20 mole-% that of hydroperoxide, the proportion increasing slightly at high dose rates.

The structures of the two filaments, B1A and B4, were markedly different: B4 was an undrawn filament with low orientation and residual elongation of 1100%, and B1A was a highly oriented hot-drawn filament with a relatively low residual elongation (160%). The γ-oxidation data for other filaments between these two extremes are listed in Table I. With one exception, all were found to oxidize at very similar rates and to give similar product ratios. The only exception is the commercial filament, which contained an unextractable phenolic stabilizer, and was used previously.[2] This commercial filament yielded much less hydroperoxide than the additive-free filaments, with carbonyl products proportionally more important (Table I). Such behavior persisted even when the filament sample was pressed into a film (Table I). However, the oxidative behavior became identical to those of the additive-free film and fiber samples when the phenolic stabilizer was completely extracted (as shown by UV spectroscopy) from this film by Soxhlet extraction with acetone for 48 hr (Table I). (The resistance to extraction of additives in oriented fibers, as compared to unoriented film, presumably results from the rigid fibrillar structure of the oriented fiber.)

TABLE I
Gamma-Initiated Oxidations

Sample	Crystallinity %	Thickness μm	Initial residual elongation,[c] %	Oxidation product concn., M[a]	
				[OOH]	[$\diagdown$C=O]
Filament B1A[b]	51	113	160	0.41	0.081
Filament B2A[b]	56	112	380	0.40	0.093
Filament B3A[b]	49	116	500	0.35	0.079
Filament B4[b]	54	114	1100	0.39	0.090
Filament B4[b] (cold drawn 3×)	—	~75	210	0.38	0.063
Amtech 6-mil monofilament[d]	45	150	80	0.14	0.068
Unextracted Amtech film	—	~70	—	0.11	0.041
Extracted Amtech film[d]	—	~70	—	0.35	0.053
Additive free film[b,d]	—	~70	—	0.42	0.060
Enjay film[d]	~40[e]	25	—	0.43	0.093

[a] From IR data, 60 hr γ-irradiation at 1000 rads/min.

[b] From M.P.L. PPH stock.

[c] Drawn at 200%/min in air at 25°C.

[d] Acetone extracted for 48 hr and vacuum dried.

[e] Calculated from density measurements. Other crystallinities obtained from x-ray data (±5%).

From the data in Table I and Figure 2, it is obvious that the PPH monofilaments studied here all oxidize in the same manner, which in turn is very similar to that of PPH films. It should, however, be noted that these film and fiber samples, although widely different in degree of orientation and fibrillar content, all have similar x-ray crystallinities (Table I).

All of the filaments studied were below 150 μm in diameter; for diameters above 150 μm, oxidation rates decreased presumably as a result of diffusion-controlled access of O_2 for these thicker fibers.

Variation of Filament Production Conditions

In the absence of morphological effects, the photostability of PPH monofilaments will depend upon the concentration and distribution of UV-absorbing impurities within them. It has often been proposed that oxidation products introduced during processing are a major cause of photo-instability.[4] Production conditions were, therefore, varied to determine precisely at what stage this oxidation occurs and how it may be prevented.

PPH filament resistance to photo-oxidation should ideally be measured by the onset of brittle failure. However, the buildup of OOH and >C=O products as measured by IR spectroscopy can be correlated with the degradation of mechanical properties and is often used as a convenient nondestructive measure of deterioration. For example, brittle failure of films and fibers usually occurs when ~0.1M —OOH has accumulated. In this paper, [OOH] or [OOH] + [>C=O] buildup is used as the criterion of photosensitivity. The more UV-
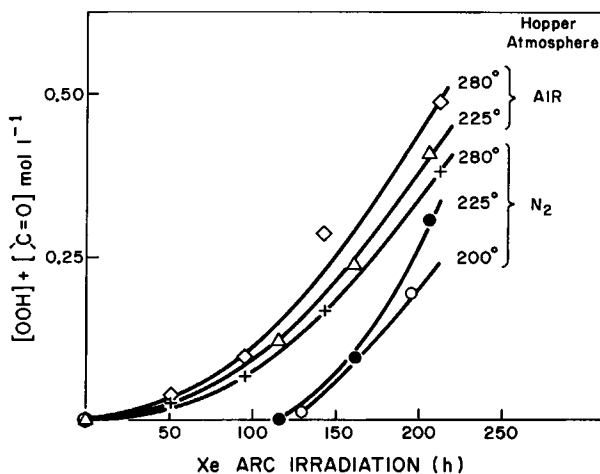
Fig. 3. Effect of extrusion temperature and hopper blanketing on PPH photostability. Filaments all extruded into air.

susceptible the sample, the more rapidly it will reach $\sim 0.1M$ —OOH. At high conversions ($>0.1M$), appreciable secondary photolysis and nonuniformity of photo-oxidation complicate photo-oxidations to the extent that rates of product formation at these conversions are difficult to compare.

Up to the brittle failure point of films or filaments, the $>C=O$ component from photo-oxidation accounts for $\sim 10\%$ of the total [OOH] + [$>C=O$] yield. After this point, the relative proportion of $>C=O$ rises, reaching $\sim 40\%$ of the total product yield at about twice the brittle failure irradiation time.

Extrusion Temperature. Figure 3 shows the photo-oxidative behavior of a series of filaments which had been prepared by extrusion at various temperatures into air. For each extrusion temperature, the photostability was significantly greater for the filament extruded with thorough nitrogen purging of the hopper. For the nitrogen-purged series, the photostability decreased appreciably with increasing header temperature. The remainder of this paper refers to filaments that were all produced with a nitrogen-blanketed hopper and a spinneret temperature of 225°C. Even with apparently identical extrusion conditions, filament photostabilities were not entirely reproducible between different batches, presumably owing to differing amounts of trace oxidation during extrusion.

Nitrogen Blanketing of the Spinline. When molten polypropylene is extruded into air, appreciable oxidation may take place as the sample cools. Several samples were, therefore, extruded into a nitrogen atmosphere ($<1.5\%$ oxygen). The filament take-up speed and hence cooling rate was also varied.[12] As is seen in Figure 4, at a fixed extrusion temperature, none of these changes appreciably affected the filament photostability.

Filament Drawing. During the early stages of the investigation, it was observed that the hot-drawn filaments photo-oxidized appreciably faster than their undrawn "parents." This behavior is illustrated in Figure 5, which shows the photo-oxidative behavior of a 120-μm filament drawn 300% through an air oven at 180°C. A reference sample received identical thermal treatment (~ 8 sec residence time) in a 180°C hot air oven but was not drawn. A more detailed investigation of draw behavior was, therefore, undertaken.
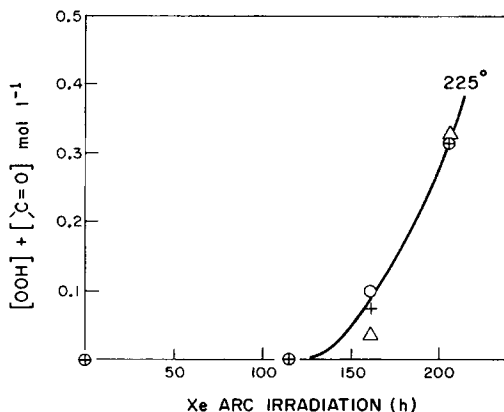
Fig. 4. Effect of windup speed and spinline blanketing on PPH photostability. Extruder header temperature 225°C: (+) extrusion into air, slow windup (20 cm/sec); (O) extrusion into air, fast windup (50 cm/sec); (△) extrusion into N_2, medium windup (30 cm/sec).
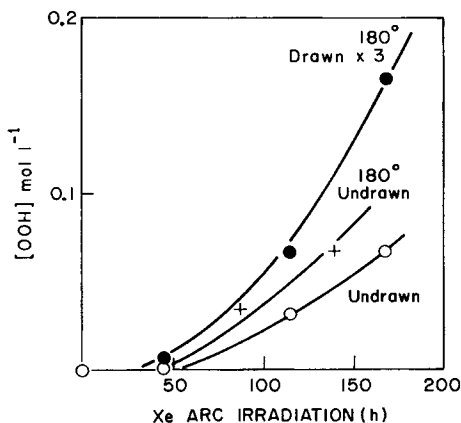

Fig. 5. Effect of hot drawing on PPH photostability: (O) undrawn monofilament; (+) undrawn, but oven treated (8 sec at 180°); (●) drawn ×3 at 180°C, residence time ~8 sec.

For filament samples all drawn 300% at 12 in./min in a water bath at various fixed temperatures, photostability was found to decrease dramatically as the bath temperature was lowered (Fig. 6). Furthermore, for a series of filaments all drawn in air at 25°C on an Instron mechanical tester (Fig. 7), increased drawing speed produced a large decrease in photostability.

To investigate whether the decrease in photostability on drawing was associated with changing fiber structure (fibrillar content, voiding, etc.) produced under different draw conditions or with trace oxidation during the draw, several samples were drawn in the absence of oxygen. The filaments shown in Figure 8 were drawn at similar rates, and so morphological effects such as voiding will be identical. The filaments drawn under vacuum were more stable than the air-drawn filament, but were still slightly less photostable than their undrawn parent. Trace oxidation would be lower for the vacuum-drawn filament since it was preevacuated for 12 hr prior to drawing to reduced O_2 in the polymer and held under high vacuum for 12 hr after drawing to allow for complete decay of any
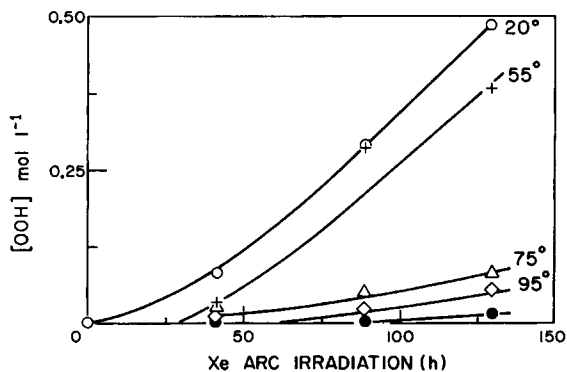
Fig. 6. Effect of drawing temperature on PPH photostability: (●) undrawn monofilament. Filaments drawn 3× at 12 in./min at 20°C (○), 55°C (+), 75°C (△), and 95°C (◇).
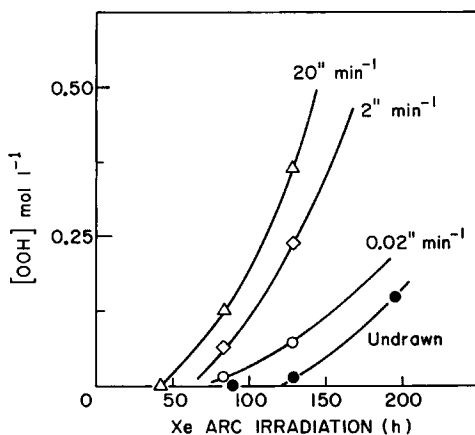

Fig. 7. Effect of draw speed on PPH photostability: (●) undrawn filament. Filaments drawn 3× in air at 25°C with draw speeds of 0.02 in./min (○), 2 in./min (◇), and 20 in./min (△).
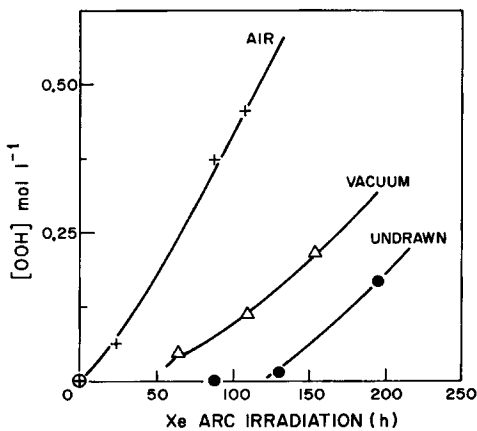

Fig. 8. Effect of drawing atmosphere on PPH photostability. Filaments drawn 3× at ~20 in./min at 25°C in air (+) and under vacuum (△).

radicals before exposure to air. The difference between the vacuum-drawn and the undrawn filaments, therefore, represents either an upper limit of possible morphological effects or the effect of traces of oxygen not completely removed from the filament. The difference between the vacuum-drawn and the air-drawn filaments must then be caused solely by oxidation during the draw step.

Further evidence for the unimportance of morphological effects is provided by the γ-oxidative behavior of a filament cold drawn in air. Such a filament was very susceptible to photo-oxidation (Fig. 8), but on exposure to γ-radiation yielded hydroperoxide levels very similar to those from the other γ-oxidized film and filament samples (Table I). In fact, the widely differing unstabilized samples shown in Table I all have identical γ-oxidation behavior.

The hydroperoxide levels of unirradiated filaments can be determined by iodometric analysis. Laboratory-extruded and commercial filaments contained $<1 \times 10^{-4}M$ hydroperoxide (the detection limit of the technique) before cold drawing, whereas a filament cold drawn in air contained $1.1 \times 10^{-3}M$ hydroperoxide. Such a concentration of extremely photosensitive hydroperoxide chromophores is obviously the origin of the subsequent rapid photo-oxidation. The hydroperoxide buildup from photo-oxidation of the cold-drawn filament followed a half-order dependence when plotted against the irradiation time,[13] with the intercept coinciding with the initial hydroperoxide level. This is consistent with a simple kinetic analysis of the early stages of photo-oxidation, based on the assumption that hydroperoxide photolysis is the dominant source of photoinitiation.[5]

The incorporation of a phenolic stabilizer, 2,4-di-*tert*-butylphenyl(4'-hydroxy-3',5'-di-*tert*-butylbenzoate), into the filament by compounding and extrusion was only partially effective in reducing oxidation during drawing. The hydroperoxide level of a cold-drawn filament was reduced from $\sim 1 \times 10^{-3}M$ (stabilizer free) to $3 \times 10^{-4}M$ (0.1 wt% of the phenol). However, even this level of draw-induced oxidation accelerated the photo-oxidation to such an extent that after 200 hr of irradiation in the xenon arc, the stabilizer had been consumed as evidenced by the loss of its characteristic IR absorbances, and the hydroperoxide level had reached $4 \times 10^{-2}M$. An undrawn filament, also containing 0.1 wt % of this phenol, suffered no observable decrease in stabilizer concentration, and the oxidation product concentration did not reach IR-detectable levels ($<5 \times 10^{-3}M$) within this 200-hr irradiation period.

Photo-oxidative Deterioration of Mechanical Properties

Large decreases in elongation at break were observed for all monofilaments before the oxidation products reached infrared-detectable levels (cf Figs. 5 and 9). In all cases, the load at break dropped less dramatically than the residual elongation. For example, after 40 hr of irradiation, the undrawn filament suffered a 30% loss in load at break while the hot drawn filament remained approximately unaltered.

Hot-drawn samples showed the greatest resistance to deterioration in mechanical properties by γ-irradiation. After 170 hr of γ-irradiation at 300 rads/min, the highly drawn filament B1A (initial elongation 160% at 200%/min) showed the greatest residual elongation of all of the similarly γ-irradiated fiber samples tested (35% at 100%/min).
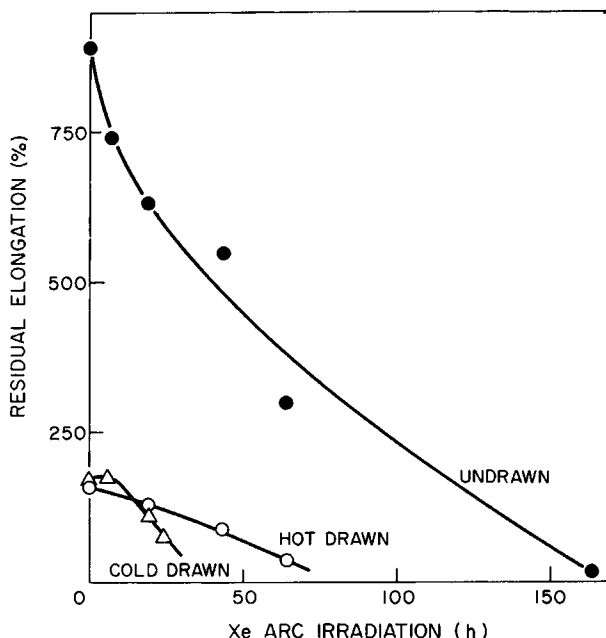
Fig. 9. Effect of photo-oxidation on monofilament residual elongation. Residual elongation to break at 200%/min at 25°C in air: (●) undrawn monofilament; (O) 5× hot-drawn filament at 180°C, residence time ~5 sec; (△) cold-drawn 3× (20 in./min at 25°C.)

DISCUSSION

The Absence of Morphology Dependence

The anomalous behavior reported earlier[2] for the Amtech filament and re-produced here (Table I) is clearly due to the presence of a phenolic stabilizer. However, it is perhaps surprising that little difference was observed in γ-oxidative behavior over such a wide range of films and filaments (Table I, Fig. 2). The orientation process, with its associated conversion from microspherulitic into microfibrillar morphology, might be expected to alter either the amount of polymer penetrated by oxygen, or the overall O_2 permeability of the PPH sample, or possibly the reactivity of the polymer, or a combination of all three. These effects will be discussed separately.

(a) At least during the early stages, γ-initiated oxidation and photo-oxidation are thought to occur solely in the oxygen-permeable, amorphous component of a semicrystalline polymer.[14,15] Sample crystallinities could, therefore, play a part in photostability. Atactic (noncrystalline) polypropylene has, however, been reported to yield only about 15% more hydroperoxide on γ-irradiation than a highly crystalline isotactic sample,[16] and so the magnitude of this effect is likely to be small. Moreover, the samples discussed here have similar overall crys-tallinities (Table I).

(b) Orientation has been suggested[17] to decrease O_2 permeability of polymers by possibly decreasing the amorphous content at the expense of the largely im-permeable crystalline zones, by increasing the tortuosity of the path followed by a diffusant, and by increasing the resistance of amorphous material to mo-lecular motions necessary to provide holes through which a gas molecule might

pass. All three effects could reduce the O_2 permeability through highly oriented filaments to such a level that O_2 depletion occurs in the bulk of the oxidizing sample. Below a critical O_2 concentration in the polymer, both the γ- and photo-initiated oxidations must then become oxygen concentration dependent and the oxidation, diffusion controlled. Peterlin[18] has shown that drawn (>8X) polyethylene is two orders of magnitude less permeable to methylene chloride vapor than polyethylene of below 4X draw. However, the data of Connor and Schertz[17] for PPH film indicates only a twofold decrease in O_2 permeability for a large increase in orientation (corresponding to a fivefold increase in tensile strength). Our own data (Table I and Fig. 2) imply that the γ-oxidation is not O_2 diffusion controlled at the highest dose rate used (1000 rads/min) because thin films and relatively thick fibers oxidize at identical rates. Furthermore, the rate of O_2 consumption at 1000 rads/min from Figure 2 is $\sim 1.7 \times 10^{-6} M$/sec, which should lead to only about a 10% reduction in O_2 concentration in the center of 100-μm fibers, assuming a permeability[17] of 1.7×10^{-10} cm^2/sec· (cm Hg). Thus, it would appear that orientation does not cause a drastic decrease in PPH oxygen permeability, perhaps because of the compensating formation of partially permeable crystalline regions as suggested by Vieth and Wuerth[19] or because of microvoid formation opening up the structure.

(c) Different components of the amorphous phase may have differing susceptibilities to photo-oxidation. Previously, it has been argued that highly strained tie molecules may be especially susceptible.[3] However, within the range of samples chosen, this effect is apparently unimportant.

Extrusion Conditions

The data presented in Figures 3 and 4 indicate that under our extrusion conditions, oxidation *within* the extruder is largely responsible for the traces of oxidation products present in the extruded undrawn filaments. `A typical filament contained about $1 \times 10^{-4} M$ hydroperoxide, but differences in hydroperoxide levels between filaments could not be reliably determined at this level. The order of photostabilities was, however, consistent with the extent of oxidation anticipated within the extruder. Raising the extruder temperature lowered the photostability, as did omission of hopper blanketing. This behavior is consistent with an earlier study by Burch on PPH extrusion stability.[20] Burch observed that the melt index increased appreciably with increasing extrusion temperature and also when the hopper atmosphere contained >3% oxygen.

Extrusion into either nitrogen or air had little effect on the filament properties, nor did the enhanced cooling produced by a faster windup rate. Presumably, after the melt emerges from the spinneret, cooling is sufficiently rapid that there is little opportunity for significant oxidation to occur.

Drawing Conditions

It is obvious from Figures 5–9 that drawing, particularly at high rates or low temperatures, reduces photostability. This must be largely due to oxidation occurring during the draw to give chromophores and not morphological or structural changes as is shown in Figure 8 and Table I. Thermal oxidation at high drawing temperatures cannot account for this effect. In fact, thermal treatment alone, without draw, failed to appreciably reduce photostability (Fig.

5). This thermal treatment was more severe than that received during hot drawing, where the filament accelerated out of the oven. The decrease in photostability with *decreasing* draw temperature also indicates that thermally induced oxidation is unimportant.

Oxidation is more likely to result from free radicals produced by bond rupture on drawing the polymer. Radical production by mechanical strain has been directly observed when polymers were crushed at liquid nitrogen temperatures.[21] More recently, strain-induced free radicals have been observed at room temperature, usually by ESR, for a wide range of polymers.[22,23] These radicals will be rapidly scavenged by oxygen, and the resultant peroxy radicals may then initiate oxidation conventionally. Oxidation products produced in this way should be randomly distributed across the fiber cross section and so should be especially effective in initiating further photo-oxidation as compared to the same quantity of radicals in localized zones. The experimentally observed photo-oxidation kinetics of cold-drawn filaments are, in fact, consistent with uniformly distributed —OOH groups from the draw process.[13]

In contrast, the photo-oxidation of PPH films has earlier been shown to occur in a surface layer a few microns thick, reputedly caused by an initial concentration of UV-absorbing impurities in this layer.[7] There is some evidence that the situation is similar in a commercial stabilized PPH monofilament.[2] Concentration of the chromophores and the resulting radicals in a surface layer lead to a reduction in the local kinetic chain length of the propagation reaction as compared to the same number of radicals spread uniformly throughout the total sample volume.

The sensitizing effects of draw at low temperatures and/or high strain rates (Fig. 6 and 7) probably result from the greater radical yield under these conditions as compared to high temperatures and/or low strain rates. The latter conditions will aid interchain slippage and unpleating of folds, rather than backbone fracture to give reactive macro-alkyl radicals.

Photo-oxidative Deterioration of Mechanical Properties

The cold-drawn filament with its high rate of photo-oxidation may be seen to be the most rapidly deteriorating (Fig. 9); however, comparing Figure 5 and Figure 9, it can be seen that for a constant degree of oxidation (e.g., $0.02M$ — OOH), the undrawn filament suffered the greater proportional loss of residual elongation. Highly drawn filaments, which are fibrillar, are therefore more resistant to photo-oxidative deterioration than undrawn filaments (microcrystalline). This behavior is consistent with an earlier study where surface cracking was reported during the photo-oxidation of a commercial filament.[3] Only during the later stages of photo-oxidation, long after the filament had become mechanically useless, did cracking occur in the fibrillar component. In an undrawn filament, no such fibrillar reinforcements are available and crack propagation can occur at low levels of oxidation.

Antioxidants and Processing Oxidation

Oxidation during the various stages of production will be important even for stabilized filaments. Few stabilizers can be completely effective in preventing

oxidation during extrusion and drawing, and even a relatively small increase in the oxidation product concentration makes it much harder for any photostabilizer to function effectively because of the increased rate of free-radical production. Clearly, the most effective stabilizers will be those that rapidly scavenge the radicals produced during processing, or those that cleanly decompose the hydroperoxide during storage.[5,24] Many conventional antioxidants such as the hindered phenols will reduce oxidation during the production stages but are poor photostabilizers apparently because they themselves tend to be photolyzed.[24]

This deficiency can obviously be overcome by a combination of an antioxidant and a conventional photostabilizer, such as a nickel chelate. However, the fact that photo-oxidations can be prevented by free-radical scavenging, as can the thermal processes, implies that processing oxidation and photodegradation may be suppressed by the use of light-stable phenolic stabilizers.[5,24]

CONCLUSIONS

1. Over the range of samples tested, films and filaments γ-and photo-oxidize in an identical manner, but the concentration of UV-absorbing impurities responsible for initiating photo-oxidation will vary with the production conditions.

2. Oxidation during extrusion is minimized by removal of oxygen from the polymer feed and a relatively low extruder temperature, whereas nitrogen blanketing of the spinline is found to have little effect.

3. Free-radical production by bond rupture occurs during the draw stage and is most marked at high draw rates and low draw temperatures.

4. Oxidation products resulting from bond breaking during the draw process markedly reduce the photo-oxidative stability of the filament.

5. The formation of UV-absorbing chromophores by oxidation during drawing is reduced by the presence of a phenolic radical scavenger, but not completely suppressed.

6. Chromophore formation during PPH deformation even in the presence of radical scavengers should lead to premature failure of PPH articles at strained points, or points briefly deformed during their lifetime, e.g., knots, tight loops, hinge points, impact zones, etc. This effect will be minimized if the residual elongation in PPH materials is designed to be as low as possible.

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