

Demonstration of the Possible Competing Effects of Oxidation and Chain Scission in Orientated and Stressed Polypropylenes

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SYNOPSIS

A series of orientated polypropylene tapes and filaments with differing draw ratio were produced from two parent polymers containing antioxidant systems of different efficiencies. Lengths of tapes and filaments were exposed in air ovens at temperatures up to 130°C under "free" conditions, held at constant length or loaded to differing stress levels for prescribed times or to failure, whichever was earlier. Those morphological effects of oven ageing treatments as are identified from their subsequent tensile behaviors and densities have been reported elsewhere; this study reports the heat flux differential scanning calorimetric (HF-DSC) observations of unexposed and exposed samples. The HF-DSC curves of treated samples show, for the postfusion oxidative exotherm for oven-exposed samples, positive shifts to lower values compared with an unexposed sample, of the extrapolated onset temperature (T_{on}). Analyses of the tensile, density, and HF-DSC data suggest that during the initial stages of thermal degradation in air, chain scission competes with oxidation. The rates of the former are enhanced by the application of stress, and scission is considered the origin of the observed deterioration in tensile behavior. Concurrent oxidation during oven exposures affects subsequent autoxidative behavior but has little immediate influence upon the mechanical properties. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermal degradation of polypropylene in air involves oxidation of the main polymer chain, which can lead to both scission and non-scission-based attacks.¹ Both reactions are considered to occur following radical initiated formation of peroxy radical and hydroperoxide moieties on the propylene tertiary carbon atom.

The addition of both primary (often hindered phenol derivatives) and secondary (usually an organic phosphite) antioxidants, which, respectively, attack these initiated sites, prevents their promoting further polymer chain degradation.²

Rapport and co-workers³ have shown that when orientated polypropylene films are oxidized under

stress, competition between oxidative nonchain scission, chain scission, and mechanically induced chain rupture exists. At low stresses, the times to failure when exposed to elevated temperature in air are independent of stress, thereby suggesting the dominance of oxidative nonchain scission reactions. However, at higher applied stresses (>0.035 GPa), the times to failure decrease, which suggests that oxidative chain scission reactions determine the overall polymer degradation. At even higher stresses oriented film durability becomes independent of the presence of oxygen, and so mechanically induced chain scission was considered to be the dominant mechanism. The concept of a "safe stress" range above which an orientated polypropylene must not be loaded has been suggested⁴ and corroborated^{5,6} by a number of authors, including ourselves.⁷ In this last study, the influence of applied tensile loads on orientated polymer durabilities during exposure to temperatures up to 130°C in air for periods less than

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the respective sample induction times for failure was investigated by measuring changes in tensile behaviors and densities of aged tapes and filaments. It was concluded that application of stress reduces times to failure and that stress sensitivity may depend on the antioxidant type and its efficiency.

This study describes the application of heat flux differential scanning calorimetry (HF-DSC) to those unaged and aged orientated polypropylene tapes previously described.⁷ It has been shown previously⁸⁻¹⁰ that oxidation of hydrocarbons generally may promote changes in thermoanalytical behavior. In particular, for polyolefins, shifts in the postfusion oxidative exotherm to lower temperatures have been identified by both HF-DSC^{8,10} and thermogravimetric¹¹ studies. The latter work in particular has also shown that techniques such as infrared spectrophotometry are unable to identify typical oxidation products such as carbonyl compounds during the prefailure stages of degradation and that thermoanalytical observations provide more sensitive procedures for identifying the presence of oxidized species generated during the induction period.

EXPERIMENTAL AND RESULTS

Filament and Tape Production

The production of a series of experimental tapes and filaments extruded from two polymer samples P1 (GYE 41, ICI Propathene) and P2 (GWE 26, ICI Propathene) with different melt flow indices and antioxidant systems has been described fully elsewhere.^{7,12} Table I summarizes the original characteristics of tapes and filaments selected for this current study.

Hot-Air Exposure Conditions

Filament and tape samples were oven-aged in a manner already described^{7,12} and that involved exposure to temperatures within the range 90–130°C under freely suspended, restrained (constant length), and positively loaded conditions for times up to maximum values below the respective induction periods for failure. All these samples were studied by HF-DSC and, because those exposed at 90 and 110°C showed little change in their thermal responses,¹² only the effects of 130°C exposure are reported here.

Table II summarizes the ageing conditions and maximum exposure times where the loadings applied to both the 4 : 1 and 8 : 1 drawn samples are expressed as a percentage of their respective breaking loads at 130°C and henceforth termed percentage (%) stress.⁷

Heat Flux Differential Scanning Calorimetry

HF-DSC was undertaken using a Stanton Redcroft 671 B thermal analyzer at 10 K/min⁻¹ in static air. Specimen masses of 0.75 mg were contained in open aluminum crucibles (5 mm dia. × 2.5 mm depth) and for each unexposed and exposed filament or tape sample two specimens were studied.

Typical records of the HF-DSC curves for unexposed, freely suspended, and stressed samples of both P1 and P2 8 : 1 drawn filaments are shown in Figures 1 and 2, respectively. The observed curves are similar for both filaments and tapes at each draw ratio. Each recorded observation shows a structured melting endotherm with defined shoulders and peaks within the temperature range 155–172°C followed by an intense postfusion exotherm. The latter is as-

Table I Raw Materials and Products

Polymer	MFI ^a g/10 min, 230°C, 2.16 kg	Antioxidant ^b	Product ^c Form	Draw ^d Ratio	Linear Density Tex
P1	12	Irganox 1330 Irgafos 168	Filament	4:1	7.25
				8:1	7.00
P2	3	Irganox 1010 Irgafos 168	Filament	4:1	6.80
				8:1	7.00
			Tape	4:1	93.0
				8:1	96.0

^a Melt flow index.

^b Analyses of the antioxidant formulations are presented in Ref. 7, Table 1.

^c Filaments were produced to have a nominal linear density of 7 tex and the tape dimensions were 2.5 mm × 50 μm.

^d The values presented are nominal draw ratios, see Ref. 7.

Table II. Filament and Tape Exposure Conditions in Hot Air at 130°C

Polymer	Form	Condition	Maximum Exposure Time, Days
P1	Filaments	Freely suspended	20
		Restrained	20
		10% stress	27
		15% stress	27
P2	Filaments	Freely suspended	7
		Restrained	7
		10% stress	7
	Tapes	Fully suspended	10
		Restrained	10
		10% stress	10

sociated with both air oxidation and autoxidation of the polypropylene chain as demonstrated in previous studies.⁹⁻¹¹ The temperature identified at the onset of the oxidation exotherm, T_{on} , which is considered to depend on the degree of oxidative deg-

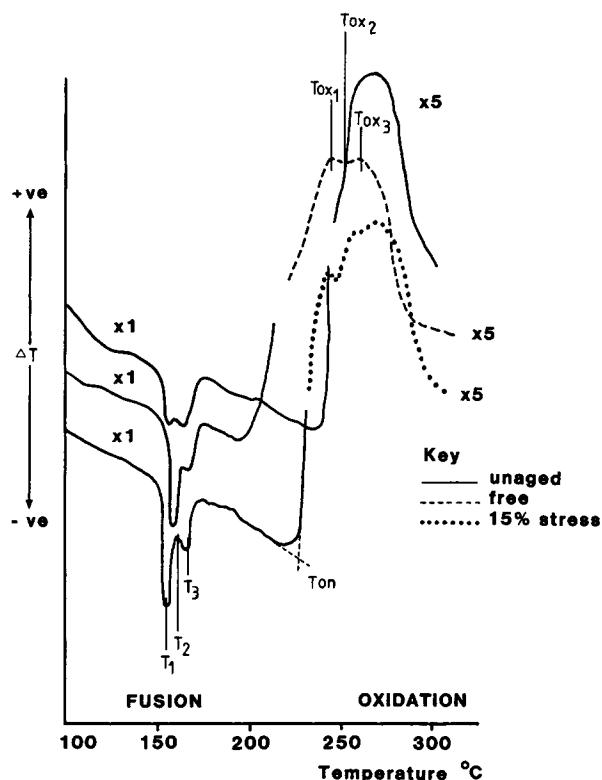


Figure 1 Recorded curves HF-DSC for P1 filaments having 8 : 1 draw ratio and before and after oven-ageing at 130°C under unloaded and loaded conditions (heating rate 10 K min⁻¹; open Al pans in air).

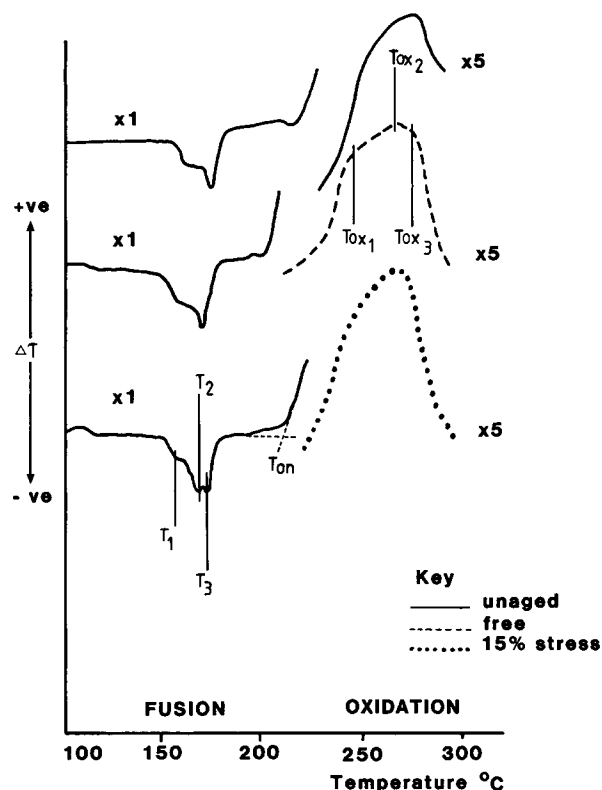


Figure 2 Recorded curves HF-DSC for P2 filaments having 8 : 1 draw ratio and before and after oven-ageing at 130°C under unloaded and loaded conditions (heating rate 10 K min⁻¹; open Al pans in air).

radation present within the filaments and tapes, may be measured at the point of intersection of the constructed tangents as shown in Figures 1 and 2. The detailed structure of the postfusion oxidative exotherms may be identified in terms of location temperatures for up to four combinations of shoulders and peaks, designated T_{ox1}, \dots, T_{ox4} at respective inflexion points or maxima. Table III presents a full description of the observed HF-DSC curve features for both unexposed and exposed P1 filaments.

The effects of a heat exposure under either free or stressed conditions produce no systematic changes in fusion endotherm characteristics or shoulder and peak temperatures within the post-fusion exotherm. The only consistent shift in the transition location following heat exposure is a shift to lower temperature of the exotherm onset T_{on} illustrated graphically in Figures 3 and 4 for P1 filaments having nominal draw ratios of 4 : 1 and 8 : 1, respectively.

Similar behaviors were observed for the HF-DSC curves from unexposed and exposed P2 filaments and tapes, and Table IV presents the collated results

Table III Thermal Transitions Identified from HF-DSC Responses for P1 Filaments Exposed at 130°C

Ageing Times, Days	Ageing ^a Condition	Nominal Draw Ratio	Melting Endotherms, ^b °C			Oxidation Exotherms, ^b °C				
			T_1	T_2	T_3	T_{on}	T_{ox_1}	T_{ox_2}	T_{ox_3}	T_{ox_4}
0	U	4:1	159	162	164	246	276	283		
5	F	4:1	159	160 ^(s)	164	234	241	273		
5	R	4:1	—	163	168	249	278	283		
5	15% stress	4:1	159	—	164 ^(s)	234	271	290		
10	F	4:1	157	161	164	225	240	245	270	
10	R	4:1	160	163	—	240	244	265	—	
10	15% stress	4:1	159	164	160	233	270	—	—	
20	F	4:1	158	162 ^(s)	164	212	240	245	268	
20	R	4:1	159	161	166	235	270	—	—	
20	15% stress	4:1	157	164 ^(s)	167	232	244	254	271	
27	10% stress	4:1	—	163	172	234	267	—	—	
27	15% stress	4:1	—	164	169	232	246 ^(s)	271	—	
0	U	8:1	157	164 ^(s)	167	241	276	—	—	
5	F	8:1	156	158	165	220	268	—	—	
5	R	8:1	155	157	165	230	268	267	290 ^(s)	
5	15% stress	8:1	157 ^(s)	159	164	234	249	268	278 ^(s)	
10	F	8:1	157	163	166	210	263	—	—	
10	R	8:1	156	161	166	230	268	275	—	
10	15% stress	8:1	157	162	—	231	247	265 ^(s)	274 ^(s)	
20	F	8:1	157	164	167 ^(s)	204	246	249	259	
20	R	8:1	157	166 ^(s)	167	230	249	268	—	
20	15% stress	8:1	158	165 ^(s)	169	229	246	261	265	271
27	10% stress	8:1	—	162	164	237	276	—	—	—
27	15% stress	8:1	—	162	169	239	250	271	—	—

^a U, unexposed filaments; F, freely suspended exposed filaments; R, restrained exposed filaments; 10% stress, filaments exposed under 10% of breaking load; 15% stress, filaments exposed under 15% of breaking load.

^b T_1 , T_2 , T_3 represent temperatures at which shoulder inflexions (s) or minima are observed. T_{on} is the extrapolated temperature of onset of postfusion exothermic oxidation. T_{ox_1} to T_{ox_4} represent temperatures at which shoulder inflexions (s) or maxima are observed.

for their respective indicated onset temperatures for the oxidation T_{on} . Samples were removed after intermediate exposure periods of days up to the respective maximum exposure period with the exception of P2 tapes, which were sampled after only a 3-h initial exposure in order to determine whether the observed rapid increase in density-derived crystallinity (annealing) are reflected in HF-DSC curve behavior.⁷

DISCUSSION

Analysis of the thermoanalytical results presented here can only be made in association with the con-

clusions drawn in the first part of this work.⁷ These latter demonstrated that while the monitoring of tensile properties of exposed filaments and tapes did not provide a very sensitive means for monitoring the presence of thermal degradation prior to specimen failure, increases in the loading for the 130°C exposure does reduce times to failure. In addition, times to failure and maximum sustainable stress levels were dependent on the contained antioxidant type and its concentration. Of particular note was the negligible change in the observed tensile properties following the thermal degradation observed in P1 filaments prior to their failure. This contrasted with the progressive reduction in tensile properties of both the P2 8 : 1 draw ratio filament and tape

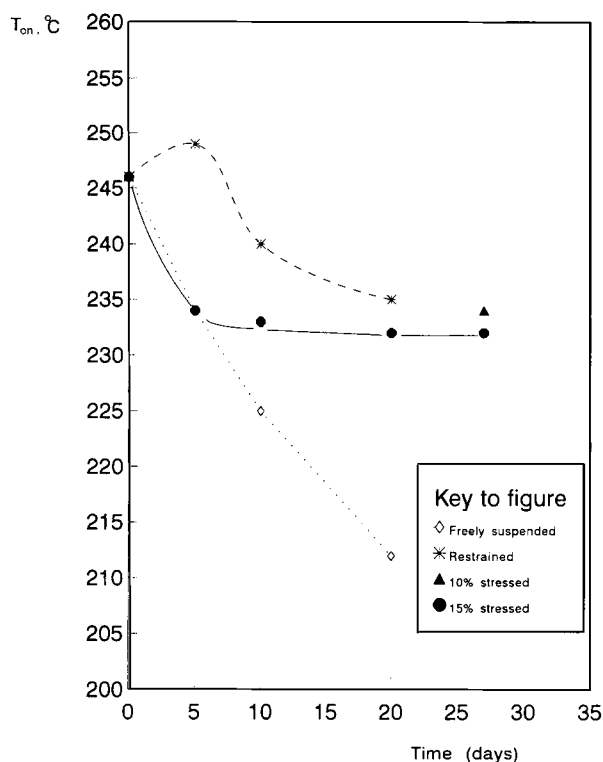


Figure 3 Effect of exposure time on HF-DSC-derived T_{on} transition temperatures for P1 filaments (draw ratio 4 : 1) exposed at 130°C.

samples prior to their failure after much shorter exposure times (see Table 2 in Ref. 7).

It is relevant, therefore, to compare these earlier results with the exposure time dependencies of T_{on} presented in Figures 3 and 4 and Tables III and IV. The more highly stabilized P1 filaments show higher values of T_{on} before and after exposure than P2 filaments and tapes. In addition, the former experience large shifts in T_{on} to lower temperatures when exposed in the free condition with the greatest effect shown by 8 : 1 drawn filaments. Application of stress, both by restraining and by directly loading the specimens, reduces the magnitude of these shifts, especially after a 5-day exposure. Except for the 27-day exposed 8 : 1 drawn filament loaded at 10 and 15% of ultimate breaking load, an approximate asymptotic trend for T_{on} is observed as filaments approach their respective times to failure. It is clear from the reductions in T_{on} that oxidation is occurring during oven exposure and that this may be greater in the lower draw ratio samples, which would possess an anticipated greater oxygen radical diffusivity^{3,13,14} as a consequence of their more limited anisotropic character. For this statement to be true it must be assumed that degrees of crystallinity and hence ef-

fective antioxidant concentrations in amorphous regions in both 4 : 1 and 8 : 1 drawn samples are the same. Comparison of density data in Figures 2 and 3 in our previous study⁷ confirms that crystallinities are indeed, within error, similar.

However, that this oxidation may not result in significant chain scission reactions is suggested by the unchanged tensile properties during exposure, although at the highest applied loading levels (15%) the time to failure is significantly reduced (see Table 2 in Ref. 7).

For the P2 filaments and tapes when exposed under high loads the converse situation to the above exists, particularly for 8 : 1 drawn samples where large reductions in tensile performance are accompanied by small shifts in T_{on} to lower temperatures. This trend is similar to that seen for P1 filaments in that results in Table IV for P2 filaments indicate that the magnitude of any time-dependent shifts in T_{on} is reduced when specimens are loaded. The thermal oxidative behavior of P2 tapes is more complex and no simple trends are recognized, except that a short-term exposure (3 h) produces an increase in T_{on} that rises concurrently with the magnitude of the applied load. If T_{on} values are compared following

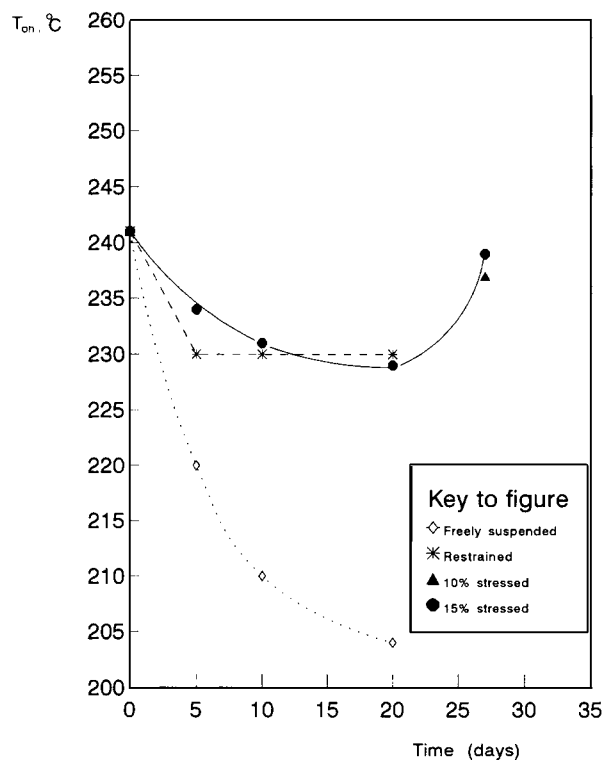


Figure 4 Effect of exposure time on HF-DSC-derived T_{on} transition temperatures for P1 filaments (draw ratio 8 : 1) exposed at 130°C.

Table IV Extrapolated Temperatures of Onset, T_{on} , of Oxidation Exotherms Observed by HF-DSC at 10 K min^{-1} in Air for P2 Filaments and Tapes Exposed at 130°C

Exposure Conditions	Time, days	$T_{on}, ^\circ\text{C}$			
		Filaments		Tapes	
		4:1	8:1	4:1	8:1
Unexposed	0	214	214	213	214
Freely suspended	0.125	—	—	219	215
	1	217	207	218	217
	5	208	202	213	212
	7	204	209	—	—
	10	—	—	209	205
Restrained	0.125	—	—	213	217
	1	209	209	209	215
	5	210	212	204	194
	7	212	212	—	—
	10	—	—	—	183
10% stress	0.125	—	—	217	220
	1	214	210	219	221
	5	202	212	219	219
	7	202	^a	—	—
	10	—	—	225	215
15% stress	0.125	—	—	222	219
	1	—	—	216	212
	5	—	—	207	209
	10	—	—	^a	^a

^a Samples broke after 5 days exposure.

longer exposures, then their shift to lower temperatures for both 4 : 1 and 8 : 1 drawn tapes is significant for both the freely suspended and restrained samples. The T_{on} fluctuates following exposure under 10% stress and shows large shifts to lower temperatures at 15% stress. It might be deduced that P1 filaments and P2 filaments and tapes after exposure at 130°C show shifts in T_{on} to lower temperatures, the magnitude of which may be reduced by the loading of the samples up to 10% of their ultimate breaking load. It is also noted that the magnitudes of the shift are greater for P1 filaments.

The lower level of thermal stability of P2 filament and tapes is reflected by both the losses in tensile behavior and their low times to failure during oven ageing. It is possible that in these samples and especially at high draw ratios and applied loadings the major thermal degradation route involves chain scission, thereby explaining the significant tensile property deterioration with little accompanying shift in T_{on} . Two concurrent degradative routes may therefore be envisaged, with competition between

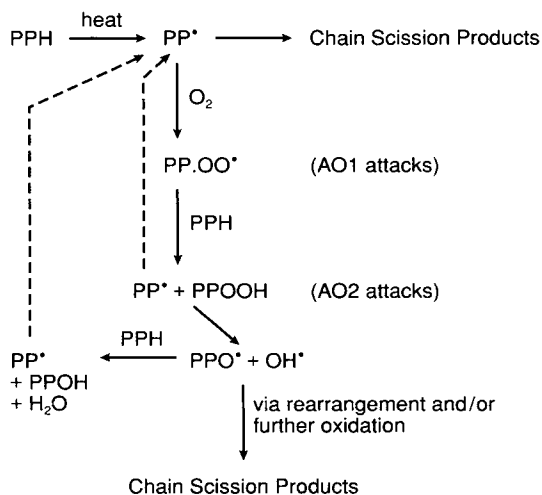
oxidative chain scission and chain oxidative non-scission reactions as shown schematically below.

Polymers P1 and P2 differ only in their average molecular weights and the antioxidant systems present. Their different behavior under the combined actions of heat and stress is most likely to be a consequence of their differing antioxidant characteristics. Their analyses, previously reported,⁷ show P1 to contain 0.17% Irganox 1330 and 0.02% Irgafos 168 while P2 contains 0.06% Irganox 1010 and 0.05% Irgafos 168. Long-term antioxidant behavior arises from the primary, hindered phenol activities (i.e., Irganox 1330 and 1010) and not usually the secondary phosphite-containing antioxidant component (Irgafos 168). The latter and secondary antioxidant reduce hydroperoxide residues and prevent autoxidative chain scission reactions from occurring. It is interesting to note that the concentration of Irgafos 168 in P2 polymer is over twice that in P1 polymer. Respective values in derived filaments and tapes are not available.

In principle, there should be little difference in

the activities of Irganox 1330 and 1010,² but the former is present at about three times the concentration than the latter in order to increase the overall long-term thermal stability of polymer P1. Both phenol derivatives should function by scavenging those peroxy radicals that would otherwise form hydroperoxides and result in chain scission products. The relative abilities of orientated tapes and filaments to retain tensile properties during thermal exposure indicates that in P1 filaments chain scission is suppressed by the antioxidant but that non-chain scission oxidation of the polypropylene chain accompanies this activity. In P2 filaments and tapes under load, chain scission reactions dominate and little chain oxidation occurs. Thus the two antioxidant systems seem to have functioned differently with regard to their preventing oxidative attack of the polymer chains and this effect becomes more apparent when orientated polypropylenes are exposed in hot air under load.

An attempt may be made to reconcile these conclusions with accepted mechanistic understanding of polypropylene oxidation and antioxidant behavior if the following simplified schemes are considered:^{3,15}



Within this scheme PPH represents polypropylene and its labile tertiary hydrogen, AO1 a primary, hindered phenol antioxidant, and AO2 a secondary, organic phosphite antioxidant. The formation of hydroperoxide represents the major precursor of chain scission and consequent formation of oxidized chain fragments. Thermal degradative scission may also occur as shown and may be particularly sensitive to high stresses.³

Evidence from this work, however, suggests that PPO*, PPOO* polymeric radical intermediates may be involved in reactions that result in either chain

scission or non-scission during exposure times less than the induction period. The latter would yield oxidatively sensitive and autoxidative products, e.g., PP.OH or even carbonyl-containing species, centered about precursor tertiary carbons in the chain. Furthermore, interaction of AO1 with either the PPO* or PPOO* radicals can lead to oxygen-containing derivatives of polypropylene, which may also have autoxidative qualities or potential.

The different polymer behaviors could be explained in terms of antioxidant concentrations alone if higher concentrations of AO1 (Irganox 1330 in P1) reduce the potential formation of hydroperoxides and consequent chain scission; lower concentrations of AO2 (Irganox 168) in P1 would result in a relative higher concentration of free hydroperoxide and hence autoxidative character as is suggested by the large shifts in T_{on} . Conversely the positive stress sensitivities of exposed, higher draw ratio P2 filaments and tapes suggest that the lower AO1 concentrations may be less effective at reducing subsequent hydroperoxide formation and chain scission reactions—the latter would be expected to be favored by applied stress.

If, as has been assumed, autoxidative behavior is related to the hydroperoxide concentration and the stress dependence of shifts in T_{on} for P1 filaments (see Figs. 3 and 4) add support to this agreement, then it is difficult to reconcile these large shifts with negligible changes in observed tensile behavior. Conversely the smaller shifts in T_{on} do not correlate with the associated, significant changes in tensile properties of P2 filaments and tapes.

An alternative explanation would involve a modification to the above scheme such that the route from PP* via PPOOH to autoxidative chain scission is accompanied by a parallel nonchain oxidative reaction sequence. In such a proposal an antioxidant system might preferentially suppress one route thereby giving rise either to reduced chain scission with increased nonchain scission autoxidation as in P1 filaments or the converse as demonstrated by P2 filaments and tapes.

Clearly, further work is required to explore this hypothesis, which, if true, poses interesting questions regarding antioxidant choice for stressed, orientated polyolefins.

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