

Physicochemical Changes in Stabilized, Orientated Polypropylene Films during the Initial Stages of Thermal Oxidation

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SYNOPSIS

Orientated, stabilized, isotactic polypropylene films have been oven-aged at 130°C for times shorter than required for their embrittlement. The structural changes occurring during this induction period have been studied using tensile tensiometric, density, thermal analytical (DTA and TGA), and infrared spectrophotometric techniques. After an initially rapid annealing, films show similar time-dependent changes in tensile, density-derived crystalline and thermogravimetric behaviors. Comparison with vacuum-aged sample properties shows that these changes reflect the effects of oxidative attack of polypropylene chains. Infrared examination shows that, even after the longest aging times studied and close to the induction period for embrittlement, the presence of oxidized chain groups is only just discernible. Oven aging reduces post-fusion oxidative onset and maximum mass loss temperatures determined by TGA. Kinetic analysis demonstrates that the apparent activation energies and Arrhenius factors are reduced during aging as the post-fusion oxidation mechanism becomes more complex. The results suggest that, during the induction period, changes in both physical and chemical structural features of orientated polypropylene occur which have possible importance in determining the lifetime of the polymer in use.

INTRODUCTION

Many orientated, fiber-forming polymers like isotactic polypropylene, when subjected to environmentally damaging conditions, show slow, often negligible losses in tensile and related properties for considerable periods of time prior to their often sudden and catastrophic failure.¹ This effective lifetime coincides with the so-called induction period after which previously slow chemical degradations became more rapid. Under ambient environmental conditions for stabilized polypropylene, these lifetimes are of the order of years and so effective laboratory testing is difficult. For example, recently reported results of soil burial exposure trials over periods as short as 32 months² to those of 7 years³ or more⁴ demonstrated that polypropylene fabrics showed excel-

lent retention of their physical properties. Because such exposure periods are within the respective fiber induction periods, such negligible property losses appear to indicate that considerable useful life remains. Since ambient-condition induction periods are not accurately known, then neither the original unexposed nor the exposed fabric expected lifetimes may be predicted.

The use of elevated temperature-derived induction periods to predict durabilities at ambient conditions is well known,^{1,5} although the tendency to overestimate lifetimes has been noted.^{1,6} Elevated-temperature or oven-aging techniques are well established^{1,5-13} for attempting to determine both high and low temperature thermooxidative stabilities of commercial polypropylene polymers, fibers, and orientated films or tapes. Low temperature (70–150°C)^{1,5-10,12-16} conditions are preferred for assessment of polypropylene aging within the solid state whereas high temperature (220–280°C) exposure¹¹ reflects polymer stabilities during melt processing. Observation of physical changes in ten-

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sile,^{2-4,6,9,10,13,15,16} mass,¹ microscopic appearance,^{2,3,9,12} and thermal behaviors^{5,9,12,16,17} coupled with oxygen sorption,⁵⁻⁸ infrared spectroscopic,^{1-3,6-10,13-15} viscometric,^{9,12,15} and mass spectrometry-gas chromatographic¹¹ studies have all been used to study the nature of the physicochemical effects of thermal oxidation. Although the exact chemistry of solid-state thermal oxidation is complex,^{18,19} essentially the initial stages involve radical formation and subsequent decomposition of hydroperoxide species to give ketonic chain segments. The latter may be identified quite easily by infrared spectroscopy.²⁰ The action of antioxidants is equally complex²¹ and the use of oven-aging studies demonstrates that their relative efficiencies may be temperature-dependent,¹ thus rendering extrapolations to ambient temperature behavior difficult. Oxidation is largely oxygen-diffusion-controlled²² and, because increased oxygen concentrations significantly reduce aging times, it has been shown that lower temperatures closer to those in service may be used and so perhaps enhance accuracy of low temperature stability predictions.¹⁴ The whole problem of relating accelerated aging tests to expected service lifetimes has been recently reviewed by Gugumus²³ for polypropylene. In particular, he corroborates previous work of Gordon,²⁴ which shows that poor correlations exist between thermal analytical measurements of polymer stability determined above the melting point and solid-state oven-aging lifetimes; however, techniques such as DTA and DSC may still be valuable as tools for quality control during antioxidant formulation. He also questions the use of pure oxygen atmospheres by Faulkner^{10,14} as a means of reducing oven-aging temperatures. Currently, therefore, because of the extremely high efficiencies of commercially available antioxidant systems,²⁵ oven-aging techniques offer the only means of assessing their efficiencies using reasonable experimental exposure times.

This paper extends the scope of a previously published short communication²⁶ and describes the use of thermal analytical methods (DTA and TGA) for investigating the effect that oven aging at 130°C has

on induction period behaviors of various differently uniaxially orientated films produced from a commercial stabilized polypropylene polymer specified for use in geotextile products. The study represents the first stage within a larger research program whereby variously stabilized polypropylene orientated tapes having acceptable commercial properties will be both oven- and ambient-temperature-aged in attempts to determine the changes in physicochemical character during the early stages of oxidation and therefore more effectively predict service lifetimes.

EXPERIMENTAL

Polymer Film Samples

Commercial grade polypropylene (ICI Propathene, GWE26) polymer having a nominal melt flow index of 3 designed for high tenacity tape end uses was selected for use in this work. It was melt extruded under nitrogen in a Plasticisers Engineering Ltd. (U.K.) Labline screw extruder. The laboratory screw extruder ($L/D = 21$) was used with barrel zone temperatures 210, 230, and 250°C and fed molten polypropylene to a 63.5×0.38 mm slit die at 250°C. A chill-roll velocity of 2 m min^{-1} was used to solidify and collect all film samples. After cooling, a tape was cut from the central film region such that, after heating to 100°C and stretching at nominal draw ratios of 4 : 1, 6 : 1, and 8 : 1, tape widths of 13 ± 2 mm were obtained. At each draw ratio, the polymer extrusion rate was adjusted to give a drawn tape having a thickness of $50 \pm 5 \mu\text{m}$. Prior to winding up, each tape was subjected to a nominal 5% linear relaxation. Actual draw ratios found by linear density determination of tapes before and after drawing/relation are presented in Table I.

Film Physical Properties. Densities were found using a Daventest density column containing an ethanol-water mixture covering the calibrated density range 0.890–0.940 g cm^{-3} at $23 \pm 0.1^\circ\text{C}$. Tensile properties of orientated tapes were found

Table I Physical Characteristics of Drawn Polypropylene Tapes

Nominal Draw Ratio	Actual Draw Ratio	f_c	Tenacity (GPa)	Breaking Strain (%)	Secant Modulus at 2% Strain (GPa)
4 : 1	3.8 : 1	0.736	0.19	34.7	2.67
6 : 1	5.4 : 1	0.908	0.39	22.7	4.41
8 : 1	7.2 : 1	0.917	0.51	20.0	6.01

initially on 100 mm lengths of full-width tapes prior to oven aging (Table I) and on 50 mm lengths of 3-mm-cut widths of oven-aged samples. An Instron 1026 tensile tester with a crosshead speed of 100 mm min⁻¹ at 20°C and 65% RH was used throughout. All reported results are the average of at least five tests per sample. The results in Table I show that a nominal draw ratio of 8 : 1 yields a tape with properties close to that for a commercially produced industrial polypropylene tape yarn.

Oven Aging

All tapes were aged in a forced-draught air oven at 130°C. Two tape geometries were selected; one series of tapes was wound about 25 mm diameter glass tubes to prevent shrinkage and so expose one side only. A second series of tapes was exposed wound around a 150 × 150 mm glass frame to enable both sides to be exposed to hot air. The former condition represented tape exposure in a woven fabric structure where sections of one side only of any component would be exposed while the latter enabled full exposure; such a condition would not normally occur in an exposed woven tape fabric. Maximum exposure times of 20 and 15 days, respectively, were chosen for all orientated tapes as representative of periods sufficient to cause oxidative aging within a period less than the induction time prior to embrittlement. For the films studied, embrittlement occurred rapidly, but rather irreproducibly, within an oven aging time range of 20–25 days. Single-sided exposed tapes were sampled at intermediate aging times of 1 h and 2, 5, 7, and 9 days and double-sided tapes at 3 and 9 days.

In order to study the effect of heat alone, samples of the 7.2 : 1 draw ratio film were sealed in glass tubes under vacuum and heated at 130°C for 2, 5, 7, 9, and 20 days.

For all aged samples, the initial 1 h exposure was necessary to fully anneal them prior to the aging experiments proper. All subsequently exposed tape properties were compared with those of the respectively 1-h-aged samples.

Thermal Analytical Studies

Differential thermal analyses of 5 mg unaged and oven-aged samples were carried out under static air at 20 K min⁻¹ heating rate in a Stanton Redcroft 671 B instrument. Selected samples were studied under static nitrogen (99.99% pure, British Oxygen Company Ltd.).

Thermogravimetric analyses of 5 mg samples were undertaken in static air both under isothermal and linear programmed temperature conditions (5–99 K min⁻¹ range) using a Stanton-Redcroft TG 760 unit.

In order to monitor the antioxidant efficiency within the GWE 26 polymer, selected DTA and TGA studies were carried out on samples of the parent, unstabilized, reactor polypropylene supplied by Chemicals and Polymer Division, ICI plc.

Infrared Spectrophotometry

A Perkin-Elmer 881 infrared spectrophotometer was used to determine measures of film orientation prior to aging and thermal oxidation following oven aging. Crystalline orientation functions f_c were determined from dichroic ratios of perpendicularly polarized 808 cm⁻¹ according to de Vries²⁷ for each drawn tape and values are reported in Table I.

The effects of oven aging were studied both by transmission and multiple internal reflection (MIR) methods. For the latter, a Specac Ltd. 25 reflection cell holder fitted with a KRS-5 prism was used with an angle of incidence of 45°.

RESULTS AND DISCUSSION

Effects of Oven Aging on Tensile Properties

In order to ascertain whether aging times were sufficient to produce small changes in tensile properties relative to the annealed (1-h-aged) values in Table I indicative of minor physicochemical structural degradation, the retentions of breaking loads are shown in Figure 1(a) for the single-side-aged tapes as a function of oven exposure time. Breaking extensions in Figure 1(b), although highly scattered because of larger experimental error (± 14 –24%), showed similar increases during the first 7 days aging followed by subsequent decreases. The initial increases in film breaking loads are inversely dependent on draw ratios, thereby suggesting orientation-dependent changes in physical and/or chemical structure. The 20-day tensile properties, however, show slight net losses for lowest draw ratios relative to the initial annealed values. Furthermore, the reduction in breaking load retention between maximum (7–9 days) and 20-day-aged values is highest for the lowest draw ratio. The converse effect of draw ratio is observed with regard to breaking extension-aging time trends.

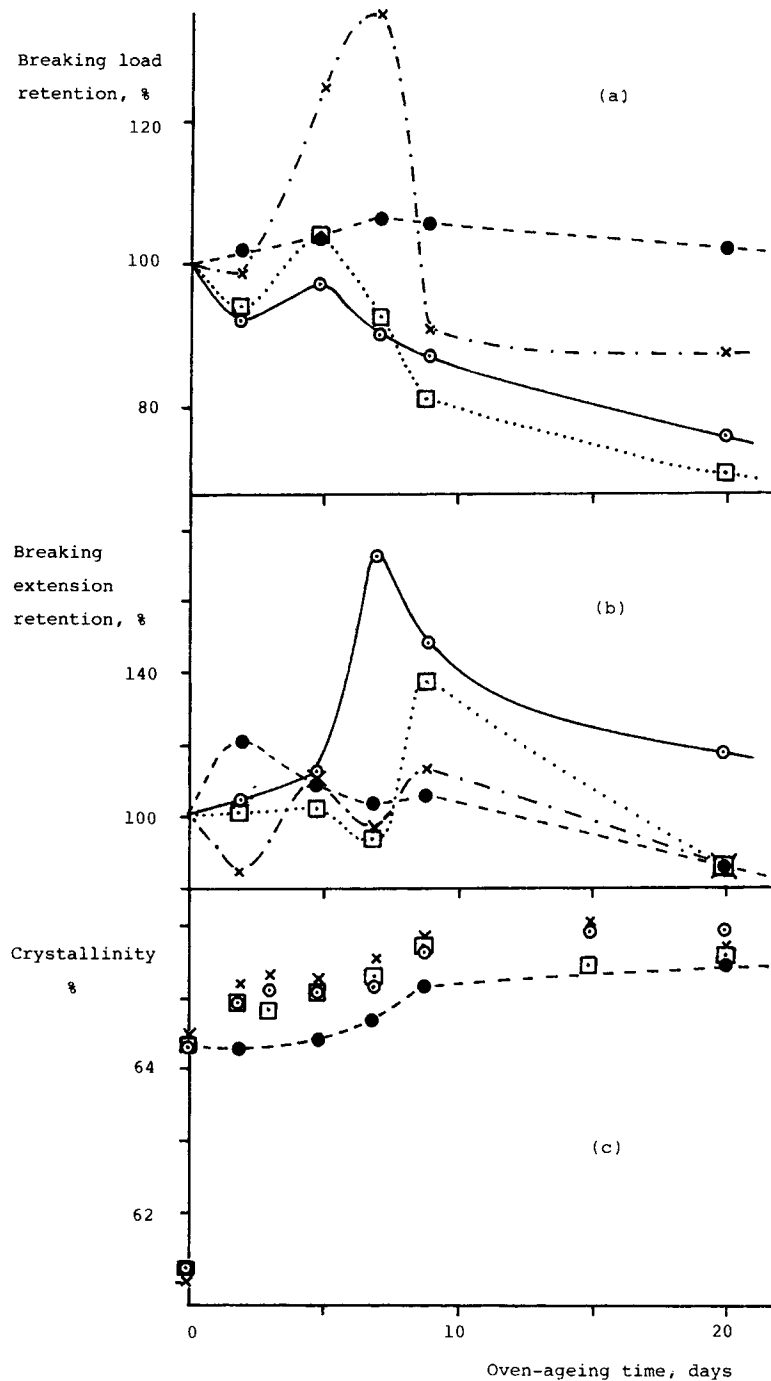


Figure 1 The effects of oven aging at 130°C on the (a) breaking load retention and (b) breaking extension retention and density-derived crystallinity: (-·×-·) 3.8 : 1; (··□··) 5.4 : 1, and (—○—) 7.2 : 1 films aged in air; (---●---) film aged in vacuum.

The 7.2 : 1 draw ratio tape when aged under vacuum, however, shows much smaller changes in breaking load and extension retentions, thereby indicating that the above changes in Figure 1 (a) and 1 (b) are caused by thermal oxidation. Mathur and

Mathur¹⁵ demonstrate that oven aging at 70 and 80°C in air shows increases in tenacity to maximum values and hence similar trends to those shown in Figure 1 (a). However, other previously reported effects of thermal aging in air show negligible changes

in tensile strength^{6,17} and breaking elongation^{1,6,9,10} during the induction period. Oswald and Turi⁶ report that aging of unstabilized and stabilized polypropylene in argon over the temperature range 75–140°C has negligible effect on tensile properties, even after exposure times greater than the air-aged induction periods. Thus it would seem that, after annealing, thermal oxidation initially promotes an increase in breaking load and extension followed by a subsequent decrease after 7–9 days aging. The effect of draw ratio on these effects is not clear, although the presence of internal stress introduced during drawing has been observed to reduce thermooxidative stability of polypropylene⁸; Roginsky¹⁹ has recently reviewed this question.

Effects of Oven-Aging on Density and Crystallinity

Density values of aged and unaged samples were used to calculate the degrees of crystallinity assuming respective densities of 854 and 938 kg m⁻³²⁸ for noncrystalline and crystalline regions. Figure 1(c) shows that when plotted as a function of oven aging time, a rapid initial increase in crystallinity for single-side aged films occurs within the first 2 days followed by a much slower, possibly stepped, increase; both regions are largely unaffected by the differences in orientation although the 3.8 : 1 film shows slightly larger increases. Table II tabulates density and crystallinity data for the double-side aged films in

which a similar effect is seen; comparison of the as-drawn film crystallinities with those for 1 h annealed films shows that most of the initial increase in Figure 1(c) occurs within the first hour. Furthermore, comparison of results in Figure 1(c) and Table II suggests that the rates and magnitudes of density changes are not influenced by whether single- or double-sided aging of tapes occurs.

Of particular note for single-side aged tapes is that the rise in crystallinity between 5 and 9 days aging time coincides with the breaking load and elongation retention maxima in Figures 1(a) and 1(b).

Increases in density and crystallinity have been shown to accompany thermal oxidation of polypropylene as oxidative chain scissions enable previously restrained chain segments to order themselves.^{1,6,9} The rise after about 7 days aging could be a consequence of thermal oxidative scission accompanied by sharp reductions in both tenacities and breaking strains of oxidized films. A more gradual increase in crystallinity occurs at longer exposure times. No significant effect of film orientation is observed on developing crystallinity after 7-day aging times, although, prior to this, the degree of order is inversely related to film orientation.

However, when the 7.2 : 1 film is aged under vacuum, although crystallinities are less than the respectively aged air-exposed samples, a similarly stepped trend is seen. It is thus possible that this step is not caused by air oxidation but by autoxidation (see below), although the generally higher crystallinities are.

Table II Orientated Film Densities and Crystallinities Before and After Double-Sided Aging

Film Draw Ratio	Aging Time (Days)	Density (kg m ⁻³)	Crystallinity (%)
3.8 : 1	0	900.9	58.1
	0.04 (1 h)	907.0	64.9
	3	908.2	66.6
	9	908.6	67.1
	15	909.4	68.0
5.4 : 1	0	901.0	58.3
	0.04 (1 h)	906.7	64.8
	3	907.4	65.7
	9	907.7	66.1
	15	908.4	66.9
7.2 : 1	0	901.0	58.3
	0.04 (1 h)	906.5	64.7
	3	907.6	65.9
	9	908.4	66.9
	15	909.3	67.9

Thermal Analytical Behavior of Aged Polypropylene Samples

Differential Thermal Analysis

The DTA traces of the parent unstabilized polypropylene in the presence and absence of static air in Figure 2 shows its oxidative sensitivity relative to those of each drawn unaged film. Under nitrogen the endothermic pyrolysis transition of the unstabilized polymer is replaced by an exotherm in the stabilized film analogues. After oven aging the enhancement of the lower temperature region of the exotherm in static air is typical of all aged films irrespective of degree of orientation. Thus oven aging sensitizes the film to subsequent thermal oxidation. It is interesting to note also that in Figure 2 that the onset of the exotherm in nitrogen has shifted to lower temperature after oven aging; it may be postulated that aging has sensitized the polymer to both post-fusion autoxidation and air oxidation. Table

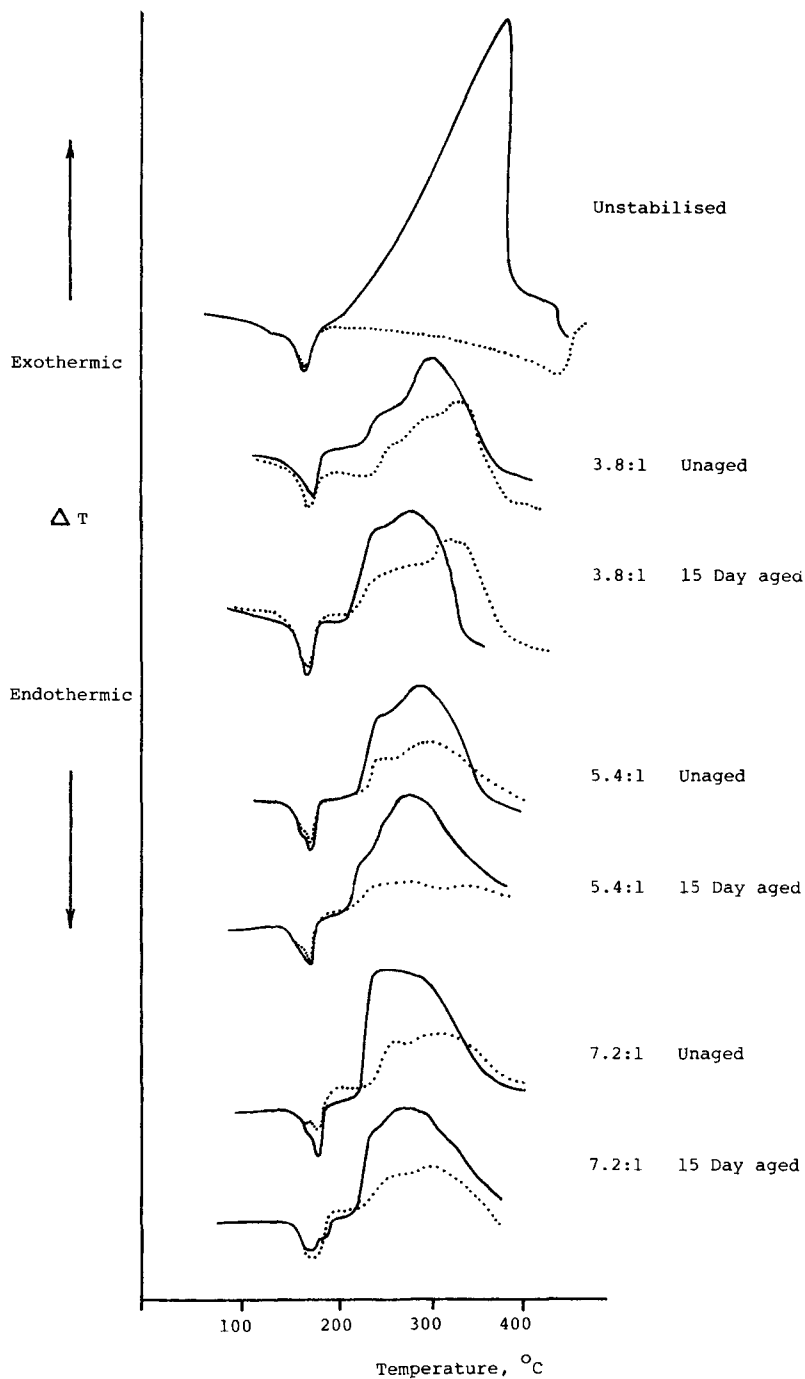


Figure 2 DTA responses under static air (—) and nitrogen (· · ·) of unstabilized and 3.8 : 1, 5.4 : 1, and 7.2 : 1 orientated polypropylene; films studied before and after double-sided oven aging in air at 130°C for 15 days.

III lists the major DTA fusion endotherm and degradation exotherms in terms of onset and minimum or maximum temperatures for unaged and the most aged films. Besides variation in post-fusion exotherm characteristics following oven-aging, slight

changes in the behavior of the fusion endotherms also occur with minima shifting from 171 to 164°C, 167 to 159°C, and 167 to 158°C during respective 20 days oven aging of 3.8, 5.4, and 7.2 drawn films.

Although annealing alone for periods up to 3 h

Table III DTA Thermal Transitions of Unaged and Aged Polypropylene^a

Draw Ratio	Aging Time (Days)	DTA Atmos (T_{ons})		Fusion T_{min} ($^{\circ}\text{C}$)				Oxidation T_{ons} ($^{\circ}\text{C}$)		
Unstabilized polymer	0	Air	149	164				207		
		N ₂	137	165				—		
3.8 : 1	0	Air	146	160 ^s	171	167		222		
		N ₂	147					234		
	15(D)	Air	148	164				207		
		N ₂	148	159 ^s	164			209		
	20(S)	Air	144	157 ^s	165			211		
		N ₂	142	157 ^s	164			219		
5.4 : 1	0	Air	144	159 ^s	167		227			
		N ₂	149	157 ^s	168		229			
	15(D)	Air	144	164 ^s				215		
		N ₂	149	159 ^s	162 ^s	167			226	
	20(S)	Air	147	157	167	167		210		
		N ₂	148	157	162 ^s	170 ^s			219	
7.2 : 1	0	Air	143	162 ^s	167	167 ^s	172 ^s	177	218	
		N ₂	144	154	164 ^s	167	172 ^s			232
	15(D)	Air	146	155 ^s	159	167 ^s		172 ^s	177	213
		N ₂	147		157	163	172 ^s		219	
	20(S)	Air	144	155 ^s	160	167				
		N ₂	147	154 ^s	158	167	173 ^s			242

^a Note: (D) denotes double-sided aging; (S) denotes single-sided aging; s denotes a shoulder.

can significantly affect the DSC melting endotherm²⁹ of polypropylene, Wyzgoski⁹ showed that prolonged oven aging at 90°C produces little further effect until after an induction period (150 h), when the DSC endotherm minimum shifts to lower temperatures. He noted also that the reduction in this minimum temperature is at least 10°C after exposure for an aging time commensurate with the induction period (500 h), after which significant loss in sample breaking strain occurs. More recent work by Mucha and Kryszewski¹² again demonstrated that annealing of polypropylene modifies the DSC fusion endotherm shape and that shifts to lower temperature occur when samples were oxidatively etched by nitric acid at 85°C; no shifts were observed following thermal oxidation at 155°C for up to 56 h, however.

Fusion endotherm structure complexity is greatest for the 7.2 : 1 draw ratio 15- and 20-day-aged samples. Figure 3 shows the DTA endotherms for unaged and aged 7.2 : 1 drawn fibers in greater detail than in Figure 2. This complexity, especially at higher draw ratios (see Table III), suggests that a number of ordered polymer populations become more diverse during thermal exposure. Erina et al.³⁰ have recently noted similarly structured DSC fusion endotherms extending to higher temperatures from polypropylene films of high draw ratio and analyzed

under isometric conditions. The effect of constraint during DSC analysis could have a similar effect on the development of order as does the thermal aging of restrained samples in this study.

Programmed Temperature Thermogravimetric Analysis

Preliminary experiments were undertaken to ascertain possible platinum crucible effects on the static air TGA post-fusion oxidations of polypropylene. These showed that use of aluminum replacements affected thermograms only with respect to the change in respective sample holder mass and specific heat. Thus it was considered that both crucible materials were inert and 166 mg, 5 mm diameter and 2 mm depth platinum crucibles were subsequently used.

Two series of TGA experiments were carried out, the first of which was to establish the influence of aging on the nature of the thermogram of all three orientated films at a constant heating rate of 20 K min⁻¹. The second was to kinetically analyze the oxidative thermograms for the unaged and the 20-day single-side and 15-day double-side aged samples.

The TGA and DTG responses of 3.8 : 1 and 7.2 : 1 unaged and 20 day oven-aged samples have been reported elsewhere.²⁶ In all drawn film samples both

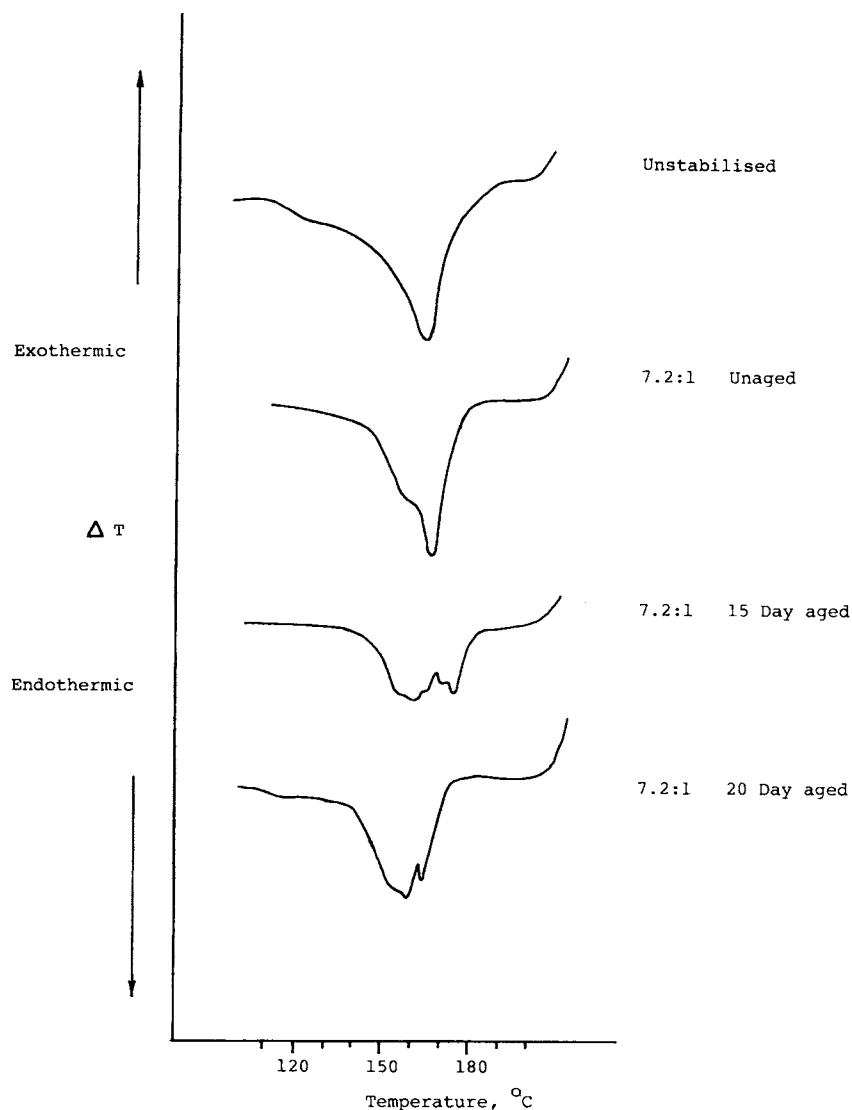


Figure 3 DTA responses under static air of fusion endotherms of unstabilized polymer and 7.2 : 1 unaged, 15-day double-sided aged, and 20-day single-sided aged polypropylene films.

the onset and maximum rate of mass loss temperatures decrease with increasing aging time and these effects are more fully analyzed in Figure 4; each transition temperature is the average of two experimental determinations. Comparison of TGA/DTG onset temperatures with similar regions of the DTA curves in Figure 2 show that, on average, the onset of mass loss temperatures are about 20°C higher than the respective DTA exotherm onset temperatures. The latter probably relates to the initial stages of oxidation, which leads to volatile formation at the subsequently higher TGA/DTG onset temperatures. Similarly, maximum rates of mass loss occur

above 340°C and are well beyond the respective unaged and aged film maximum exothermic reactions signified by DTA.

Comparison of the trends in Figures 1 and 4 shows similar discontinuities during the 5–9-day aging period. Thus aging-dependent physicochemical changes occurring are significant, in that changes in tensile, density, and thermal analytical behaviors are concurrent within experimental error.

TGA responses under nitrogen are less influenced by oven aging than those analyzed under static air. As shown in Figure 4, the 7.2 : 1 drawn film has onset (T_{ons}) and maximum (T_{max}) mass loss tem-

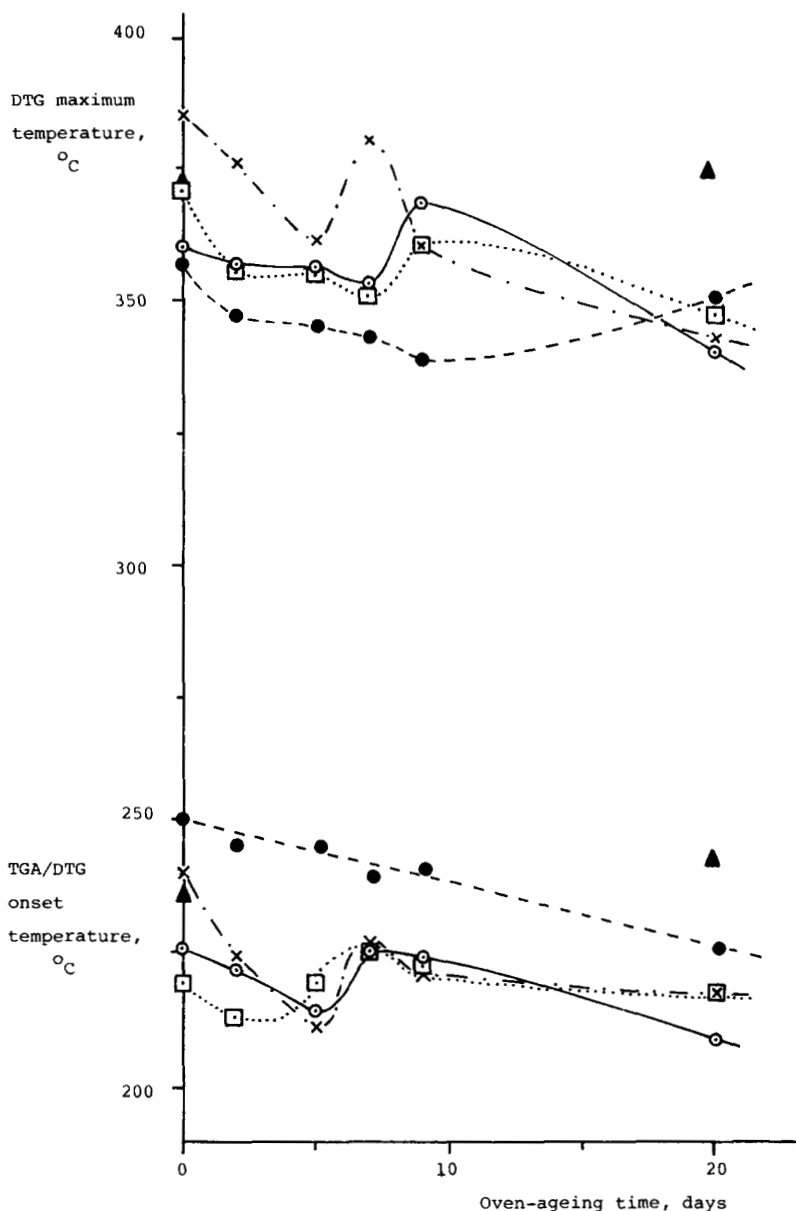


Figure 4 TGA/DTG onset, T_{ons} , and DTG maximum mass loss, T_{max} , temperatures under static air conditions for (— \times —) 3.8 : 1, (\cdots □ \cdots) 5.4 : 1, and (—○—) 7.2 : 1 orientated films aged in air at 130°C and (—●—) 7.2 : 1 films aged under vacuum at 130°C: (▲) respective transition temperatures determined under static nitrogen of 7.2 : 1 unaged and air-aged films.

peratures, of 241 and 370°C before aging and 244 and 375°C after 20 days oven exposure. A similar situation was observed for the DTA responses in Figure 2, where post-fusion autoxidative degradation occurs at higher and less aging-dependent temperatures.

The effect of oven-aging under vacuum on the static air TGA responses in Figure 4 for the 7.2 : 1

films shows less oven-exposure dependence than for respective air-aged films. The vacuum aging experiment was carried out 1 year after the air exposure experiments, during which time films were stored in the dark. It was noticed (see Fig. 4) that the unaged T_{ons} value of the 7.2 : 1 film had increased from 227 to 251°C whereas T_{max} had been reduced from 360 to 357°C. Reexamination of the 5.4 : 1 and 3.8 : 1

films showed similar increases in T_{ons} from 220 to 238°C and from 237 to 240°C, respectively; the apparent shift increases with higher draw ratio. Conversely, the magnitude of the reduction in T_{max} was largest for the film with the lowest draw ratio; shifts from 367 to 343°C and from 385 to 342°C for 5.4 : 1 and 3.8 : 1 films, respectively, were noted following this 1-year storage period. This ambient temperature aging effect was accompanied by the appearance of a second higher temperature DTG peak in all films.

Clearly this commercial quality, stabilized polymer is not as stable as might be anticipated, and the effects of ambient temperature aging require further investigation.

Kinetic Analysis of Programmed Temperature TGA

In order to study the apparent kinetics of the post-fusion oxidative behaviors of the unaged and most oven-aged films, respectively, a second series of TGA experiments was undertaken. In static air, 5-mg samples were subjected to various heating rates over the range 5–99 K min⁻¹. Figure 5 shows the effect of heating rate on the TGA curves for the 7.2 : 1 draw ratio films before and after oven aging double-sided for 15 days. Analyses of sets of TGA curves obtained were undertaken using the Ozawa method,³¹ following the observation by Cooney et

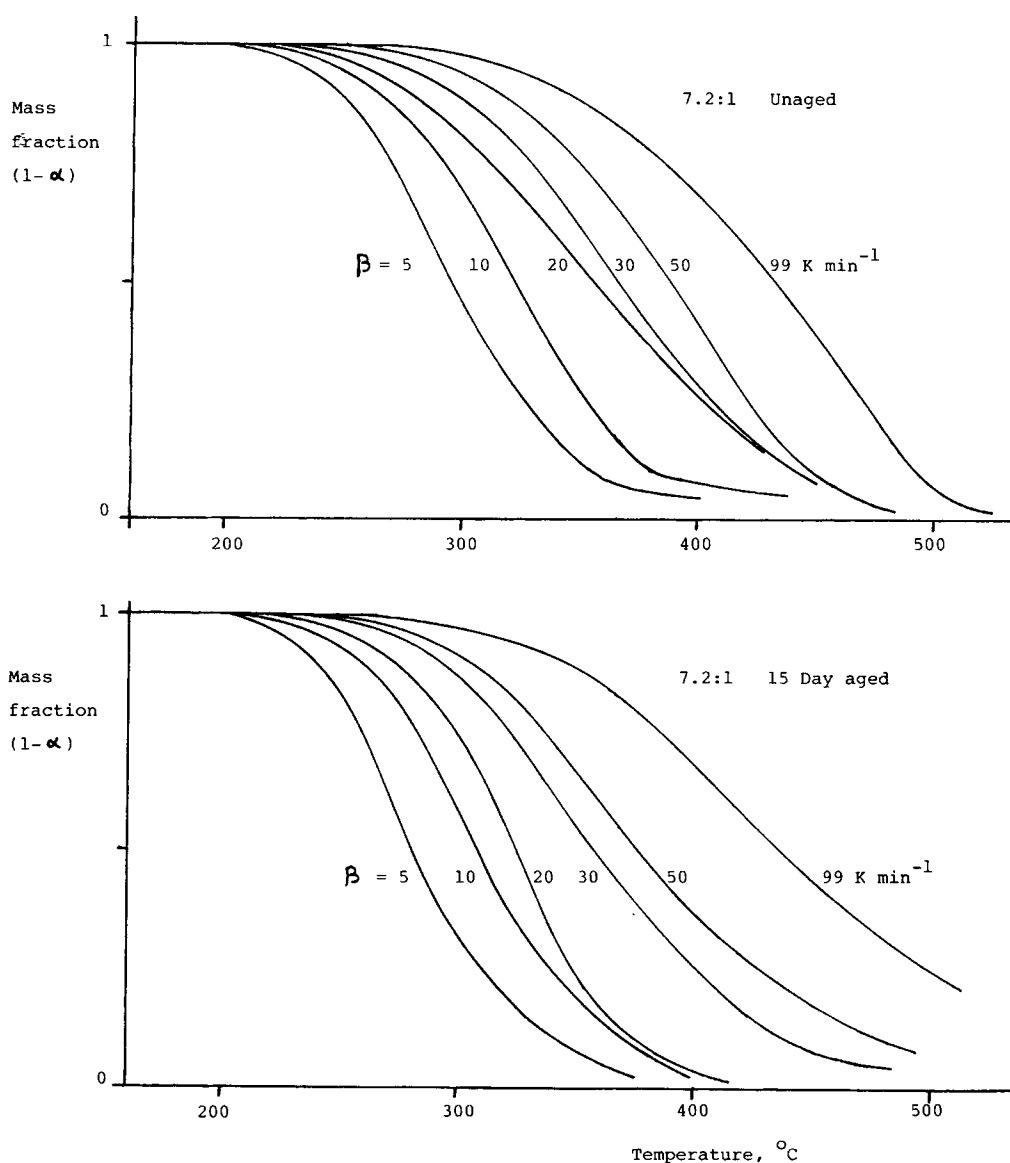


Figure 5 Effect of heating rate, β , on TGA mass fraction ($1-\alpha$) vs. temperature curves of 7.2 : 1 unaged and 15-day double-sided 130°C aged polypropylene films.

al.,³² who demonstrated its recent satisfactory use for analyzing the TGA data derived during the thermal degradation of poly(ethylene terephthalate). This method follows the assumption that at any temperature T the degree of thermal degradative conversion, α , of polymer to volatile products changes as a function of time according to the equation

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where k is the rate constant. The function $f(\alpha)$ for an n th order of reaction is defined by

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

from which

$$d\alpha/dt = A(1 - \alpha)^n \exp(-E/RT)$$

where A is the Arrhenius factor, E is the apparent activation energy of the thermal degradation, and R is the gas constant. If a polymer is heated at a rate of ($\beta = dT/dt$), then this equation becomes

$$d\alpha/(1 - \alpha)^n = A/\beta \cdot \exp(-E/RT) \cdot dT \quad (3)$$

Ozawa³¹ shows that this equation may be integrated and solved if A , $(1 - \alpha)^n$, and E are independent of T and both A and E are independent of α . Simplification of the resulting function for $E/RT \approx 20$ ³³ enables a plot of $\log \beta$ versus $1/T$ at constant α to yield a straight line having a slope of $-0.4567(E/R)$. The Arrhenius factor may be found from the intercept if the reaction kinetics are assumed to be first order.

The families of TGA curves, as exemplified in Figure 5, were analyzed at $\alpha = 0.1, 0.25, 0.5,$ and 0.75 for the 3.8 : 1, 5.4 : 1, and 7.2 : 1 films in the unaged, and 15-day double-side and 20-day single-side aged conditions. The derived E and A values are shown in Table IV.

Price et al.³⁴ have recently published an iterative method to solve the integral of eq. (3) and thus claim that more accurate values of E and A are thereby achievable. Application of their method to our results give the respective E and A values on the right-hand side of Table IV. Comparison of these latter results show that E and $\log A$ values for respectively identical film types, aging conditions, and degrees of conversion, α , tend to be slightly lower than for the Ozawa-method-derived values. Within error, E values for each unaged film are independent of α

Table IV Apparent Activation Energies and Preexponential Factors from Isoconversional TGA Plots Using the Methods of Ozawa³¹ and Price et al.³⁴ for Unaged and Aged Samples (TGA Responses in Static Air Conditions Unless Otherwise Stated)

Film Draw Ratio	Aging Time (Days)	Ozawa's Method, ³¹ Degree of Conversion, α								Price et al.'s Method, ³⁴ Degree of Conversion, α							
		0.1		0.25		0.50		0.75		0.1		0.25		0.50		0.75	
		E^a	$\log A^b$	E	$\log A$	E	$\log A$	E	$\log A$	E	$\log A$	E	$\log A$	E	$\log A$	E	$\log A$
3.8 : 1	0	72.3	5.7	68.4	5.4	70.9	5.6	79.1	6.2	67.1	5.0	62.5	4.6	64.9	4.8	72.4	5.3
	15(D) ^c	72.6	6.0	65.2	5.4	57.7	4.9	60.7	5.2	67.5	5.2	58.3	4.5	51.2	3.9	54.1	4.2
	20(S) ^d	70.5	5.7	65.9	5.4	69.5	5.7	72.6	5.8	65.4	5.0	60.2	4.5	63.4	4.8	65.6	4.9
5.4 : 1	0	74.3	5.9	76.2	6.2	67.1	6.6	71.5	5.6	69.2	5.2	70.9	5.4	60.2	4.4	64.7	4.7
	15(D)	66.2	5.5	62.0	5.2	58.2	4.9	50.5	4.4	61.0	4.7	56.2	4.3	51.6	3.9	43.0	3.2
	20(S)	66.5	5.4	61.8	5.1	57.2	4.7	52.7	4.4	61.4	4.6	55.9	4.2	50.5	3.7	45.7	3.3
7.2 : 1	0	73.9	6.0	72.8	5.9	73.5	6.0	73.8	6.0	69.1	5.3	67.2	5.2	56.4	4.2	67.3	5.1
	15(D)	70.6	5.8	59.4	4.9	59.4	5.0	53.3	4.5	64.6	4.9	53.5	4.0	52.8	4.0	46.3	4.4
	20(S)	75.2	6.2	69.1	5.8	64.5	5.4	52.7	4.4	70.3	5.5	63.6	5.0	58.3	4.5	45.8	4.4
Unstabilized polymer 7.2 : 1	0	64.0	4.9	56.5	4.3	54.8	4.3	56.8	4.5	58.3	4.0	49.9	3.3	47.6	3.2	49.5	3.4
	(TGA under N ₂)									69.0	5.1						
	20(S)	72.2	5.2							65.6	4.7						

^a Units: kJ mol⁻¹; error in computed E values within the range ± 3 -13%

^b A values have units of min⁻¹.

^c Double-sided exposures.

^d Single-sided exposures.

and so the post-fusion thermal oxidation of these polypropylene samples seems to be isokinetic; furthermore, both E and $\log A$ values are independent of the respective film extrusion and drawing histories. However, these respective values are both lower for the unaged, unstabilized polymer. The absence of antioxidants is considered to explain these reductions. Apparent E and $\log A$ values for post-fusion degradation under nitrogen are, within error, of similar magnitude to the corresponding air-oxidized values for the 7.2 : 1 unaged and aged films. The post-fusion air oxidation mechanism is therefore apparently similar to the autoxidative degradation occurring under inert atmospheric conditions.

The effect of aging on the kinetic parameters especially for $\alpha > 0.1$ shows significant reductions in both E and $\log A$ values. Thermal aging thus enhances the ease with which subsequent thermal oxidative degradation will occur and in fact respective values after 15-day double- and 20-day single-sided aging approach those for the unstabilized polymer. The apparent decrease in both E and $\log A$ values for all aged fibers with increasing α shows that, following thermal oxidation, polypropylene post-fusion degradation kinetics become more complex, especially after the initial stages. This seems to be noticeably so at higher draw ratios. The Ozawa and similar kinetic treatments cannot be applied³⁵ in any case where parallel, competitive reactions occur, and this condition is likely to hold following the introduction of oxidative reaction centers within the polymeric backbone. A major aim of this present study, however, has been to establish whether aging influences subsequent thermal behavior rather than to establish defined kinetic mechanisms. Not only are the apparent E values purely empirical and hence not related to a specific reaction pathway but also the derived A values are similarly so. These latter do not lend themselves to simple interpretation either as "collisional factors" or as entropy of activation-related parameters describing heterogeneous solid-state reactions.³⁶ The magnitude of $\log A$ values presented in Table IV are far too low for such interpretations to be valid.

Isothermal Thermogravimetric Analysis

Because it has been previously noted that activation energies for polymer degradations are often lower when determined by TGA methods than by isothermal procedures,³⁷ a selected series of isothermal degradations were undertaken in this current work. The 7.2 : 1 draw ratio unaged and 20-day single-side

aged tapes were subjected to isothermal TGA in static air at temperatures over the range 158°C (just below the melting point) to 300°C. Induction times were recorded for temperatures up to about 200°C, above which they become less than 20 min and, because of the sample heating up times being of about 10 min, were difficult to measure under the chosen conditions. These times are listed in Table V along with that for the parent GWE 26 polymer at 160°C. Induction times were, as expected, much shorter for the unstabilized polymer and so were recorded at temperatures as low as 129°C (see Table V). It was found that for induction times greater than 3 h or so, they became very irreproducible, possibly because of the effect of sample shape and surface area.³⁸ Use of flowing air (60–100 cm³ min⁻¹) did not improve reproducibility and considerably increased induction times. This was possibly because volatile oxidation products were removed which, under static air conditions, would normally remain on the polymer surface and enhance the reaction rate. Thus isothermal conditions were chosen so that conveniently long, yet reproducible induction periods were recorded.

It is evident that thermal aging, both during extrusion and during oven aging, greatly reduces induction periods and so sensitizes the polypropylene to further oxidation as demonstrated by the changes in kinetic parameters in Table IV. Similar reductions in induction periods were observed at 176°C by Rose and Mayo⁵ for both oven-aged and γ -irradiated polypropylene and at 170°C by Steiner and Koppelman¹⁶ in their attempts to predict oxidative stabilities of various antioxidant-polymer formulations.

Plots of \ln (reciprocal induction time) versus reciprocal temperature are shown in Figure 6. Only the unstabilized polypropylene gives a linear plot which is independent of the state of the polymer. For the 7.2 : 1 unaged and 20-day-aged tapes, linear regions exist above the melting point of about 167°C. The observation for stabilized polypropylene is in agreement with those of Billingham et al.³⁹ but in contradiction to the more recent results of Steiner and Koppelman.¹⁶

The estimated activation energy of unstabilized polypropylene of 73 kJ mol⁻¹ in Table V may be compared with that of 130 kJ mol⁻¹ (31 kcal mol⁻¹) reported by Stivala et al.,¹³ which was found to compare favorably with cited, previously reported values and more recently with that of Oswald and Turi.⁶ More recent work reports values of 100¹⁰ and 102 kJ mol⁻¹,¹⁶ which compare well with that reported by Miller et al.⁴⁰ of 92–109 kJ mol⁻¹ (22–26 kcal mol⁻¹).

Table V Induction Periods and Kinetic Parameters from Isothermal TGA in Air

Sample	Aging Temperature (°C)	Induction Time (h)	Kinetic Parameters		
			1st Order, $\alpha = 0.1$		Induction Period E (kJ mol ⁻¹)
			E (kJ mol ⁻¹)	log A (A , min ⁻¹)	
7.2 : 1 Unaged film	158	16.50	60.7	4.5	56 ^a
	166	1.40			
	175	0.55			
	184	0.40			
	198	0.25			
	212	0.20			
7.2 : 1 20-day-aged film	163	0.70	63.6	4.8	34 ^a
	175	0.35			
	184	0.30			
	192	0.25			
	204	0.20			
	Unstabilized polymer	129			
	137	2.00			
	151	0.80			
	161	0.95			
	177	0.23			
	181	0.15			

^a Liquid state oxidation.^b Liquid and solid state oxidation.

The polypropylene used by Faulkner,¹⁰ while considered commercially to be unstabilized in fact, contained a trace of stabilizer (0.005 wt % 2,6-di-*t*-butyl-4-methyl phenol). Table V also shows the estimated activation energies for the 7.2 : 1 stabilized tapes. The value $E = 56$ kJ mol⁻¹ for the 7.2 : 1 unaged film is much lower than that quoted for an Irganox 1330 (Ciba-Geigy) stabilized polypropylene of 212 kJ mol⁻¹.¹⁶ Figure 6 shows that E is greater for oxidation when solid than when the polymer is liquid. Aging causes E to reduce (34 kJ mol⁻¹) as noted also in Table IV. However, the error in our computed E values from induction time data is probably considerable.

Post-induction isothermal TGA responses for temperatures up to 300°C for aged and unaged 7.2 : 1 film and the unstabilized polymer sample were kinetically analyzed during the initial stages of oxidative volatilisation. All responses were approximately linear over the range $\alpha = 0-0.1$ and hence approximately zero order. For $\alpha > 0.1$, the plots became curved. Assuming first-order kinetics to occur following the initial stages, tangents drawn at the $\alpha = 0.1$ condition enabled $-\ln(dx/dt)$ vs. $1/T$ plots to be made as shown in Figure 7. All three plots are

essentially linear (except for unstabilized polymer at temperatures above 250°C) and almost superimpose. Most points are for liquid phase oxidation. Linear regression of each enables the respective E and log A values shown in Table V to be derived from the slopes and intercepts. These values compare favorably, although they are slightly less than those in Table IV. It would seem, therefore, that perhaps analysis of the isoconversional vs. heating rate data according to the method of Price et al.³⁴ and to a lesser extent of Ozawa³⁵ are yielding realistic kinetic parameter values. However, the isothermally determined values are less dependent upon both aging history and presence or absence of antioxidant.

Published E values¹³ of 92 kJ mol⁻¹ for nonvolatile oxidation product formation in unstabilized polypropylene and 87 kJ mol⁻¹ for trace-stabilized polymer under air oxidation have been recorded. This last result followed aging at lower temperatures of 60–90°C compared with the higher ranges used by Stivala et al.¹³ Similar values have been reported for pure oxygen oven-aged polypropylene.^{7,10} Our E values are consistently lower for both stabilized and unstabilized polypropylene than these cited results.

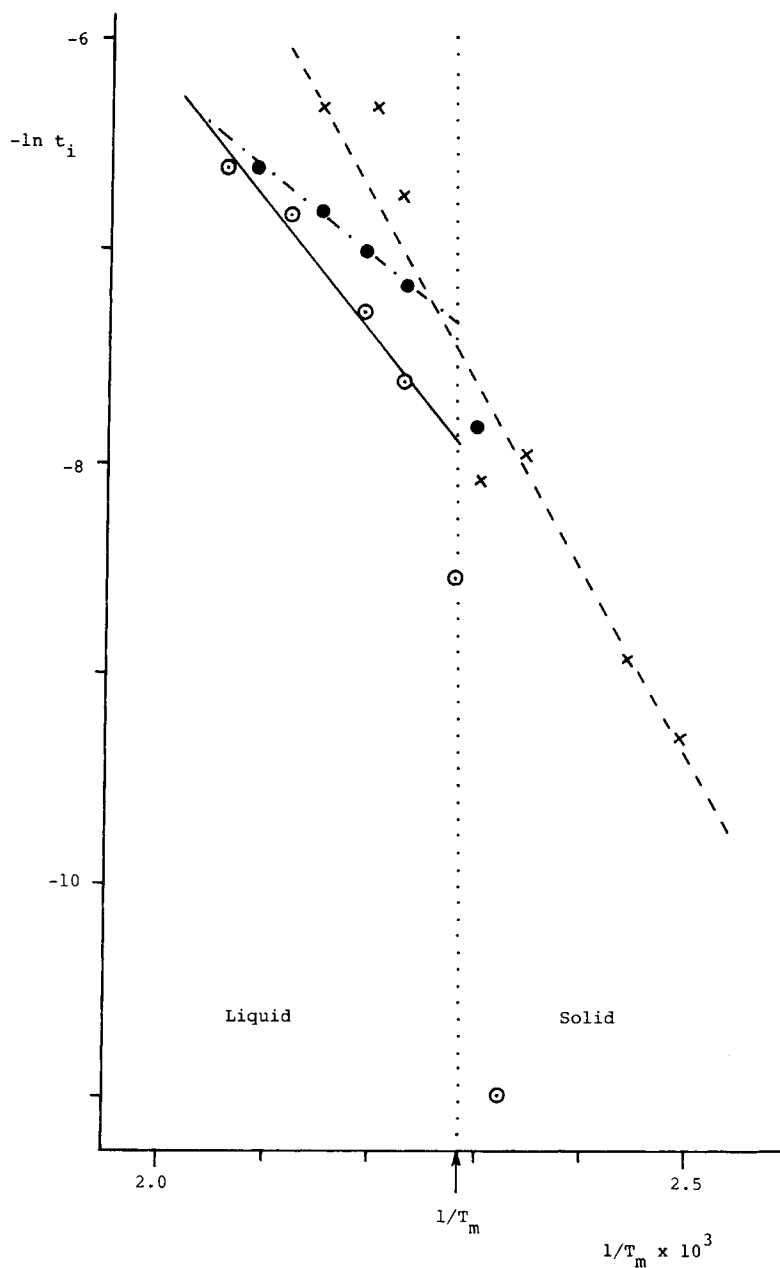


Figure 6 Plots of $\ln(\text{reciprocal induction time})$, $-\ln t_i$, vs. reciprocal temperature, $1/T$, for (---X---) unstabilized polymer and 7.2:1 unaged (—○—) and 20-day oven-aged (—●—) orientated polypropylene film; T_m is the melting point, 167°C .

Infrared Spectrophotometric Examination of Aged Films

MIR Studies

Spectra of both unaged and aged film surfaces showed the presence of an intense, structureless absorption band at 1730 cm^{-1} quite unlike those previously associated with carbonyl group-containing oxidation products.²⁰ This band is typified by spec-

trum 1 in Figure 8 for the 20-day-aged, 3.8:1 drawn film. Close inspection of both unaged and especially aged films showed the presence of a surface deposit. This could possibly comprise migrated additive³⁹ as well as low molecular, atactic polymer. Washing with cold petroleum ether (boiling range $40\text{--}60^\circ\text{C}$) removed this deposit.

In order to attempt to observe underlying oxidatively generated carbonyl species, subtracted

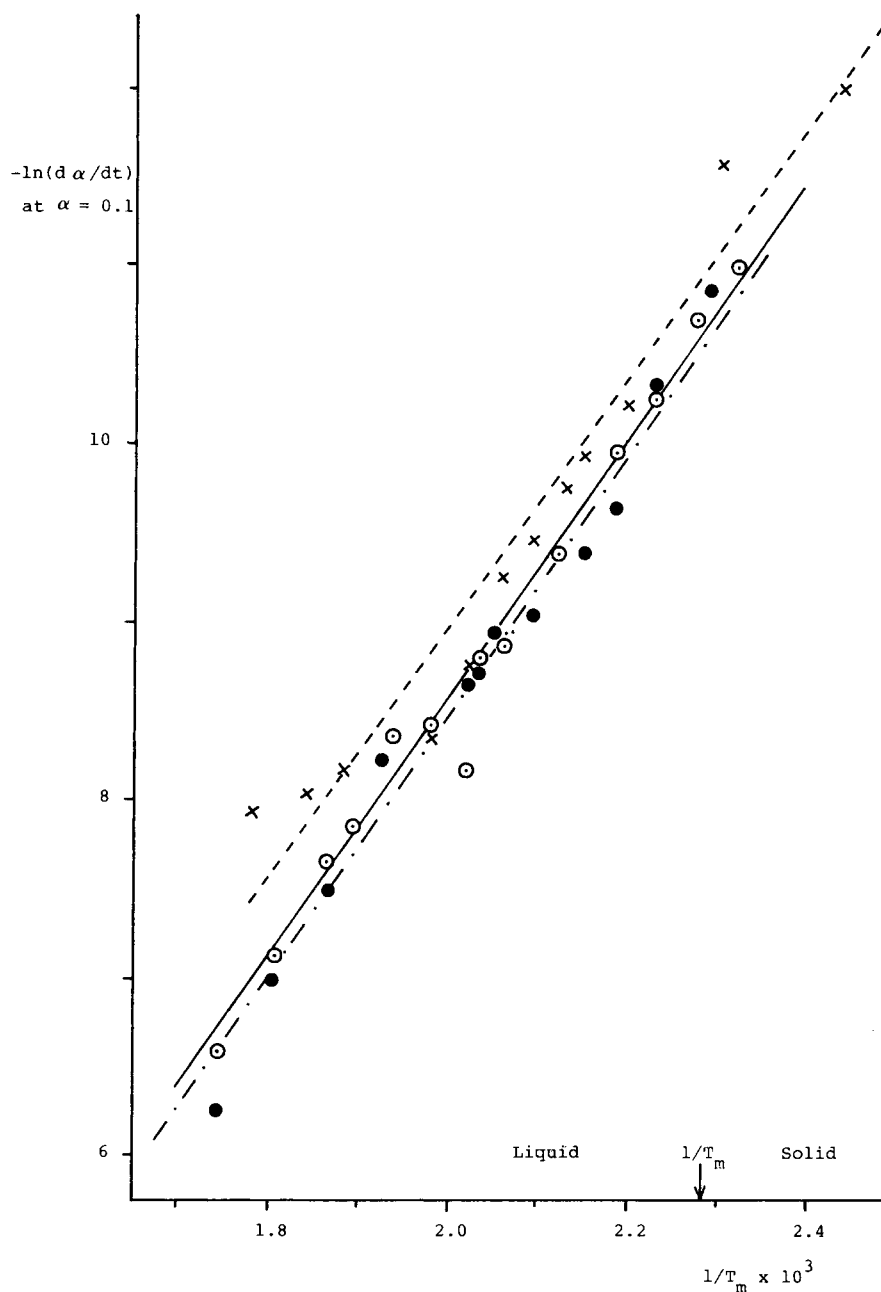


Figure 7 Plots of $-\ln(d\alpha/dt)$ vs. $1/T$ for assumed first-order postinduction period oxidative volatilization at $\alpha = 0.1$ over the temperature range 158–300°C; (—×—) unstabilized; (—○—) 7.2 : 1 unaged, and (—●—) 7.2 : 1 20-day oven-aged polypropylene.

spectra of aged and unaged, solvent-washed films were recorded. Spectrum 2 in Figure 8 is that for the outer surface of the solvent washed 20-day single-side aged 7.2 : 1 sample with respect to its solvent washed unaged analogue. Although the maximum is at 1730 cm^{-1} , other absorption bands at 1702, 1709, and 1720 cm^{-1} are evident. This latter group of bands is similar to that observed by other workers^{9,10,13,20,41} in oxidized polypropylene.

If the major band at 1730 cm^{-1} is associated with additive (a typical feature of ester-containing antioxidant species²⁵), then its concentration at or near the surface, as a consequence of oven aging, renders observation of oxidized polymer carbonyl species difficult using MIR techniques. Additive migration was obviously not of importance in the previously successful use of this technique for observing carbonyl products in UV degraded polypropylene.²⁰

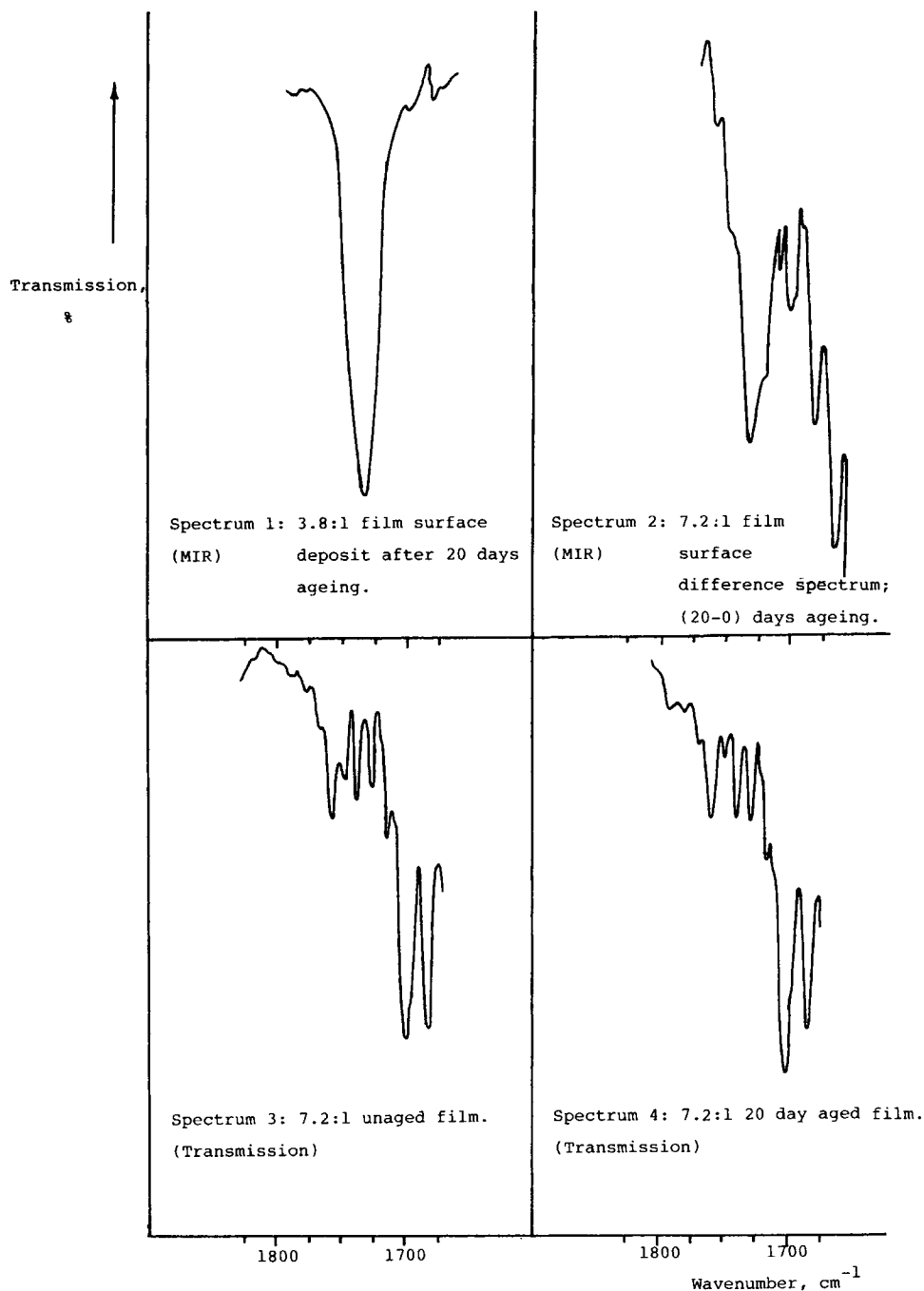


Figure 8 Multiple internal reflectance (spectra 1 and 2) and transmission (spectra 3 and 4) IR spectra of unaged and oven-aged orientated polypropylene films.

Transmission IR Studies

Film spectra, each the average of 10 repeat scans, showed low intensity structured absorption bands between 1700 and 1800 cm^{-1} . Spectra 3 and 4 in Figure 8 of respectively unaged and 20-day oven-aged 7.2 : 1 draw ratio films are typical of all orientated film spectra in that considerable structure

is present but oven aging promotes little obvious change in this structure. Although absorption bands are present in the 1730–1740 cm^{-1} region, they do not overawe the neighboring lower frequency absorptions as seen in the MIR spectra.

Quantitative analysis of transmission spectral bands between 1758 and 1699 cm^{-1} was undertaken by calculating optical densities and normalizing each

with respect to that at 974 cm^{-1} for the $-\text{CH}_3$ rocking combination band. In order to monitor the often-called isotacticity fraction or index as a function of oven aging, the optical density ratio of the 998 and 973 cm^{-1} bands were also found.⁴¹ All results are listed in Table VI.

Within experimental error, oven aging for up to 20 days has almost negligible effect either with respect to changes in isotacticity or to increase in carbonyl species absorption. There is a suggestion, however, that both the 1728 and 1714 cm^{-1} absorbing species increase in intensity consistently for all three films. The unusually high results for the 15-day aged 3.8 : 1 drawn film species at 1738 and 1728 cm^{-1} species are both reproducible and inexplicable. The 1728 and 1714 cm^{-1} bands, however, are close to those identified by Carlson and Wiles²⁰ at 1726 and 1718 cm^{-1} and associated with thermooxidatively derived ketonic products in isotactic polypropylene. Both these bands have been shown to increase in intensity after an initial induction period during oven aging.^{6,7,9,10,13,14} Oswald and Turi⁶ and Faulkner¹⁰ demonstrated that significant increases in the intensity of the 1710 cm^{-1} band occurs only after aging times greater than the induction period for tensile property deterioration. Wyzgoski,⁹ however, recorded increases in the same (1708 cm^{-1}) absorption maximum after an induction period relating to observed reductions in DSC fusion endotherm minimum temperatures. This period, as mentioned previously, was about one third of the induction period related to loss of tensile elongation following 90°C oven aging.

In this current study significant decreases in DTA fusion endotherm minimum temperatures occurred only after 7 days aging and even after 20 days single-sided aging shifts were considerably less than those observed by Wyzgoski. It would seem, therefore, that the initial stages of thermal oxidation prior to the induction period for catastrophic tensile property deterioration and ensuing film embrittlement are not easy to monitor using conventional infrared techniques.

CONCLUSIONS

The variously orientated polypropylene films have been oven-aged at 130°C for times less than those required for embrittlement and consequent loss in useful properties. The induction period physicochemical structural changes monitored by tensile, density, thermal analytical, and infrared spectrophotometric procedures have enabled the following conclusions to be drawn:

- i. During the initial stages of aging and after a 1-h annealing treatment, both tenacities and breaking strains increase in parallel with crystalline order, possibly because of a reorganization of physical structure following oxidative polymer chain scissions.
- ii. Subsequent induction period aging shows that tensile properties pass through respective maxima and then reduce as further ox-

Table VI Relative Intensities of Infrared-Absorbing Bands in Unaged and Aged Polypropylene Films

Film Aging Time (Days)	Normalised Optical Densities at Wavenumbers Shown ($\text{cm}^{-1}/\text{cm}^{-1}$)						
	998/974	1758/974	1747/974	1738/974	1728/974	1714/974	1699/974
3.8 : 1							
0	0.659	0.0465	0.0530	0.0512	0.0415	0.0470	0.0940
15(D) ^a	0.673	0.0436	0.0555	0.0868	0.0703	0.0503	0.0971
20(S) ^b	0.700	0.0421	0.0547	0.0507	0.0387	0.0430	0.0948
5.4 : 1							
0	0.688	0.0405	0.0314	0.0382	0.0321	0.0348	0.1017
15(D)	0.620	0.0422	0.0268	0.0371	0.0383	0.0483	0.1055
20(S)	0.671	0.0393	0.0264	0.0365	0.0347	0.0488	0.1006
7.2 : 1							
0	0.651	0.0411	0.0302	0.0332	0.0348	0.0445	0.0933
15(D)	0.726	0.0462	0.0313	0.0356	0.0353	0.0462	0.1076
20(S)	0.646	0.0417	0.0279	0.0423	0.0432	0.0523	0.1027

^a Double-sided exposures.

^b Single-sided exposures.

- oxidative degradation occurs; crystalline order again increases during these changes.
- iii. Infrared spectroscopic analyses shows that thermally generated ketonic species are only just observable during the whole induction period.
 - iv. Differential thermal analysis shows that small shifts to lower temperatures of the onsets of fusion endotherms occur during the initial stages of thermal oxidation. Furthermore, aged films become more sensitive to post-fusion oxidation in air.
 - v. Thermogravimetric analysis demonstrates that post-fusion oxidation of unaged, stabilized polypropylene films is essentially isokinetic and that oven aging reduces the activation energies and renders more complex this reaction, especially at higher orientations. Kinetic parameters derived from both programmed temperature and isothermal TGA methods are comparable during the initial stages of oxidation ($\alpha = 0.1$), yielding values $E = 60\text{--}75 \text{ kJ mol}^{-1}$, depending on the method of their computation.
 - vi. Differential thermogravimetric studies show that both onset and maximum rate of mass loss temperatures for each aged film show changes which reflect those in tensile properties and crystallinity at the same aging times.
 - vii. Oven aging greatly reduces isothermal TGA induction periods, and this is reflected by a reduction in the activation energy of induction observed.
 - viii. The effects of film orientation are difficult to resolve and do not consistently influence aging behavior, although small effects are seen with respect to tensile and thermal analytical behavior.

In use, polypropylene orientated films and fibers which are exposed for times approaching their induction periods are about to reach the end of their useful lives. The approaching potential catastrophic failure about to occur may not be evident from cursory examination of gross properties, however. This study has shown that careful monitoring of tensile, density, and thermal analytical behavior can be useful in following induction period structural changes. Future work will attempt to demonstrate how this methodology may be applied to assess the remaining effective lifetime of a given polypropylene film or fiber sampled during its end-use exposure conditions.

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