Time and Temperature Effects on the Tensile Yield Properties of Polypropylene

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ABSTRACT: Tensile tests were made on polypropylene films as a function of aging temperature from 80 to 130°C at a strain rate of 5 cm min^{-1}. Polypropylene films aged at 60 and 100°C and at time intervals up to 180 min were also stretched at the same strain rate. The yield stress and initial modulus were found to be linear functions of temperature, extrapolating to a zero value close to the thermodynamic melting point of the polymer (170°C). The work of yield, the plastic and yield strains also decreased with increase in aging temperature but the elastic strain increased. The plastic strain, yield strain, yield stress, and initial modulus for the 60°C aged film had larger values than the corresponding values for the 100°C aged film at equivalent time intervals and all properties decreased with increasing log time of aging. These decreases in properties were explained in terms of decrease in the density (crystallinity) of aged PP films. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 625–633, 1997

Key words: polypropylene films; tensile tests; stress; strain; thermal aging

INTRODUCTION

The thermal oxidation of polypropylene (PP) has generated much research interest, probably because of its utility in various applications. It has been well established that the presence of chromophores and impurities introduced during manufacturing processes initiates both photo- and thermal oxidation.[1-7] In addition, prior thermal or ultraviolet exposure history is known to affect the subsequent thermal stability of PP.[8-10] The degradation in the presence of air is due mainly to chain scission by the well-known Norrish types I and II mechanisms of the initially formed keto and hydroperoxide intermediates.

The thermal oxidation of PP close to the processing temperature gave 23 major products, mainly aldehydes, ketones, acids, and alcohols, while a higher temperature of aging (240–290°C) gave 39 products.[11] Camino et al.[12] degraded PP under a helium atmosphere and using a combination of subambient–thermal volatilization analysis (SA–TVA), infrared spectroscopy, and gas chromatography obtained two fractions—the lower volatility fraction (30%) made up of C_{15}–C_{25} saturated hydrocarbons and a higher volatility fraction (70%) made up of saturated and unsaturated hydrocarbons, C_1–C_5. In addition, the same workers reported that the addition of chloroparaffin-fire retardants before thermal aging changed the composition of the volatile products. On the contrary, Samuels[13] reported that a minimum annealing temperature required to transform a moderately oriented spun PP fiber into a hard elastic fiber is 130°C.

While the deterioration of physicomechanical properties of PP films has been studied at temperatures lower than the processing tempera-

ture by Osawa et al.[14] and Adams and Good-rich,[15] changes in such properties as plastic strain and elastic strain with temperature have not been investigated. It was the aim of this article to present results of recent investigations on the effect of temperature and exposure times on the plastic and elastic strains, the yield stress, the initial modulus, and the yield energy U_y of the thermally oxidized PP films. Also, the yield energy is discussed using well-known thermodynamic relationships.

EXPERIMENTAL

Materials

The polypropylene (PP) films, 0.12 mm thick, density, 0.90 g cm^{-3}, and percent crystallinity, 48, were kindly supplied by Bag Manufacturing Co. (BAGCO), Lagos, Nigeria.

Method

The PP films were cut into suitable lengths and weighed in a sensitive Mettler digital balance with a precision of ± 0.05 mg. The films were loaded onto a wooden plate in a Gallenkamp hot box oven after the oven air temperature had equilibrated (15 min) and then heated at 80, 100, 110, 130, and 150°C for 24 h. After the heating, the samples were removed from the oven and cooled to room temperature and weighed again to determine the weight loss for each sample. The density ρ of treated films was measured in a water/propan-2-ol density gradient column. The percent weight loss, density, and changes in the film thickness are recorded in Table I.

Also, PP films were heated in the oven at different temperatures and time intervals. The temperatures used were 60 and 100°C and the time intervals were 30, 60, 90, 120, and 180 min but not necessarily for both temperatures. The aged films were cooled to room temperature.

All the films were put into the oven at the same time for a particular test. The treated films were cut into dog-bone-shaped structures and then stretched at a strain rate of 5 cm min^{-1} and a gauge length of 5 cm using an Instron tensile testing machine (Model 1122) at 25°C and 65% RH. The film thickness was measured using a Shirley Development thickness gauge. Five samples from each heat treatment were analyzed and the mean values were recorded. Four mechanical properties were evaluated from the stress–strain curves: yield stress σ_y, initial modulus E, yield strain λ_y (the strain being defined by the ratio of increase in length to the original gauge length $\Delta L/L_0$), and the yield energy U_y, using ASTMD, 882-81. The elastic strain λ_e is defined by the ratio of yield stress to the initial modulus. The plastic strain λ_p was obtained from the difference between the yield strain and the elastic strain ($\lambda_p = \lambda_y - \lambda_e$). The standard deviation of the five test samples to the average value in respect to stress were about ± 5 and $\pm 1.5\%$ for the strain. The data on these properties and their variation with temperature and time of thermooxidative degradation are presented in Tables II and III.

RESULTS AND DISCUSSION

Weight Loss and Change in Film Thickness

The percent weight loss of oxidized PP films after 24 h at different temperatures of exposure are

Table I   Density, Weight Loss, and Change in Film Thickness of Aged PP Films at Different Temperatures

Temperature (°C)	Density (g cm^{-3})	Initial Mass (g)	Percent Weight Loss	Final Film Thickness[a] (mm)	Percent Increase in Thickness
80	0.915	0.8152	0.183	0.13	8.3
100	0.912	0.8053	2.215	0.13	8.3
110	0.905	0.8255	0.225	0.15	25.0
130	0.901	0.7771	0.273	0.16	33.3
150[b]	[b]	[b]	[b]	[b]	[b]

[a] Initial film thickness 0.12 mm.
[b] Film destroyed.

Table II Variation of Tensile Properties with Temperature

Temperature (°C)	Yield Stress σ_y (MPa)	Yield Strain λ_y	Initial Modulus E (MPa)	Plastic Strain λ_p	Elastic Strain λ_e	Work of Yield U_y (MPa)
80	27.0	0.15	600	0.105	0.045	7.5
100	23.1	0.10	450	0.049	0.051	5.4
110	22.3	0.12	380	0.061	0.059	4.0
130	18.6	0.11	300	0.048	0.062	3.0
uPP (27°C)	18.3	0.17	1000	0.152	0.018	5.0

Strain rate 5 cm min^{-1}; uPP, untreated PP.

given in Table I. The percent weight loss appears to increase fairly linearly with increase in temperature. This is expected, as a higher temperature will melt and vaporize a lower molecular weight polymer and products of chain scission from thermal aging. However, the relatively low percent weight loss over the temperature range suggests thermal stability in support of the highest service temperature of 160°C.

The increase in film thickness with temperature as demonstrated in Table I may be explained by increased chain folding. Also, from Table I, increase in film thickness correlates with a decrease in density. Jourdan et al.[16] correlated an increase in density with an increase in the crystallinity ratio of heat-treated PP samples from X-ray data.

Stress–Strain Curves

The shapes of the stress–strain curves for the thermally oxidized PP films in the yield region

are shown in Figure 1(a) to illustrate the effect of increasing oxidation temperature and in Figure 1(b,c) to elucidate the effect of the time of oxidation at 60 and 100°C. From Figure 1(a), it would appear that increase in the oxidation temperature decreased the stress on the treated PP films. From Figure 1(b,c), it appears that the stress decreased with the time of thermal aging at the two temperatures of 60 and 100°C. Mathur and Mathur[17] showed that PP films aged in air in the temperature range 70–90°C resulted in reactions involving a change in the molecular structure and the formation of oxygenated and unsaturated groups which increased the molecular weight ($\bar{M}_v$) produced by recombination of alkyl and alkoxy radicals which produced nonradical products. Such decreases in stress are explained by a decrease in the density (crystallinity) of PP samples with thermal aging (Table I).

Yield Stress

The yield stress was estimated from the maximum of the stress in the yield region. From Table

Table III Variation of Tensile Properties with Time of Thermal Oxidation at Two Temperatures

Time (min)	Density (g cm^3)	Yield Stress σ_y (MPa)	Yield Strain λ_y	Initial Modulus E (MPa)	Elastic Strain λ_e	Plastic Strain λ_p	Work of Yield U_y (MPa)
At 60°C							
60	0.907	26.6	0.20	900	0.027	0.173	9.0
90	0.904	24.8	0.16	760	0.033	0.127	6.0
120	0.903	23.8	0.14	733	0.032	0.108	5.5
180	0.902	22.0	0.14	667	0.330	0.107	4.8
At 100°C							
30	0.906	26.0	0.16	875	0.030	0.130	6.5
60	0.903	25.6	0.16	720	0.036	0.124	6.2
120	0.902	23.5	0.14	667	0.035	0.105	5.3
180	0.901	21.5	0.14	583	0.039	0.101	5.5
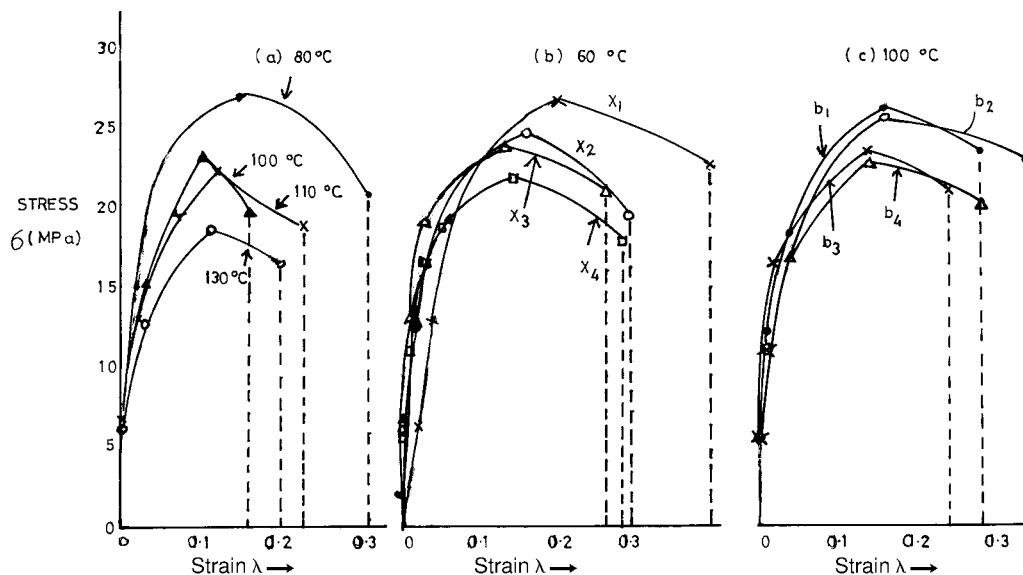
Figure 1 Change in shape of stress–strain curve in the yield region: (a) at different temperatures; (b) at 60°C for different time intervals; (c) at 100°C at different time intervals: X_1 = 60 mm; X_2 = 90 mm; X_3 = 120 mm; X_4 = 180 mm. b_1 = 30 min; b_2 = 60 min; b_3 = 120 min; b_4 = 180 min.

II and the yield stress σ_y versus temperature plots (Fig. 2), it appears that yield stress decreased linearly with increase in aging temperature. The yield stress extrapolates to zero at 167°C. Magill and Peddada[18] in their DSC studies on the heat capacity of PP showed that PP crystallized with the shish-kebab fibrils with an extended backbone structure melted in the range 168–171°C, with a minor peak at 180–190°C.

The plots of variation of yield stress σ_y with increasing log time (min) of thermal oxidation at a particular temperature are given in Figure 3. The yield stress is shown to decrease, although marginally, with log time. The decrease in yield stress corresponds to the decrease in the density (crystallinity) of aged PP samples as shown in Table I. Figure 3 also indicates clearly that the curves for the two temperatures are fairly parallel, i.e., the decrease rates are equal, with the lower temperature-oxidized (60°C) films having larger values of yield stress at equivalent time intervals.

Yield Strain, Elastic Strain, and Plastic Strain

The data on yield strain λ_y, elastic strain λ_e, and plastic strain λ_p are presented in Table II for the effect of temperature and in Table III for the effect of time of oxidation at 60 and 100°C. The plots of strain against temperature in Figure 4 show that

the yield strain λ_y and plastic strain λ_p decreased with increase in temperature, while the elastic strain λ_e increased with increase in temperature. A possible reason could be a drop in the density (crystallinity) of the aged samples, as seen in Table I. From Table II, the elastic strain λ_e averaged 0.054, which is higher than the range predicted for untreated polymers (0.017–0.030),[19,20] increasing linearly from 0.045 for 80°C aged PP films to 0.062 for 130°C aged films at a strain rate of 5 cm min^{-1}. These values are higher than the values of 0.021 and 0.059 obtained at room temperature and the 117°C test temperature, respectively, by Hartman et al. for polyethylene at a strain rate of 2 cm min^{-1}, nylon 6,6, and poly(4-methylpent-I-ene), all of which exhibited shear deformation.[20–22] In these results, the decrease in the yield strain λ_y and plastic strain λ_p differs from the results of Hartmann et al. for PE.[20] The disparity was largely due to the effect of the changed morphological structures resulting from thermal oxidation, leading to a decrease in density (crystallinity) and use of differing strain rates since elastic strain is known to decrease with increase in the strain rate. Moreover, Hartmann et al.'s work dealt with the variation of these properties with the temperature of mechanical stretching.
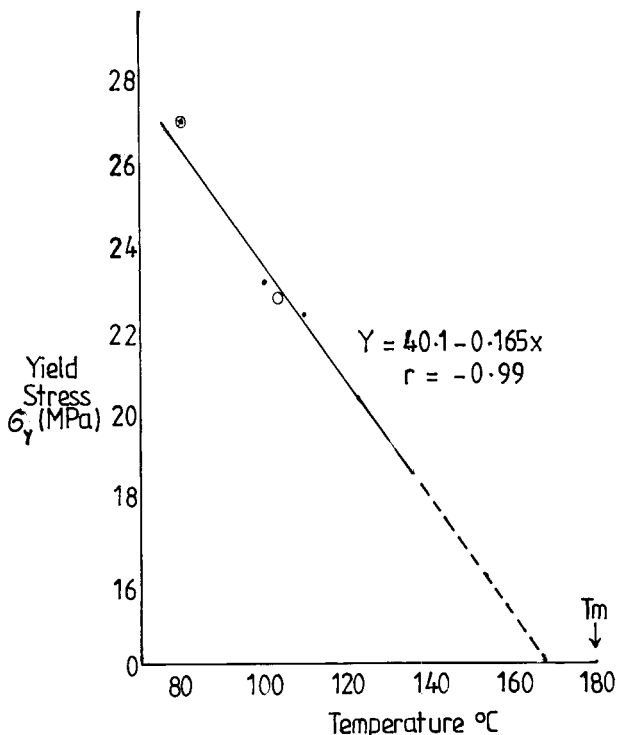
The effect of the time of thermal aging at 60

and 100°C on the strain properties of oxidized PP are shown in Figure 5. The mean elastic strain λ_e of 0.035 at 100°C and 0.031 at 60°C over the time of aging are close to the values predicted for polymers. The variation in these values with the earlier ones may be attributed to the shorter time of exposure in the present case when thermal aging had not produced significant changes in the morphology of the PP films.
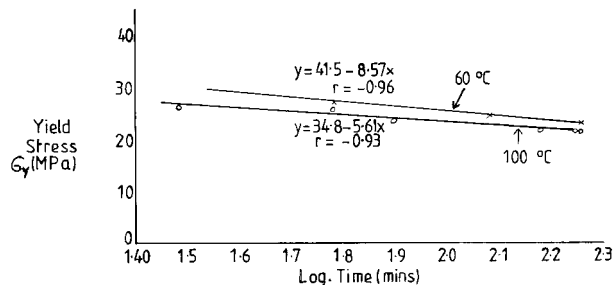
Figure 5 shows that while elastic strain λ_e increased with the log time of oxidation at the two temperatures, yield strain λ_y and plastic strain λ_p decreased with increase in the time of oxidation of the PP films. However, while the elastic strain λ_e for 60°C oxidized PP film is generally lower than that for the 100°C aged PP, the yield strain λ_y and plastic strain λ_p for 60°C aged PP films are larger than those of the 100°C aged PP films at equivalent time intervals. This is explained by the recognition that 60°C aging resulted in fewer degradation effects on the density (crystallinity) than did the 100°C aging.

Initial Modulus

The variation of the initial modulus of thermally oxidized PP films showed a decreasing relation-

Figure 3   Graph of yield stress G_y (MPa) as a function of log time (min) at 60 and 100°C oxidation.

ship with increase in temperature. The data on the initial modulus presented in Table II and plotted in Figure 6 extrapolate to zero at 177°C, which is close to the thermodynamic melting point of PP. It is clear, too, that the thermal aging caused a significant reduction in the initial modulus compared to that of untreated PP samples (Table II). The data on the initial modulus E and log time (min) of the thermal oxidation given in Table III are plotted in Figure 7 and they also show a de-

Figure 2   Plot of yield stress G_y (MPa) against temperature of thermal oxidation. r is the regression coefficient.
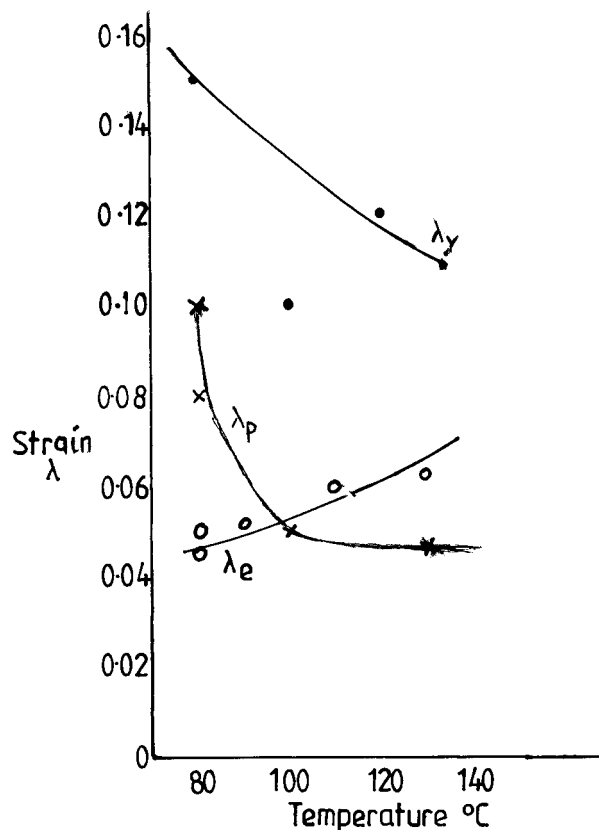
Figure 4   Plots of yield strain λ_y, elastic strain λ_e, and plastic strain λ_p against temperature of oxidation.
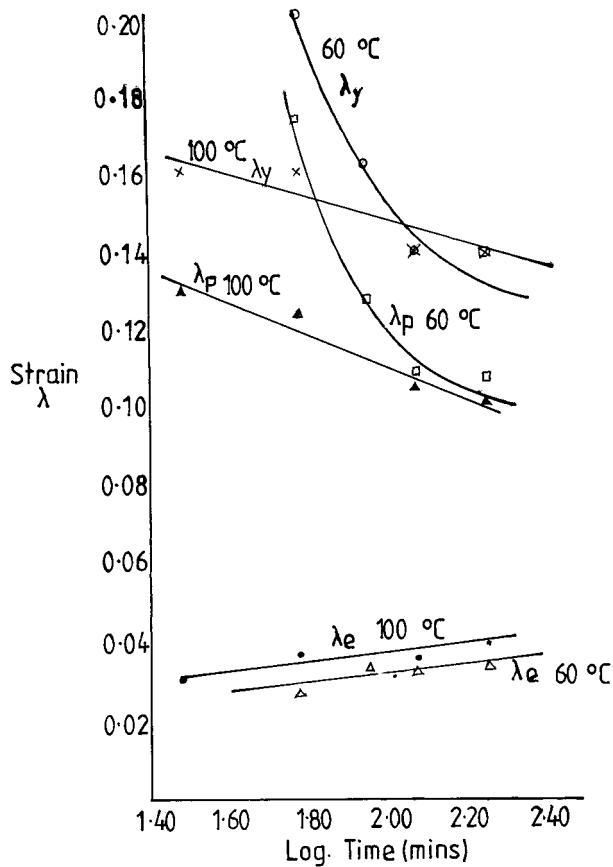
Figure 5 Plots of yield strain λ_y, elastic strain λ_e, and plastic strain λ_p against log time (min) for 60 and 100°C oxidized PP.

creasing relationship between the initial modulus and log times, with the curve for the 60°C oxidation having larger values than those of the 100°C aging at equivalent time intervals. The decrease in the initial modulus with temperature and time of treatment at a particular temperature is due to a drop in the density (degree of crystallinity) of the aged PP films.

Work of Plastic Yielding U_y

The work of yield or energy expended in yielding, U_y, is defined as the energy dissipated for plastic yielding to take place. It is estimated from the area of the stress–strain curve from the origin to the yield point. The data at different temperatures of aging and different times of aging at 60 and 100°C are presented in Tables II and III, respectively. From Figure 8, a plot of the work yield against temperature, it is evident that the work of
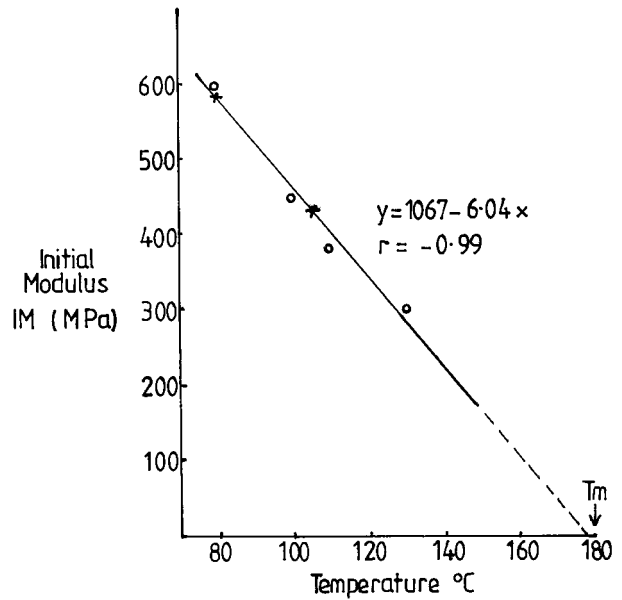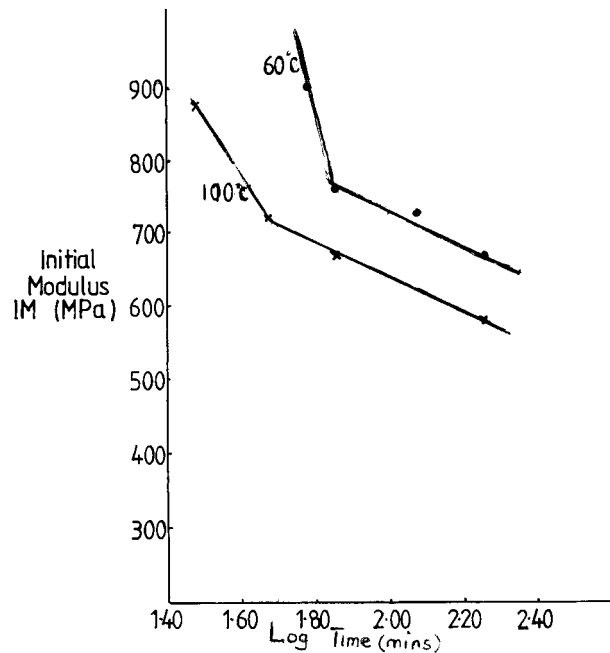

Figure 6 Plot of initial modulus IM (MPa) against temperature of oxidation. r is the regression coefficient.

yield, U_y, decreased with increase in temperature. The work of yield U_y is given by eq. (1):

$$U_y = K\rho C_p (T_m - T) \qquad (1)$$

where K is a constant that depends on the Kelvin

**Figure 7** Plot of initial modulus IM (MPa) against log time (min) for 60 and 100°C oxidized PP.

temperature of aging T; T_m, the melting point; and ρ and C_p, the average density and heat capacity, respectively, over the temperature range T and T_m. Equation (1) was obtained by putting K in place of the b/b' term, representing the ratio of fraction of the thermal to mechanical energy available to overcome the activation barrier to yielding, used by Hartmann et al.[20–22] to estimate the yielding energy from thermodynamic effects for semicrystalline polymers. It is assumed that changes in the temperature of thermal oxidation of the PP film will affect the morphological structures by the development of oxygenated products and chain cleavages which will then influence the density (degree of crystallinity) and other physical properties of heat capacity, and heat of fusion.

The temperature derivative of eq. (1) is eq. (2):

$$-dU_m/dT = K\rho C_p \qquad (2)$$

Using average values of density (0.908 g cm^{-3}) and heat capacity C_p $1.94 \text{ J K}^{-1} \text{g}^{-1}$ and the average value of $K = 0.047$ determined from the slope of the estimated yield energy versus the oxidation temperature curve (Fig. 9), the yield energy due to thermal aging may be calculated.

The energy of yielding due to thermal aging at a particular temperature may be extended to
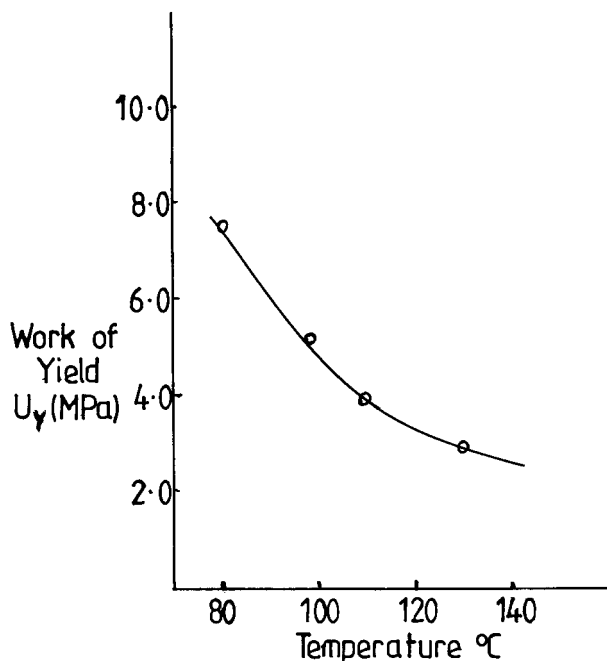
Figure 8 Plot of work of yield U_y (MPa) against temperature of thermal oxidation.

include time effects. The data on yielding energy U_y are plotted in Figure 10 against log time (min) for 60 and 100°C aged PP films. From Figure 9, it is evident that there is a decrease in U_y with log time (min).

The time effects on yield energy U_y may be given by eq. (3):

$$U_y = K\rho C_p \Delta T(t_f - t_t) \qquad (3)$$

where ΔT represents $(T_m - T)$ of eq. (1) and t_f and t_t are the melting and the aging times, respectively, at aging temperature T. The time derivative of eq. (3) is given by eq. (4):

$$-dU_y/dt = K\rho C_p \Delta T \qquad (4)$$

The quantities on the right-hand side of eq. (4) are constants at a particular aging temperature and can be estimated from known parameters or can be estimated from the slope of the yield energy vs. log time of the aging plot. The calculated value of $-dU_y/dt$ of eq. (4) using average C_p values[23] of $1.94 \text{ J K}^{-1} \text{ g}^{-1}$ over the range of 60 and 100°C thermal aging are 9.88 and 6.56 MPa min^{-1}.

Morphological changes resulting from the thermal aging of PP films may be responsible for the changes in the properties. It has been established that oxidation of PP takes place in the amorphous region[24–25] and the formation of alkyl ($R^{\bullet}$) and alkyl peroxy ($ROO^{\bullet}$) radicals from the primary oxidative process.[24] The helical structure of iPP affords intra- and intermolecular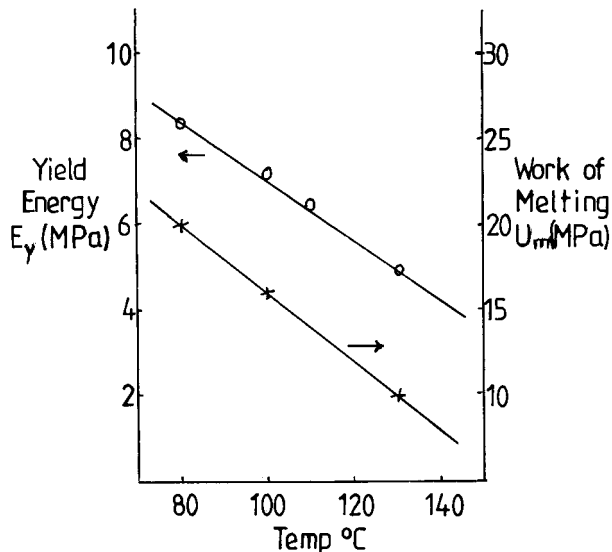 hydrogen abstraction, and in the presence of oxygen, oxygenated groups such as carbonyl $\diagdown$C$=$O and peroxide —OOH groups are formed.[24–26] Several workers[16,24,27] have investigated the changes in the physicochemical properties of thermally aged PP films.

The decrease in initial modulus, yield stress, plastic strain, yield strain, and work of yield with aging temperature indicated a decrease in the crystallinity of the treated samples. Mathur and Mathur[17] reported an increase in density and isotactic content resulting from increased molecular ordering, i.e., a crystallinity increase during low-temperature aging. At the higher temperatures used for this study (up to 130°C), a decrease in the density would be expected to lead to a decrease in the crystallinity as implicated by the reduction
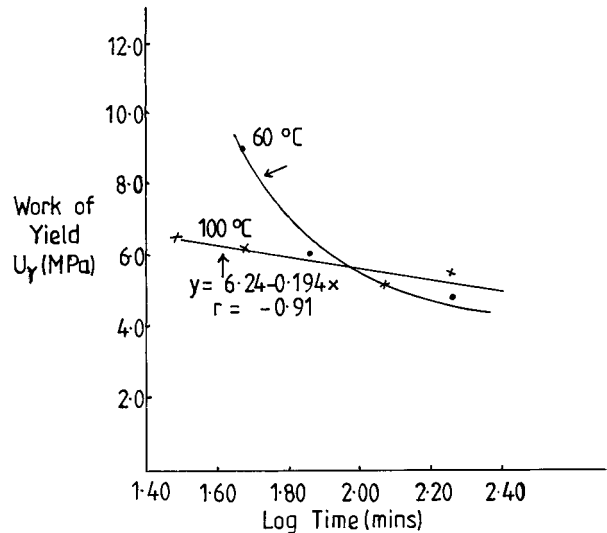
in the properties of the treated films. The effect of time revealed that 60°C aging resulted in less deterioration of properties than did the 100°C aging at equivalent time intervals and these decreased with time of aging. Moreover, a shorter time of aging (24 h) at higher temperatures up to 130°C was enough to produce a significant reduction in the properties. Mathur and Mathur[17] obtained a loss in properties over a very long time interval and aging at low temperatures (70–90°C). At the early stages of aging, at a low temperature ordering in the amorphous matrix, recombination of alkyl radicals in a more ordered form and chemicrystallization resulting from increased oxygenated groups are reported to increase density and, hence, crystallinity.[17] A higher aging temperature needed a smaller time interval to cause a significant reduction in the properties. At longer time intervals and higher temperatures, faster rates of chain scission and volatilization of products rather than recombination of oxygenated products would cause a decrease in density (crystallinity) and lead to the deterioration of PP films.

CONCLUSIONS

Tensile yield measurements were made on thermally aged PP film samples. The study focused on the effects of temperature and time of thermal

Figure 10 Plot of work yield U_y (MPa) as a function of log time (min) for 60 and 100°C oxidized PP. r is the regression coefficient.

oxidation at a particular temperature on the yield properties, yield stress, initial modulus, yield strain, elastic strain, plastic strain, and energy of yielding. The following conclusions were reached:

- Yield stress and initial modulus are linear functions of temperature, extrapolating to zero at the thermodynamic melting point.
- Yield stress, yield energy, and initial modulus decreased with increase in time of thermal aging with the values for the 60°C aged films remaining larger than those for the 100°C aged PP films at equivalent times.
- The yield strain, plastic strain, and work of yield decreased with increase in temperature while the elastic strain increased with increase in temperature as the density (crystallinity) of aged PP film decreased.
- The plastic strain and yield strain for 60°C aged PP film had values larger than the corresponding values for the 100°C aged film at equivalent time intervals, while the 100°C aged film exhibited a larger elastic strain than that of the 60°C aged PP film at equivalent times of aging.

Figure 9 Plot of yield energy E_y (MPa) and work of melting U_m (MPa) against temperature (°C).

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