Time and Temperature Effects on the Ultimate Properties of Thermally Oxidized Polypropylene Films

T. C. UZOMAH, S. C. O. UGBOLUE

Department of Polymer and Textile Technology, Federal University of Technology, Owerri, Imo State, Nigeria

ABSTRACT: The ultimate properties of thermally oxidized polypropylene (PP) films have been determined. Attention was focused on the variation of draw stress, tensile strength, draw ratio, breaking extension, breaking factor, work of draw, and work of rupture, with a change in temperature and time of heat treatment. While the draw stress and draw ratio increased with increase in temperature, the tensile strength, breaking extension, work of rupture, and work of draw decreased with increase in temperature. The breaking factor, rather, attained a maximum at 110°C before decreasing with further increases in temperature. The PP films thermally oxidized at 60°C exhibited larger values for the following properties: tensile strength, breaking extension, draw ratio, work of rupture, work of draw, and breaking factor, than for the 100°C oxidized PP films. While breaking extension and tensile strength just decreased with increasing the log time (min), the draw stress, draw ratio, work of rupture, and work of draw were linear functions with negative slopes of log time (min) of thermal oxidation at a particular temperature. The decrease in all properties studied were explained by decrease in the density of aged PP films. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1217–1226, 1997

INTRODUCTION

The thermooxidative degradation of polyolefins, especially polyethylene and polypropylene (PP), has been extensively investigated. It has been established that the thermooxidative sensitivity of these polymers is largely due to the presence of impurities—hydroperoxides and carbonyl groups introduced during high-temperature manufacturing processes.[1–8] Secondary bond forces formed between the polymer chains and chain scission result in the change in the morphology of the molecules and these bring about oxidation products.[5,6,9] Intramolecular hydrogen abstraction, especially from the helical structure and intermolecular hydrogen abstraction from the PP chain, has

been proposed as the mechanism for the radical chain scission.[4,6,10]

The deterioration of the useful physicomechanical properties, e.g., density, elongation at break, and tensile strength of the PP films following thermooxidation, have been studied.[6,11–16] Madan and Gent[17] included the variation of yield stress, draw ratio, and draw stress with temperature of stretching. In our contribution,[10] we reported the effect of time of exposure and temperature on the density and the tensile yield properties of PP. In addition to the usual yield properties studied, attention was focused on the seldom-discussed properties: plastic strain, which decreases, and elastic strain, which marginally increases with increasing temperature of degradation. All the properties studied exhibited larger values for the 60°C oxidized PP film than for the 100°C oxidized PP film at equivalent time intervals.

The present article was concerned with time and temperature effects on the ultimate properties of

Table I   Variation of Ultimate Properties with Temperature of Oxidation

Temp (°C)	Density (g cm^{-3})	Draw Stress σ_d (MPa)	Draw Ratio λ_d	Tensile Strength σ_b (MPa)	Breaking Ratio λ_b	Breaking Factor (BF) kN m^{-1}
80	0.915	23.0	5.3	50.2	9.9	25.1
100	0.912	20.0	3.5	49.7	9.4	24.9
110	0.905	18.8	3.3	53.2	9.7	26.6
130	0.901	15.0	2.0	39.3	8.7	19.8
27 (uPP)		15.6	5.3	33.1	10.3	20.8

The data for untreated PP, uPP at 27°C are included for comparison.

thermally oxidized PP films. The changes in the ultimate properties, viz., tensile strength, extension at break, draw stress, draw ratio, and the seldom-studied breaking factor, were investigated.

EXPERIMENTAL

Materials

Polypropylene (PP) films (thickness 0.12 mm, density 0.90 g cm^{-3}) were supplied by the Bag Manufacturing Co. (BAGCO), Lagos, Nigeria.

Method

The method of heat treatment was fully described in Ref. 18. The cooled heat-treated films were cut into dog-bone-shaped structures and stretched at a strain rate of 5 cm min^{-1} and gauge length of 5 cm, using an Istron tensile testing machine (Model 1122) at 25°C and 65% RH. Several ultimate prop-

erties were determined from the stress–strain curve. The standard deviation from the average value for the five test samples with respect to stress was about ±5%, and the strain was ±1.5%. The density of aged PP films was determined in a water/propan-2-ol density gradient column.[18]

The following ultimate properties were determined; draw stress σ_d, draw ratio λ_d (defined by the increase in length at the drawn portion over the original gauge length), tensile strength σ_b, breaking ratio λ_b (defined by the ratio of elongation at moment of rupture to original gauge length), and works of plastic deformation, i.e., work of draw U_d and work of rupture U_r. Data on these quantities and their variation with temperature and log time of aging are presented in Tables I–IV.

RESULTS AND DISCUSSION

The ultimate properties of interest are draw stress σ_d, draw ratio λ_d, tensile strength σ_b, breaking ratio λ_b, and breaking factor (BF).

Table II   Effect of Time of Aging on the Ultimate Properties of Aged PP Films at 60 and 100°C Aging

Time (min)	Density (g cm^{-3})	Draw Stress σ_d (MPa)	Draw Ratio λ_d	Tensile Stress σ_d (MPa)	Breaking Ratio λ_b	Work of Draw U_d (MPa)	Work of Rupture U_r (MPa)
60°C							
60	0.906	22.5	4.5	50.5	10.3	101	300
90	0.904	19.5	4.0	42.2	9.8	78	241
120	0.903	21.0	3.8	45.3	10.5	80	296
180	0.902	17.0	3.6	38.3	9.8	61	221
100°C							
30	0.907	23.2	1.9	47.6	8.9	44	93
60	0.903	23.1	1.8	43.0	8.0	42	86
120	0.902	20.5	1.7	34.0	6.6	35	61
180	0.901	20.2	1.6	36.7	6.7	32	60

Table III   Effect of Temperature on Works of Drawing U_d and Rupture U_r.

Temp (°C)	Work of Draw U_d (MPa)	Work of Rupture U_r (MPa)
80	122	290
100	70	265
110	62	262
130	23	222
27 (uPP)	98	265

uPP = untreated PP film.

Draw Stress and Draw Ratio

The data on the draw stress σ_d and draw ratio λ_d are shown in Table I and plotted in Figure 1 against the temperature of oxidation. The draw
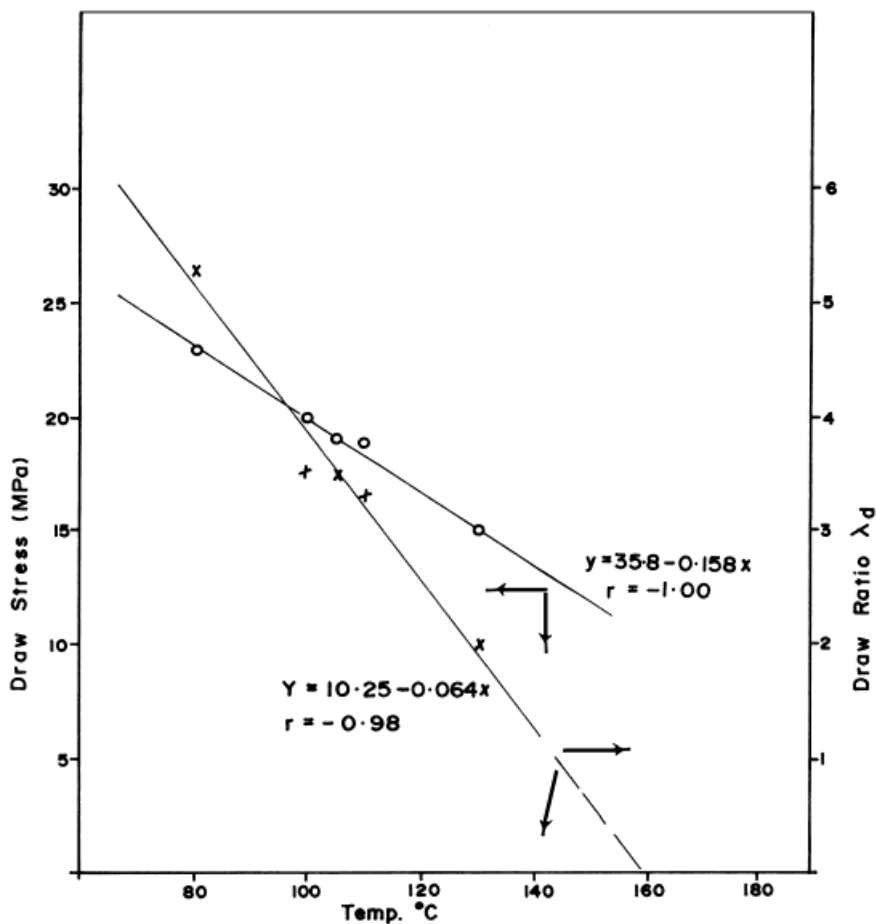
Table IV   Effect of Time of Aging on Work of Draw U_d and Work of Rupture U_r at 60 and 100°C on PP Films

Time (min)	Work of Draw U_d (MPa)	Work of Rupture U_r (MPa)
60°C		
60	108	300
90	78	241
120	80	295
180	61	221
100°C		
30	44	93
60	42	86
120	35	61
180	32	60

Figure 1   Plots of draw stress σ_d and draw ratio λ_d as a function of aging temperature, r = regression coefficient.
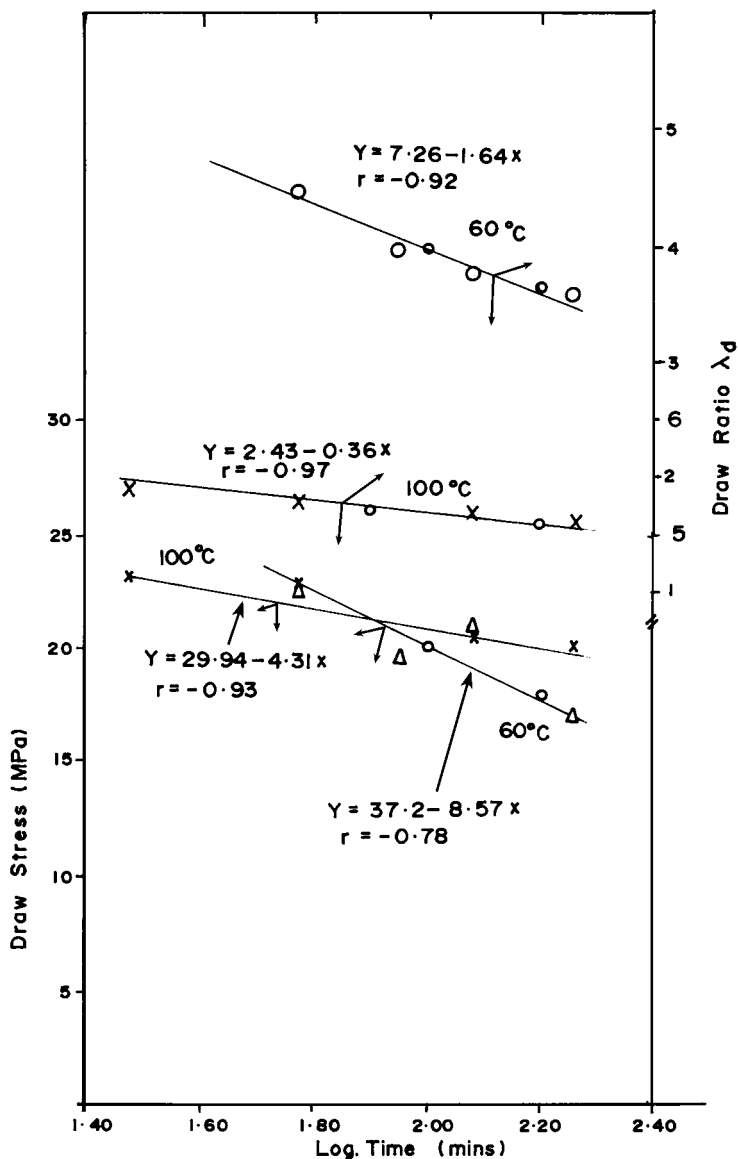
Figure 2 Plots of draw stress σ_d and draw ratio λ_d vs. log time. γ = regression coefficient.

stress and draw ratio decreased sharply with increasing aging temperature, with the draw ratio extrapolating to zero when the treated film should become brittle at 160°C below the melting point of untreated PP film (170°C), while the draw stress is expected to extrapolate to zero above the melting point of PP film. The results for the draw stress are similar to those obtained for other semicrystalline polymers by Gent and Madan,[17] who measured draw stress with stretching temperature. The decrease in draw stress and draw ratio which correlates with decrease in density (Table

I) can be explained by the effects of thermal aging. However, the data on the draw ratio λ_d are different from those obtained by the same workers.[17]

The data on draw stress σ_d, draw ratio λ_d, and the time (min) of thermal degradation at 60 and 100°C are presented in Table II and plotted in Figure 2. The draw stress–log time (min) curve for 60°C aging exhibited a steeper slope than did the corresponding curve for the 100°C aged film and intersected unexpectedly at log time 1.90 (80 min). The draw ratio λ_d for the 60°C-aged film was significantly larger than that of 100°C-aged
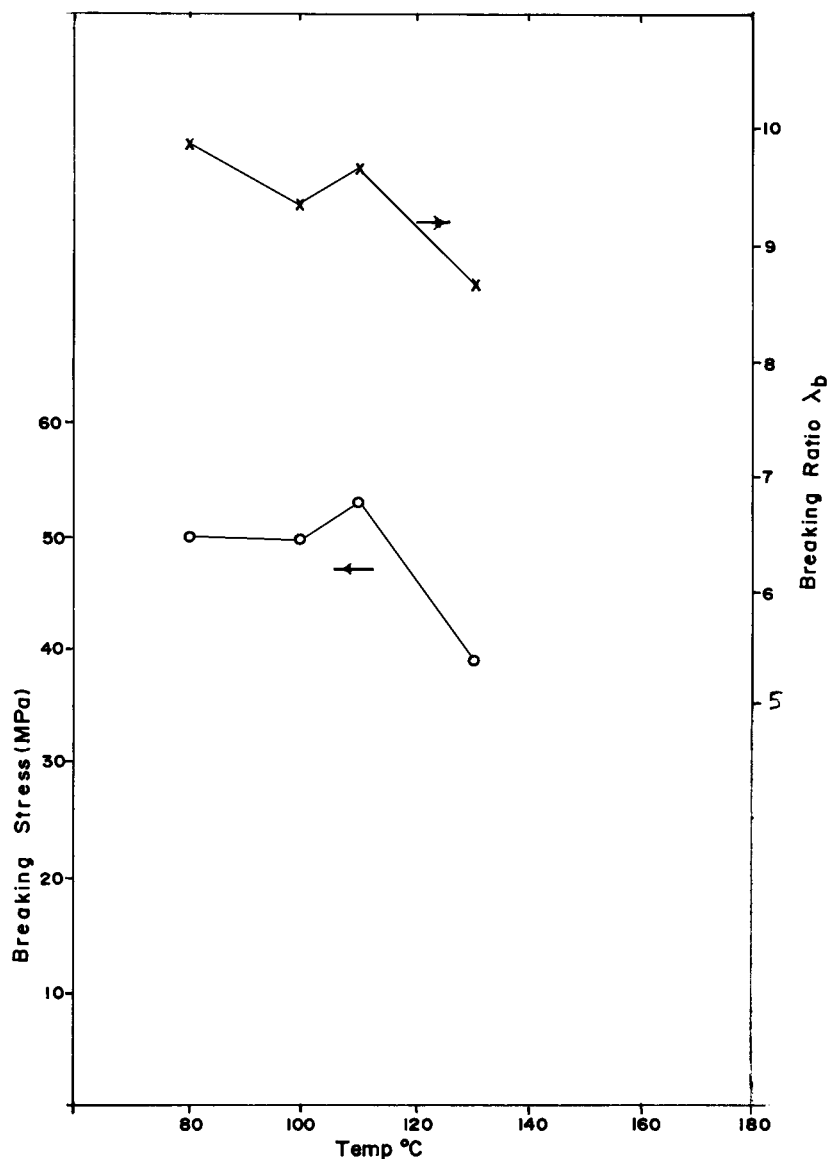
Figure 3   Plots of breaking stress and breaking ratio λ_b.

film at equivalent times of aging. This is expected as thermal aging effects are more effective at higher temperature: 100°C.

Tensile Strength and Breaking Ratio

The data on tensile strength σ_b, breaking ratio λ_b, and temperature of thermal aging are given in Table I and plotted in Figure 3. From Figure 3, it is clear that the tensile strength σ_b, initially constant up to 100°C, increased, reached a maximum for 110°C-aged film, and then decreased rapidly with increase in temperature as had earlier been reported.[14] On the other hand, Figure 3 indi-

cates a steady decrease in breaking ratio λ_b, up to 100°C aging, then increased to a maximum for the 110°C-aged film before decreasing with further increases in temperature. The increase in tensile strength has been attributed to higher ordering in the amorphous matrix and recombination of the alkyl radical in a more ordered arrangement, while chain scission decreases the value.[14]

The data on variation of tensile strength σ_b and breaking ratio λ_b with time at the two temperatures of thermooxidative degradation are presented in Table II and plotted in Figure 4. From Figure 4, it is clear that the tensile strength σ_b for the 60°C aging decreased monotonically, while
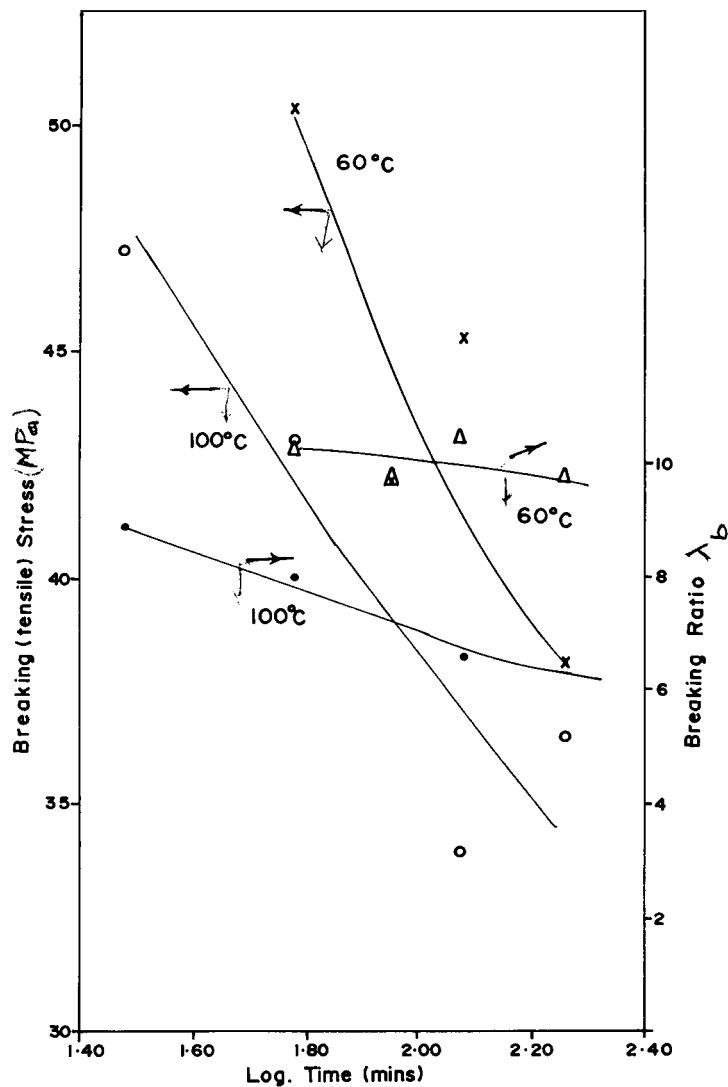
Figure 4 Plots of breaking (tensile) stress σ_b and breaking ratio λ_d against log time at two temperatures.

the breaking ratio λ_b remained fairly invariant to increasing log time, and the tensile strength σ_b and breaking ratio λ_b for 100°C aging decreased linearly with the log time of oxidation at equivalent time intervals. This was expected, as higher aging temperature caused more degradation of the polymer film, which led to a decrease in tensile strength and breaking ratio. The kinetics of tensile strength σ_b at the two temperatures were apparently similar, but it must be noted that 100°C aging would lead to "zero" tensile strength long before the 60°C aging. For linear polyethylene PE, Popli and Mandelkern[19] showed that the tensile strength decreased markedly with increasing molecular weight, but was invariant to different mo-

lecular structures, crystallinity, and crystallite thickness.

The same investigators[19] who used the ambient stretching temperature also showed that the breaking ratio was dependent on the molecular weight. Thus, thermal aging of PP films led to the formation of oxygenated and carbonyl products with different molecular weights from unaged PP films, and these affected tensile strength and breaking ratio similarly.

Breaking Factor (BF)

The BF is probably the most seldom discussed ultimate property of polymer materials. The di-
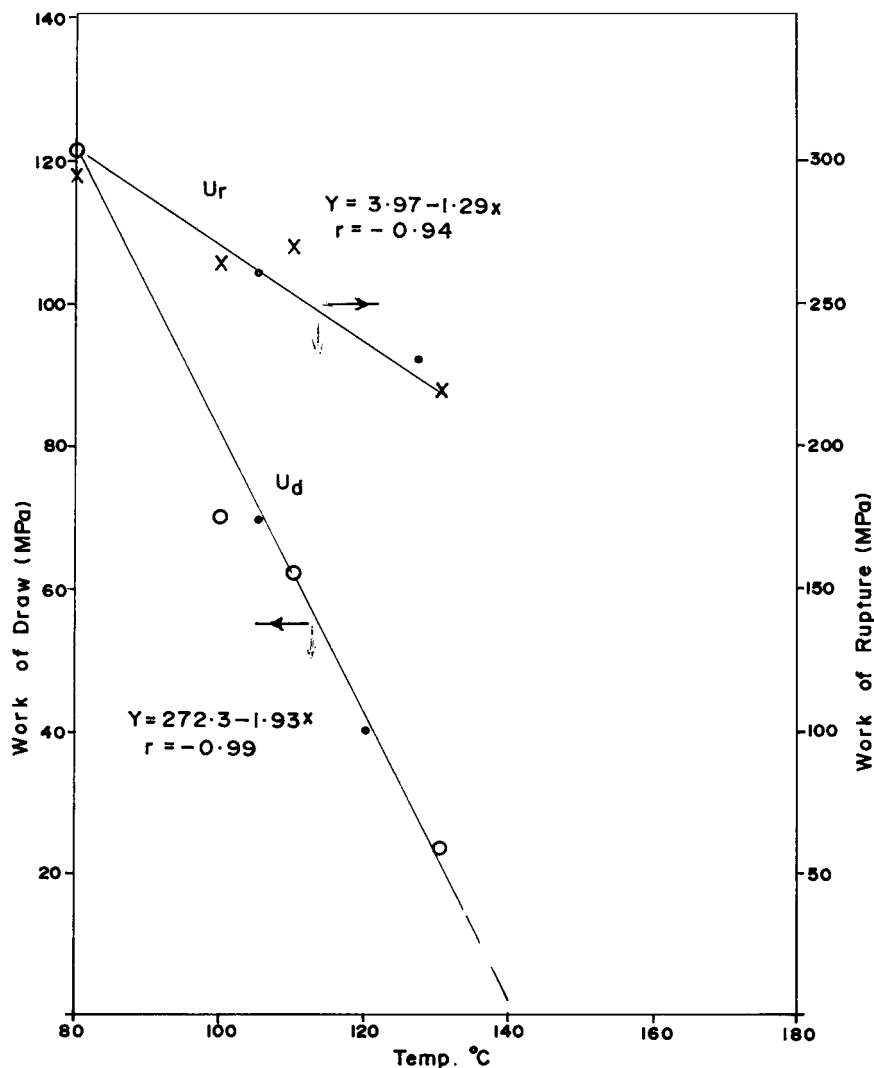
Figure 5 Plots of work of draw and work of rupture against aging temperature. γ = regression coefficient.

rect relationship with tensile stress σ_b probably explains why this is so. Even though it is not a measure of strength, it defines the tension in the drawn films at the moment of rupture.

The data on the variation of the BF with temperature and time of aging at 60 and 100°C, respectively, are presented in Tables I and II. From Table I, it would appear that the BF increased monotonically, reaching a maximum at 110°C before decreasing with further increases in the aging temperature, following the same trend as the tensile strength. From Table II, it is clear that the BF for 60°C-aged PP films had higher values than those of the 100°C-aged films at equivalent time intervals. This is expected, as the higher temperature and longer time of aging resulted in

more chain scission and carbonyl formation in the polymer chain than did the 60°C aging. From Table I, it is evident that the 130°C-annealed and the untreated PP films had about an equal BF value. This finding is in support of the claim that some properties increased before decreasing with increase in temperature.[14]

Ultimate Works of Plastic Deformation

The ultimate works of plastic deformation studied are the work of draw, U_d, and work of rupture, U_r. Data on these quantities are presented in Tables III and IV.
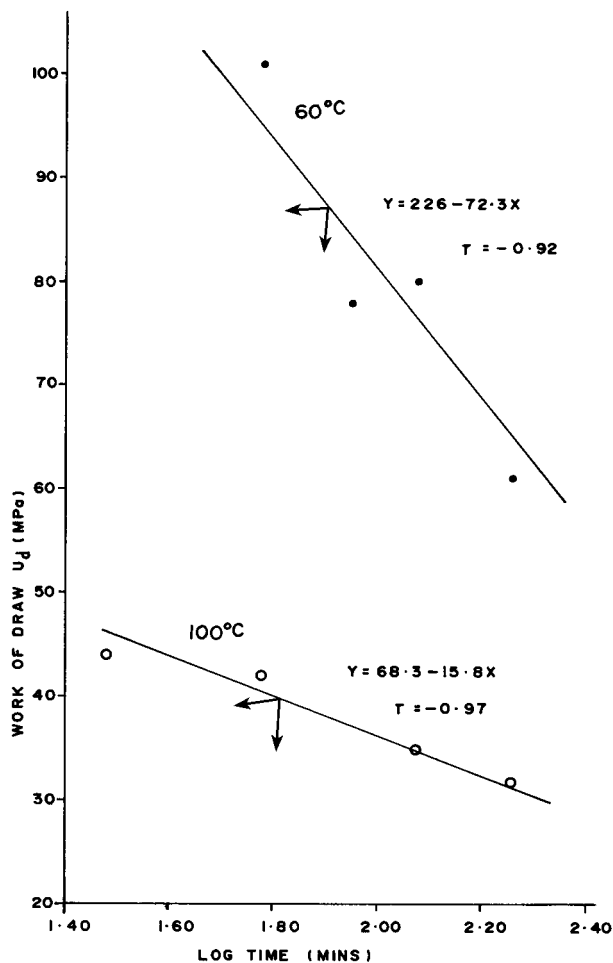
Figure 6 Plots of work of draw U_d against log time at two temperatures. r = regression coefficient.

Work of Draw

This is the energy expended in the drawn portion of the deformation process. It is estimated from the area of the stress–strain curve in the drawn portion, where σ_d is the draw stress and λ_d is defined by the elongation divided by the original gauge length given by eq. (1):

$$U_d = \int \sigma_d \cdot \delta \lambda_d \qquad (1)$$

$$U_d = \sigma_d \cdot \lambda_d \qquad (2)$$

Equation (2) is useful for the estimation of U_d when σ_d and λ_d have constant values.[17] The work of draw U_d, presented in Table III for the different aging temperatures and in Table IV for the time intervals for 60- and 100°C-aged PP films, are plotted in Figures 5 and 6, respectively.

From Figure 5, it is clear that the work of draw

is a linear function of temperature of thermooxidative degradation. The curve, however, extrapolates to zero at 140°C, well below the thermodynamic melting temperature.

Carbonyl formation and chain scission resulted in a decrease in density (crystallinity) which caused a decrease in the draw stress σ_d and draw ratio λ_d. From eq. (2), for PP with a low draw ratio λ_d,[2–5] and at constant draw stress σ_d, the work of draw will have values ranging from $\frac{1}{5}$ to $\frac{1}{2} \sigma_d$, as the temperature increased from 60 to 130°C (Table III).

From Table III, a presentation of the effect of time on the work of draw at two aging temperatures, 60 and 100°C, and plotted in Figure 6, it is evident that the work of draw decreased linearly with aging time. Clearly, the work of draw for 60°C-aged film generally had larger values at equivalent time intervals and ranged from $\frac{1}{2}$ to $\frac{2}{3}$ σ_d from 30 to 180 min aging than that for the 100°C-aged film, which ranged from $\frac{1}{5}$ to $\frac{1}{4} \sigma_d$ from 60 to 180 min treatment. Thus, higher-temperature aging resulted in more serious degradation effects.

Work of Rupture U_r

The impression had been created that the characteristics of plastic deformation could be obtained from a full understanding of the yielding process.[19] This is probably the reason why the work of rupture is the least studied ultimate work of deformation. But subtle differences in the experimental conditions may result in significant departure from the expected correlation between the yielding process and fracture behavior and, in particular, between the work of yield and the work of rupture.

From Table III and Figure 5, it appears that the work of rupture decreased with increase in the aging temperature; as the density of the aged PP film decreased, the work of rupture for the 100–110°C aging was approximately equal to that of unaged (27°C) PP film (ca. 265 MPa). The data for the unaged PP film and the 60°C-aged film indicated an initial increase in the work of rupture.

The work of rupture plotted against log time at the two temperatures, 60 and 100°C, is given in Figure 7. It is clear that the work of rupture U_r for the 100°C thermal aging was significantly less than that of the 60°C-aged PP film. The work of rupture at a particular aging temperature de-
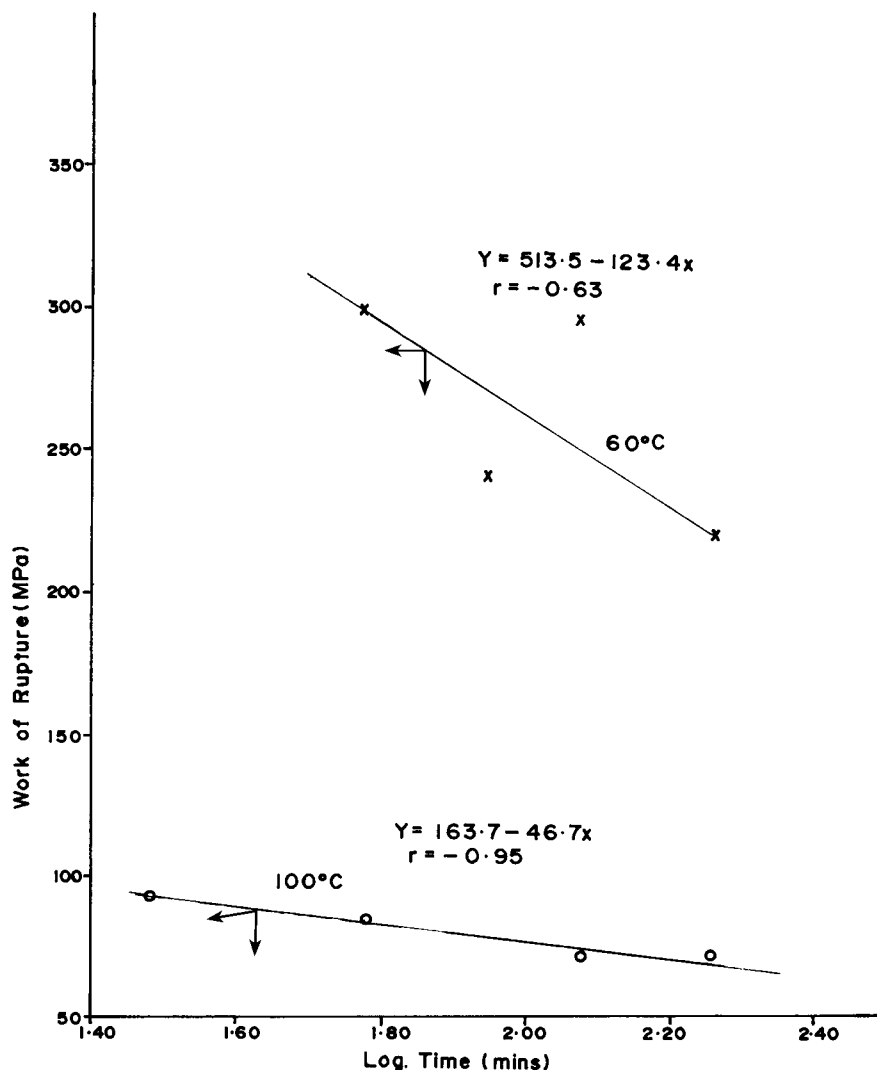
Figure 7 Plots of work of rupture against log time at two aging temperatures. γ = regression coefficient.

creased with increasing log time of thermal aging, the decrease being monotonic for the 60°C-aged and linear for the 100°C-aged film.

The thermal stability and consequent deterioration of PP films have been studied by several workers. The stability depends on unavoidable trace amounts of impurities, carbonyl and hydroperoxide groups, and catalyst residue.[4–7] Radical mechanistic bond cleavages and intra- and intermolecular hydrogen abstraction result in the formation of oxygenated products, which lead to the deterioration of the physicochemical properties.[4–7,11–14] Mathur and Mathur[14] reported an initial increase in the viscosity-average molecular weight $\bar{M}_v$, which later decreased to values lower than that of unaged film after a long time interval (1200 h) for 90°C-aged

film. A competition between ordering in the amorphous region and recombination of the alkyl radical, on the one hand, and a faster rate of chain scission, on the other, has been proposed as affecting the tensile strength.[14] The former improves crystallinity and density and, hence, tensile strength, while the latter decreases the value. Also, cleavage of the polymer chain in the amorphous region may cause the nonhelical poorly ordered molecular chains to adopt a more ordered helical form, which results in an increase in the local order and density.[14] Considerable increases in crystallinity and density have been explained by increased ordering of low molecular weight segments in the amorphous matrix.[14] Chain scission has been reported to take place mainly by β-cleavage reactions

of macroalkoxy radicals which lead to the formation of carbonyl esters, carboxylic acids, and other unsaturated groups.[11]

CONCLUSION

The ultimate properties of thermally oxidized PP films have been determined. The emphasis was on the effects of temperature and the time of thermal oxidation at a particular temperature on the following properties: draw stress, tensile strength, draw ratio, extension at break, work of draw, and work of rupture. We may conclude that thermal aging caused a decrease in crystallinity which results as follows:

- Draw stress and draw ratio are linear functions of aging temperature, with the draw stress extrapolating to zero close to the thermodynamic melting temperature.
- The draw stress and draw ratio at 60 and 100°C were linear functions of log time (min) of exposure, with the draw ratio for the 60°C oxidized PP films generally having larger values.
- The tensile strength and breaking ratio decreased with increase in temperature of oxidation.
- The tensile strength and breaking ratio which had higher values for the 60°C oxidized PP film relative to the 100°C oxidized film decreased with increase in the time interval of exposure at a particular temperature.
- The work of draw and work of rupture decrease with increase in temperature of oxidation, and also the work of draw and work of rupture which had higher values for the 60°C oxidized PP films decreased linearly with increase in the log time of thermal oxidation.
- While the breaking factor exhibited a maxi-

mum value at 110°C, the 60°C oxidized PP film had larger values with log time (min) as compared to the 100° oxidized film.

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