Natural Weathering of Polypropylene Films. II. Ultimate Properties and Exposure Time

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ABSTRACT: Changes in the ultimate properties brought about by outdoor weathering during the rainy season of polypropylene (PP) films were studied. The results obtained showed that the draw ratio λ_d, tensile stress σ_b, breaking ratio λ_b, breaking factor (BF), work draw U_d, and work for rupture U_r all increased with increase in outdoor exposure time, attaining a maximum at about 240-h exposure time, before decreasing with further increases in exposure time. On the other hand, the draw ratio δ_s remained practically constant up to about 100-h exposure time. The changes in the former set of properties were corroborated by the changes in the apparent crystallinity of the PP samples. In addition, it was shown that a 504-h exposure time was not enough to reduce the properties to damaging levels. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2533–2540, 1998

Key words: tensile stress; draw stress; breaking ratio; draw ratio; apparent crystallinity

INTRODUCTION

The deterioration in the physicochemical properties of polyolefins during photo- and thermodegradation and outdoor weathering was studied by several workers.[1–8] Largely, attention was focused on the changes of the chemical evidence. Such changes are expressed by the carbonyl index growth at 715 cm^{-1}.[2,4,8] The hydroperoxide index increases at 3400 cm^{-1} (refs. 3 and 5) from IR spectra have been correlated with the ultimate properties, namely, tensile strength σ_b and elongation at break λ_b. Chain scission along the polymer chain results in decrease in the molecular weight and this leads to a decrease in the properties. For polypropylene (PP) and other semicrystalline polymers, it has been reported that preferential oxidation takes place in the amorphous region[7] and a higher concentration of tertiary carbon on the PP chain favors higher rates of oxidation.[6,7] Outdoor weathering of PP film is presumed sensitive to light intensity, and wetness/humidity and these depend on the location and time (season) of the year.[4]

Not much published work is available on the ultimate properties of outdoor weathering of PP films from this part of the world. The changes in the yield properties and percent apparent crystallinity of 504-h outdoor weathering of PP films in the rainy season have been reported.[9]

It was the purpose of this work to report the results of the natural weathering of PP films during the rainy season with respect to tensile strength σ_b, draw stress σ_d, draw ratio λ_d, and breaking ratio λ_b. In addition, changes in other ultimate properties of the breaking factor (BF), work of draw, and work of rupture are discussed. It is shown that the BF could also be an early indicator of the deterioration of exposed films like tensile strength and breaking ratio.

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Table I   Properties of Exposed PP Films

Exposure Time (h)	AC (%)	Draw Stress (MPa)	Draw Ratio λ_d	BF (kNm^{-1})	Tensile Stress (MPa)	Breaking Ratio λ_b
0 (unexposed)	0	19.8	2.45	4.91	28.9	4.58
48	13.7	19.4	3.75	5.19	20.5	6.78
98	7.0	19.8	4.00	6.56	38.6	7.78
144	−17.6	19.8	3.61	4.57	26.9	5.67
240	−33.3	27.7	4.25	9.69	57.0	9.20
504	−60.0	28.8	3.10	8.71	51.2	6.74

EXPERIMENTAL

Materials

The polypropylene (PP) film (0.17 mm) of density 0.90 g/cm^3 was a homopolymer sample obtained by the kind permission of the Bag Manufacturing Co. (BAGCO; Lagos, Nigeria).

Method

The procedure for outdoor weathering was fully described in an earlier work[9] for the location at latitude 5°21′ N and longitude 7°2′ E. The apparent crystallinity developed was estimated from the critical dissolution time (CDT) data.[10] The CDT was determined in hot toluene and the apparent crystallinity (AC) was determined from eq. (1):

Apparent crystallinity (AC) (%)

$$= \frac{\mathrm{CDT_{treated} - CDT_{control}}}{\mathrm{CDT_{treated}}} \times 100 \quad (1)$$

The ultimate mechanical properties studied were obtained from the stress–strain curve as described earlier.[9] The draw stress σ_d is defined as the constant stress on the film at the draw portion of the stress–strain curve and is usually lower than the corresponding yield stress. The draw ratio λ_d is the change in length to the original gauge length, and the breaking ratio λ_d is increased length up to the moment of rupture divided by the original gauge length. The tensile stress σ_b is the maximum stress at the moment of rupture, while the BF is the maximum stress divided by the initial gauge length.

RESULTS AND DISCUSSION

Critical Dissolution Time (CDT) Data and Apparent Crystallinity (AC)

The data on the CDT and AC of the PP films from outdoor weathering are presented in Table I. The CDT technique[10] assumes that

1. The treated films consist of two phases: the impermeable crystalline region embedded in an amorphous region.
2. The solvent molecules permeate the amorphous phase only.
3. The larger crystallites take a longer time to dissolve than do the smaller crystallites.

In Table I, it is evident that there is an initial increase in the AC of the exposed PP films, reaching a maximum at the 48-h exposed films, before decreasing to lower values. In particular, films exposed to more than 110 h with negative AC values have an AC lower than that of unexposed PP film. The ultimate properties of the exposed PP films, namely, draw stress σ_b, draw ratio λ_d, BF, tensile stress σ_b, and breaking ratio λ_b, with the outdoor exposure time are presented in Table I.

Draw Stress

The data on draw stress σ_d plotted against exposure time (Fig. 1) shows that the draw stress was fairly constant for the first 144 h and then increased with further increases in the exposure time. By the 504-h exposure, the draw stress was 45% higher than that of the exposed PP sample.

Draw Ratio

In Table I and Figure 1, it would appear that the draw ratio λ_d increased with exposure time, attaining a maximum at about 200-h exposure time, before decreasing with further increases in expo-
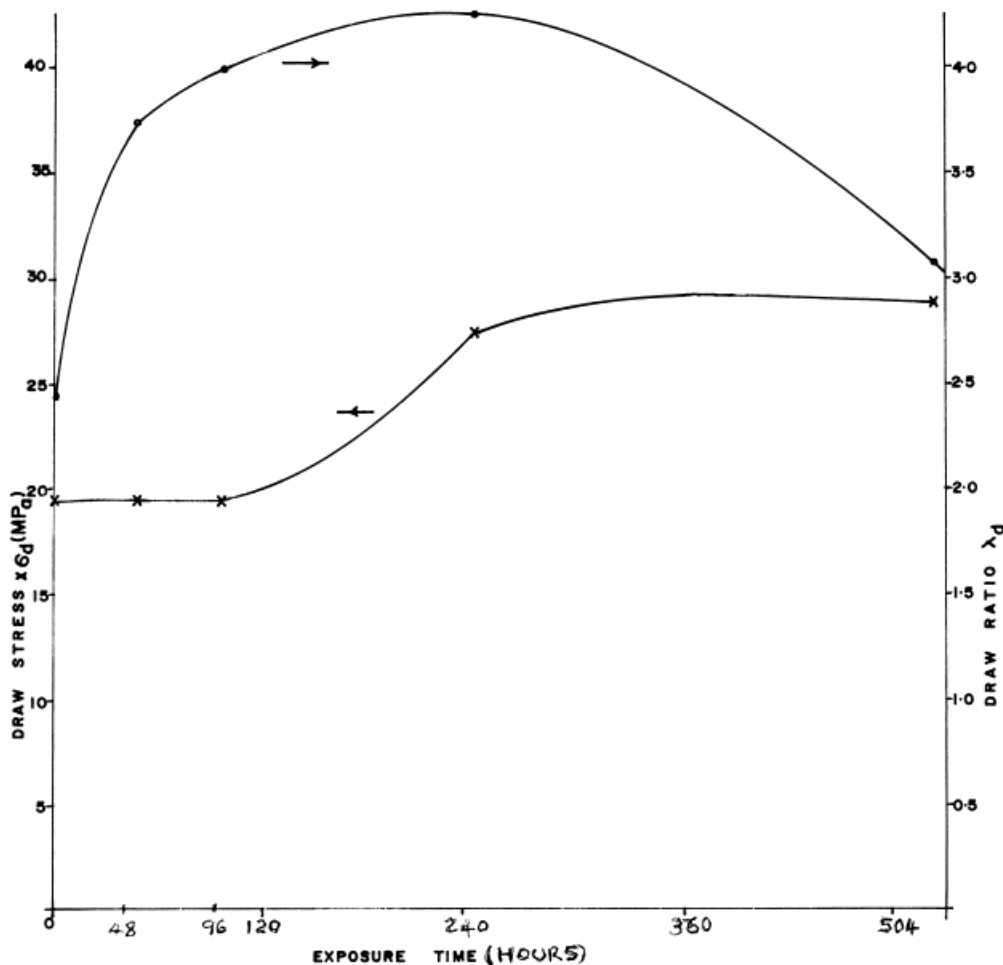
Figure 1 Graph of ($\times$) draw stress σ_d (MP$_a$) and ($\bigcirc$) draw ratio λ_d against exposure time (h).

sure time. The draw ratio λ_d after 504-h exposure remained significantly higher by about 27% of that of the unexposed sample.

Drawing takes place by the strengthening of the crystalline and amorphous molecular chains[11,12] and, therefore, implicates the degree of crystallinity and crystallite thickness. However, the data in Table I show an initial increase in the AC, reaching a maximum before decreasing to values even lower than that of the unexposed films. As pointed out by Johnson and Popoola,[10] the AC is not an absolute degree of crystallinity since the unexposed sample has some measurable degree of crystallinity, but in this case, it has a zero AC value. The AC therefore only depicts a trend in the variation of the crystallinity developed during treatment. On that score, in comparison of the data on the AC (Table I) and Figure 1, a plot of the draw ratio against the exposure time, it can be said that the AC data for up to 98-h

exposure support data on the draw ratio λ_d. However, for greater than 144-h exposed films, the relatively larger draw ratio λ_d compared to that of the unexposed sample may be explained by the plasticization of the oxidized PP chain, an observation corroborated by the loss in AC (negative values with respect to unexposed samples). Gent and Madan[11] showed that for PP there is limited amount of molecular reversal and reentry during drawing. Chain scission and oxidation resulting from outdoor weathering is bound to reduce the molecular reversal and reentry and increase plasticization, respectively. The observed property therefore depends on the net balance of two opposing factors: enhanced crystallization and plasticization.

Tensile Stress

The data on tensile stress σ_b and exposure time (h) presented in Table I are plotted in Figure 2.
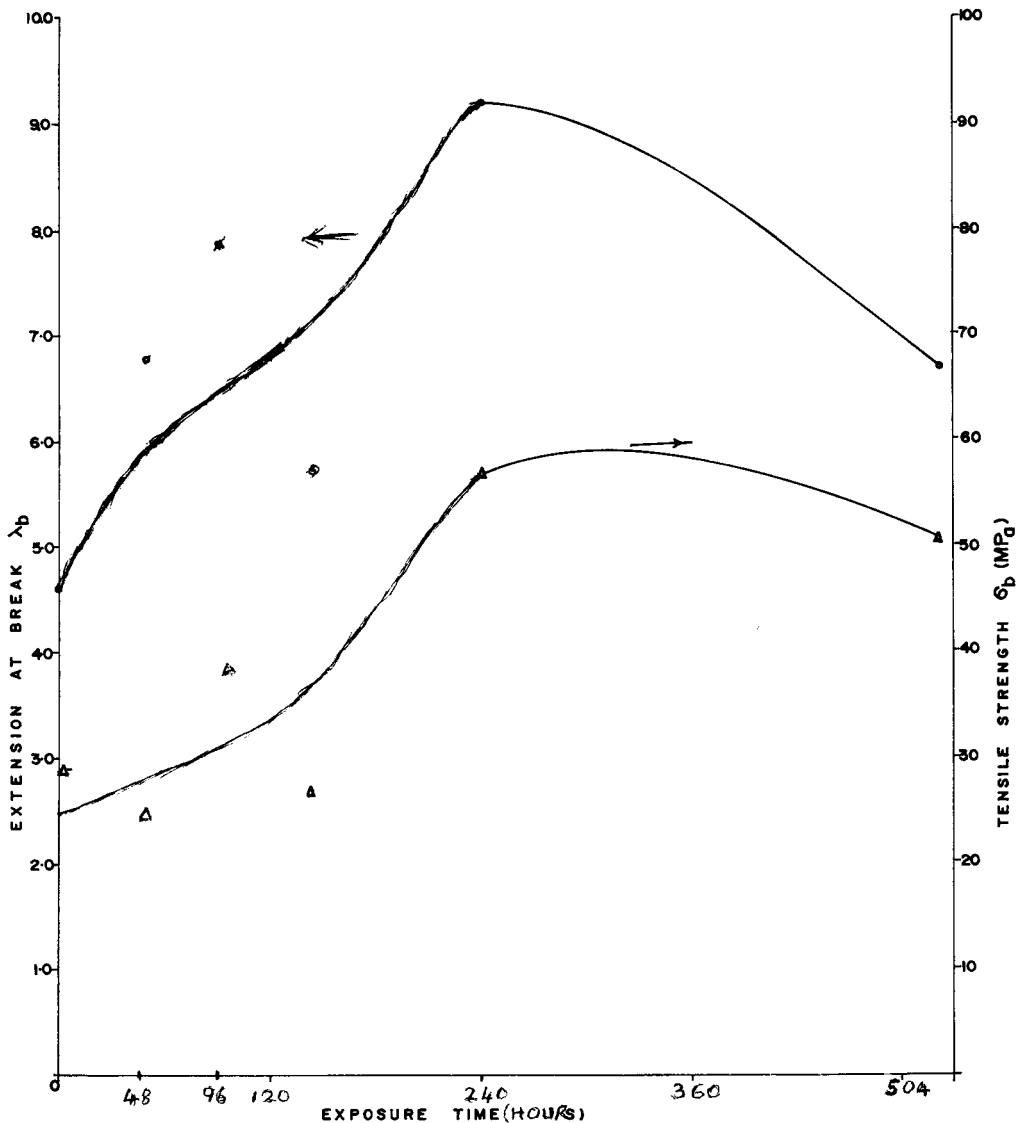
Figure 2   Graph of (○) extension at break and (△) tensile stress against exposure time (h).

Tensile stress is one of the two major ultimate properties of the semicrystalline properties studied. In Figure 2, the tensile stress σ_b increased monotonically and attained a maximum with the 240-h exposed film, about 97% higher than the value for the unexposed film. The higher value of the tensile stress σ_b at 504-h exposure, 77% higher than that of the unexposed film, suggests that a longer exposure time was needed for significant reduction of the property to result in the deterioration of the PP film.

Breaking Ratio

The variation of the breaking ratio λ_b with outdoor exposure time presented in Table I is plotted in

Figure 2. In congruence with the variation of the tensile stress σ_b, the breaking ratio (λ_b)–exposure time plot exhibited a monotonic rapid increase, attaining a maximum at the 240-h exposed PP film sample before decreasing to lower values with further increases in exposure time. Again, a 504-h exposure of the PP film in the rainy season, with 78% of the breaking ratio higher than that of the unexposed film, was shown not to be enough to reduce the strain property to levels unsuitable for its load-bearing application.

The initial increase in the breaking ratio λ_b and tensile stress σ_b up to the values at the 240-h-exposed PP film may be explained by the improved restructuring of the sample by the chemi-
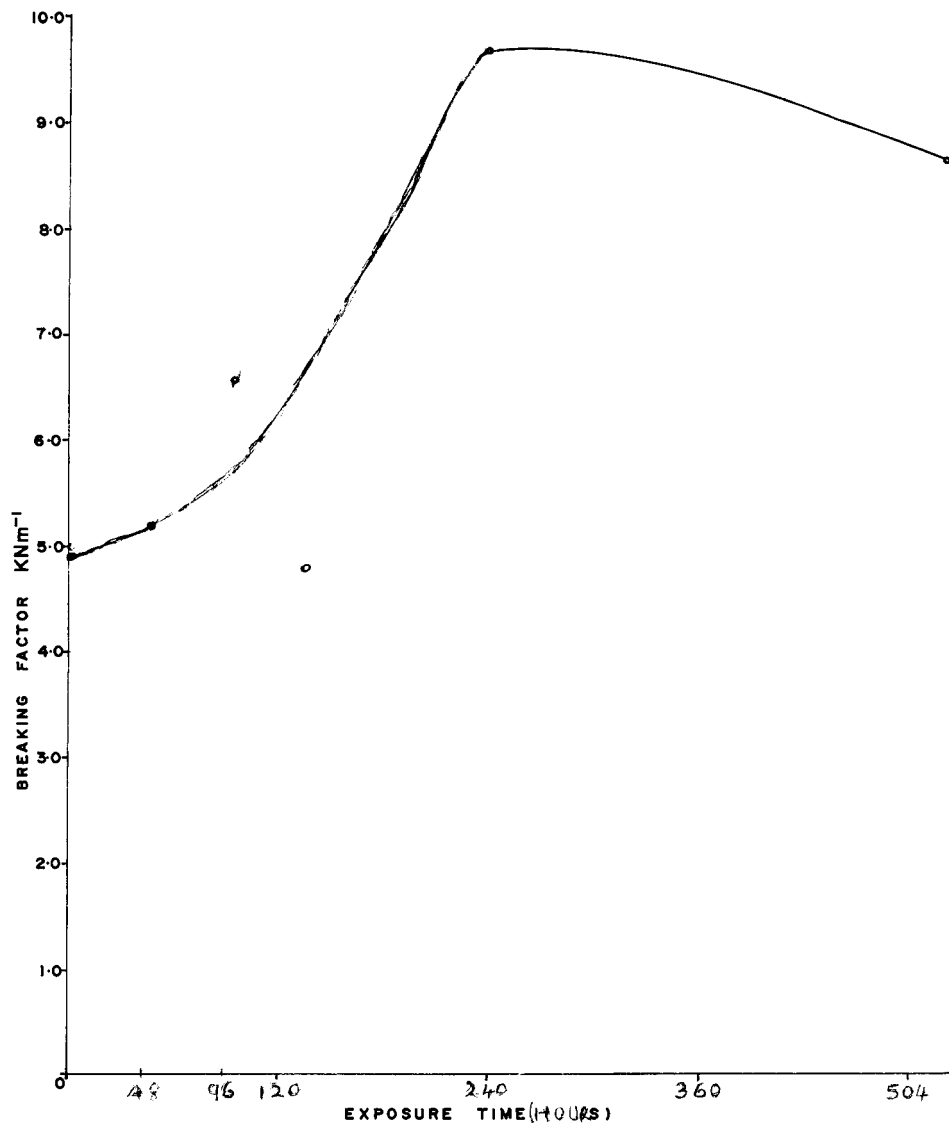
Figure 3 Graph of breaking factor (kN m^{-1}) against exposure time (h).

crystallization resulting from the presence of oxygenated polar groups and concomittant plasticization. The decrease in the properties are explained by the cleavage of the PP chain resulting from outdoor weathering. The variation of the two properties with outdoor exposure time are corroborated by the AC data (Table I).

Breaking Factor (BF)

Although the BF is not a measure of force, it measures the surface tension at the weakest point along the deforming film at the moment of rupture. It is closely related to the embrittlement time, which is generally acknowledged as a more convenient measure of the deterioration of polymer films.[12] The variation in BF with outdoor exposure time is presented in Table I and plotted in Figure 3. A similarity between the BF–exposure time plot, on the one hand, and the tensile stress–exposure time and breaking ratio–exposure time, on the other, is easily noticeable by comparison of the Table I data and Figures 2 and 3. In Figure 3, one notices an initial monotonic increase in the BF with increasing outdoor exposure time, reaching a maximum at the 240-h-exposed PP film before decreasing with further increases in exposure time. By the end of 504-h rainy season exposure, PP films exhibited a BF 79% higher than that

Table II   Ultimate Works of Plastic Deformation and Outdoor Exposure Time

Exposure Time (h)	Work of Draw U_d (MPa)	Work of Rupture U_r (MPa)
0	13.2	37.8
48	25.4 (92%)	58.7 (55%)
96	28.8 (118%)	77.4 (105%)
144	21.1 (60%)	42.9 (13%)
240	43.6 (230%)	130.0 (224%)
504	33.0 (150%)	90.0 (138%)

Values in parentheses are the percent increase relative to the unexposed film.

of the unexposed films. The variation of the BF also seems to agree with the changes in the AC of outdoor-exposed PP films.

Ultimate Works of Plastic Deformation

The effect of outdoor weathering on the ultimate works of plastic deformation: work of draw U_d and work of rupture U_r, are presented in Table II. The work of draw U_d was obtained from the area under the stress–strain curve in the draw portion, while the work of rupture U_r was obtained from the area under the stress–strain curve from the origin to the point of rupture. In Figure 4, it appears that the work of draw and rupture increased monotonically with exposure time and each attained maximum value at the 240-h-exposed PP film, before finally decreasing with further increases in exposure time. The larger value of these works for the period under study relative to the unexposed PP films are due to large draw stress and tensile stress resulting from chemicrystallization and recombination of the radicals and the plasticization of oxidized films which results in a large draw ratio and breaking ratio, respectively. The change in these energies were approximately constant, for instance, at the 96-h-exposure time, work of draw U_d and work of rupture U_r had increased by 118 and 105%, respectively, and at 504-h-exposure time, the observed increases were 150 and 138%, respectively, of the values for the unexposed PP films.

The changes in the ultimate properties of outdoor weathering of PP films have been correlated with the chemical microstructure, namely, carbonyl, hydroxyl/hydroperoxide growths, decrease in molecular weight, and crosslinking.[13,14] Natural weathering is caused by solar ultraviolet radiation and the heat of the sun; local variations of

outdoor weathering applicable are rainfall (wetness) and humidity. The increases in the properties as recorded may be explained by increase in the density, crystallinity, and crosslinking (molecular weight) and recombination of radicals (for stress) or plasticization (for strain). Increase in the density and crystallinity result from improved ordering of the PP chains in the amorphous phase and chemicrystallization brought about by increase in the oxygenated polar groups in the PP chain.[15–17] At early exposure times, the crosslinking of PP chains and recombination of the macroradicals are expected to be more preponderant than chain scission; thus, increase in the molecular weight is expected. The plasticization of the shorter polymer chains that results from longer exposure time degradation is manifested in decrease in the draw stress and breaking stress.

The decrease in the breaking ratio λ_b and tensile strength σ_b with exposure time is due to the chain scission of the PP chains and such decreases have been monitored by carbonyl growth and hydroxyl/hydroperoxide growth[13,14] and have been correlated with a drastic decrease in molecular weight. Popli and Mandelkern[18] established that for polyethylene (PE) the breaking ratio and tensile stress are molecular weight-dependent but independent of the level of crystallinity, crystallite thickness, and different supermolecular structure. One strong factor that will aggravate carbonyl, hydroxyl, and hydroperoxide growth during the rainy season is the loss of stabilizers by leaching and the stabilization process. Weimer and Conner[19] reported that the wash–dry cycle of PP yarns, by bringing more stabilizers to the surface and leaching, led to the loss of stabilizers. They concluded that the rate of stabilizer loss increased with drying temperature and rate of water flow and is greater for the wash–dry cycle process than is ordinary washing with detergents. The successive heavy rain–dry periods are assumed analogous to the wash–dry cycle. Although Mantia[1,2] explained the effect of a light stabilizer as arising from a decrease of microstructural defects and weak sites that resist outdoor weathering, loss of the stabilizer either by leaching or a chemical process leads to increased carbonyl and hydroxyl/hydroperoxide formation and these aggravate the chain scission and deterioration of PP films. Even though the data on leaching/leachate are unavailable, it may not be too speculative to suggest that the leaching of stabilizers may have aided the reduction in the properties.
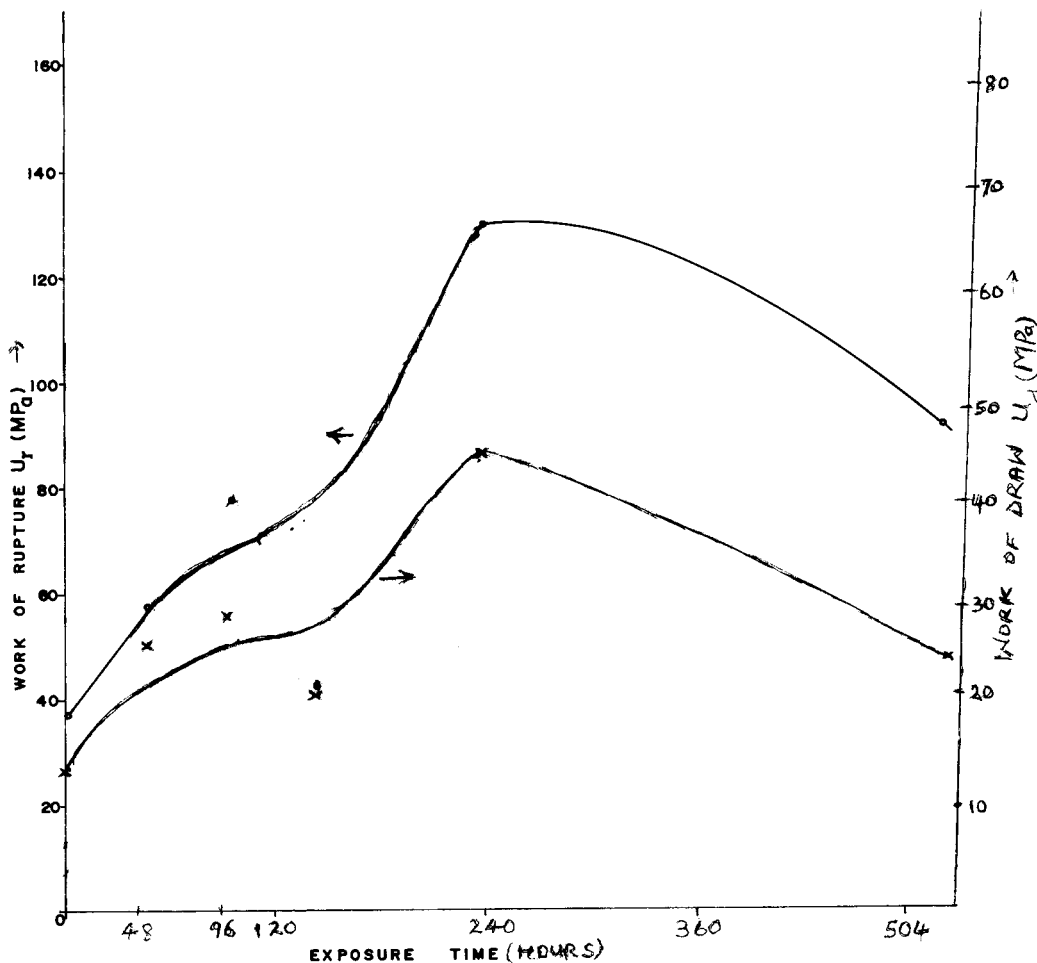
From the value of the breaking ratio λ_b, the

Figure 4   Graph of ($\bigcirc$) work of rupture (MP_a) U_r and ($\times$) work of draw U_d against exposure time (h).

tensile stress σ_b, BF, and works of plastic deformation, it is clear that 504-h outdoor exposure of PP films during the rainy season was not enough to cause significant deterioration of the PP film. In addition, the changes in the properties are corroborated by the AC data (Table I). It had been reported that a shorter time of outdoor exposure during the summer months (dry weather) caused more reduction in the breaking ratio of PP monofilaments.[19] Such a comparison may have to wait until data from the dry season outdoor weathering of PP films in this location are available.[20] It had been suggested that only the breaking ratio λ_b, tensile stress σ_b,[2,8,13,14] and embrittlement times[21] can be used as sensitive indicators of the degree of deterioration (photodegradation) for polyolefins, but following the close relationship among the breaking ratio λ_b, tensile stress σ_b, (Figs. 2 and 3), and the BF measurements of tension at rup-

tures, the BF can also be a useful indicator of the degree of degradation.

CONCLUSIONS

The ultimate mechanical properties of the outdoor weathering of PP films were investigated. The results obtained from the study showed a time-dependent relationship between properties and exposure time.

The tensile stress σ_b, breaking ratio λ_d, BF, work of draw U_d, and work of rupture U_r all increased with increase in the outdoor exposure time, attaining maxima at 240-h exposure time, before decreasing with further increases in exposure time. The data on these properties were corroborated by the AC data. It was established that a 504-h exposure time was not enough to reduce

these ultimate properties to levels below those of the unexposed PP films. The increase in draw stress σ_d, tensile stress σ_b, and BF were explained in terms of the improved restructuring arising from enhanced chemicrystallization and recombination of radicals, while the decrease was due to PP chain cleavage, resulting from the outdoor exposure. The increase in draw ratio λ_d and breaking ratio λ_b were due to plasticization, which at longer exposure time diminished due to the presence of shorter PP chain segments. Because of the close similarity between the tensile stress (usually accepted as an indicator of degradation) and the BF, it is suggested that BF could also be a useful indicator of photooxidative degradation.

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