# Natural Weathering of Polypropylene Films. I. Exposure Time and Yield Properties

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**ABSTRACT:** The yield properties of about 500 h of outdoor weathering (in the rainy season) of polypropylene (PP) films have been studied. The yield strain, plastic strain, and initial modulus, work of yield attained local maxima at 48- and 240-h exposure time; elastic strain attained near double maxima at these times. The yield stress reached a local minimum for the 144-h exposed film before increasing with further exposure hours. The increase in yield strain, plastic strain, and initial modulus were explained in terms of crosslinking chemocrystallization; decreases were due to chain scission and leaching. Critical dissolution time data, interpreted in proportion to density, crystallite thickness, and percent crystallinity, increased with PP exposure time, reaching a maximum at 48 h before decreasing to values even lower than that of unexposed film from the 120-h exposure. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 667–673, 1998

**Key words:** natural weathering; polypropylene films; exposure time; yield properties

## INTRODUCTION

It is well known that pure unsaturated polypropylene (PP) should be unaffected by exposure to outdoor weathering. However, it has been recognized that the presence of carbonyl[1-8] and hydroperoxide[6-8] impurities introduced during processing are capable of UV absorption that initiates a photochemical reaction. Zeigler–Natta catalyst impurities[9,10] and aromatic impurities[2,11] are presumed to have a collaborative effect on photoinitiation. In the wake of photochemical initiation, other reactions such as chain scission, crosslinking, and subsequent formation of carbonyl, hydroxyl, and vinyl groups, and evolution of volatile products[6,7,12,13] arise.

Thus, the morphological changes in exposed PP films have been interpreted in terms of competition between ordering of PP chains, chain scission, crosslinking, leaching of stabilizers, and volatilization of products. The deterioration of polymer films by photodegradation has been monitored by the growth of the carbonyl index[14,15] and/or the decrease in hydroperoxide index.[16,17] In particular, such studies have only been limited to reduction of extension at break, tensile strength[14-17] and elastic modulus of exposed PP film with exposure time.[18] Atmospheric factors that affect outdoor weathering are light intensity, temperature, humidity, and wetness that are subject to seasonal, yearly, and locational variations.

In this work the results of outdoor exposure of PP films during the rainy season relate to yield properties such as yield stress, yield strain, plastic strain, elastic strain, and work of yield that have received limited scientific studies. The highlights of the weathering of PP films from Nigeria with its high humidity and wet and hot rainy season are presented. Kolawole[19] reported results of outdoor weathering of binary blends of polyisobutylene and poly(methyl methacrylate) in a northern part of Nigeria. A second article on the changes of the ultimate properties of outdoor weathering of PP film will subsequently follow.

**Table I    Yield Properties, Percent Crystallinity, and Exposure Time for Naturally Oxidized PP Film**

| Exposure Time (h) | Percent Crystallinity | Initial Modulus, $E$ (MPa) | Yield Stress, $\sigma_y$ (MPa) | Yield Strain, $\lambda_y$ | Plastic Strain, $\lambda_p$ | Elastic Strain |
|---|---|---|---|---|---|---|
| 0 | 0 | 200 | 23.3 | 0.24 | 0.12 | 0.12 |
| 24 | 13.0 | 400 | 24.5 | 0.36 | 0.30 | 0.06 |
| 48 | 7.0 | 333 | 24.3 | 0.21 | 0.14 | 0.07 |
| 144 | −17.6 | 360 | 20.2 | 0.21 | 0.154 | 0.06 |
| 240 | −33.3 | 667 | 33.3 | 0.27 | 0.22 | 0.05 |
| 504 | −60.0 | 371 | 36.9 | 0.17 | 0.07 | 0.10 |

## EXPERIMENTAL

### Materials

The 0.17 mm thick PP films were obtained from the Bag Manufacturing Company (BAGCO, Lagos, Nigeria).

### Method

The PP films were hung on a cross-bar in open air at the Geographical Experimental Station of the Alvan Ikoku College of Education (Owerri, Nigeria) situated at latitude 05′21″ N and longitude 07′02″ E. The films were exposed during the rainy season from September to October. Strips of films were cut at varying exposure intervals of 2, 4, 6, 10, and 21 days and stored at 24.5°C and 65% relative humidity (RH) in a calcium nitrate desiccator.

Dumbbell-shaped film specimens were cut from each sample and stretched to the breaking point on an Instron tensile testing machine (model 1122) using a gauge length of 5 cm. Five test specimens from each set of samples were tested, and the mean values of the properties derived from the stress−strain curves were obtained (ASTM-D 882-81). The mechanical properties studied were yield stress $\sigma_y$, initial modulus $E$, yield strain $\lambda_y$, plastic strain $\lambda_p$, elastic strain $\lambda_e$, and the work of yield $U_y$. Data on these properties are given in Table I.

### Apparent Crystallinity Measurement

The apparent crystallinity of exposed films was obtained from critical dissolution time (CDT) data.[20] The CDT technique involved immersing cut films (2 × 1 cm) into hot solvent (toluene) at 100°C and noting the time it took the film to dissolve. The percent crystallinity was then obtained from the simple expression

% crystallinity

$$= \frac{\text{CDT exposed} - \text{CDT control}}{\text{CDT exposed}} \times 100 \quad (1)$$

Data on the percent crystallinity are given in Table I.

## RESULTS AND DISCUSSION

### Yield Stress

Data on yield stress presented in Table I are plotted in Figure 1 against the hours of exposure. It can be seen from Figure 1 that $\sigma_y$ increased slowly for the first 48 h and then remained constant for another 48 h. After this, the yield stress increased gradually until 504 h, at which time a 58% increase of the unexposed value had been attained. Increase in the $\sigma_y$ of semicrystalline polymers has been correlated with the increase in density and degree of crystallinity of the sample but not with the molecular weights, spherulites, and other supermolecular structures.[21] The increase in percent crystallinity from the CDT data seems to support this claim. The proposition by Popli and Mandelkern[21] that $\sigma_y$ and maximum crystallite size $(L_R)$ exhibit linear dependence are therefore partly corroborated by these results. The negative value of the apparent crystallinity from the 144-h exposure is an indication that the crystallinity is less than that of the unexposed PP film.

### Initial Modulus

The initial modulus $E$ represents the initial response by the polymer film to stretching, and it was estimated from the stress−strain curve in the limit of small strain (<3%). The data on initial modulus given in Table I are plotted in Figure 1 against hours of natural weathering. Figure 1
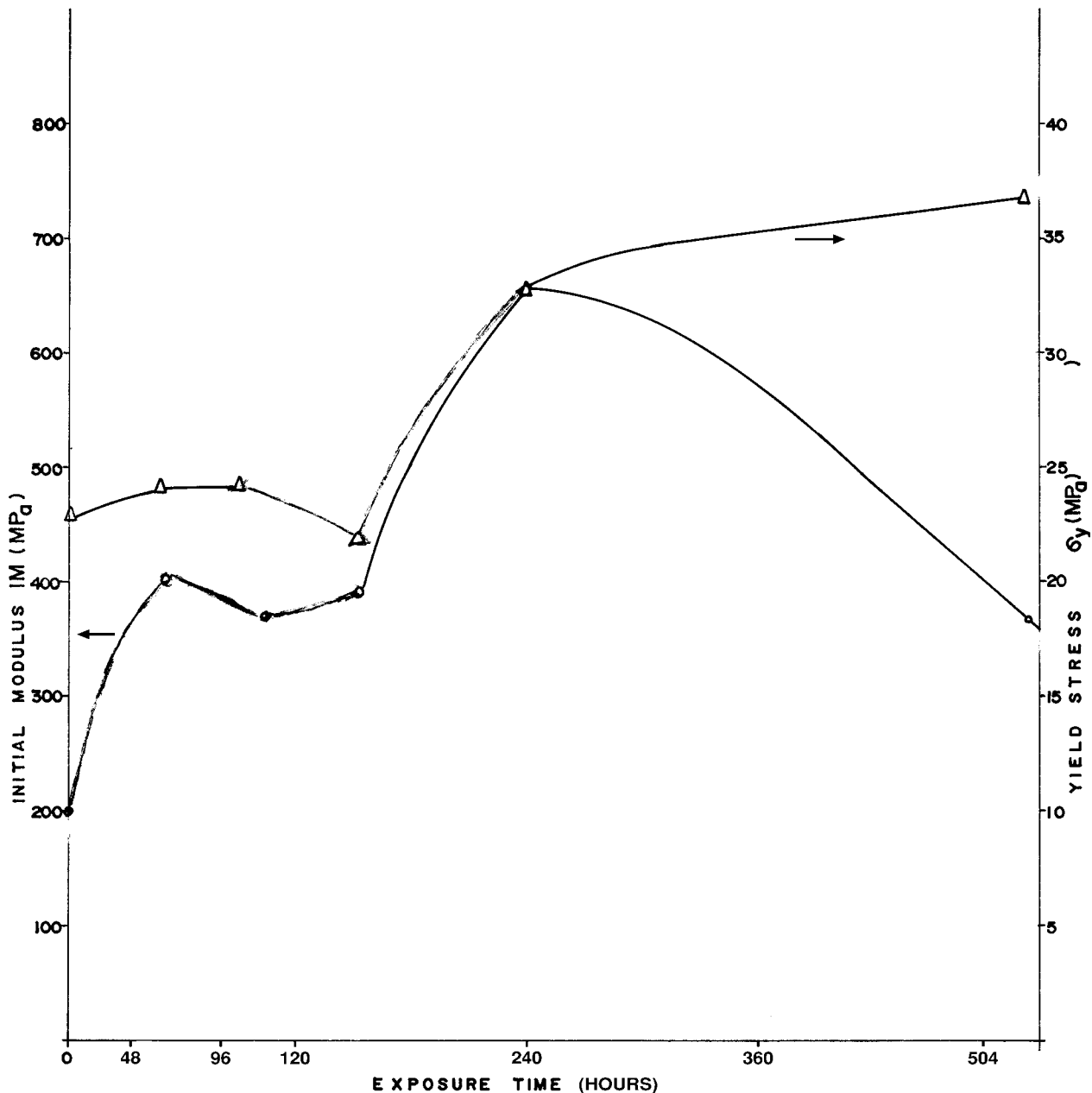
**Figure 1**    Graph of ($\bigcirc$) initial modulus and ($\triangle$) yield stress against exposure time.

shows that the $E$ of exposed PP films doubled by 48 h decreased during the following 48 h before increasing, reaching a maximum (about 3 times of the control) at about 240 h before decreasing to lower values. It is clear that after the 504-h exposure the value of $E$ for the PP films still remained 86% higher than the $E$ value of the unexposed sample. It had been suggested that an increase in $E$ could be due to two structural modifications: crosslinking of PP chains and improved crystallinity.[18] Improved crystallinity could arise

from higher ordering in the amorphous region and recombination of alkyl radicals from the mechanistic radical degradation in more ordered forms or from chemicrystallization arising from the polar oxygenated groups formed.

## Yield Strain, Plastic Strain, and Elastic Strain

Table I gives the data for the strain properties yield strain, plastic strain, and elastic strain. Previous workers have ignored the variation of plas-
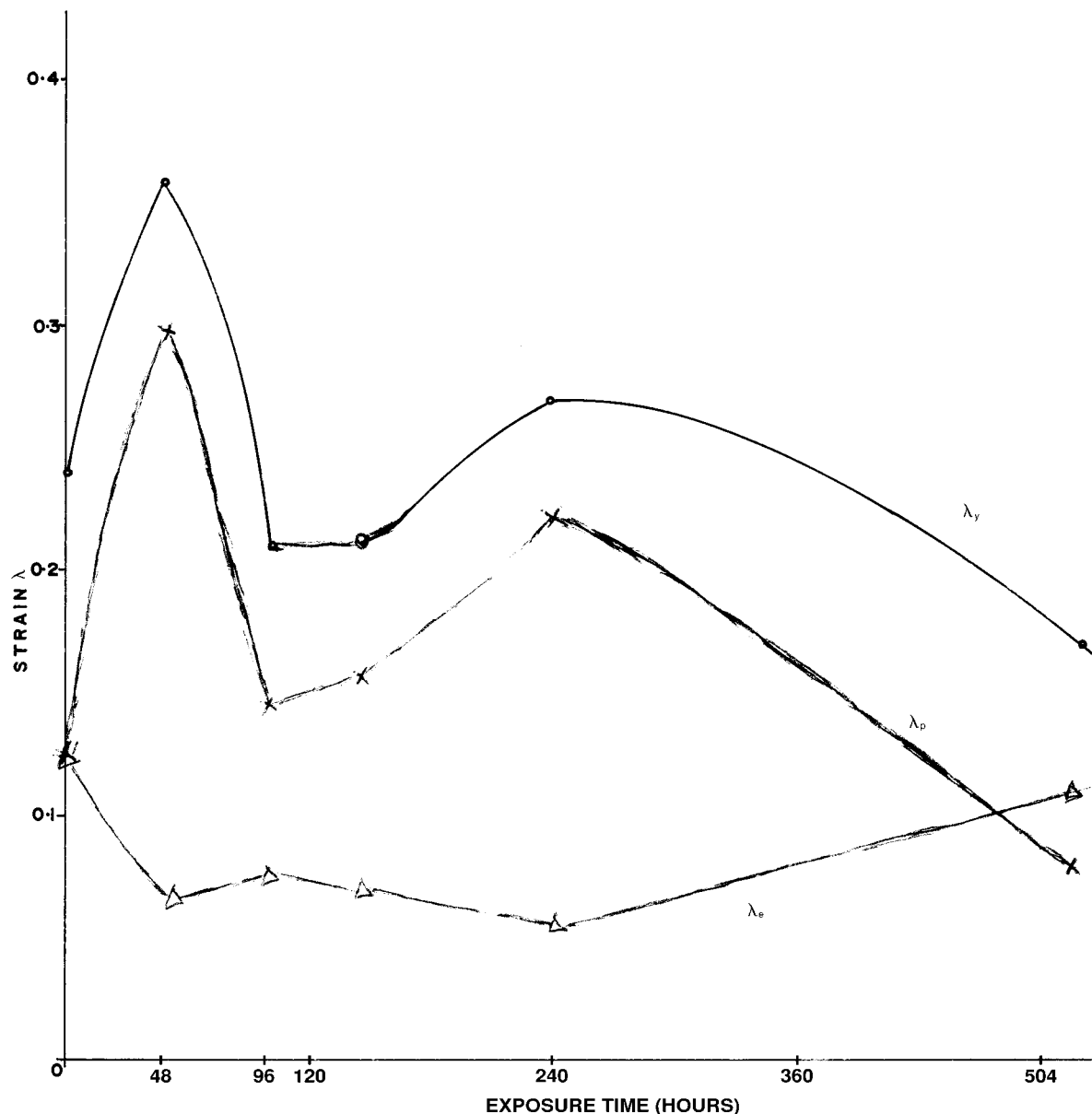
**Figure 2**   Graph of yield strain ($\lambda_y$), plastic strain ($\lambda_p$), and elastic strain ($\lambda_e$) against exposure time.

tic strain and elastic strain.[18] The elastic strain ($\lambda_e$) is defined by the ratio of yield stress ($\sigma_y$) to $E$, and plastic strain ($\lambda_p$) is estimated from the difference between the $\lambda_y$ and $\lambda_e$ ($\lambda_y - \lambda_e$). Plastic deformation is known to be induced when the polymer substance has exceeded the elastic deformation.

From the Table I and Figure 2 plots of the various strain properties against exposure hours of PP films, it appears that $\lambda_y$ increased and attained a maximum of about 50% more than that of unexposed film at 48 h of exposure and then decreased

to a lower value (by 12.5%) at 144 h. Another local maximum was observed at the 240 h before it finally decreased to 29% of that of unexposed PP films after 504 h. The $\lambda_p$ − exposure time and $\lambda_y$ − exposure time plots have similar profiles (Fig. 2). The $\lambda_p$ increased and reached a local maximum about 75% greater than that of the unexposed sample at 48 h and then decreased to a lower value, but it was still larger than that of unexposed PP films before attaining a second local maximum at 240 h before it decreased finally to 42% less that of untreated sample at 504 h. How-
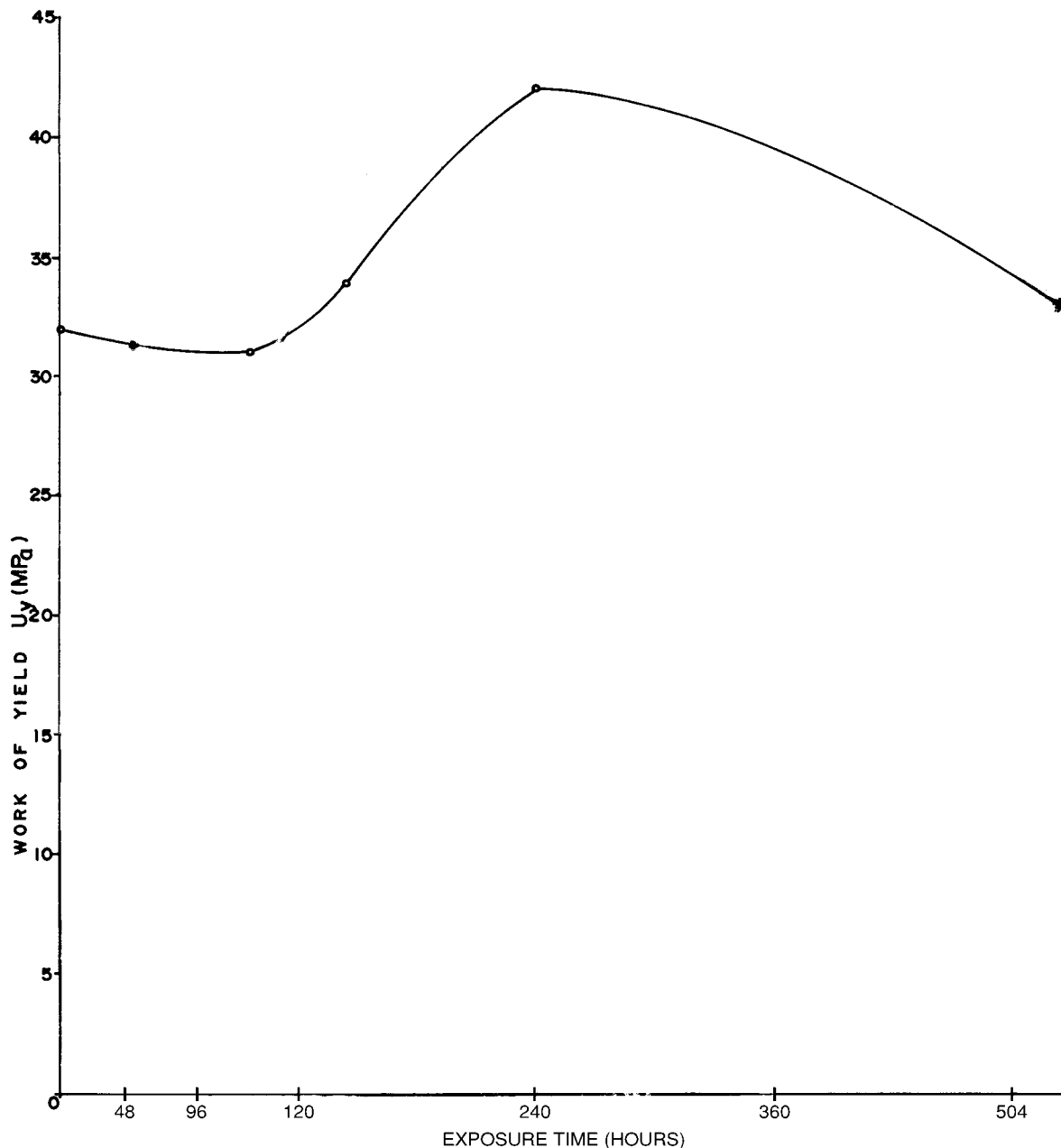
**Figure 3**  Graph of work of yield against exposure time.

ever, $\lambda_e$ decreased with exposure time and attained a minimum value of 42% less than the value for the unexposed sample at 240 h before the gradual increase with further exposure time.

From the profile of the three plots (Fig. 2) it appears that the increase in $\lambda_p$ and $\lambda_y$ corresponds to a decrease in $\lambda_e$. At the early stage of weathering, the increases in $\lambda_y$ and $\lambda_p$ may be due to a rapid improvement of the crystallinity of the PP chain, but subsequent decreases may be due to a

loss in crystallinity. The $\lambda_e$ is bound to decrease with an increase in $E$, so that the decrease in $\lambda_e$ may be due to chemicrystallization. Chemicrystallization arises from the improved mobility of short chain segments brought about by the photooxidative scission of PP chains in the amorphous phase.[12,22,23] The increase in $\lambda_e$ may be explained by the crosslinking of PP chains that leads to gel formation. Le Mantia[18] explained the changes in $E$ of exposed low density polyethene films by these

**Table II   Work of Yield ($U_y$) and Exposure Time**

| Exposure Time (h) | $U_y$ (MPa) |
| --- | --- |
| 0 | 3.2 |
| 24 | 4.2 |
| 48 | 3.1 |
| 144 | 3.4 |
| 240 | 4.2 |
| 504 | 3.3 |

opposing factors. Figure 2 shows that even though an increasing trend of elastic modulus after the 240-h exposure is observed, it is probable that with longer exposure time, in particular toward embrittlement time, elastic yield will reduce drastically. It may also be proposed that the increase in $\lambda_y$ and $\lambda_p$ was due to chemicrystallization while the decrease was due to crosslinking, gel formation, loss of stabilizers by leaching, or stabilizing action. The drop in $\lambda_y$ and $\lambda_p$ at 48 h may have been aggravated by heavy rain that facilitated leaching under gravity and in addition increased the concentration of dissolved oxygen and hydroxyl groups that enhanced photooxidative degradation.

## Work of Yield

The work of yield ($U_y$) 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 on the $U_y$ of naturally weathered PP film and the exposure time are presented in Table II and plotted in Figure 3.

The $U_y$ showed two local maxima in the 48- and 240-h exposed films. However, during the period of exposure the $U_y$ did not decrease significantly below that of unexposed PP film. Rather it is observed that an increase of work yield of 31% of that of the unexposed film had occurred at the two maxima and that the 504-h exposed sample and the unexposed sample had approximately the same value. The $U_y$ is determined by the $\sigma_y$, which was observed to increase with exposure time, and the $\lambda_y$, which had a maximum value for 48- and 240-h exposed film. This explains why the 48- and 240-h exposed PP films had the largest $U_y$ values. Thus, factors that increase yield stress (crystallinity, density, maximum crystallite size, $\lambda_y$ and chemicrystallization) all increase the $U_y$.

The results of natural weathering of PP films during the rainy season may be interpreted as manifesting the morphological changes that took place during outdoor exposure. The density and crystallinity increase indicates molecular ordering.[24] The scission of the PP film backbone in the amorphous region led to more local ordering in the matrix.[25,26] The increase in the $\sigma_y$ that appeared to behave in the same way as that from thermooxidative aging at lower temperature below 100°C may be due to higher ordering in the amorphous region and recombination of alkyl and alkoxy radicals in more ordered form[24]; an increase in oxygenated polar groups, and enhanced ordering of such groups, often referred to as chemicrystallization.[12,22,23] The course of the sudden decrease in $E$, $\lambda_y$, and $\lambda_p$ at the 96-h exposed sample is not clear. It is probable that chain scission in the PP amorphous zone with subsequent leaching and volatilization of products may be responsible for this.

Leachability of stabilizers from a polymer is a surface phenomenon and leads to loss of stabilizer concentration at the surface layers that are exposed to weathering conditions. Leachability has been estimated by comparing the stability of nonexposed and exposed polymer samples. In addition to leaching, stabilizer loss from PP films has been attributed to chemical consumption (i.e., the stabilization process). Weimer and Conner[27] studied the effect of the complete washing cycle of repeated washing and drying on the loss of stabilizers in PP yarn and concluded that the rate of stabilizer loss increased with drying temperature and rate of water flow, almost independent of the presence of a synergist, and is greater for a cyclic wash–dry process. Hydrolyzable derivatives of stabilizers were also readily washed away.[27] It is thus proper to liken the repeated heavy rain and sunny periods of the rainy season to the repeated washing cycle. Thus, reduction in yield properties can be explained not only by chain scission and volatilization of products but also by the leaching of stabilizers. Loss of stabilizers by leaching, chemical consumption, or hydrolysis of hydrolyzable antioxidants leads to higher oxygen and hydroxyl uptake and both enhance outdoor weathering during the rainy season. Data on yield properties of exposed PP films during the dry season will be needed to confirm this preposition. However, Mckellar and Allen[28] reported that shorter time of exposure during summer months caused a 50% reduction in the properties of PP monofilament.

The extraction of stabilizers from the surface sets up a concentration of gradient between the

interior and the polymer surface. With the two exposed PP film surfaces, this will mean that the diffusion gradient is applicable to both surfaces, leaving the interior with low stabilizer concentration; and this condition aggravated the photochemical deterioration of exposed PP films during the 504-h rainy season exposure. During the cyclic wash–dry process, the high temperature of drying and diffusion of stabilizers to the surface present more stabilizers from the interior to the surface for subsequent leaching.

## CONCLUSION

The changes in the yield properties of the natural weathering of PP films during the rainy season have been investigated. From the results we may conclude the following:

1. The CDT data, interpreted proportionally to density and percent crystallinity increased with time of exposure before decreasing to values lower than that of unexposed film.
2. The initial modulus, plastic strain, yield strain, and work of yield attained double maxima for the 48- and 240-h exposed films; these corresponded to near double minima for the elastic strain.
3. The yield stress rather attained a local minimum for the 144-h exposed PP film before increasing to higher values up to the 504-h exposed film, and the variation was explained in terms of a decrease and subsequent increase in crystallinity with exposure time.
4. The major physicochemical reactions, crosslinking and chemicrystallization on the one hand and chain scission and leaching on the other, were evoked to explain the major changes in many properties.

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