

A Durability Index in the Weathering of Low-Density Polyethylene (LDPE) Films

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Synopsis

Degradation resulting from weathering in low-density polyethylene (LDPE) films used in agricultural applications was investigated by a series of mechanical and spectroscopic characterization techniques. An easy, nondestructive, and comparatively sensitive test for measuring the durability of these films based on microhardness indentations is presented.

INTRODUCTION

Methods for monitoring weathering effects, for predicting durability, and for providing an early warning of failure rate are of interest in many areas of polymer applications. This is the case in the measurement of the degradation processes resulting from the exposure of LDPE films used for agricultural applications to light, air, and moisture. Degradation and embrittlement of films exclude the use of this material in greenhouse covering even if its optical characteristics remain unaffected by weathering. Obviously, these studies have been focused on the relationship between weathering and the changes in chemical and tensile properties. In fact, the most obvious chemical effect induced on LDPE by exposure is the formation of carbonyl and vinyl groups, which is accompanied by significant tensile property losses, e.g., on the elongation at break. In general the effective lifespan of an agricultural film is defined in terms of the time required for a given environment to promote a sudden change in a macroscopic property.

The aim of this paper is to present a simple new test (Vickers microhardness) for measuring this lifespan of stabilized LDPE films, a significant factor in establishing its durability outdoors or under artificial weathering conditions. Microindentation testing has proved to be very popular in many fields because of its relative simplicity and nondestructive nature, and it is a technique in which our laboratory has a wide experience.¹⁻⁴

EXPERIMENTAL

Materials

The polymers used in this investigation were two LDPE samples (CP-117 and CP-124), long-life thermic agricultural films for greenhouses, supplied by

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REPSOL QUIMICA (Spain). Molecular and mechanical characteristics of these films are shown in Table I.

The films were mounted, without stress, in frames inclined at 30° to the horizontal, and were exposed facing south on the cover of a greenhouse at about 4 m above ground, in a place where the average radiation in the experimental period was 148 kcal/cm² per year. The average air temperature in this area varied generally between 13°C (winter) and 28°C (summer). The program was initiated in October 1985 at El Ejido, Almería (Spain).

Sections of these films were removed at different exposure intervals for analysis of weathering effects. These analysis include elongation at break, spectroscopic, and microhardness measurements.

Apparatus and Procedures

Tensile tests were performed on an Instron Universal testing machine (traction rate, 500 mm. min⁻¹). Elongations at break, together with the tensile strength, were measured according to processes specified in ASTM D882-75. These measurements in films, generally yield results with considerable scatter due to the presence or generation of weak points in the sample.

Microhardness measurements were obtained in square samples (20 mm length) at room temperature using a Zeiss tester with a square-pyramidal indenter. Values were calculated by computing the ratio of the applied load to the contact area of the resulting indentation. The experimental setup was essentially the same as those used in previous work.^{2,4} The optimal conditions for these measurements were a load of 5 pounds applied for a period of 60 sec; measurements were made immediately after the load was removed. Ten hardness values were measured at random on each sample and the average taken; the standard deviation in the MHV values was found to be less than 5%.

The measure of the absolute hardness value in polymers is always problematic, because in general they creep under load and exhibit a time-dependent recovery when the load is removed, so that the apparent hardness would be greater than the real hardness. This difficulty is critical in the study of the hardness as a fundamental property but is not so when, as in this case, we try to use the technique only as a specific method of characterizing relative variations in other properties correlated with the microhardness.

Apart from measuring the mechanical properties, the changes in the microstructure have also been studied by monitoring spectral changes. Usually the development in the relevant absorption peaks have served as tracers for the rate and nature of degradation. In our experiments VIS/UV and IR spectroscopy were used in order to follow the weathering of films. Measurements were per-

TABLE I
Characteristics of the LDPE Samples Studied

Sample	Melt flow index (g/10m)	Nominal density (Kg/m ³)	Thickness (microns)	Tensile strength (MPa)	Elongation at break (%)	M_w	M_w/M_n
CP-117	0.3	922	180	~ 18	500	115,500	6.4
CP-124	0.4	950	200	~ 18	500	98,000	7.0

formed on a UV/VIS Philips PU 8740 and FTIR Mattson/Cygnus 100 spectrometers.

RESULTS

Figure 1 (a) shows that the elongation at break decreases slightly in the first 20 months of exposure (270 kcal/cm^2); afterwards it decreases rapidly in a meaningful way; tensile moduli do not alter in this significant manner.

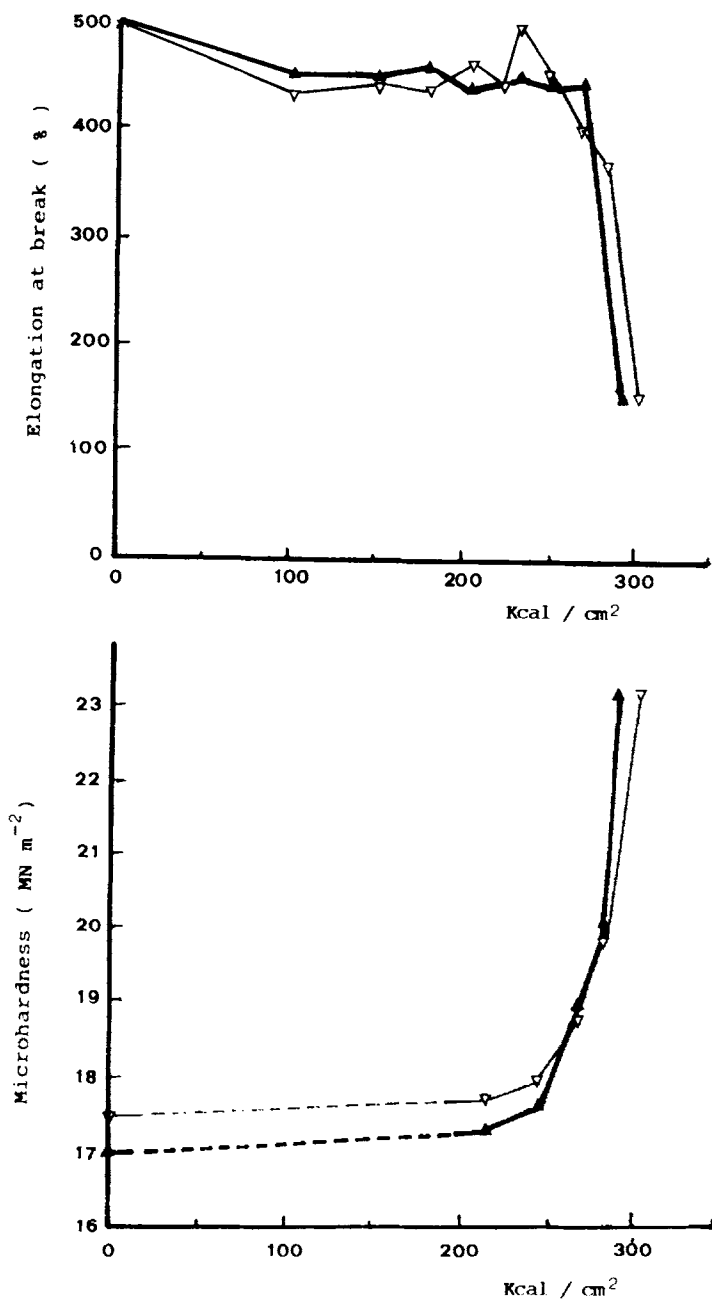


Fig. 1. Changes in the elongation at break (a) and microhardness (b) resulting from weathering.

After March 1987 (200 kcal/cm²) irregular tearing is clearly visible by SEM in the exposed surface of films. The result of the IR measurements in original and degraded samples indicates the existence of a photooxidation process with formation of carbonyl groups as the major final estimable degradation products. There is no simple relationship between the changes in the concentration of these groups and the lifespan of the films because of the proximity of the strong > C=O absorption peak proceeding of the stabilizer (1740 cm⁻¹) and that due to the > C=O formed in the chain (1712 cm⁻¹) during exposure make difficult a significant deconvolution. Only the general observation of a development of carbonyl group absorbance at 1712 cm⁻¹ as a function of exposure time, is evident in our experiments.

No significant change in the optical performance of these films is registered in all samples for wavelengths of 350 nm and above. In each case increased absorption was observed in the region of 275–350 nm with the exposure time. These changes are typical of weathered LDPE compounds and have been attributed to carbonyl groups and to carbonyl groups with conjugated unsaturation superimposed.

The greatest reduction in the elongation at break takes place at the same exposure range than a substantial growth in the MHV values [Fig. 1(b)]. Apart from the initial scission of LDPE chains and in the later exposure stage considered, probably simultaneously with the chain scissions, a predominant crosslink phenomenon, with a three dimensional network formation, may be the reason for the increase in the microhardness and deterioration in the properties of the degraded material.

CONCLUSION

The methods available for measuring the degradation of LDPE are many and varied. The validity of these measures obviously depends on the mode of deterioration and applications of the product. In the case of the stabilized LDPE films studied in this investigation, because of their practical significance, much emphasis has been put on the estimation of the mechanical changes induced by exposure. Our results show the important information supplied by destructive tensile measurements and the only semiquantitative values obtained by spectroscopic methods. Furthermore we present an easy, sensitive, and nondestructive test, based on conventional microhardness measurements, which can give very significant information on the durability of the LDPE films used for agricultural applications.

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