

# The Three Stages in Degradation of Polymers—Polyethylene as a Model Substance

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## Synopsis

Data relating to the degradative conversion of  $^{14}\text{C}$  present in low density polyethylene (LDPE) film to respiratory  $^{14}\text{CO}_2$  during a 10-year aerated cultivation with soil are presented. The degradation was performed with two sets of LDPE samples, one without additive (PE) and the other containing UV sensitizer (NDPE). Samples were exposed to UV irradiation for 0, 7, 26, and 42 days. The degradation is characterized by three stages: (I) a constant degradation rate, (II) a parabolic decline in the rate of degradation, and (III) a subsequent final increase in the rate of degradation. The first step (I) is probably dependent on the environment. The material changes rapidly until some kind of equilibrium with the environment has been achieved.  $\text{CO}_2$  is evolved, oxygen uptake is rapid, and a rapid change in mechanical properties is also observed. The second step (II) is characterized by low oxygen uptake, a low evolution of  $\text{CO}_2$  and slow changes in the mechanical properties, crystallinity, and molecular weight. The changes in mechanical properties are not necessarily synchronous with the decrease in molecular weight. Step III, finally, is a rapid deterioration of the structure. The degradation rate increases again, and all the mechanical properties are more or less lost due to the final collapse of the structure. For an inert material such as PE, 10 years is a short time, so that only small indications of step III and a coming mineralization point can be observed. The changes are more evident for NDPE. The use of degradable materials, for example polypropiolactone, however, means that it is possible during a 2-year period to study all three stages. An understanding of the mechanisms in each step will give a better base for lifetime predictions.

## INTRODUCTION

Polymers are to varying degrees susceptible to degradation. Degradation occurs by the action of heat, stress, radiation, oxidation, hydrolysis, and chemical agents as well as by biological processes.

In a sequence of papers the interest is focused on the degradation of low density polyethylene (LDPE) and high density polyethylene (HDPE) under the influence of different environmental factors.

The studies have shown that the biodegradation is affected by preliminary irradiation by a UV source,<sup>1,2</sup> by the morphology and surface area of the material,<sup>3,4</sup> by antioxidants,<sup>5</sup> by additives,<sup>6,7</sup> and by molecular weight.<sup>2</sup> We have also proposed a mechanism for the biodegradation of polyethylene (PE) and compared it with the biodegradation of paraffin.<sup>8</sup> There is a synergistic effect between photooxidation and biodegradation. The initial photooxidation facilitates the attack on PE by microorganisms.<sup>7,9,10</sup>

The degradation is usually followed in periods of 2 years, but in a few cases for a longer period, one series of  $\text{C}^{14}$ -labeled LDPE has been followed since

1973, and it is still under constant control. In this work the degradation of LDPE was followed as the  $^{14}\text{CO}_2$  evolved and the results were presented schematically for the first time in 1976.<sup>1</sup>

In curves showing the  $^{14}\text{CO}_2$  evolution over a period of about 800 days duration neither the values of the individual measurements nor the mean values of the parallel runs were indicated. Instead the trends were estimated simply by comparing the arithmetic readings within the same group and within the same fine range.

If the earlier results are summarized with regard to degradation rate, it is obvious that the degradation rate curves are characterized by a linear progression in the first 100 days of observation. Thereafter, the evolution of  $^{14}\text{CO}_2$  declined.

In the next publication after a further 4 years, a fairly complete presentation of the results was given.<sup>2</sup> The extended readings were displayed in two figures where degradation in the absence or presence of a UV sensitizer was shown. In both cases, means and variation ranges based on 3–7 runs were presented for each experimental series. The liberation of  $^{14}\text{CO}_2$  was very small for most LDPE material. The small differences between the runs subjected to different treatments were, however, quite significant, being greater than the deviation between parallel runs within the same series.

Four years was still too short a period for a reliable final judgement of all the molecular processes in the ageing polyethylenes. In some individual cultivations, the degradation did not stabilize to a minimum or zero rate, but instead occasionally the trend towards a declining degradation was reversed to a progressive increase in the degradation rate.

Now the results of 10 years degradation of polyethylene are presented. The aim of the present publication is to show how the degradation rate changes during a 10-year period and to compare the results with the catastrophic structural deterioration earlier predicted. The degradation of LDPE mixed with soil are also compared with the degradation of LDPE in nutrient solutions inoculated with *Fusarium redolens* to give an example of influence of the environment.

Finally the shape of the degradation curves of the rather inert polyethylene are compared with the degradation curves of the degradable polymers poly(tetra methylene adipate), polypropiolactone, and copolymers of poly(ethylene succinate)-6-poly(tetramethylene glycol).

## EXPERIMENTAL

LDPE labeled with ( $^{14}\text{C}$ ) was produced by Imperial Chemical Industries, London, and generously supplied by Åkerlund and Rausing AB, Lund, Sweden.

From ethylene a polymer with a rather high concentration of  $^{14}\text{C}$  is first made using a high pressure free radical process. Secondly, this polymer is blended with another batch of similar commercial polymer to give a polymer with a rather low concentration of  $^{14}\text{C}$ . This results in a distribution of  $^{14}\text{C}$  where the labeled carbon is located in a few molecules.

The density of the LDPE granulate was 0.922 g/cm<sup>3</sup>, and its molecular weights were  $M_n = 18,200$  and  $M_w = 84,000$ . Thick and thin films were made by heating and moulding the LDPE granulates. The thick films have a

thickness of 0.16 mm and the thin films 0.02 mm. One set of the polyethylene samples contained an additive (NDPE) which increased the photochemical degradation rate. A parallel set of samples was used without additive (PE).

Samples were exposed to UV light (Osram Ultra Vitalux, 300 W at a distance of 0.3 m) for periods of 0, 7, 26, and 42 days. After exposure, the LDPE films were cut into pieces and mixed with soil, water, or nutrient medium. Nonsterile as well as sterile samples were prepared. In soil, the relative humidity was adjusted to 40%. To maintain a relative humidity of 40%, water was periodically added to the soil. Aeration of the mixtures and the controls was performed at 10 mL/min in all cases.

LDPE samples were also maintained in aerated nutrient media inoculated with *Fusarium redolens*. This *Fusarium redolens* was originally isolated from polyethylene samples mixed with non-sterile soil. The controls in these experiments always contained the polymers either in aerated uninoculated nutrient media with 0.05% AgNO<sub>3</sub> added (as fungal growth inhibitor) or in sterile distilled water only.

<sup>14</sup>CO<sub>2</sub> was trapped in KOH solutions and measured in a liquid scintillation counter, Packard Tri Carb, Model 3375 by conventional methods.<sup>1</sup> All samples were placed in a dark cultivation room at a constant temperature of 25°C. During the 10-year period, samples were continuously taken from the flasks. The amount of <sup>14</sup>CO<sub>2</sub> evolved was calculated. Background radiation was subtracted from the calculated values.

## RESULTS

We can now present the results after ten years of scintillation readings. We are interested in the degradation rate and especially in the random increases in individual cultivations, and we therefore present the results of each run separately instead of as earlier in terms of means and variations.

Figure 1 shows the <sup>14</sup>CO<sub>2</sub> captured in extended long-term biodegradative experiments, measured as liquid scintillation of <sup>14</sup>C but expressed as the percentage degradation of the total polymer material. The two LDPE films, one with UV sensitizer (ND-0) and one without (PE-0), were kept in humid composted soil under aeration. These samples had not been exposed to UV irradiation. There are obvious differences between the four runs of PE-0 and the four runs of ND-0. There is only a very slow evolution of CO<sub>2</sub> from the PE-0 film, less than 0.2% by weight in 10 years, but the evolution from the ND-0 film is five times greater. In the ND-0 runs it is also possible to see the increase in the degradation rate after each addition of water (to maintain 40% humidity in the soil).

As mentioned earlier, irradiation by UV light increases the degradation rate of polyethylene. Figure 2 shows two irradiated LDPE samples, one irradiated for 7 days (PE-7) and one for 26 days (PE-26). The samples were irradiated before mixing with composted soil, and this led to loss of material. PE-26 lost more material than PE-7 but was at the same time more oxidized and oxidation increases the weight. The total weight loss figures after 10 years are corrected for the loss due to irradiation. During a 10-year period the PE-7 evolved 0.3% and the PE-26 0.5% by weight in the form of CO<sub>2</sub>. The irradiation was not so intense as to result in brittle films and the increase in

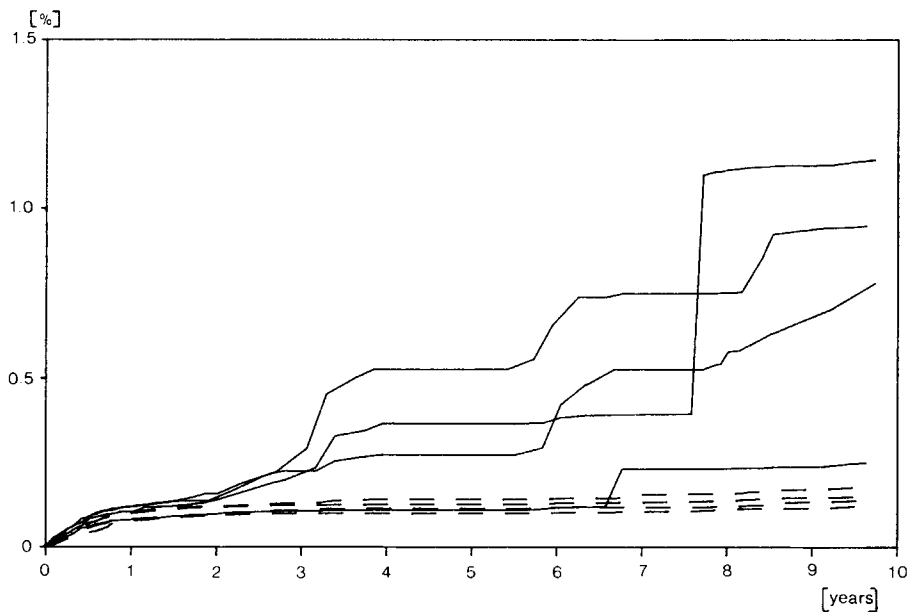


Fig. 1. Captured  $^{14}\text{CO}_2$  in extended long term biodegradative experiments, measured as liquid scintillation of  $^{14}\text{C}$  but expressed as percentage degradation of the total amount of polyethylene. Nonirradiated LDPE film maintained in humid composted soil under aeration for times according to the abscissa: (---) samples without UV sensitizer.

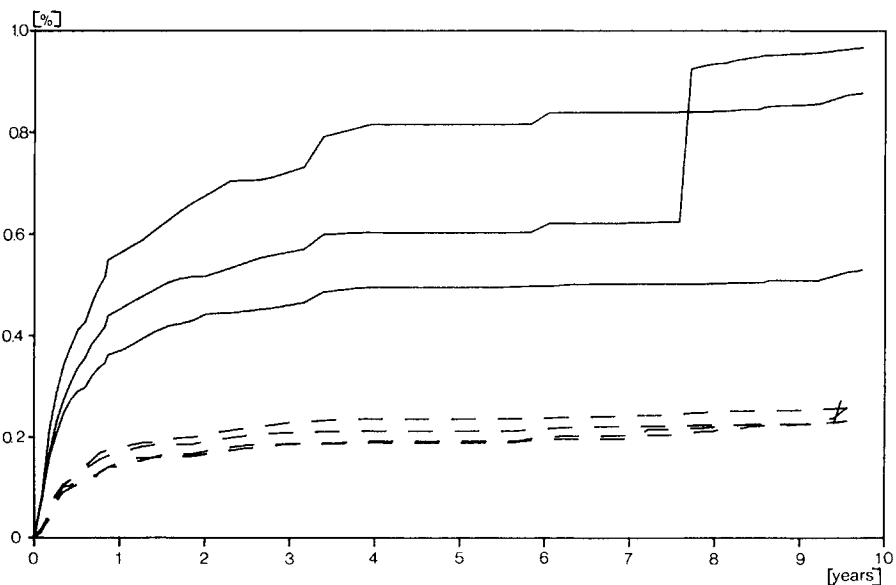


Fig. 2. Same as Figure 1. LDPE film without UV sensitizer, 7 days initial UV irradiation (PE-7, ---) and 26 days UV-irradiation (PE-26, —).

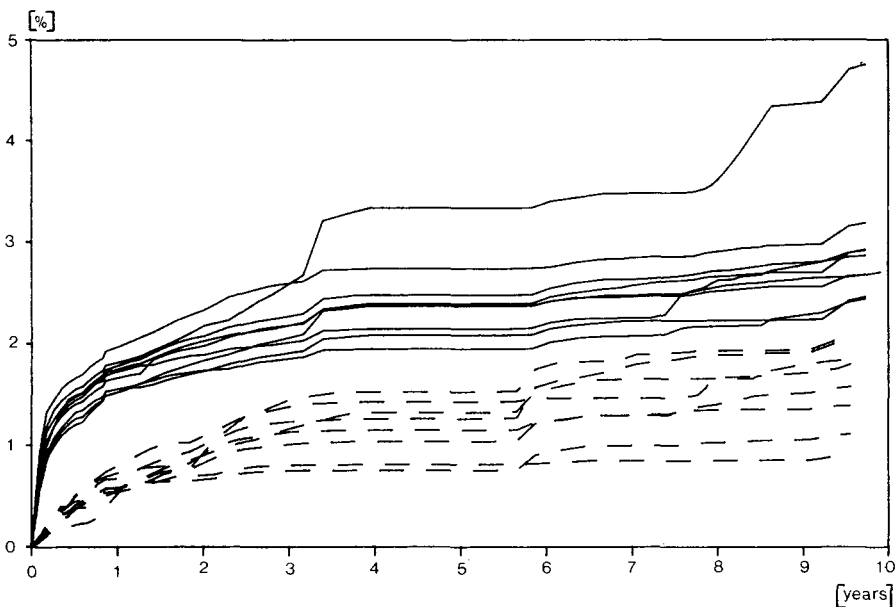


Fig. 3. Same as Figure 1. LDPE film with UV sensitizer, 7 days UV-irradiation (NDPE-7, ---) and 26 days UV-irradiation (NDPE-26, —).

the degradation rate after each addition of water is smaller than for ND-0 but greater than for PE-0. After 7 years, however, one of the PE-26 runs show an extra jump in the degradation rate curve and the variation between the PE-26 runs is larger than for the PE-7.

Figure 3 shows data for NDPE with different exposure times. When the exposure time was increased from 7 days (ND-7) to 26 days (ND-26), the NDPE film became brittle. During a 10-year period mixed with soil, the different ND-7 samples diminished 0.9–2.0% by weight and at the same time the ND-26 runs lost 2.4–4.8% by weight as  $\text{CO}_2$ . In many of the ND-7 and ND-26 runs it is possible to see an occasional increase in degradation rate after water addition. In one ND-26 run there also was a continuous increase in degradation rate over the last two years.

Figure 4 shows LDPE film with and without UV sensitizer which has initially been exposed to 42 days UV irradiation. This is a very high irradiation dose; both the PE-42 and ND-42 films were extremely brittle, and both the materials lost weight during irradiation. During a 10-year period mixed with soil, the PE-42 evolved 1.3–5.7% by weight as  $\text{CO}_2$  and ND-42 3.5–8.4%. In each series, one of the samples showed an extreme jump in the degradation rate, and the final level of degradation seems to be close to a decomposed structure.

Cumulative degradation values have been a convenient way to present the evolution of  $^{14}\text{CO}_2$  from C-14, labeled PE. But the changes in degradation rate are not so evident if these values are used. Using mean values, we have in an earlier paper even further decreased the changes in degradation rate at different moments.<sup>5</sup> Instead it is possible to visualize how the degradations have shifted during the processes by picking out those values corresponding to

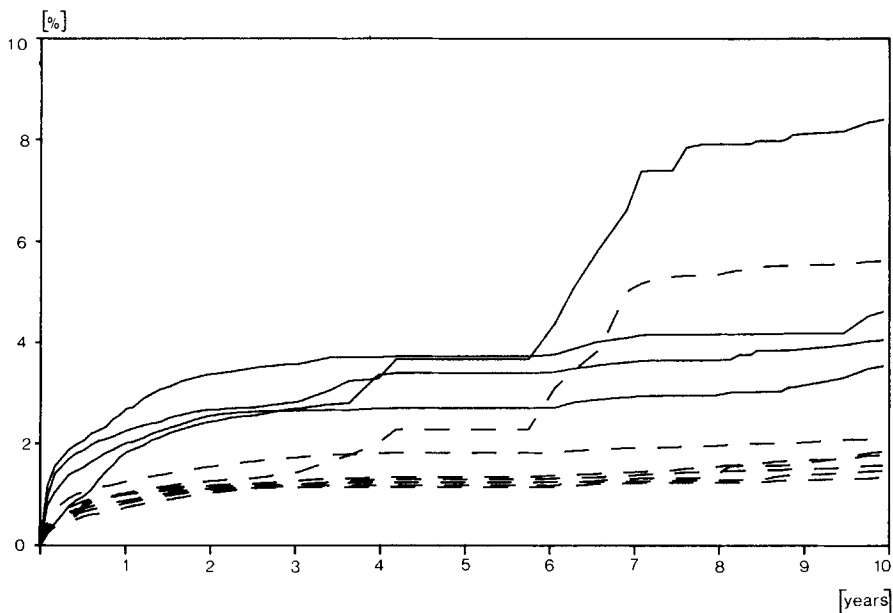


Fig. 4. Same as Figure 1. LDPE-film with and without UV-sensitizer. Irradiation time 42 days (PE-42, ---; NDPE-42, —).

maximum evolution of  $^{14}\text{CO}_2$ . The maximum value appears when the degradation rate is at its peak. Each measured value calculated as percent per year is plotted against total time for soil burial. The highest degradation rate (in percent) recorded on each occasion is shown as a vertical line at the appropriate point on the time scale on the abscissa (Figs. 5 and 6). Since it is a microbial system we are studying, these changes are of great importance in order to properly describe the degradation system.

Figures 5(a) and (b) show data for samples PE-0 and PE-7. Initially the degradation rate decreases with time, up to about 1 year, i.e., the degradation rate is rather high during the first year and then during years 3–6 the degradation rate is lower. The rate again increases randomly after 7 years. The irradiated PE-7 has, of course, a higher degradation rate than the nonirradiated PE-0. On a few occasions the degradation rate for PE-7 is as high as about 0.5% per year but for PE-0 the highest values are around 0.2% per year.

For samples which have been irradiated for 26 and 42 days, Figures 5(c) and (d), the more extensive degradation is of course associated with a higher degradation rate. For PE-42, the degradation rate decreases from a peak value close to 6% during the first year down to low values during year three. A gradual increase is noticed during year 4; this increase in degradation rate continues during years 7 and 8 with a new peak value close to 4%. Occasional sudden increases in the degradation rate are apparent.

Figures 6(a) and (b) show samples of NDPE. A higher degradation rate is as expected observed in the irradiated ND-7 than in the ND-0 sample. A sudden very high degradation rate is observed in the ND-0 sample during the eighth year.

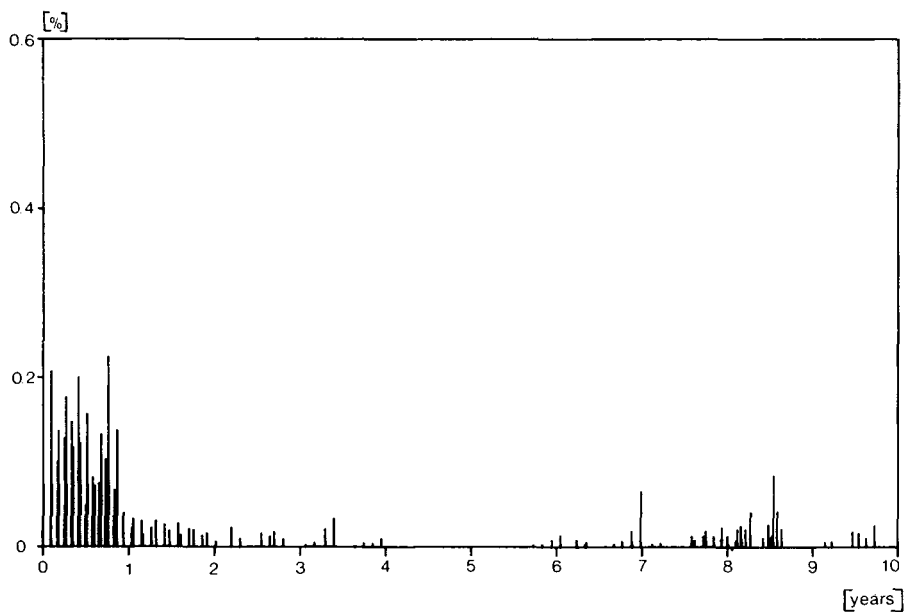


Fig. 5(a). The degradation rate at different times over a 10-year period for nonirradiated LDPE samples without UV-sensitizer and maintained in humid composted soil under aeration. The degradation rate is expressed as evolution of  $\text{CO}_2$  per year given in as percentage by weight per year. The vertical lines indicate the maximum degradation rate for different samples.

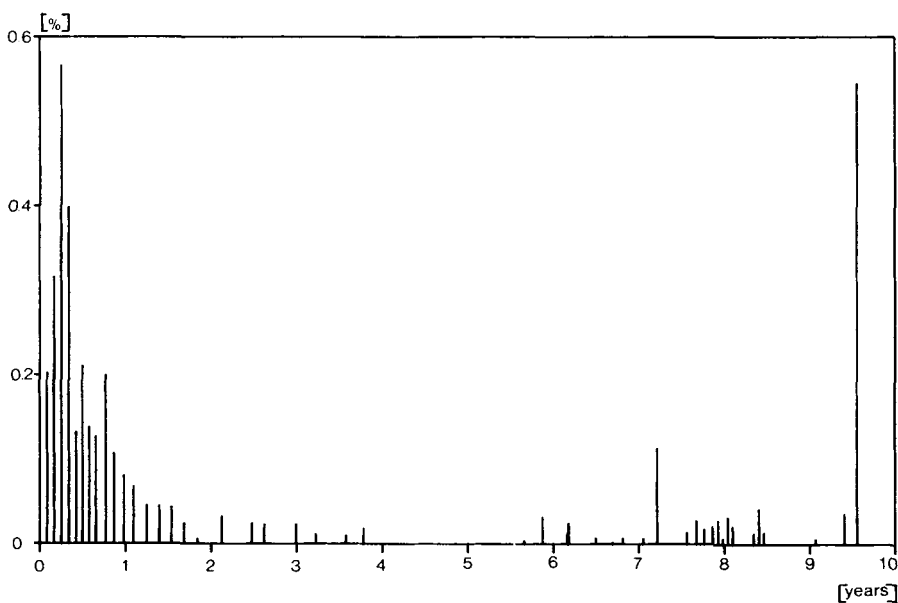


Fig. 5(b). LDPE samples without UV sensitizer, 7 days irradiation, as in Figure 5(a).

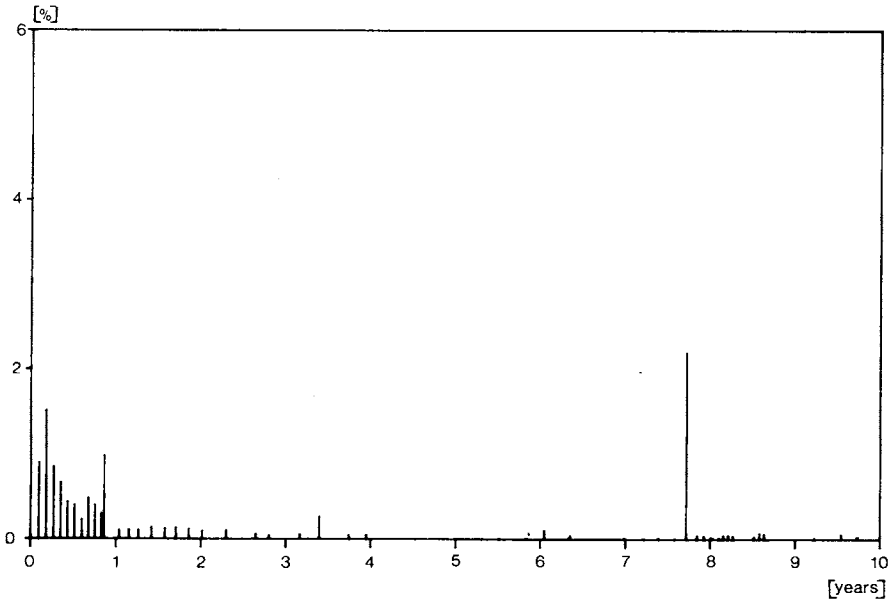


Fig. 5(c). LDPE samples without UV sensitizer, 26 days irradiation, as in Figure 5(a).

Figures 6(c) and (d) show NDPE with 26 and 42 days of initial exposure to UV light. Both samples show a high initial degradation rate which decreases very rapidly during the first 100 days of incubation. Samples ND-26 and ND-42 were both very brittle after exposure to UV radiation and disintegrates to powder. The samples irradiated for 42 days have a higher degradation rate overall than the samples irradiated for 26 days. The peak value of ND-42 is almost as high as 15% per year and for ND-26 nearly 10% per year.

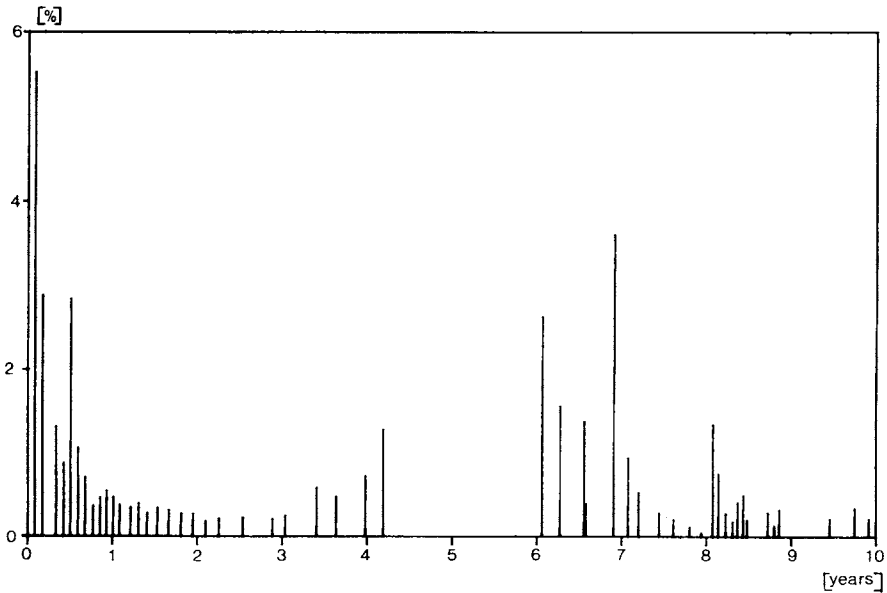


Fig. 5(d). LDPE samples without UV sensitizer, 42 days irradiation, as in Figure 5(a).



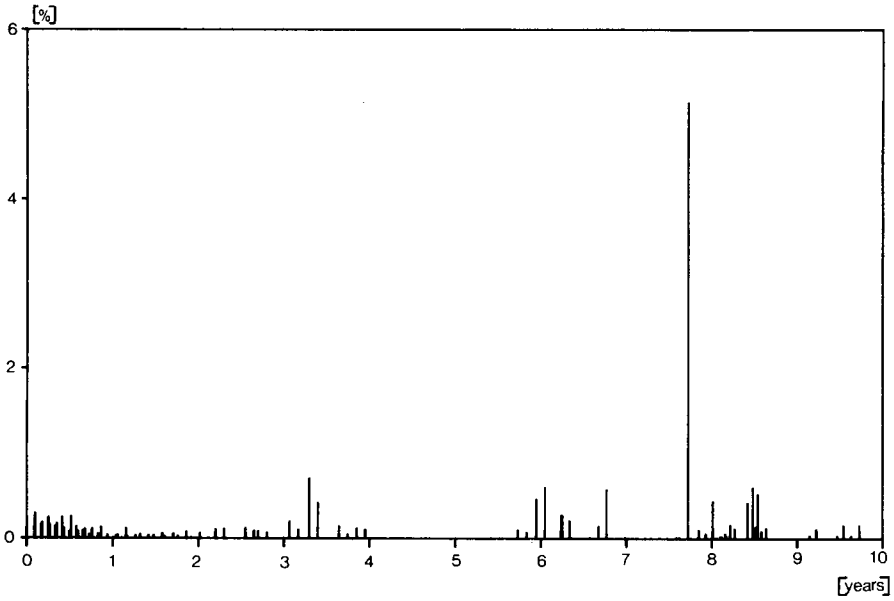


Fig. 6(a). LDPE samples with UV sensitizer nonirradiated, as in Figure 5(a).

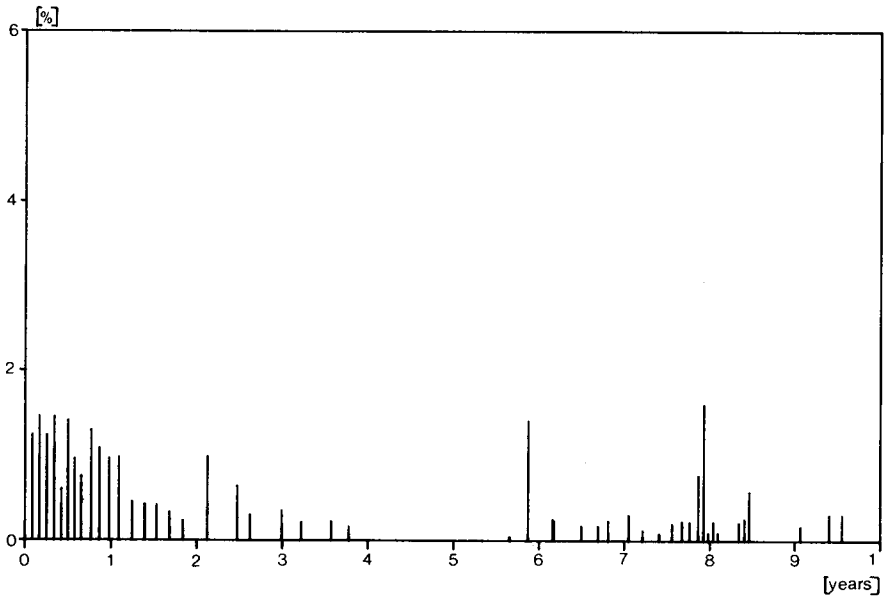


Fig. 6(b). LDPE samples with UV sensitizer, 7 days irradiation, as in Figure 5(a).

## DISCUSSION

The first report describing the behavior over a 2 year period characterizes the degradation curves by a straight line progression over the first 100 days of observation. Thereafter, the curves decline parabolically both for HDPE and LDPE samples in different biotic environments. When the experimental period was extended to four years, the trend was occasionally reversed to a

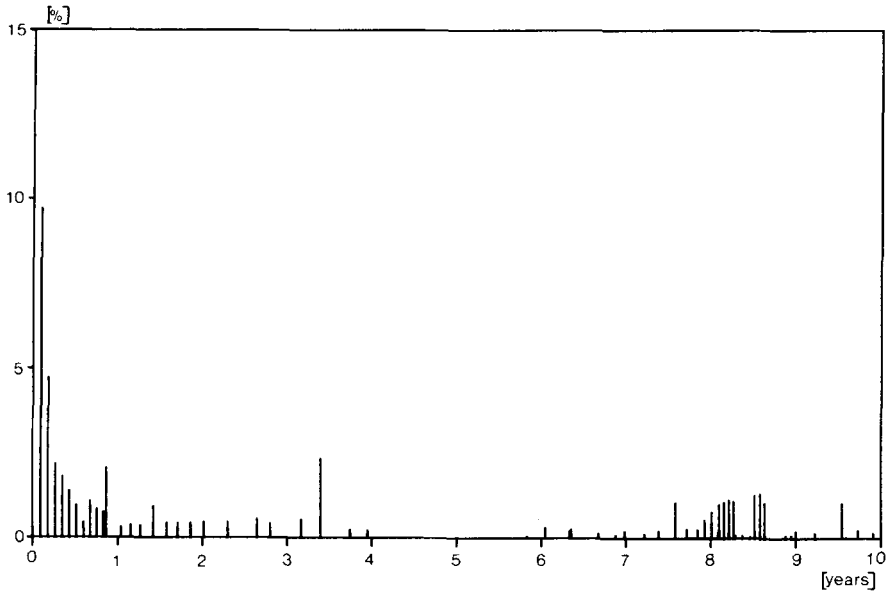


Fig. 6(c). LDPE samples with UV sensitizer, 26 days irradiation, as in Figure 5(a).

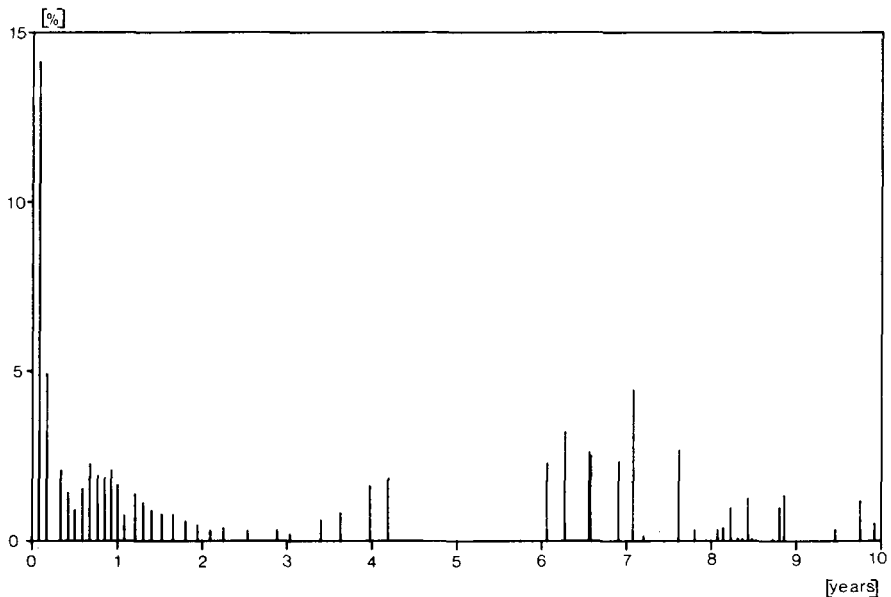


Fig. 6(d). LDPE samples with UV sensitizer, 42 days irradiation, as in Figure 5(a).

progressive increase in  $^{14}\text{CO}_2$  liberation for some of the LDPE samples. The results from 10 years of scintillation readings are now available, and we can report that the amount of  $^{14}\text{CO}_2$  developed increased at times in nearly all the samples.

The onset of such periods of rapid degradation was not simultaneous in all cultures of a set, nor was the rate the same for each sample. All the

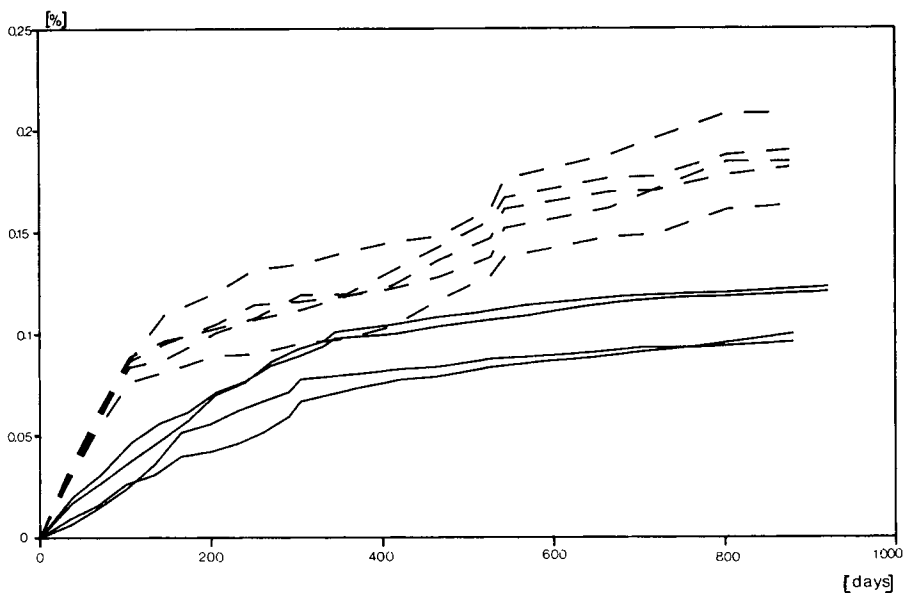


Fig. 7. LDPE-film (without UV sensitizer) noninoculated (—) and inoculated (---) with *Fusarium redolens*. Percentage degradation by weight as a function of time.

phenomenon appeared to occur randomly; the fact that it occurs for most of the samples of a given series indicates that this is certainly not a single, rare deviation but instead a confirmation of the earlier predicted<sup>2</sup> shape of the degradation curves. First there is a constant degradation rate (I), secondly a parabolic decline (II), and thirdly an increase in the rate of degradation (III), leading to a final destruction and mineralization of the material.

The LDPE has been tested mixed with soil. This is a traditional way of testing degradation because of its similarity to actual conditions, but the method lacks reproducibility. Dolezel<sup>11</sup> has given a summary of different methods used for soil tests, and Griffin<sup>2</sup> has discussed the complex nature of the biodegradation process and the tremendous variability of the natural environment. Griffin therefore suggests a "standard" degradation in an environment of compost with sugar and fat additives. This active system would probably have given a higher degradation rate than our system with LDPE mixed with soil. We have, however, also tested LDPE degradation with fungi.

Figures 7 and 8 show how the degradation increased when we changed the system from PE mixed with humid soil to PE in nutrient solution inoculated with *Fusarium redolens*. Both curves in Figure 7 with PE-0 and both in Figure 8 with ND-0 show the same shape, even though the system with fungi shows a slightly higher degradation rate. We have earlier discussed the differences between different test methods<sup>4</sup> and in all our tests on HDPE and LDPE we have always observed the same shape of the degradation curves with periods I and II. The time has often been too short for period III to develop. The degradation of <sup>14</sup>C-labeled PE in soil has also been followed by Henman,<sup>13</sup> but over too short a time to see the typical shape of the degradation curves. The maximum amount of PE conversion detected was then 0.2%, about the same as without PE-0.

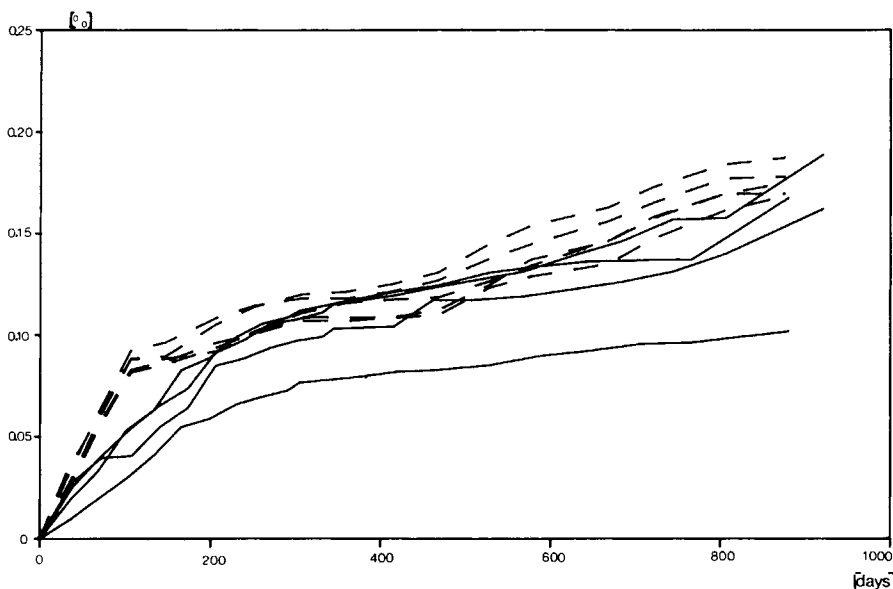


Fig. 8. LDPE-film (with UV sensitizer) noninoculated (—) and inoculated (---) with *Fusarium redolens*. Percentage degradation by weight as a function of time.

Jones et al.<sup>9</sup> have instead estimated the biodegradation of polyethylene from the consumption of oxygen, and the shapes of the curves show a stage I with high oxygen consumption and a stage II with lower oxygen consumption. They also showed similar results for polypropylene.<sup>10</sup> The polystyrene is <sup>14</sup>C-labeled, and it is possible to compare the oxygen uptake with the formation of <sup>14</sup>CO<sub>2</sub> and the later curves also show stages I and II. The time is less than 200 days so there is no sign of a stage III.

Colin et al.<sup>14</sup> have also studied polyethylene under soil burial conditions and say that the small, but significant, embrittlement of the polyethylene could not be explained simply by thermal oxidation or microbial attack. Our results demonstrate, however, that there is always a greater degradation in a biotic environment than in an abiotic environment.<sup>2-6,8</sup> Both Scott<sup>15</sup> and Griffin<sup>12</sup> call this biotic effect a secondary process, and we have earlier shown the synergism between environmental factors and the subsequent biodegradation.<sup>8</sup>

There are very few results in the literature related to very long periods of degradation of inert polymers such as PE. For comparison and in contrast to the inert PE, we have instead synthesized a <sup>14</sup>C-labeled degradable polymer and followed the <sup>14</sup>CO<sub>2</sub> emission. Poly(tetramethylene adipate) (PTMA) in a nutrient solution was inoculated with a mixture of microorganisms, and we could follow the typical shape of the degradation curves.<sup>16</sup> Each period was shorter and the degradation rate in each period higher than for PE. However, for some samples there was an induction period when we first failed with the inoculation of microorganisms. We compared PTMA of two different molecular weights ( $M_n = 4200$  and  $M_n = 14\ 000$ ) and the degradation was lower for the higher molecular weight sample. During the degradation, we followed the

decrease in molecular weight, crystallinity, and mechanical properties. The mechanical properties in particular showed the typical change in three stages: first a period of rapid change, then a period of slow change, and finally a third period of rapid change.

We have also synthesized other nonlabeled degradable polymers and followed the changes in the materials.<sup>17-19</sup> Polypropiolactone, in particular, stored abiotically at 37°C in a pseudoextracellular fluid for 2 years, shows the three steps in the degradation process as changes in mechanical properties,<sup>18</sup> even though it was not a biotic environment. The third period was here associated with the total catastrophic structural deterioration of the fibers. We have also followed the change of crystallinity, molecular weight, and properties during the three stages.

### CONCLUSION

The first step (I) involving a constant rate of degradation is dependent on the environment. The material changes rapidly until some kind of equilibrium with the environment has been achieved. CO<sub>2</sub> is evolved, oxygen uptake is rapid, and a rapid change in mechanical properties is also observed. The second step (II), a parabolic decline, shows low oxygen uptake, a low evolution of CO<sub>2</sub>, and low changes in mechanical properties, crystallinity, and molecular weight. The change in mechanical properties is not necessarily synchronous with the drop in molecular weight. Step III, finally, is associated with a rapid deterioration of the structure. The degradation rate increases again, but the mechanical properties are more or less lost due to the final collapse of the structure. Different polymer materials behave differently and many may not show all three characteristics steps at the same times. Another important factor if the three steps are to be studied is the time when the degradation studies start. If the material is old, step I may already have passed.

For an inert material such as PE, 10 years is a short time so that it is only possible to see small indications of stage III and coming mineralization point. Using degradable material a period of 2 years is sufficient to show all three stages and the influence of the environment on the degradation steps. Further studies of the three stages and the mechanisms in each step will give better possibilities for lifetime predictions.

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