Appendix "B"

A Collection of Research Papers Concerned with Degradability of Plastics Utilizing Modified Starch Additives

By:
PCL & Eastern Packaging Limited
May, 1989

MAKING PLASTICS BIODEGRADABLE USING MODIFIED STARCH ADDITIONS

Dr. Wayne J. Maddever
St. Lawrence Starch Company Limited

Dr. Graham M. Chapman
St. Lawrence Group Limited

INTRODUCTION

The plastics industry has developed countless numbers of applications for polymers. Many of these applications are short lived by definition while the material used is extremely long lived by nature. The increasing awareness of the potential problems caused by these materials has brought us together for this Symposium. While research efforts in recycling and incineration are proceeding there will inevitably be a certain amount of plastic which will be disposed of in landfill sites or elsewhere. For example, certain applications such as garbage bags will not be recycled while other applications such as fishing nets will be disposed of, either accidentally or purposely at sea.

This paper will discuss a method of rendering common polymers degradable through the use of a starch-based additive system. This relatively inexpensive material has the additional advantage of being a renewable resource which both the United States and Canada have in abundance.

BACKGROUND

In the mid 1970s when plastic carry bags were being introduced in Britain, Colorell, a bag manufacturer, wished to develop a polymer film which had some of the characteristics of paper. In conjunction with Brunel University, a polyethylene film was developed which felt and printed much like paper and which exhibited desireable antiblock and antistatic properties.

Further development resulted in an additive system which would render common polymers, such as polyethylene, polypropylene, polystyrene and polyurethane, biodegradable.

The rights to this technology were acquired by St. Lawrence Starch Company Limited. St. Lawrence is developing applications for the product in North America and in Europe under the name Ecostar.

MANUFACTURE AND PROPERTIES OF ECOSTAR

As Canada's second largest corn wet miller, St. Lawrence has concentrated its applications development efforts on corn starch, although other starches may be used to advantage in certain applications.

During the manufacture of Ecostar, regular corn starch is treated with a silane coupling agent to render it hydrophobic. It is then dried to a moisture content of less than 1% (in comparison to the normal 10–12% moisture content of dry starch). The resulting starch has the physical characteristics shown in Table I. Temperature stability of various starches is illustrated in Figure 1 which indicates the removal of water at approximately 100° C. and the endothermic collapse of the starch grain beginning at approximately 250° C.

BIODEGRADATION MECHANISMS

The Ecostar system entails the addition of starch and an unsaturated fatty acid or auto-oxidant to the polymer. Degradation proceeds by two interactive mechanisms.

Starch is present in the polymer as granules as shown in Figure 2. These granules are attacked by microorganisms, such as fungi and bacteria, as shown in Figure 3, until they are completely removed as illustrated in Figure 4. This weakens the polymer matrix as well as greatly increases the surface area of the plastic.

The second mechanism is a result of the formation of peroxides by the auto-oxidant when it comes into contact with metal salts present in soil, fresh water or sea water. These peroxides begin then to break the polymer chain as indicated by the change in molecular weight shown in Figure 5. This second mechanism is tremendously enhanced by the increase in surface area provided by the first mechanism.

Breakdown of the polymer chain not only weakens the material but reduces the chain length, and thus molecular weight, to a level that the polymer can then be metabolized by microorganisms. As the process is purely biological the products of degradation would be those of normal biological activity, namely carbon dioxide and water.

In addition to the above mechanisms it has been shown that macrodegradation of thin films can take place through attack by certain insects such as woodlice.

As the degradation mechanism is biological in nature the rate of degradation depends greatly on factors such as:

- moisture
- presence and type of microorganisms
- temperature
- pH

TABLE I: Physical Properties of Ecostar

Description:	natural polymer, free flowing white powder
Particle Size:	15 micron average
Density:	1.25
Thermal Stability:	stable to 230°C.
Moisture Content:	less than 1%

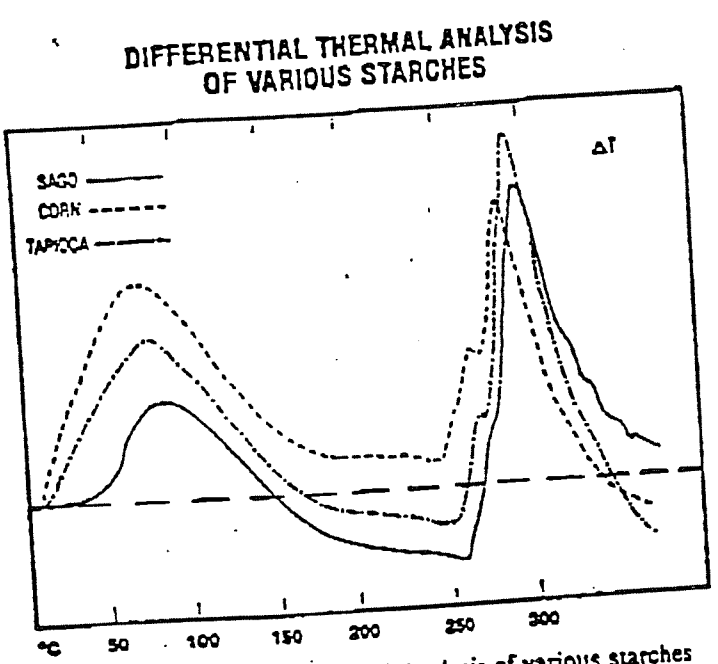

Figure 1: Differential Thermal Analysis of various starches indicating thermal stability to approximately 250° C.

— presence of metal salts
— relative proportions of polymer and active ingredients
— polymer type
— surface area and thickness of article.

Examples of the loss of strength of samples of starch-filled plastics in different conditions are shown in Figure 6. It is estimated that a typical carry bag containing 6% starch, disposed of in a sanitary landfill site, would degrade completely in 3 to 6 years. Increased levels of starch and auto-oxidant would decrease this time in similar environments.

PROCESSING AND PROPERTIES OF STARCH-FILLED PLASTICS

Ecostar is easily introduced into the polymer as a masterbatch during conventional processing operations such as film blowing,

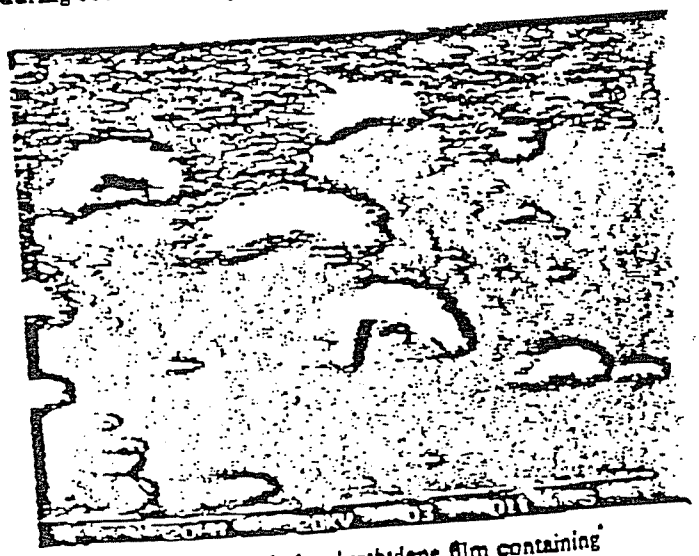

Figure 2: Undegraded polyethylene film containing 6% starch showing starch present as granules (× 1000).

Figure 3: Polyethylene film containing 6% starch after 60 days in sea water showing fungal hyphae and bacteria (× 6000).

blow moulding or injection moulding. The masterbatch contai not only the starch but appropriate amounts of the auto-oxidar Direct addition of starch and auto-oxidant are possible b special addition equipment may be required to assure adequ dispersion and elimination of moisture pick-up by the starc Thus the economy of direct addition would only be realized large volume applications.

During processing, temperatures above 230° C should avoided. In addition, due to the hygroscopic nature of t starch it is necessary to avoid prolonged exposure of t masterbatch to the air.

Physical properties of polyethylene films with various amoun of Ecostar are shown in Table II. The effect on film properti is similar to that expected from the addition of other fillers similar levels.

The addition of the Ecostar system has no effect on shelf li of the polymeric materials in which it is incorporated. As it a truly biodegradable material, no degradation will occur un

Figure 4: Polyethylene film containing 6% starch after 60 days in compost showing removal of starch granules (× 1000).

the material is placed in a biologically active environment such as compost, soil, landfill sites or, fresh or sea water.

APPLICATIONS

The Ecostar system can be used in virtually any application in which biodegradability is an asset, subject to the processing conditions described earlier.

As all of the elements of the system, including the chemicals used for surface treatment of the starch, are FDA approved, the system is applicable to food packaging materials. Formal USFDA and Health and Welfare Canada approvals are being sought. The use of Ecostar has been approved in new legislation recently written by the European Economic Community.

Levels of Ecostar addition are dependent on the application. "Commodity" products such as carry bags, garbage bags or film packaging materials in which degradability is not the primary function would contain 6% starch. Commodity rigid or thick walled forms would contain 10–15% starch. Specific biodegradable applications such as composting garbage bags would contain levels of starch of approximately 15%.

Carry bags containing starch have been successfully made for several years. Several hundred tonnes of masterbatch have been made and used in Europe this year reflecting the growing interest in biodegradable plastics. Co-extruded carry bags have recently been made in Europe. Blow moulded bottles of high density polyethylene and composting bags of low density polyethylene have been made in both Europe and Canada. Other applications including polypropylene binder twine, and thermoformed polyethylene and styrene sheet have also been tested.

While the average corn starch particle is 15 micron in diameter, some particles can be as large as 22 micron. This limits the minimum thickness of film containing corn starch to approximately 25 micron (1 mil). In applications in which lower gauges are required rice starch, with its 3 to 5 micron particle size, may be used. Similarly, potato starch may be used in applications in which its large particle size (approx. 50 micron) is of some particular advantage.

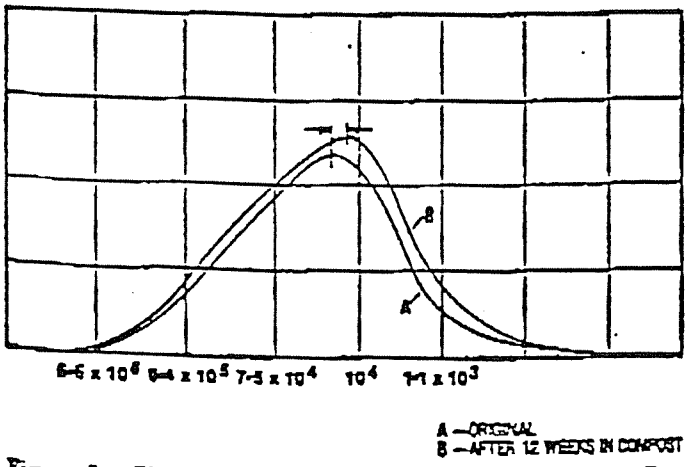

Figure 5: Size exclusion chromatograph of polyethylene film containing 7% starch (a) before and (b) after 12 weeks in compost showing reduction in molecular weight.

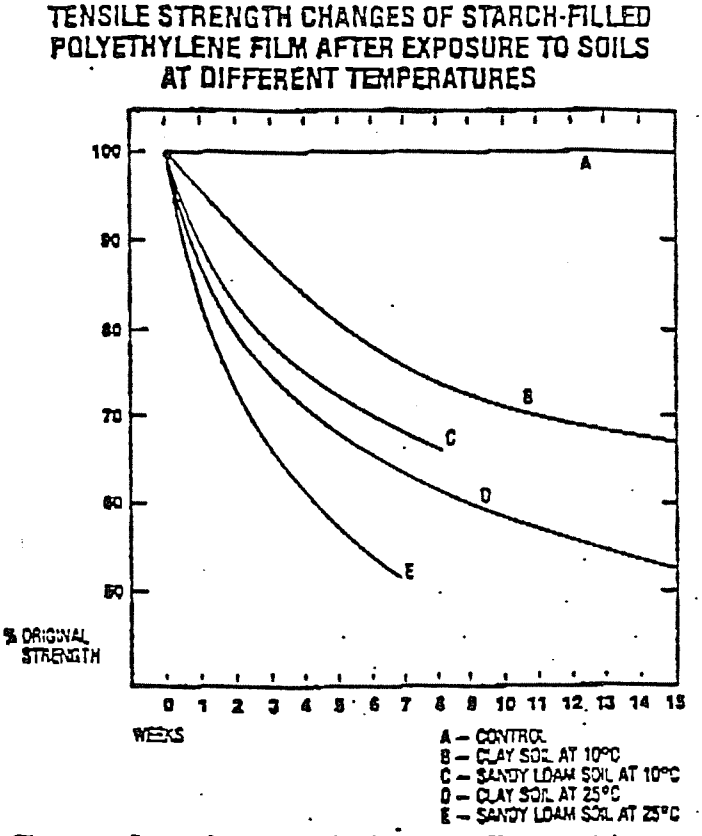

Figure 6: Loss of strength of polyethylene film containing 6% starch after exposure to various environments.

Ecostar without the auto-oxidant has been used in several nondegradable applications as a lightweight filler which can also impart desirable texture qualities to an item. Examples of these applications are vinyl wallpaper, glass reinforced polyester and injection moulded polypropylene parts. Of these only the first is commercial at this time.

ECONOMICS

The current price of Ecostar is approximately 10–15% lower than that of polyethylene resin, depending upon location. In addition, North America is self-sufficient in corn. As a result

TABLE II: Physical Properties of Linear Low Density Polyethylene Films Containing Various Amounts of Ecostar

Starch Content (%)		0.0	3.0	6.0	9.0
Gauge (mil)		2.1	2.2	2.1	2.2
Elmendorf Tear (gm)	MD	579	634	637	797
	TD	1190	1113	1133	1126
Tensile @ Yield (kg/cm²)	MD	124	128	126	128
	TD	128	126	124	130
Tensile @ Break (kg/cm²)	MD	299	257	260	223
	TD	286	230	222	198
Elongation (%)	MD	807	717	734	667
	TD	889	774	764	702
Dart Impact (gm)		192	160	174	118

the prices of corn and corn starch are far less influenced by the price of petroleum than are polymer prices.

In applications in which direct addition is possible, significant material cost savings can be realized. In applications in which the additional masterbatching process is required, material costs are increased slightly. For example, at current masterbatch concentrations and prices the material cost increase for polyethylene film containing 6% starch would be approximately 10%. This differential would be lower for higher priced resins. In filler applications the low density of starch compared with mineral fillers must be taken into account as fillers are purchased by weight but are utilized on a volume basis.

As corn prices are expected to remain constant or decrease in the future while polymer prices are beginning to exhibit a slight upward movement, this differential will be reduced. Increased levels of masterbatch production should also help in this regard. This differential is also less significant in a packaging application in which the package forms only a small portion of the product price, than in an application such as carry bags.

CURRENT AND FUTURE BIODEGRADABILITY STUDIES

At present the University of Surrey is conducting a study of starch-filled carry bags in a number of laboratory and in sim environments including compost, garden soil, fresh water and sea water.

Diversified Research of Toronto is testing film samples a and 15% starch loading and blow moulded bottles at 10% load using ASTM standards for fungal and bacterial attack polymeric materials.

In Switzerland several different compost bag formulatic are being tested. A further development in this area is degradable composting bag containing Ecostar and anoth additive which biodegrades in less than four months.

A large scale two- to three-year comprehensive study of t parameters affecting biodegradability of starch-filled materi will start later this year. The effects of material thickness a type, active ingredient loading and environment will be studie

SUMMARY

Ecostar has proven to be a viable method of renderi common polymers biodegradable. The system is currently use in several applications.

The method is complimentary to current development wo in the area of recycling and incineration. Ecostar should ha no effect on those processes when they are developed ye provides a method of eliminating those products which will n pass through the recyling or incineration streams. Furthermo Ecostar is available now as a method of making biodegradab plastics in applications or geographic areas in which legislatic may be pending.

BIOGRAPHIES

Dr. Wayne J. Maddever

Dr. Maddever received his degree from the Department of Metallurgy and Materials Science at the University of Toronto in 1977. He subsequently was employed by the Linde Division of Union Carbide and held a number of positions in Research and Development, Sales and Product Management both in Canada and the United States.

He joined the St. Lawrence Group of companies in 1985 and as Manager, Business Development he is currently responsible for the development and marketing of Ecostar in North America.

Dr. Graham M. Chapman

Dr. Chapman received his Ph.D. in Organic Chemistry fron Imperial College in London in 1966.

He held a number of Research and Development position with Mars Limited and Spillers Limited before becoming Re search and Development Director of Lucas Ingredients Limited a Division of Dalgety U.K.

Dr. Chapman is currently General Manager of the St. Law rence Group Limited and is responsible for the developmen and marketing activities of St. Lawrence Starch in Europe particularly those activities relating to Ecostar.

Proceedings of Symposium on Degradable Plastics. The Society of the Plastics Industry, Inc., Washington, D.C., June 10, 1987

STARCH-BASED DEGRADABLE PLASTIC FILM

Felix H. Otey and William M. Doane
Northern Regional Research Center
Agricultural Research Service
U. S. Department of Agriculture

Starch from cereal grains such as corn and wheat shows promise as a component of plastics, especially where the introduction of a biodegradable component is important. For many years up to the early 70s, petroleum was readily available at $2 to $4 per barrel and starch sold for about 5 cents per pound. Since that time, petroleum has increased 5- to 10-fold while starch maintained a steady price or increased little more than 2-fold. These price changes and increased availability now make starch economically attractive as a substitute for petroleum.

Most common starches contain 17–27% amylose, a linear polysaccharide consisting of 400–1,000 1,4-linked α-D-glucose units, and 73–82% amylopectin, a branched molecule consisting of D-glucose units linked α-D(1→4) with branches at the C-6 position once every 26 or more D-glucose units. Starch readily gelatinizes (or disperses) in hot water to form a paste that can be cast into film. However, such films are sensitive to water and become quite brittle upon drying due to retrogradation of the starch. To alter these properties, starch has been blended with water-soluble plasticizers and synthetic polymers. Unfortunately, starch is quite incompatible with most commercially available synthetic resins used in plastic production such as low density polyethylene (LDPE). Aqueous blends of gelatinized starch, polyvinyl alcohol and glycerol or other polyols can be cast into flexible films (1). For large-scale applications, water-extractable plasticizers must be avoided, and the formulations must be adaptable to more economically feasible extrusion blowing techniques now used for most synthetic film production. Also, relatively high levels of starch (40% or more) may be required to achieve desirable rates of biodegradation. We have had considerable success in achieving these objectives by blending gelatinized starch with poly(ethylene-*co*-acrylic acid) (EAA).

$$-(CH_2CH_2)_x-(CH_2CH)_y-$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad CO_2H$$

Films made from this system require no plasticizer, yet they remain flexible even after exposure to water and drying. Although the mechanism is not known, we envision that as internal bonding within the starch molecule is reduced during gelatinization and extrusion, new bonds are formed between the starch hydroxyls and the EAA carboxyl groups that retard retrogradation of the starch.

Starch not only serves as a biodegradable, renewable component but reduces oxygen permeability and can introduce semipermeable characteristics into the film. Starch-containing films may have application as agricultural mulch for which the removal and disposal of conventional films is expensive and disposal sites are increasingly difficult to find.

Film Preparation. Several techniques have been explored for making the films. Initially, they were made by casting aqueous dispersions of starch and EAA (2). These films are promising for applications where up to 90% starch is needed for rapid biodegradation but where strength, flexibility, and water resistance are not critical. When lower levels of starch were used, good physical properties and water resistance were achieved; however, the cost could prohibit certain large-scale applications because casting is a relatively slow process and aqueous dispersions of EAA are more expensive than pelletized EAA.

A second method, which allowed the use of EAA pellets, involved premixing film formulations with excess water (50% or less solids concentration) at 90–100°C in heavy-duty Sigma- or Banbury-style mixers for 45 minutes (3). The resulting dough-like product was repeatedly extrusion-processed into strands until the moisture content of the extruded product was about 5 to 10%. The product was then blown into film by extruding it through a 0.5-inch blown film die. Small amounts of alkali were essential to obtaining quality film. Ammonium hydroxide is the preferred alkali for general purpose film because any excess readily escapes during processing of the films. When strong alkali is added, such as sodium hydroxide, the resulting films have semipermeable properties. This premixing method allows the addition of various formulating aids such as LDPE to lower the formulation cost or various polyols and sugars to increase the amounts of biodegradable composition. Films have been made by this method with up to 60% starch; however, the preferred maximum starch level is about 40–50%.

One major concern to potential manufacturers was the need to premix the starch and EAA in a heavy-duty mixer with large amounts of water before extrusion processing and blowing into film. Quality films have now been made without this premixing step and with much lower initial moisture, by incorporating urea into the system. The major function of the urea is to reduce the amount of water and time needed to gelatinize the starch. Using this technique, a 35-lb. pilot-plant run was successfully completed. A semidry composition of 45% EAA, 40% starch, and 15% urea plus about 17 parts per hundred of aqueous ammonium hydroxide was mixed in a ribbon blender and then extruded into small strands. The extruded product was fed through a commercial blown-film extruder by Rex

Plastics, Thomasville, N.C. The extruder had a 2-inch diameter screw and a 4-inch die. The bubble had a lay-flat width of 12 inches.

Film Properties. In general, starch-EAA films had tensile strengths that remained constant at 2000–2300 psi, but their percentage elongation dropped from 130% to 20% as the starch level was increased from 20% to 50%. Substituting up to half of the EAA with LDPE caused some loss in both strength and percentage elongation, especially with aging; however, cost reduction may outweigh these slight property losses.

Incorporating 10–15% urea into a starch-EAA formulation, to eliminate the heavy-duty mixing step, lowered tensile strengths of films with 40% starch to about 1600 psi, but the percentage elongation increased slightly due to the plasticizing effect of urea. After soaking in water, which removed the urea, tensile strengths and percentage elongations were comparable to those made, without urea, by the premixing method.

No field studies have been conducted on the films to determine effect of long-term outdoor exposure on decomposition rate. In laboratory studies, films containing 40% or more starch develop mold growth within one month after being sprayed with a mixture of microorganisms, and they lost 50% or more of their mechanical properties when in contact with soil for few months.

REFERENCES

1. Otey, F. H., Mark, A. M., Mehltretter, C. L., and Russell, C. R., Ind. Eng. Chem. Prod. Res. Dev. *13*, 90–92 (1974).
2. Otey, F. H., Westhoff, R. P., Russell, C. R., Ind. Eng. Chem. Prod. Res. Dev. *16*, 305–308 (1977).
3. Otey, F. H., Westhoff, R. P. and Doane, W. M., Ind. Eng. Chem. Prod. Res. Dev. *19*, 592–595 (1980).

BIOGRAPHIES

Felix H. Otey

Felix H. Otey, Research Chemist, Plant Polymers Research, Northern Regional Research Center, Peoria, Illinois earned a B.S. degree in chemistry from Murray State College in 1948 and a M.A. degree from the University of Missouri in 1950. Since joining the Peoria Center in 1956, his research work has been concerned with developing industrial uses for starch as raw materials in surfactants, coatings, controlled release pesticides, rubber, and plastics. He has authored about 90 scientific publications including 12 patents and has made about 50 technical presentations.

William M. Doane

William M. Doane is Research Leader of Plant Polymer Research at the United States Department of Agriculture Northern Regional Research Center, Peoria, Illinois. Since receiving his Ph.D. in Biochemistry from Purdue University in 1963, he has conducted and led a wide range of research on the development of technologies for using agricultural materials as sources of chemicals to reduce our dependence on petroleum. As both a researcher and team leader, Dr. Doane has received several awards for scientific accomplishments. During his scientific career he has published more than 150 papers and given numerous invited technical presentations.

(A)

UNIVERSITY OF SURREY

Guildford Surrey GU2 5XH Telephone (0483) 571281 Telex 859331

DEPARTMENT OF MICROBIOLOGY

4TH June 1987

This is to certify that researches in the Department of Microbiology at the University of Surrey have shown that low density polythene suitably formulated to contain surface modified starch grains* is biodegradable in a range of natural environments. These include soils of different types as well as fresh water. Biodegradation was assessed by measurements of the decrease in tensile strength resulting from exposure to these environments.

Dr P. J. Whitney
LECTURER IN MICROBIOLOGY

DEPARTMENT OF MICROBIOLOGY
UNIVERSITY OF SURREY

* The rights for the patents relating to these modifications are assigned to the St Lawrence Group.

Sago-76: Papers of the First International Sago Symposium
(Ed.) Koonlin Tan, Kuala Lumpur;1977.

(B)

A Study on Biodegradation of Starch-Filled Plastics in Malaya

K.C. ONG and W.R. STANTON
University of Malaya
Kuala Lumpur

Ordinary plastics (polyurethane and polyethylene) are widely used as disposable packaging materials in Malaysia. These synthetic polymeric materials are noted for their resistance to biodegradation, and therefore pose environmental problems after disposal as the elemental components in the plastics cannot be recycled.

A new generation of plastics has recently been developed. These plastics are manufactured with incorporation of starch polymers in the process. Four types of starch-filled plastic sheets were kindly supplied by Dr. Griffin (Brunel University, England) for this study; their formulations are listed in Table 1.

Table 1: Formulations of Polyurethane and Polyethylene Samples

Sample	*Type of Plastics*	*Maize Starch % (w/w)*
I	Thermoplastic polyurethane	30.0
II	Low-density polyethylene	9.1
III	Ethylene vinyl acetate copolymer	13.0
IV	Low-density polyethylene	9.1

Samples II, III and IV all contain less than 1% of an unsaturated fatty acid ester, and all samples were manufactured by the process of extrusion blowing.

The plastic sheets were cut into strips 40 cm x 200 cm (Samples I, II and III) and 20 cm x 100 cm (Sample IV); they were buried in garden soil on the campus of Universiti Malaya. Samples (in triplicates) were removed and examined 15, 30 and 60 days after soil burial; Plates 1–2 show the extent of biodegradation of these plastics. The loss in weight of the plastics was also recorded (Table 2). The combined action of insects, fungi and bacteria was found to be responsible for the degradation; insects in particular played an important role in this aspect.

All of these samples supported the growth of microorganisms. Patches of pink, yellow, brown and black staining by fungi and bacteria were detected on the sheets. Plate 3 shows the fungi grown on the 60-day sample.

B-2

Plate 1. Biodegradation of four types of plastic sheets after 15, 30 and 60 days' burial in soil.

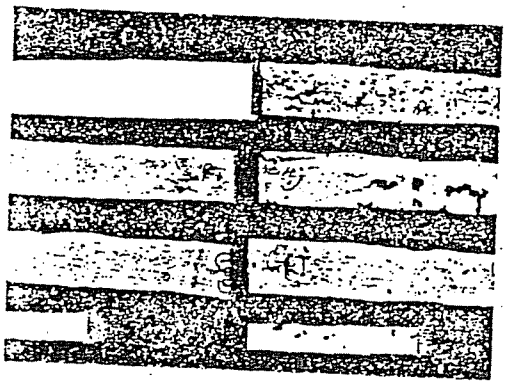

Plate 2. Closer view of plastic sheets in Plate 1.

Table 2: Weight Loss of Plastics Buried in Garden Soil

Sample	*% Weight Loss after Burial for*		
	15 days	*30 days*	*60 days*
I	0.20	10.31	21.80
II	0.24	4.23	5.82
III	0.64	1.31	2.57
IV	1.02	3.74	4.21

Table 3: Weight Loss of Plastics Suspended in Garden Soil Solution

Sample	*% Weight Loss after Suspension in 10% (w/w) Soil Solution for 7 days at 30° C*
I	0.82
II	1.30
III	2.20
IV	0.90

Biodegradability of these plastic sheets by microorganisms alone was also studied by suspending in soil water; strips of the samples were placed in flasks containing 10% (w/v) garden soil solution and incubated in a rotary shaker for 7 days at 30° C. The results indicate the biodegrading power of soil microorganisms (Table 3).

B-3

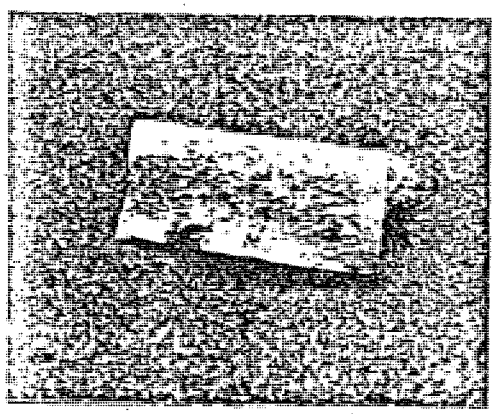

Plate 3. Exhumed degraded plastic sheet: Fungi growing out of the sheet on the right.

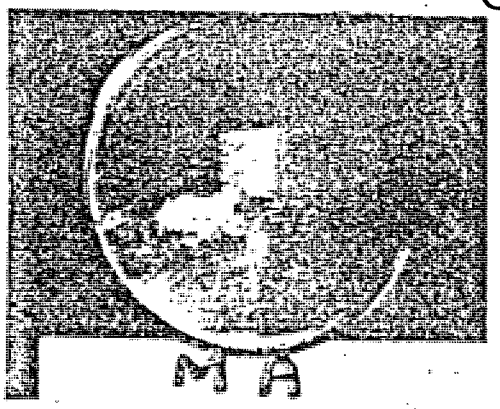

Plate 4. Microorganisms growing out on malt extract agar plate from exhumed plastic sheet.

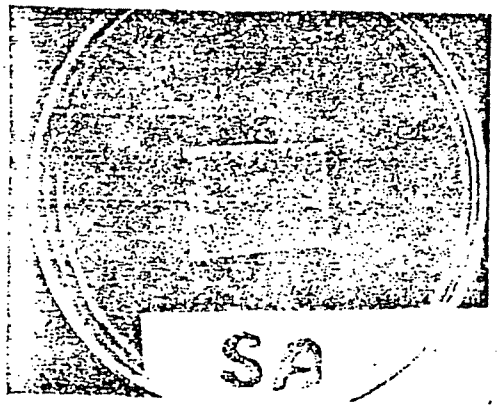

Plate 5. Microorganisms growing on starch agar plate from exhumed plastic sheet.

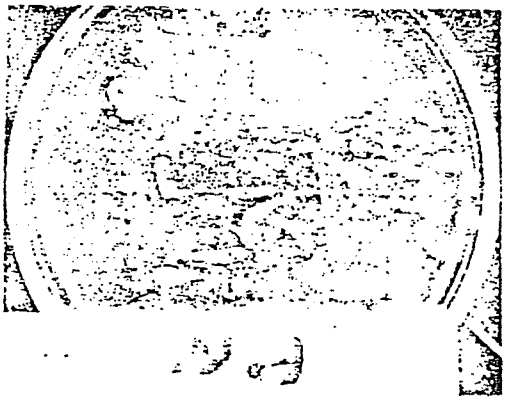

Plate 6. Microorganisms growing on nutrient agar plate from exhumed plastic sheet.

Further study was carried out to determine the types of fungi and bacteria responsible for the biodegradation. Malt-extract agar (Oxoid), starch agar (1% w/v, commercial grade) and nutrient agar (Oxoid) were used for isolating and culturing microorganisms from the exhumed degraded plastic samples (Plates 4, 5 and 6).

Subsequent isolation and purification of these microorganisms revealed that the fungi include *Trichoderma* sp. (Plate 7), *Mucor* sp. (Plate 8) and *Streptomyces* sp., and the bacteria are mainly bacilli and cocci (Plate 9).

It is concluded that the starch-filled plastic sheets under study are all susceptible to insect and microbial degradation.

B-4

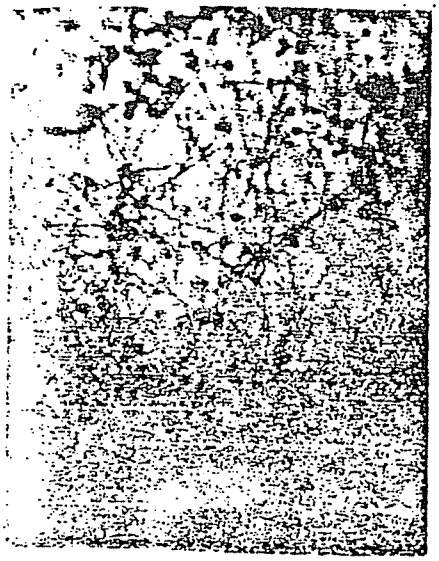

Figure 7. *Trichoderma* sp. isolated from exhumed plastic sample.

Figure 8. *Mucor* sp. isolated from exhumed plastic sample.

Figure 9. *Bacilli and Cocci* isolated from exhumed plastic sample.

BIODEGRADATION OF ETHYLENE/VINYLACETATE CO-POLYMERS

G. J. L. GRIFFIN and H. MIVETCHI

Brunel University, Middlesex, U.K.

Summary

The common synthetic plastics have not generally been regarded as biodegradable, apart from the special case of plasticised PVC. Because of the conflicting technological objectives in, on the one hand, maintaining the stability of plastics used in exposed conditions as structural materials and, on the other hand, in achieving some control of the interaction between throw-away plastics packaging and the environment, any observed exceptions to the biological inertness merit special study. This work reports observations on the growth of fungi in association with EVA co-polymers. The extent of the growth is shown to increase with the vinyl-acetate content and also the presence of starch as a filler. A simple optical technique is described for recording the extent of fungal invasion, and the actual penetration of hyphae into the body of the samples is confirmed by microscopy. The results of experiments with pure cultures and burial in soil are listed. Gross changes in the physical properties of some samples are reported with, in the extreme case of pure polyvinyl acetate, the appearance of partial water solubility.

INTRODUCTION

If we limit our definition of biodegradation to 'a direct utilization of a major component of a material in the metabolic processes of microorganisms', this, in practice, implies a situation in which the normal enzyme secretions of that microorganism may be regarded as corrosive agents toward the material and also that the corrosion products diffuse back into the microorganisms with nutritionally beneficial results. This happens in the case of plasticised PVC and it is generally accepted (Booth and Robb, 1968) that the mechanism involves a diffusion of the low molecular weight plasticiser out of the body of the plastics material to the surface region which is being depleted by the corrosion process. Let us call this Type I. In this particular case, the physical consequences would be a loss in weight accompanied by an increase in hardness and tensile strength. There is, as yet, no evidence for attack on the vinyl chloride polymer chain itself. If we restrict the definition still further to 'utilization of part of the polymer chain structure proper', then the ability of the microorganism to cause a real collapse of the structure is implied and there are very few authenticated examples of synthetic polymers which can be quoted as demonstrations of this type of process, which we can call Type II. The most celebrated are fungal corrosion of certain of the polyester polyurethanes and the effect was originally identified by Levisohn and Evans, (1966) in these materials. It is very clear from microscopy that, in this case,

Table I

Supplier	*Code*	*Melt flow index*	*Density g cm⁻³*	*Vinyl acetate content %*
ICI	Q1388	2	0·916	0
ICI	EVA 49	10	0·937	18
USI Chemicals	UE 631	1·4	0·941	18–21
USI Chemicals	UE 633	20	0·941	17–19
USI Chemicals	UE 634	3	0·950	26–28
USI Chemicals	UE 636	22	0·948	26–28
USI Chemicals	UE 646	16	0·949	26–28
USI Chemicals	UE 643	9	0·941	18–20
USI Chemicals	EY 902	34·2	0·967	41·7
USI Chemicals	20150	7·3	0·973	
Cairn Chem. Co.	S7	Mw 86 000	—	100

Assessment methods

Optical. Gross changes could be noted visually and recorded photographically. Less dramatic effects needed a more refined approach. In an attempt to quantify the extent of the overall change in the samples, they were scanned by a standard microdensitometer and the change in optical density between the exposed sample and a stored control sample recorded as an index of attack. Figure 1 shows a typical scan across a control and a soil

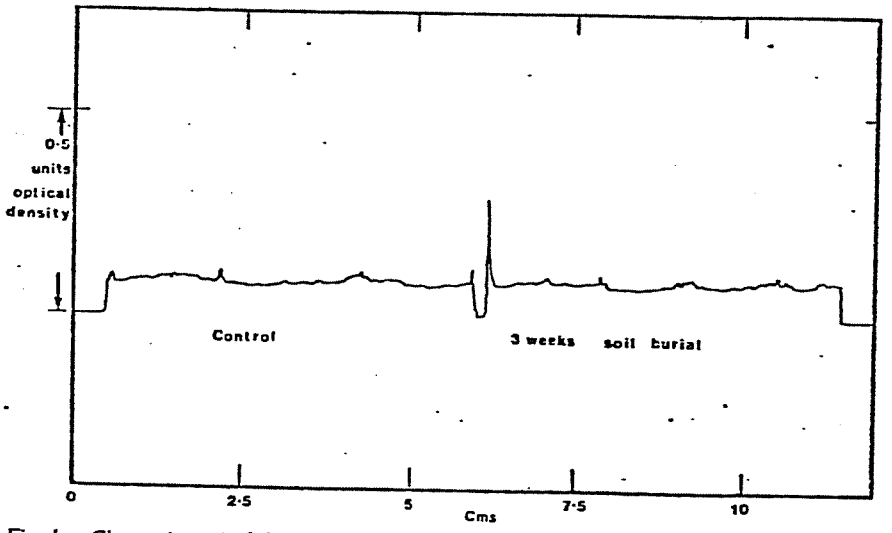

Fig. 1. Change in optical density of a typical EVA sample sheet after exposure to soil burial for 3 weeks. Reproduced from a single microdensitometer trace. Sample was a proprietary partly hydrolysed EVA moulded sheet.

burial sample with almost no effects, while Fig. 2 shows the effect of starch addition to an otherwise identical pair. Data extracted from six sets of samples for a typical EVA/starch blend are shown in Fig. 3 plotted against time of burial. Even when the growth was irregular and the traces correspondingly broadened, it was easily possible to draw in a mid-line for the purposes of extracting a single density change figure. The method was sensitive to lack of parallelism between the faces of the samples and, if present,

this became evident in the form of an imposed gradient on the trace which could be accommodated by, again, drawing in the mid-line and taking its centre as the measurement point.

The samples were also examined by a high power optical stereo-microscope and, in certain cases, sections cut, stained in lactophenol cotton blue, and mounted in lactophenol for photomicroscopy.

Mechanical. Because of the extreme difficulty of handling the quantity of material that would have been necessitated by a decision to use conventional tensile testing procedures, hardness was adopted as an alternative index of mechanical change. Because the specimens were thin (ca. 0·5 mm), it was necessary to use a very small indentor and this was available in the ICI pattern microhardness tester.

Metabolic. Because evidence for major breakdown of the material was being sought, this aspect of the work was confined to following weight loss of the samples after careful conditioning to constant weight at 35°C.

RESULTS

Because the test period was limited to 15 weeks and the testing environments were mild, as compared to the more chemically aggressive nature of a composting garbage environment as reported by Wallhäuser (1973) and Griffin (1975), polyethylene itself showed very little reaction in any of these tests. At the other end of the scale, however, polyvinyl acetate (Mw 86 000 visc. 26–32 cps 86 g/1000 ml benzene) developed a high degree of water sensitivity very quickly, especially if starch filled, and could not then be separated from the soil. On drying the soil a 'biscuit' of impregnated soil could be recovered.

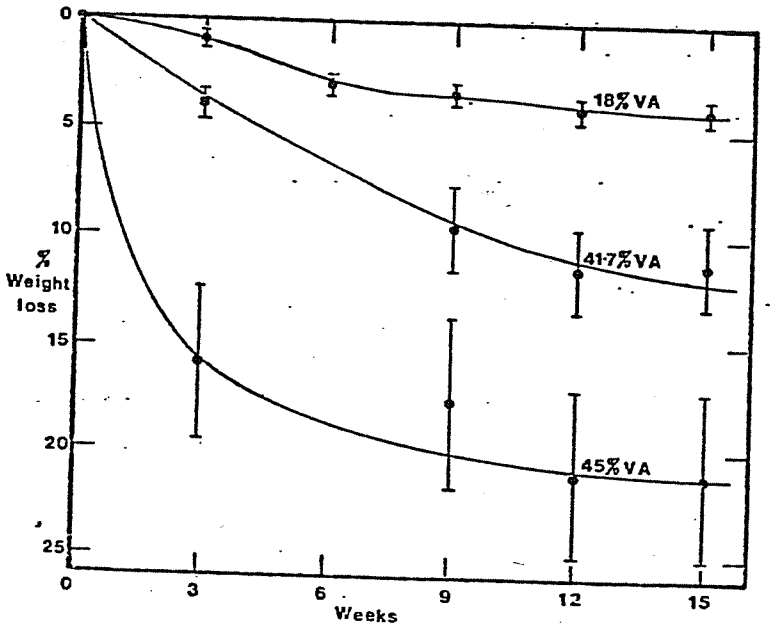

Fig. 4. Variation in percentage weight loss with time on exposure to soil burial conditions of low maize starch loaded EVA with three different vinyl acetate contents.

In all other intermediate cases the dominant influences were, first, the vinyl acetate content and, second, the addition of the auxiliary starch nutrient. These impressions are confirmed by the weight loss measurements, typically as in Fig. 4, and it is significant that for a few of the high VA content samples with added starch, at the end of the 15-week period the weight loss exceeded the weight of the starch addition.

Microhardness was a rather more puzzling quantity, as Fig. 5 suggests, although the general trend was still evident. It has to be remembered that the results here would be very different in the presence of moisture as was evident when handling the samples immediately after removal from the culture dishes.

Studying the surface of the soil burial samples yielded views of micro-organisms typified by Fig. 6 and it was easily apparent with the stereo-microscope that hyphal penetration had occurred especially with the high vinyl acetate/starch loaded samples. This is not so clearly apparent in 2D and therefore cut sections were prepared and stained in cotton blue. From these it was clear that hyphal penetration had occurred through the body of the sample.

CONCLUSIONS

Polymerized vinyl acetate is clearly capable of being attacked by micro-organisms, especially fungi, in a manner which increases its water sensitivity to the point of incipient dissolution. Its co-polymers with ethylene all show this effect to a degree and the attack is very greatly stimulated by the presence of starch as a filler. It would appear to offer an alternative degradation route avoiding the oxidative chain scission requirement for the microbiological digestion of polyolefines, *i.e.* make an initial stage that of enzymatic hydrolysis of side chain ester groups in order to achieve a degree of water dispersability as a hydrophyllic colloid. There is a strong indication from the achievement of hyphal penetration through the polymer films between the starch grains that a major breakdown of the polymer is occurring. This is supported by the fact that some of the buried samples lost more weight than the actual starch content would permit if the polymer were remaining inert. Furthermore, the hardness eventually increased in all cases, just the opposite to what would be expected for simple starch removal.

REFERENCES

Booth, G. H., and Robb, J. A. (1968). *J. Appl. Chem.*, 198, 194.

Griffin, G. J. L. (1975). Preprints. Degradation and stabilisation of polyolefins. 15th Prague Microsymp.

Levisohn, I., and Evans, D. M. (1966). Fungal growth on polyurethane printing rollers. Patra Report No. 71.

Potts, J. E., Glendinning, R. A., and Ackhart, W. B. (1973). *Preprints Degradability of polymers and plastics.* Plastics Institute, London.

Wallhäuser, K. H. (1973). *Preprints Degradability of polymers and plastics.* Plastics Institute, London.

Worne, H. E. (1970) Biodegradability of synthetic organic polymers. S.P.E. Plastics and Ecology, pp. 5–8. Reg. Tech. Conference Proc., Cherry Hill, N.J.

IUPAC STOCKHOLM 1976

AUTHORS: P.J. Whitney & W. Williams

(D)

BIODEGRADATION OF A POLYETHYLENE COMPOSITE

A composite film of polyethylene and starch (6%) together with an unsaturated fatty acid ester (circa 0.5%) and calcium stearate (circa 0.5%) was subjected to tests to determine its biodegradability in soil and freshwater environments. Samples were exposed to microbial attack in the test environments and in simple laboratory models of these environments.

Biodegradation was investigated by light microscopy following both staining the intact film and sectioning and staining the film. Scanning electron microscope studies of the intact film were also made during microbial attack.

Changes in the mechanical properties of the composite were assessed at time intervals during degradation by tensile strength measurements. Some of the organisms involved in the degradative process were isolated and pure culture studies were carried out to confirm that degradation was due to microbial attack. Preliminary enzyme studies have been initiated in an attempt to further understand the nature of this attack.

The composite was found to be substantially degraded in both soil and water environments and similarly degraded in laboratory models and pure culture studies. The rate of degradation being found to be related to the type of microbial flora present.

A sample of a commercially available polyethylene film was not found to be degraded during exposure to microbial attack in these test environments.

P.J.W./9.6.76

D-2

BIODEGRADATION OF A POLYETHYLENE COMPOSITE

by P.J. Whitney and W. Williams
Department of Microbiology, University of Surrey

The material investigated was a commercially available low density polyethylene containing 6% starch, 0.5% unsaturated fatty acid ester and 0.5% calcium stearate. The starch grains in thie composite produced a textured surface to the film (plate 1) each grain appearing to be covered by a thin membrane of polyethylene. The material used had undergone considerable handling including manufacture into polyethylene bags. Much of the surface debris is thought to have been accumulated during this handling.

Samples were buried in soil in the field and in pots in an incubator and also suspended in a fresh-water lake. Degradation was not measured by the most obvious method of loss of dry weight because of the possibility of nutrients being transported to the film during the early stages of colonisation by filamentous fungi masking a genuine weight loss by the film; instead loss of tensile strength was measured. Very simple apparatus was used to measure tensile strength (Fig. 1). The film was cut into the shape indicated around a metal template and replicates were carried out with different orientations of the film.

The effect on tensile strength of a number of treatments are shown in figure 2. Not surprisingly degradation occurred more rapidly in soil in the field at or below 12°C than in soil in a laboratory incubator at 10°C, but interestingly the greatest loss of strength was in the samples suspended in a fresh-water lake, (down to about 57% of original strength).

Soil type and temperature were further investigated in the laboratory where it was clear that again degradation was greater at higher temperatures and also greater in a sandy loam than in a clay soil (Fig. 3). This probably reflects a higher microbial activity at higher temperatures and

Very interestingly it was found that some bacteria and fungi appeared to attack the polyethylene matrix itself resulting in a cracking of the film. The actual cracking may be an artefact produced by the freeze drying process used in preparing the sample for S.E.M. but if this cracking is an artefact, considerable breakdown of the polyethylene must have occurred to make the polyethylene so fragile that it cracked during drying (Plates 3 & 4). This cracking not only occurred around mature fungal hyphae but also around the tips of developing hyphae, where shrinkage of the polyethylene could also be seen (Plate 5). The degradation of the polyethylene would seem to be due to extracellular attack extending a small distance from the hyphae and bacterial cells. One can speculate that this breakdown is due to oxidase or peroxidase enzymes as these have been shown to be involved in the breakdown of other carbon chains.

Not all bacteria or fungi found growing on the surface of the film produce this apparent degradation (Plate 6) but it was fairly common and distinct where it occurred.

The same material that was used for S.E.M. studies was also used for light microscopy. Sections were cut after embedding in a hard ester wax (Steedman, 1960 - Difco) and were stained with iodine. The large dark areas in the figures are stained starch grains and the small dark areas titanium oxide pigment.

Incubation in the petri dishes containing water agar did not result in the complete hydrolysis of starch even in the surface grains. Some loss of starch may well have occurred but the sensitivity of the iodine reaction is such that even a small amount of starch remaining would result in the characteristic blue/black reaction. There did, however seem to be a detectable change in the surface of the entire film which also tended to break away into small 'whiskers' during sectioning (Plate 7) and often to tear away as a sheet during sectioning (Plate 8), a phenomenon not observed

with the better oxygen availability in the loam.

It was thought that the loss in strength could be due at least in part to hydrolysis of the starch grains. Clearly there is a problem of enzyme penetration to starch grains covered by more than a very thin or incomplete membrane of polyethylene. Staining with iodine caused practically all the surface starch grains to blacken, so obviously small molecules such as iodine can gain relatively easy access to the starch grains, but the penetration by large enzyme molecules is more difficult to envisage. Treatment of the film of polyethylene composite with a bacterial amylase resulted in at most a 10% loss in strength but there did appear to be hydrolysis of at least some of the surface grains as they no longer stained so strongly with iodine.

Mechanical penetration by fungal hyphae would of course greatly extend the depth of enzyme attack and to investigate this scanning electron micrographs were taken of degraded polyethylene film. Pieces of unsterilized film were laid on water agar and inoculated with soil crumbs, soil water or left uninoculated and were then incubated for 7 or 14 weeks at 15°C. Tensile strength changes were not statistically significantly different between the three treatments and they were similar to those found in the soil burial experiments. It would seem therefore that after normal handling procedures there was sufficient deposition of bacteria and fungal spores to cause degradation in a suitable environment without further inoculation with organisms from soil or water.

We could find no clear evidence of any penetration by fungal hyphae (this does not of course prove it does not occur, simply that we could not see it in our S.E.M.). There did, however, appear to be examples where surface starch grains were distorted and shrinkage had occurred causing folding of the overlying polyethylene film (Plate 2). This effect could be due to hydrolysis of the starch by extracellular enzymes, provided they are able to penetrate the polyethylene covering the starch grain.

in the undegraded material (Plate 9).

The organisms capable of colonising the plastic were isolated and cultursd on soil water agar supplemented with starch as a carbon source and their ability to cause a loss of strength in the plastic investigated. All organisms found colonising the plastic with any frequency with the exception of Pseudomonas sp. produced amylases resulting in a clear area in the region of the colony when the plate was flooded with iodine. The ability of the organisms to degrade the plastic was tested by inoculating the organism onto soil water agar or soil water plus starch agar and a piece of plastic previously sterilized in 70% alcohol placed on top. The changes in strength of the pieces of plastic were measured after 4 and 8 weeks incubation at 25°C (Table 1). Interestingly the Bacillus species caused greatest loss in strength on the medium supplemented with starch but none of the bacteria were able to degrade the plastic in the absence of an external carbon source. The fungi on the other hand caused greater loss in strength of the plastic when grown on a medium containing soil water alone.

These results may give a somewhat erroneous picture of the relative importance of fungi and bacteria in the degradation of this starch-filled polyethelene composite because in the natural environment there are likely to be significant amounts of external nutrients both in the soil as plant debris and in the water as epiphytes colonising the surface of the plastic start to die, so that the role of bacteria is likely to be significant and may well be as important, or more important than that of fungi.

In conclusion, I would just like to say that we know the biodegradation of this, and probably all plastics, is a complex one which is further complicated by such factors as the interaction of different organisms attacking it at the same time, the probable succession of organisms as the material changes its character during degradation and the influence of the environment affecting all the degradative changes.

D-6

		PERCENT OF ORIGINAL STRENGTH (Incubated 25°C)			
		Soil extract + starch medium		Soil extract medium	
	ORGANISM	4weeks	8weeks	4weeks	8weeks
1	Bacillus sp.(i)	67.9	46.4	100.0	100.0
2	Bacillus sp.(ii)	70.0	47.1	100.0	100.0
3	Bacillus sp.(iii)	67.9	45.0	100.0	100.0
4	Bacillus sp.(iv)	71.4	50.0	100.0	100.0
5	Enterobacteriacea sp.	85.7	72.1	100.0	100.0
6	Flavobacterium sp.	89.3	67.1	100.0	100.0
7	Aeromonas sp.(i)	98.6	90.0	100.0	100.0
8	Aeromonas sp.(ii)	99.3	90.0	100.0	100.0
9	Pseudomonas sp.(i)	92.9	85.7	100.0	100.0
10	Pseudomonas sp.(ii)	92.1	84.3	100.0	100.0
11	Botrytis sp.	84.3	62.1	71.4	57.1
12	Aspergillus sp.	85.7	64.3	57.1	39.3
13	Cladosporium sp.	85.7	68.6	85.0	68.6
14	Monilia sp.	90.0	70.7	82.9	70.7
15	Pestazzolia sp.	88.6	69.3	55.0	38.6
16	Epicoccum sp.	100.0	90.0	100.0	90.0

Table 1 The reduction in tensile strength caused by attack from bacteria (1 - 10) and fungi (11 - 16) isolated from the surface of starch filled polyethelene after burial in soil when grown on soil water agar and soil water agar supplimented with 2% starch

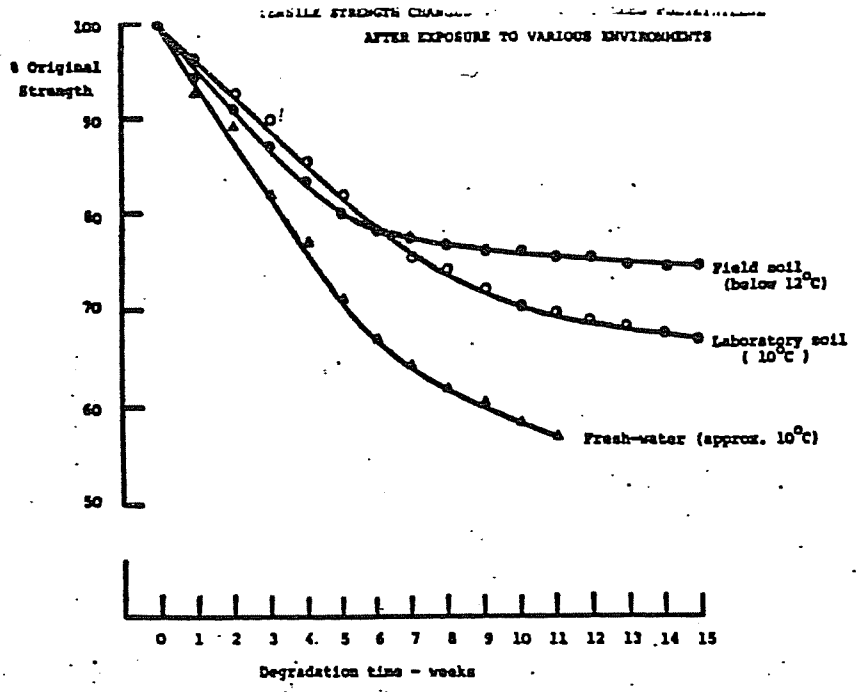

Figure 2

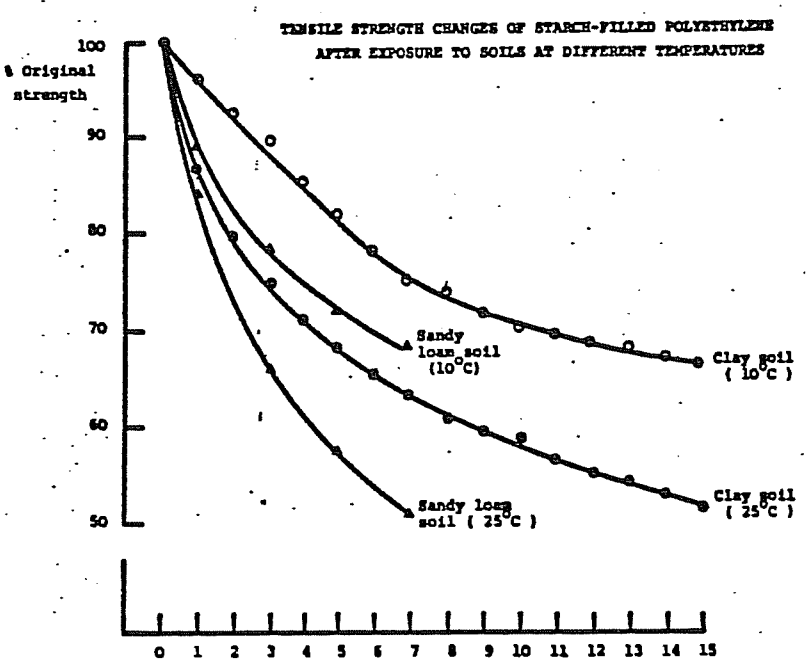

Figure 3

D-8

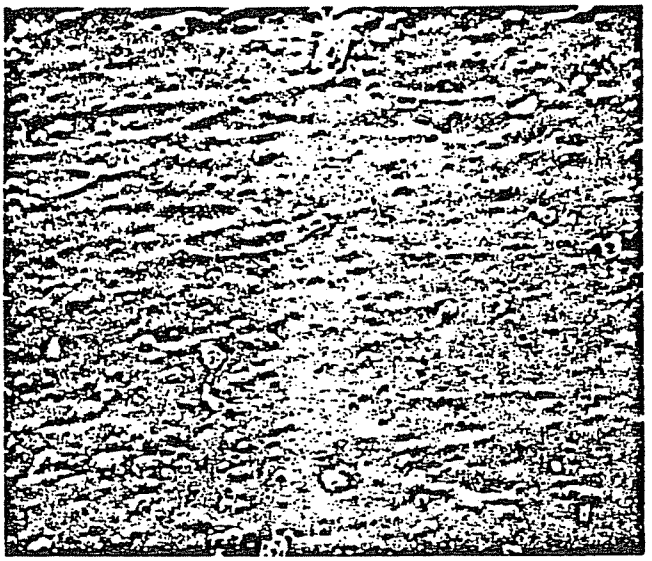

Plate 1 Scanning electron micrograph showing surface of starch-filled polyethelene (x 100).

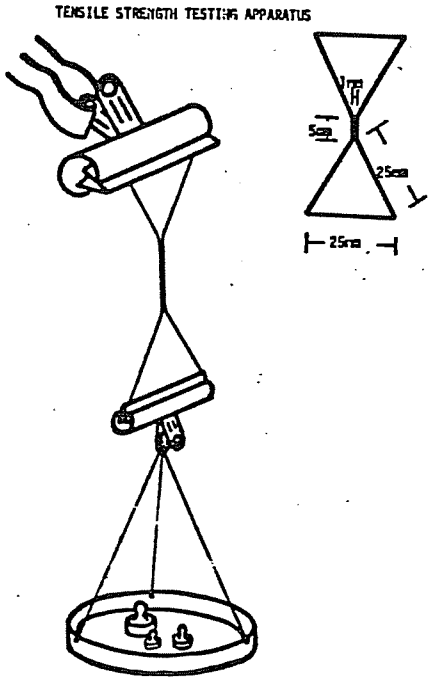

Figure 1

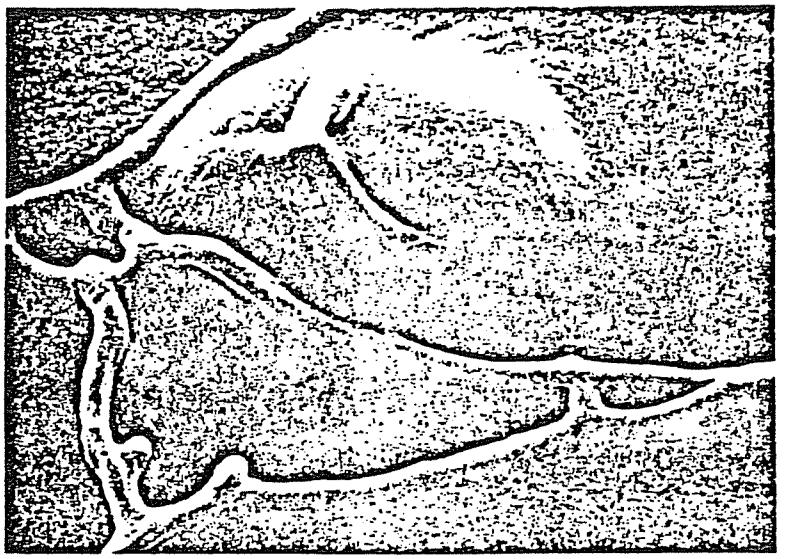

Plate 2 Scanning electron micrograph showing collapse of starch grains on surface of starch-filled polyethelene (x 3,500)

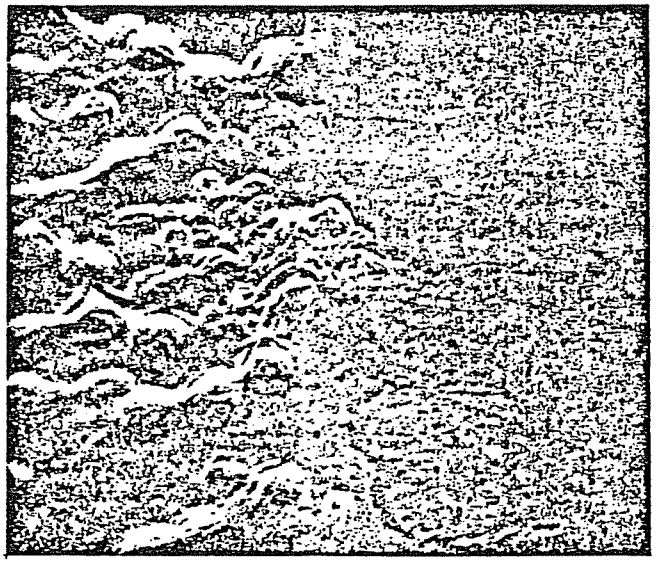

Plate 3 Scanning electron micrograph showing cracking of the starch-filled polyethelene caused by bacteria (x 7,500)

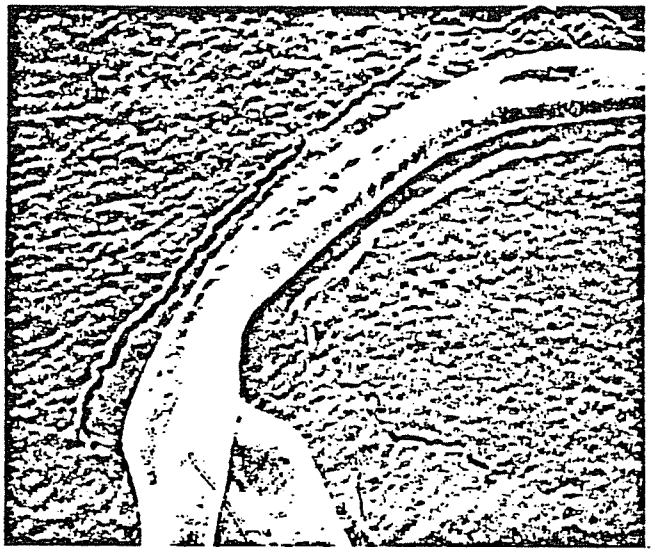

Plate 4 Scanning electron micrographs showing cracking of starch-filled polyethelene caused by fungal attack (x 6,000)

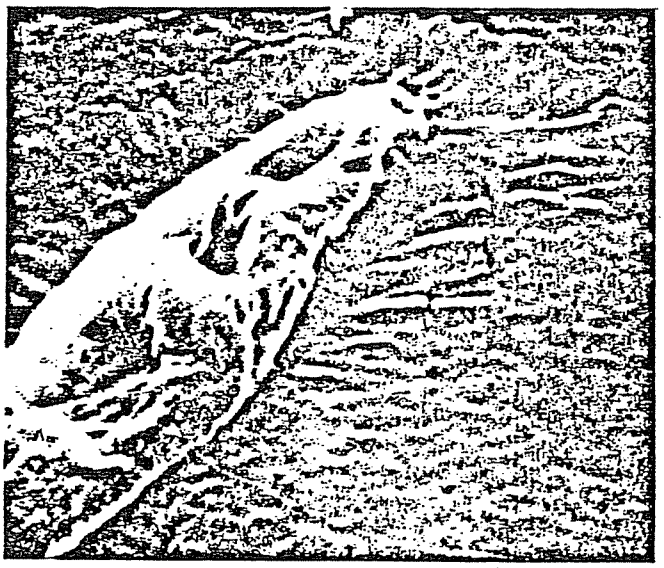

Plate 5 Scanning electron micrograph showing cracking and shrinkage of starch-filled polyethelene at around the tip of a fungal hypha

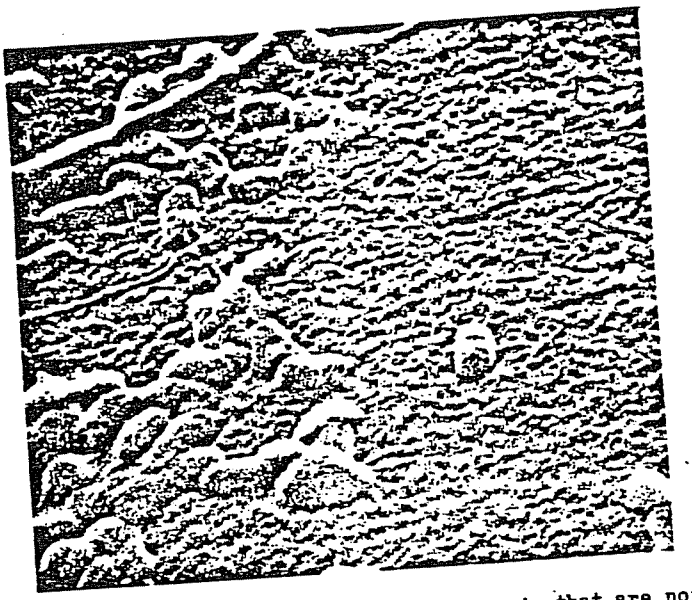

Plate 6 Scanning electron micrograph showing bacteria that are not causing cracking when growing on starch-filled polyethelene (x 7,500)

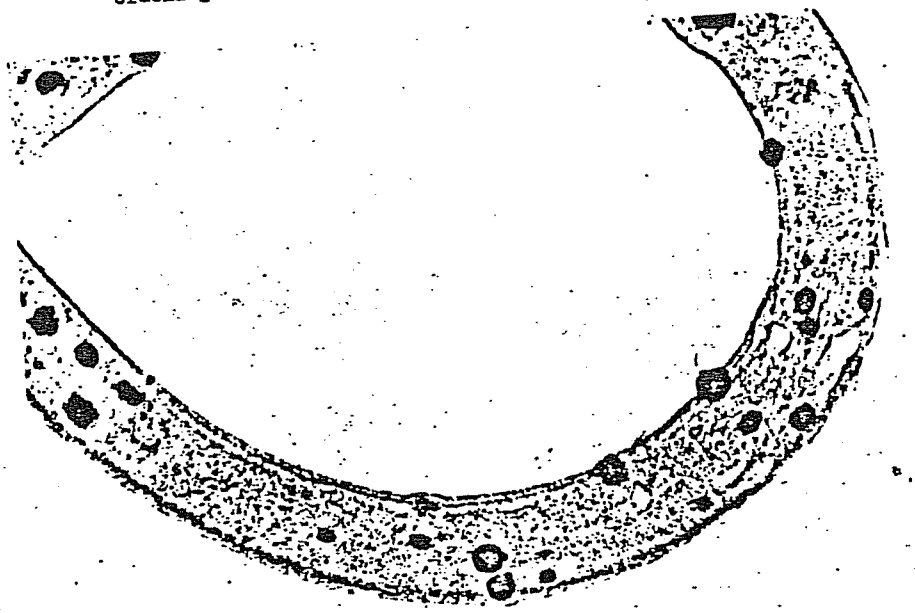

Plate 7 Light micrograph of a section through starch-filled polyethelene stained with iodine after microbial attack showing degradation of the surface of the film

Plate 8 Light micrograph of a section through starch filled polyethelene after microbial attack showing tearing away of the surface layer that occurred during sectioning.

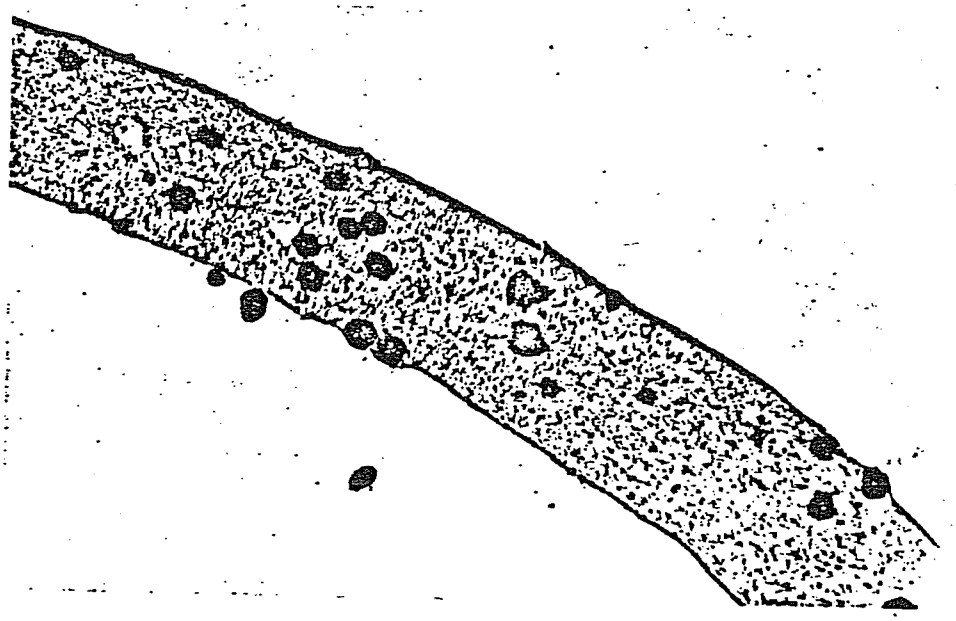

Plate 9 Light micrograph of a section through starch filled polyethelene film stained with iodine

SYNTHETIC POLYMERS AND THE LIVING ENVIRONMENT

G.J.L. Griffin

Department of Non-metallic Materials, Brunel University, Uxbridge, Middlesex, UK.

Abstract - The interaction between synthetic polymers and the physical environment, especially in terms of the effects of oxygen and radiant energy, has been extensively studied and reported and directly useful results have been obtained by the use of experimental techniques of a kind very familiar to physical chemists. The introduction of living organisms to the system, however, adds to the acknowledged difficulty of polymer characterisation other problems more familiar to the biologist. Attempts to reduce the complexity of the system and create study models such as a single homodisperse polymer in contact with a single organism are very misleading because of the mutual dependancy of living things and the delicate balance between organisms, polymer, and auxiliary nutrition.

This field is reviewed here, and extended with observations on the interdependance of macro and micro biological phenomena in the destruction of plastics together with the significance of oxidation as an intermediate stage in the sequence of events.

INTRODUCTION

The primary object of this paper is to summarise the evidence for the breakdown of synthetic polymers in the natural environment under the influence of living organisms. Certain new experimental information is also offered on the question of an oxidative first step in the process of biodegradation of polyolefines. The precise meaning of the term biodegradation has been the subject of some questioning over the last decade. It would appear to imply a very clear organism/material relationship where a conjunction of the specific biological vector and the precise material will always produce a given set of changes implying that a particular process in the life action of the organism, such as the excretion of an identifiable enzyme, is linked to a chemically recognisable cleavage of the molecular structure of the substrate material. Current activity in this field is here reviewed as a survey of recent literature.

It can be equally argued, however, that a particular case of functional decay of a material, e.g. loss of strength, substance, transparency, or good dielectric properties should be termed biodegradation where it is known to be identifiable with exposure of the material to a living environment, which may itself be very complex, and the property loss may be attributable to physical or chemical actions as first steps in an elaborate chain of processes. The exposure of a cotton fabric based resin laminate to a humid tropical environment would be typical of this latter situation in which the initial activity could be the colonisation of the surface by a damp film of fungi encouraged by surface dirt with a subsequent swelling of the laminate surface layers caused by seepage of moisture along the cellulose fibres. The swelling of the fibres causing cracking and disintegration of the resin matrix would be the first stage of properties loss followed rapidly by 'true' biodegradation of the fibres. Biological attack on the resin matrix might, indeed, never occur or might itself be preceded by atmospheric oxidation of the fractured surfaces.

Finally, we must also acknowledge the contribution of a macrobiological vector, this being the mechanical destruction of plastics materials by creatures larger than the bacteria and fungi in the course of nest building , burrowing in search of food, or direct chewing or attrition due to a presumption of nutritive value. This latter situation may be deliberately e[illegible]raged by a modification of the plastic to make it attractive to particular insects [illegible] crustaceans whose habitat and life cycle is appropriate to achieving destruction of a plastic artefact after it has served its useful purpose and especially if it has been improperly discarded.

We can summarise the probable degradation routes thus :

i) Direct biodegradation, involving a direct enzymic scission of the macromolecule which

assimilation of the macromolecule starting from chain ends.

(ii) Indirect biodegradation, oxidative cleavage of the macromolecule followed by metabolisation of the fragments.

(iii) Macrobiological degradation, mechanical attrition of the plastic by rodents, insects, crustacea etc. probably followed by type (i) or (ii) action accelerated by the fine state of subdivision of the material.

E-2

General

The one type of degradation where direct enzyme dissolution of synthetic polymers seems to be beyond dispute is in those cases where actual penetration of a solid polymer matrix by fungal hyphae can be established visually. The classic example is the interaction between polyester polyurethane elastomer and Ulocladium Chartarum as described by Levisohn (Ref. 2). A recent photomicrograph of a discrete event of this kind is seen in Fig.1.

E-3

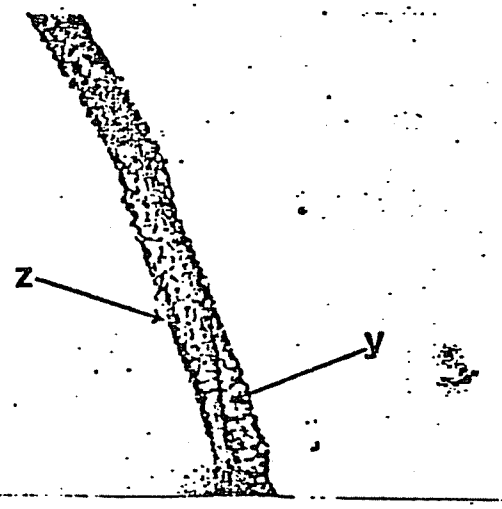

Fig.1. An optical photomicrograph of a fungal hypha in its tunnel etched into ICI 'Daltonol' cast polyester polyurethane elastomer. The hypha y is about 2 micrometres in diameter and the tunnel X about 10.

Similar action has been noted in Starch/EVA blends by Griffin & Mivetchi (Ref. 43). The Author has found it possible to monitor the growth of single hyphal tips within small blocks of clear polyester polyurethane cast on glass cover-slips. Time-lapse cinematography through a microscope over periods of 6-10 hours gave excellent recordings of tip growth, although the extraction of quantitative data was made difficult by apparently random variations in direction, growth velocity, and branching.

It is clear to the observer that no mechanical forces are at work in this hyphal penetration, the fungal filament lies slack in its generous excavation whilst the hole simply grows longer ahead of the growing tip. It is therefore tempting to place the investigation on a more precise footing by attempting a formal analysis of the action. We can list the variables affecting such a venture as follows :-

Subject to direct visual observation -

i. Geometrical factors
ii. Growth kinetics
iii. Branching frequency
iv. Relative growth rates of branches

Measurable local environmental influences -

i. Ionic strength
ii. pH
iii. Surface charge
iv. Temperature
v. Concentration of auxiliary nutrients

The geometrical and kinetic data can be derived by the frame by frame analysis of the cinematographic records subject only to errors of growth velocity components along the optical

leaves the focal plane of the microscope to any significant extent.

The microenvironmental conditions at the hyphal tip present more serious experimental problems and would probably have to be derived from bulk values.

(E 4)

Biological Principles

Experience with bacterial cultures suggests the possibility of an induction of enzyme production by the substrate (Ref. 48). However, macromolecular substrates with their highly restricted molecular mobility pose the problem of access to the protein-synthesis activity, within the microorganisms, although general biological evidence might admit the possibility of surface receptors responding to such a substrate despite their gel or solid form. We have examples in bacterial membranes and in the hormone receptors of higher animals. There seems also, no fundamental reason why the surfaces of fungal hyphae should not be capable of responding to macromolecular substrates. In the case most studied, however, we do not know whether the PU degrading enzymes are constitutive (i.e. substrate independent), or induced.

In order to explain hyphal growth kinetics in terms of enzyme kinetics the enzymes responsible must first be isolated and studied in vitro. This done, then theoretical models could be formulated.

The simplest would involve two growth phases –

A) Initiation of tunnel & B) growth by extension of the tunnel.

A naive model would thus be a steady state kinetic scheme in which a constant concentration of active enzyme(s) is/are maintained in the growing zone and where growth is assumed to be restricted to the tip region. Given the surface area of the polymer tunnel at the growth zone (noting the problem of its indefinite boundary) and the enzyme concentration in the growth zone extracellular fluid we can calculate the local rate of dissolution of the tunnel end simply from the enzyme kinetics. The tunnelling geometry might be depicted simply as in Fig.2.

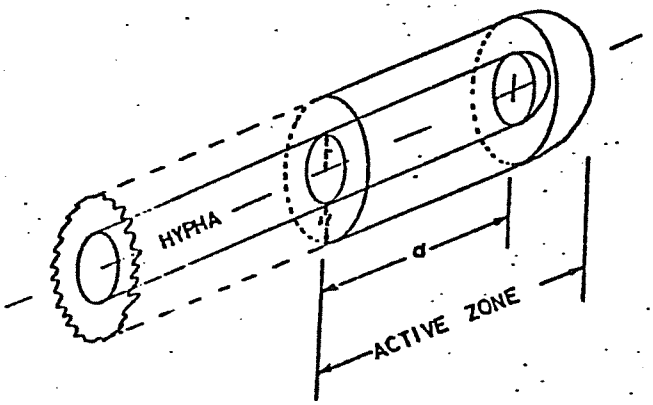

Fig.2. Diagrammatic representation of fungal penetration into an homogeneous polymer by direct enzyme etching.

However, the form of kinetic equation must depend on the mode of heterogeneous catalysis involved and there will be effective concentrations (that is local thermodynamic activities) of chain ends and loops. Different enzymes or different subunits of the same multimeric enzyme may be required to degrade these different sections of polymer. There may also be different rates applicable to areas of different chain enlargement. The differential etching of polymer surfaces by oxidising agents is a reminder of this possibility.

These observations will only relate to short time periods because there are statistical variations amongst the hyphae in a mycelium and the growth may even be oscillatory. The real situation with possible induced enzyme generation and multi-step enzyme processes could prove to be exceedingly complex (Ref. 49) but it is hoped that calculated averages might lead to bulk invasion rates being deduced and it is this latter quantity that related to the progressive destruction of the bulk polymer.

work existing on the degradation of natural macromolecules such as cellulose but the refractory nature of the common plastics and their often complex formulations combine with the complexity and variability of live biological systems to present some formidable problems.

(E-5)

INDIRECT BIODEGRADATION

General

It is generally accepted that high molecular weight is a major factor in inhibiting the microbiological assimilation of polymers. There is, therefore, no difficulty in accepting published descriptions (Refs. 50-51) of the biological assimilation of certain polymers after massive exposure to ultraviolet radiation in the presence of appropriate degradation catalysts. There has, however, been accumulating evidence that the 'difficult' polymers are also very slowly degraded by processes whose final stages are biological under certain environmental contact situations even in the absence of light. The earliest observation is the work of Oppenheimer and his colleagues in the medical field (Ref. 4) where implants of radioisotope labelled polymers, including polyethylene, were seen to be steadily and progressively losing carbon judging by the appearance of radioactivity in the urine of the experimental animals. Subsequently the observations of Wallhauser (Refs. 52-53-54) on polymer samples retrieved from landfall excavations and composting plants confirmed that very slow attack was occurring. Then we find the radioisotope labelling experiments of Nykuist (Ref. 55) designed to show the biological sensitivity of light degraded polyethylene but incidentally showing a small level of carbon metabolization occurring in the unexposed controls. This could have been attributed to scavenging of low molecular weight polymer normally present in the commercial material but when this work was extended by Albertsson (Refs. 44-45-46) in the form of experiments lasting several years, it became apparent that the tailing off of activity that would have been expected of the low molecular weight fraction explanation was correct did not occur, in fact an actual increase in activity was observed. Such a continuing metabolization must mean a progressive breakdown of the polymer.

The apparent contradiction is resolved if we accept that, under certain conditions a two stage process can operate in which the polymer molecular weight is first reduced by oxidation followed by biological scavenging of the oxidation products. Evidence in support of this action in the composting domestic garbage environment was put forward by Griffin (Ref. 56) on the basis of the detection of peroxides and carbonyl groups in low density polyethylene which had been exposed to warm fermenting garbage containing autoxidising fats.

Experimental

On the assumption that it must be possible to reproduce the composting results using clean and characterised materials the Author set up a series of compositions based on a low additives content polyethylene (I.C.I. Q.3188 with MFI of 2 and density 910kg m^{-3} blended with 1% of various unsaturated oils and 0.01% of cobalt added in the form of a commercial cobalt naphtherate solution in xylene).

The compositions were mixed in a miniature internal mixture of 10g capacity in an atmosphere of nitrogen, the discharged material being immediately pressed into sheets, about 100 micrometres thick between polyester foils in a hydraulic press with steam heated platens. These sheets, stripped of their protective foils, were examined by ESR spectroscopy whilst maintained at 80°C in an oxygen atmosphere. Specimens were also mounted for IR spectroscopy, maintained in a circulated air oven at 80°C, being removed for spectroscopy at regular intervals. A further set of 12mm wide strips were cut from the pressed sheets and mounted between roller grips in an Instron tensile tester set to record a 10% elastic elongation slope every hour. The sample and grips were maintained at 80°C in a precision oven fitted in the working area of the tester.

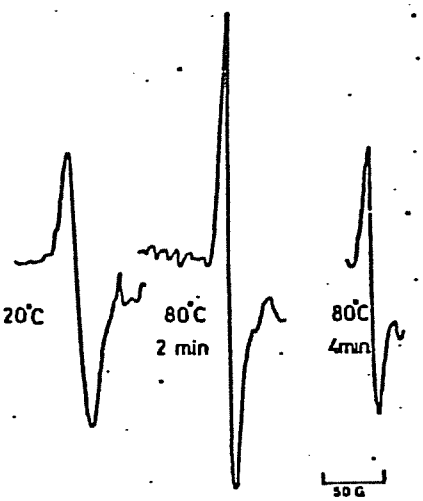

Fig.3. Free radical ESR responses from a low density polyethylene film containing 1% alkali refined linseed oil and 0.01% cobalt as naphthenate.

Fig.3 shows the way in which a typical ESR response appeared and diminished in an LDPE sample containing 1% of alkali refined linseed oil and 0.01% of cobalt as naphthenate. All the indications are that the spectrum is associated with hydroperoxy radials, although the shape is not quite as expected. Because of the competing reactions in this complex system it is difficult to ensure that the specimen is put into the spectrometer at such a stage in its oxidation as to produce the spectrum reliably and it may be desirable to simplify the procedure in some way.

By deriving a carbonyl concentration index from the infra red spectra it was possible to plot the growth of carbonyl content against time and this is shown in Fig.4.

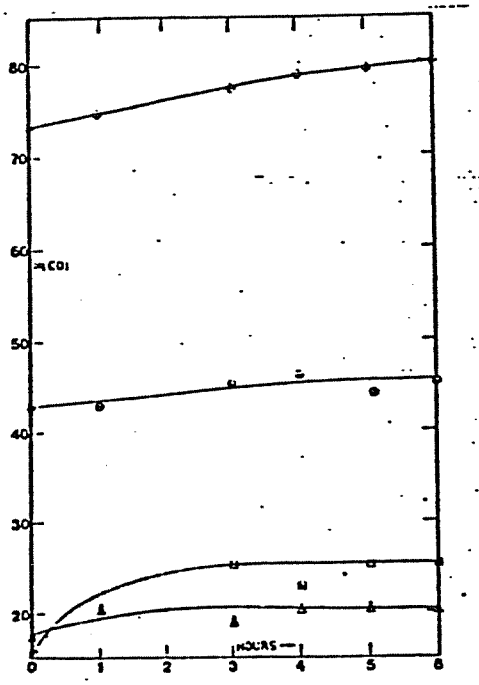

Fig.4. The carbonyl content index of low density polyethylene film (△), the same polymer containing 0.01% of cobalt as naphthenate (⊡), 1% soya oil (⊙) and 1% soya oil with 0.01% cobalt as naphthenate (◈). The index is shown as a function of time at 80°C in air.

In this it is evident that cobalt alone has very little effect on LDPE under these mild conditions, whereas the combination in the case recorded of refined soya oil and cobalt

greater than would be expected from the minute amount of oil actually present in the IR beam path but it is clearly necessary to demonstrate in some positive way that oxidative transfer is taking place between the oil and the polymer. The simplest demonstration of this effect is to show the corresponding changes in the elastic properties of the polymer which might be expected to stiffen initially with crosslinking and then degenerate as the molecular weight diminished. These changes can be seen clearly in Fig.5 which records the tangent modulus of LDPE containing these co-oxidants, and controls, as a function of time at 80°C. It is frustrating not to be able tp get closer to zero time because of the technological problems of sample preparation, but the effect is clear enough. This work has been extended and confirmed by molecular weight change and this will be reported separately.

E-7

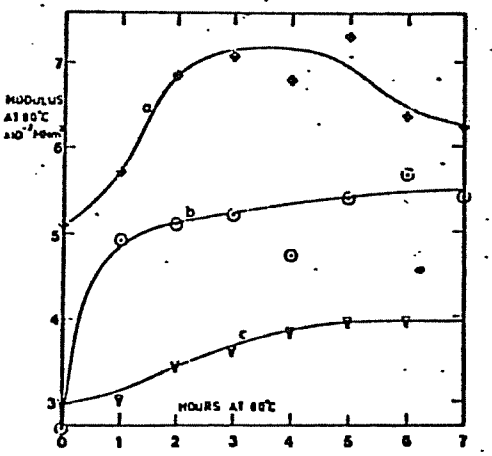

Fig.5. The change in tangent modulus with time of exposure to air at 80°C of low density polyethylene film alone (▽), the same polymer plus 0.01% cobalt as naphthenate (⊙), and with 1% soya oil and 0.01% cobalt as naphthenate (◇).

MACROBIODEGRADATION

The subject of plastics under attack by living creatures larger than bacteria and fungi was extensively reviewed by this Author with Turner in 1978 (Ref. 57) and need not, therefore, be considered in such detail here. Its scattered early literature, entirely concerned with the harmful influence of the attack on man-made artefacts, was given a more formal structure with the appearance of publications from Becker and his Berlin colleagues. For example on insect attack in 1962 (Ref. 58), and again in 1972 (Ref. 59). In a similar manner Schreyer wrote on rodent attack in 1972 (Ref. 60). An opposite view of the situation, i.e. macrobiological attack as a beneficial component of the natural cycle, became possible with the observation, reported initially in (Ref. 57) that controlled attractiveness of material to the animal vector could be achieved with the special case of the crustacean isopoda, the woodlouse, and the novel composite polyethylene/starch (Ref. 61). It now seems possible to engineer a composite by choosing filler ratio, filler particle size, and product geometry so as to create a particular degree of attraction to the woodlouse thus elevating this ubiquitous and attractive creature to the status of potential plastics litter scavenger. Current experimentation confirms the willingness of the woodlouse to discharge this function optimally when it is enjoying its normal humid environment and diet on decaying leaves or wood, that is to say it does not have to be starving to resort to eating starch/polyethylene composite. It is possible to make a film 50 micrometres thick such that 50mm squares will be totally consumed by woodlice in a few weeks. The polymer is discharged in the faeces of the crustaces as submillimetre particles harmless to the environment and in an ideal condition for slow indirect biodegradation to continue. It is clearly likely that other small scavengers could become involved in this action and, most important, the parallel creatures active in the marine environment could be dragooned into beneficial environmental housekeeping to deal with the alarming burden of novel artefacts finding their way into deep water (Ref. 62).

It is interesting to note how the early interest in polymer/environment interactions changed from a preoccupation with damage by micro-organisms to military equipment having plastics components and stored goods wrapped in plastics films, as is typified by the papers of Klausmeier (Ref. 1) to a concern with pollution by discarded plastics items made from embarrassingly long lived polymers. This latter interest built up a large body of publications starting from around 1970 many of which were more . alarmist than informative. A mild conflict appeared between those who contended that many polymers were everlasting in the absence of UV radiation and those who thought otherwise. In 1966 a very factual paper appeared (Ref. 2) first as a PATRA report in which Miss Levisohn reported a clear case of a micro-organism/synthetic polymer interaction involving polyester PU. Later observations of polylactones (Ref. 3) originally synthesised for fibre improvements is a second such clear case. Meanwhile medical research work on implants and prostheses had stimulated studies of biocompatability in which as early as 1955 we find Oppenheimer (Ref. 4) using C14 labelling to demonstrate a progressive biological metabolisation of polystyrene in the bodies of experimental animals.

If we look now at the more recent literature spanning 1976 to 1978 it is interesting to note a sharp growth in research work on biosensitive polymers intended for medical work. Vezin & Florence at Glasgow are investigating Poly-N-alkyl cyanoacrylates (Ref. 5) whilst at the University of Naples Ferruti & others (Ref. 6) are examining Polysaccharide succinic esters as biodegradable drug release matrices.

At the University of Connecticut Bell, Huang, Knox & Others have been studying polyurethanes, -benzylated nylons, polyurea, poly (ester-urea) blends with phenylalanine and hydroxyacid copolymers (Refs. 7-11). At North Carolina State University Penn (Ref. 12) & Lynn (Ref. 13) have been working on block copolymers such as those containing amylose units.

At the National Cancer Institute, Bethesda, Bergman (Ref. 14) and others are examining the biodegradation of polylactic acid in the form of urethral grafts. The US Army Medical Bioengineering Laboratory at Fort Detrick are reviewing biocompatability by biodegradation testing in order to achieve short term evaluation of materials (Refs. 15-16).

At the University of Maryland, Bailey (Refs. 17-18) has started work on rather complex polyamides which, by ingenious chemistry, achieve hydrophilicity and biodegradability. The US Army Dental Research Institute in Washington D.C. has been looking at the biological hazards of using polylactate and polyglycollate materials as implant materials (Ref. 19). These same polylactic acid materials have interested Chang at McGill (Ref. 20) and are a commercial development of the Dynatech Research and Development Co (Ref. 21). A variation is seen with the work of Schindler and others (Ref. 22) at the Research Triangle Institute N.C. using caprolactone dilactide for drug release systems. At the University of Groningen, Netherlands, Marck and others (Ref. 23) have looked at the biodegradability of random copolymers of l-leucine, l-aspartic acid and l-aspartic acid esters. An extensive study of the biodegradation of Polylactones by hydroxybutyrate specific bacteria and fungi has been described in three papers by Tanaka of the Industrial Fermentation Research Institute, Chiba, Japan (Refs. 24-25).

Another approach to surgical implant elastomers is to be found in work at the University of Liverpool by Reed and others (Ref. 26) using poly (ethyleneoxide)-poly (ethyleneterephthalate) copolymers. Rather more exotic chemistry comes from Japan with Tabuse and colleagues at the Kohjin Chemical Co. claiming biodegradability for polyol modified phosphonitrilic polymers (Ref. 27), and from Russia where Sukharukova and others have been producing biodegradable polyurethane semicarbazides bearing alkyl thio side groups (Ref. 28).

A common feature of all this medically oriented work is a willingness to accept complex chemistry with attendant high cost. The actual goal of direct, i.e. enzyme chain breaking, biodegradation seems to be achievable provided only that at least the continuous simple carbon chain backbone is avoided by introducing N substituted amide links, ester links or, under some circumstances, ether links. A warning note by the US Army Bioengineering and Dental Units reminds us that the breakdown products of these exotic polymers cannot automatically be assumed as acceptable in toxicological terms but we should remember that they are concerned with the very specialised environment of body tissues.

When we consider non-medical application areas we find a much poorer yield. The USDA laboratory at Peoria describes various cellulose and starch graft copolymers (Refs. 29-30) and also water sensitive films cast from ethylene/acrylic acid copolymers extended with soluble starch (Refs. 31-32). The water sensitive route to biodegradation is also reflected in studies by Casey and Manley in an elaborate examination of Polyvinyl alcohol metabolisation in activated sludge (Ref. 33), a field also reviewed by Hahn and his colleagues at Hydroscience Inc of New Jersey (Ref. 34). Evidence of commercial activity using PVA in applications other than as textile sizes, comes from the Patent of Comerford and Kapur of Personal Products Inc. USA (Ref. 35).

Early observations of the biodegradability of ester plasticisers has led to a few studies of polyesters as biodegradable polymers, for example Tsuji of the Kuriraay Co. Japan, has

N.J. (Ref. 37). We also have Hatakeyama and his colleagues at the Industrial Products Research Institute, Tokyo, working steadily on methoxy-hydroxystyrene polymers, seen as models of the natural material lignin (Refs. 38-40). Finally the Author's work on starch-autoxidant polyolefine formulations as economically feasible degradable films and mouldings continues to develop (Refs. 41-43).

Few papers are devoted specifically to studying the 'mechanics' of biodegradation and the work of Albertsson at Stockholm is unique in many respects (Refs. 44-46) reporting an impressively lengthy investigation using the C/14 labelling technique.

Also interesting is a Patent by Yogo and Minoda of the Mitsubishi Oil Co (Ref. 47) claiming biodegradation of Polyethylene by Acinetobacter calco aceticus and cunninghamella elegans. In this work it is claimed that HDPE loses 8.9% of its weight in 60 days incubation in a medium of nutrients at 30°C. The specified presence of Fe in the nutrient may be significant in view of the importance of oxidation in these situations.

ACKNOWLEDGEMENTS

The Author would like to record his gratitude to his son, Dr. W.G. Griffin, for valuable suggestions and discussions on the subject of enzyme/polymer interactions. He is also grateful to Dr. R.A. Lott of the Chemistry Department, Brunel University, for assistance with ESR spectroscopy. and to Mr. C. Bewick for skilful experimental assistance with time-lapse photography.

1. Klausmeier, R.E. Internat. Biodet. Bull. 8, 1, p3 (1972).
2. Levisohn, I. Patra (UK) Printing Laboratory Report 71 (1966).
3. Potts, J.R. Glendinning, R.A. and Ackart, W.B. P.I. Conference Preprints 12-1. Deg. of Polymers and Plastics, London (1973).
4. Oppenheimer, B.S. et al Cancer Research 15, p335-340 (1955).
5. Veein, W.R. and Florence, A.J. J.Pharm. Pharmacol 30, Brit. Pharm. Conf. Supp 5, (1978).
6. Ferruti, P. Tanzi, M.C. Vaccaroni, F. Makromol. Chem. 180, 2, p375-82 (1979).
7. Huang, S.J. Knox, J.R. et al J.App.Pol. Sci. 23, No.2, p429-437 (1979).
8. Huang, S.J. Knox, J.R. A.C.S. Symp. Series 49, Text. Pap. Chem. Technol. Symp. p73-80 (1977).
9. Leong, K.W. Diss. Abs. Intl. B. 38(1), 216 (1977).
10. Bell, J.P. Huang, S.J. and Knox, J.R. U.S. NTIS Rep. Issue AD-A 029935 (1975).
11. Huang, S.J. Bell, J.P. and Knox, J.R. et al. Proc. 3rd Int. Biodegradation Symp. p731-741 (1976).
12. Penn, B.J. Diss. Abs. Int. B. 39(5) 2330-1 (1978)
13. Lynn, M.M. Diss. Abs. Int. B. 39(5) 2330 (1978)
14. Bergman, S. et al. Invest. Urol. 16, p48-49 (1978)
15. Megyeli, A.F. et al. Coll. Proc. of 1st and 2nd Conference on short term in vitro test for Carcinog. Mutagen. Tox. p50-75. Pub. Franklin Inst. Press, Phil. Pa.
16. Wade, C.W.R., Hegyeli, A.F. and Kulkarni, R.K. J.Test.Eval. 5,(5) p397-400 (1977).
17. Bailey, W.J. et al. Proc. 3rd. Int. Biodegradation Symp. p765-773 (1976).
18. Wu, Y.S.H. Diss. Abstr. Int. B. 38 (10) p4837-8 (1978).
19. Nelson, J.F. et al. Oral Surg. Oral Med. Oral Path 43 (6) p836-843 (1977).
20. Chang, T.M.S. J.Bioeng 1 (1), p25-32 (1976)
21. Wise, D.L. Acta. Pharm. Suec. 13, (Supplement) 34 (1976).
22. Schindler, A. et al. Contemp. Top. Polym. Sci. 2, p251-289, (1977).
23. Mark, K.W. J.Biomed. Mater. Res. 11, (3) p405-422 (1977).
24. Tanaka, H. et al. Biseibutsu Kogyo Gijutsu Kenkyusho Hokoku 48, p67-74 and p75-79 (1976).
25. Tanaka, H. et al. Nippon Nogei Kagaku Kaishi 50, (9), p431-436 (1976).
26. Reed, A.M., Gilding, D.K. and Wilson, J. Trans. Am. Soc. Art. Int. Organs. 23, p109-115, (1977)
27. Tabuse, I. et al. Japan Patent No.76134800 of 20 May(1975). Japan Kokai Pub.22 (1976).
28. Sukhurukova, S.A. et al. Sint. Fiz. Khim. Polim. 18, p24-27 (1976).
29. Dennenberg, R.J. et al. J.App. Pol. Sci. 22 (2), p459-465 (1978).
30. Bagley, E.B. et al. US Patent 4026849 (1975).
31. Otey, F.H. and Westhoff, R.P. US Patent 4133784 (1977)
32. Otey, F.H. and Westhoff, R.P. US Patent App. 837931 (1977)
33. Casey, J.P. and Manly, D.G. Proc. 3rd Internat. Biodegradation Conf. p819-833 (1976)
34. Hahn, W.H. Barnhart, E.L. and Meighan, R.B. Proc. Ind. Waste Conf. 30, p530-539 (1977).
35. Comerford, J. and Kapur, C. Fr.Pat. 2308656 (1975)
36. Tsuji, M. and Icihara, Y. Hakko Kogaku Kaishi 56 (6) p799-801 (1978)
37. Weisfeld, J. Diss. Abstr. Internat. B 38 (4) 1939 (1977)
38. Nakamura, K. and Hatakeyama, H. Plast. Age 24 (8) p88-9 (1978).
39. Hatakeyama, H. Plast. Age 23 (4) p88-91 (1977)
40. Hatakeyama, H., Hayashi, E. and Haraguchi, T. Polymer 18 (8), p759-63 (1977).
41. Griffin, G.J.L. US Patent 4125495 (1973).
42. Griffin, G.J.L. Brit. Patent 1 489 050 (1973).
43. Griffin, G.J.L. and Mivetchi, H. Proc. 3rd Int. Biodeg. Symp. p807-813 (1976)
44. Albertsson, A.C. J.App. Pol. Sci. 23(12), p3419-33 (1978).
45. Albertsson, A.C. and Ranby, B. Proc. 3rd Int. Biodeg. Conf. p743-51 (1976).
46. Albertsson, A.C. J.App. Pol.Sci. 22 (12), p3435-47, (1978).
47. Yogo, M. and Minoda, Y. Japan Patent No.77 56175 (1975).
48. Watson, J.D. Molecular Biology of the Gene, 2nd Ed. p438. Pub. Benjamin, New York (1970).
49. Boyer, P.D. The Enzymes, Kinetics and Mechanism, Vol.II, pub. Academic Press, New York (1970).
50. Potts, J.E. Glendinning, R.A., Ackart, W.B. & Niegisch, W.D. Polym.Sci.Tech. 3, p61-79 (1973).
51. Guillet, J.E. Regulski, T.W. & McAneney, T.B. Envir.Sci. & Tech., 8, No.10 p923-925 (1974).
52. Wallhauser, K.H. Verpackungs Rundschau, 3, p266 (1972).
53. Wallhauser, K.H. Mull. U. Abfall, 1, p10 (1972).
54. Wallhauser, K.H. Plastics & Rubber Inst. Conf. Degrad. of Polymers, Preprint Vol. London (1973).
55. Nykvist, N.B. Plastics and Polymers, Vol. p195-199 (1974).
56. Griffin, G.J.L. J.Polym.Sci. Symposium No.57, p281-286 (1976).
57. Griffin, G.J.L. and Turner, Ruth D. International Biodeterioration Conference, Berlin, August 1978 (In press).

59. Becker, G. and Seydlitz-Kirzbach, E. Material u Organismen, 7, p161-176 (1972).
60. Schreyer, G. Konstruiren mit Kunstoffen, Pub. Carl Hanser Verlag, Munchen, p743 (1972).
61. Griffin, G.J.L. Advances in Chemistry, Series 134, Fillers and Reinforcements for Plastics, A.C.S., p159-170 (1974).
62. Cundell, A.M. Environmental Conservation, 1, p63-68 (1974).

E-11

(F)

BIODEGRADABLE PLASTICS

G. J. L. Griffin,

Ecological Materials Research Institute,
Brunel University,
Runnymede Campus,
Egham,
Surrey, TW20 0J2

Summary

In the absence of economic constraints there seems to be little difficulty in preparing synthetic or semi-synthetic polymers which are quite rapidly decomposed by the direct action of bacterial or fungal enzymes. Conversely by selecting particularly refractory synthetic polymers and compounding them with adequate protective agents it is possible to prepare useable plastics compositions with a very high life expectancy in biologically active environments. Much more difficult is the problem of designing polymer compounds which are economically and technically acceptable to a specific industry, that of packaging goods for retail distribution. This paper considers the constraints imposed by the packaging technologists on the development of environmentally preferred materials, in particular the conflict between the requirements for lengthy in-store life possibly in contact with food, and subsequent breakdown in garbage disposal operations. Test methods are described and the importance of their selection is considered in the light of experience with starch/polymer blends used as packaging films.

What is Biodegradability?

We can recognise decay as an important element in the dynamics of biological processes: living things eventually die and the products of their decay return key substances into the cycle thus tending to restore the fragile equilibrium of life on earth. The most familiar substances cycled are carbon and nitrogen and it is generally accepted that the processes of decay and decomposition of vegetable and animal residues are complementary to the processes of reproduction and growth. The consequences of disturbing this balance are only too often revealed in land erosion, deforestation, and the associated famine and drought.

The process of decay is slower and more complex than is often thought. Pine needles falling to the floor of a European forest may take as long as fourteen years to become assimilated into the soil. The route from dead

matter to soluble or gaseous products may pass through many stages involving large animals, then smaller creatures such as insects and crustaceans and, finally, fungi, yeasts and bacteria. Freak circumstances may freeze these processes for long periods of time especially when natural or man-made events happen to change the environment from oxygen rich to anaerobic. The geological curiosities - oil, bitumen, peat and coal - are examples of such happenings of natural origin, whilst the millions of tonnes of raw urban garbage being buried each year near our large towns is just such an example of a man-made event. The excavation of rubbish burial sites by Wallhauser (1972) in Germany gave a startling indication of the durability of 'natural' materials in anaerobic burial sites when readable pages of seven year old newspapers were discovered. The earliest attempts to manage and utilise biodegradation were undoubtedly associated with the perfection of composting as an important contribution to horticulture and in the vital developments of organised sewage processing. It should also be remembered that much has been learned about the mechanics of decay by those whose professional concern is the preservation of man-made objects and, for them, the same processes of decay would be called 'biodeterioration'.

The most formal definition has come from Hueck (1974) who insists that true biodegradation can only be claimed if there is a unique association between an identified micro-organism and an event leading to molecular breakdown and loss of properties of a particular substance. Where human concern, however, is for the avoidance of the nuisance caused by over-intrusive materials which are, themselves, only an insignificant part of the total organic cycle, then a degradative process which resulted in fragmentation rather than chemical disintegration would be equally acceptable on practical grounds. It is common practice to refer to all cases of progressive loss of physical properties, as well as those where an actual weight loss is associated with the activities of fungi, yeast and bacteria, as 'micro-biodegradation'. I have found it also useful to use the 'macro-biodegradation' to denote those cases where insects or crustaceans are involved. There appears to be no need to classify the less important, but very conspicuous, contributions made by rodents, birds, bears and other animals. The effect of the climate - rain, wind and sun - may be a major mechanical or photochemical element in environmental breakdown, but is generally excluded from the biodeterioration concept.

Biodegradable Polymers

Most natural organic solids such as wood, flesh, horn casein, straw etc., are themselves polymers of sugars or amino acids and in every case there exist corresponding enzyme systems arising from microbiological sources capable of depolymerising the molecules by clearly recognisable chemical mechanisms. It should be possible, therefore, to simulate these processes in suitable contrived synthetic polymers. Such materials have in fact been produced, some by design, such as polycaprolactone, and some by accident, such as polyester polyurethanes, and in these cases specific enzyme/polymer interactions can be recognised. This area of polymer chemistry has been reviewed by this Author (Griffin, 1980) and has given rise to a number of products which are of interest in the development of absorbable prosthetic devices and slow-release drug systems. The unfortunate aspect of such specialised polymer synthesis is that all the products are extremely expensive

and are, therefore, effectively barred from application to such areas as retail packaging. The interesting question remains as to whether the plastics materials most familiar to the packaging industry, polyethylene, polyvinyl chloride and polystyrene are directly biodegradable to any degree. Most hotly debated has been the case of polyethylenes with some authorities (for example see Potts et al., 1973) insisting that polyethylene is virtually everlasting in the absence of sunlight. Wallhauser (1972), however, noted that polyethylene retrieved from his garbage dump excavations had deteriorated physically with some indication of bacterial presence. Evidence from the early work of Albertsson (1976), in which ^{14}C carbon from labelled polymer appeared as radioactive $^{14}CO_2$ evolution in the air above the buried samples, was explained by suggesting that only the very low molecular weight fractions known to be present in commercial synthetic polymers were involved in microbia metabolism. Albertsson (1980) continued the work, however, and showed that after several years of soil contact, instead of the oligomeric residue becoming exhausted, the rate of $^{14}CO_2$ evolution actually increased. The most reasonable explanation of these events is that progressive slow chemical oxidation is taking place under soil burial conditions with microbial scavenging of the polar oxidised material. It seems extremely improbably that direct enzymic attack of the high molecular weight polyolefin is occurring. Support to this view is derived from the more recent studies of Colin et al. (1981) who have made careful observations on the embrittlement and chemical degradation of polymer films in soil burial for periods of up to thirty-two months and conclude that progressive oxidation does occur and that biological action may be involved. Cornell et al. (1984) have also studied the biological sensitivity of the oxidised fraction of photodegraded polymers and confirm that bacterial populations are readily supported by this polar material; they also observed the development of cross-linked structures as evidenced by differential solubility. This is remarkably parallel to the embrittlement and initial increase in tensile strength seen in soil burial studies of polyethylene at Brunel University (Griffin, 1976). It can now be stated with some confidence that high molecular weight polyethylenes are not directly accessible to enzymatic attack in soil contact but a slow two-stage process appears to occur which is not in itself rapid enough to return carbon to the natural cycle or to cause problems with increased oxygen depletion or spontaneous combustion. The embrittlement and reduction in tensile strength properties does, however, offer a route towards reducing the obtrusive physical presence of gross polymer artefacts in the environment. The two-stage process is conspicuous in the garbage environment because of the role played by the auto-oxidation of unsaturated fatty materials leached from food residues into the polymer resulting in the generation of peroxides which appear to be the active agents in the initial scission of the polymer chains.

Work carried out with polystyrene and polypropylene suggests that these materials are even more highly resistant to degradation in soil burial than polyethylenes. The other low cost polymer common in packaging applications, polyvinyl chloride, is extremely resistant to environmental attack in the absence of photochemical breakdown. Flexible plasticised PVC compounds, however, behave quite differently because the plasticiser itself, which may comprise as much as 40% of the composition, can be very sensitive to biological attack and, when removed in this way, leaves behind a porous brittle shell of PVC which is easily fractured by the mechanical disturbances of wind action or agricultural machinery (Griffin, 1984).

Clearly, if the very modest and rather complex breakdown processes of some of the common plastics widely used in the manufacture of disposable packaging items could be accelerated by some economical means without introducing toxic hazards or processing difficulties, then a useful industrial product would result. Such a possibility arose when the special value of particulate starch as a filler was recognised.

Starch-filled Plastics - Origins

The work on starch fillers, started at Brunel University, was concerned with the need to solve a particular industrial problem which called for the creation of a paper-like texture in LDPE blown film. Because of the very tight financial limitations imposed by the originators of the project it was not possible to consider any methods involving significant changes in manufacturing methods or the use of more costly polymers. Any idea of developing novel polymers was quite out of the question. It was clear that the only direction open for seeking an economically viable solution was to examine the possibility of finding a novel filler which could be incorporated into the LDPE before the film blowing operation and to choose the particle size such that, after the thinning of the melt in the film blowing process, the surface of the product film would be gently textured. The search for a suitable filler was made interesting by the peculiar demands of the film blowing process. Mineral powders were rejected because of their abrasive character, the opacity induced by the great difference in refractive index between the mineral and the polymer, and the density increase of the product. Organic fillers, traditionally one of the forms of cellulose, were rejected because of the unacceptable effect of the fibrous material on the flow properties of the polymer melt. Powdered polymers were rejected on the grounds of cost as well as their effect on flow properties. What seemed to be a hopeless situation was rescued by the recognition that natural starch offered a possible combination of low density, matching refractive index, no abrasive action, uniform and appropriate particle size, and reasonable economics which could qualify it as the ideal filler for the task if a technique could be evolved for incorporating it successfully into LDPE. Such a technique was developed by the Author, as a result of which a specially prepared starch is now regarded as a standard filler for thermoplastics and is consumed on a tonnage scale for modifying PVC plastisols for paper coating as well as for the manufacture of extrusion-blown LDPE film (Griffin, 1975; Griffin, U.K. Patents).

At an early stage in the industrial development of the starch filler it became apparent that this new combination of a natural polymer, starch, with the synthetic polymer LDPE could reasonably be expected to be more rapidly broken down in the environment than the synthetic polymer alone. This was shown to be the case and, in consequence, the LDPE/starch blend found ready commercial acceptance in the manufacture of shopping bags, some 400,000,000 of which have been made in the U.K. The shape and size of the maize starch particles gave exactly the required texture to the surface, as is evident from Figure 1.

Starch Filled Plastics - Biodegradability

The first consideration in establishing whether the hypothesis of starch

F-5

enhanced degradability was reflected in fact was to establish the accessibility of the starch itself to biological action. Some doubts were reasonable because it was clear from microscopy that the starch granules were almost perfectly "wrapped" in polyethylene. It was found that if these starch filled films were immersed in starch digesting enzymes (amylases) under the appropriate conditions a substantial proportion, depending on the starch concentration, of the starch filler was digested. This surprising event implied that the polythene was permeable to the enzyme, unexpectedly so in view of the high molecular weight of the enzyme. In fact this behaviour was later proved to be characteristic of polyethylene films of less than one micrometre thickness and was confirmed by preparing very thin films and showing them to be protein-permeable by ingenious biophysical procedures (Griffin and Nathan, 1979). When we consider the situation in a typical packaging film 50 micrometres thick in which are distributed at random starch granules 15 micrometres in diameter, it is not surprising that some of them will be spearated by only 1 micrometre of polymer or less, whilst all those near the surface will have the thinnest covering skin because of the melt stretching that occurred in the film blowing process. This means that most of the starch granules near the surface will be rapidly degraded to sugar and gummy substances while much of the more deeply sited starch will be reached by a kind of "stepping stones" action (a percolation process). The sugar-filled pockets swell by osmotic attraction of water and actual physical disruption of the polymer surface takes place creating a sticky rough surface which is very receptive to the growth of adherent microbial colonies by contrast with the usual smooth waxy polyethylne. Encouraged by these results, laboratory tests were established to examine and confirm the degradation properties of the starch extruded films at Brunel University, the University of Surrey, I.C.I. laboratories in England, and the University of Malaysia at Kuala Lumpur. At Brunel the work was based on a miniature Dano garbage composting drum. Whitney and Williams (1976) at Surrey used a viety of aquatic environments, I.C.I. laboratires used soil burial and sewage sludge for their test environments (P. G. Edgerley, I.C.I. personal communications 1980 - 1982), whilst Ong and Stanton (1977) at Kuala Lumpur used soil burial sites in the botanical gardens of their university.

Comparison between the early composting trials and soil burial tests revealed the importance of auto-oxidisable oils as polymer chain breakers, referred to earlier, because the cooking fats leached by polyethylene from the garbage cuased a much faster breakdown than was observed in temperate region soil burial using starch filler alone. In general the physical properties of the buried or immersed films changed in a characteristic manner in which the first visible evidence would be a dulling of the surface followed by bacterial and fungal overgrowth. The film would become progresively harder and the elongation at break would diminish associated with a slow drop in tensile strength after an initial increase. Failure occurred by the appearance of numerous cracks and after about a twelve month period, mechanical disturbance of the soil would cause fragmentation of the film.

The samples exhumed after a few months from soil burial in tropical Malaya showed extensive fungal and bacterial attack, and also gross perforations were were obviously of insect origin (Ong and Stanton, 1977). Rather surprisingly, similar events were noted in European experimentation (Griffin and Turner, 1978) and the principal active creature was discovered to the humble and ubiquitous woodlouse. Subsequent studies by Griffin and

(F-6)

Tarverdi (1981) have confirmed the willingness of the woodlouse (Isopoda; spp Oniscus asellus; Armadillium vulgare; Porcellio scaber) to attack starch extended plastic films of various types presumably in search of decaying starch granules because the polymer is simply reduced by their mastication to small particles and ejected with their faecal pellets. It is very remarkable that these creatures, which will totally ignore normal plastic films, will attck polymers such as polyethylene, PVC and polystyrene if starch filled, and perform best when they have access to their normal diet and are in damp cool surroundings (Figures 2 and 3). It is fortunate that these are just the conditions, under buildings, in the entrance to culverts and at the base of hedgerows, where neither sunlight exposure nor true soil burial conditions are available and where much plastics litter tends to accumulate.

The Technology of Starch Filled Polymers

Commercial starch filler for plastics is, generally, refined maize starch which has been intensively dried to reduce its moisture content from the normal 12% to less than 1% and has then had its granule surfaces chemically modified so as to render them hydrophobic. This latter operation greatly simplifies the process of mixing the filler with 'oily' polymer melts and also considerably enhances the mechanical properties of the final films or other products. In most applications, for economic reasons, the route to inclusion in the final product involves the familiar intermediate stage of masterbatch preparation. The very dry starch product is thermally stable at temperatures up to 230°C for short exposure times and will withstand temperatures below 200°C for long periods, it therefore offers no problems in masterbatching into the common industrial thermoplastics. Because the particles have an almost uniform size of 15 micrometres diameter (Figure 4) without fines or agglomerates, no special demands are made on the mixing and dispersing action of the machinery used. Care is needed, however, to protect the masterbatch from extended contact with water, although water ring coolers have been successfully used in conjunction with face cutters in systems where the pellets drop immediately onto a separating screen and emerge hot from water contact within 2 - 3 seconds. With masterbatches of starch content higher than 50% WW more care has to be exercised because the pellet surface becomes rougher as the starch content reaches the limit (at around 70% WW) and physical separation from cooling water becomes almost impossible. Using these masterbatches in film blowing or extrusion equipment requires no modification to plant or special procedures other than to protect the masterbatch from extended exposure to moist air. The smooth rounded starch particles have a remarkably small effect on the melt viscosity of polymers and no difference in film area production will be detected at the common loading percentage of 6% as a result of melt viscosity changes.

Mechanical Properties of Starch Filled LDPE Films

Adding large volume fractions of fillers to polymers generally has the effect of reducing tensile strength. Because of the low density of starch filler it has to be remembered that 6% of starch is equivalent in volume terms to 13% of chalk, yet the effect of such a level of addition is less than the commonly experienced day to day fluctuations in the 'standard' physical properties attributable to polymer quality variation, test method inaccuracy, and gauge wandering. a typical set of test figures from an independent test house is presented in Table 1 to confirm this assertion. It can also be

(F-1)

Table 1 Mechanical Properties of Starch filled LDPE film

Test	No. of reps	Sample type, starch content						
		0%	0.7%	1.4%	2.8%	4.2%	5.6%	7%
Thickness (um)								
Apparent Mean		98.3	101.3	111.4	103.1	101.7	120.5	114.7
Min	5	96	92	108	92	93	106	108
Max		101	106	115	109	111	126	122
Calculated Mean		100.0	102.7	103.1	92.7	92.8	93.7	92.7
Grammage (g/m^2) BS2782 Method 512A								
Mean		92.2	95.0	96.1	86.6	87.2	88.3	87.2
Min	5	88.4	91.1	95.1	82.6	84.3	86.8	82.5
Max		94.0	97.7	97.4	92.6	91.0	90.4	95.6
Density (g/cm^3)								
Mean BS2782 Method 509D	3	0.921	0.924	0.932	0.934	0.939	0.942	0.949
Burst Strength (N/cm^2/100um film thickness)								
Mean		12.8	12.8	12.6	12.1	12.2	11.6	11.6
Min	5	12.0	11.7	12.1	10.8	11.8	11.2	10.7
Max		13.0	13.6	13.1	12.9	12.4	11.7	11.5
PFMS 3/67								
Dart Impact (F_{50}) (g/100 um film thickness) BS2782 Method352D	20	404	385	365	399	365	360	345
Tensile Strength (N/mm^2)								
MD Ultimate Mean		103	92	96	91	88	87	87
Min	5	92	83	92	87	80	78	80
Max		112	102	103	95	99	94	91
CD Yield pt Mean		49	49	49	47	44	49	46
Min	5	48	46	47	43	41	48	45
Max		50	52	50	49	47	50	47
CD Ultimate Mean		76	97	100	91	77	90	79
Min	5	66	81	92	86	62	80	68
Max		87	107	109	98	98	101	88
BS2782 Method326B								
Elongation %								
MD Mean		357	402	320	319	325	390	370
Min	5	280	382	280	283	286	334	346
Max		426	440	408	394	368	426	404
CD Mean		469	600	639	611	501	591	538
Min	5	384	482	598	564	365	536	412
Max		536	644	685	644	613	663	609
Resistance to Tear Propagation (g/100 um film thickness)								
MD Mean		122.4	130.3	116.4	113.1	121.1	145.1	114.3
Min	5	118	117	107	95	103	124	106
Max		124	138	124	123	138	162	123
CD Mean		239.2	240.7	316.0	288.2	287.9	272	279.6
Min	5	224	222	217	242	250	235	255
Max		272	280	399	345	271	329	319
BS2782 Method360A								

(F-8)

reported that supermarket check-out operatives find that carrier bags made from these films are easy to handle because there is zero blocking and the surface texture stabilises the stacks of bags.

Economics

The economics of filled polymer manufacture must obviously be totally based on local commodity prices, plant capital costs and depreciation procedures, and labour costs. These elements vary so much from one country to another that it is virtually impossible to include specific examples. However, certain general points can be made which are important in avoiding some common sources of confusion. It has to be remembered that the criteria of technical acceptability vary from product to product, thus a line producing LDPE film for carrier bags will be judged by its output in area units per hour at a particular gauge and this output will be sensitive to changes in density, whereas a polystyrene extrusion line serving a thermoforming unit making cups will be judged by the number of cups made per tonne of feed material, their thickness being less important than the measured stiffness - a property which is actually increased by the inclusion of starch filler.

A familiar complication is that of allowing for the cost ofthe mixing operation needed to incorporate the starch. This can vary from nothing, in those cases where the line is fed with powder preblends, to the full cost of masterbatch preparation. Masterbatching cost is acutely sensitive to the scale of operation and is an activity deserving most careful planning. Costs can often be reduced by incorporating other ingredients in the one mixing operation and, obviously, working with the highest possible starch loading.

A general case, which can be conveniently set up as a simple computer operation, can be derived thus:-

Q = % by weight of dry starch in the finished compound.
s = cost of the dry starch per tonne.
P = cost of the polymer per tonne.
M = cost per tonne of the masterbatch making.
D_s = density of starch, in tonnes per cubic metre.
D_p = density of polymer, in tonnes per cubic metre.
K = % by weight of dry starch in the masterbatch.

Then the density of any mixture D_m is given by:-

$$D_m = \frac{100\, D_s D_p}{D_p Q + D_s(100 - Q)}$$

An important quantity is the ratio by which the density has been changed by the introduction of Q% of starch, i.e. D_p/D_m, because in the manufacture of goods costed on an area basis at set gauge, this factor decides the reduction in area yield per tonne of compound which will have to be offset against the lower cost of the starch filled compound. Thus:-

$$\frac{D_p}{D_m} = \frac{D_p Q + D_s(100 - Q)}{100\, D_s}$$

Now the cost of producing a tonne of compound in its finished state containing Q% by weight of starch will be:-

$$\frac{(100 - Q)P + QS + (100/K)QM}{100} \quad \text{cost units per tonne.}$$

As has been explained, in cases where the product has to be area costed, the calculated cost must be increased slightly because of the density increase. Thus the cost of producing the same volume, i.e. area at fixed gauge, as would have come from one tonne or original polymer is:-

$$\frac{((100 - Q)P + QS + (100/K)QM)D_s}{D_p Q + D_s(100 - Q)} \quad \text{cost units per tonne equiv. volume.}$$

Now the density of superdried maize starch can have values between 1.23 and 1.45 tonnes per cubic metre according to type and the nature of the drying process, and starch is cheaper than the common plastics by a factor ranging from 2 to 16, therefore the maximum economic benefits will come from optimisation of the following factors:-

1. Achieving the highest starch content in the finished product short of

interfering with the manufacturing operation or the physical character of the product.

2. Working with the highest concentration of starch in the masterbatch subject to the limitations of the compounding machinery, or avoiding masterbatching entirely.

REFERENCES

ALBERTSSON, A. C., and RANBY, B (1976) Biodegradation of Synthetic Polymers: the ^{14}C Method Applied to Polyethylenes Proc. 3rd Int. Biodeg. Conf. 743 - 751. Ed. Sharpley and Kaplan. Appl. Science.

ALBERTSSON, A. C. (1980). The Shape of the Biodegradation Cures for Low and High Density Polyethylenes in prolonged Experimental Series. Europ. Polymer.J.

COLIN, G., COONEY, J. D., CARLSSON, D. J., and WILES, D. M. (1981). Deterioration of Plastic Films under Soil Burial Conditions. J. App. Polymer Sci., 26, 509 - 519.

CORNELL, J., KAPLAN, A. M., ROGERS, R. (1984) Biodegradability of Photo-oxidised Polyalkylenes. J. app. Polymer Sci. 29, 2581 - 2597.

GRIFFIN, G. J. L., U.K. Patents 1,485,833; 1,487,050 and etc.

GRIFFIN, G. J. L., (1975) Biodegradable Fillers In Thermoplastics ACS Advances in Chemistry Series No. 134.

GRIFFIN, G. J. L. (1976) Degradation of Polyethylene in Compost Burial. J. Polymer Sci. Sympos. No. 57, 281-286.

GRIFFIN, G. J. L., and TURNER, Ruth D. (1978) Macrobiodeterioration of Plastics Proc. 4th. Int. Biodet. Symposium, Berlin. Eds. Oxley, Allsopp and Becker: Pitmans.

GRIFFIN, G. J. L., and NATHAN, P. S. (1979) Enzyme Permeability of thin Polyethylene Membranes, J. App. Polymer Sci. 35, 475-484.

GRIFFIN, G. J. L. (1980) Synthetic Polymers and the Living Environment Pure and Appl. Chem., 52, 399-407.

GRIFFIN, G. J. L. and TARVERDI, K. (1981) Macrobiodeterioration of Thermoplastics Proc. of 5th Int. Biodet. Symp. Aberdeen. Eds. Oxley and Barry: Wiley.

GRIFFIN, G. J. L. (1984) Biodegradation of Plasticised Polyvinyl Chloride, 6th Biodet. Soc. Symp. Washington D.C. USA, Commonwealth Agricultural Bureau.

HUECK, H. (1974) Criteria for the assessment of the Biodegradability of Polymers. Int. Biodet. Bull. 10, (3), 87.

ONG, K. C., and STANTON, W. R. (1977) Biodegradation of Starch filled Plastics in Malaya. Proc. of 1st. International Sago Symp., Sarawak.

POTTS, J. E., CLENDENNING, R. A., ACKART, W. B., and NIEGISCH, W. D. (1973) The Biodegradability of Synthetic Polymers. Polym. Sci. Tech. 3, 61.

WALLHAUSER, K. H. (1972) The Disposal of Plastics in Controlled Dumping. Mull and Abfall, 1, 10.

WHITNEY, P., and WILLIAMS, W. (1976) Biodegradation of a Polyethylene Composite. IUPAC Conference Proceedings, Stockholm.

J. POLYMER SCI.: Symposium No. 57, 281–286 (1976)

(G)

DEGRADATION OF POLYETHYLENE IN COMPOST BURIAL

G. J. L. GRIFFIN

Department of Polymer Science and Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, England

SYNOPSIS

Degradation of buried low-density polyethylene has been reported but only in the composting garbage environment. Evidence is offered linking the initial stage of the breakdown with the transfer by diffusion of unsaturated lipids from the compost to the polymer associated with the generation of peroxides by autoxidation.

INTRODUCTION

Concern about the longevity of low-density polyethylene (LDPE) in land-fill disposal has been widely expressed and discussed. Efforts to achieve rapid chemical breakdown have caused speculation about possible attendant problems of increased bological oxygen demand (BOD)[1]. The view proposed, for example, by Potts[2] that LDPE is indefinitely stable in the dark damp conditions of soil burial has been widely accepted by the polymer industry as the basis of a claim that the material offers no environmental problems. The first recorded study known to this author of plastics materials recovered from old rubbish dumps, and thus having experienced extended contact with soil burial conditions, is due to Wallhäuser[3] and, apparently, completely contradicts the work of Potts. Extensions of Wallhäuser's work[4] to samples deliberately buried in accelerated composting units confirmed his first work. Nykvist[5] in a laboratory investigation of soil/polymer interaction, using radiocarbon tracer techniques, reported slow degradation of LDPE and he specified compost as the burial medium. Most recently Guillet et al.[6] have confirmed Nykvist's findings, also confirming the greater speed of degradation in sewage sludge and composted garbage, and offering their results as a rebuttal of Potts's observations. In view of the fact that these faster degradation reports are exclusively associated with compost burial it would seem reasonable to look for an explanation in this circumstance and thus avoid a conflict of opinions. I have repeated the tracer work on certain other polyolefins in contact with compost and found again positive indications of breakdown and there would seem to be little doubt that composting garbage is, in general, a mildly aggressive environment for plastics, much more so than garden soil. Observations of the changed physical appearance of LDPE film

after transit through a municipal composting plant lead me to the belief that some substance had been acquired from the garbage and this has been investigated.

EXPERIMENTAL

Commercial Composting Unit

Access was arranged to a "DANO" horizontal cylinder composting unit whence large numbers of samples of LDPE packaging film were recovered from the output screens. This material had a peculiar dull appearance and feel and shared the rancid odor characteristic of the fresh output of these units. The transit time in the composting cylinder is ca. 5 days. During this time the temperature peaks to 60–70°C, aerobic conditions being maintained by a forced draught.

Initial Examination of Samples

Solvent extraction with petroleum ether in a conventional Soxhlet apparatus disclosed that the LDPE which had been through the composting unit contained an average 9% of hydrocarbon soluble material which took the form of a translucent soft brown wax. It was partly soluble in alcohol but, initially, no further attempt at analysis was made. Normally, LDPE film would yield only minute amounts of soluble matter to petroleum ether, mostly derived from antioxidants and slip agents.

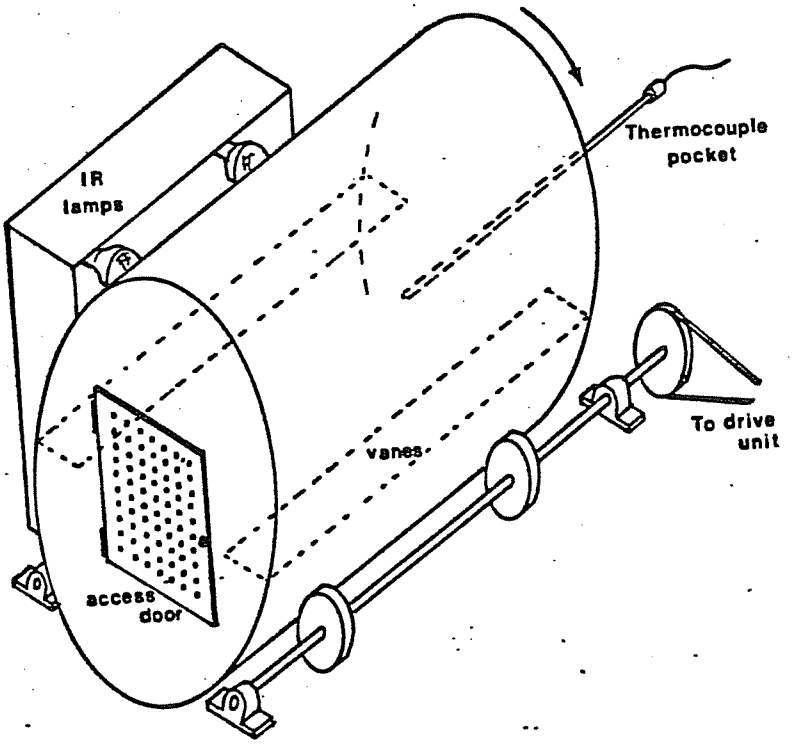

FIG. 1. Sketch of laboratory compost exposure unit.

G-3

Laboratory Composting Unit

Because of the inconvenience of working with a composting unit remote from the laboratory and the near impossibility of recovering from the outlet screens samples which had been intentionally introduced into the feed stream of the Dano plant, it was decided to construct a small version of the equipment in the laboratory (Fig. 1). An aluminum drum 0.56 m in diameter by 0.92 m long was set upon 4 small rollers with its long axis horizontal. One end was fitted with a ventilated access door and two internal fixed vanes 0.15 m wide running the length of the drum served to keep the contents aerated when the drum was rotated slowly at 0.0033 H_z. A temperature of 35 ± 2°C was maintained in the drum by a combination of an internal thermocouple linked to an external bank of four infrared lamps. Approximately 30 kg of fresh compost, taken from the screens of a Dano plant, was charged into the drum and renewed each week. It was not practicable to use the initial raw garbage/sewage sludge blend in this small drum but the conditions were reasonably well re-established by making additions of water, olive oil, sugar, and potato starch so as to match the raw compost analyses available in the literature.[7] Subsequent

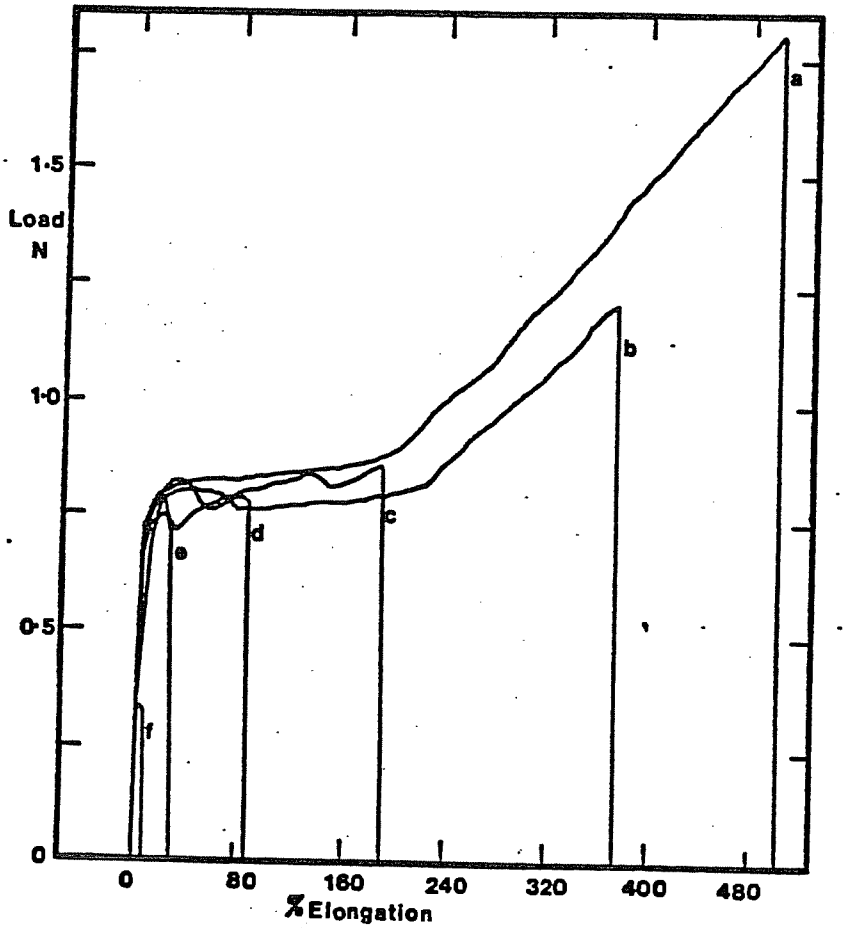

FIG. 2. Superimposed load/extension recordings from an "Instron" tensile testing machine showing the progressive reduction in breaking energy of LDPE film after exposure to warm compost. (a) control; (b) 6 weeks; (c) 7 weeks; (d) 9 weeks; (e) 11 weeks (f) 13 weeks.

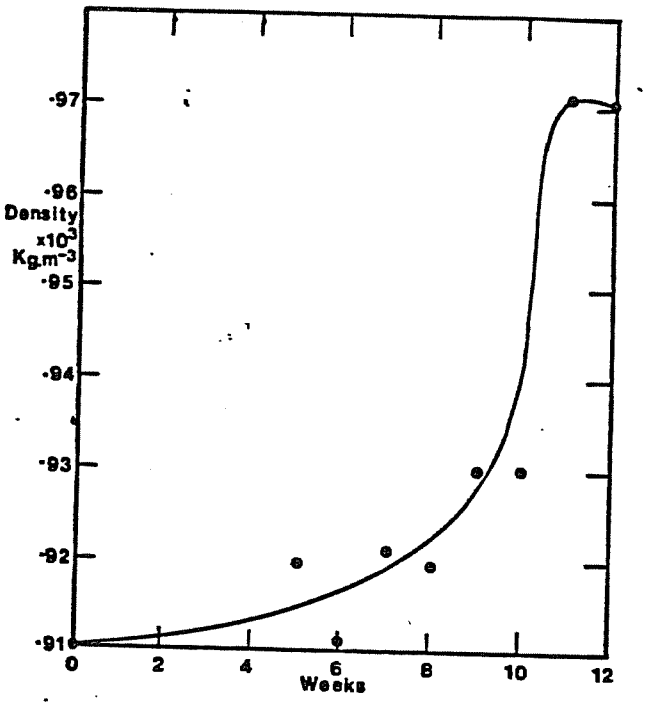

FIG. 3. Density of LDPE film after exposure to warm compost environment for periods up to 12 weeks. These density gradient column measurement show an induction period followed by a steep increase to a plateau.

comparisons with the full size plant were very encouraging. The polyethylene samples were introduced as sheets 150 × 100 × 0.075 mm cut from film extrusions blown in the laboratory using an ICI polymer grade Q3188 which is substantially free from additives and has a density of 910 kg m^{-3} and melt flow index (MFI) 2.

Quantitative Examination of Samples

At regular intervals sample sheets were removed from the composting drum, washed in deionized water, and used for the cutting of standard tensile strength specimens. The ultimate tensile strength (UTS) decreased steadily with time although initially, the yield point changed very little, the best "degradation index" being the area under the load/extension curve. This is clear from Figure 2 in which six successive Instron autographic tracings are superimposed. From the same sample sheets small fragments were cut for density measurement using a density gradient column. The progressive increase in density with composting time reaching a plateau at 10 weeks is typified by the results recorded in Figure 3. At the end of the experimental period the final samples were washed and examined for peroxide content by solvent extraction with isopropanol in an all glass Soxhlet apparatus followed by iodometric titration following the method of Wagner et al.[8] In the same way LDPE film samples recovered from the Dano unit were examined for extractable peroxides and the results, tabulated as active oxygen content, were as follows:

Sample identity	Active oxygen, %
LDPE film ex laboratory composter	0.0039
LDPE film ex Dano composter	0.0059
Control, solvent only	0.000019

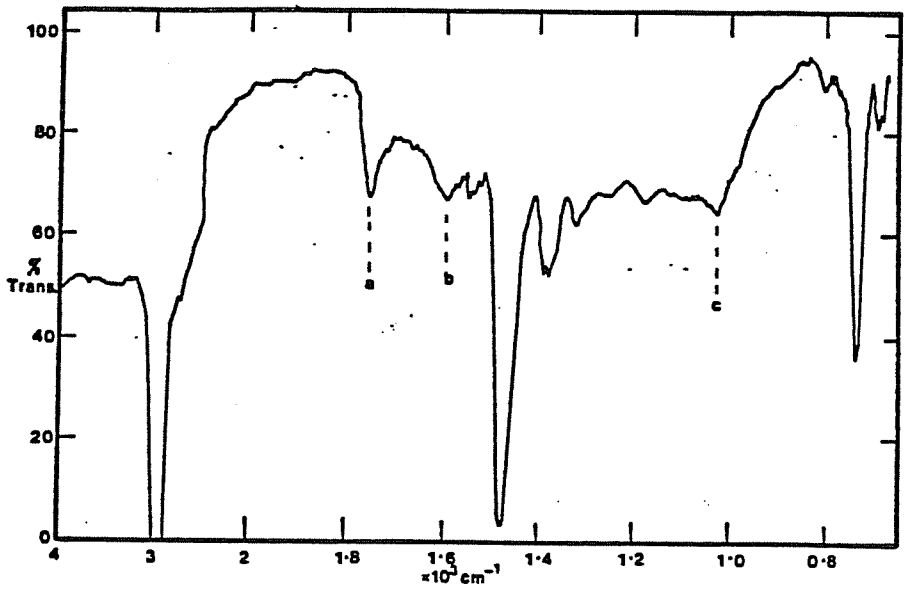

FIG. 4. IR spectrum of compost exposed LDPE sheet (in the Dano unit) showing three new peaks, "a" being identifiable as associated with the carbonyl group.

The samples of the film recovered from the Dano unit were checked for polymer identity by recording their infrared spectrum; a typical recording is shown in Figure 4. The spectrum is considerably modified from the usual LDPE shape, three novel peaks are easily discernible, one of which is clearly associated with the presence of carbonyl groups.

CONCLUSIONS

It has been shown that thin LDPE film can absorb lipids from warm composting garbage and that the plastic film is then found to contain significant amounts of peroxides. At the same time the density increases rapidly after an initial 5 weeks and reaching a plateau at 11 weeks accompanied by a falling away of mechanical properties to virtually zero strength at 13 weeks. Although some loss of strength is attributable to abrasive damage, it is nevertheless reasonable to see a causal link between autoxidative peroixde generation in the unsaturated fatty acids of the lipids and the subsequent degeneration of the polyethylene. Because the autoxidation process is very sensitive to heavy metal catalysis this work is being extended to "clean" systems with very pure fatty acid esters.

The author wishes to acknowledge the contribution of Mr. D. K. Lennard, formerly of Brunel University, whose final year project contained much of the data reported. He is also most grateful to Mr. J. Anderson, Manager of the Leatherhead Refuse and Sludge Utilisation Plant in Surrey U.K., and his staff for allowing access to the Dano unit in their charge and for helpful discussions.

REFERENCES

1. B. Oberbacher, Battelle Information No. 19, 1974, p. 14.
2. J. E. Potts et al., *Polymers and Ecological Problems*, J. Guillet, Ed., Plenum, New York, 1973.

3. K. H. Wallhäuser, *Mull. Abfall.*, *1*, 10 (1972).
4. K. H. Wallhäuser, *Degradability of Polymers and Plastics*, Preprints, Plastics Institute, London, 1973.
5. N. Nykvist, *Degradability of Polymers and Plastics*, Preprints, Plastics Institute, London, 1973.
6. J. E. Guillet et al., *Environ. Sci. Technol.*, *8*, 919 (1974).
7. R. G. Bond and C. P. Straub, Eds. *Handbook of Environmental Control, Vol. II: Solid Waste*, CRC Press, Cleveland, Ohio, 1973, p. 501.
8. C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, *19*, 976 (1974).

olefins of the markets of paper, board and other conventional materials.

Bibliography

Wolpert, V.M., "LINEAR LOW- AND MEDIUM-DENSITY POLYETHYLENE", Volume 1, (polymer, processing, products, and markets and trends), 122 pages, incl. 14 pages with mounted samples, issued in April, 1981;
Supplement I to this survey, 32 pages, issued in November, 1981;
Volume 2, 125 pages, issued in September, 1982.

(H)

DEGRADABLE POLYETHYLENE IN THE PACKAGING FIELD

G.J.L.Griffin *

Widespread use of polythene in packaging has triggered a growth in public concern about the consequential environmental pollution and radically altered load upon our waste disposal services. American and Swedish workers have debated the intrinsic biodegradability of LDPE; it seems that this polymer is probably not biodegradable in the strict academic sense. However the multi-stage autoxidation/biodegradation approach has provided a commercially viable modified polyethylene which does degrade more rapidly in the rural or garbage environment than LDPE itself.

PLASTICS IN THE ENVIRONMENT

The past 50 years has witnessed a growing awareness of the need for polymer technologists to take head of all the consequences of their ingenuity, they must now surely feel obliged to look beyond the successful conclusion of their precise and ingenious manufacturing developments. Soothed by the comfortable notion that most polymers were inert, non-toxic, and harmless materials, they gave little thought in the past to the environmental problems that might be generated by their astonishing success in the packaging industry. The fact that such problems were first brought to the notice of the plastics industry by a vigorous over-reaction in the American environmental concern lobby was particularly unfortunate in that it found the industry largely unprepared and the new 'anti-plastics' outcry gained strength from association in the generally un-informed public mind with older fears about fire hazards and vague resentments against unnatural synthetic "substitute" materials. The public debate, in the main, largely ignored the fact that by the mid 1960's the evolution in food distribution techniques had reached a stage of total dependence on plastics materials and the associated automated processing and converting technologies.

Much has been said and written by way of attempts to define and quantify the environmental problem and such comment can, in turn, be roughly classified. Firstly there are the specific environmental comments such as the finding of plastic wastes on remote Alaskan beaches (1), and various newspaper reports of specific accidents with animals involving, usually, PP baler twine. Secondly we find more broadly based comments on the progressive consequences of the proven contamination of the marine environment by suspended plastics debris (Colton et al (2), Cundell (3), Lyons (4), Lyons (5), Anon (6)) with marine biologists now regarding polymer fragments as a 'normal' ingredient of plankton net sweeps, and expressing concern about the possible fatal effects of such an indigestable diet on immature fish. Finally there

*Ecological Materials Research Institute of Brunel University

is a massive literature on the subject of the disposal of Municipal garbage that would call for a five day symposium to do it justice. Briefly, it is beyond question that the physical nature of garbage has changed progressively as packaging methods have developed (Fig. 1), landfill operatives do find that the low density of present day waste gives them problems with excessive volume demand and wind pick-up of plastic film. Wallhauser's pioneering observations (Wallhauser (7)) on the gradual deterioration of the common packaging plastics in old landfill sites have been supported by other evidence (Griffin (8)) but the process is too slow to be useful in reducing the density of buried garbage. Accelerated mechanical composters such as the Dano plant (Fig. 2) have helped to accelerate the process and give useful density increases before the landfill operation, and some tentative efforts have been made to recover organic materials from garbage for use as fuel and as mixed plastics waste of limited commercial usefulness (Anon (9), Baum (10)).

DEGRADABLE PLASTICS

Old hands in the plastics business may be forgiven for having regarded the outburst of enthusiasm for "degradable plastics" that occupied the period around 1971-1976 with a certain cynicism when we recall that their formative years had been spent in an endless and expensive struggle to protect their 'new' substances from the evils of sunlight, water, and oxygen. Most polymers could be rendered photodegradable by simply omitting the UV protective agents and ingenious work by the photochemists (Guillet (11) and Scott (12)) soon produced limited action agents conferring a certain measure of 'lifetime control'. The extra costs and responsibilities presented to the distributive trades by such systems, however, were not welcomed and they have found their application in the specialised area of agricultural mulch film rather than in their original target area. Photodegradable plastics were intended as a response to the problems presented by the surface pollution of seashore and countryside and had little or no relevance to the landfill problem or marine pollution.

The term 'Biodegradable' was being used by water engineers grappling with the problems of indestructable detergents and industrial effluents long before the plastics industry appropriated it in a rather clumsy fashion. The 'rottable' plastics called for were going to solve all environmental and disposal problems without any consideration of consequential difficulties associated with the inevitable large increases in biological oxygen demand and heat generation. There is, in fact, no great problem in finding natural or synthetic polymers that interact strongly with certain micro-organisms and such polymers can be used wherever their high cost or limited properties are acceptable (Griffin (13)). The deliberate creation of a biodegradable polyethylene, however, is a separate issue.

IS POLYETHYLENE BIODEGRADABLE?

Before approaching this question we must attempt to agree a definition of the term, a task first formalised in the plastics context by Hueck (14) with his ideas based upon the classical demonstration of a micro-organism/substrate relationship evolved in other disciplines by bacteriologists. This formal approach was extended by Kaplan (15) who insisted, further, that i) a positive demonstration of metabolisation of the polymer must be made, e.g. by proving that carbon for the polymer structure is identified as CO_2 in the associated gas phase and ii) the total disappearance of the original material must be demonstrated.

If we adhere closely to these definitions then it is difficult to avoid the conclusion that polyethylene is not biodegradable because no laboratory has, so far, succeeded in demonstrating a high molecular weight hydrocarbon/specific enzyme interaction of measurable rate and with demonstrable metabolite production. Even speculation about the possible future evolution of micro-organisms capable of generating appropriate enzymes gives no grounds for optimism when we reflect on the circa 1.3×10^6 generations of bacteria that have occurred since the commercial advent of polyethylene. It is even possible that the polyethylene molecular structure has been on offer to bacteria for geological time periods if the structure determination of the elastic mineral Elaterite by Heidberg and Graf (16) has correctly identified it as a polyethylene type.

A non-biodegradable conclusion, however, leads us into difficulties with the observations of the Stockholm school of Ranby, Albertsson and Nykvist (17,18,19,20) where, by using C^{14} labelled high and low density polyethylene they were able to demonstrate an unambiguous transfer of carbon from the polymer to the gas phase where the polymer was in contact with 'live' compost, but not where the environment was sterile. The reaction from the American workers was to suggest that what was being demonstrated was the scavenging of low molecular weight fragments of the polymer and to predict that the CO_2 liberation would pass a peak and then decrease with the exhaustion of the biologically accessible fraction. In fact when Albertsson extended her experiments to periods of years, rather than months, she reported that the CO_2 evolution did not decrease but actually increased with time.

This result suggests that a 2-stage process could be in operation with the induction period containing the build up of activity which is cleaving the macromolecule into truly biodegradable fragments. It is also evident that the presence of compost is important, suggesting links with the observations of Wallhauser (7) and Griffin (21) on the mild but real aggressiveness of the compost environment towards polyethylene.

It was on the basis of such observations that the present Author developed a composite based on polyethylene compounds with minor additions of unsaturated oils and, as a filler, desiccated and hydrophobic whole grain starch (Griffin, (22,23,24)). In this system the polymer breakdown was initiated by an oxidation stage triggered by the inclusion of the unsaturates, typically very pure autoxidisable materials such as octyl oleate which, whilst remarkably stable in the clean polymer, became oxygen sensitive on contamination by garbage or by soil contact presumably by transfer of transition metal ions into the polymer.

The presence of the starch was shown to accelerate those processes because, in blown film, it is found very close to the surface (Fig. 3) by virtue of the mechanics of the blowing process, and Griffin and Nathan (25) have shown that very thin layers of polyethylene are permeable to the starch dissolving enzymes produced by fungi and bacteria. The consequences are that shortly after soil contact the surface of the film loses its hydrophobic nature and becomes pitted and easily wettable, greatly aiding the oxidation stage. Material of this type has been in continuous manufacture in the U.K. since 1976 and during that time some 350,000,000 shopping bags have been produced.

The complex nature of the degradation process with these autoxidation/biodegradation system LDPE films is further observed by the tremendous variability of the natural environment into which they may be introduced. Efforts at Brunel University to find a 'standard' degradation environment

have concentrated on sieved 'Dano' compost revived with sugar and fat additions, the University of Surrey have examined forest soil and natural waters Whitney (26), and I.C.I. Laboratories (27) have found very slow but more consistent loss of physical properties using activated sewage sludge as the experimental environment.

MACROBIODEGRADATION

The wide distribution of the British made degradable polyethylene shopping bags has had one surprising and agreeable consequence, in that a number of schools have examined the material as sixth form projects: because of the need to compress these projects into periods measured in months rather than years, attention was given to larger scavengers than the microorganisms which had dominated the University laboratory work. The findings of Miss V. Parris on the positive attraction as "food" of starch/LDPE composites to varieties of woodlouse (a crustacean isopods) drew attention to earlier unexplained events where film samples in soil burial had disappeared completely or, as reported by Ong & Stanton (28), tropical soil burial tests regularly yielded samples perforated by numerous irregular holes. It was clear that a number of insects and crustaceans were active scavengers of starch/LDPE whilst being uninterested in pure LDPE. Interestingly, the attraction is a positive one in that the creatures attack the degradable film faster when they have access to their own normal food and are in their normal dark and humid environment. This work, first reported in Berlin by Griffin and Turner (28) in 1978, has expanded into a new subject area and further publications are appearing (Griffin and Tarverdi (29)), and it seems that a gap in the environmental pattern could well have been filled in that waste plastics deposited in situations where they are neither buried nor exposed to sunshine could well be made attractive to the natural scavengers of these sites, under hedgerows, in covered drains, and trapped below buildings. The first product of this style of scavenging has been shown to be finely powdered polymer which is environmentally innocuous and can be safely left to degrade further by oxidation and microbiodegradation.

H-3

Bibliography

1. U.S. Dept. Commerce Newsrelease, "Plastic Wastes found on isolated Alaska Beaches", March 29, (2) (1973)
2. Colton,J.B.;Burns,B.R.;Knapp,F.D."Plastic particles in Northwest Atlantic Surface Waters", Science, 185, (Aug.9th,1974) 491
3. Cundell,A.M.;"Plastics in Marine Environment", Environmental Conservation, 1 (1) (1974) 63
4. Lyons,R.D.;"Chemical Debris is Fouling the Atlantic", New York Times Feb. 13th,(1973) 22
5. Lyons,R.D.;"Ocean Pollution, the very dirty sea", New York Times, Feb 18th,(1973) 4, Sec 4
6. Anon.;"Marine Scientists Warn of High Sea Contaminants", NOAA News Release, Feb 13,(1973) (4)
7. Wallhauser,K.H.;"The disposal of Plastics in Controlled Dumping" Mull u Abfall, 1, (1972) 10-18
8. Griffin,G.J.L.;"Degradation of Polyethylene in Compost Burial", J.Polymer Sci. Symposium No. 57 (1976) 281-286
9. Anon.;"One way packaging and the Recuperation of Plastic Refuse", Paper No. 13 Europlastique 82 Lecture series (1982)
10. Baum,B.;"Plastics Waste Management", Pub. Debell & Richardson Inc. (1974)
11. Guillet,J.E.;"Polymers with Controlled Lifetimes", Conference Proceedings, Degradability of Polymers and Plastics, Plastics & Rubber Institute, London 1973
12. Scott,G.;Plastics, Rubbers, Textiles, 1 (1970) 361
13. Griffin,G.J.L.;"Synthetic Polymers in the Living Environment", Pure & Applied Chemistry, 52 (1980) 399-407
14. Hueck,H.J.;"Criteria for the Assessment of the Biodegradability of Polymers", Internat. Biodetn. Bull.(ISSN 0020-6164)10, (3) (1974) 87
15. Kaplan,A.M.;"Microbial Decomposition of Synthetic Polymeric Materials", Proceeding of 1st Inter. Congress of International Association of Microbiological Societies, Tokyo Sep (1974)
16. Anon; "Fossil Polythene Keeps its Suppleness", New Scientist, 15 Oct (1970), 111
17. Nykvist,N.B.; Plastics & Polymers, (1974), 195-199
18. Albertsson,A.C. & Ranby,B., Proc. 3rd Internat. Biodeg. Conf. (1976), 743-751

19. Albertsson, A.C. "Biodegradation of Synthetic Polymers", J. Appl. Pol. Sci. 22 (12), (1978) 19-33

20. Albertsson, A.C. "Biodegradation of Synthetic Polymers II,"J. Appl. Pol. Sci., 22 (12) (1978) 3435-3447

21. Griffin,G.J.L.,"Degradation of Polyethylene in Compost Burial", J. Pol. Sci., Symposium No. 57 (1976) 281-286

22. Griffin, G.J.L. "Synthetic Resin Based Compositions", U.S. Patent 4,125,495 (1973)

23. Griffin,G.J.L. "Synthetic Resin Based Compositions", U.S. Patent 4,016,117 (1973)

24. Griffin,G.J.L. "Synthetic Resin Based Compositions", U.S. Patent 4,021,388 (1973)

25. Griffin,G.J.L. and Nathan,P.S. "Protein Permeability of Thin Polymer Membranes" J. Appl. Pol. Sci. App. Pol. Symp. 35 (1979) 475-484

26. Whitney,P. and Williams,W "Biodegradation of a Polyethylene Composite", IUPAC Conference Proceedings, Stockholm (1976)

27. Edgerley,P.G. I.C.I. Welwyn, Private Communications, 1980-1982

28. Griffin,G.J.L. and Turner,Ruth D. "Macrobiodegradation of Plastics" Symposium Vol, 4th International Biodeterioration Symposium, Berlin (1978) 117-122

29. Griffin,G.J.L. and Tervardi,K. "Macrobiodegradation of thermoplastics" Symposium Vol. 5th International Biodeterioration Symposium, Aberdeen (1981)

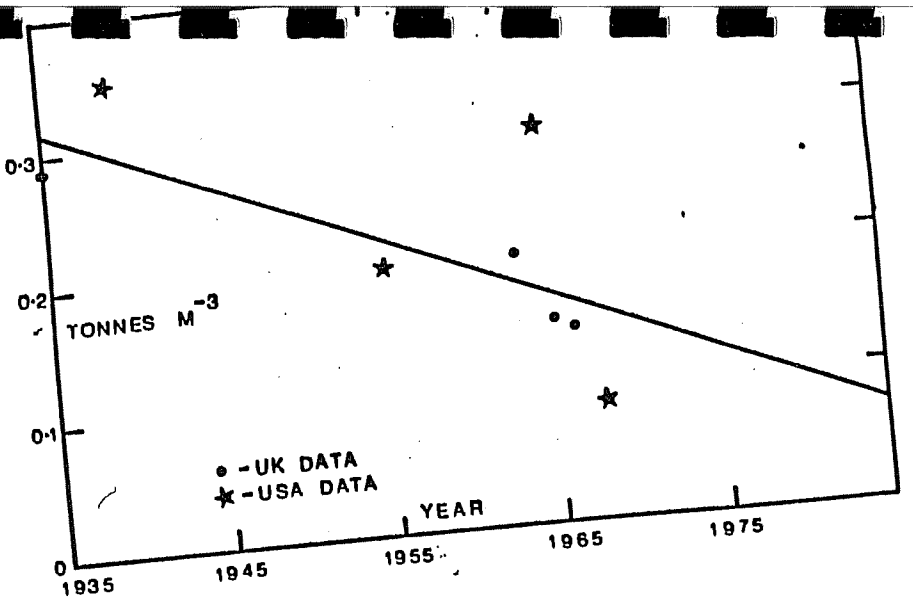

Fig.1 Municipal garbage density plotted against year.

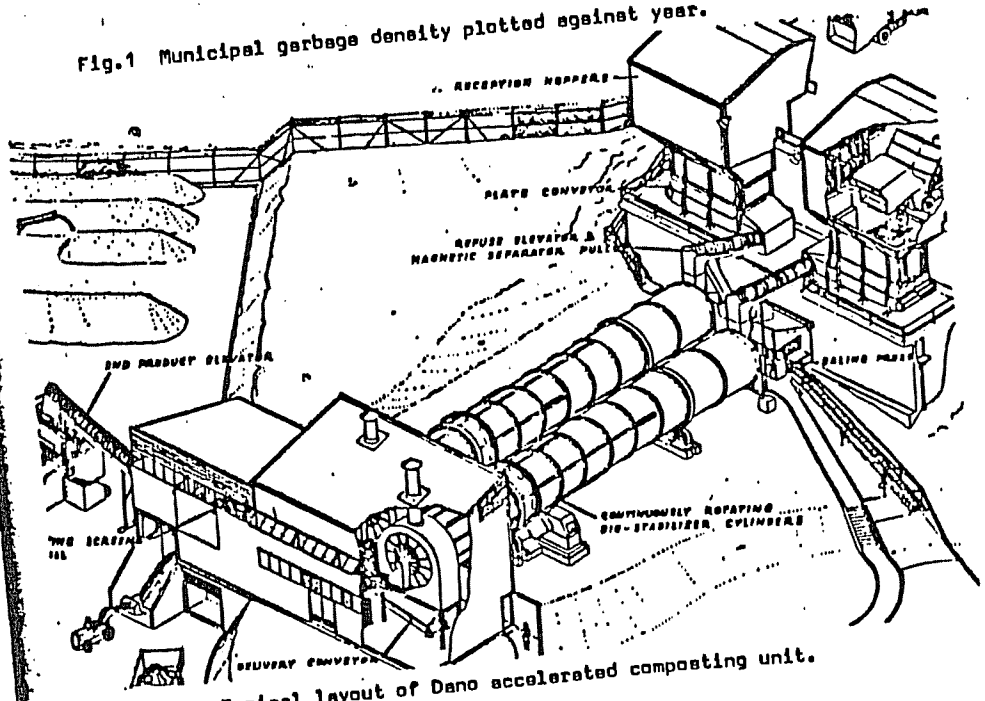

Fig.2 Typical layout of Dano accelerated composting unit.

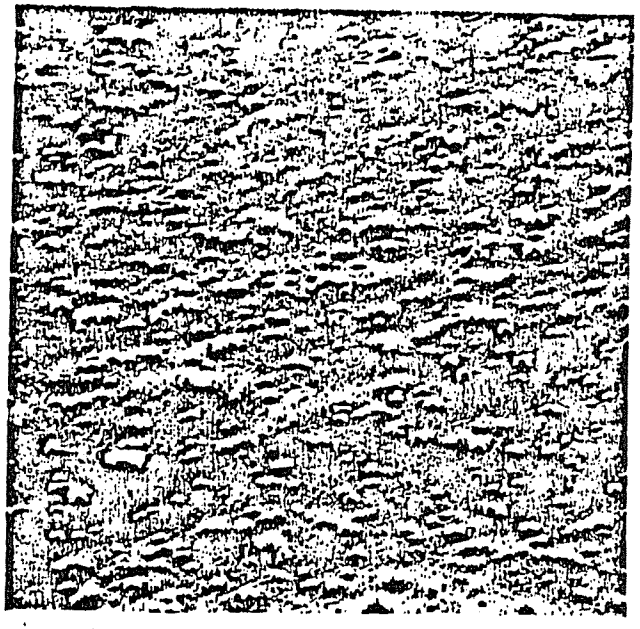

Fig.3 SEM picture of surface of starch-modified LDPE packaging film showing 15–20 micrometre bulges caused by the starch particles.

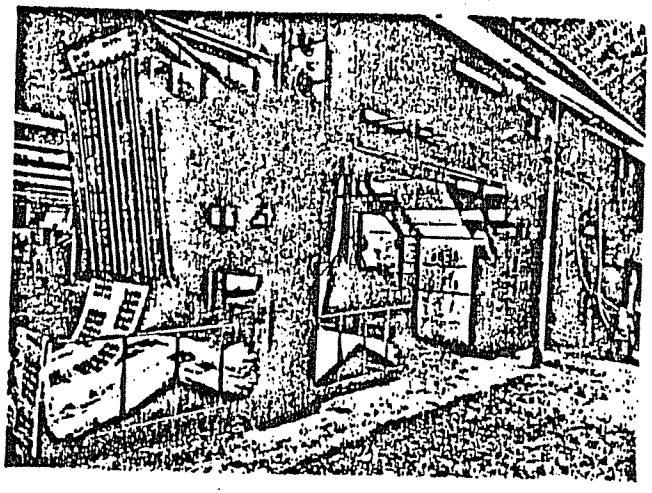

Fig.4 Part of the Coloroll Ltd carrier bag plant at Nelson showing the printing of degradable LDPE layflat tubing.

H-C

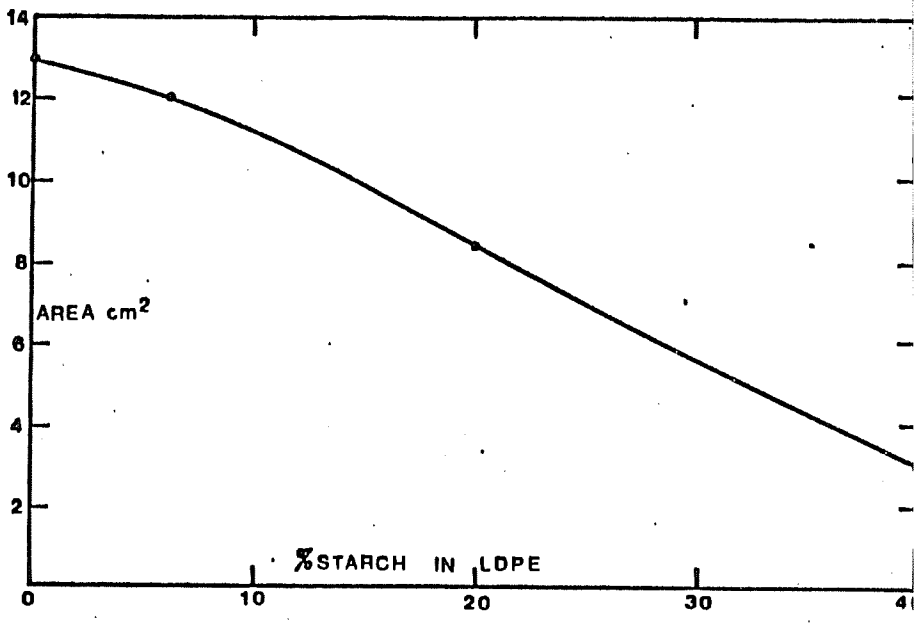

Fig.5 The effect of varying the starch concentration on the area left uneaten of 50 micrometre starch/LDPE blown film after 12 weeks exposure to woodlouse colonies.

diversified research

Diversified
Research
Laboratories Ltd.

1047 Yonge Street
Toronto, Ontario
M4W 2L2

Telex: 065-28057

Telephone: 416-922-5100

September 24, 1987

(1)

Dr. Wayne Maddever
St. Lawrence Starch
P.O. Box 1050
Port Credit Postal Station
Mississauga, Ontario
L5G 1E8

Dear Wayne:

Re: Report Update - Project #86-A-768
Biodegradation of Plastic Films and Bottles

According to the ANSI/ASTM standard test procedures G-21-70 and G-22-76, we found that LLDPE plastic film containing starch was susceptible to bacterial and fungal growth and, as expected, specimens with 15% starch were more susceptible than specimens with 6% starch.

It was also observed that HDPE bottles containing 10% starch were susceptible to fungal growth.

Yours truly,

DIVERSIFIED RESEARCH
LABORATORIES LIMITED

Maria Enriquez
Manager,
Physical Testing and
Packaging Development

c.c. Dr. Don Potts