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An Investigation of the Biodegradability of Packaging Plastics

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AN INVESTIGATION OF THE BIODEGRADABILITY OF PACKAGING PLASTICS

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FOREWORD

To find, through research, the means to protect, preserve, and improve our environment, we need a focus that accents the interplay among the components of our physical environment - the air, water, and land. The missions of the National Environmental Research Centers -- in Cincinnati, Ohio; Research Triangle Park, North Carolina; Corvallis, Oregon; and Las Vegas, Nevada -- provide this focus. The research and monitoring activities at these centers reflect multidisciplinary approaches to environmental problems; they provide for the study of the effects of environmental contamination on man and the ecological cycle and the search for systems that prevent contamination and recover valuable resources.

Man and his surrounding air, water, and land must be protected from the multiple adverse effects of pesticides, radiation, noise, and other forms of pollution as well as poor management of solid waste. These separate pollution problems can receive interrelated solutions through the framework of our research programs -- programs directed to one goal, a clean livable environment.

This publication, issued by the National Environmental Research Center, Cincinnati, reports on a 14-month research contract study of one of today's more pressing solid waste disposal problems--disposing of the plastics that inexpensively and attractively clad and protect so much of what we buy. That these plastics will continue to be used is indisputable; and it follows that solutions must be found for their disposal. The findings here will contribute greatly to solving this problem.

ANDREW W. BREIDENBACH, Ph.D.
Director, National Environmental
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ABSTRACT

An Investigation Of The Biodegradability Of Packaging Plastics

This study investigates the effects of various structural parameters on the biodegradability of plastics. It includes a determination of the effect of molecular weight and polymer end group composition on the biodegradability of polyethylene and polystyrene, and an evaluation of the biodegradability of various block, graft and random copolymers containing polyethylene or polystyrene chain segments. Also included is a study of the biodegradability of organic chemicals used commercially as additives to plastics.

The study verifies the popular belief that the current high volume, high molecular weight packaging plastics are not biodegradable at practical rates. Aliphatic polyesters and derivatives were the only synthetic, high molecular weight polymers found to be biodegradable. The report also establishes that the structural modification of polyethylene and polystyrene by random copolymerization with other monomers will not lead to biodegradability.

This report was submitted in partial fulfillment of Contract No. CPE-70-124 under the sponsorship of the Solid Waste Research Division of the National Environmental Research Center, Cincinnati, U.S. Environmental Protection Agency.

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SCOPE OF INVESTIGATION

This is the final report of a 14 month investigation of the biodegradability of packaging plastics performed by the Research and Development Department of the Union Carbide Corporation, Chemicals and Plastics, under a research contract with the Solid Waste Research Division of the National Environmental Research Center, Cincinnati, U.S. Environmental Protection Agency.

The major objectives of this investigation, as described in the work statement of the contract are:

1) to screen the major commercial packaging plastics for biodegradability

2) to determine the biodegradability of other plastics that might be useful as packaging plastics

3) to determine the effect of polymer molecular weight on the biodegradability of polyethylene and polystyrene

4) to determine the effect of placing metabolically active polymer end groups on the biodegradability of polystyrene and polyethylene

5) to determine the biodegradability of additives that are customarily found in packaging plastics (antioxidants, slip agents, and plasticizers, for example)

6) to examine the biodegradability of random copolymers of ethylene and of styrene

7) to study the effect of block and graft polymer structure on biodegradability, and

8) to examine the effects of thermal, ultraviolet, and ionizing radiation on polymer biodegradability.

The commercial polymer samples used in this investigation were either obtained in-house or purchased from other plastic manufacturers. The experimental polymers and copolymers involved in this program were synthesized in the laboratories of the Union Carbide Corporation and contributed without cost to the investigation.

SUMMARY

In a study embracing the large volume thermoplastic packaging plastics and several hundred experimental polymers, aliphatic polyesters and derivatives were the only synthetic, high molecular weight polymers found to be biodegradable. Although high molecular weight polyethylene is not biodegradable, pure linear paraffin molecules below about 500 mol wt were found to be utilized by microorganisms. Lower molecular weight polyethylenes, prepared by either direct polymerization or by pyrolysis of high molecular weight polymers, also supported the growth of microorganisms. Evidently, the polymer fractions being utilized were those below 500 mol wt. Low molecular weight polystyrene, down to 5,000 mol wt , did not support the growth of microorganisms. The placement of metabolically active organic functional groups at the end of polyethylene and polystyrene chains did not observably enhance biodegradability. Copolymers of ethylene with comonomers such as vinyl acetate, ethyl acrylate, lauryl acrylate, acrylic acid, carbon monoxide, aconitic acid, itaconic acid, and vegetable oils such as safflower, linseed, and soy bean oil, did not support fungal growth. Copolymers of styrene with acrylic acid, dimethyl itaconate, 2-ethyl-hexyl fumarate, and dodecyl acrylate were also inactive.

An explanation of these observations from the viewpoint of molecular biology was outside the scope of this investigation. When the insolubility in water and the inertness of most plastics to biological attack is considered, it is not surprising that most published fundamental studies of microbiological decomposition involving polymers were carried out with naturally occurring polymeric materials such as cellulose, starch, protein, lignin, etc. From these studies we can elicit general principles that may well be relevant to the systems examined in this investigation.

The first principle is that a living cell must take food materials inside itself to obtain energy and organic buildup blocks for growth. Soluble organic substances diffuse into the cell or are carried in by various transport mechanisms involving enzymes called permeases. Inside the cell, the food substances are attacked by digestive enzymes and the fragments used for growth or energy.

For insoluble materials such as many natural polymers, the organism prepares one or more enzymes that leave the cell and break down the insoluble material in the vicinity of the cell to a soluble substance that can be assimilated by the cell and utilized.

A second general principle involving the metabolism of living cells is that as a result of evolutionary processes, microorganisms utilize many metabolic processes in common with other more complex organisms such as man. These metabolic pathways involve the action of many highly specific enzymes.

As mentioned above, low molecular weight linear polyethylene molecules are biodegradable, even though they are of synthetic origin. These products are closely related structurally to the paraffin based crude oils which are of natural origin. It would appear that the oxidase enzymes developed by nature to facilitate the biooxidation of naturally occurring linear paraffinic hydrocarbons are also specific for low molecular weight linear polyethylene fractions.

The mechanism of biodegradation of paraffinic hydrocarbons involves the action of oxidase enzymes, which catalyze the beta oxidation of the molecular chain by removing two carbon atoms at a time from the end of the chain. Why are the enzymes that must catalyze the decomposition of low molecular weight polyethylene seemingly unable to bring about the decomposition of high molecular weight polyethylene used for packaging applications? Rodriguez[1] suggested that this may be due to the fact that polyethylene crystallizes in a folded chain configuration in which chain ends are unlikely to be

found near the surface of the polymer. In order for the enzyme to catalyze the oxidation of the polymer, it must be able to complex with the ends of the polymer chains that are both low in concentration and not very accessible. This steric hindrance may play an important role in inhibiting the biodegradability of high molecular weight polyethylene.

Other factors that must be considered in addition to enzyme specificity and steric hindrance are the effect of pH and the tendency of the polymer to absorb water. The water repellant nature of polyethylene certainly does not facilitate the attainment of the aqueous conditions (pH and swelling) favorable to the optimum functioning of enzymes, which are proteins.

Although this investigation did not establish which enzymes are responsible for the biodegradability of the aliphatic polyesters examined, it is reasonable to assume that initial attack is by esterase enzymes, which catalyze the hydrolysis of ester linkages along the chain.

In summary, this study has verified the popular belief that the current high volume, high molecular weight packaging plastics are not biodegradable at practical rates. It has also established that structural modification of

polyethylene and polystyrene by random copolymerization with other monomers will not lead to biodegradability. The economics of the plastic packaging industry indicate that polyethylene, polystyrene, and polyvinyl chloride will continue to be used in large volume for packaging applications because of their low cost, light weight, eye appeal, and functional utility. For these materials to be made biodegradable, the molecular weight of the polymer will have to be reduced substantially. This deliberate degradation of molecular weight must be carried out after the plastic package is discarded, because degradation results in a severe reduction in the strength properties of the package.

Two methods of achieving this degradation require no prior modification of the plastic packaging material. The discarded plastic is either pyrolyzed (thermally degraded) or treated with oxidizing chemicals in an autoclave. The third method involves modification of the plastic formulation during manufacture so that the plastic package is rendered much more susceptible to oxidative attack by environmental oxygen. The plastic formulation can be modified either by adding substances that will enhance the rate of oxidation in a controllable manner, or by modifying the structure of the polymer sufficiently to make it more susceptible to oxidative degradation.

The development of packaging plastics that will undergo controlled auto-oxidation will help alleviate the plastic litter problem and will insure that such products will be recycled back into the natural carbon cycle of the planet.

INTRODUCTION

Plastics in Solid Waste

It has been estimated[2] that by 1976, the U.S. will be generating about 450 billion lb of solid waste per year, compared with 375 billion lb estimated for 1970. By 1976, total plastic wastes are expected to be about 9.5 billion lb per year, with packaging plastics accounting for about 6.6 billion lb. Thus plastics represent less than 5% by weight of the total solid waste generated annually in this country.

Table 1 lists the types of plastics found in municipal refuse as of 1966.[2] It can be seen that 90 percent of the total plastic waste is made up of polyethylene (38%), polyvinyl chloride (31%), and polystyrene (21%).

TABLE 1

TYPES OF PLASTICS FOUND IN MUNICIPAL WASTE

Type of plastic	Weight (in millions of pounds)	% of total
Nylon	7.9	0.2
Phenolics	22.5	0.6
Polyacetals	3.5	0.1
Polycarbonate	3.4	0.1
Polyethylene	1446	37.6
Polypropylene	71	1.8
Polyvinyl chloride	1204	31.2
Polyesters	51	1.3
Polystyrenes	823	21.3
Urea and melamine	79	2.0
Urethane foam	89	2.3
Cellulosics	60	1.5

Because these three plastics account for the bulk of packaging plastics, it is felt that they should be the focus of attention of research and development pertaining to the disposability or recycling of plastic waste.

A recent report prepared for the Solid Waste Management Office of the Environmental Protection Agency by Battelle Memorial Institute[3] presented data on the expected ranges in municipal refuse composition (see Table 2).

TABLE 2

EXPECTED RANGES IN MIXED MUNICIPAL REFUSE COMPOSITIONS

Component	Percent composition as received (dry weight basis)	
	Anticipated range	Nominal†
Paper	37-60	55
Newsprint	7-15	12
Cardboard	4-18	11
Other	26-37	32
Metallics	7-10	9
Ferrous	6-8	7.5
Nonferrous	1-2	1.5
Food	12-18	14
Yard wastes	4-10	5
Wood	1-4	4
Glass	6-12	9
Plastic	1-3	1
Miscellaneous	<5	3

†Battelle estimate.

The anticipated range for plastics is 1 to 3 percent, a figure that is quite low compared to paper and paper board (37-60%) and other solid wastes such as glass and metals.

Definition of Biodegradability

Strictly speaking, biodegradable materials are those whose chemical structures make them susceptible to assimilation by microorganisms such as molds, fungi, and bacteria when buried in the ground or otherwise contacted with the organisms under conditions conducive to their growth. Some nonbiodegradable plastics are erroneously believed to be biodegradable because they often contain biodegradable additives that will support the growth of microorganisms without causing the plastic itself to become assimilated.

The term "biodegradable" is often used indiscriminately to refer to various types of environmental degradation, including photodegradation. Because a polymeric material is degraded by sunlight and oxygen does not necessarily mean that the material will also be assimilated by microorganisms. The term "biodegradable" should be reserved for that type of degradability that is brought about by living organisms, usually microorganisms.

Biodegradability as a Means of Recycling

The reclamation and recycling of plastic wastes are already being practiced to some extent in those applications where the plastic waste can be kept homogeneous and clean, or in applications where substandard plastics are completely acceptable. In almost all large volume plastic applications, however, very rigid standards of product quality, including cleanliness, are absolutely necessary for several reasons:

1. In many packaging applications, the plastics fabrication must meet very demanding standards set by the Food and Drug Administration with regard to the cleanliness, absence of toxic or undesirable additives, or presence of material which may be extracted by the food being packaged. The vendor must guarantee the compositional uniformity of his product.

2. The plastic material must be suitable in melt flow properties and in heat stability for the particular fabrication process used and must emerge from fabrication without any loss of mechanical strength or appearance properties.

3. The packaging material must exhibit the proper balance of physical properties for the specific application for which it was designed -- modulus, impact strength, stress crack resistance, softening temperature, abrasion resistance,

and permeability to gases and liquids to name a few. Properties required for a plastic milk bottle are quite different from those of a meat wrap, for example. Many of these physical properties requirements are subject to regulation by State and National agencies, and by organizations such as the National Sanitation Foundation.

In order to meet these demanding and varied requirements, the plastics industry has developed thousands of formulations containing various plastics in combination with many different additives that are necessary for different applications. Even if techniques for separating mixtures of waste plastics from other municipal waste are eventually developed, such mixtures may not be suitable for most plastic applications because of their nonuniformity with respect to such characteristics as color, composition, additives, molecular weight, molecular weight distribution, softening point, and heat resistance. The resulting inability to predict the performance of mixed waste plastics discourages their use in most plastics applications.

As stated above, another way to recycle organic substances is by way of the carbon cycle of the earth -- nature's way. A simplified diagram of the carbon cycle is given in Figure 1. Green plants convert carbon dioxide gas from the

atmosphere into organic carbon with the aid of sunlight by the process known as photosynthesis. Animals and plants ultimately revert to dead organic matter, which yields CO_2 when decomposed by microorganisms. Animals and plants also produce CO_2 by respiration. Note that animals are true parasites in the carbon cycle - they can only utilize it for growth and energy. It should also be observed that the CO_2 used by plants in photosynthesis comes from many sources, including the burning of gasoline, oil, coal, wood and the incineration of solid waste, as well as from the respiratory processes of plants, animals, and microbes.

In principle, biodegradable plastics would decompose in sanitary landfills and backyard compost heaps, and would disappear more rapidly when littered. Biodegradable plastics would not be expected to cause any unusual incineration problems.

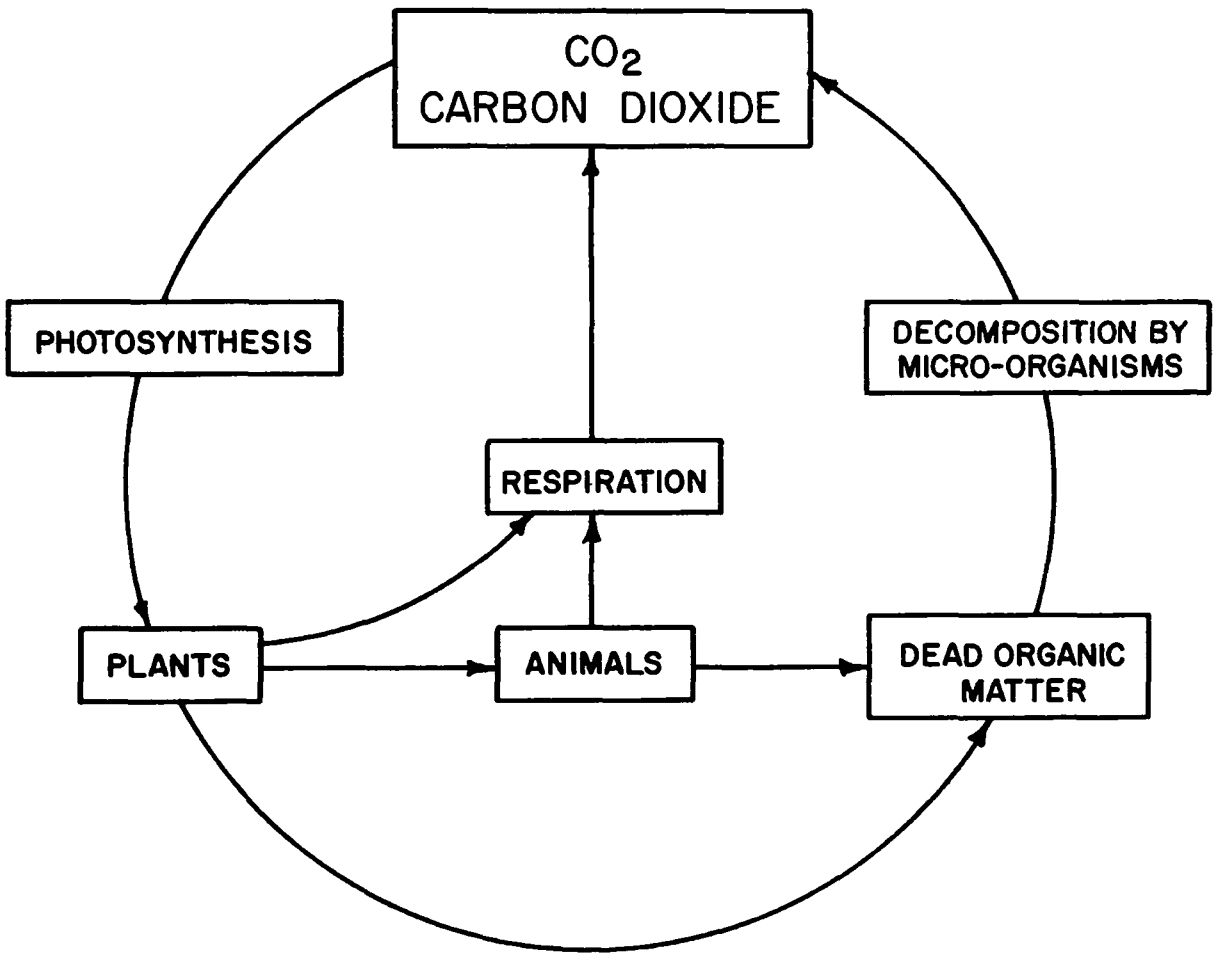

Figure 1. A simplified diagram of the carbon cycle.

PREVIOUS STUDIES OF THE BIODEGRADATION OF PLASTICS

The literature in this field is almost entirely concerned with the problem of preventing or retarding attack on plastics by microorganisms. H. J. Hueck[4] discussed the biological deterioration of plastics by microorganisms, insects, and rodents in a short review article written from the point of view of a biologist. An excellent, more comprehensive review of the effects on plastics of attack by fungi, bacteria, and other larger organisms was published by C. J. Wessel.[5] In a similar vein, but restricted to plasticized polyvinylchloride, is an article by G. Tirpak.[6] Darby and Kaplan[7] discussed the fungal susceptibility of 100 experimental polyurethanes, using a mixed-culture petri dish method. Polyether polyurethanes were moderately to highly resistant to fungal attack, whereas all polyester polyurethanes tested were highly susceptible. P. K. Barua and co-workers[8] demonstrated that Trichosporon species utilized only normal paraffins from a mixture of n- and iso-paraffins. Utilization of individual n-alkanes ranging from n-decane to n-eicosane was generally good. In mixtures, however, the shorter chains (decane, undecane, and dodecane) were consumed faster and at a more uniform rate than longer chain paraffins.

Rodriguez[1] reviewed the published information pertaining to the biodegradation of rubber, cellulose, paraffinic hydrocarbons, polyester plasticizers, and polyurethanes in a recent article, which gives 72 references. He suggests that the resistance of high molecular weight polyethylene to attack by microorganisms may be due to the fact that polyethylene crystallizes in a folded chain configuration in which chain ends are unlikely to be found near the surface of the polymer. Accessibility of chain ends is undoubtedly a rate-determining factor in beta-oxidative degradation catalyzed by oxidase enzymes.

Jen-Hao and Schwartz[9] studied the rate of increase of bacteria in contact with a series of polyethylenes as the sole source of carbon. The bacteria count increased for a week and dropped slowly toward the value for the carbon-free control. The data suggested that only the low molecular weight fractions were being assimilated.

MICROBIOLOGICAL PROCEDURES

Samples of polymers of high molecular weight were pressed or molded into plaques from which test specimens were cut. These specimens were tested for degradation by fungi, using ASTM Method D-1924-63.[10] This procedure requires the placement of test specimens in or on a solid agar growth medium that is deficient only in carbon. The medium and specimens are inoculated with the test microorganisms and incubated for 3 weeks. Any growth that may occur is dependent on the utilization of the specimen as a carbon source by the test organism. The test fungi consisted of a mixture of Aspergillus niger, Aspergillus flavus, Chaetomium globosum, and Penicillium funiculosum.

Because of the possibility that growth might occur as a result of additives in the polymer, it was necessary that the polymers tested be free from stabilizers, plasticizers, lubricants, and other extraneous organic substances, or that the presence of such additives be recognized. If a pure polymer sample showed heavy growth and concurrent loss of weight and mechanical properties, this was considered good evidence of its degradability.

Method D-1924-63 was also used to examine semisolid waxes and greases through the use of biologically inert fiberglass cloth that was impregnated with the test substance and then examined as above.

In a few instances, ASTM-D-2676T[11] was used in addition to D-1924. This test uses Pseudomonas aeruginosa bacteria in place of fungi. Because the fungi are more active than the bacteria, D-1924 was the test of choice in this work.

After various exposure times (up to 3 weeks), samples were examined and assigned growth ratings as shown below:

Growth ratings:

0 = No growth

1 = Traces (less than 10% covered)

2 = Light growth (10 - 30% covered)

3 = Medium growth (30 - 60% covered)

4 = Heavy growth (60 - 100% covered)

In addition to the agar plate methods described here, some plastic samples were buried in a mixture of equal parts by volume of garden soil, builders sand, and peat moss, which was placed in flower pots and watered daily.

BIODEGRADABILITY OF COMMERCIAL PLASTICS

Packaging Films

Table 3 gives the growth rating (GR) for several of the most widely used packaging films. The GR of 2 exhibited by the polyethylene film (sample 1) is evidently due to the presence of an additive that is readily removed by extraction with cold toluene. The extracted polyethylene is not attacked by fungi. Two samples of polyvinyl chloride film, both containing plasticizer, were also found to be biodegradable. Removal of the epoxidized soy bean oil plasticizer by toluene extraction reduced the GR from 3 to 1. The plasticizer in the Resinite film, though not identified, is almost certainly responsible for the observed growth. Samples of vinylidene chloride-vinyl chloride copolymer, polypropylene, polystyrene, and polyethylene terephthalate in film form were all resistant to attack by fungi.

TABLE 3

BIODEGRADABILITY OF PACKAGING FILMS

Sample no.	Characterization	Growth rating
1	Polyethylene household wrap	2
2	Sample 1 extracted with toluene	1
3	PVC-epoxidized soy bean oil plasticizer	3
4	Sample 3 extracted with toluene	1
5	Polypropylene	1
6	Polystyrene	1
7	Polyethylene terephthalate	1
8	Saran Wrap copolymer	1
9	PVC-plasticized Resinite	3

The susceptibility of various additives customarily found in plastics is treated in detail in a later section of this report.

Other Commercial Plastics

Table 4 lists 31 commercially available plastics; almost all are resistant to attack by microorganisms. Thermolastic gave a GR of 3, which dropped to 1 on extraction, thus indicating the presence of a degradable additive. Kydene also gave a GR of 3, but neither polyvinyl chloride nor polymethyl methacrylate are susceptible. This suggests the presence of a biodegradable plasticizer in the blend.

In contrast to the above are the results obtained with Estane polyurethane (sample 22) and caprolactone polyester (sample 24). The biodegradability observed for samples 23 and 24 is in agreement with the results of Darby and Kaplan[7], who demonstrated the susceptibility of aliphatic polyesters and urethanes derived from such polyesters to microbiological attack. Since Darby and Kaplan also found polyether polyurethanes much more resistant than polyester urethanes, it is likely that Estane polyurethane is made from an aliphatic ester diol.

It should be noted that Barex 210 and LOPAC plastics, both of which are used for soft drink bottles, are not biodegradable.

TABLE 4

BIODEGRADABILITY OF COMMERCIAL PLASTICS

Sample no.	Characterization	Growth rating
1	Acrylonitrile-butadiene-styrene copolymer (ABS) (Kralastic	0
2	ABS-PVC blend (Cycovin)	0
3	ABS-polycarbonate blend (Cycoloy)	0
4	Butadiene-acrylonitrile rubber (Hycar)	0
5	Styrene-acrylonitrile copolymer (C-11)	0
6	Rubber modified polystyrene	0
7	Styrene-butadiene block copolymer (Thermolastic)	3
8	Thermolastic extracted	1
9	Polymethyl methacrylate-PVC (Kydene)	3
10	Polymethyl methacrylate (Lucite)	0
11	Rubber modified polymethyl methacrylate	0
12	Polyethylene terephthalate (Arnite)	0
13	Polyethylene terephthalate-isophthalate (Vitel)	0
14	Polycyclohexanedimethanol terephthalate (Kodel)	0
15	Bisphenol A polycarbonate (Lexan)	0
16	Poly(4-methyl-1-Pentene) (TPX)	0
17	Polyisobutylene	0
18	Chlorsulfonated polyethylene (Hypalon)	0
19	Cellulose acetate	0
20	Cellulose butyrate	0
21	Nylon-6, nylon-66 (Zytel), nylon-12	0
22	Polyurethane (Estane)	4
23	Caprolactone polyester urethane	4
24	Caprolactone polyester	4
25	Polyvinyl butyral	0
26	Polyformaldehyde (Celcon)	0
27	Barex 210 soft drink bottle	0
28	Lopac soft drink bottle	0
29	Polyvinyl ethyl ether	0
30	Polyvinyl acetate	1
31	Polyvinyl acetate 50 percent hydrolyzed to alcohol	1

EFFECT OF POLYMER MOLECULAR WEIGHT AND BRANCHING

Polyethylene

The preceding section has demonstrated the remarkable resistance of almost all types of high molecular weight polymers to attack by microorganisms. These results are generally in agreement with other published data.[4,5,12,13] It has also been observed by a number of investigators that low molecular weight normal paraffins are readily utilized by microorganisms,[8,14] but their branched isomers are very poorly utilized. Barua[8] reported utilization of n-paraffins up to n-eicosane ($C_{20}H_{42}$, mol wt 282.5). Miller and Johnson[15] cultivated a mixture of Candida lipolytica and C. intermedia on gas oil samples and paraffin wax and found that the organisms utilized n-paraffins ranging from dodecane through dotriacotane ($C_{32}H_{66}$, mol wt 450.9), with the maximum efficiency of alkane removal in the nonadecane ($C_{19}H_{40}$, mol wt 268.5) to tetracosane ($C_{24}H_{50}$, mol wt 338.7) range.

The biodegradability of several pure linear hydrocarbon samples in the molecular weight range 170-620 was measured by the screening test described earlier. The growth rating results are shown in Table 5.

TABLE 5

BIODEGRADABILITY OF STRAIGHT CHAIN HYDROCARBONS

Compound	Formula	Mol wt	Growth Rating
Dodecane	$C_{12}H_{26}$	170	4
Hexadecane	$C_{16}H_{34}$	226	4
Octadecane	$C_{18}H_{38}$	255	4
Docosane	$C_{22}H_{46}$	311	4
Tetracosane	$C_{24}H_{50}$	339	4
Octacosane	$C_{28}H_{58}$	395	4
Dotriacontane	$C_{32}H_{66}$	451	4
Hexatriacontane	$C_{36}H_{74}$	507	0
Tetracontane	$C_{40}H_{82}$	563	0
Tetratetracontane	$C_{44}H_{90}$	620	0

These data show clearly that biodegradability diminishes sharply above 450 mol wt for the test organisms and is negligible at 619 mol wt.

The effect of chain branching in alkanes has been studied by Barua[8] and others who have found that isoparaffins are utilized poorly or not at all. The biodegradability of several branched hydrocarbons were measured and compared to their corresponding straight chain analogs. The data are shown in Table 6. Here, the first, third, fifth, and seventh samples are the straight chain hydrocarbons, as reported in Table 5. The second, fourth, and sixth samples are branched chain hydrocarbons. The chain length of each of these samples is the same as the preceding hydrocarbon, but methyl groups have been introduced along the chain. In each case, the introduction of branching points decreases the susceptibility of the hydrocarbon to fungal attack, and a growth rating of 0 is obtained. Note that the molecular weight of all of these compounds is below the 450 cutoff point found in Table 5.

The above data can be used to explain the results we have found for low and high density polyethylene of varying molecular weights. Before presenting these results, however, it will be helpful to discuss the concept of molecular weight distribution as it applies to polymers. Each of the above

pure organic compounds (Tables 5 and 6) consists of a collection of molecules having the same chain length and molecular weight. In a polymer sample there are molecules of different chain lengths, and the measured molecular weight of the sample is an average value. Because of kinetic considerations during polymerization, there is an approximately gaussian distribution of molecular weights about the average value. This is illustrated by Figure 2, in which the probability of a given molecular weight molecule being present in a polymer sample is plotted versus the average molecular weight of the same sample.

As the average molecular weight of the polymer is decreased (by varying polymerization conditions or by post-polymerization treatment to bring about random chain scission), the proportion of low molecular weight polymer in the sample increases.

In addition to the complication of molecular weight distribution, polymer molecules may fall into three main structural shape classification. They may be linear, branched, or crosslinked. Linear molecules are those in which the monomer units are linked together to form one long continuous molecule. Branched molecules are those in which side branches of monomer units of varying length extend

TABLE 6

EFFECT OF BRANCHING ON HYDROCARBON BIODEGRADABILITY

Compound and structure	Mol wt	Branched	Growth rating
Dedecane $C_{12}H_{26}$			
$(CH_3CH_2CH_2CH_2CH_2CH_2)_2$	170	no	4
2,6,11-Trimethyldodecane $C_{15}H_{32}$			
$CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2CH(CH_3)CH_3$	212	yes	0
Hexadecane $C_{16}H_{34}$			
$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_2$	226	no	4
2,6,11,15-Tetramethylhexadecane $C_{20}H_{42}$			
$(CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2)_2$	283	yes	0
Tetracosane $C_{24}H_{50}$			
$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_2$	339	no	4
Squalane $C_{30}H_{62}$			
$(CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_2)_2$	423	yes	0
Dotriacontane $C_{32}H_{66}$			
$CH_3(CH_2CH_2CH_2CH_2CH_2CH_2)_5CH_3$	451	no	4

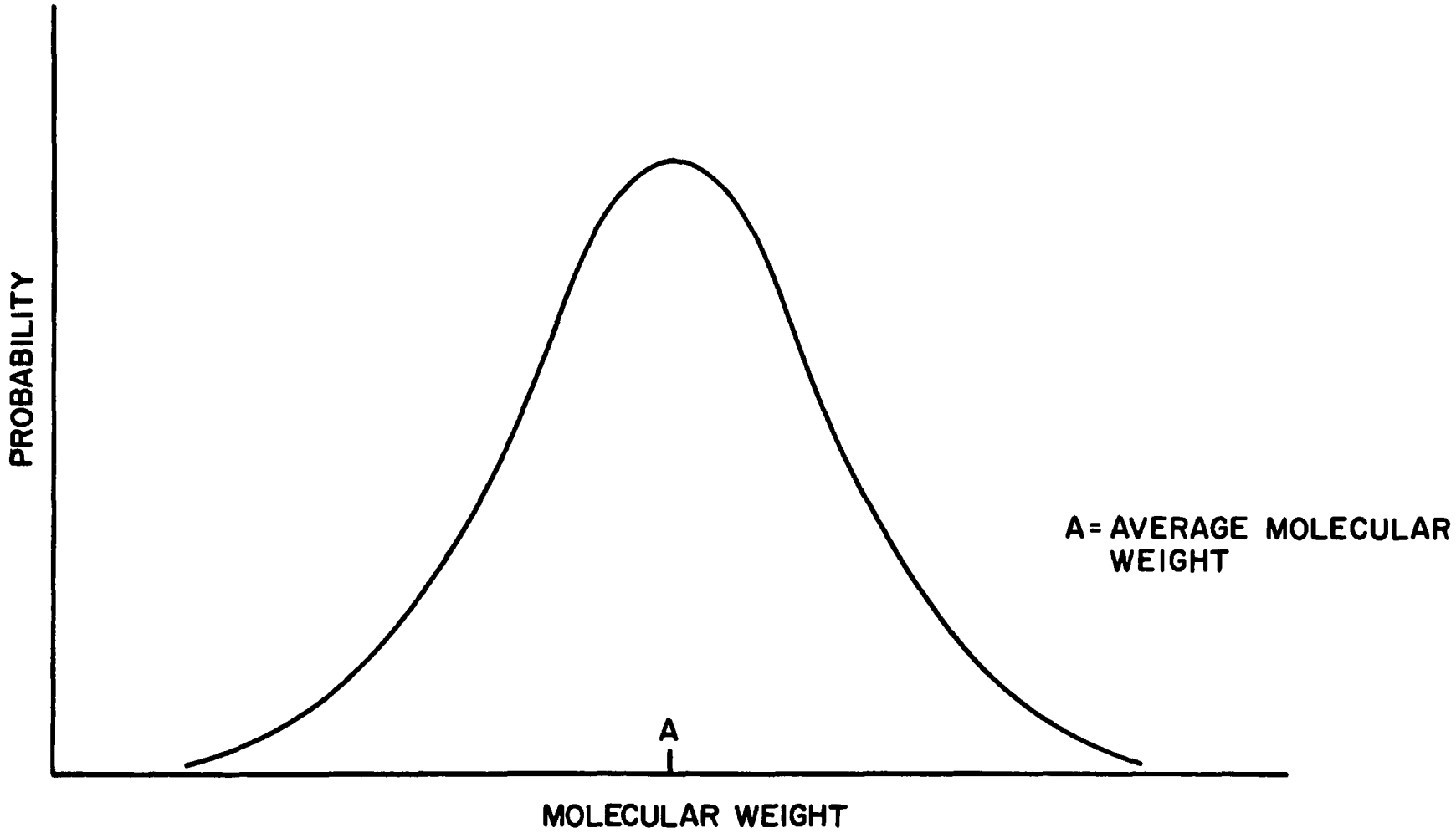

Figure 2. Polymer molecular weight distribution.

from a main polymer chain. Cross-linked molecules are those in which main polymer chains are connected to each other at points other than the ends by "bridges" of varying length. These types of structures can be illustrated as shown in Figure 3.

Based on the data in Table 6, it can be seen that branching could seriously interfere with the ability of a microbe to utilize a polymer chain, since a branch point on a polymer molecule is like a methyl group in the compounds of Table 6. Branching is also related to crystallinity and density. Thus as the amount of branching increases, the density decreases and the crystallinity decreases because the polymer chains can no longer fit easily into a crystal lattice. High density polyethylene, for example, is a more crystalline, linear polymer than low density polyethylene, which is more branched.

Table 7 shows the effect on biodegradability of varying molecular weights in low and high density polyethylenes. Since the high density polyethylene is a linear, nonbranched molecule, the molecular weight distribution in

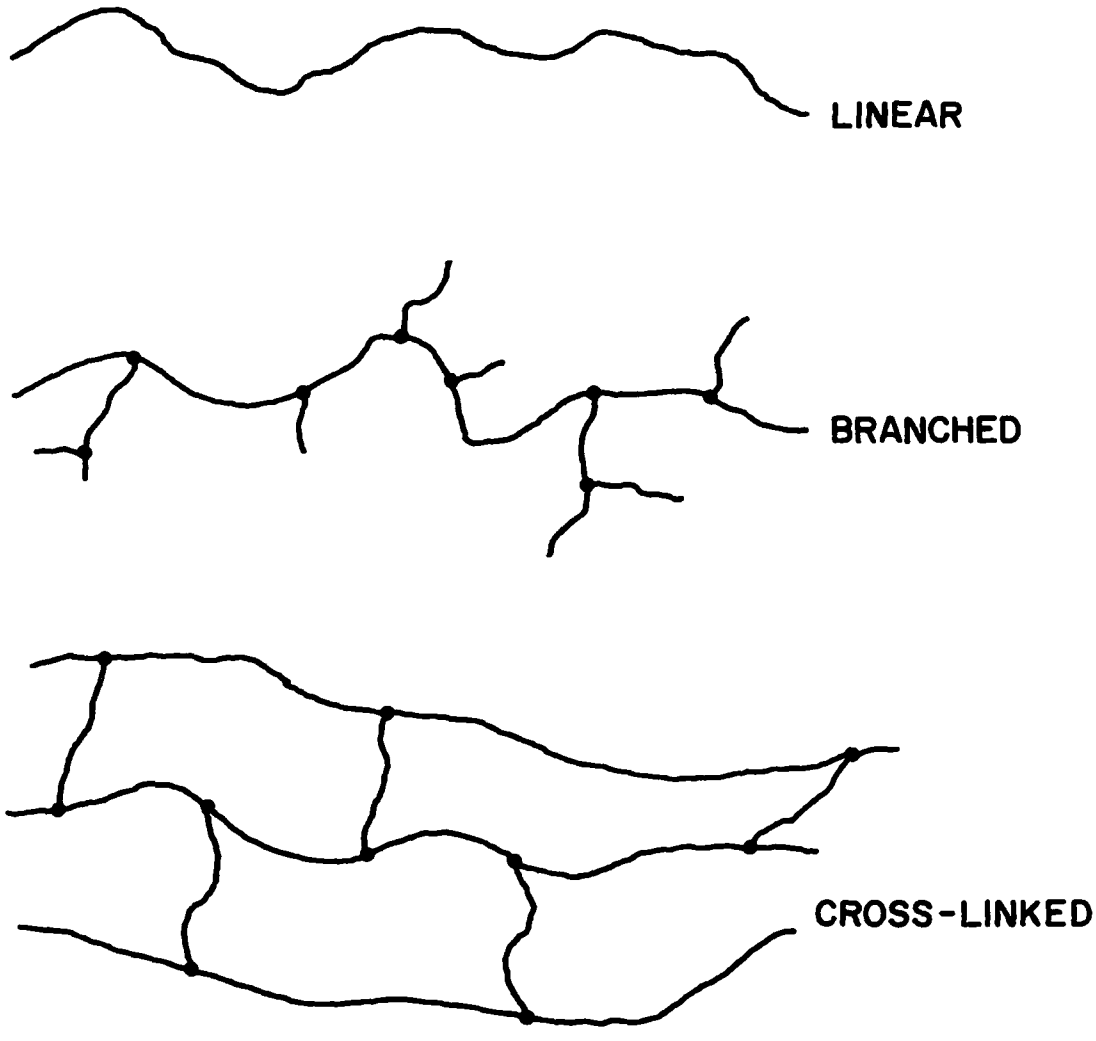

Figure 3. Linear, branched, and cross-linked polymer molecules.

samples 1 and 2 is evidently such that the low molecular weight, biodegradable molecules are present in sufficient concentration to give a positive reading in the test. As the average molecular weight increases into the commercial range, the molecular weight distribution is shifted so that there is not a sufficient quantity of these low molecular weight species present to be detected by the test.

The same conclusion can also be applied to the low density polyethylene, except that samples 6 and 7 appear to be anomalous. The discussion of branching offers an explanation here. Sample 6 is a grease, which is a very low density, highly branched sample that contains very few linear molecules. It received a low GR. Sample 7 is a crystalline wax with a high density and a higher crystallinity than sample 6. It therefore contains more straight chain molecules below about 500 mol wt than sample 6 and hence receives a higher rating. Sample 6 represents a borderline case since it showed no growth in one test and slight growth in another.

TABLE 7

EFFECT OF POLYETHYLENE MOLECULAR WEIGHT

ON BIODEGRADABILITY

Sample no.	Product type	Mol wt	Growth rating
1	High density polyethylene	10,970	2
2	High density polyethylene	13,800	2
3	High density polyethylene	31,600	0
4	High density polyethylene	52,500	0
5	High density polyethylene	97,300	1
6	Low density polyethylene	1,350	1
7	Low density polyethylene	2,600	3
8	Low density polyethylene	12,000	1-2
9	Low density polyethylene	21,000	1
10	Low density polyethylene	28,000	0

Pyrolyzed Polyethylene

Samples of high and low density polyethylene have been thermally degraded using a unique, continuous process which was developed by the Union Carbide Corporation and recently described by Potts.[16,17,18] This process converts high molecular weight polymers into lower molecular weight polymers by thermal treatment in the absence of air in a continuous, hydraulically filled system. Because the polymer is thermally degraded under isothermal conditions, it is possible to obtain lower molecular weight polymer without the gassing and charring associated with conventional thermal decomposition.

Samples of polyethylene pyrolyzed at temperatures between 400 C and 535 C were examined for biodegradability (Tables 8 and 9).

High density polyethylene, with an initial molecular weight of 123,000, exhibits biodegradability when pyrolyzed to a molecular weight of 3,200 or below (Table 8). Low density, pyrolyzed polyethylene shows a lesser GR at 2,100 mol wt than high density polyethylene at 3,200 mol wt. This can be accounted for by the difference in chain branching in the two types of polyethylene, as mentioned earlier. Perhaps the most significant fact is that the pyrolysis process yields biodegradable polyethylene derivatives and thus increases the usefulness of this process as a waste plastic recycling tool.

TABLE 8

BIODEGRADABILITY OF PYROLYZED,

HIGH DENSITY POLYETHYLENE

Pyrolysis temperature (C)	Viscosity average molecular weight	Growth rating
Control	123,000	0
400	16,000	1
450	8,000	1
500	3,200	3
535	1,000	3

TABLE 9

BIODEGRADABILITY OF PYROLYZED,

LOW DENSITY POLYETHYLENE

Pyrolysis temperature (C)	Viscosity average molecular weight	Growth rating
Control	56,000	0
400	19,000	1
450	12,000	1
500	2,100	2
535	1,000	3

Polyethylene Containing Terminal Functional Groups

Low molecular weight polyethylene was synthesized by the high pressure, free radical process using acetic acid in one experiment and acetone in another as chain transfer agents. Because of the chemistry of the chain transfer process, a carboxyl group is placed at the end of the chain in the acetic acid experiment, and a methyl ketone group in the case of the acetone experiment. The purpose of these experiments was to determine the effect on biodegradability of placing nominally biologically active functional groups on the end of the polymer chain.

The presence of carboxyl groups and carbonyl groups in the appropriate polymers was shown by infrared spectroscopy. The products were low molecular weight, brittle waxes. The molecular weight of the carboxyl terminated sample was determined by titration and found to be about 3,000, assuming monofunctionality. For the acetone transfer product, the molecular weight was calculated from the intensity of the carbonyl peak in the infrared spectrum and found to be about 1,500, again assuming monofunctionality. Both of these products gave a GR of 1, indicating no susceptibility to attack by fungi. These results, along with those obtained for low mol wt polyethylene samples described earlier, suggest that these terminal functional groups in some way interfere with biodegradability. Another possibility is the presence of undetected branching in these samples.

Polystyrene

Table 10 shows the effect of molecular weight variation on the biodegradability of polystyrene. Samples 1 through 5 represent a series of polystyrenes prepared with an initiator that places carboethoxy groups at the end of the polymer molecule. Samples 6 through 11 are polystyrene samples having a carboxylic acid group at one end of the molecule. Samples 12 and 13 have -CN groups on the end of the molecules. All of the samples of polystyrene showed a zero GR over the molecular weight range 5,900 to 214,000. The presence of metabolically active ester and carboxylic acid end groups did not increase the susceptibility of polystyrene to biodegradation.

Pyrolyzed Polystyrene

Polystyrene was pyrolyzed using the Union Carbide continuous plastics pyrolysis process, which was described earlier under Pyrolyzed Polyethylene.[16,17,18] Pyrolysis temperatures were the same as those used in the polyethylene pyrolysis study. The products were characterized by determining their viscosity average molecular weights and subjecting them to the agar screening procedure for biodegradability. As the data in Table 11 show, the susceptibility of polystyrene to attack by fungi is not enhanced by the lowering of molecular weight.

TABLE 10

EFFECT OF POLYSTYRENE MOLECULAR WEIGHT

ON BIODEGRADABILITY

Sample no.	Molecular weight M_v	End group composition	Growth rating
1	89,000	Carboethoxy (Ester)*	0
2	43,600	Carboethoxy (Ester)	0
3	18,600	Carboethoxy (Ester)	0
4	11,700	Carboethoxy (Ester)	0
5	5,900	Carboethoxy (Ester)	0
6	214,000	Carboxylic acid†	0
7	62,400	Carboxylic acid	0
8	43,600	Carboxylic acid	0
9	18,600	Carboxylic acid	0
10	13,800	Carboxylic acid	0
11	5,900	Carboxylic acid	0
12	47,300	Cyanide‡	0
13	11,700	Cyanide	0

* $-COOC_2H_5$

† $-COOH$

‡ $-CN$

TABLE 11

BIODEGRADABILITY OF PYROLYZED POLYSTYRENE

Temperature of pyrolysis (C)	Viscosity average molecular weight	Growth rating
Control	220,000	1
400	93,000	1
450	67,000	0
500	26,000	0
535	4,000	0

In terms of chain length, the molecular weights of pyrolyzed polystyrene are comparable to those generated in the pyrolysis of polyethylene. A polyethylene chain with a molecular weight of 1,000 has about 35 monomer units, and a polystyrene chain with a molecular weight of 4,000 has about 40 monomer units. It is evident that this study will have to be extended to even lower molecular weights in order to determine if the problem is due to the lack of a specific enzyme for metabolizing polystyrene chain fragments. Because of the branched structure of polystyrene, the latter explanation is probably correct.

BIODEGRADABILITY OF RANDOM COPOLYMERS OF ETHYLENE OR STYRENE

Copolymers of Ethylene

Several dozen ethylene copolymers were tested for biodegradability during this investigation. A description of the copolymers and their GR are given in Tables 12 and 13. All of the samples were made by free radical, high pressure copolymerization. Several of the samples were also tested in the form of derivatives, such as the vinyl alcohol (samples 4 and 5) or the partial sodium or ammonium salt (samples 7, 8, 9, 11). The composition (parts by weight) is listed after the name.

With the exception of sample 1 in Table 12, all of the ethylene copolymers tested gave GR of 0 or 1. The rating of 2 shown by sample 1 is out of line with the results for samples 2 and 3 which are of similar structure.

Table 13 gives the results of the copolymerization of ethylene with several vegetable oils. The copolymers were carefully purified before analysis and testing to remove unreacted vegetable oil. None of the copolymers containing vegetable oil were susceptible to fungus attack.

TABLE 12

BIODEGRADABILITY OF ETHYLENE COPOLYMERS

Sample no.	Characterization	Growth rating
1	Ethylene-vinyl acetate 82-18	2
2	Ethylene-vinyl acetate 67-33	1
3	Ethylene-vinyl acetate 55-45	1
4	Ethylene-vinyl alcohol 30-70	0
5	Ethylene-vinyl alcohol 70-30	0
6	Ethylene-acrylic acid 85-15	0
7	Sample 6, 35% converted to NH_4 salt	0
8	Sample 6, 100% converted to NH_4 salt	0
9	Ethylene-acrylic acid 80-20, 100% converted to sodium salt	0
10	Ethylene-ethyl acrylate 82-18	0
11	Sample 10, 35% converted to Na salt	0
12	Ethylene-carbon monoxide 52-48	1
13	Ethylene-carbon monoxide 94-6	0
14	Ethylene-aconitic acid 82-18	0
15	Ethylene-itaconic acid 79-21	1
16	Ethylene-lauryl acrylate 75-25	1

TABLE 13

COPOLYMERS OF ETHYLENE WITH VEGETABLE OILS

Sample no.	Vegetable oil	Percent oil in copolymer	Growth rating
1	Castor oil	26.1	0
2	Linseed oil	28.3	0
3	Safflower oil	26.6	0
4	Soybean oil	27.1	0
5	Neat's foot oil	40.8	0
6	Peanut oil	20.0	0
7	Rapeseed oil	19.2	0
8	Olive oil	15.7	0
9	Corn oil	18.0	0
10	Oleic acid	8.6	0

Copolymers of Styrene

Since polystyrene was shown not to biodegrade at a measurable rate, it was thought that copolymers of styrene containing metabolically active groups along the chain might be more susceptible to attack. Accordingly, copolymers of styrene with one or more monomers such as acrylic acid, sodium acrylate, ethyl acrylate, dibutyl maleate, and dimethyl itaconate were synthesized and tested for susceptibility to fungus attack. As seen in Table 14, the presence of such groups did not alter the resistance of the styrene polymer to attack.

TABLE 14

BIODEGRADABILITY OF STYRENE COPOLYMERS

Sample no.	Characterization	Growth rating
1	Styrene-acrylic acid 84-16	0
2	Styrene-sodium acrylate 84-16	0
3	Styrene-acrylic acid-dibutyl maleate 85-10-5	0
4	Styrene-acrylic acid-dimethyl itaconate 85-10-5	0
5	Styrene-dimethyl itaconate 70-30	0
6	Styrene-ethyl acrylate 50-50	0
7	Styrene-2-ethyl hexyl fumarate 85-15	0
8	Styrene-methacrylonitrile 13-87	0
9	Styrene-dodecyl acrylate 85-15	0
10	Styrene-ethyl acrylate-dodecyl acrylate 85-10-5	0

BIODEGRADABILITY OF POLYESTERS

Thus far in this investigation, the only synthetic high molecular weight polymers that have been found to be biodegradable are those having aliphatic ester linkages in the main chain, as for example samples 22, 23, and 24 of Table 4. Those polymers having aliphatic ester linkages in a pendant position on the main chain (polyvinyl acetate, for example) are not utilized by microorganisms. Previous investigators have also observed the susceptibility of aliphatic polyesters to attack by microorganisms, as cited above. This situation is being re-examined in the hope of better understanding the structural factors in a polymer that favor biodegradability. Table 15 lists polyesters of varying structure and molecular weight (as measured by reduced viscosity) and the GR observed for each. Sample numbers in the following discussion refer to Table 15.

Sample 1, an epsilon caprolactone polyester that has a molecular weight of about 40,000 and no branching is quite readily utilized by fungi and bacteria. Sample 2, a branched polyester derived from pivalolactone and of much lower molecular weight, was not utilized at all.

TABLE 15

BIODEGRADABILITY OF POLYESTERS

Sample no.	Characterization	Reduced viscosity	Growth rating
1	Caprolactone polyester	0.7	4
2	Pivalolactone polyester	0.1	0
3	Polyethylene succinate	0.24	4
4	Polytetramethylene succinate	0.59	1
5	Polytetramethylene succinate	0.08	4
6	Polyhexamethylene succinate	0.91	4
7	Polyhexamethylene fumarate	0.25	2
8	Polyhexamethylene fumarate	0.78	2
9	Polyethylene adipate	0.13	4
10	Polyethylene terephthalate	high	0
11	Polycyclohexanedimethanol terephthalate	high	0
12	Polybisphenol A carbonate	high	0

Polyesters based on fumaric acid, which is an unsaturated, dibasic acid, appear to be utilized more poorly than those based on saturated dibasic acids such as succinic and adipic acid.

A marked dependence of biodegradability on molecular weight was observed for polytetramethylene succinate (samples 4 and 5). Aromatic structures as exemplified by samples 10, 11, and 12 render the polyester unassimilable.

Soil burial tests have been carried out on epsilon-caprolactone polyester to determine the rate of weight loss as a function of length of burial. The results are discussed in the following section of this report.

SOIL BURIAL TESTS ON EPSILON-CAPROLACTONE POLYESTER

The polyester derived from the ring opening polymerization of epsilon-caprolactone was chosen for further biodegradation testing by the soil burial technique. A polymer sample of about 40,000 mol wt was molded into tensile test bars, which were found to have an ultimate tensile strength of 2,610 psi, and an ultimate elongation of 369 percent, measured at room temperature. Test bars of this material were buried in a mixture of equal parts of New Jersey garden soil, Michigan peat moss and builders sand. At intervals of 1.25, 2.0, 4.0, 6.0 and 12 months, samples were removed, tested for tensile strength and elongation, and measured for weight loss. With increasing length of soil burial, the test bars became more pitted and eroded (Figure 4) and were much weaker (see Table 16). At the end of 12 months, the samples were too weak to measure strength properties and had lost 42 percent of their original weight. The break in the 2-month sample in Figure 4 is the result of our physical testing, not of attack by the fungi.

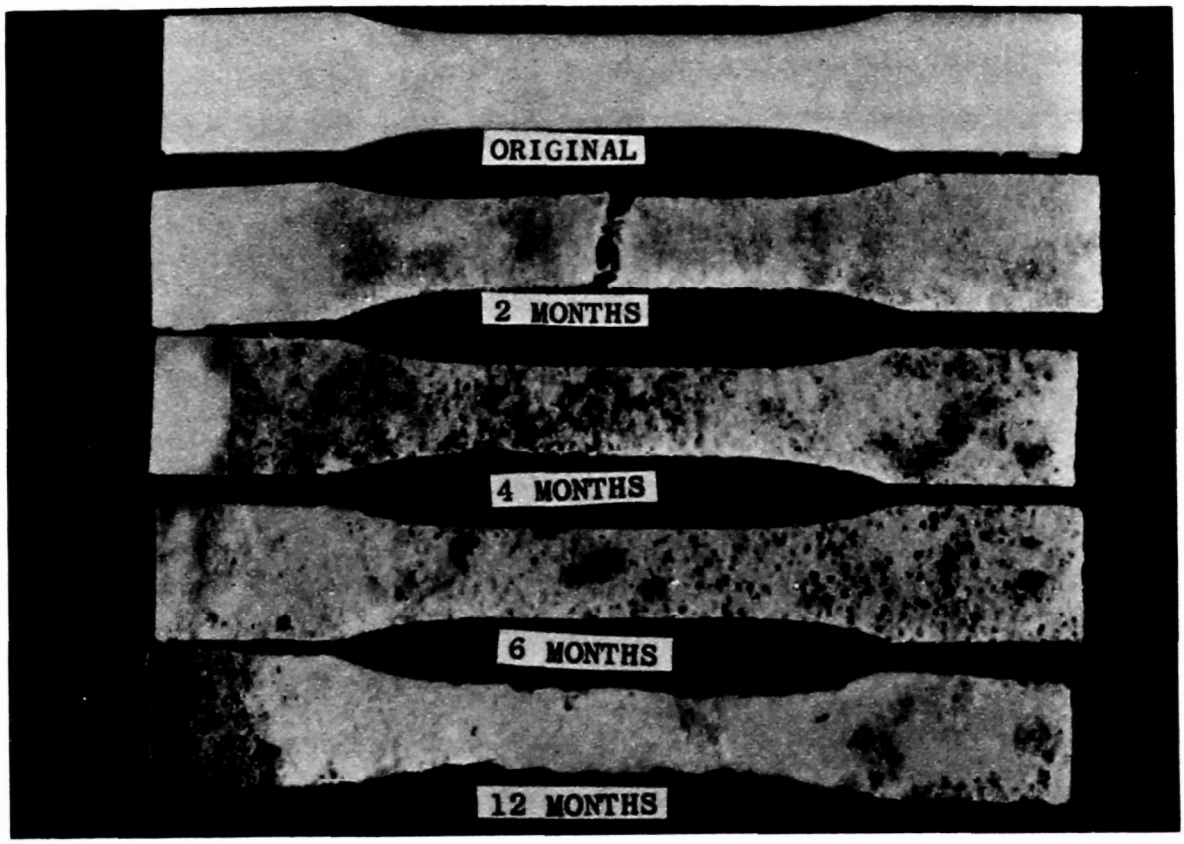

Figure 4. Soil-buried caprolactone polyester (about 1.5x).

TABLE 16

EFFECT OF SOIL BURIAL ON CAPROLACTONE POLYESTER

Months of burial	Tensile strength psi	Percent elongation	Percent weight loss
0	2,610 ± 103	369 ± 59	0
1.25	1,890 ± 215	9 ± 1.4	---
2.0	1,610 ± 180	7 ± 2.0	8
4.0	520 ± 220	2.6 ± 1.1	16
6.0	100	Negligible	25
12.0	Negligible	Negligible	42

Scanning electron micrographs of the surface of the 2-month, soil-buried sample reveal the extent of the attack (Figures 5, 6, and 7).

Figure 5 is a photo of the surface magnified about 980 times before any degradation. The streaks and straight lines are indicative of the surface of the mold in which the tensile bar was made. Figure 6 shows the surface of a tensile bar at about the same magnification (950x) that has been soil-buried for 2 months. Figure 7 is a similar photo at a slightly lower magnification (about 600x). The deep pitting, channelling, and cavernous appearance resulting from the degradation process is readily apparent in these pictures.

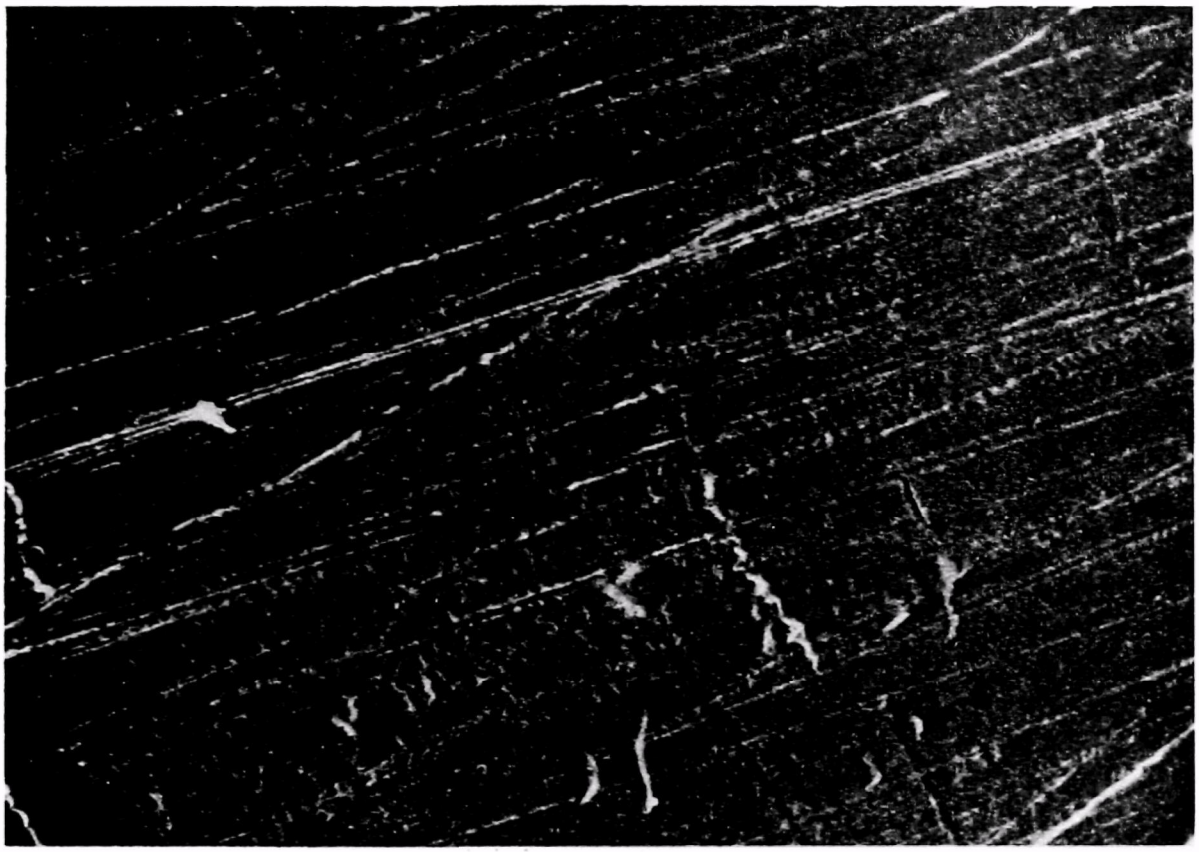

Figure 5. Scanning electron micrograph (about 980x) of caprolactone polyester. Not soil-buried.

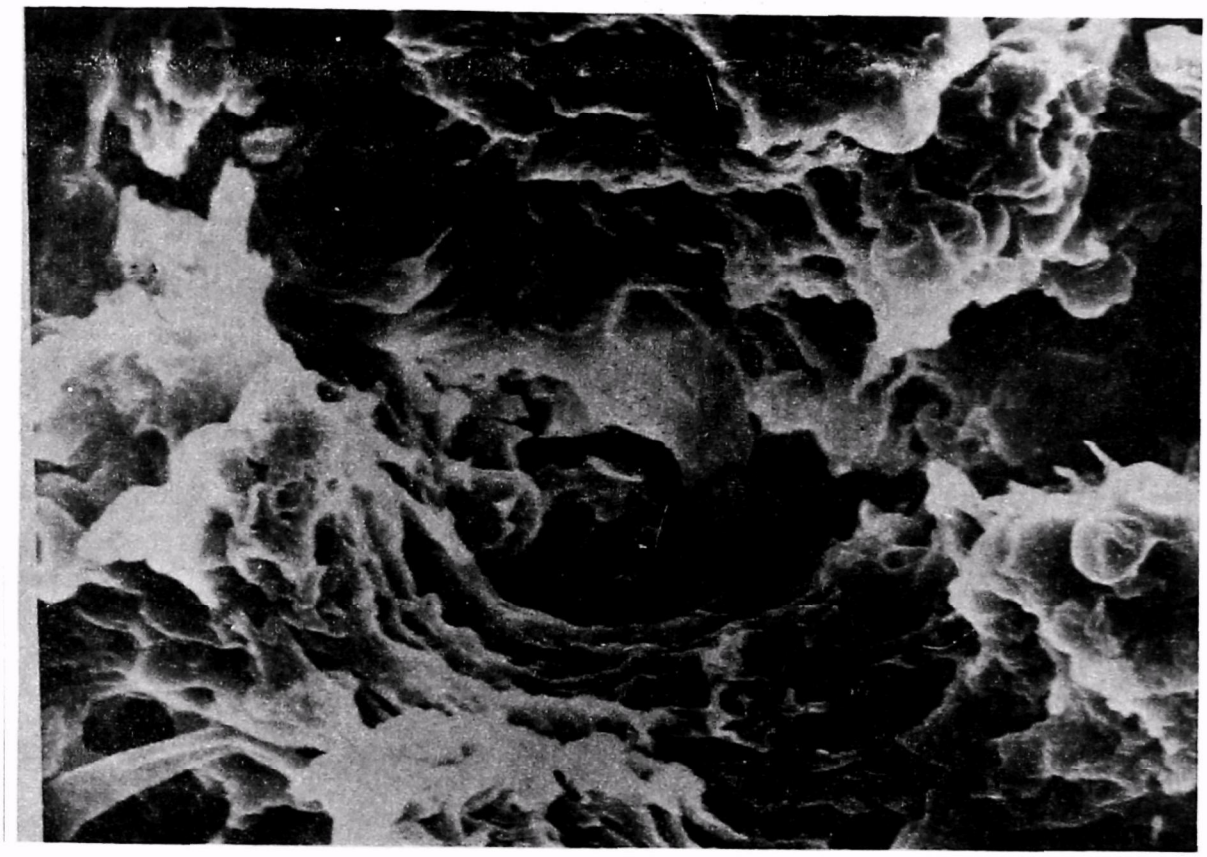

Figure 6. Scanning electron micrograph (about 950x) of caprolactone polyester soil-buried for 2 months.

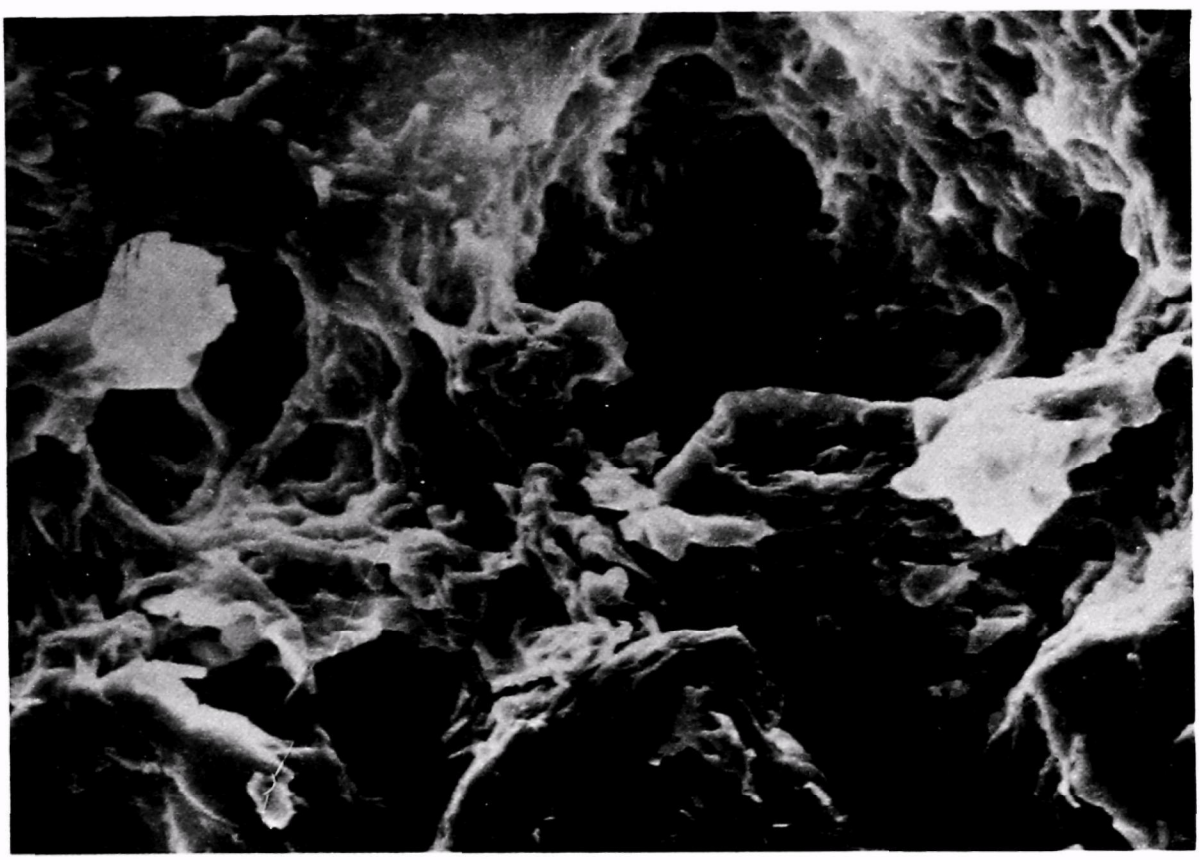

Figure 7. Scanning electron micrograph (about 600x) of caprolactone polyester soil-buried for 2 months.

In addition to tensile bars we have also soil buried 1.5 ounce injection molded containers. Weight loss measurements on these samples are given in Table 17 and photographs of the samples are shown in Figure 8. The greater percentage weight loss observed for these samples relative to the tensile bars is due, of course, to their larger surface areas.

TABLE 17

WEIGHT LOSS ON CAPROLACTONE POLYESTER CONTAINERS

Months of burial	Percent weight loss
0	0
2	12
4	29
6	48
12	95

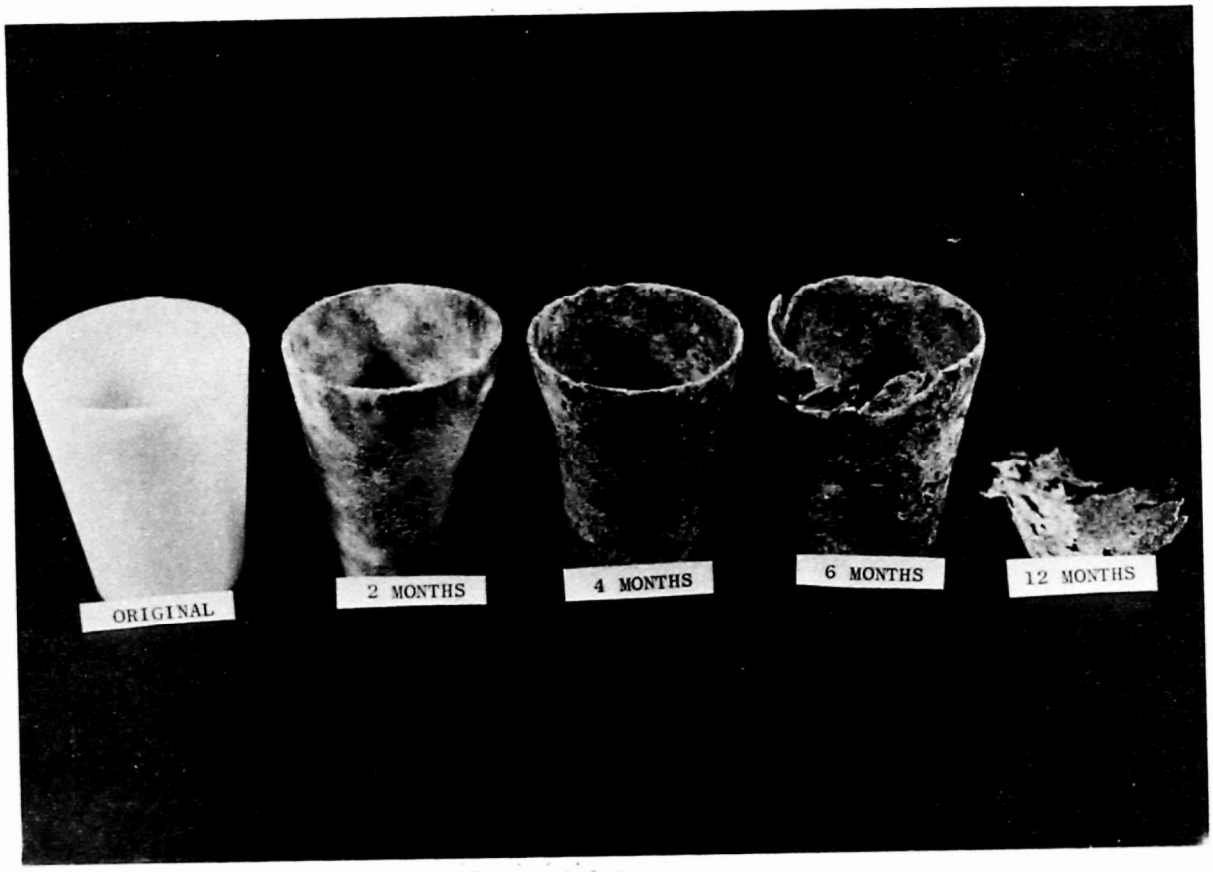

Figure 8. Soil-buried caprolactone polyester.

BIODEGRADABILITY OF BLOCK AND GRAFT COPOLYMERS

One synthetic approach to biodegradable polymers is to construct a polymer molecule containing chain segments or blocks of nonbiodegradable polymer connected to chain segments of a biodegradable polymer. Such products can be made either by block polymer synthesis or graft polymer synthesis. Several of these block and graft copolymers have been synthesized and subjected to our screening program. The nonbiodegradable polymer, or A segment, of the graft copolymers can be a polyethylene type chain or a polystyrene type chain. The biodegradable, or B segment, is based on an aliphatic polyester. The data obtained on the ethylene based polymer is presented in Table 18, and data for the styrene based polymer is presented in Table 19.

TABLE 18

BIODEGRADABILITY OF GRAFT COPOLYMERS BASED ON AN ETHYLENE POLYMER AND A POLYESTER

Sample no.	Percent of ethylene polymer	Percent of polyester	Growth rating
1	24	76	4
2	48	52	4
3	60	40	2
4	88	12	0

TABLE 19

BIODEGRADABILITY OF GRAFT COPOLYMERS BASED ON A STYRENE POLYMER AND A POLYESTER

Sample no.	Percent of styrene copolymer	Percent of polyester	Growth rating
1	23	77	4
2	65	35	4
3	80	20	2
4	92	8	1

Note that in both of these tables, the biodegradability of the system increases as the degradable polyester content increases. Thus, having small amounts of a biodegradable polymer chemically bound to a nonbiodegradable polymer is not sufficient to impart rapid disintegration to the overall system. It appears in the above case that it is necessary to have about 40 percent of the degradable polymer present in order to get reasonably rapid degradation rates; but more data is needed to clearly define the lower limit, since in Table 19 a growth rating of 2 is reported for a system containing 20 percent of the biodegradable segment.

In the area of block copolymers, some preliminary experiments have been done in which a commercially available

nondegradable polyester, polyethylene terephthalate, has been modified with a degradable polyester to yield products that support microbiological growth. The data obtained are reported in Table 20.

TABLE 20

BIODEGRADABILITY OF BLOCK COPOLYMERS OF DEGRADABLE POLYESTER (DP) WITH POLYETHYLENE TEREPHTHALATE (PET)

Sample no.	DP (% by weight)	PET (% by weight)	Growth rating
1	73	27	4
2	43	57	2
3	27	73	0
4	17	83	0

As might be expected, the biodegradability of the block copolymers is directly related to the biodegradable polyester content, which was also true of the graft copolymers reported above.

No property evaluation of these systems has been done with regard either to their utility or to their loss of properties as biodegradation proceeds. Both of these are beyond the scope of the current investigation. What has been demonstrated is that biodegradability of block

and graft copolymers is dependent on the content of the biodegradable segment of the copolymer, and that appreciabe contents are required to confer biodegradability on these particular systems.

BIODEGRADABILITY OF ADDITIVES USED IN PLASTICS

Additives are used in plastic formulations for a variety of reasons -- to inhibit oxidative degradation, and to act as plasticizers, molding lubricants, ultraviolet absorbers, and heat stabilizers, to mention a few. Accurate determination of the biodegradability of a polymer cannot be accomplished without knowing what additives are present and whether they are biodegradable, inert, or perhaps growth inhibiting. Some paints contain fungicides, such as phenyl mercuric acetate.

Table 21 lists commonly used additives, their function, and the GR observed for each. In some instances where the chemical name of the substance was not available, the trade name was used. Inclusion of an additive in the list does not imply that it is in any way preferable to other additives not included in this study. The additives are classified according to the polymer with which they are most commonly associated.

Generally, hindered phenol antioxidants are not biodegradable, and thio esters are readily utilized by microorganisms. Nonyl phenyl phosphite was found to be a growth inhibitor. Plasticizers also vary widely in their biodegradability-aliphatic polyesters are readily utilized

by microorganisms, while those based on aromatic acids are inert. A more complete discussion of plasticizer utilization can be found under Plasticized Polyvinyl Chloride.

TABLE 21

BIODEGRADABILITY OF ADDITIVES

Common trade name	Chemical name or chemical type	Growth rating
POLYETHYLENE AND OTHER POLYOLEFINS		
Antioxidants:		
Butylated hydroxy toluene (BHT)	Hindered phenol	0
Santonox R	Hindered phenol; also thioether	0
Topanol CA	Hindered phenol	0
Irganox 1010	Hindered phenol	0
DLTDP, dilauryl thiodipropionate	Thioether ester	4
DSTDP, distearyl thiodipropionate	Thioether ester	4
Polygard	Nonylphenylphosphite	Z.I.*
Slip or anti-block agents:		
Erucamide	C_{22} unsaturated primary amide	4
Oleamide	C_{18} unsaturated primary amide	4
Stearamide	C_{18} saturated primary amide	4
Behenamide	C_{22} saturated amide	2
HTSA-1	Olealyl palmitamide (a secondary amide)	2
UV absorbers:		
Eastman DOBP	2-hydroxy-4-dodecyloxy-benzeophenone	0
Eastman OPS	p-octylphenylsalicylate	0

*Zone of inhibition. These compounds are essentially fungicides.

TABLE 21

BIODEGRADABILITY OF ADDITIVES -- Continued

Common trade name	Chemical name or chemical type	Growth rating
	POLYVINYL CHLORIDE	
Plasticizers:		
Phthalates Flexol DOP	Di-2-ethylhexyl phthalate	0
Phosphates Flexol TCP	Tricresyl phosphate	1
Epoxies Flexol EPO	Epoxidized soy bean oil	4
Trimellitates Rucoflex 2, 5TM	Tris-2-ethylhexyl trimellitate	0
Polyesters Plastolein 9765	Aliphatic polyester	4
Santicizer 409	Aliphatic polyester	4
Adipates Flexol A 26	Di-2-ethylhexyl adipate	0
Heat stabilizers:		
Vanstay HTA	- - -	4
Vanstay SD	Phosphite	0
Dibutyltin dilaurate	Tin compound	4
Lubricants:		
Zinc stearate	Metal salt	4
Hoechst wax E	Hydrocarbon	2

TABLE 21

BIODEGRADABILITY OF ADDITIVES -- Continued

Common trade name	Chemical name or chemical type	Growth rating
POLYVINYL CHLORIDE -- Continued		
Antioxidants:		
Butylated hydroxy toluene (BHT)	Hindered phenol	0
Processing aids:		
Acryloid K 120 N	Acrylic polymer	0
POLYSTYRENE AND RELATED POLYMERS		
Plasticizers:		
Mekon white wax	Microcrystalline wax	2
Lubricants:		
Zinc stearate	Metal salt	4
Antioxidants:		
Butylated hydroxy toluene (BHT)	Hindered phenol	0
Polygard	Nonylphenyl phosphite	Z.I.*
Rubber:		
Diene 35	Polybutadiene	0

*Z.I. = Zone of inhibition. These compounds are essentially fungicides.

PLASTICIZED POLYVINYL CHLORIDE

Of the approximately 3 billion lb of polyvinyl chloride (PVC) and copolymers sold in the United States in 1970, about 75 percent, or 2.3 billion lb, falls into the category of plasticized or nonrigid PVC. The susceptibility of many types of PVC plasticizers to microbiological attack is well documented in the literature and in an earlier section of this report. There are no instances, either in our work or in the literature, where biological assimilation of the PVC molecule has been proven. In addition to plasticizers, PVC contains other additives such as heat stabilizers that prevent thermal decomposition and hydrogen chloride evolution. Some of these stabilizers such as dibutyltin dilaurate are biodegradable. Loss of these stabilizers could result in a system more susceptible to dehydrohalogenation and subsequent oxidative attack. Certain types of tin stabilizers are the preferred stabilizers for food contact applications such as wraps for luncheon meats, bottles, etc.

The major additive present in PVC formulations however, is the plasticizer. Work by Tirpak (6) and by the Union Carbide Corporation has shown that as the plasticizer is utilized by microorganisms, the vinyl

becomes stiff, brittle, and increases in tensile strength and modulus. We have examined three samples of PVC film containing different plasticizers to show the variability of the attack and to demonstrate that not all plasticizers are biodegradable. The data are presented in Table 22.

TABLE 22

EFFECT OF PLASTICIZER ON PHYSICAL PROPERTIES OF POLYVINYL CHLORIDE AFTER EXPOSURE TO BACTERIA

Plasticizer		Tensile modulus of elasticity (psi)		Percent of
Code	Type	Unexposed	Exposed	change
R2H	Polyester	2,373	2,887	22
H707	Hercules proprietary	1,372	4,895	258
DOP	Dioctyl phthalate	1,102	1,166	6

The amount of plasticizer consumed in these experiments was not determined, but the surface of the film was severely pitted. The increase in modulus on exposure to the bacteria indicates that the sample was becoming embrittled. Additional environmental degradation would be required before a product is obtained that will crumble to a dust. Plasticizer utilization by microorganisms can, however, leave a material with a much

larger surface area, thus enabling environmental degradation to proceed at a faster than normal rate.

From the data in Table 22, we conclude that the polyvinyl chloride containing DOP (the most common, workhorse plasticizer) is essentially unaffected by the bacteria. The sample containing R2H is attacked to a slight degree, and the sample containing H707 is severely attacked.

At present, biodegradable plasticizers are used in PVC in one-time use applications. A good example is PVC film for packaging meats. In the packaging-marketing area in 1970, film and sheet markets accounted for the use of 175 million lb of PVC resin.

Although this study did not make detailed studies of the progressive embrittlement of PVC film as the plasticizer is removed by microorganisms, there is definite evidence, as indicated in Table 22, that the sample becomes more friable, as one would expect. In addition to the samples examined in Table 22, PVC meat wrap film containing epoxidized soy bean oil plasticizer was buried in the soil for 3 months and then removed for examination.

Whereas the original meat wrap film was limp and flexible, the film that had been buried for 3 months

had the appearance of parchment paper and cracked when flexed more than once. Although the test was not continued it was judged that soil burial for a year or more would result in eventual removal of all of the plasticizer from the film, leaving a brittle film of greatly increased surface area.

Simultaneous removal of the biodegradable stabilizer (dibutyltin dilaurate) further enhances the susceptibility of the film to dehydrohalogenation, which results in an unsaturated polymer of greatly increased oxidative and microbial susceptibility.

EFFECT OF ENERGY TREATMENT ON PACKAGING FILMS

The treatment of plastics with ionizing radiation, corona discharge, ozone, etc. has been proposed on several occasions as a means of increasing the susceptibility of plastics to attack by microorganisms. In an attempt to demonstrate the feasibility of these approaches, we have treated several of the more prominent packaging materials with (1) high energy electrons from a van de Graaff electron accelerator, (2) corona discharge, and (3) ozone.

The irradiation with van de Graaff electrons was carried out at three different dose levels: 5 megareps, 10 megareps, and 20 megareps. The higher the dose, the more intense the radiation and the more pronounced the effect should be. Radiation doses of 20 megareps are considerably higher than those normally used in commercial radiation processes.

The film exposed to the corona discharge was exposed on one side for 15 seconds at 120 volts and 2.3 amps. This is approximately what is used to surface treat film to improve the acceptance of printing inks by the film.

For treatment with ozone, the films were exposed in a flow system at 50 C to an atmosphere containing 2 percent ozone. The ozone was generated at a rate of 9 g per hr over a 6-hr period, thus exposing the film to a total of 54 g of ozone.

After exposure to these treatments, the samples were submitted to our standard screening procedure. The results are presented in Table 23.

It is obvious that none of the treatments used in this experiment has enhanced the biodegradability of any of these film samples enough to be measurable by the standard screening test. The vinyl films contained plasticizers that are biodegradable.

In addition to the above physical methods, some preliminary experiments were done on outdoor-weathered polyethylene in which a GR of 2 was observed. The deterioration of physical properties upon outdoor weathering or aging of a polymeric material is due to sunlight activated oxidative attack on the polymer structure. This oxidative attack generally leads to a decrease in the molecular weight of the polymer. Although the average molecular weight of the polymer at the stage where it crumbles to a powder is still relatively high, continued

oxidative attack over a longer period of time could lead to sufficient molecular weight reduction so that, depending on the structure of the polymer, assimilation by soil microorganisms might take place. For hydrocarbon polymers such as polyethylene, evidence was presented earlier that a reduction in molecular weight to about 500 would be sufficient for assimilation by fungi in the soil. It should be recognized that microbiological growth on the degraded polyethylene would be in evidence before all of the molecules in a given plastic object were reduced to the 500 mol wt level because of the distribution of molecular sizes that exists in polyethylene even after oxidative degradation.

There has been a great deal of publicity recently devoted to the degradation of polymer systems by the action of ultraviolet light. Work in England, Canada, and the United States has pointed out several ways that the ultraviolet degradation of plastics can be accelerated. Most of this work is pointed towards alleviating the litter problem. In some cases this approach has been claimed to result in a biodegradable product. Because of the profound effect that chain branching has on inhibiting biodegradation of synthetic polymers (an effect that persists even to low molecular weights), it is essential that such claims be substantiated by adequate experimental data.

TABLE 23

EFFECT OF PHYSICAL METHODS OF TREATMENT ON PACKAGING FILMS

Film sample	Growth rating of treatment method					
	Control	Corona discharge	Ozone	Radiation (megareps)		
				5	10	20
Polyethylene	0]	0	0	0	0	0
Polystyrene	0	0	0	0	0	0
Resinite vinyl film	3	3	3	3	3	3
EPO plasticized vinyl film	3	3	3	3	3	3
Saran wrap polyvinylidene chloride	0	0	0	0	0	0
Mylar polyethylene terephthalate	0	0	0	0	0	0
Polypropylene	0	0	0	0	0	0

RECOMMENDATIONS FOR ACTION

1. Additional studies are needed to determine the effects that the use of biodegradable additives, such as plasticizers and stabilizers, will have on the disintegration of plastic packaging, particularly polyvinyl chloride. Investigations would include data on the optimal use of additives with regard to both the end use and eventual disintegration of the plastic packaging when buried. The ultimate purpose of such studies would be to assess the use of such additives as a standard practice in packaging plastics such as PVC.

2. Further studies of biodegradable, aliphatic polyesters are needed to assess their usefulness as packaging materials. These studies would include fabrication of selected polyesters into various packaging containers and evaluation of their physical properties with regard to various packaging applications. The objective of these studies is to provide the basic technical data needed to determine the commercial feasibility of this approach to biodegradable packaging plastics. These studies will also include an evaluation of blends of the biodegradable polyesters with polyethylene, poly-

styrene, and polyvinyl chloride.

3. The studies of block and graft copolymers containing blocks that were found to be attacked by microorganisms should be continued to determine which of these types of block copolymers show promise in packaging applications. This would involve (a) synthesis of larger quantities of specific products carefully screened for promising physical properties, (b) fabrication into various useful packages, and finally (c) measurement of their rate of assimilation by microorganisms. The purpose of these studies would be to demonstrate the feasibility of this approach to biodegradable packaging materials.

4. Preliminary studies reported in a previous section of this report demonstrated that pyrolyzed polyethylene becomes more biodegradable as the average molecular weight decreases. These pyrolysis studies should be extended to other plastics to determine the effect of thermal degradation on their biodegradability. The Union Carbide continuous pyrolysis process will be used in these studies because of its freedom from tar formation and its greater degree of control over the molecular weight of the pyrolyzed polymers.

5. Perhaps the most practical route to biodegradability for polyethylene involves the development of polyethylene packaging containing additives that will protect the package during its useful life but that will promote its disintegration and ultimate degradation to a low molecular weight polymer that will be biodegradable. It is recommended that sufficient work be done to demonstrate the feasibility of this approach.

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