

THE RECYCLING OF PLASTIC WASTES
IN PACKAGING

Thesis for the Degree of M. S.
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YUGO SUZUKI

1974

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ABSTRACT

THE RECYCLING OF PLASTIC WASTES IN PACKAGING

By

Yugo Suzuki

The technology of plastic waste disposal has been researched and developed to overcome the nuisance disposal problem, and many results have already appeared on the market. There are several chemical approaches: stabilized plastics for recycling, blends of different sorts of plastics, and bio- or chemically degradable plastics.

Engineering methods are reviewed briefly to compare with these chemical approaches.

Landfill has played a great role in disposal because of its cost advantage. However, facing a land shortage, incineration and pyrolysis will come to be much appreciated and they are now being employed to dispose of a lot of wastes including plastics.

After the oil crisis in 1973, prices of petroleum products increased at an incredibly high rate, and so reclamation has been reconsidered both from the economical and environmental points of view.

It is likely that we need a long time before we will establish a valuable technology of polymer blending. A successful example of high density polyethelene milk bottle recycling gives us only a small market and a small profit even now. However, it will be a great aid for a petroleum-inclined economy to develop reclamation and blend technologies.

For a new technology to be adopted in a community and economic market, economics are very important. The total cost estimation and the prediction of disposal methods in future indicate to us very interesting solutions. The pyrolysis for the collected refuse and the biodegradable plastic developed for non-collected refuse will give us an outstanding result without high costs or pollution.

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IN PACKAGING

By

Yugo Suzuki

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1. PLASTICS IN PACKAGING

Packaging has long enjoyed first place as a market for plastics; one-fifth of all the plastics produced in the United States is consumed by the packaging industry, though it is expected to drop into second place, yielding to building and construction (1). But this does not mean a decline in demand or growth. Still the growth rate is expected to be around 10% per year in the next decade in spite of the predicted low GNP growth rate (1).

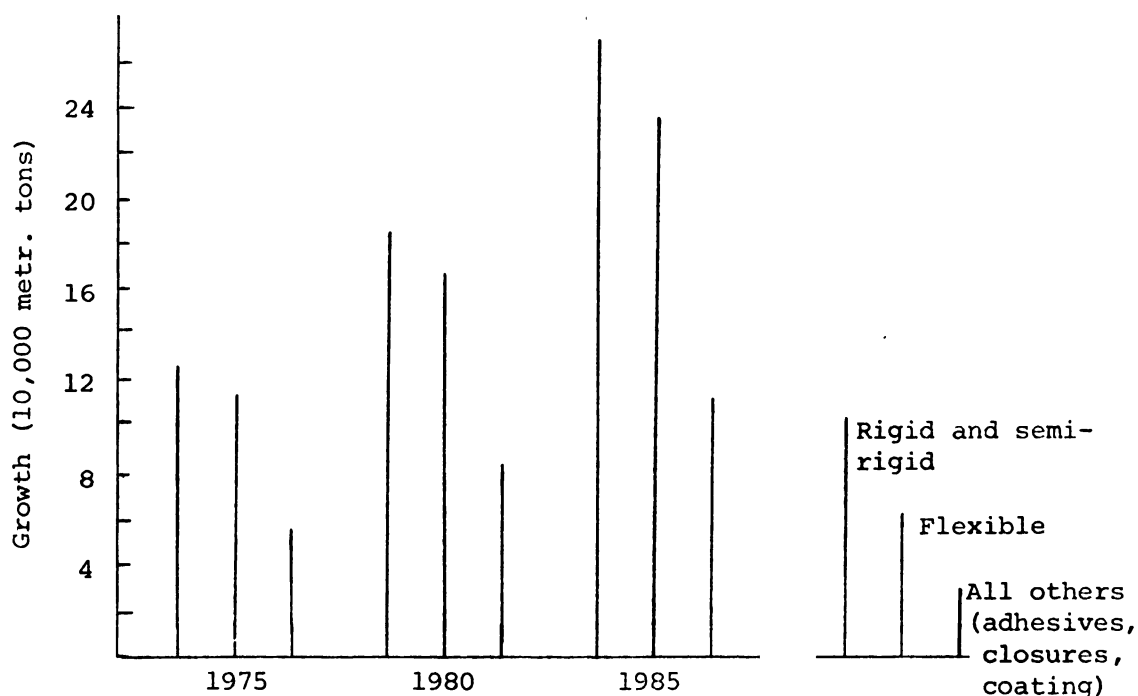


Figure 1.1.--Plastics in Packaging; Growth by 1985 (1).

There are two main motivating factors for the increase of plastics in packaging: (1) consumers prefer plastic containers to other materials, and (2) plastics are more flexible in terms of design and market oriented properties than other materials. New technologies such as copolymerization, coextrusion, laminating and alloying have expanded into plastic packaging, and there is active research in new materials development and processing improvement.

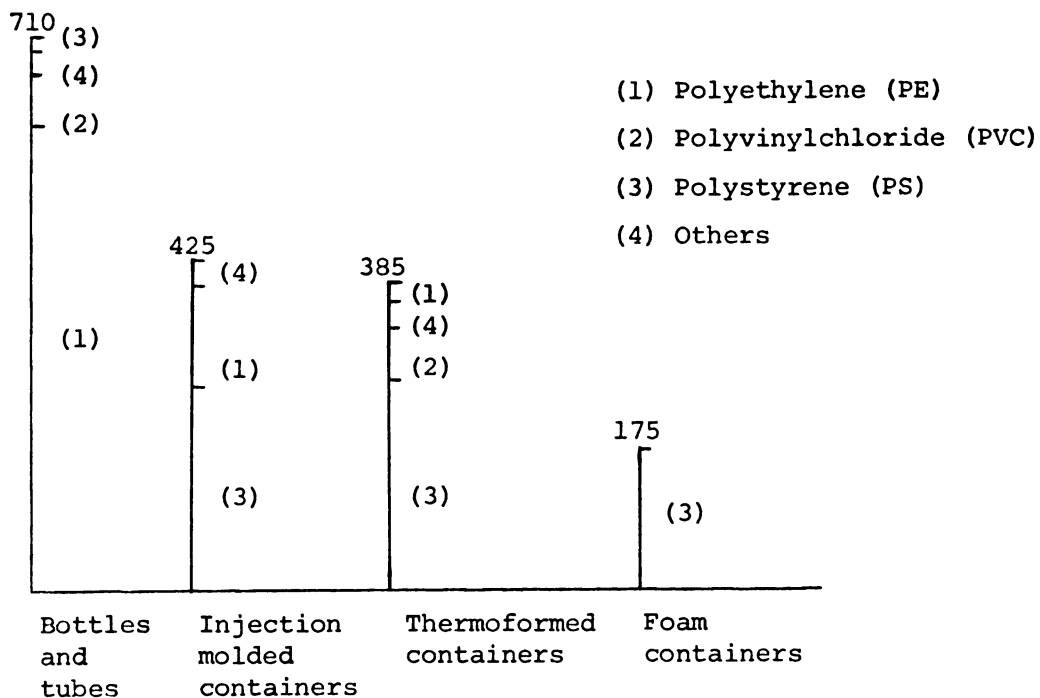


Figure 1.2.--Rigid Plastic Packaging Market in 1970 (2). (In millions of pounds.)

Surely there are problems. One is today's "stagflation"; that is, the average growth rate for packaging is linked to the growth of the Net National Product (Gross National Product adjusted for inflation) which is weak at this time. Secondly, litter control singles out plastic packaging for special treatment, and makes ecology one of today's tough issues. Third, the high price of crude oil and tight supply of resin for all thermoplastics raises their cost radically, making them less competitive.

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2. RECYCLING SYSTEMS FOR PLASTICS

The excellence of plastics as industrial materials is recognized as well as their economic superiority, and in the future they are expected to rank with steel as a major industrial material. But the environmental questions about plastics and the oil crisis of October 1973 have put a shadow of doubt over their glorious future.

TABLE 2.1.--Plastics Production, 1970 (3).

	%	Billions of Lbs.
PS	17.1	3.35
PVC	19.4	3.80
PE	30.6	6.00
Phenolics	5.5	1.07
PP	5.1	1.01
Others	<u>22.3</u>	<u>4.37</u>
Total	100.0	19.60

TABLE 2.2.--Plastics in Packaging, 1970 (3). (In millions of pounds.)

	PE	PVC	PS	PP	Other	Total
Adhesives	--	41	--	--	10	51
\ Bottles and tubes	584	65	18	--	40	707
Coatings	400	143	--	--	57	600
\ Closures	42	12	10	19	31	114
\ Film and sheet	1,250	197	10	85	53	1,595
Containers	150	--	730	--	17	897
Miscellaneous	<u>--</u>	<u>--</u>	<u>--</u>	<u>--</u>	<u>23</u>	<u>23</u>
Total	2,426	458	768	104	231	3,987

TABLE 2.3.--Composition of Residential Solid Wastes, 1970 (4).

Paper products	43.8%
Food	18.2
Metals	9.1
Glass and ceramics	9.0
Garden wastes	7.9
Plastics, rubber, and leather	3.0
Textiles	2.7
Wood	2.5
Rock, ash, etc.	3.7

In the data announced in 1970 (4), the composition of plastics, rubber, and leather wastes is only 3.0% of residential solid waste in the United States, and this composition is similar for other industrialized countries such as England, France, and Japan as indicated by statistical data.

The troubles with waste plastics are (1) the quantity has increased rapidly with production rates, while the disposal techniques did not follow this expansion; (2) the research effort for plastics was limited mainly to production, molding, and applications, rather than disposal; (3) the use cycle time for plastics is short in urban areas and they are disposed with other residential solid wastes; and (4) the chemical conformation of waste plastics is such that they do not degrade in biological systems without treatment. Nowadays, urban refuse is disposed by landfill or incineration. There has been criticism of plastic wastes in incineration due to the HCl produced by burning polyvinylchloride (PVC) and damage to incinerators from the high temperatures produced in plastics combustion.

World affairs since last October, the so-called oil crisis (high cost of crude oil supply), changed the problem with plastics refuse to another one.

Plastics have as high an energy of combustion as petroleum and they have good chemical conformation. That

has demonstrated to us that plastics are another precious resource even after use. Therefore the reclamation of waste plastics should receive a good deal of research effort. The reason that less than 5% of total refuse collected as urban solid waste is so much criticized, especially by environmentalists, is that plastics are (1) particularly inert materials, littered everywhere people move and gather, and highly visible; (2) found in disposable and short-lived products, especially for packages and containers which are colorful eye-catchers that are felt to be unnatural; and (3) a rapidly increasing waste component in this decade though they are still a small minority.

The trend of plastics in city life is that (1) plastic packages and containers have increased with automation, self-service systems, and the mobility of people, and with the market competition among retailers; (2) consumers appreciate that plastic packages are shatterproof, sanitary, and transparent.

2.1. Introduction to Recycling

The disposal of plastic wastes has briefly been considered. In the issue of disposal technology, each method was authorized unless it contributed another kind of pollution, but the oil crisis has dramatically changed this easygoing approach to recyclability of precious natural resources. All the effort to reuse, recycle, and

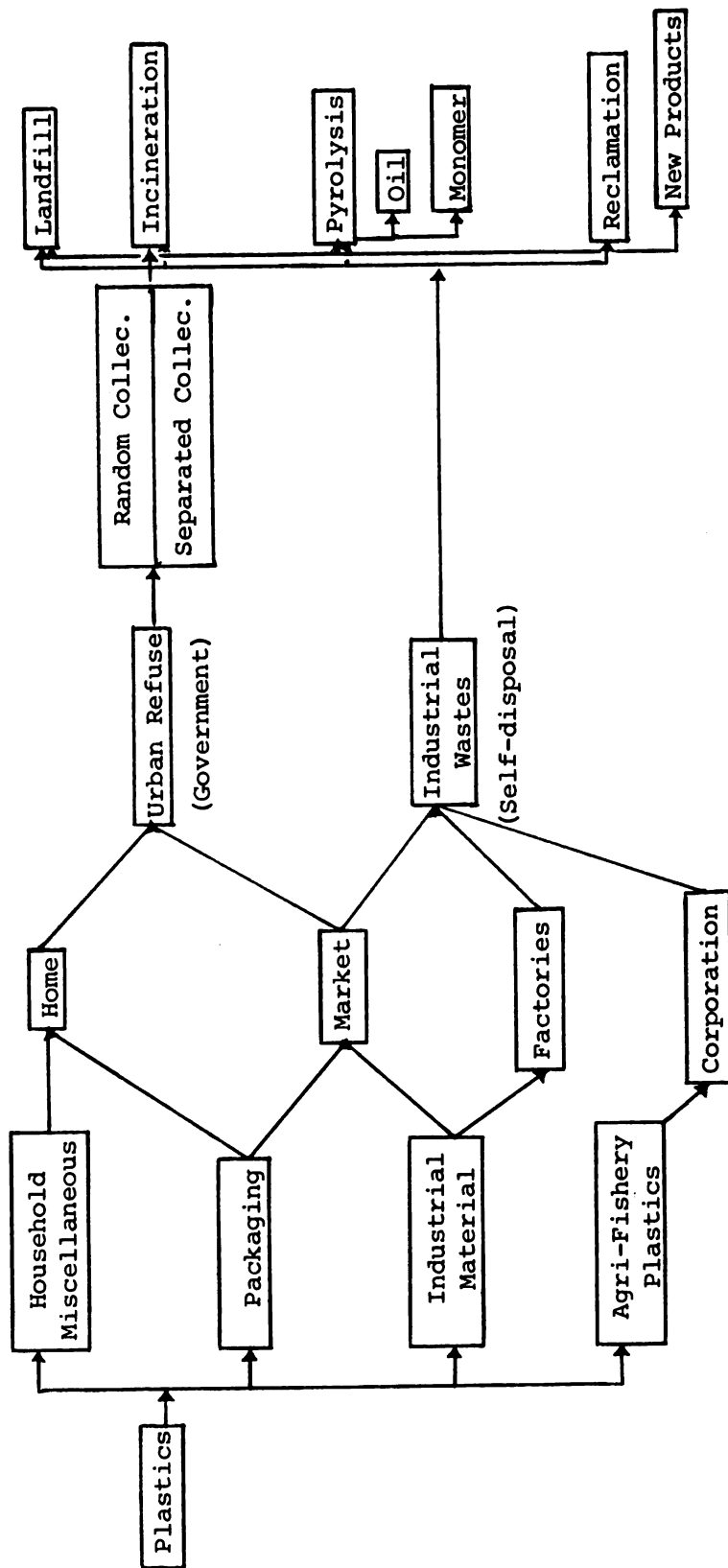


Figure 2.1.--Flow Sheet of Waste Plastics Disposal.

reclaim cannot be economically justified, so only a proper disposal technology can be applied. Considering the environment a system of complete recycling either through material reuse, pyrolysis or incineration with heat recovery is desirable. A product must not just have disposability but recyclability, which means we create a new concept of material rotation; we do not throw away urban refuse, thinking it only useless. A recycling system should have complete technology to separate the useful resources, to classify into each material, and to remake it into another product.

In general, the market value of wastes depends on space and time, where and when they exist, as well as on their intrinsic value; accordingly, widely dispersed materials become less valuable. If collection, classification, and remanufacturing methods and mature markets for a product are once established, a total recycling system built in the community really works. Examples of this already developed are recycling for paper, aluminum cans, and glass containers. The same problems as with plastics are discussed in other recycling systems such as rubber (tires), glass, fibers, and waste oils. In consideration of the recycling process, we do not only develop a new technology. Just as important are product innovations and the development of markets for recycled products. Some help from legislation and cooperation between governmental units

and plastics industries will be needed considering both the environment and energy affairs in these days.

2.2. Disposal of Plastics

2.2.1. Landfill

Landfills are the most common disposal method of urban refuse; 90% of United States and United Kingdom wastes is landfilled (5). Landfills are classified as open landfill and sanitary landfill, but only sanitary landfills are now legal in the United States.

TABLE 2.4.--Waste Disposal Methods.

	France (1972)	U.K. (1972)	U.K. (Estim. 1980)	U.S.A.
Incin.	30%	10%	20%	9%
Compost.	13	--		1
Landfill	57	90	80	90

Reclaimed land from a high quality landfill operation has more than 890 kg/cu.m (55 lb/cu.ft.) density, while common landfill is about 475~600 kg/cu.m and some inferior lands have less than 300 kg/cu.m. The densities of various plastics are around 0.8~1.0 g/cu.cm (800~1000 kg/cu.m) which indicates that many plastics theoretically satisfy the density condition (6). Mixed plastics in the soil of landfills do not present problems for the reclaimed

land, because most plastics are not naturally degradable or unstable, but the low friction coefficient of plastics sometimes makes them slippery, so usage in construction of heavy buildings is not advisable without special precautions. Recently even in the United States, which has a great deal of land, many cities cannot get enough space for landfill, and so other developed areas such as in Europe and Japan, can no longer depend on this major method of disposal.

2.2.2. Incineration

The easiest and most practical engineering method for disposal, working all over the world, is incineration. The principle of combustion is not so difficult. Nowadays the combustion heat in an incinerator is used to make steam which is distributed to the community as a heat source.

About 20% of U.S. incinerators are the heat recycling type, where incoming air is warmed by exhaust gases. Larger plants, more than 600 tons per day, use the waterfall furnace, where the circulating water is heated around the furnace. Fumed gases released from chambers include toxic ones such as hydrogen chloride (HCl), carbon monoxide (CO), sulfur dioxide (SO₂), and nitrogen oxides (NO_x); the technology for treating them is available and claimed in many patents, but still not completed for practical use. Some people indicate that an improved

device attached to the incinerator or improved furnace designs such as the double chambers work well to minimize toxics. But still these are very expensive and energy-consuming methods for market competition. The removal of HCl originated from combusting PVC is hard even for a modern technology without a large investment. As heat sources plastics show superior properties, high combustion energy and flammability, particularly PE, PP, and PS, but not PVC, among the popular plastics.

TABLE 2.5.--Combustion of Packaging Wastes.

	Ignition °C	Cal. Kcal/Kg
PE	340	11,100
PP	350	11,050
PVC	390	5,060
PS	350	10,170
Phenols	520-540	5,850
Melamines	475-500	4,260
Uretanes	310	4,450
Corrugated paper		4,130
Paper cartons		4,300
Textiles		4,470
Hardwood, oak		4,830
Softwood, pine		5,090

Mixed combustion of household refuse, above all with wet garbage that is carried out by many local governments, is aided by the high energy of plastics. The ratio of plastics can be controlled to keep temperatures constant and to generate the same amount of heat per hour during a long run.

2.2.3. Pyrolysis

The flow chart of pyrolysis of plastic wastes is presented, which shows these four branches: (1) tar, (2) water soluble mixture, (3) organics, and (4) gas mixture. Much equipment and many pilot plants have been developed for plastic pyrolysis, and each plant is proud of its excellent capacity to dispose of refuse.

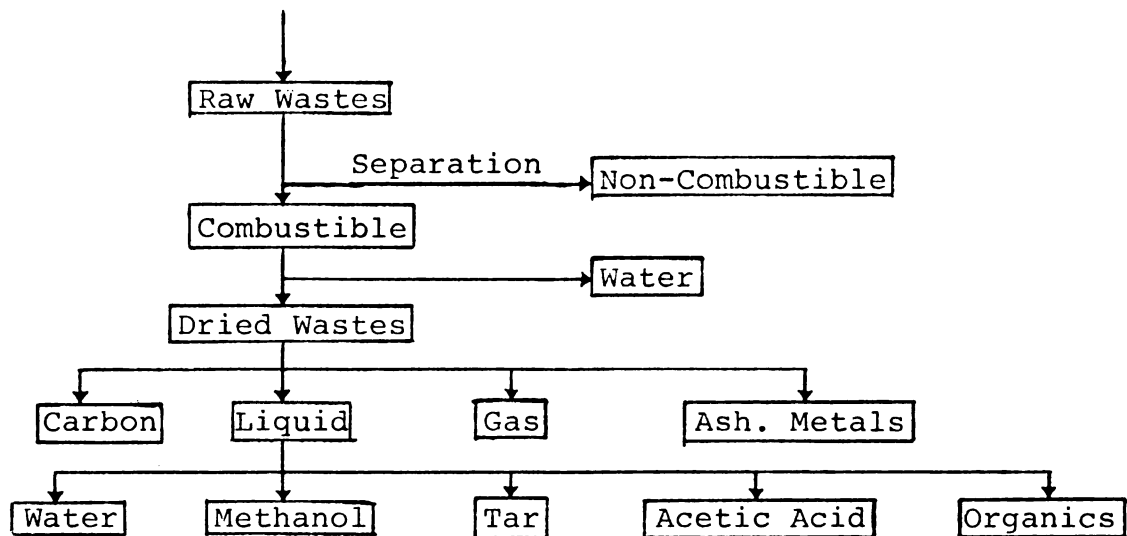


Figure 2.2.--Flow Chart of Pyrolysis.

TABLE 2.6.--Pyrolysis of Plastics (8).

	Temp. of Pyrol. (°C)	Liquid (%)	Gas (%)	Residue (%)
PE	465	89.2	7.9	0.6
PE	470	93.6	6.0	0.4
PP	460	91.0	7.6	0.2
PP	550	94.7	5.0	0.3
PS	465	96.5	0.4	3.2
PS	530	97.8	0.9	1.9

Some companies have been developing the pyrolysis technology and running experiments with pilot plants. Not so long from now commercial plants for community needs will be running, while some small plants are already in commercial use. A lot of information about pyrolysis is available and every paper claims superiority for its own method. Some examples are (9):

(1) Destrugas process (Denmark): This works for fuel gas, has a capacity of 18 ton/day, and the following pyrolyzed product composition of solid, liquid, and gas, and can easily be scaled up. Eighty percent of product gases is burned in the plant and the remaining 20% is supplied to the outside community.

(2) Union Carbide process: Controlling the pyrolysis temperature and time, this process can select the

product composition among wax, grease, oil, and even gas. The process consists of a premelting process and a pyrolysis furnace, hence HCl from PVC can be removed at a stage of preheating.

(3) Monsanto process: This is developed for the purpose of urban refuse disposal, and has four stages: crushing, pyrolysis, gas purification, and residue treatment. Ninety-four percent of the gas is released in a low oxidation state and purified at high temperatures, removing toxic gases and washing out particles with water.

(4) Lentz converter process: A closed rotary kiln as a furnace is operated at around 1,200 °F. Steam, volatile oil, carbon dioxide, and carbon are converted from plastics, then the steam and carbon dioxide are removed. The volatile oil includes hydrogen, methane, and propylene, which have the heat capacity to generate 400,000 kw of electricity per day.

With relation to these methods, a tire reclamation process is running in the U.S. Bureau of Mines and U.S. Rubber Reclaiming Company, which claim to produce many chemicals as well as hydrocarbons (10).

It is said that pyrolysis is more favorable than incineration among experts, because (1) a closed system is possible to minimize air pollution; (2) a large-scale plant and recycled heat can decrease the investment and running cost; (3) recycled gas is reformed to raw materials

for other processes; (4) urban refuse is reduced to less than 50% by volume, so post treatment becomes easier. The result in San Diego after three years of experience indicates that (1) the volume of wastes was decreased to 50% of starting; (2) a new energy supply was not necessary; (3) the remaining ash or other materials are favorable to landfills; (4) recycled gas and oil are available for new products for the market; (5) on a large scale, it is estimated that the total cost of building and operating is about 65% of that of an incineration plant.

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3. CHEMICAL APPROACH TO DISPOSAL

We have now come to the point to discuss the chemical approach to the recycling of plastics found in collected solid waste and litter.

Since the birth of synthetic plastics, research chemists have devoted themselves to the stabilization of plastics against heat and light. Tough and clear plastics were their dream for a long time. To apply this idea in the recycling of plastics, and how we can make a stable plastic through its use and reclamation, is the chemist's big interest now.

The techniques of polymer blending are some of the most difficult areas and, therefore, only less advanced technology has been developed there. However, once it is developed we would not need a classification process, which is another difficult technique even for modern technology except the human eye.

Littered plastics are a main target at which a lot of environmentalists and ecologists throw sharp accusations. If plastics would disappear before their eyes it would be a big relief for all these people unless they pay attention to the toxicity of the degraded plastics. They will no longer hurt the beautiful scenery around us.

There are two methods to degrade plastics: biodegradation and chemical degradation. Biodegradation is literally a degradation by bio-organisms and chemical degradation is a photodegradation by ultraviolet (UV) energy, or an oxidation with an oxidizer.

3.1. Stabilization of Polymers

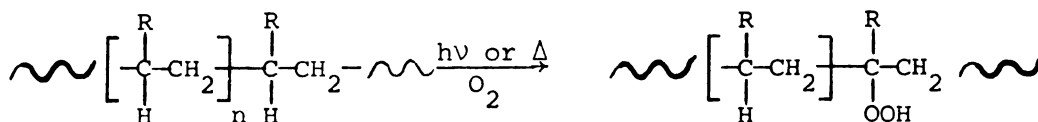
3.1.1. Background Theory

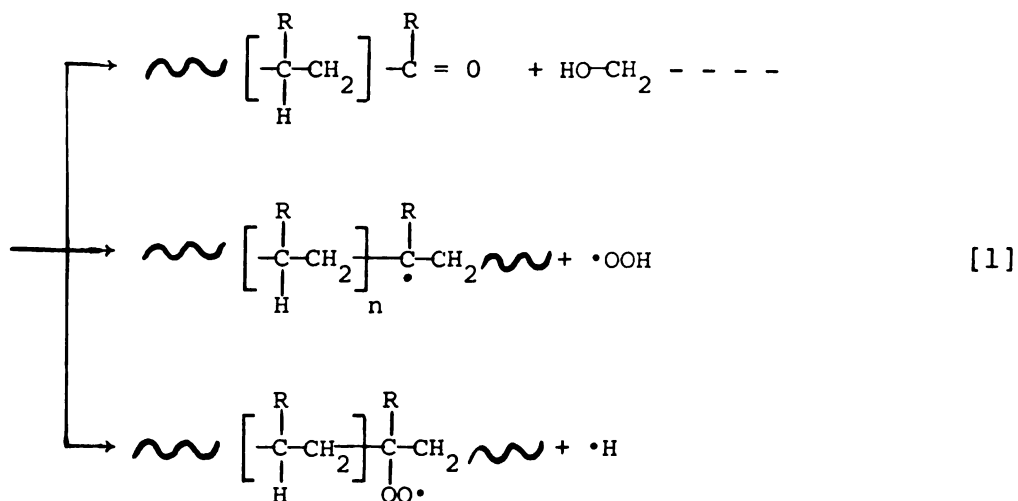
Synthetic polymers require stabilizers to be processed into products, and the stability of physical and chemical properties of plastics depends on these stabilizers and the proper technique of using them. The ideas of stabilization and of degradation are opposite, however the chemical approach to each is similar. The chemical bonds in polymers generally have an energy of about 40-90 kcal/mole, corresponding to about 720-320 μm of wave length. Carbon-carbon, carbon-hydrogen and carbon-halogen bonds are generally 65-85 kcal/mole and typical carbon-carbon bonds in polymers are about 80 kcal/mole. Carbon-hydrogen bonds are somewhat more reactive, especially when the hydrogen is tertiary or alpha to an activating group such as C=C. On the other hand, a bond energy of 40-90 kcal/mole corresponds to the visible and ultraviolet light region. This indicates that polymers are degradable in the natural environment and commercial plastics need stabilizers for most applications. Commercial plastics

undergo a lot of thermal processes that cause oxidation of the polymer chain and branches, and degrade or color them. So we need various kinds of stabilizers for various polymers, above all heat resistant ones.

An outstanding new development of stabilizers has not been seen in recent years, because commercial stabilizers were developed in the 1950s and they have been effective enough as market needs. Stronger polymers are not realistic or hopeful, because here you see the physical limitation of bond energy: 40-90 kcal/mole. The more we add additives for strength, the less plastic polymers become. This is a dilemma for the chemist.

Factors of polymer degradation are classified (1) oxidation by UV light, (2) oxidation by heat, (3) oxidation catalysis by transition metals, (4) oxidation with ozone, (5) thermodegradation, (6) degradation by radiation; (1)-(3) are important. In the samples of vinyl polymers, degradation from oxidation is indicated by [1].

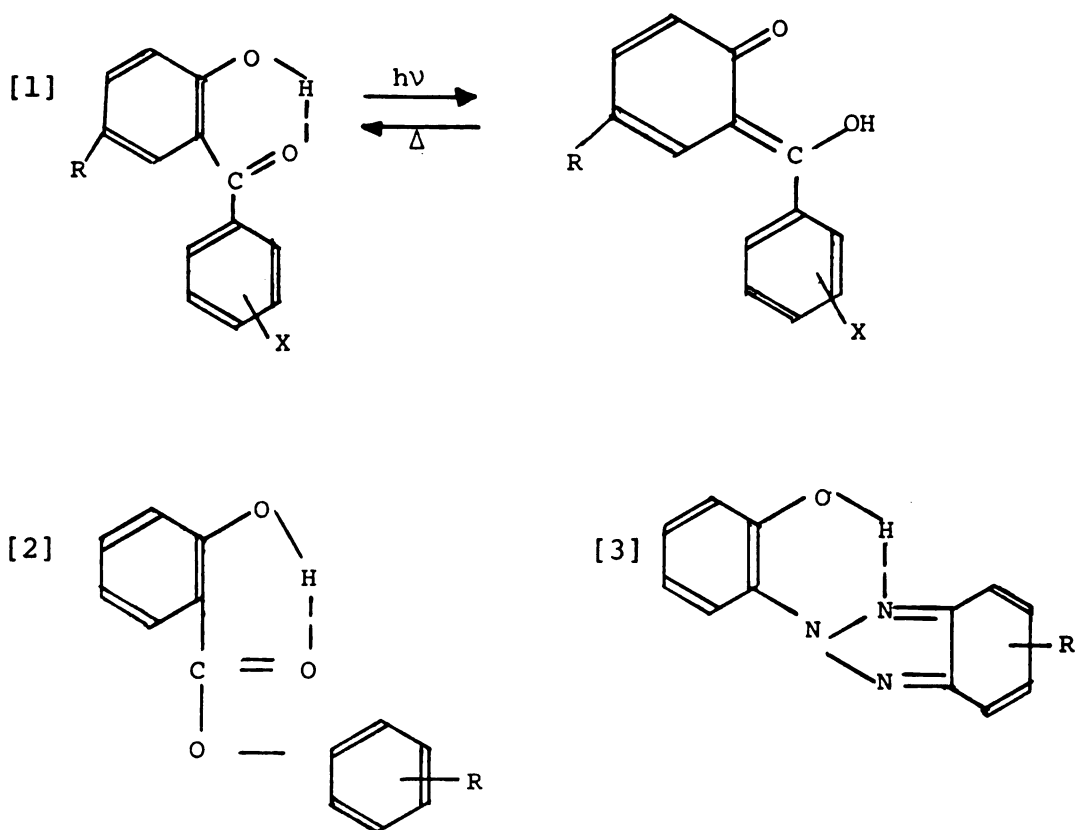




This kind of oxidation is generally seen in various kinds of polymers, so to maintain the physical strength of polymers, we have to overcome these degradation reactions under environmental conditions. Such ideas are applied to stabilizers. Stabilizers have to deactivate the oxidation radical or absorb the UV energy that causes the oxidation.

3.1.2. Ultraviolet Absorbents

The UV absorbent absorbs UV light but does not drive other reactions. Many data of experiments indicate these three types of compounds are effective as UV absorbents: [1] oxybenzophenone, [2] phenylsalicylates, [3] 2-(2'oxyphenyl)benzotriazoles.

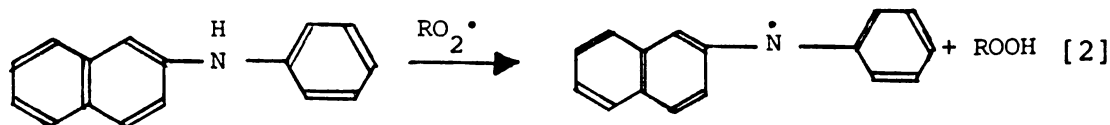
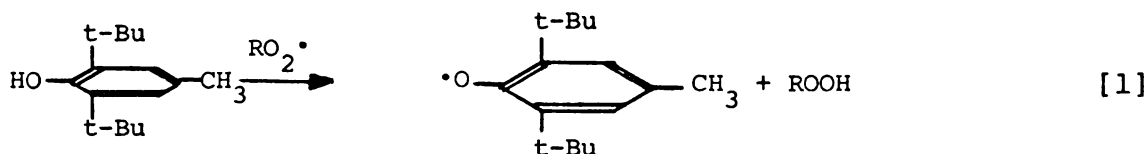


These three absorb UV energy to become enoles and release heat to return to the starting compounds, which means they have the function of an energy exchanger between photo and thermal energy. In blending of these compounds, compatibility with polymers, volatility at molding, and deformation by heat or migration to the outer system is influenced by R or X, which are the secrets covered by many patents. Any mixing methods cannot perfectly overcome these defects. Recent developments concentrated in making chemical bonds between polymers and additives by graft copolymerization or other polymerization methods (11, 12).

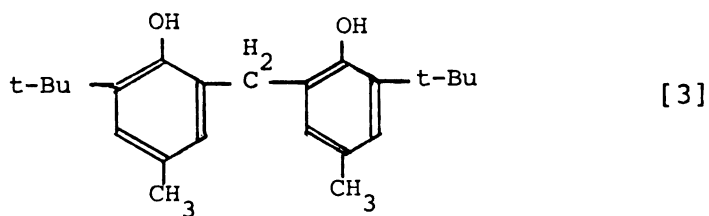
We find some marketed copolymerization methods that are better than the mixing method, and that support perfect dispersion, which is very important for stabilizers.

3.1.3. Antioxidant

An antioxidant requires a molecular structure that is able to catch reactive radicals and become inert after the combination. Some representative antioxidants, known to exist as stable radical compounds, are [1] hindered phenols, [2] aromatic amines shown in the figure.



Reactions with stabilized radicals are not expected, because they are protected by large components. But radicals emerging from polymers are comparatively easy to recombine with stabilized radicals to make inert products. The mixing of antioxidants has the same technical problems as UV absorbents, therefore high molecular weight antioxidants with high molecular modifiers are devised such as [3] and [4] (13).



But the perfect dispersion is an ideal state to receive the complete effect of the stabilizers. And this indicates that chemically bonded (e.g., graftcopolymerization) additives are more desirable than conventional mixing methods. Copolymerization with a vinyl compound, which has an antioxidant in it, is a very favorable method considering its ideal dispersion. This method contains some other applications such as degraders and other stabilizers (14).

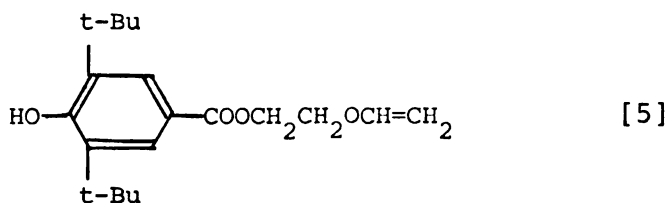


TABLE 3.1.--Heat Stability of Copolymer; PS+[5].

Time	[η]			
	0 (Hr)	20	144	240
PS	0.43	0.42	0.40	0.38
PS+ [5]	0.41	0.42	0.42	0.41

Other stabilizers are proposed in the plastic market, polymer types such as polysiloxane, which not only work effectively as antioxidants, but are less volatile and do not migrate. However the market share of these compounds is still small. The development of stabilizers is moving toward graftpolymerization (15) or copolymerization, but these procedures are available only in the laboratory. Even now many additives on the market are modified compounds of [3] or [4].

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3.2. Polymer Blend

3.2.1. Background on Polymer Blends

The polymer blend is a mixture of different kinds of polymers. Since the various properties of the blend polymers depend on compatibility, state of dispersion and the mixture state, we have to think not only of the mixture of polymers but of the mixture of additives and moreover of macromolecular reactions.

From the micro point of view, copolymers are a mixture of more than one polymer and, of course, homopolymers are also a mixture of various molecular weights and lengths. However, the one type of polymer, such as HDPE for blow molding, will have a similar molecular distribution from various sources.

The mixture of the polymer molecules, if it is thoroughly mixed (one molecule surrounded by another kind of polymer molecule) has definitely different properties, but this is hard to obtain. The polymer blends that have been produced consist of molecular dispersions from 1 μ to a few hundred μ .

3.2.2. Research on the Blend

The approach to the blend is quite old, for instance natural rubber with natural resins, rubber with asphalt, or phenolic rubber with phenol polymers. Then other combinations were studied, but they have not been successful until the introduction of ABS (polyacrylonitrilbutadienestyreneterpolymer).

In the production process, polymer blending is carried out at the final molding process to meet the particular market needs. At this time raw material makers are starting to pay attention not only to the new technology but to the innovating treatment of recycling plastics.

The blend polymers must have compatibilities between polymers, meanwhile other incompatible combinations should be investigated, since they sometimes have interesting properties as raw materials. We cannot neglect them because they may be needed for purposes of recycling and industrial materials. For example, incompatible blends indicate a phase separation phenomenon and may be applicable as a material for some important parts of several electronics products. Most scientists have researched only pure materials, even though natural polymers and materials are not pure. For example, wood and bamboo are composed of different structures and materials.

3.2.3. Properties of Blend

(a) Factors of mixture: In the case of a mixture of more than one polymer, it is necessary to know the properties of the polymers and the mixing methods as well as the mixing ratio.

(1) Property of a polymer

- a. Chemical conformation, configuration, stereoregularity, solubility parameter δ (16), phase separation.
- b. Degree of polymerization.
- c. Crystallinity (HDPE, LDPE)
- d. Reactivity of polymer; reaction between polymers, reaction between polymers and additives (cross linking).

(2) State of polymer

Solid--plastics, fibers, rubber emulsion (latex).
Liquid--liquid polymer (oligomer).

(b) Density of blend polymer: In the sample of roll blended polystyrene (PS) and polymethylmethacrylate (PMMA), the correlation between the blend ratio and density tells us that an actual density is lower than an arithmetic average (17). Evidence of this poor compatibility is shown in a whitened film. The expansion of the volume is caused by the incompatible phase of polymers; the larger the contact surface, the greater the expansion. On the other hand, if two polymers come close enough, the density will be greater than the arithmetic average.

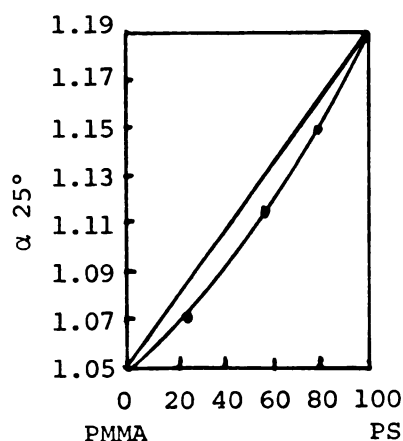


Figure 3.1.--Density of Polymer Blend PMMA+PS.

(c) Transparency: The transparency of the blend polymer does not depend much on the refraction of the materials. The refraction of PMMA is 1.49; PS, 1.59; and PVC, 1.54; but blended PVC-PS is white, while PVC-PMMA is clear. This mainly is the result of the proximity or closeness of the polymers.

(d) Physical property: The physical property of the blend is affected by the contact surface and the tensile strength of the blend depends on the degree of deformation given to the dispersed phase. Suppose a discontinuous phase B dispersed in a continuous phase A does not deform when A is charged by physical power. This shows that the compatibility between A-B is much smaller than the phase strength of B. The blend which does not transmit a load between A-B has the lower strength. However, if a chemical bond is formed between A-B, it must have stronger properties than without it, because of the increase of the molecular weight (18). The main factor in impact resistance is whether impact energy is absorbed by the blend. Deformation is also one of the important factors in absorbing the energy. However, the impact time is always so short that the deformation is an elastic one, therefore we should form the elastic element in the blend polymers. The toughness of materials needs a good balance between load and deformation when considering the impact resistance.

(e) Precipitation in cosolvents: The precipitation test is a method to precipitate two polymers in a solvent in which a precipitizer is added to measure their compatibility. The interaction between two polymers shifts a precipitation curve as shown at Figure 3.2 (b), but non-interaction between them indicates no clear shift at Figure 3.2 (a) (19).

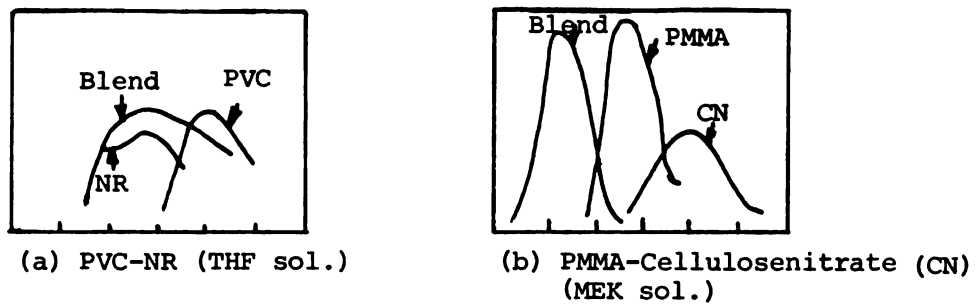


Figure 3.2.--Precipitation Curve.

(f) Phase separation: Two polymers dissolved in a solvent sometimes separate into multiple phases. A polymer which has a big clinging energy to itself results in the separation phenomenon because this energy excludes other polymers in the solvent.

(g) Measuring the glass transition temperature: On measuring the glass transition temperature of the blend polymer, some examples show different transition temperatures from those of the pure polymers. The glass transition temperature is the point at which the thermal activity is frozen. When there are two transition temperatures, the interaction energy between the two polymers is not great enough to shift the temperature curves. In general, a compatible blend gives a different thermal property from any of the pure polymers.

(h) Heat of mixing: For the mixing of materials, whether it is endothermic or exothermic depends on the thermal properties of the phase change. In the case that

the mixing is exothermic, blending is easy. From the thermodynamic characteristics the solubility parameter, δ , of polymers is obtained (21).

TABLE 3.2.--Heat of Mixing (20).

Polymer 1	Polymer 2	Solvent	Heat of Mix. (cal/mol)
PB	PS	Benzene	0.3
PB	NR	Benzene	0.3
NR	SBR (Styrenebutadiene)	Benzene	-0.3
Butylcellulose	PS	Anone	-1.3
Bytylcellulose	PS	Chloroform	-3.9
Nitrocellulose	Acetylcellulose	Acetone	+5.9
Nitrocellulose	PVA	Acetone	+0.9
Acetylcellulose	PVA	Acetone	-2.9
Polymethylacrylate	Polybutylacrylate	Acetone	0.0
Polymethylacrylate	PMMA	Acetone	-2.5
Polybutylacrylate	Polybutylmethacrylate	Acetone	-0.6
PVA (Polyvinylacetate)	PMMA	Acetone	-1.0

TABLE 3.3.--Solubility Parameter d (21).

Polymer	d (cal ^{1/2} /cm ^{2/3})	Polymer	d
PE	7.7~8.35	Polypropylacrylate	9.05
PP	8.2~9.2	Polybutylacrylate	8.8~9.1
Polyisobutene	7.8~8.1	Polyisobutylacrylate	8.7~11.0
PB	8.1~8.6	PMMA	9.1~12.8
PS	8.5~9.3	Polyethylmethacrylate	8.7~9.0
PVC	9.4~10.8	Polybutylmethacrylate	8.2~10.0
Polyvinylidenechloride	9.9~12.2	Polybenzylmethacrylate	9.8~10.0
Polyvinylbromide	9.5	Polyacrylonitrile	12.5~15.5
Polychlorotrifluorethylene	7.2~7.9	Polymethacrylonitrile	10.7
Polytetrafluoroethylene	6.2	Polymethylenoxide	10.2~11.0
Polychloroprene	8.2~9.25	Polytetramethylenoxide	8.55
PVA	9.35~11.05	Polypropyloxide	7.55~9.9
Polyvinylpropionate	8.8	Polyethylensulfite	9.0~9.5
Polymethylacrylate	9.7~10.4	Polydimethylcyloxane	7.3~7.6
Polyethylacrylate	9.25~9.4	Polyepychlorhydrine	9.4
Polyisoprene	7.9~10.0	Polyethyleneterphthalate	9.7~10.7

(i) Mixing state: The experimental methods to determine the mixing state are (1) measuring the refraction: transparency or phase microscopy; (2) polymer crystallinity: electrosopy or X-ray refraction; (3) glass transition temperature: T_g .

We can judge whether two certain polymers are soluble or not by the phase separation method or by the

heat of mixing measurement. Also, we can judge by the value of the solubility parameter, d . A phase separation may not appear in a polymer-polymer mixture, because of the high viscosity of the polymers. Examples of the mixing state of rubbers are described in Table 3.4 which reveals the relation between dispersed particles and the solubility parameters (21).

TABLE 3.4.--Mixing State of Rubbers.

Rubbers	Diameter of Particle (μ)	d
NR/SBR	2	8.15/8.54
Polychloroprene/SBR	0.5	9.38/8.54
Buna 85/NR	0.5	8.65/8.15
PB/NR	0.5	8.38/8.15
CisBR/NR	0.5	8.38/8.38
NR/Polyisoprene	2	8.15/8.15
NR/Butyl rubber	1	8.15/7.87
SBR/BR	2	8.54/8.38

3.2.4. Copolymers and Blend Polymers

A copolymer has the different segments or components in the molecular chain, while the blend polymer is the mixture of the different molecules. The random copolymer has the intermolecular plasticization phenomenon related to the random configuration, while the blend of

the different segments shows various phenomena such as repulsion and adsorption. It is a good advantage for the blend to add a third copolymer that has the same segments as blending polymers, and a good affinity to both polymers in the blend. However, it is impossible to synthesize all of these copolymers now. And so we set up a reaction in the blend; that is, a polymer reaction in the blended polymer. A chemical reaction needs a very short distance between reacting sites, therefore some techniques are devised to force functional sites closer together in the polymer blend. If the polymer has a dipole moment and a good tendency to come closer, we do not have to form a new bond. In some cases, heat, light, or a reagent is added to initiate the reaction between the less compatible phases. The conversion of this reaction does not have to reach up to 100%, because products can still contribute to a desirable property such as elongation strength.

3.2.5. Examples of the Blend

PVC blends.--The purpose of the blend is to improve processability, to improve plasticity, to improve physical and chemical properties, and to reduce cost, but the improvement of impact resistance is the main consideration in industrial research. However, in this section we are concerned with the multimixtures for the reclamation of the recycled plastics.

A high impact resistant PVC is marketed such as described in this summary.

(1) An ABS blend with PVC or an MBS (polymethylmethacrylate-PB-PS) blend with PVC: ABS and MBS are the most familiar blends with PVC, that are produced by a post polymerization method or graft polymer blend method. The good impact resistance of the blend depends on the graft ratio, graft components, and rubber particles. Transparent MBS-PVC is not unusual for certain market needs (24, 25).

(2) EVA blend: The copolymer EVA [PE-polyvinylacetate (PVA)] has a variable compatibility with PVC due to the PVA content. When more PVA is added, more compatibility with PVC is given to EVA, and the blend is more transparent and more highly impact resistant. So far a high PVA content of EVA has appeared in the market for blending with PVC, and it is said that crosslinked PVC with EVA has outstandingly high impact resistance.

(3) Chlorinated PE (CPE): The history of chlorinated PE began in the 1950s, however it is only lately that CPE received wide application in industry, for instance "Placon CPE" of Allied Chemicals, "Tyrine" of Dow Chemicals, and "Holoflex" of ICI (27).

The physical and chemical properties of chlorinated polyethylene depend on the distribution of chlorine, degree of chlorination, distribution of molecular weights, and

crystallinity. It is said that non-crystalized CPE with 35% chlorine is most favorable for PVC blending.

In view of the fluctuating market, it is unwise to invent a new polymer for a single use, therefore an improvement of the general purpose polymers by way of the polymer blend methods and the graft copolymerization method has attracted wide attention. Recent trends of blending are toward multicomponent systems, which are the mixture of the intermediate graft copolymers to retain the characteristics of blending component polymers (28, 29).

A good product is the nonflammable PE blend with CPE proposed by Dow's "MX2243.04," where CPE has 36% of Cl, 1740 lb/sq.in of tensile strength, 69% of elongation, 111 lb/sq.in of tear strength (30).

In Table 3.5, they describe remarkably improved tear strength of the blended PVC and PE.

(4) EVA/PVC graftpolymer: Bayer Chem. (Germany) developed 1:1 PVC/grafted EVA, that has more impact resistance than EVA blended with PVC and better weather resistance, but not tensile strength (31).

This graft polymer is available to produce both hard and soft PVCs without changing the plasticizer.

ABS and MBS do not have good weather resistance because of the double bonds in the main chains, so EVA without double bonds in the main chains takes their place.

TABLE 3.5.--MX 2243.04 Blend with PVC and PE.

Blend Polymer	Additives (%)	Tensile (lb/in ²)	Elongation (%)	Tear (lb/in ²)	Melt Viscosity (poises)
--	--	1740	690	111	3660
--	A ₁ 20	1910	775	128	3820
--	T ₁ 10	1860	760	156	3770
20% PVC	--	1730	550	163	3890
20% PVC	A ₁ 20	1540	400	161	4060
20% PVC	T ₁ 10	2220	480	194	4015
20% LDPE	--	1600	725	180	2310
20% LDPE	A ₁ 20	1260	610	178	2560
20% LDPE	T ₁ 10	1410	650	209	2375
10% HDPE	--	2090	740	207	3355
10% HDPE	A ₁ 20	1580	635	187	3650
10% HDPE	T ₁ 10	1970	720	221	3445

A₁: Calcium acetate.

T₁: Talc.

In the PVC group such multicomponent plastics as PVC-PVC/polycarbonate, PVC-EVA-CPE, PVC-EVA-SBR, PVC-EVA-PMMA, PVC-PVC/PE-ABS, PVC-PVC/PE-PB, PVC-PE chlorosulfonate-AS, PVC-polychloroprene-AS, PVC-PVC/PE-CPE have been developed(33), and PVC-PE-CPE is reported to have better impact resistance than PVC-ABS (34). The high flowing PVC-PP copolymer or low molecular weight PVC such as postchlorinated PVC is under development to be blended for heat resistance improvement (35, 36).

PS blends.--In addition to the high impact resistance, efforts for improving ABS and MBS were aimed at getting high heat resistance and better transparency and a processability of foamed plastic (37). Since low weather resistance is the major defect for the high impact polymers, the sunlight resistant plastics such as PS and AS (acrylonitrile-styrene) are coated on ABS or MBS (38).

The blend of ABS with polycarbonate ("Cycloy" of Marbon Co.) shows better impact resistance and processability than polycarbonate, and better weather resistance than ABS (39). However, PS/PB (polybutadiene) block copolymer (by Shell Chem. Co.) has almost the same compatibility with PS as the blended PS/PB, and the same stress-strain curve as PB rubber (40).

Olefin blends.--The poor properties of PE are stress cracking, low weather resistance, and poor printing ability, and those of PP are low weather resistance, impact resistance at lower temperatures, and poor dyeing ability.

Polyvinylbutylol and polyethyleneisophthalate as well as synthetic rubbers are blended with PE to improve stress cracking. A graft copolymer of PE with diene or vinyl is impact resistant. A halogenated copolymer blend is devised to lower the inflammability of polyolefins, though incompatibility is a severe problem. PP has improved impact resistance by adding butylrubber, polyisobutylene, EPrubber (ethylenepropylene), and polybutene-1

(alkylrubber); however, due to the research development ethylene/butene-1, EVA, propyleneoxide rubber, ethylene/acrylate, polybutadiene or ethylene/propylene block copolymer are mixed to create even better impact resistance nowadays. Also, the multiblend systems such as PP-polyisoprene-PE, PP-PE-EPT, PP-polyisobutylene-EVA are proposed to mend impact resistance of PP. A dyeing ability of PP is crucial when it is formed to fibers, and so vinylpyridin and epoxy-polymer which have significant dyeing ability are blended. The particular blend such as PE-Nylon-polymer with metal ion has properties both of PE and of nylon. The other blends such as CPE-AS blended with butyl rubber or PMMA, and CPE-EVA, EVA-PS are suggested for the impact resistance improvement of PP (41).

Other polymer blends.--The aliphatic polyamide blended with aromatic polyester has been attempted to produce a new fiber.

PMMA is blended with EVA/MMA (methylmethacrylate) graft copolymer or PMMA-EVA blend to raise impact resistance. Polycarbonate blended with polyacrylate or PE-PS has improved cracking resistance and impact resistance (42). Polyacetal mixed with ABS, PB or polybutene is stable against heat and impact. Polycarbonate, polyacetate or polyamide blended with PE and their grafted copolymers with PE show the good processability and impact resistance (43).

Ultrasonic welding.--The ultrasonic welding (20,000 cycle/sec) of plastics is applied to the process to connect parts in plastic manufacturing. The material should be a thermoplastic which gets the frictional heat being generated between the two plastics to be joined. This results in a molten flowing and fusion of two parts into a permanent bond. The compatibility between two components is a crucial one for this process, and melting temperatures are also significant, because this is a kind of heat process. The data of the compatibility of thermoplastic materials shown in Table 3.6 is applied for the polymer blend and the possibility of the manufacturing development. The mass scale process of ultrasonic welding will be developed to treat a vast amount of plastics at once, however many barriers are predicted at this time of the beginning of the research (44).

3.2.6. Future of Blending

The aim of the polymer blend is mainly to improve physical properties such as high impact resistance. The compatibility of additives such as plasticizers, pigments and filler has been paid less attention than that of polymers. However, from this time on, polymeric additives will be developed to reform the additive system and enhance the physical properties of the polymers. The application of the polymer blends in metals, woods, glasses (glassfibers), cement and paper industries will be further studied in the future.

TABLE 3.6.--Compatibility of Thermoplastics (44) in the Ultrasonic Welding.

	ABS	ABS/Polycarbonate	PVC/ABS alloy	Acetal	Acrylics	Acrylic/PVC	AS	Butylates	Nylon	Polycarbonate	PE	PST	PPO	PVC	SAN/NAS
ABS	⊗	⊗	○		⊗	○	○	○				○			○
ABS/Polycarbonate	⊗	⊗	○		○	○	○			⊗					○
PVC/ABS alloy	○	○	⊗		○	○	○							○	
Acetal				⊗											
Acrylics	⊗	○	○		⊗	○	○			○					○
Acrylic/PVC	○	○	○		○	⊗	○							○	
AS	○	○	○		○	○	⊗					○			○
Butylates								⊗							
Nylon									⊗						
Polycarbonate		⊗			○					⊗					
PE											⊗				
PST	○						○					⊗			○
PPO													⊗		
PVC			○			○								⊗	
SAN/NAS	○	○			○		○					○			⊗

⊗ denotes compatibility.

○ denotes some but not all grades and compositions compatible.

Japan Steel Works disclosed a plastics recycling installation with a capacity of 440 lb/hr. In this pilot plant, waste plastics are composed generally of 40% of LDPE, 10% of HDPE, 10% of PP, 15% of PS, 15% of PVC, and 8% of thermoset or other plastics. The remaining 2% is made up of non-ferrous metals and other wastes. This plant consists of crushing, separating of heavy materials, grinding, magnetic separating, washing and pelletizing, in which polymixture pellets were produced at a cost of about 3¢/lb in 1973; however, the mechanical strength is not good enough to meet the market needs (45). As shown in Figure 3.3, plastics made by blending methods have desperately poor compatibilities to build a mass recycling system and to produce a wide market root.

There will be big barriers to pass over before we will have completed the technology to blend these commercial plastics successfully.

TABLE 3.7.--Scrapped Plastics and CPE (46).

	Elong. (%)	Tensile (psi)	Impact (psi)
100% scrap	11	1,450	0
15% CPE	11.7	1,715	0.45
17.5% CPE	12.7	1,690	0.54
20% CPE	15.7	1,715	0.76
22.5% CPE	17.7	1,712	1.5
25% CPE	20	1,600	1.6
27.5% CPE	22	1,600	2.83

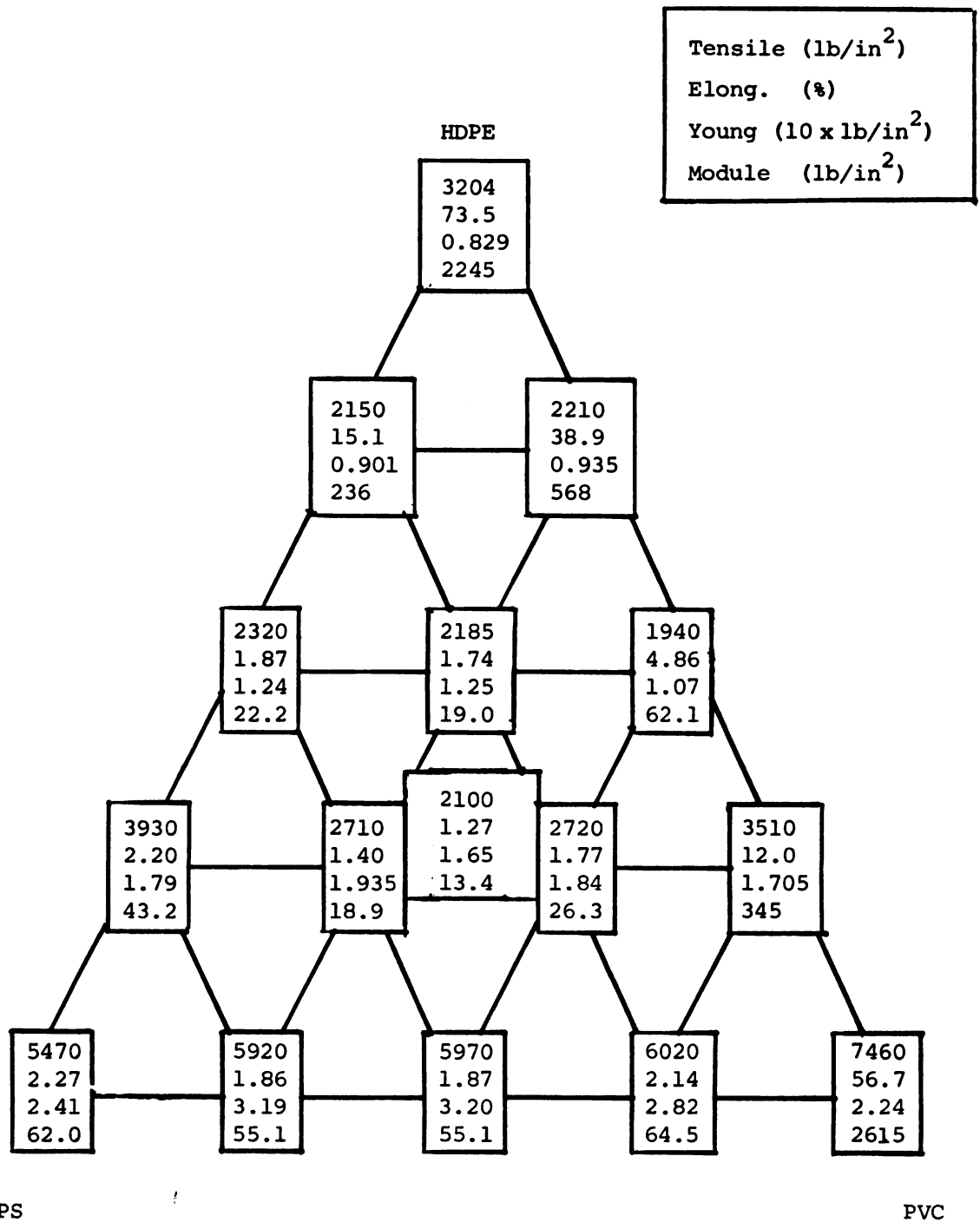


Figure 3.3.--Properties of the Blended PE, PS and PVC (46).

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3.3. Biodegradation

Biodegradation is a process of degradation initiated by living organisms or by products directly derived from such organisms. There are many reports indicating that general purpose commercial plastics such as PE, PP, PVC, and PS are not biodegradable. However, some reports revealed that even such kinds of polymers are degradable by a few strains of bacteria. These biodegradation phenomena are crucial for plastic manufacturers.

The biodegradation reaction is generally classified as:

- (1) degradation of polymers including biodegradable copolymer and hetero chain polymer,
- (2) degradation of the low molecular weight polymer,
- (3) biotic attack to the impurities, such as additives, fillers, and plasticizers.

With the significant mechanism in the degradation context, it is

- (1) simple oxidation,
- (2) hydrolysis,
- (3) other reactions by microorganisms,
- (4) stresscracking,
- (5) attack by insects, rodents, and marine creatures.

3.3.1. Basic Data of Biodegradation

The biodegradability of commercial plastics has been investigated by many researchers by ASTM test, D-1924, and D-2676T; which requires 3-week exposure to the environment, then assigned growth ratings as shown (47):

Growth ratings: 0--no growth
 1--trace (less than 10% covered)
 2--light growth (10 to 30% covered)
 3--medium growth (30 to 60%)
 4--heavy growth (60 to 100%)

Table 3.8 indicates that most commercial plastic products are resistant to bio-attack, although some samples are susceptible. No growth was seen on the samples extracted with toluene, which explains that the

TABLE 3.8.--Biodegradability of Commercial Plastics.

Plastics	Growth Rating
1. PE household wrap	2
2. Sample 1, extracted with toluene	1
3. PVC-epoxidized soybean oil plasticizer	3
4. (3) extracted with toluene	1
5. PP	1
6. PS	1
7. PE terephthalate	1
8. Polyvinylidenechloride	1
9. ABS	0
10. ABS-Polycarbonate blend	0
11. Butadiene-acrylonitrile rubber	0
12. AS	0
13. Rubber modified PS	0
14. Styrene-butadiene blockcopolymer	0
15. PMMA	0
16. Rubbermodified PMMA	0
17. PET (Polyethyleneterephthalate)	0
18. Polycyclohexanedimethylterephthalate	0
19. Bisphenol A polycarbonate	0
20. Bisphenol A polysulfone	0
21. Poly (4-methyl-1-pentene)	0
22. Polyisobutylene	0
23. Chlorosulfonated PE	0
24. Celluloseacetate or butylate	0
25. Nylon-6, nylon-66, nylon 12	0
26. Polyurethane	4
27. Polyvinyl butylal	0
28. Polyformaldehyde	0
29. Polyvinylethylether	0
30. Polyvinylacetate	1

polymermolecule itself is not attacked, but most commercial plastic samples have biodegradable additives. Some papers did not explain even whether additives in the polymer are extracted or not, but stated only the conclusion of their experiments.

The antioxidants and the ultraviolet absorbents are definitely resistant to bioreaction and do not allow any growth on the test samples. But the slip agents and plasticizers are receptive to biodegradation, since some of them have amide, phosphate, and ester groups in their structures. PVC, which contains many additives, is easily attacked by bacteria in the air, which is supported by the result of the experimental data in Table 3.9.

The effects of the molecular weight of a polymer and of branching are important to biodegradation, and a number of investigations have been reported in papers. Interesting results are given in Table 3.10. It is observed that when the molecular weight increased from 451 to 507 the growth rating had drastically shifted from 4 to 0, which confirms that the biotic reaction must have a high degree of specificity. Branching hydrocarbons are also resistant to biodegradation as seen in the petroleum protein reaction where only normal parafins (no branching) are consumed by the fungi.

Even in the low molecular weight region, branched samples do not indicate biodegradability, while straight

TABLE 3.9.--Biodegradability of Additives (47).

Additive		Growth Rating
1. Antioxidant		
Hindered phenol		0
Nonylphenol phosphate		0
2. Slip agent		
C ₂₂ primary amide		4
C ₁₈ "		4
Olealylpalmitliamide		2
3. UV absorbents		
2-hydroxy-4 dodecycloxy benzophenone		0
P-octylphenyl salicylate		0
4. Plasticizers		
Di-2-ethylhexylphthalate		0
Tricresil phosphate		1
Epoxidized soybean oil		4
Aliphatic polyester		4

TABLE 3.10.--Biodegradability of Straight Chain Hydrocarbons (47).

Compound	Formula	MW	Growth Rating
1. Dodecane	C ₁₂ H ₂₆	170	4
2. Hexadecane	C ₁₆ H ₃₄	226	4
3. Octadecane	C ₁₈ H ₃₈	255	4
4. Docosane	C ₂₂ H ₄₆	311	4
5. Tetracosane	C ₂₄ H ₅₀	339	4
6. Octacosane	C ₂₈ H ₅₈	395	4
7. Dotriacontane	C ₃₂ H ₆₆	451	4
8. Hexatriacontane	C ₃₆ H ₇₄	507	0
9. Tetracontane	C ₄₀ H ₈₂	563	0
10. Tetratetracontane	C ₄₄ H ₉₀	620	0

chain hydrocarbons give a growth rating of 4 as shown in Tables 3.10 and 3.11.

The result from these data is supported by LDPE samples, in which the structure of the polymer is similarly branching to the samples of Table 3.11.

TABLE 3.11.--Effect of Branching (47).

Compound of Structure	MW	Growth Rating
2, 6, 11-trimethyldodecane $C_{17}H_{32}$		
$ \begin{array}{ccccccc} & C & & C & & C & \\ & & & & & & \\ C & -C & -C & -C & -C & -C & -C \end{array} $	212	0
2, 6, 11, 15-tetramethylhexadecane $C_{20}H_{42}$		
$ \begin{array}{ccc} & C & & C & \\ & & & & \\ (C & -C & -C & -C & -C & -C) \end{array} $	283	0
2, 6, 11, 15-tetramethylhexa Squalane $C_{30}H_{62}$		
$ \begin{array}{ccccccc} & C & & C & & C & \\ & & & & & & \\ (C & -C & -C & -C & -C & -C & -C & -C & -C) \end{array} $	423	0

Since HDPE is linear and non-branching, the lower molecular weight samples 1 and 2 in Table 3.12 are as degradable as the low molecular weight straight chain olefins (47).

TABLE 3.12.--Effect of MW on Biodegradability (47).

		MW	Growth Rating
1.	HDPE	10,970	2
2.	HDPE	13,800	2
3.	HDPE	31,600	0
4.	HDPE	52,500	0
5.	HDPE	97,300	1
6.	LDPE	1,350	1
7.	LDPE	2,600	3
8.	LDPE	12,000	2
9.	LDPE	21,000	1
10.	LDPE	28,000	1

Also, in the experimental data of Table 3.12, LDPE indicates the same trend as observed in HDPE except 6 and 7, where 6 is branching and greasy, while 7 is straight chained crystalline sample.

The same kind of discussion is described with the pyrolyzed HDPE and LDPE in Table 3.13, in which the lower molecular weight is favorable on biodegradability.

TABLE 3.13.--Biodegradability of Pyrolyzed PE (47).

Pyrolysis Temp. °C		Viscosity av. MW	Growth Rating
HDPE	Control	123,000	0
HDPE	400	16,000	1
HDPE	400	8,000	1
HDPE	500	3,200	3
HDPE	535	1,000	3
LDPE	Control	56,000	0
LDPE	400	19,000	1
LDPE	450	12,000	1
LDPE	500	2,100	2
LDPE	535	1,000	3

Notice the growth rating of PS shown in Tables 3.14 and 3.15 is different from PE because of its aromatic pendant --benzene.

TABLE 3.14.--Biodegradability of PS (47).

Average MW	Growth Rating
214,000	0
62,000	0
44,000	0
19,000	0
14,000	0
5,900	0
2,100	0
600	0

TABLE 3.15.--Biodegradability of Pyrolyzed PS (47).

Pyrolysis Temp. °C	Average MW	Growth Rating
Control	220,000	1
400	93,000	1
450	68,000	0
500	26,000	0
535	4,000	0

The only degradable synthetic high polymers are those having aliphatic ester linkages in the main chain. The biodegradability of the polymer in which the pendant component is composed of esters such as polyvinylacetate is different from the main chain polyesters.

TABLE 3.16.--Biodegradability of Polyester (47).

Esters	Reduced Visc.	Growth Rating
1. Caprolactone polyester	0.7	4
2. Pivalactone 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

Since polyester does not have a simple formation like PE and PS, the discussion of its biodegradability has to cover different aspects. However, it may be summarized that this is the copolymer which has the bioreactive comonomer.

3.3.2. Biodegradable Polymers

Biodegradable copolymers and heterochain polymers.--

An attempt to synthesize a biodegradable copolymer has not much been carried out, and some specialists say it is still very hard to predict the completion of this technology. Especially, commercial polymers such as PE, PP, and PS are not treated by this method. A few biosensitive comonomers which have hydroxide, acid, and ester branches are tested

for the purpose of degradation; however, the result indicates that only a negligibly small growth is allowed on the samples.

TABLE 3.17.--Biodegradability of Comonomers (47).

	Comonomer	% Comonomer	Growth Rating
1. PE	Vinyl acetate	18, 33, 45	1
	Vinyl alcohol	13, 70	0
	Acrylic acid	15	0
	Sodium acrylate	20	0
	Ammonium acrylate	20	0
	Ethyl acrylate	18	0
	Dodecyl acrylate	25	1
	Carbon monoxide	6, 8	0
2. PS	Acrylic acid	16	0
	Sodium acrylate	16	0
	Dimethyl itaconate	30	0
	Ethyl acrylate	50	0
	Acrylonitrile	28	0
	Methacrylonitrile	87	0
	Dodecyl acrylate	15	0

As mentioned above, the biodegradable copolymers are considered very hard to synthesize, because they have the carbon chains which are inactive to microbial reaction even when they contain some amount of biosensitive branches. The branch, even if it is consumed by bacteria, does not make the main chains biodegradable. But heterochain

copolymers (they may not be classified as copolymers, actually) such as polyester, polyurethane, and nylon, are comparatively sensitive to biodegradation and so they may have a big potential for future development.

Darby and Kaplan examined the biodegradability of diols, polyesters, and urethanes, and as the experimental result, they indicated that polyesters support heavy growth on samples in a few weeks, as shown in Table 3.18 (48).

TABLE 3.18.--Maximal Growth Rating of Fungus Mixture on Polyurethanes and Polyesters.

Diol	Monomer	Polymer	
		TDI	MDI
1. Ethyleneglycol	2	0	1
2. 1.3--Propanol	2	1	2
3. 1.4--Butanediol	4	2	2
4. 2.3--Butanediol	4	2	0
5. 2-Methyl-1.4-butanediol	4	2	1
6. 2.2-Dimethyl-1.3-propanediol	3	2	0
7. 2.3-Dimethyl-2.3-butanediol	2	0	1
8. Diethylene glycol	2	1	1
9. Triethylene glycol	2	1	1
10. Polypropylene glycol (MW 400)	2	2	2
11. Polypropylene glycol (MW 1320)	2	3	2
12. Bis (4-hydroxyphenyl) dimethylsilane	1	0	0
<u>Polyesters</u>			
1. Polyethyleneglycoladipate	4	4	4
2. Poly-1.3-propanedioladipate	4	4	4
3. Poly-1.4-butanedioladipate	4	4	4

TDI: Tolylendiisocyanate.

MDI: Methylenediisocyanate.

Generally speaking, nylon is resistant to fungal attack, but its monomers are sensitive. However, some reports mentioned that even nylon is biodegradable in the soil burial test.

On the other hand, since most natural polymers such as natural rubber and cellulose are biodegradable, modified natural polymers have been applied as thermoplastics. For example, hydroxypropyl cellulose (brand name is Klucel) does not only show thermoplastic properties, but is soluble in water below 45°C, biodegradable, non-caloric, and non-nutritive when digested (49).

Amylose starch film is edible, water-dispersible, and mechanically strong. When adopted as a packaging material, its fermented starch also provides modified cellulose which is thermoplastic, water soluble, and easily modified with acid to make polyesters (50).

Impurities for biodegradability.--Many fillers, plasticizers, and modifiers such as oligomeric esters for PVC mixed in the plastics are regarded as biodegradable. In 1973, a very simple but practical method was discovered by Griffin. He mixed only starches to control the biodegradation rate of commercial plastics. In his report, starches are added from 20 to 50 wt. % to the polymer (51). The physical properties are reported not worse than expected, moreover even high molecular weight polymers are degradable as well as low molecular weight ones. He

mentioned that the biodegradability depends on the surface condition of the polymers exposed to air and all the plastics could be biodegradable by the surface reformation with the readily decomposed starches. When plastics are manufactured most of commercial ones are processed with plasticizers such as oligomeric esters and alcohols. However, these additives are not stable to the bioreaction, and therefore commercial plastics are sometimes decomposed while stored if Griffin's proposal is right. The examples of highly biodegradable plasticizers are di-2-ethylhexyl azelate, di-n-hexyl adipate, di-isooctyl adipate, tetrahydrofurfuryl oleate, triethylene glycol, epoxidized soybean oil, and butyl ricinolate (52).

3.3.3. Particular Approach to Biodegradability

A practical approach was carried out by Wallhauser, who has studied the behavior of composting of urban refuse with the systematic treatment in a bioreaction vessel. Collected refuse is bioreacted in aerated cells at 65-85°C for 10-20 days and the finished compost remains as a byproduct. In his data this method shows a few defects such as a long reaction time, non-continuous process, and high cost of disposal (53).

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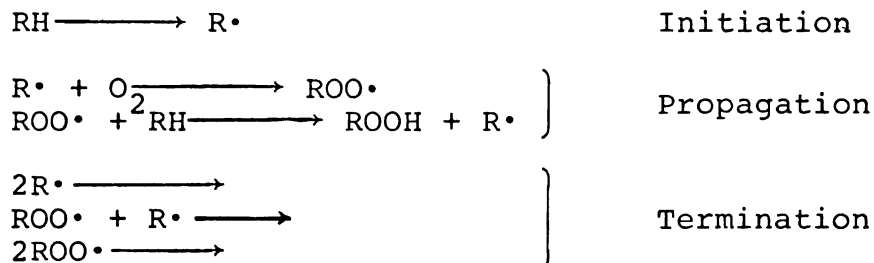
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3.4. Chemical Degradation

3.4.1. Background of Chemical Degradation

The factors influencing photochemical degradation reactions are (1) factors external to the polymer and (2) inner factors of the conformation of the polymer. The external factors are light, oxygen, ozone, corrosive gas like nitrogen oxide, and impurities mixed in the polymer. The internal factors affecting the degradation reaction are the conformation of polymers. The reaction processes of the chemical degradation contain radical or non-radical pathways. The first example of the radical degradation reaction is a spontaneous oxidation called auto-oxidation.



The second one is the radical initiation with peroxides and halogenated compounds, and the third one is the reaction of photosensitizers. One of them is a radical initiator like benzophenone which extracts hydrogen from a molecule. Another one is an oxygen-sensitizer like methylene blue.

The decomposition step of polymer hydroperoxides and peroxides is so slow that light, or heavy metals or their salts are added in the reaction system as catalysts.

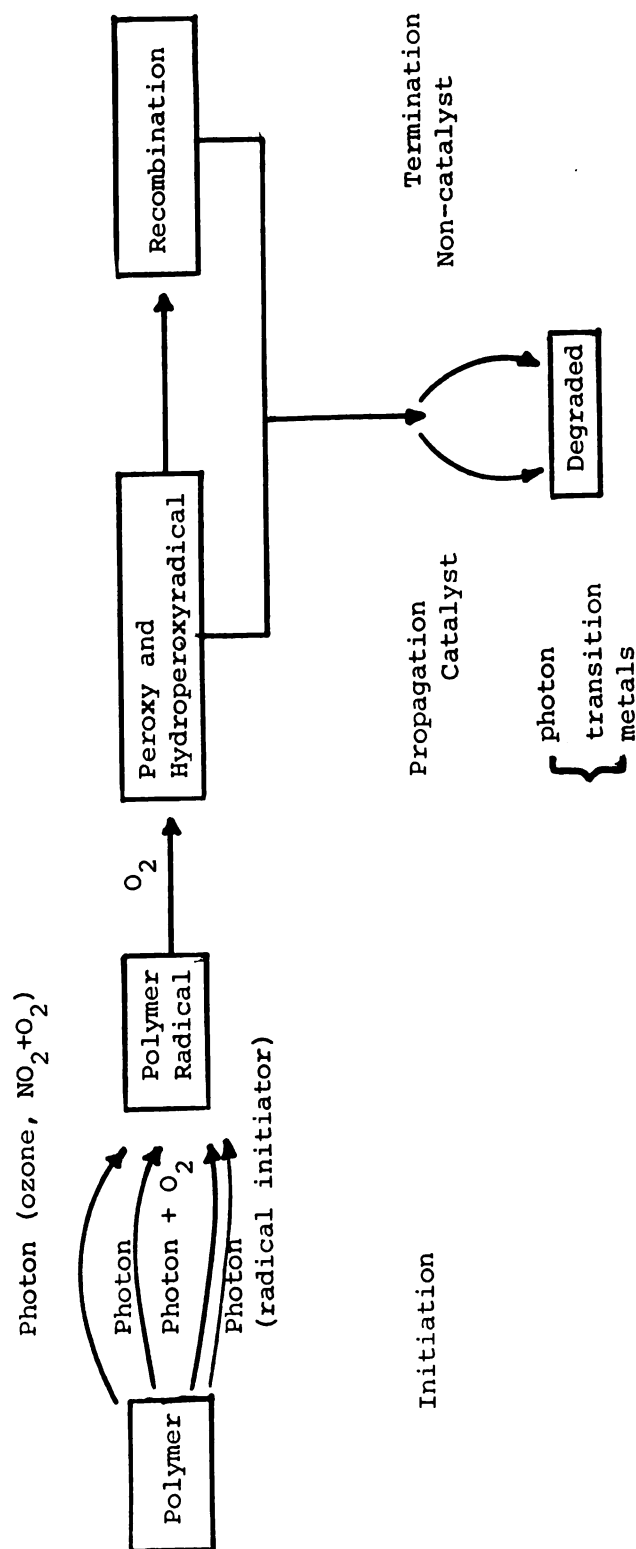


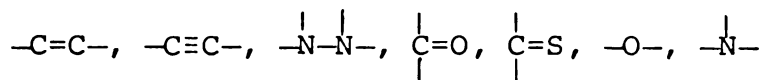
Figure 3.4.--Degradation Process.

The chemical degradation without the production of any toxic degraded products needs some particular configurations in main chains, as described in Table 3.19.

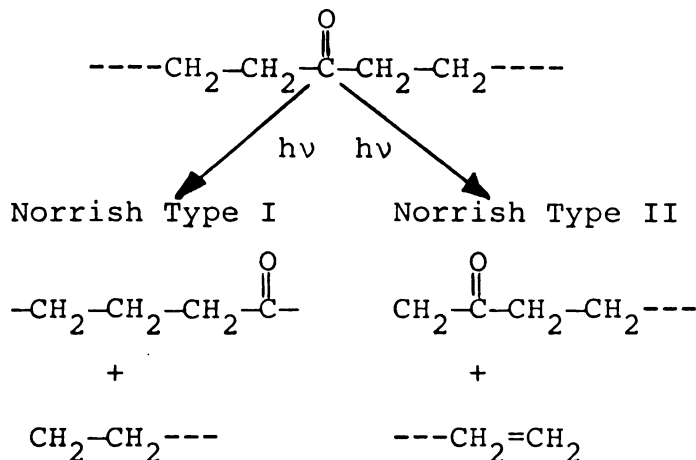
TABLE 3.19.--Examples of Easily Oxidized Polymers.

Configuration	Polymers
$\begin{array}{c} \\ -C-C-C- \\ \\ R \end{array}$	PP, HDPE, EP rubber
$\begin{array}{c} & & \\ -C-C=C- \\ \end{array}$	Polydiolefin, SBR, NBR, ABS
$\begin{array}{c} H \\ \\ -C-N- \\ \end{array}$	Polyethyleneimine
$\begin{array}{c} \\ -C-O-C \\ \end{array}$	Polyether
$\begin{array}{c} O-R \\ \\ -C- \\ \\ H \end{array}$	Polyvinylether
$\begin{array}{c} H \\ \\ -C-N-C- \\ \quad \\ \quad O \end{array}$	Polyamide, polyurethane

In general the polymer which has a pi bond or a lone pair in the main chain is photosensitive



Photosensitive structure



for example, the Norrish Type II reaction in ethylene-carbonmonoxide copolymer is common when it is photodegraded (54).

3.4.2. New Developments in Accelerated Degradation

Photosensitive polymers.--Guillet has established the authoritative technology of the photodegradable copolymer with vinylketone at wave length, 300-350 mμ, where vinylketon is copolymerized with many kinds of vinylcomonomers, and the degradability is controlled by light exposure time from a few days to 6 months depending on comonomers. He explains that there are no changes on chemical and

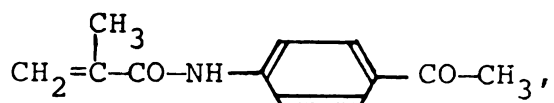
physical properties and no side effects on heat stability of polymers even if modified with vinylketon. The cost increase is only minimal (he claims) because of low content of vinylketon, hence Guillet has licensed with Ecoplastique (Canada) and Royal Packaging Ind. (Holland) to distribute his know-how in the market (55).

Such companies as Union Carbide, Eastman Kodak, Ethylene Plastique and Mitsubishi have applied Guillet's method to copolymerize ketoniccarbonyl into polymer main chains (56).

As presented in Figure 3.5, Kato modified vinylketone with aminoacetophenone (MAA) and 2, 6-di-tert-butylaminomethylphenyl (TBAP) which he explains more degradable and controllable when mixed with antioxidants (57).

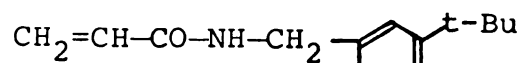
Eastman Kodak has a patent of ethylene-carbonmonoxide copolymer for temporary food packages. The company claims that when 8% of carbonmonoxide is copolymerized with ethylene, the wrapper is decomposed by the end of the fourth day.

Ethylene Plastique also developed ethylene-carbonmonoxide copolymer containing 0.2-9% of carbonmonoxide, which is applied as coating materials, and this copolymer, when copolymerized at 2% content of carbonmonoxide, gets badly cracked and torn after 2-3 months (58).



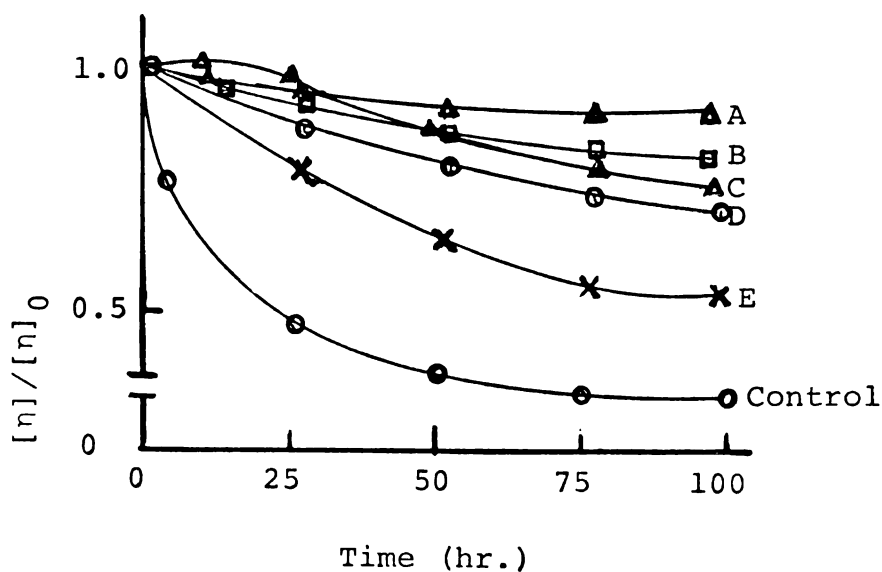
MAA (aminoacetophenone)

Ketone derivatives



TBAP

(2,6-di-tert-butylamino-ethyl phenyl)



- (A) 2.5 mol % of phenyl- β -naphthylamine
 (B) 2.5 mol % of 2,6-di-tert-butyl-p-cresol
 (C) 2.5 mol % of 4,4'-thio-bis-(6-ter-butyl-m-cresol)
 (D) 0.5 mol % of 2,6-di-tertbutyl-p-cresol
 (E) 2.5 mol % of 2-(octadecyloxylcarbonylethylethyl) sulfide

Figure 3.5.--Controllability of Degradation of PMMA-MVK (5,6 mol %) Copolymer in Toluene.

Mitsubishi has studied the copolymerization of methylvinyl ketone to such polymers as PS, PVC, PE, PP, and PMMA, and when 0.3%-10% of methylvinyl ketone is added, the gradual degradation was obtained (59).

Low stable polymers.--Takeuchi presents an example of the polymer which has a low stability to light. As shown in Figure 3, 6-syndiotactic 1, 2-polybutadiene is photo degradable without any sensitizers, and controllable with stabilizers. It is suitable for food packaging materials because of nontoxicity, and the service life of this polybutadiene film can be controlled by a proper selection and combination of stabilizers (60).

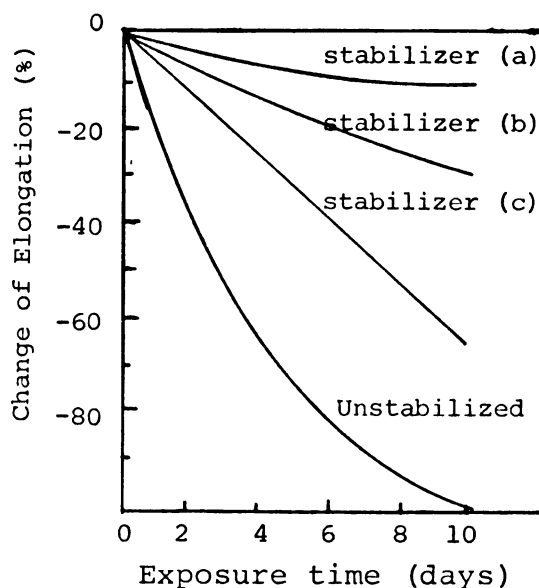


Figure 3.6.--Weathering Test of Syndiotactic 1,2-Polybutadiene Film by Outdoor Exposure.

Mitsui Toatsu Chem. developed the same type of copolymer as Takeuchi's of styrene and butadiene by 1,2-polymerization method. Now it is surveyed in the market to set a good reputation and to get more information for Suntax, the brand name of this copolymer (61).

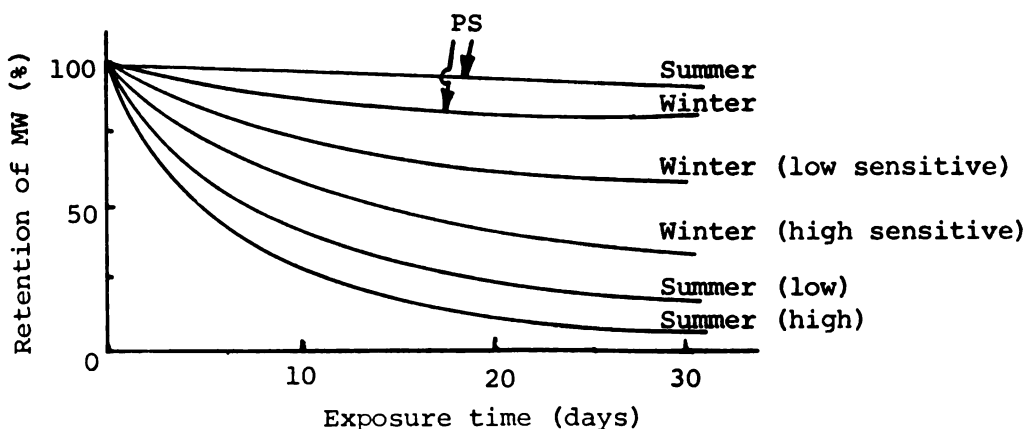
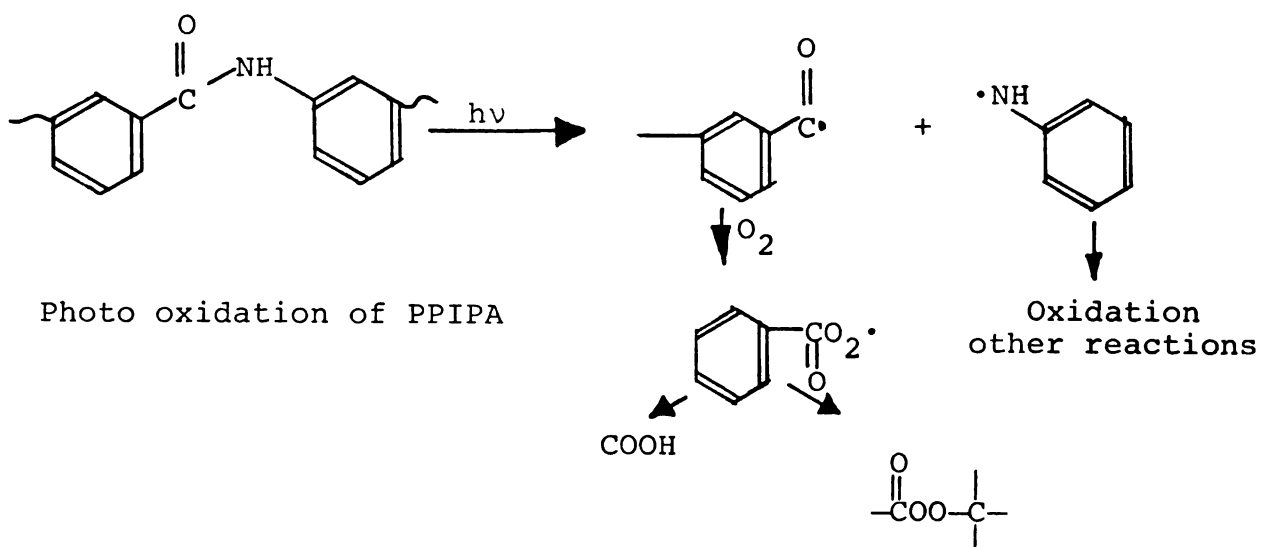


Figure 3.7.--Degradation Rate of Suntax in Seasons.

Poly (1,3-phenylene isophthalamide) (PPIPA) is not a general purpose plastic but its fibers and papers are marketed by Du Pont by the trade name Nomex, and enjoys a good reputation. Du Pont explains that it is remarkably susceptible to UV degradation, because it absorbs most of the energy of sunlight in the wavelength range of 355 mμ to 400 mμ. According to the disclosed data, Nomex retains only half of the original breaking strength and one-third of elongation strength, and discolors noticeably after 100 hour exposure in an Atlax xenon arc weatherometer (62).



Photosensitive additives.--On the pathway of radical reactions, the additives form free radicals which pull out hydrogen from the polymer chains directly or indirectly through an intermediate hydroperoxide, and then they make polymers break down.

Scott suggests the effective photosensitizers such as iron stearate at 1.3% content and iron dibutyldithiocarbamate at 0.013%, and also refers to cobalt, copper, chromium, manganese and cerium metal salts, and numerous other anti-oxidants. In his paper, he reported on the photodegradation of LDPE, HDPE, PP, PS, high impact PS, polyvinylchloride-acetate and PVC. The effect of prooxidants on the UV degradation of polyolefin is shown in Figure 3.8, where the carbonyl index in the polymer is related to the physical properties of the plastic; that

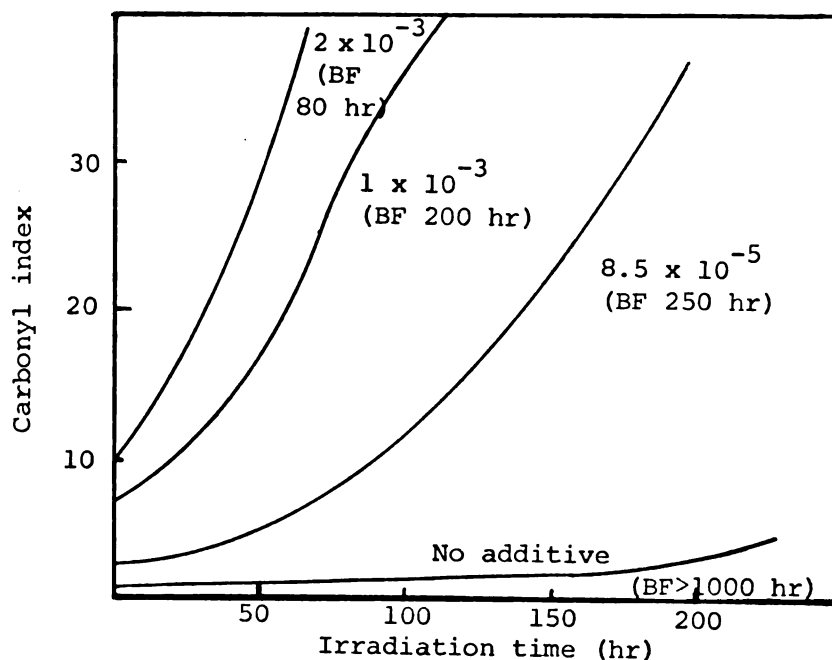


Figure 3.8.--UV Degradation of LDPE Containing Fe(III)-acetylacetonate, conc. [Moles/100 g] (BF = Brittle Fracture).

is, the high carbonyl index polymer rapidly loses its strength and becomes brittle (63). Also, it is well known that metal ions such as aqueous ferric chloride catalyze the photodegradation. Scott mentions that metal ion chloride initiates the photooxidation of PP. According to the feature of a magazine, he has patents of these photosensitizers all over the world and is licensing with many manufacturers including U.S. companies (63).

AB Tetrapack developed a new type of plastic for packaging which decomposes rapidly when discarded outdoors but retains its strength inside. In this plastic, the

additive has double bonds which are attacked by oxygen and light, and decompose the polymer chains. Also they disclosed the data that LDPE makes crosslinks between chains with the ultraviolet ray energy; however, the additives such as parafin, oleic acid, and soya oil blended in the LDPE film inhibit this crosslinking reaction and cause a more rapid decomposition (64, 65).

Princeton Chemical Research invented the easily decomposing film of polybutene-1 used on farms, where they devised a balanced combination of antioxidants, UV absorbents, and other additives. Since polybutene-1 is susceptible to UV degradation, UV may not always be necessary. In any event, Princeton Chemical will soon be marketing a polybutene-1 version called Ecolan. In spite of the expensive monomer costs of polybutene-1 compared to ethylene, they believe that the overall cost of polybutene-1 mulch will be almost the same as that of PE mulch considering the high labor costs to dispose of the non-degradable PE mulch after use.

Eastman Kodak disclosed the application of prooxidant additives with pacifying agents (e.g., carbon black) to LDPE, PP, and polybutene films. Eastman's prooxidants include cobalt, acetate, copper oleate, manganese stearate, manganous dodecyl acetoacetate and cobalt acetyl acetate (67).

Mobil Oil Co. also developed an additive system for polybutene-1. They prepared 30 mil plaques and 2 mil films and produced bags from polybutene-1 films with mixed compounds containing an oxidation catalyst of cobalt, which is a free radical producer (polyterpene) and a UV light sensitizer (benzophenone). After exposure outdoors for 30 days, all samples containing prooxidants, except those mixed with 2.5% carbon black, had degraded. Within 13 days, the bags containing 1000 ppm of cobalt octoate and 0.05% ionol broke and in 31 days they disappeared completely. However, as explained before, polybutene-1 is inherently more unstable than PE, therefore without any prooxidant, polybutene-1 still degrades within 3 months. On exposure to sunlight, the principal reaction in polybutene-1 is a kind of chain scission, while crosslinking reactions occur simultaneously in PE (68).

ICI presented the additives of ketone and its derivatives which should be mixed at around 0.001 to 10% in polyolefins. This ketone is composed of the structure $R_1-(CO)-R_2$, where R_1 and R_2 are aliphatic or aromatic and ketone derivatives are $R_3-\overset{\overset{X}{\parallel}}{C}-R_4$, also aliphatic and aromatic for R_3 and R_4 , X is sulfur, oximino, imino, hydrazone or their derivatives. They claim that this polymer is available for disposable packages, containers, and cups (69).

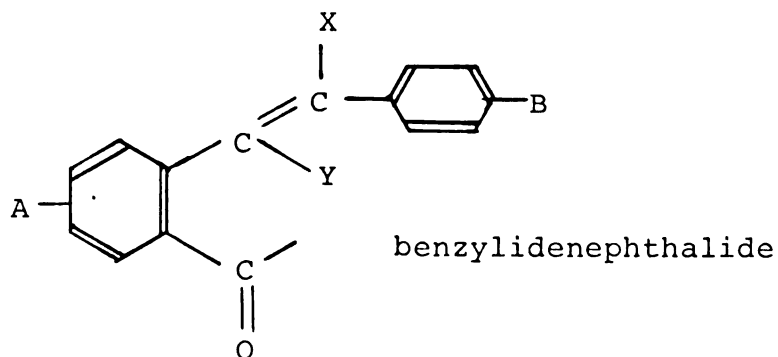
ICI established one more technique of degradable polyolefins with ferrocene and its derivatives at 0.01 to

2%. They also devised the degradable PE with 0.01 to 10% of poly (4 methylpentene-1) and 0.001 to 2% of photosensitizer, and this polyolefin is applied for various kinds of films and packages (70).

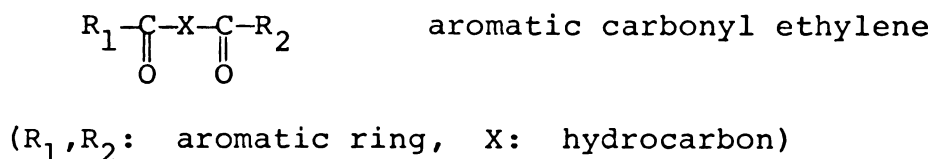
Another method is discussed by Dow Chemical where PE is mixed with absorbents such as aliphatic and aromatic ketones, aromatic ammonia, quinones and aldehydes. They explain that this PE is available for many purposes such as disposable kitchen goods, packages, and items for farms (71).

Societe Anonym Ethylene Plastique (France) is working on polyaromatic chloride at 2% to α -polyolefins (72).

Mitsubishi thought about new sensitizers for polyolefins such as 3-benzylidenephthalide or its derivatives, and 3-(α -cyanobenzylidene)-phthalide or its derivatives and imidine compounds, which are sensitive to sunlight and other lights of no longer than 400 m μ , and so available for the plastics for indoor furniture and packages (73).



They also invented the degradable polyolefins with sensitizers such as modified ethylene, which is principally modified with aromatic carbonyl (74).



Sumitomo Chem. concentrated in quinone compounds, transition metals and metals such as Cu, Ag, Zn, Cd, at 0.01 to 10% applied for almost all the polymers (75).

Kagiya added various kinds of carbonyl compounds to the polymer, particularly halogenated carbonyls and their metallic salts such as ferric chloride to PVC, PS, and PE by his own experimental method, where plastic films are dipped into solutions of carbonyl compounds. He found that films so treated lost tensile strength and durability on exposure to UV radiation and in atmospheric oxygen at room temperature. He researched more of this UV radiation method, for example, methylacetylene and tetrafluoroethylene which are light sensitive when mixed into PE causing bridge formation between polymer chains. But both techniques are not practical yet to be used in manufacturing processes which generally require simple and marketable methods (76).

We can find many reports and papers of degradable plastics, and they are indicating a lot of techniques of

additive system and degradable copolymers, however, they are not completely ready for an industrial application and market needs.

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4. DISCUSSION AND CONCLUSION

4.1. Discussion of Waste Disposal System

We have discussed the technologies of polymer stabilization, polymer blending, biodegradation, and chemical degradation as a chemical approach to the waste plastic disposal problems. And also we have briefly mentioned chemical engineering methods such as landfills, incineration, and pyrolysis. We have now come to conclude our discussions; what is the most favorable technology to overcome the so-called plastic pollution surrounding our community? The new technology of plastic waste disposal, of course, should not result in secondary or another type of pollution or contamination.

Let us consider the advantages and disadvantages of various disposal methods from the point of social, economic, and environmental aspects, as shown in Table 4.1.

The degradable plastics must certainly be of great benefit to our environment as far as the degraded products are not another nuisance. The research work with the degraded plastics is surprisingly delayed compared with the efforts to develop degradable plastics, and there are few reports of how these degraded plastics react in the soil. Above all, biodegradable plastics have a lot of unknown areas; what kind of bioreaction, bioorganism or

TABLE 4.1.--Advantages and Disadvantages in Waste Disposal.

Disposal	Advantage	Disadvantage
(1) Degradation in littering	•no collection •beauty in environment •go to natural cycle	•cost-up •processability •high price •short life •low strength •food contamination •ground water contamination •hygiene (biodegradable) •littering behavior •resource loss
(2) Recycling	•save resource •products •beauty in environment	•products limited •low demand in market •difficult technology •low property •difficult collection •high cost
(3) Incineration	•heat •high temperature •volume reduction	•toxic gas (open system) •furnace collapse •gas recycle system--cost up •loss of resource
(4) Pyrolysis	•products •no fuel •no toxic gas (closed system) •lower cost •residues available	•difficult technology •separation system →cost up
(5) Landfill	•claimed land •easiest method •low cost	•natural resource loss •ground water contamination •wide land needed

bioproduct is harmful or not for the human environment. Optimistically speaking, if we can produce edible proteins from the waste plastics, it would be a great benefit for human life. However, the various compositions of recycled plastic yield multiple bioreactions and bioorganisms, meanwhile for example, petro-protein is cultivated only in normal parafins of petroleum.

The presence of degradable plastics in refuse may give rise to flammable gases such as methane, and toxic or undesirable products which might contaminate the groundwater. And therefore we should take precautions to prevent the formation of such contaminants, particularly as low molecular organic chlorides from degraded PVC.

The manufacturers of degradable plastics have to invest more for the process to produce these plastics and they will be faced with problems of processability of easily degradable plastics and with the necessity of increasing their assortments. Furthermore, the use of sensitizers like metal complexes which accelerate the degradation reaction may cause even more pollution problems, and so more scientific controversy should be made by both consumers and health authorities.

All photodegradable plastics will be more expensive than their unmodified ones because of the higher cost of the modifier. So far a few degradable brands have been available in the market, however they get less demand

than their sales forecasts, and so they do not get to the break-even point.

The public will have to be warned of the limited shelf life of degradable containers, and more, we do not yet know exactly whether the physical and other mechanical properties of degradable plastics are inferior to those of unmodified plastics, and degraded products of containers impart undesirable smells or colors, and in particular whether they can support the growth of micro-organisms, which would be very objectionable for reasons of hygiene.

The reclamation by way of polymer blending is certainly one of the most difficult methods, and so it has been the least advanced or most neglected method.

In the blend, the compatibility, which is the definite obstacle before the practical reclamation method by way of blending different types of polymers, is very crucial to recycle waste plastics and this compatibility between low affinity polymers cannot be improved more than the physical limitation.

In the metallurgical industry, metals can make more excellent metal alloys with physical strength and electrical properties greater than each component, and they can produce the same quality of steel from scrap as from iron ores. Meanwhile, in the plastic world, only a few examples of polymer alloys are available in the market such as ABS and high impact resistant PS. Of course,

they are not included in a category of the plastic disposal, but of the improvement of mechanical properties. Even if a thorough mixture is acquired in the multiple polymer blend system, the deterioration of various properties is too big to compete with non-blend materials. However hard the recycling by way of stabilization and polymer blend is, we should not forget those methods have outstanding potential in the plastic recycling system.

The plastics, usually polyolefins, HDPE, LDPE, and PP, are probably the largest source of refuse material in the form of reject film. Oxidation is the mode of breakdown of HDPE and LDPE resulting from continued recycling--a breakdown that leads to an increase in the melt flow index. On the other hand, PE is not sensitive to contaminants and can be readily recycled without too many problems.

It is said that favorable regrind levels for PP are about a 10% blend with virgin polymer depending on the thermal history of the material. Recycling results in an increase in the melt flow index reflected by a decrease in molecular weight and a fall-off of impact strength. PP is also susceptible to contamination promoting degradation, which is signified by a noticeable increase in the brittleness of moldings and an increase of over 30% in the melt flow index of the recycled material compared with that of the virgin one. PS can be readily processed but with a

reduction in some physical properties, a tendency for colors to become opaque, and with contamination by other materials.

Reworked PVC can be used in proportions up to 100%, but on continued recycling, the stabilizer, necessary for processing and an effective length of service life, becomes exhausted and plastics readily degrade. The presence of degraded material promotes the further degradation of other materials with which it is blended and PVC is also susceptible to contamination.

Clear non-degraded reground ABS plastic can be mixed with virgin pellets of the same grade in any proportion. A fall-off in physical properties, particularly impact strength, and a darkening of the material are indications of continuously reworked ABS.

The original water white color of acrylics tends to deteriorate slightly with repeated reworking, and when the molded color is critical, rework should be limited. Acrylics are not compatible with other molding materials and contamination results in a loss of transparency and coloring effects.

As mentioned above, a stabilizer, especially one that is non-volatile and stable during reprocessing, is required to rework most plastics with less deterioration in the mechanical properties. From now on, polymeric

stabilizers with antioxidants and UV absorbents will be the goal of research in this area.

There is optimism with regard to several projects of stabilized plastics and plastic blending to reuse consumer plastics as they are--without attempting to sort plastics by polymer types. But some selectivity is usually still necessary to remove nonplastic items--except in the case of certain industrial wastes.

For instance, PVC and PE are essentially incompatible and their combined scrap is useless to manufacturers. However, if we introduce chlorinated PE as a compatibilizer for PVC-PE, it will require extensive research to develop the new technology.

Paul has done this research (28) and a chlorinated PE producer, Dow Chemical, has conducted similar experiments and both efforts indicate that this material, added to mix plastics at 10 to 30% levels, can act as a mutual binder, enabling such blends as PVC-PS-PE and PS-PV to be reprocessed conventionally for selected commercial products.

Introducing this mutual binder into the compatibilizers for all the waste plastics, there could be interesting methods to modify polymers with fluorine, bromine, and iodine (by fluorination, bromination, and iodination) as well as chlorine to make each plastic compatible--to produce mutual compatibilizers among waste plastics.

Furthermore, if we can add general substrates to waste plastics, which could change incompatible plastics into compatible ones, we would be able to develop mutual compatibilizers without blending other binds. This method might be established by special techniques such as radiation reactions and other sophisticated methods.

At least two entrepreneurial groups are known to be engaged in developing chemical additives that also function as compatibilizers. One of them asserts that their proprietary agents work as process aids, speeding cycle times when high-nitrile and other difficult materials are blow molded. Many other chemical companies also are reported to be investigating similar compatibilizing chemicals. One foresees the day, not many years off, when entire new families of compatibilized compounds will be used.

A more direct method of reprocessing various mixtures of plastics has been developed by such companies in Japan as Japan Steel Works and Mitsubishi Petrochemicals. As briefly mentioned before, the machine reportedly can rework any mixture of PE, PP, PS, ABS, PVC, polyester, and even nylon--in molded part, film, or fiber form. Depending upon end-use specifications, this machine will accept up to 50% nonplastic materials including glass, paper, cloth, etc.

In England, Regal Packaging, Ltd., has designed a system for pressure forming pellets from sheets rolled from mixed waste. Royal Kent Co. has launched a similar program, using an air classification system to retrieve plastic from municipal refuse.

Summarizing these two technologies--stabilization and blending with a compatibilizer--the recycling route shown in Figure 4.1 will be likely soon after the completion of the search for an effective compatibilizer which is now under investigation. A direct method of reprocessing recycled plastics with mechanical blending has been almost developed by some companies, and there are only a few problems left with this mechanical process.

In any event, both the stabilizer and compatibilizer will be polymer types, considering volatility, stability against heat, and compatibility.

Incineration is a common method adopted by a lot of local governments to dispose of daily household refuse. Due to the advanced technology, controlled combustion systems and improved furnace materials have been found to cope with the high temperatures released from plastics burning. Conventional furnaces have not endured high temperatures and could not remove molten viscous plastics clinging to their walls.

When plastics are burned, toxic emitted gases such as HCl , NO_x , and CO are troublesome from the environmental

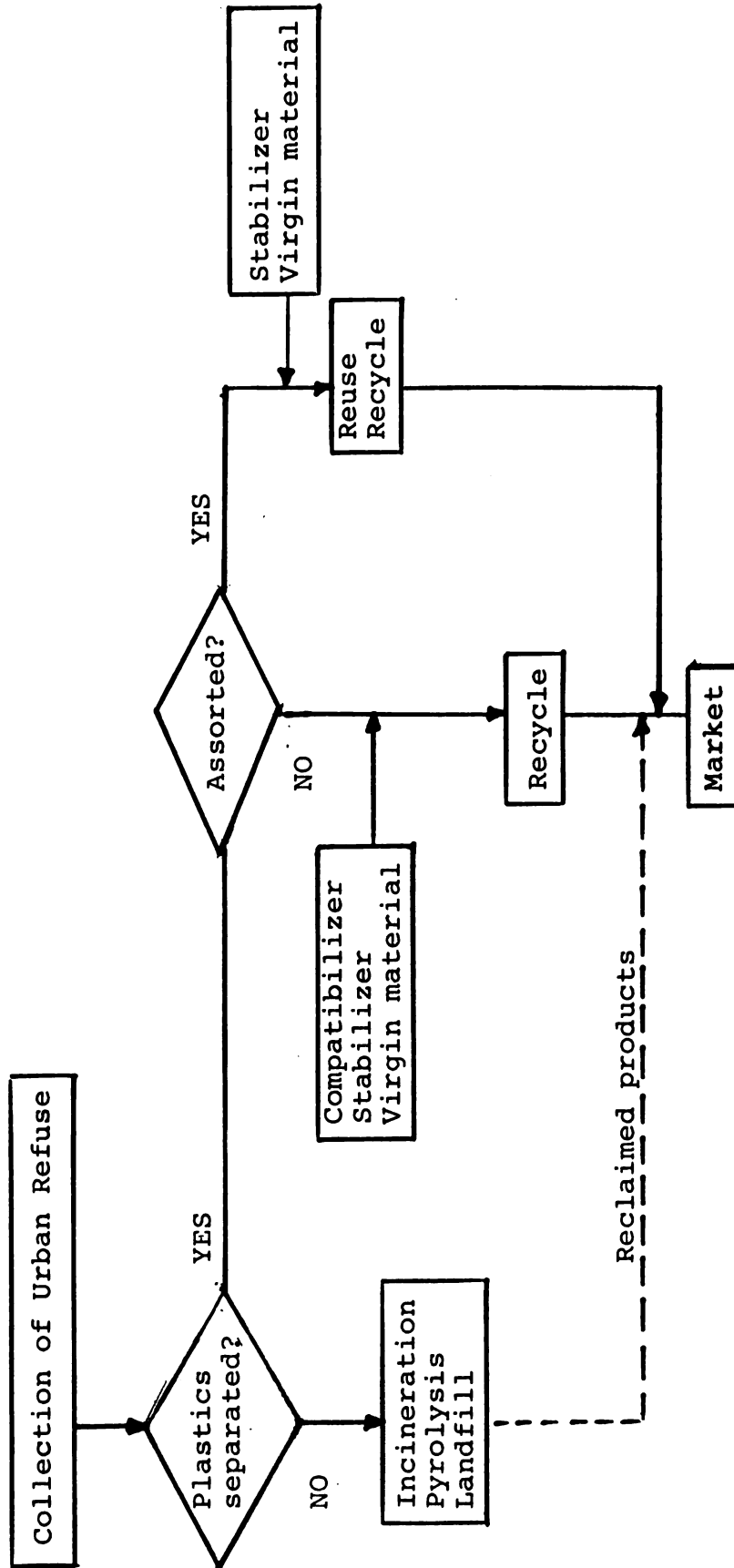


Figure 4.1.--Flow Chart of Plastics Recycling

and public health point of view. The HCl removal equipment has been available for more than 10 years in the incineration plant, and a highly concentrated HCl solution is made as a byproduct with a remarkably low cost.

On the other hand, the method to lower NO_x in the emitted gases, particularly when the incineration is operated at high temperatures like other combustion facilities such as the inner combustion engine of the automobile, is much more difficult. For the furnace to burn industrial wastes and plastics at high temperatures, it is hard to absorb emitted NO_x at chimney from the standpoint of both technology and economy.

Heat of steam delivered from an incinerator is supplied to the community as a heat source for homes and factories.

Considering the reclamation of plastics, if once incinerated, there is no hope to recycle a natural carbon resource except remaining ash which is used for limited purposes such as landfills and compostings.

Pyrolysis is not a completed method for the disposal of urban refuse, but has attracted a lot of attention recently, because it is a closed system which can avoid another pollution.

According to the disclosed information, it reclaims organic compounds at controlled pyrolyzing temperatures,

and moreover once the pyrolysis plant starts up, no more fuel is fed to the plant because the pyrolysis reactions are exothermic.

Pyrolyzed products can be controlled by catalysts such as Fe_2O_3 , FeCl_3 , NiCl_2 , etc.

Landfills dispose of about 90% of urban refuse in many countries and they claim lands along seashores in some areas.

As described before, the densities of many plastics are fortunately close to soil, around $0.8\text{--}1.0\text{ g/cm}^3$, and the non-corrosive property of carbon chain polymers in the real environmental condition is favorable for landfills in spite of their frictional smoothness to cause partial landslides.

Landfills are the method to use volume properties of plastics not energy properties, and so it is quite hard to compare their benefits with technologies which use the heat energy of waste plastics.

4.2. Conclusion

4.2.1. Cost Estimation of Disposal

Since the waste disposal technology is concerned with the social factors, any cost estimation should be considered, whether by a private handling corporation or a governmental organization, to minimize the total consumption of precious capital and energy. The total cost

is fluctuating at this time of soaring inflation and rapid technical innovation. Above all the scale merit of a new disposal plant when built on a large scale reduces the installation cost and running cost per unit, and so we should not regard the cost estimation as a solid and fixed one but an index to compare proposed disposal methods and find the less expensive one.

Costs of modified plastics.--Some amount of higher cost is predicted for producing such modified plastics as developed by Scott or Guillet, and to manufacture stabilized plastics. For instance, Ecolite, PE copolymer with vinylcarbonyl at 0.02 to 2%, is wholesaled at \$27.5 to \$29.0, which originally sold at \$25 when unmodified, so there is a 10-16% increase (79). It could be estimated that modifying comonomer costs 5-8 times as much as main monomer. According to this assumption, degradable PE developed by Guillet costs \$18-\$30/ton more, and that by Scott, \$2-\$3/ton more than unmodified PE which cost around \$200/ton in 1970. Of course, if a vast amount of demand emerges in the market, mass production would reduce these costs. By the same assumption as above, stabilizers in PE are mixed at 1-2% level and they cost 3-8 times as much as ethylene monomer, which adds \$10-\$30/ton in cost to PE pellets.

Collection systems.--Solid waste disposal is primarily a management decision, not a technical one. It is said that the collection and transportation costs account for up to 90% of all waste disposal costs (77), and so a small technical improvement here should open vast new areas for economical dumping. The Solid Waste Office of the Environmental Protection Agency (U.S.) reports collection and transportation costs ranging from \$1 to \$420/ton (78).

Here is an interesting assumption. A 20 cu.yd. truck with rear compactor and a three-man crew costs \$150/day to operate when fuel, amortization, and maintenance are figured in. The average truck is driven about 50 miles a day, disposing of two 4-ton loads. Thus operating costs are about \$19/ton. If a new dump site 10 miles further away is needed, the increased travel time is more than 1.5 hour at 25 miles/hr. So only 1.5 loads a day, or 6 tons, could be collected, raising the collection cost close to \$26/ton. The \$7 difference could be applied to a secondary transportation and landfilling (77).

Separation.--Stabilized plastics may be recycled in an exclusive circulation for their reclamation, but waste plastics are generally recycled in a random manner.

In the total disposal system the separation process is to select plastics from other urban refuse and to classify them into each group such as PE, PP, PS, etc.

As far as we have investigated, the classification of plastics is the hardest technology in the plastics industry, and so far only one example that may be successful in the reusing process does not require separation--that is, recycling only HDPE milk bottles, which are circulated in a small community.

Since the proposed separation methods such as air classification and the sink-float method that are actually the separation of plastics from other refuse are at an experimental stage, we can hardly estimate their installation and operation costs, but we assume that they are not far from other processes such as pyrolysis (78).

Disposal.--Sanitary landfill is a solid waste handling method which disposes of up to 90% of urban refuse in developed countries. In Figure 4.2, we have good estimates of sanitary landfill costs with cover materials purchased at \$1.50/cy.yd. and in the same figure, we recognize the total cost of incineration is about \$7/ton at 1,000 ton/mo. disposal capacity, and also a cost estimation is given for pyrolysis assuming that it has a similar trend to incineration.

According to the test result for pyrolysis, the total disposal cost is about \$10/ton at a 1,000 ton/mo. capacity plant (corresponding to a city population of 100,000) (78).

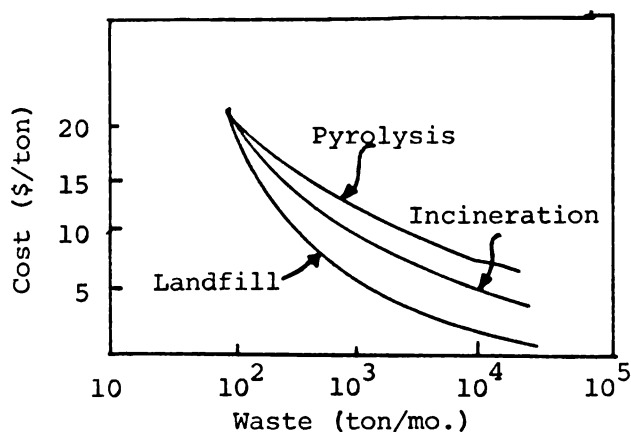


Figure 4.2.--Cost Estimation with Tonnage, 1970.

Sale value of new products.--Landfill reclaims new lands when the dump sites are acquired along the seashore or the lake shore. The price of land varies a lot depending on where it is located. In this cost prediction to compare the relative values, we assume a temporary value of the reclaimed land.

Incineration produces steam and remaining ash used for landfills which make only a small amount of profit. On the other hand, pyrolyzed municipal refuse provides organic liquids and char which could be reclaimed for other raw materials. In the available data, these raw materials are valued at as much as \$20-\$30/ton, depending on the forms of chemical compounds (78). Suppose that the reclaimed products sell at a price of one-third of the products of virgin plastics and the profit rate is 25% of the sales price, considering this raw material is cheap, but the product quality is inferior. The profit

of products is about \$15/ton for the case of PE, where the price of virgin PE is assumed to be \$180/ton in 1970.

Conclusions from the cost estimation.--The total cost estimation of disposal methods indicates very interesting results. In engineering methods, pyrolysis is more recommended than the other two methods as far as the cost estimation is concerned, and pyrolysis is also praised from the environmental point of view because of its closed operation which discharges less pollution.

In the reuse technology, if we consider these two points--that the recycling circle of plastic is very small and the blending technology is not completed yet--the total cost assumption is not accurate; however, we assume here that it is not so high if compared with other methods.

Considering its cost competitiveness and chemical toxicity, there is a remarkable innovation in the degradable plastics, which is developed by Griffin. In an interview Griffin explained that the starch blended in plastics did not result in a cost increase, because the starch sold at a price 1/2-1 times as high as ethylene monomer.

This starch degradable plastic does not appear in the market yet, but it will be likely to get a good reputation, especially as farm materials, judging from its cost and non-toxic additives. The other two methods, presented in Table 4.2, are more expensive and toxic than

TABLE 4.2.--Cost Estimation of Disposal (\$/ton) in 1970.

	Cost-Up	Collection Transition	Separation	Disposal	Profit of Products	Total Cost
Landfill	--	25~29	--	5	0.5~1	29~33.5
Incineration	--	25~29	--	7	0.5	33.5~37.5
Pyrolysis	--	25~29	--	10	20~30	5~19
Stabilization	10~30	25~29	0	--	15	20~45
Blend	10~30	25~29	10	--	15	30~50
Griffin (Starch)	0	--	--	--	--	0
Scott (Oxidants)	2~3	--	--	--	--	2~3
Guillet (Carbonyl)	18~30	--	--	--	--	18~30

Assumed: PE Cycle; disposal capacity--1,000 ton/mo. (100,000 population).
 Cost Data: base in 1970.

Griffin's, although each of them claims to have more effective degradability than others.

Our conclusion with waste plastic disposal is that (1) plastics circulated with urban refuse should be disposed of by pyrolysis and (2) those plastics out of the collection should be made environmentally degradable.

Hence there are lots of exceptional cases from our assumption; we, of course, must think about a detailed plan to come up with various problems which may occur in our environment. However, as we have predicted, the solutions to the disposal problem will be these two methods--pyrolysis and degradable plastics, judging from the cost analysis and environmental situation within the next decade.

4.2.2. Movement of Disposal in the Future

The plastic reclamation by way of the separation from urban refuse is not carried out in a plastic society--the reasons are (1) the classification of a tiny ratio of plastics, about 3%, from huge amounts of urban refuse is very difficult, considering its technology and the economic benefits; (2) recycled products cannot compete with virgin ones in a real market. In any way, the necessary terms to which we should pay attention for the successful recycling of plastics are:

1. sanitation--recycled plastic cannot be supplied in the food market.

2. cost--cost competition with virgin plastics should be improved, especially collection and reclamation should definitely be cheap.
3. supply of refuse--urban refuse must be supplied with stable quality and quantity for a long term.
4. composition--recycled materials must not have random composition, particularly incompatible ones should not be included.
5. market root--a solid and profitable market for recycled plastics should be developed.

We will expend a lot of investments and efforts before we solve this hard question--waste plastic disposal.

Considering general aspects of the disposal method, the basic technology has progressed more rapidly than its followers; in other words, the hardware has moved faster than the software which is defined in this discussion as the controlled disposal system, administration of the government's litter control or regulation by law and public or private organization for waste disposal.

Meanwhile, more improvement in the hardware is expected in such cases as the recycling-inclined plastic developed by Monsanto, which is a nitrile based, light, safe, easy-storing, and recyclable polymer. And Monsanto claims it has low energy consumption while processing and recycling, meeting the recent energy shortage demands (80).

There is a very interesting proposal from the U.S. Atomic Energy Commission, which suggests a promising method of treatment of municipal refuse with fusion-powered electrical generating stations of the future.

The plasma produced during nuclear fusion is so hot that anything fed into it becomes dissociated and ionized. The wastes are fed into the immensely hot plasma produced for the fusion of deuterium. This magnetically bottled plasma is around 50 million °C, a temperature that obviously causes any solid not just to vaporize but to dissociate into its elements and to ionize. When treating typical refuse, these elements would include oxygen (44%), carbon (33%), iron (6.6%), hydrogen (4.8%), silicon (4.6%), aluminum, copper, sodium, magnesium, and other elements with significant reuse value.

All of this is still very conceptual, because nuclear fusion is a long way from being commercial, but the potential attractions of this waste-disposal route would likely far outweigh the cost of the high energy level required. Furthermore, this new waste disposal concept is good in that, unlike many other disposal techniques, it does not introduce any pollution of its own, and there is very little energy loss because the process takes place at very high temperatures.

We hope the plasma will overcome the nuisance, waste disposal problem, not far away from now, because it must be a more perfect technology than mankind has ever experienced (81, 82).

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