

RECYCLING OF SOLID WASTES AS SOLID WASTE-POLYMER
COMPOSITES FORMED BY RADIATION INDUCED POLYMERIZATION

by

WAYNE OTIS VANDERPOOL

B. S. , University of Colorado, 1969

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

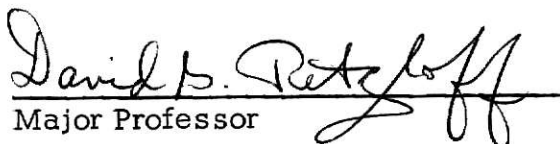
MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1971

Approved by:


Major Professor

LD
2668
T4
1971
V29
Spec. Coll.

TABLE OF CONTENTS

	Page
1.0 INTRODUCTION	1
2.0 LITERATURE SURVEY	6
2.1 Sources of Solid Wastes	6
2.1a Urban Waste Sources	8
2.1b Industrial Waste Sources	14
2.1c Agricultural Waste Sources	15
2.1d Mineral Waste Sources	15
2.1e Federal Waste Sources	17
2.2 Collection of Solid Wastes	19
2.2a Collection of Urban Wastes	19
2.2b Collection of Non-Urban Wastes	23
2.3 Disposal of Solid Wastes	24
2.3a Disposal of Urban Wastes	26
2.3b Industrial Waste Disposal	37
2.3c Disposal of Agricultural Wastes	40
2.3d Disposal of Mineral Wastes	42
2.3e Disposal of Federal Wastes	42
2.4 Summary	43
3.0 OBJECTIVE	46
4.0 THEORETICAL	47
4.1 Sources of Radiation	47
4.2 Primary Processes	47
4.3 Polymerization Mechanisms	50
4.4 Activation and Inhibition	51
4.5 Graft Polymerization	53
4.6 Polymer Degradation	58
4.7 Vinyl Monomer Survey	60

	Page
5.0 EXPERIMENTAL	64
5.1 Equipment and Supplies	64
5.2 Sensitivity of the Composite Process to the Type of Solid Waste Used	75
5.2a Procedure	76
5.2b Results	80
5.2c Discussion	88
5.3 Polymerization of MMA in the Presence of Com- pressed Paper	88
5.3a Procedure	92
5.3b Results	96
5.3c Discussion	101
5.4 The Effect of Air and Pressure Used to Compress the Paper on the Polymer-Paper Composite Process	101
5.4a Procedure	101
5.4b Results	105
5.4c Discussion	109
5.5 Testing the Physical Properties of the Composites	109
5.5a Procedure	109
5.5b Results	114
5.5c Discussion	117
6.0 CONCLUSIONS	119
7.0 RECOMMENDATIONS	127
NOMENCLATURE	131
ACKNOWLEDGMENTS	132
REFERENCES	133
APPENDIX A	140
A.1 Tensile Strength Testing	140
A.2 Compressive Strength Testing	143
A.3 Hardness Testing	143
A.4 Water Absorption Tests	152

LIST OF FIGURES

FIGURE		Page
1	RESPONSIBILITY FOR COLLECTION PERFORMANCE	20
2	CHAIN STRUCTURE OF CELLULOSE	55
3	TYPICAL SEGMENT OF THE CELLULOSE-PMMA GRAFT POLYMER	56
4	EFFECT OF RADIATION ON VINYL-TYPE POLYMERS	59
5	GENERAL FEATURES OF MECHANICAL SHREDDER USED TO SHRED PAPER	65
6	SMALL COMPRESSION DYE USED TO COMPRESS PAPER	66
7	LARGE COMPRESSION DYE USED TO COMPRESS PAPER	68
8	VACUUM VESSEL	70
9	MONOMER INTRODUCTION SYSTEM	72
10	WATER ABSORPTION RATE OF LAYERED COMPUTER PAPER-PMMA COMPOSITE	91
11	CONVERSION OF MONOMER USING PAPER COMPRESSED AT 2500 psi	103
12	EFFECTS OF OXYGEN AND PAPER COMPRESSION PRESSURE ON THE CONVERSION OF MONOMER	110
13	PREPARATION OF SAMPLES FOR TESTING	113

LIST OF TABLES

TABLE		Page
1	GENERATION OF SOLID WASTES FROM FIVE MAJOR SOURCES IN 1967	7
2	COMPOSITION OF SOLID WASTES FROM URBAN SOURCES	9
3	ESTIMATE OF COMPONENTS OF DOMESTIC REFUSE IN SANTA CLARA COUNTY, CALIFORNIA	11
4	COMPOSITION AND ANALYSIS OF COMPOSITE MUNICIPAL REFUSE (1966)	12
5	POTENTIAL VALUES IN TRASH	13
6	COMPOSITION OF SOLID WASTES FROM AGRICULTURAL SOURCES	16
7	GENERATION BY TYPE OF SOLID WASTES FROM THE MINERAL AND FOSSIL FUEL INDUSTRIES (1965)	18
8	COMPOSITION OF TYPICAL MUNICIPAL INCINERATOR RESIDUE (AVERAGE OF FIVE WASHINGTON, D.C. INCINERATORS)	27
9	COMPARISON OF MAJOR TRASH RECYCLING PROCESSES	38
10	SURVEY OF MONOMER SYSTEMS FOR COMPOSITES	63
11	SOLID WASTES COLLECTED TO BE USED IN PRODUCING SOLID WASTE-PMMA COMPOSITES	77
12	RESULTS OF IRRADIATION EXPERIMENTS	84
13	WATER ABSORPTION TEST RESULTS	89
14	RESULTS OF THE POLYMERIZATION OF MMA IN THE PRESENCE OF COMPRESSED PAPER	97
15	PERCENT POLYMER AND POLYMER TO PAPER WEIGHT RATIO OF THE COMPRESSED PAPER-PMMA COMPOSITES AT 100% CONVERSION OF MONOMER	100
16	CALCULATION OF POLYMER TO PAPER WEIGHT RATIO OF THE PAPER-PMMA COMPOSITE AT 100% CONVERSION OF MONOMER USING PAPER COMPRESSED AT 2500 psi	100
17	PERCENT CONVERSION OF MONOMER FOR PAPER-PMMA COMPOSITES USING PAPER COMPRESSED AT 2500 psi	102

TABLE		Page
18	EFFECT OF OXYGEN ON THE PERCENT CONVERSION OF MONOMER IN THE PAPER-PMMA COMPOSITES	106
19	THE EFFECTS OF THE PRESSURE USED TO COMPRESS THE PAPER AND THE PRESENCE OF OXYGEN ON THE CONVERSION OF MONOMER IN THE PAPER-PMMA COMPOSITES	108
20	POLYMER CONTENT OF THE "LARGE" PAPER-PMMA COMPOSITES	112
21	PROPERTIES OF THE PAPER-PMMA COMPOSITES	115
22	COMPARISON OF PROPERTIES OF THE PAPER-PMMA COMPOSITE WITH OTHER STANDARD MATERIALS	123
23	RESULTS OF TENSION TESTS	142
24	RESULTS OF COMPRESSION TESTS	144
25	RESULTS OF HARDNESS TESTS	150
26	RESULTS OF WATER ABSORPTION TESTS	154

CHAPTER 1

1.0 INTRODUCTION

For every pound or cubic foot of finished product produced, there is two or three times (and possibly a 1000 times) as much solid waste produced. When the finished products lose their usefulness they are discarded and add to the volume of solid wastes. Industries, agricultural activities and mining operations all generate solid type wastes that must be dealt with. Most of the service industries also create waste products that must be disposed of. Up until a few years ago, these wastes were not too much of a problem. Traditionally, they were burned, buried or carted off somewhere out of the way and dumped. With a few new twists, these are still the major methods in use today. While in the past these practices presented few problems, today's escalating population, the concentration of this population in urban centers, and skyrocketing consumption has fashioned a triple threat to the age-old practice of dumping trash into the nearest unoccupied space. More people consuming more things in a confined area have created a threat to our environment and to the public well-being.

The relationship between public health and improper disposal of solid wastes has been known for quite some time (73). Rats, flies and factors propagating diseases thrive in the open dumps and among the wrecklessly discarded trash (25). Statistical evidence shows that the illness-accident rate for sanitation workers is several times higher than that for industrial employees (74).

Many problems associated with air and water pollution have been linked to mismanagement of solid wastes (84). Leachate from open refuse dumps and poorly engineered landfills has contaminated surface and ground waters. Polluted water from mineral tailings can be particularly hazardous if the leachate contains toxic substances such as arsenic, radiation, mercury or copper. Many residues resulting from poor management of solid wastes are not readily eliminated or degraded. Some are a threat to human health; others adversely affect desirable plants and animals.

Nature has the capacity to disperse, degrade, absorb or otherwise dispose of unwanted residues in the natural sinks of the atmospheres, inland waterways, oceans and the soil. But these natural sinks could be sites where undesirable residues may accumulate from indiscriminate solid waste disposal. These residues may poison, damage or otherwise affect one or more species in the biosphere, with a resultant ecological shift.

Other present practices that have complicated the solid waste problem include planned obsolescence, a never ending variety of new products, increased use of plastics and other nondegradable materials, single-use containers (nonreturnable bottles), and other gadgetry and conveniences that swell the amount as well as types of wastes to be managed within a community.

However, it is impractical to think of impending urban affluence, progress of industry, and advances of agriculture by strict control. The trend for the future must include pollution abatement systems which provide progress without the harmful side affects. Within such systems, there must be solid waste management to provide the preservation of public health, aesthetics and quality of the environment.

In order to achieve such goals, authorities are concentrating on long range solutions to the solid waste problem (39). Support is beginning to crystalize around the concept of reclamation - or recycling, as it is more popularly known. Rather than viewing trash as a useless waste to be stored away somewhere, the recycling concept views it as a resource to be exploited.

There are three powerful reasons supporting the recycling approach.

(1) First, the waste material is diminished or eliminated. Considering all the sources of solid waste, the average daily per capita production is approximately 100 pounds of wastes (74). Most of these are visible heterogeneous wastes generated in areas with little storage space. These wastes cannot be tolerated for long on individual premises or public places. One way eliminating or reducing the volume of these wastes is to transform them into something useful.

(2) Second, credit may be obtained toward the cost of managing the waste material. The disposal of solid wastes has been anything but a money making operation. The collection and disposal of wastes in the cities are paid for through utility fees, taxes, or payment to private disposal agencies. Industries pay private collectors or purchase land to stockpile their wastes. Even agricultural and mineral wastes are becoming an expensive problem. The treatment of waste has always been an expense and very few of the recycle methods show any indication of being otherwise. Those areas which are profitable involve the recycling of some of the industrial wastes. This practice is responsible for a sizable part of the production of those materials. (Thirty percent of all the aluminum currently produced, 45 percent of the copper and brass, 52 percent of the lead, and 20 percent of the paper come from the secondary (waste) materials industry (64,65).) However, these represent only a very small portion of the wastes produced. To begin with it appears that any form of recycling will have to be subsidized by federal funds, or by a tax incentive or the public will foot the bill by paying higher prices for goods to cover subsequent disposal of the goods consumed. However, the more potential value recovered from the wastes, the lower the overall cost.

(3) Third, the pressure on the corresponding virgin material source is reduced. People, especially in the U.S., have the attitude that materials are to be used once and then discarded. Man extracts metals from ores and transforms other materials from a natural state to man-made products. When these products have fulfilled their usefulness, and are classified as solid wastes, the valuable and nonrenewable cost of materials are often lost. In most instances, it is still cheaper to extract the needed substances from the natural resources than it is to try to recover them from discarded wastes. However, earth's resources are limited. Iron, and other metals oxidize, other valuable substances degrade, and these materials may never be available again for use by future generations. Shortages in resources for some of the less common

elements have been created already by many indiscriminate waste disposal practices. In spite of the excellent programs of many pulp manufacturers and conservation groups, the ever increasing use of pulp wood may in time present a problem of supply (1,8). Unless the present consumption of materials is cut drastically, and without reuse, the cost of all raw materials will skyrocket because of depleted resources.

Recycling literally means returning to the beginning of the cycle. This suggests separating the trash into its components which may then be returned to the place of manufacture; for example, paper waste may be remade into paper products, tin cans returned to the steel mill, and bottles to the glass furnace.

However, it is not necessary to return the components of trash to their original form in order to obtain some further usefulness from them. The current aim of recycling efforts is simply to return the wastes to the economy in a way that will produce some utility in any form. The question is, can we utilize trash in a more useful way and still eliminate the wastes and their harmful side effects.

Under this definition, the common practices of sanitary landfilling, incineration (used as a source of heat), and composting could qualify for recycling methods. The problem is that the value regained by these methods is nominal compared to the potential that the wastes contain. There have been numerous methods proposed to try to regain a bigger percentage of this potential value. A common problem among these methods (besides being very expensive) is that they only apply to certain wastes (e.g. urban, industrial, agricultural or mineral; or possibly even more specific, e.g. paper, metal, glass, etc.). When using a particular method there are always residues or wastes which must be processed by other means. As the volume of waste goes up and as dumping and burning become less tolerable, there will be a higher percentage of this type of waste to treat.

Most of the solid wastes are shreddable, that is they can be ground up (or already are in some shredded form). New sensors have been developed to separate shredded solid wastes into five or six major categories (68,94). It may be possible to use these shredded wastes as filler in some kind of composite material, using a polymer as a binder. Even if a great deal of the wastes are recycled back into their original form, there will always be some residues which must be disposed of, such as ashes, mineral tailings or other types of unusable residues.

It is the purpose of this study to review the current solid waste problem, develop requirements met by successful recycling methods in general; and using these criteria, investigate a possible recycling method for all types of shreddable, granular, or powdered solid wastes. The proposed method involves the making of a composite material using the shredded wastes as a filler and an acrylic polymer as a binder. To form the composite, the waste material is impregnated with a monomer which is in turn polymerized to a polymer upon exposure to gamma-radiation. Shreddable wastes from all kinds of sources have been used for filler in the composite. The process appeared rather insensitive to the waste used and good binding properties appeared in all the composites formed with methyl methacrylate (MMA). To further investigate the properties of such a composite, a waste paper-poly-methyl methacrylate (PMMA), composite was produced using different pressures to compress the paper before impregnation. The effects of the paper compression pressure and irradiating atmospheres (air or nitrogen) on the composite properties were determined. These paper-PMMA composites were tested for compression and tensile strength, resistance to indentation and water absorption. The results of these tests were then compared to the properties of some standard building materials and possible uses of such composites were projected.

In addition, the effect of air on the polymerization of the monomer in the formation of the composite was investigated with respect to time required to give complete conversion of the monomer.

CHAPTER 2

2.0 LITERATURE SURVEY

To develop criteria for evaluating possible recycling methods, it is necessary to review past practices and current technology in the area of solid waste management. This chapter is broken down into: (1) sources of solid wastes; (2) collection of solid wastes; and (3) the disposal of solid wastes.

The first section separates the sources of solid wastes into five major categories. The components in the wastes of each category are given and, where possible, an attempt is made to present the potential value that is in the wastes. The second section describes the collection of the wastes. The third section gives the common methods of waste disposal and discusses some of the recent recycling approaches. Finally, in the summary, the common requirements met by those most successful recycling methods are formulated.

2.1 Sources of Solid Wastes

Approximately 200 million tons of trash are collected each year by towns and cities alone in the U.S. (29,74). This amounts to about five pounds of trash per person per day. If one considers all the sources of solid wastes, the total amount was 3.65 million tons (in 1967) equivalent to 100 lbs. per capita per day for a national population of 200 million. By 1980 the total amount is expected to increase to 5 billion tons.

According to the Federal Office of Science and Technology (74), these solid wastes fall into five major source categories: urban (including domestic, commercial and municipal); industrial; agricultural; mineral; and Federal establishments.

Estimates of the quantities of solid wastes generated from all of these sources in 1967 is given in Table 1. Before the information in this table can take on much meaning, the different categories must be defined and explained to a certain extent. This table was taken from the technical report of the

TABLE 1.* GENERATION OF SOLID WASTES FROM FIVE MAJOR SOURCES IN 1967

Source	Solid-Wastes Generated	
	lbs/cap./day	million tons/yr.
Urban		
domestic	3.5	128
municipal	1.2	44
commercial	<u>2.3</u>	<u>84</u>
Sub-total	7.0	256
Industrial	3.0	110
Agricultural		
vegetation	15.0	552
animal	<u>43.0</u>	<u>1563</u>
Sub-total	58.0	2115
Mineral	30.8	1126
Federal	1.2	43
TOTALS	100.0	3650

*Reference (74).

Office of Science and Technology on Solid Waste Management (74) which contains a full explanation of each category presented in Table 1. In this review the categories will not be covered in detail but the sources and their composition will be discussed to some degree.

2.1a Urban Waste Sources: This category has been grouped into three different sources: domestic or residential, commercial-institution and municipal. The residential source involves that solid waste collected from the individual households in the community. Commercial waste sources are wholesale and retail trade, hotel, restaurant, hospital and institutional, finance, insurance, corporate, general offices and services excluding private households. The commercial sector of the American economy primarily manages its solid wastes on an individual basis. Municipal sources of urban solid wastes include street litter, discarded auto bodies, power plant and incinerator ashes and residue, and sewage sludge. A summary of the composition of the solid wastes produced by these sources is given in Table 2 (74).

Several attempts have been made to determine the percentage of these components in urban wastes (29,36,74). The results of some of these studies are given in Table 3 and Table 4 (74). At this time it should be pointed out that the values in Table 1 are only rough estimates at best, taken from various studies conducted at different locations, like ones just discussed. For example, reported estimates on the size of the garbage fraction of domestic and commercial refuse ranged from 5 to 15 percent. The reported ratios of combustible and noncombustible rubbish also varied extending from 15 to 25 percent for the noncombustibles and 64 to 75 percent for the combustibles. Examples of the more common constituents are: paper, 42 to 57 percent; metals, 1.5 to 8 percent; glass, 2 to 15 percent; rags, .6 to 2 percent; garden debris, 10 to 12 percent; and ashes, 5 to 19 percent.

Now that rough estimates have been established it is possible to determine some approximation of the potential value in trash. Table 5 (29) represents the

TABLE 2. * COMPOSITION OF SOLID WASTES FROM URBAN SOURCES.

Urban Sources	Waste	Composition
Domestic, household	Garbage	Wastes from preparation, cooking and serving of food; market wastes from handling, storage, and sale of food.
	Rubbish, trash	Paper, cartons, boxes, barrels, wood, excelsior, tree branches, yard trimmings, metals, tin cans, dirt, glass, crockery, minerals.
	Ashes	Residue from fuel and combustion of solid wastes.
	Bulky wastes	Wood furniture, bedding, dunnage, metal furniture, refrigerators, ranges, rubber tires.
Commercial, institutional, hospital, hotel, restaurant, stores, offices, markets	Garbage	Same as domestic.
	Rubbish, trash	Same as domestic.
	Ashes	Same as domestic.
	Demolition wastes, urban renewal, expressways	Lumber, pipes, brick masonry, asphaltic material and other construction materials from razed buildings and structures.
	Construction wastes, remodeling	Scrap lumber, pipe, concrete, other construction materials.
	Special wastes	Hazardous solids and semiliquids, explosives, pathologic wastes, radioactive wastes
Municipal, streets, sidewalks, alleys, vacant lots, incinerators, power plants, sewage treatment plants, lagoons, septic tanks	Street refuse	Sweepings, dirt, leaves, catch basin dirt, contents of litter receptacles, etc.
	Dead animals	Cats, dogs, horses, cows, marine animals, etc.
	Abandoned vehicles	Unwanted cars and trucks left on public property.
	Fly ash, incinerator residue, boiler slag	Boiler house cinders, metal scraps, shavings, minerals, organic materials, charcoal, plastic residues

TABLE 2. (cont'd)

Urban Sources	Waste	Composition
Municipal, etc.	Sewage treatment residue	Solids from coarse screening and grit chambers, and sludge from settling tanks.

*Reference (74).

TABLE 3. * ESTIMATE OF COMPONENTS OF DOMESTIC REFUSE IN SANTA CLARA COUNTY, CALIFORNIA (1967)^a

Classification	Percent of total	Lbs/cap/day	Tons/yr
Garbage	12	0.42	75,240
Rubbish			
paper	50	1.75	313,500
wood	2	0.07	12,540
cloth	2	0.07	12,540
rubber	1	0.04	6,270
leather	1	0.04	6,270
garden wastes	9	0.31	56,430
metals	8	0.28	50,160
plastics	1	0.04	6,270
ceramics & glass	7	0.24	43,890
nonclassified	<u>7</u>	<u>0.24</u>	<u>43,890</u>
TOTALS	100	3.50	627,000

*Reference (74).

^a A per capita production of 8 lbs per day, of which 44 percent is domestic refuse, was assumed in estimating values.

TABLE 4. * COMPOSITION AND ANALYSIS OF COMPOSITE MUNICIPAL REFUSE
(1966)^a

Components	Percent by weight
1 Corrugated paper boxes	23.38
2 Newspaper	9.40
3 Magazine paper	6.80
4 Brown paper	5.57
5 Mail	2.75
6 Paper food cartons	2.06
7 Tissue paper	1.98
8 Wax cartons	0.76
9 Plastic coated paper	0.76
10 Vegetable food wastes	2.29
11 Citric rinds and seeds	1.53
12 Meat scraps, cooked	2.29
13 Fried fats	2.29
14 Wood	2.29
15 Ripe tree leaves	2.29
16 Flower garden plants	1.53
17 Lawn grass, green	1.53
18 Evergreens	1.53
19 Plastics	0.76
20 Rags	0.76
21 Leather goods	0.38
22 Rubber composition	0.38
23 Paint and oils	0.76
24 Vacuum cleaner catch	0.76
25 Dirt	1.53
26 Metals	6.85
27 Glass, ceramics, ash	7.73
28 Adjusted moisture	9.05
TOTAL	100.00

*Reference (74).

^aSource: Kaiser, E. R. Chemical analyses of refuse components, 1966.

TABLE 5.* POTENTIAL VALUES IN TRASH

	Percent by Weight	\$/Ton of Component	\$/Ton Trash
Paper, paperboard	50	100	50
Ferrous metal ^c	9	20	2
Aluminum	1	200	2
Glass, ceramics	10	10	1
Garbage, yard waste	20	5 ^a	1
Misc.: Plastics, textiles, etc.	10	5 ^b	0.50

*Reference (29).

^aValue as compost.

^bValue as fuel.

^cScrap steel being processed at Granite City Steel mill, Granite City, Illinois.

generally accepted average percentage values for the different components in domestic trash.

The second column of the table lists the values of the bulk material (scrap iron, aluminum, scrap glass, and clean wastepaper). For the food/yard waste fraction, the value of compost is used. The miscellaneous materials including plastics, rubber, fabrics, wood and leather, is assigned only fuel value since the fraction contains little of any one material, and its fuel value is high.

The final column, the product of the first two columns, gives the potential value of the components of trash if these materials could all be recycled as the forms shown. These potential values represent only the upper limit of the value in these materials, nevertheless, this gives an ideal of the maximum value that a recycling method might produce.

The interesting picture that comes from this analysis is that the potential value of paper literally dwarfs the other values in ordinary trash. This is a result of the predominance of paper products in trash and the relatively high value of the cellulose fiber.

2.1b Industrial Waste Sources: By definition, industrial solid wastes are any discarded solid materials resulting from an industrial operation or deriving from an industrial establishment. They include processing, general plant, packaging and shipping and office and cafeteria wastes. Specifically excluded are dissolved solids in domestic sewage and any dissolved or suspended solids in industrial waste waters. These types of waste are less obvious than the urban wastes but solid wastes of industrial origin comprise a category of major magnitude (Table 1). In warehouses and backlots of industrial properties there are piles and acres of sludges, slags, waste plastics, scrap metal, bales of rags and paper and drums of off-grade products. The magnitude of the problem of their disposal is compounded by the fact that industrial wastes are as diversified as industry itself. Unlike residential solid wastes, with characteristics generally similar throughout the United

States, the quality and quantity of industrial wastes varies from industry to industry. There are a few materials that are common in all industrial wastes but it is impossible to give a usual composition of wastes generated by industries. For examples of the waste generated by the different industries, see the report on Solid Waste Management (74). In general, these waste materials are reintroduced into the industrial process whenever possible but often the percentage of such incorporation is very nominal. Those wastes not re-used are then stored on company property or disposed of by some other means.

2.1c Agricultural Waste Sources: The principal agricultural and forestry wastes generated in the United States are animal manures, vineyard and orchard prunings, crop harvesting residues, animal carcasses, greenhouse wastes, and pesticide containers. The composition of these wastes is given in Table 6 (74).

In 1967, major agricultural crop wastes amounted to 550 million tons per year and animal wastes, 1,560 million tons per year. In addition to this, 25 million tons of lodging debris are left in forests during the average year which involve residue and trash in forestry operations.

Domestic animals produce over 1 billion tons of fecal wastes a year and over 400 million tons of liquid wastes. Used bedding, paunch manure from abattoirs, and dead carcasses make the total annual production of animals' wastes close to 2 billion tons. As much as 50 percent of these animal wastes is generated in concentrated growing operations close to urban areas, creating waste disposal problems, as well as offensive odors and other threats to the environment (44).

2.1d Mineral Waste Sources: During the past 30 years, over 20 billion tons of mineral solid wastes have been generated in the United States by the mineral and fossil fuel mining, milling and processing industries. It is estimated that in 1967, the generation of mineral solid wastes was 1.1 billion tons per year (Table 1). By 1980 this estimate goes over 2 billion annually. If, as expected, ocean and oil shale mining become major commercial

TABLE 6.* COMPOSITION OF SOLID WASTES FROM AGRICULTURAL SOURCES

Agricultural Source	Waste	Composition
Farms, ranches, green-houses, livestock feeders, and growers	Crop residue	Cornstalks, tree prunings, pea vines, sugarcane stalks (bagasse), gree drop, cull fruit, cull vegetables, rice, barley, wheat and oats stubble, rice hulls, fertilizer residue.
	Forest slash	Trees, stumps, limbs, debris.
	Animal manure (Paunch manure)	Ligneous and fibrous organic matter, nitrogen, phosphorus, potassium, volatile acids, proteins, fats, carbohydrates.
	Poultry manure	Same as animal manure.
	Animal carcasses, flesh, blood, fat particles, hair, bones, oil, grease	Ammonia, urea, amines, nitrates, inorganic salts, various organic and nitrogen-containing compounds.
	Pesticides, insecticides, herbicides, fungicides, vermicide and microbicide residues and containers	Chlorinated hydrocarbons, organo-phosphorus compounds, other organic and inorganic substances, e.g., strychnine and lead arsenate.

*Reference (74).

enterprises, approximately 4 billion tons of wastes will be generated. Increased waste generation can be expected in nearly every commodity area, including coal, phosphate rock, clay and mica among others, not only because of increased production but also because of the need to process lower-grade ore.

Although some 80 mineral industries generate wastes, eight industries are responsible for 80 percent of the total. For a breakdown of the wastes produced by the different industries see Table 7. Of these, the copper industry contributes the largest tonnage, followed by the iron and steel, bituminous coal, phosphate rock, lead, zinc, alumina and anthracite industries. Smelting, nonmetallic mineral mining including sand and gravel, gold dredging, stove and clay, and the chemical processing of ores and products account for most of the remaining 20 percent of the mineral solid waste generated.

Mineral wastes are, for the most part, barren overburden or submarginal grade ore from open pit or surface mining of copper and iron ores, phosphate pebble rock, a multitude of nonmetallic minerals such as clays, mica and kyanite, and from the underground mining of lead and zinc ores. These spent ores, called tailings, generally consist of the carbonates and silicates of calcium, magnesium, aluminum, and other metals, together with silica and other oxides (71). The exact proportions in which the compounds exist vary from mine to mine and from industry to industry. These large volumes of wastes usually accumulate near the mining operations. Sometimes this is in remote, sparsely populated areas and sometimes they are not. When they are near populated areas, wind erosion contaminates the air with dust. The wastes from the coal industry often ignite and fill the air with noxious, corrosive pollutants, and during rainy seasons, pose slide threats. In both cases, silt and chemicals washed from these waste accumulations could poison nearby streams and rivers.

2.1e Federal Waste Sources: There are approximately 6,000 major defense installations located in the United States and throughout the world, with approximately 3.5 million persons in the uniformed military services.

TABLE 7. * GENERATION BY TYPE OF SOLID WASTES FROM THE MINERAL AND FOSSIL FUEL INDUSTRIES
(1965)

Industry	Mine waste	Mill tailings	Washing plant rejects	Slag	Processing Plant wastes	Total (thousands of tons)
Copper	286,600	170,500	---	5,200	---	466,700
Iron and steel	117,599	100,589	---	14,689	1,000	233,877
Bituminous coal	12,800	---	86,800	---	---	99,600
Phosphate rock	72	---	54,823	4,030	9,383	68,308
Lead-zinc	2,500	17,811	970	---	---	20,311
Aluminum	---	---	---	---	5,350	5,350
Anthracite coal	---	---	2,000	---	---	2,000
Coal ash	---	---	---	---	24,500	24,500
Other ^a	---	---	---	---	---	229,284
Totals	419,571	288,900	144,593	23,919	40,233	1,146,500

*Reference (74).

^a Estimated waste generated by remaining mineral mining and processing industries.

Civilian employees of government number approximately 2.6 million, and the varied nature of their work results in solid wastes of every conceivable nature.

Some solid wastes produced by Federal installations, and particularly those associated with the military, require special considerations in disposal, or certain aspects of the solid-waste system must satisfy special requirements. For example, the disposal of defective bombs create problems that are seldom encountered outside of government.

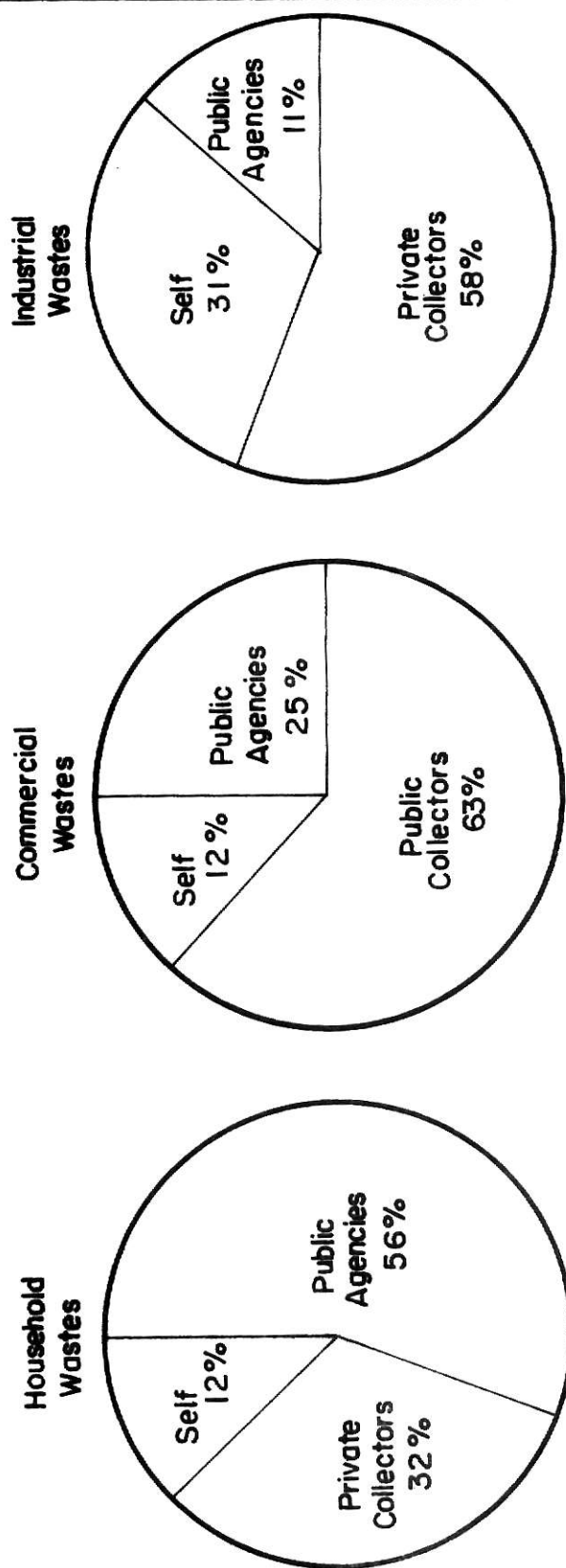
On the other hand, the military installations and federal industries generate wastes similar to their civilian counterparts.

The big difference in the Federal and civilian sources is the wide spread control the Federal Government has over the policies on the handling of the solid wastes.

2.2 Collection of Solid Wastes

2.2a Collection of Urban Wastes: Urban solid wastes constitute only about one-twentieth of the national solid waste production, yet their management requires a great deal of continuous effort. This is because they are visible heterogeneous wastes generated where people live and in areas with limited storage space. These wastes cannot be tolerated for long on individual premises or public places; they must be moved.

Urban wastes are collected and transported in one of three ways; public agencies, private collectors or the wastes are handled by individuals themselves. In the report National Survey of Community Solid Waste Practices (9), some 6300 communities were surveyed with respect to their handling of solid wastes. In the case of household collections, some 56 percent of community inhabitants are served by public agencies and 32 percent by private collectors, while 12 percent of the population perform their own collection and transport of their household refuse. In Fig. 1 it is noted that these proportions are entirely different for commercial and industrial collection. The public agencies tend to concentrate on household and commercial collections, with an appreciable amount being expended on street cleaning. Private collectors give somewhat



NATIONAL AVERAGES
(Population Basis)

Fig.1. Responsibility for Collection Performance.(74)

more attention to industrial customers. Since collections of household and commercial wastes are frequently combined, the data does not give a clear indication of the extent to which public agencies concentrate on households and private collectors concentrate on commercial sources.

Individual waste collection practices vary with each municipality. In the case of public agencies or private collectors, household garbage and rubbish are usually collected once a week. For other types of household wastes such as yard refuse, ashes, and bulky items, collections tend to be sporadic.

Collection organization concepts are based on route and crew organizations, container handling and type of pickup service. Semi-truck and trailer, long distance transfer hauling, and transfer station operations are more commonly used in the collection and transfer of municipal refuse. These transfer costs run about \$2 to \$3 per ton. Conveyor belt and water slurry transport may be less expensive for short haul distances than rail and motor transport.

By far the most expensive phase of solid waste management is the collection and transportation of the wastes. Collection and transport accounts for approximately 75 to 80 percent of the \$4 billion annual cost of urban solid waste management (86). This service costs \$30 to \$50 per household per year. Even with the present inadequate solid waste systems, these expenditures account for a major portion of community expenditures. Among city public services, such expenditures are exceeded by only a few other activities such as schools, welfare, and roads. Not only is collection and transportation the biggest cost involved, it is reported also as being the most inefficient area of operation. Some of the problems involved were pointed out by Richard Stevens, President of University Byproducts, Inc. (Sun Valley, California), at one of the National Industrial Solid Waste Management Conference sessions (71). He maintained that mechanized equipment available today is inadequate, but its use is far from efficient. The reasons are complex but Stevens did cite a few examples. First, optimum use of collection equipment is often thwarted by

obsolete highway codes. Loading capacity of most collection and compaction equipment is far greater than that legally allowable. In order to achieve maximum efficiency, waste contractors must be allowed to use maximum loading capacity. Another drawback is the unwillingness of health agencies and the public in general to accept such innovations as a once a week collection rather than twice weekly, and curb-side service of backyard pickup. The recent introduction of disposable paper and plastic refuse sacks has rendered health codes obsolete in terms of a need for frequent collection and once a week collection of bagged refuse at curb-side would lower collection costs dramatically with little or no inconvenience to home owners. Another of the stumbling blocks to efficient industrial waste management has been the fact that in the design of new industrial and commercial centers, the designer and architects are often insensitive to the waste management requirements. As a result the refuse handling arrangement receive little attention and often are the last facility allowed for in the design.

Recently with the new emphasis on ecology, there has been an increase of voluntary sorting of trash at home and delivery to collection centers, where it can be turned over directly to industries. This movement by numerous ecology-oriented volunteer groups around the U.S., and assisted by the industries involved, has been responsible for much of the new awareness of the recycling problem in this country.

It is doubtful, however, that the private collectors and the individual volunteer practices will provide an acceptable alternate for the public collection agencies.

First, the secondary materials industries now work mainly with commercial or industrial scrap and obtain very little of their material from domestic trash sources. If they tried to expand by sorting material from trash, it would be a very costly operation. Presently it would probably require expensive hand labor, plus some additional processing to clean up the material for sale.

With some form of subsidy from voluntary effort or public treasury, a lot more value could be skimmed from trash. However, neither the volunteer movement nor the commercial scrap dealers seem likely to be able to handle the entire urban trash problem, including the disposal of the final residue remaining after sorting out the materials of value.

Also, using an alternate collection system will require some means of moving the waste materials. Since in conventional trash management practices, the collection process is responsible for 80 percent of the cost, further fragmentation of the collected system seems like a step in the wrong direction.

The volunteer recycling drives and commercial scrap industries have made a great impact on the American public in the form of increased education and awareness about the solid waste problem. Through the efforts of recycling drives and through the publicity given these efforts, many Americans are becoming aware that paper can be recycled and that aluminum is a relatively expensive material. This is bringing about a change of attitude about using materials once, then discarding them without concern of environmental consequences.

2.2b Collection of Non-Urban Wastes: For many industries, including mineral extraction and agricultural operations, collection is a minor portion of solid waste management because the wastes are either stored, processed or disposed of on-site.

If a municipality offers free municipal pickup to industrial establishments, most industries will avail themselves of the service because they pay for it in taxes. In some cities municipal regulations may prohibit municipal pickup of industrial wastes and therefore, the industries will use self disposition or contractor collection, depending on economics.

Because of the lack of information, it is impossible to determine how much of the industrial, agricultural and mineral wastes are collected and what percentage is disposed of on-site. However, among those private collection agencies there exists commercial scrap dealers. These scrap dealers collect

or buy scrap metal, paper, glass, fabrics, plastics and other materials, usually from commercial and industrial sources, sort it if necessary, and sell it to manufacturing industries. This eight billion dollar secondary (waste) materials industry is responsible for most of the recycling done currently, including 30 percent of all the aluminum produced, 45 percent of the copper and brass, 52 percent of the lead, and 20 percent of the paper (64,65).

Most of the urban wastes are being picked up and carried to the disposal sites, but much of the industrial and almost all the agricultural and mineral wastes are disposed of on-site. While certain types of solid wastes from Federal installations also require special handling, the bulk of Federal solid wastes are collected in a manner similar to municipal and industrial processes. As the practices of open dumping and burning become illegal, the volume of wastes to be collected will go up drastically, especially in the agricultural and mineral areas. In order to be economical, large scale operations will be needed to process these wastes. This will require collecting of the wastes at their source and transporting them to the processing site.

Many of the problems discussed in the previous section apply to the collection and transportation of these wastes. To keep down the costs, high volume handling must be used. At this time, the greatest future in the collection of solid wastes lies in regionally integrated facilities, handling urban, industrial, agricultural and mineral solid wastes. This use of centralized operations is one way of taking advantage of modern waste collection and processing techniques, most of which depend on large scale operations for efficiency.

2.3 Disposal of Solid Wastes

The final step in the management of solid wastes is the processing or final disposal of the collected wastes. As mentioned previously, this step did not present too much of a problem in the past. These unwanted materials were disposed of in the cheapest, most convenient way possible. The general

attitude was that materials were to be used once, then discarded. This idea seemed acceptable partly because of an abundance of natural resources, availability of unused real estate of low value and a lack of knowledge about some environmental consequences of mismanagement of solid wastes. Even today, about 90 percent of the trash collected in the U.S. is disposed of either by open dumping and burning or by landfilling (29,74).

Gradually as the awareness of pollution and public health has grown, this attitude is giving way to a more resourceful one. Dwindling resources, urban concentration of an escalating population, soaring consumption of goods, and environmental factors have made past practices and attitudes unacceptable. Authorities are now endeavoring to utilize these discarded materials in such a way that will eliminate the wastes, protect the quality of the environment and do it economically (16).

Currently a great deal of attention is being given to the concept of reusing or recycling wastes. This concept is not limited to the recycling of waste components back into their original form but also includes direct use of the wastes, reclaiming certain values in it and recycling the wastes in some useful form (29).

The major categories of disposal in use today are open dumping, open burning, ocean disposal, mulching, land spreading, animal feeding (45,88), and sanitary landfilling. These methods are far from the most efficient ways of handling the resources and value that is contained in the wastes of the nation. These approaches give some idea of the gap between actual and desirable methodology.

How and where the wastes, generated by the different sources described in the earlier part of this report, end up is rather difficult to determine. There is very little data about whose wastes go where and the figures and data are only approximate. Most of the literature quoting facts about urban wastes are based on the National Survey of Community Solid Wastes Practices, 1968 (9), or other similar studies. These studies are far from comprehensive facts about

the wastes other than urban have even less substantial basis. The lack of regional control, both private and public participation in waste management, on-site disposal and unsupervised, random dumping make accurate data impossible to get.

The remainder of this section discusses correct waste disposal methods with respect to the source which generated them. Also given are some new recycling methods which may prove practical in the future.

2.3a Disposal of Urban Wastes: Before the 1960's, the most predominant type of urban waste disposal was open dumping. Little effort was made to manage land disposal sites and as a result general public health was threatened. During the 1960's there was an extensive change from the open dumps to the development of sanitary landfills. In 1969 about 90 percent of the trash collected in the U.S. was disposed of either by open dumping and burning or by landfilling (74).

The landfill process, however, is a ravenous devourer of land. New York City has been consuming land for this purpose at the rate of about 200 acres a year. Some cities, including San Francisco, have already run out of space and are shipping their trash to other areas. The concentration of the growing population around urban centers is making it impossible to continue landfilling practices.

Incineration is about the second largest method used in the disposal of urban wastes. The heat generated can possibly be reclaimed and the volume of trash can be reduced substantially to a mineral residue (13,17,71). This will extend the life of a landfill and improve its quality but this method is not a final solution to landfills because of the residue disposal (see Table 8 on next page). The incinerator method also faces other problems. The air pollution restrictions are becoming stiffer and presently only about one-fourth municipal systems meet current air codes (72). At the same time the toxicity and corrosiveness of the flue gas is increasing due to the gases produced by burning certain materials, especially plastics (2,87). These factors drive up

TABLE 8.* COMPOSITION OF TYPICAL MUNICIPAL INCINERATOR RESIDUE
(AVERAGE OF FIVE WASHINGTON, D.C. INCINERATORS)^a

Material	Percent by Weight
Tin cans	17
Other iron and steel	11
Other metals	2
Glass	44
Ceramics, stones, bricks	2
Partially burned or unburned organic matter	9
Ash	15

*Reference (29).

^aSource: U.S. Bureau of Mines Report 7204, 1968.

the capital and operating cost making this method less and less attractive especially for smaller communities. Incineration will probably be more and more popular in the immediate future but in the long run it is not an ideal solution.

These and other methods, with just as many or more disadvantages, have caused authorities to look for longer range solutions. In the 1970's the trend has been toward the reuse of the solid wastes. This does not necessarily mean returning the discarded material back into its original form. The current recycling efforts are simply to return the wastes to the economy in a way that will provide some utility, in any form. With this definition, even landfilling can be termed a recycling use. Los Angeles, for example, has filled pits and gullies which afterwards are golf courses and botanical gardens. Virginia Beach, Virginia, is building a 60-ft. high hill of trash on which will be built an amphitheater, a soapbox derby run and a winter sledding course. Heat provided by incineration can also be utilized, thus meeting the recycling definition. In Montreal and Chicago heat produced by burning trash supplies steam used to produce electricity.

Yet the value of a landfill material (approximately \$2/ton) and of incineration heat (from \$1/ton to \$5/ton) is rather nominal considering the relatively expensive material which went into the trash (29). The question is whether or not there is a more valuable way to utilize the trash.

Current technology has generated many new methods for reusing wastes as well as a greater percentage of recycling of waste materials into its original form (for example the return of returnable glass bottles, recycle of scrap iron and other metals like aluminum, etc.).

One such method of recycling is that of pyrolysis which produces an oil similar to crude petroleum. The oil, used mainly as a fuel, has a fuel value two or three times that of raw trash, but even this is not enough to make the process very economically attractive. Only about half of the trash weight is obtained as oil, and little, if any, increase in the overall fuel value is likely.

This type of recycling approach uses an old process known as "destructive distillation". Pyrolysis, as it is called, is similar to incineration except that air is excluded and heat is applied externally. This is the process that is used to convert wood and coal into charcoal and various chemical products. Recent studies using trash as a feed have shown that various liquid and gaseous organic materials, such as methyl alcohol, acetic acid, and some heavier oils are driven off and charcoal and some ash are left as residues (4,26,46,67,70). The ash is similar to that from incinerators but the other products are combustible and are thought to be saleable mainly as fuels. Little credit is expected from the chemical products produced, however; the reason being that the market for the chemicals reported as being produced can absorb only a small percentage of the huge quantities of these chemicals potentially available in the urban wastes.

The first major trash pyrolysis plant was to be built in Delaware and operated by the Hercules Corporation (63). The 10 million dollar plant will handle 500 tons of waste a day, and is based on a composting step handling the bulk of the material, followed by the removal of the metal and glass for recycling and then the residual material is pyrolyzed.

One area that the pyrolysis technique may prove to be very attractive is in the disposal of old rubber tires (62). Approximately 100 million tires are discarded annually in the U.S. The Firestone Rubber Company announced a process where tires are pyrolyzed to give about 45 percent solid carbonized residue and the other 55 percent is a mixture of gases and liquids similar to petroleum products (91).

Another area where pyrolysis may prove valuable is in the treating of plastic wastes. These gum up and chemically attack the walls and grates of incinerators and produce toxic vapors in the stack gases. In the pyrolysis process they are reduced to a crude oil which can be handled quite easily (59,60).

The important feature of the pyrolysis process is its ability to convert most organic materials to charcoal which is saleable as fuel and volatile organic compounds. This conversion of trash makes it easier to manage its fuel value and possibly simplify air pollution problems.

Two related processes have been developed by the U.S. Bureau of Mines. The first involves reacting trash with carbon monoxide at high temperature and the pressure to produce an oil similar to crude petroleum (4). The second involves the reaction of municipal wastes with gaseous hydrogen to produce mainly methane (called hydrogasification). Again these are major technological achievements but the product has rather low value (22).

Another type of disposal method that may qualify as a recycling method is composting (61). Composting is essentially the biological oxidation of the organic components of trash to relatively stable compounds. The trash is usually ground or shredded then allowed to cure. This is done by spreading the shredded trash in windrows which are turned occasionally over a several-week period, or cured for three to five days in a large, slowly rotating, horizontal cylinder. Paper and other cellulose materials undergo composting readily. Thus the largest part of the urban wastes can be processed by this method. Sewage sludge is often added to provide moisture and nutrients which add to the composting process, while metal plastic and larger pieces of glass are removed from the product by screening (69). Composting costs are in the range of five to ten dollars per ton of trash which produces one-half to two-thirds ton of compost. The finished product sells for about six dollars per ton, but is low in fertilizer nutrients and finds its main value as a soil conditioner for high-value speciality crops. Compost can be used to improve the fertility of barren or dry land and strip-mined coal fields or for stabilization of steep slopes, road embankments and mine-tailing piles.

A typical composting plant is run by the Metropolitan Waste Conversion Corporation in Houston, Texas (89). Here, as in most instances, the emphasis is shifting toward salvaging as much material as possible prior to the composting process. Iron is removed magnetically and paper and other easily

identifiable materials are sorted, partly by hand and partly by mechanical methods.

Although widely used in Europe, large scale composting has not been attractive in the U.S. Only three composting sites were operating in 1969. The large market for compost present in Europe has not developed here and the market that does exist is located in the rural areas far from the urban areas where the compost is produced. Since the value of the compost is low and the trends seem to be away from making compost a saleable product, and viewing it as a means of converting trash into a material which can be returned to the environment without harming it. If this continues, composting will be reduced simply to a disposal method for organic wastes and is no longer a recycling approach. In urban areas, incineration and pyrolysis are more versatile means of accomplishing the same end. The residues from incinerators and pyrolysis are smaller, and the by-produce power available from both have a ready market in the urban areas. Thus in the more densely populated areas, composting is probably heading toward the same fate as sanitary landfilling, which is becoming obsolete.

Because of the high volume of paper in urban wastes (roughly 50 percent) special mention will be made concerning the recycling of paper. In the U.S. approximately 11 million tons of waste paper a year are directly recycled back into paper or paperboard products. This accounts for roughly 20 percent of the total paper production in the U.S. The waste, however, does not come from collected urban trash but from commercial and industrial sources. Over 70 percent of the recycled paper consists of either corrugated board, newsprint or what is known as N_0 mixed (a low-grade paper waste collected from office buildings and other similar commercial establishments). Much newsprint comes from volunteer organizations, but the remainder is collected by dealers, who sort, bale and ship it to papermills. Most of this waste goes into cardboard or construction paper, where bulk, rather than high strength or whiteness, is the major concern.

To try to reclaim some of the paper in urban trash, two approaches have been developed in the U.S. within the past few years. The first method is the separation of the paper from the raw trash by hand or by mechanical means (12). Some composting plants such as Metropolitan Waste, have done so and are selling the paper back to the papermills.

The second approach was developed by the Black Clawson Company, a manufacturer of papermaking equipment (33,54). This method involves the pulping of raw trash in a large blender. A series of mechanical separations including screens and centrifugal devices remove large objects which cannot be pulped such as cans, shoes, bones and broken glass, after which a fine screen catches the cellulose fibers. About half of the cellulose fiber present in the trash is recovered as a crude product valued, according to the company officials, at about \$25 a ton. The metal and glass which are separated are also saleable.

With the aid of a grant from the U.S. Bureau of Solid Wastes Management, the city of Franklin, Ohio, is constructing a 50-ton-per-day trash reclamation plant which will use this process (93). The Black Clawson Company claims that a 1000-ton-per-day plant (an amount equivalent to a city of about 500,000 people) would break even, while larger plants could produce a profit.

Dr. Jetzel from Purdue has proposed a related process which combines the hydropulpers and reverse osmosis to treat sewage and solid wastes to produce a solid slurry for land application, metals for reclaiming and drinkable water (53).

Another similar project is underway at Madison, Wisconsin. Their process uses the "dry sort" methods of the composting plants along with the Black Clawson's wet-pulping process (24). The FPL officials are planning to upgrade the crude pulp by chemical processing, creating a recycled fiber which can compete for uses currently filled by virgin fiber.

In their analysis, the FPL investigators have found that the bottleneck limiting preparation of high-grade pulp is probably not the usual contaminants in trash, such as grease, food or other garbage put into a paper during use and disposal by the user, but rather the waxes, pigments and plastics put into the paper by the manufacturer.

Another major issue related to the recycling of paper is a marketing problem. Most paper products ultimately end up in the trash - some estimate as high as 70 to 80 percent. If a substantial amount of this paper could be recycled as high-grade pulp, the fiber would compete with virgin material for paper products.

The market is large enough to absorb this recycled fiber, if the quality of the fiber is competitive. The reuse of fiber will reduce the demand for raw materials, much to the delight of conservationists. The pulp manufacturers on the other hand will face a new competitor and will not be so optimistic about the advantages with this type of paper recycling.

Two other common components in the urban wastes are metal and glass. With few exceptions, these are almost unaffected by the disposal methods that have been previously described. Thus, the recovery of metal or glass can be accomplished at the feed or from the residue of the processes discussed and the similar equipment could be used in either case. In the processes involving heat, the alloying of the metallic constituents with each other complicates the subsequent separation of metals. Once separated the metal and glass can be returned to their original manufacturers and in this way recycled.

At the present time the most effective means for sorting out these materials are, for iron, various magnetic devices, and for glass, some form of air classification (12) in which an upward air stream carried lighter materials away. No simple means has been reported for removing the aluminum, but the problem is under study. The value of the separated waste glass and metals are quite high (scrap steel is worth about \$20/ton and aluminum \$200/ton, glass \$10/ton) but because of their low weight percentage in trash, it is

doubtful that the credit obtained by selling the glass and metal back to the original manufacturer will be enough to offset the separation and transportation charges. Their separation, however, is essential in most recycle operations so for the process to be profitable separating costs must be made up for by credit somewhere else in the process.

The major metal item in trash is the notorious "tin" can, which accounts for about two-thirds of the metal found there. The total amount of iron and steel items in trash is estimated to be about 10 to 15 million tons per year or approximately 10 percent of the U.S. steel production. Another million tons or so of other metals, mainly aluminum, are discarded in trash. Sizeable quantities of cans are already being used in the western U.S. for recovering copper from low-grade-ore processing. This is a limited market and it appears that eventually steel-can reclamation will require recycling them to steel furnaces, where the cans are now generally unacceptable because of their tin coating. The technology of detinning is well known but expensive. However, a big boost to can recycling may be on the way because of TFS cans, (tin-free steel cans) which are directly acceptable into the steel furnace. The tin coating is replaced by a chromium and resin film.

A large source of steel scrap is the junked automobile. There are some 7 or 8 million autos junked each year in the U.S., most of which end up in junkyards. However several hundred thousand are abandoned in the countryside and in cities where they become a part of the urban trash problem. New York City, for example, hauled away 50,000 such cars in 1969.

The major technical problems of recycling cars are the same as those of recycling cans; that of removing undesirable materials and the transportation of the steel to a buyer, such as a scrap yard. In the U.S. the principal development for separating these metals for recycle is a shearing machine which produces fist-sized chunks that are separated by magnetic equipment to yield iron and steel.

Once the metal has been separated from trash, further separation is necessary by most recycling processes to remove other materials such as glass. The glass content of trash is mainly bottles and jars, but most bulk-separation methods would probably pick out stones, ceramics and concrete, in addition to glass of nearly every shade of the visible spectrum. Scrap glass can be recycled to glassmaking furnaces but it must be sorted by color and separated from extraneous materials such as rocks and metal.

The problem of sorting glass by color is being approached from two directions. The U.S. Bureau of Mines uses a very high-intensity magnetic field to separate colored glass according to its iron content which is related to its color. Other devices divert glass fragments passing a sensor to appropriate bins, depending on the color of light transmitted by the fragment.

The scrap glass, called cullet, is valued at about fifteen dollars per ton, thus it is questionable whether large quantities can be economically reclaimed from trash, sorted and transported to the glass factory. In many locations the problem may be one of how to return the glass to the environment without harming it. The current trend has been to dispose of the glass by incorporating it into building blocks, tiles, or "black top" aggregate (14, 25). The cullet which is similar to sand has been used by the Owens Illinois Company to pave a street (61). While the value of this type scrap glass is only that of sand or crushed rock (3 or 4 dollars/ton), construction and paving uses represent large outlets in populated areas, eliminating the need for transportation to distant glass furnaces.

The municipal sources of solid wastes almost always are handled by the same agency that is handling the domestic wastes of a community. Therefore like domestic trash, most municipal wastes end up in a sanitary landfill or being incinerated.

The recycling method being used in the area of domestic wastes will naturally be applied to those wastes generated by the municipalities. The recycling of junked autos has already been discussed previously as well as

the composting of sewage sludge. It was also mentioned that fly ash generated at the power plant from the burning coal or the ash residue from incineration could be used as filler in asphalt or concrete (6,23). Another development has occurred in the area of fly ash disposal.

At the University of West Virginia, J. W. Leonard has developed a brick which is made of fly ash (43). The difficulty in working with ash, as in most waste materials is that its physical and chemical characteristics vary considerably depending on the fuel being burned as well as temperature, season, etc.

The disposal of commercial wastes (wastes from hospitals, restaurants, hotels, general office buildings, etc.) are somewhat different than the domestic and municipal waste disposal. In many of the downtown areas, municipal collection services are provided to these commercial enterprises. Some of these enterprises, however, are located outside the normal service area of the public collectors; therefore, they turn to private collectors and disposal agencies or take care of their wastes themselves. There is no accurate data on a national basis about the disposal of these wastes but it has been pointed out that much of the recycling of waste paper comes from these commercial sources. The scrap dealers frequent many of these commercial installations collecting paper and other valuable reusable wastes whenever the situation is profitable. Most of the current recycling is attributed to these scrap dealers.

Most of the commercial wastes collected by the public agencies and a lot of that collected by the private collectors (that which is not desirable and other residues) will end up at the municipal dump site or incinerated like other urban wastes. Thus the same problems are encountered as before. There are some specialty wastes from hospitals, explosive and other toxic wastes from other institutions, etc. which are banned from the normal municipal disposal system because of the possibility of a public hazard. If a large integrated system is to be instigated, it must have provisions for the handling of these specialty wastes generated by the commercial sources.

There have been numerous other methods of recycling proposed, ranging from biological processes for production of alcohol, sugar and protein (81), to a suggestion that trash be put through a hydrogen fusion torch which would break it down into its constituent elements (20). Building materials have been made by pouring tar over compressed garbage (39,90), and many other exotic recycling methods have been proposed. At the present it is impossible to tell which of these methods will prove to be best.

In an attempt to compare the different methods presently available Grinstead has drawn up a table comparing some of the present disposal methods. His results are given in Table 9.

Estimates of final nonrecyclable residue have not been included, since most proposals envision burning or pyrolyzing any such residue to an ash. The only conclusions that could be made from this analysis is that the classical methods - landfilling, incineration and composting - recycle paper produced into an end use of fairly low value and do not reduce the burden on virgin materials. Presently this may be sufficient, since the one to ten dollars-per-ton cost of the disposal process is secondary when compared to the twenty to fifty dollars-per-ton cost of the collection system which precedes it (94). In the long run, however, there will probably be a shift toward reclamation of cellulose fibers, where the value of the product offers a better chance for positive returns.

This does not mean that other methods will disappear. Because of the variety of situations where domestic trash is generated, condition may favor in one case a process which is not applicable in others.

2.3b Industrial Waste Disposal: Burning and dumping are the most widely used methods for industrial solid wastes. The methods are increasingly unacceptable in the face of more stringent air and water pollution regulations along with the decreasing availability of land for disposal sites. A serious problem arises in the lack of information on the quantity and type of wastes generated. A large percentage of industrial waste is of similar

TABLE 9.* COMPARISON OF MAJOR TRASH RECYCLING PROCESSES

Process (Use)	Ton of Product Recovered per Ton of Trash	\$ Value, per Ton of Product	\$ Value Gained per Ton of Trash Processed	Processing Complexity and Cost	Marketing Fit	Probable Net Credit (+) or Cost (-) of Process, \$ per Ton of Trash
Landfill	1	1	1	low	becoming poorer in urban areas	-1 to 2
Incineration ^a (fuel)	1	3	3	low to moderate	good	-1 to 5
Compost	.5-.67	6-10	3-5	moderate	poor	-5 to 10
Pyrolysis (fuel)	(.5)	5-10	2-5	moderate	good	similar to incineration
Carbon Monoxide (oil)	(.5)	20	10	high	good	probably (-) and large
Fiber Recovery ^b	(.25)	25	6	moderate to high	good	about zero

*Reference (29).

^aFor incinerator utilizing heat.^bBased on Black Clawson process.

nature, being independent of the specific industry involved. For example, shipping waste, plant trash and office wastes are very much alike from one industry to another. The remainder of the wastes produced, however, are often peculiar to the processes involved. The amount and make-up of these wastes is seldom known by municipal authorities. Therefore, rather than risk overburdening their already taxed wastes disposal system or creating new environmental problems, these officials prevent the specialty wastes from reaching the municipal systems. Unless the municipalities have more accurate information about the industrial process wastes, they will continue to prohibit these unique wastes from entering their disposal systems while they accept the burden of the "routine" solid wastes from the industrial establishments (89). Again if some type of an integrated system of total solid waste management is to be developed, more detailed information is needed about the type, quality, and best methods of handling all industrial wastes.

One significant point is made by the 1969 "Solid Waste Management" report (74). It indicates that even at that time it was estimated 48 percent of the industrial wastes were being utilized or recycled in some manner which is the highest recycle rate of all the sources. The highest waste utilization occurs in the lumber industry. In 1965, the total industrial waste produced was estimated to be 229 million tons of which 65 million tons was from sawmills. Of that 164 million tons remaining, only 27 percent was recycled.

Again most of the recycling is in the form of the individual industries reusing their wastes or selling it to scrap dealers (47). Fifty percent of industrial waste disposed of in private facilities and 36 percent went to municipal facilities. Forty percent of those industrial wastes collected were disposed of in dumps. Excluding sawmills, 57 percent of the wastes collected went to dumps.

Although the largest reuse is in the wood and wood-products industries, it seems that the disposal of the large volume of sawdust and shavings without aggravating air and water pollution is a growing problem. The wood-products industry produces many types of materials from these wastes, but

the existing markets are often quite reluctant to use these unfamiliar products when the "old standard" products are available at competitive or lower prices. The standard products, made from virgin materials, may become more expensive as the supply of raw material depleted, thus making the recycled products more competitive.

The industrial phase of the solid wastes problem has an impressive re-use rate, but there is still a great need for more of it. Many industrial plants are disposing of large volumes of wastes by using liquid carriage to streams, sewers and by spray irrigation. Being pressured by higher and higher waste water quality requirements, the industries will have to recapture these wastes in a solid form, and as a result, there will be an even greater increase in the volume of industrial solid wastes.

2.3c Disposal of Agricultural Wastes: The agricultural sector of this country is the largest producer of solid wastes (see Table 1) and use the least sophisticated methods of disposal. Most of the vegetation wastes are burned, returned to the soil, or left piled at some convenient location. In the past, animal wastes did not create much of a problem and were considered an asset used to augment the fertility of the nation's soils. The animal manures were left in the pastures or hauled from the feeding lots to fields where they were incorporated into the soil. Currently it is cheaper for the farmer to use concentrated chemical fertilizer than it is to haul manure in sufficient amounts from his own farm to his fields. This coupled with the concentration of livestock and poultry production has magnified the problems of handling animal wastes.

Problems arising from present management of agricultural wastes include air pollution resulting from the burning of wastes, insect and rodent breeding because of improper storage, generation of offensive odors and dusts through improper handling, and surface and ground water pollution from indiscriminate dumping and spreading on land (74). Accumulation of pesticide containers may occur in agricultural areas, constituting a hazard to humans and animals.

Plant residues from crops, orchards and forests contribute to pollution in two ways; as a source of smoke and other air pollutants when burned, and as reservoirs of plant disease and other pests. Until means are found for controlling the survival of plant pathogens in the buried wastes, burning will continue to be the only safe way (with respect to plants) of disposing of the vegetation wastes.

The contribution of burning agricultural waste to photochemical air pollution has been investigated to some extent (74). The studies indicated that concentrations of photochemically active hydrocarbons were negligible at a mile and a half from the fire where more than 1000 acres of wastes were burned. The emissions of hydrocarbons and oxides of nitrogen from burning of agricultural wastes were considerably less per ton of fuel consumed than those in auto exhaust. The burning of vegetation wastes produced an average of 12 lbs. of hydrocarbons compared to 130 lbs. of the same hydrocarbons in auto exhaust per ton of fuel consumed. It appears from this limited study that the burning of agricultural wastes does not significantly add to the burden of pollutants in the community air, however, the smoke may be an important aesthetic factor.

Disposal of animal manures from concentrated livestock and poultry productions have been associated with fish kills, eutrophication of lakes, off-flavors in surface waters, excessive nitrate contamination of aquifers, odors, dusts and increased production of flies and other noxious insects (44).

Current disposal methods used by feedlot operations include manure storage in tanks when it undergoes incomplete anaerobic decomposition followed by land spreading of the remaining wastes, and anaerobic lagoons which provide low cost manure storage and significant solids destruction (48). The problems involved in these processes are many and these large scale producers are faced with the disposal of the wastes without the technology or finances to cope with modern requirements.

2.3d Disposal of Mineral Wastes: Because of the cost of transportation, the mineral wastes are deposited adjacent to or within short distance from the mining or processing operation concerned. Some of these accumulations of solid wastes pose a threat to life and property, and most of them are real eyesores. Only a small portion of the wastes generated is recycled to the economy, usually in the form of low value commodities used for local construction. Some progress has been made in fabricating useful products from mineral wastes. For a brief discussion of these see reference 71. The problem is that raw materials for the products in markets that these waste materials might enter are already very cheap. This economic factor is compounded by the fact that most mines are located far from potential markets. What's more, the products made from wastes must be of high quality to be competitive. In those cases where the waste product has been successfully utilized, the product has been the best choice with respect to both quality and price. For example blast furnace slag (and to a lesser extent, steel slag) is being used in the construction industry as an all-purpose aggregate for road building and in all manner of concrete products (71). Indeed, this particular material is the preferred product and the steel industry cannot make enough of it.

Mineral waste, like agricultural wastes, have received little attention in the past and only recently have any efforts been made to reclaim some kind of value from them. As their volume grows and as their effects on the environment become better known, a great deal more effort will have to be devoted to their handling.

2.3e Disposal of Federal Wastes (74): The handling of Federal wastes differ from others only in that there is greater possibility of control over the disposal of the wastes. However, it does not appear that the government is taking advantage of this opportunity. There are no sweeping recycling method being used by the Federal installations but instead they use the standard

methods of landfilling, incineration, etc. In fact in the disposal of some specialty wastes (nerve gas containers, etc.), it is leaving a very poor recycling example.

2.4 Summary

In the past (and even today) the most widely used methods of waste disposal were dumping and open burning. To protect our environment it is becoming necessary to prohibit such practices. To provide the necessary environmental protection, to keep control over indiscriminate waste disposal, and to capitalize on large volume processing, there is a need for an overall solid waste management system. This system (whether community wide, county wide, state wide or nation wide) should be responsible for, not only urban wastes, but also those wastes of the industrial, agricultural and mineral sectors of the economy. The volume of wastes to be handled by such a system is phenomenal and the costs involved will also be very high. Such systems have been investigated and a variety of methods proposed to handle all the different wastes (26,50).

Presently the highest costs incurred are those involving the collection of the wastes, but a high volume system will help lower these costs. With the collection costs lowered, the economics of the disposal methods will become focused upon. There will be a great need for ways of removing some of the potential value that is present in the wastes collected to offset the processing costs. To regain value from these wastes they must be transformed to produce some utility, that is recycled. The most widely used recycling methods have been the sanitary landfilling, incineration or composting. These methods have been attractive because they require a minimum amount of treatment of the wastes to regain value from them. However, due to the lack of space, stricter air quality standards and the lack of a market for composting, these methods are losing their attractiveness. Besides, the value gain from the final product (see Table 9) is nominal compared to potential value of the components in the wastes.

The ideal waste management system would involve the recycling of most of the solid wastes back into their original form. With the increased public awareness of the problem and recent advances in technology, more of the waste materials are being so recycled; for example paper (78), aluminum (10,51,77), and plastics (56,76). However, not all wastes can be recycled into their original form, like mineral tailings, ashes from powerplants, etc. There are many other new types of recycling methods (other than recycling wastes into their original form) evolving from the present research and some of these new approaches may prove valuable if a total waste management system does materialize. In using these methods to produce products of high quality, it is taking more sophisticated techniques requiring a great deal of waste separation and complicated processing. Initially, the value gained from the products will not be sufficient to cover the costs, therefore most methods must be subsidized in some way (taxes, tax breaks, government subsidies or high prices for product or utility fees). As the technology improves and with a more efficient handling system, some of the methods may be able to break even or might even become profitable.

From an analysis of the possible recycling processes, several common requirements have been met by those methods which have shown to be reasonably successful. The following paragraphs summarize these requirements.

1. In those processes which succeeded, there has existed markets which are large enough to absorb the volumes of recycled materials and are close enough to provide acceptable shipping costs.

2. In this market, the recycled materials must have the quality to successfully compete with those products made from virgin materials.

3. The amount and difficulty of disposal of final residue (those wastes remaining after all materials which can be recycled have been removed) must be reasonable and not harmful to the environment.

4. Finally the cost of collecting the recycleable material from the solid waste source and then converting it to a form which can be used by the

appropriate industry must be offset by the value derived from the material recycled. The costs of the process must be covered by the sale of the products.

In light of these requirements it is the purpose of this study to investigate the feasibility of a possible recycling method.

CHAPTER 3

3.0 OBJECTIVE

The object of this report was to carry out a preliminary analysis on the possibility of recycling shreddable solid wastes and/or shredded or powdered residues from other methods of waste treatment into solid waste-polymer composites. This recycling process was investigated in light of those requirements met by previous successful recycling methods as determined from the Literature Survey.

First the selectivity of this process toward the type of solid waste that could be used was investigated. This would determine, to some extent, the type of residues that cannot be treated by this method.

Second, the basic processing steps necessary were determined as a basis for future economic studies.

Third, using paper as a representative waste, waste paper-polymer composites were made and tested for some of its physical properties. These results were compared to some standard materials with which the composite material might compete or replace.

Finally, a brief market analysis was made to try and get some idea of the areas where the composite material might compete effectively.

CHAPTER 4

4.0 THEORETICAL

The plastic-solid waste composites used in this study were produced by radiation-induced polymerization. Therefore, before discussing the results of the experiments, a short survey of the radiation chemistry aspects of this study is given in this chapter.

4.1 Sources of Radiation

Any radiation-initiated commercial process requires a convenient, efficient and economic source of radiation energy. There are a multitude of sources of radiation available, however only a few are practical. In the area of ionizing radiation, the current practical choices are electron accelerators, and a cobalt-60 or cesium-137 source. For a discussion of these sources, their details, maintenance, economics and suppliers see reference 31.

4.2 Primary Processes

When electromagnetic radiation passes through matter its intensity decreases, primarily as a result of scattering and energy absorption by some of the irradiated molecules. The three major processes are:

- (1) The photoelectric effect
- (2) Compton scattering
- (3) Electron-pair production

A brief description of each process is given below (15, 80).

(1) The photoelectric effect. X- and gamma-rays of very low quantum energy (< 1 MeV) are all exclusively absorbed by photoelectric absorption. In this process, all the energy carried by the incident photon is transferred to an electron of the irradiated substance. In the case of ionizing radiations, the energy of the photon ($h\nu$) is usually much larger than the binding energy of the electron (Q) in its orbital. Thus an electron is freed and acquires a kinetic energy of $(h\nu - Q)$ which is greatly in excess of the electronic binding

energy and as a result is capable of liberating several other electrons from molecules along its path. In each photoelectric event a photon disappears and is replaced by a fast moving electron which has a much shorter range and so dissipates most, if not all, of its energy in the irradiated medium. The probability of photoelectric absorption increases rapidly both with the wavelength of the radiation and with the atomic number of the irradiated medium.

(2) The Compton effect. For more energetic X- and gamma-radiation (> 1 MeV) a large proportion of the energy is dissipated through Compton recoil electrons. In this process, only a fraction of the photon energy is transferred to the electron. The incident gamma photon interacts with an orbital electron of an atom, ejects it (with varying amounts of kinetic energies) and a photon of somewhat longer wavelength (lower energy) emerges from the collision in a direction different from that of the original photon. Compton electrons produced from a radiation of given quantum energy have a very broad spectrum of energies which varies from 0 for a photon which is undeflected, to a maximum of $(2h/mc)$ for a photon scattered through 180° .

The total energy transferred by Compton absorption in any volume is directly proportional to the total number of electrons in that volume element and is predominantly in the .2 to 2 MeV range. The Compton effect is the most important primary absorption mechanism in the range of photon energies, usually employed for radiation chemical processes.

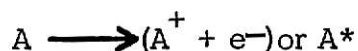
(3) Electron-pair production. For electromagnetic radiation having quantum energies above 1.02 MeV, a fraction of the radiation energy is absorbed by electron-pair production. In this process, the photon is changed into an electron plus a positron which share equally the available kinetic energy. The absorption coefficient for pair production is proportional to the square of the atomic number of the absorbing molecule and increases with increasing photon energy.

It follows from the foregoing analysis that when electromagnetic radiation traverses matter, the absorbed photons are rapidly converted into fast

moving electrons. These electrons produce most of the observed ionizations and are responsible for nearly all the chemical changes that take place. In the case where matter is exposed to Co-60 gamma radiation, the most important primary absorption mechanism is the Compton effect.

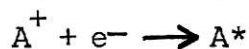
The chemical bond energies of organic materials lie in the range of 1.5 to 8.5 ev. Therefore actinic radiation can lead to direct production of organic free radicals or atoms of such elements as the halogens. In the case of photochemical reactions, direct internal rearrangement may occur. These occur at a rather specific chemical-bond site and whether or not the overall conversion of one chemical to another is also specific depends upon the reaction mechanism of the propagation steps that may follow.

High energy radiation (2/Mev), on the other hand, does not result in the deposit of its energy in a specific bond during the primary absorption process. All the interactions of ionizing radiation and matter lead to the formation of positive ions and ejected electrons, and/or excited species. This can be represented by the equation

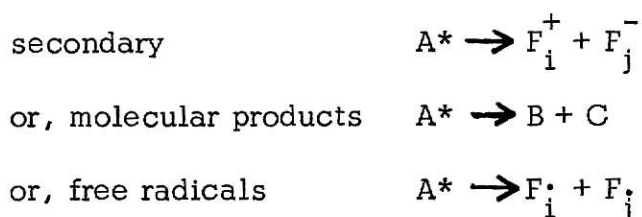


in which A is a molecule in the irradiated system, and e^- is the ejected electron. The asterisk indicates a molecule in an electronically excited state.

If the ejected electron is not captured by another molecule, it may recombine to neutralize the original or another positive molecule. This recapture can leave the molecule in a highly excited state.



Unless some other means is at hand for dissipation of the excess energy present in the excited molecule, dissociation will occur. This decomposition may yield:



where F is a fragment of the original molecule and where B and C are molecular products. The radicals or ions formed by these processes will then react according to the usual chemistry of free-radical or ionic reactions. The dissociation of the excited molecule A^* into free radicals F_i^\cdot and F_j^\cdot is believed to be one of the most important sources of free radicals in radiation-chemical processes. These radicals are thought to be chiefly responsible for the subsequent chemical changes. This is especially true for polymerization vinyl monomers by irradiation.

4.3 Polymerization Mechanisms

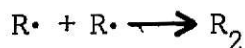
The radiation-initiated polymerization of numerous vinyl monomers such as styrene, methyl methacrylate, etc. leads to high-molecule-weight products having products almost identical to those of the corresponding polymers obtained when using conventional methods of initiation. It is thus concluded that radiation polymerization proceed by a long chain reaction process similar to ordinary polymerization. A single radical or ion can initiate a polymerization chain reaction. Experimental work has shown that most radiation polymerizations at room temperature proceed via free radical chain reactions. In radiation polymerization the initiation step is brought about by the absorption of the radiation energy, and this results in various secondary processes which finally lead to the production of free radicals. In the propagation step, a free radical adds on to a double bond of a monomer molecule, thereby regenerating another free radical. This process goes on until the activity of the growing chain is destroyed, known as termination.

A detailed kinetic scheme in which all the mutual reactions involving all free radical intermediates are taken into consideration is given below (15).

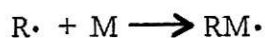
(a) Initiation: (Formation of primary radicals)



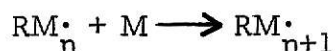
(b) Recombination of Primary Radicals:



(c) Addition onto Monomer:

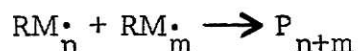


(d) Propagation:

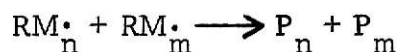


(e) Mutual Termination:

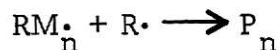
by combination:



by disproportionation:



(f) Termination by Primary Radicals:



Here A^* is any molecule present in the reacting mixture (monomer, solvent, initiator, etc.), $R\cdot$ is a primary radical, M the monomer, $RM_n\cdot$ a growing polymer chain and P_m , P_n , and P_{n+m} are "dead" polymers.

At low dose rates and in systems with low conversions, the monomer traps all the primary radicals and steps (b) and (f) do not occur at any appreciable extent. In this case, it can be shown that the overall polymerization rate is linear with respect to monomer concentration and is a function of the square root of the dose rate. At higher conversions, all the reaction schemes must be considered and the polymerization rate is no longer linear with monomer concentration nor a function of the square root of the dose rate.

4.4 Activation and Inhibition

The polymerization reactions of vinyl monomers are susceptible to both activation and inhibition.

There are a large number of organic and inorganic compounds which form free radicals ($B\cdot$) upon decomposition and act as an initiator for vinyl polymerization. Initiation is caused by the reaction of the free radical ($B\cdot$) with a monomer (M) to form a new radical ($BM\cdot$). This radical is progressively generated terminally ($B(M)_n M\cdot$) by the further addition of monomer molecules. The radical $B\cdot$, thus, becomes a part of the polymer chain. These activating compounds include the acyl and aryl peroxides and hydroperoxides, diazonium compounds, persulfates, and aliphatic azobisisobutyronitriles. Triphenyl methyl chloroform and carbontetrafluoride have also been used in the polymerization of styrene.

Inhibitors may act in a number of different ways. One class of these substances completely prevents polymerization. Such compounds combine with and thus inactivate the active centers as soon as they are formed in the monomer or by initiators. As the inhibitor reacts with the active sites, it is gradually consumed. Thus there will be an induction period during which substantially no polymerization can be detected, followed by a normal reaction after consumption of the inhibitor. This consumption is of zero order, that is the induction period is proportional to the amount of inhibitor initially present, and the rate of consumption is independent of its concentration.

A second process acts by providing an alternative to the normal processes of propagation and termination. The net effect of these substances is to cut down the overall rate and lower the average chain length. Ideal retarders only interfere with the growth and termination of polymer chains.

Some compounds do not fit in either the first or second class of inhibitors but interfere with the initiation, propagation and termination steps. These compounds produce an induction period as well as reduces the overall rate of production of polymer chains and lowers chain length.

All commercial monomers contain some kind of inhibitor to prevent polymerization during storage. Some common inhibitors include hydroquinone, various quinones, phenols, and various aromatic nitro compounds. Inhibitors of this type can be removed by washing or distillation.

In this study, methyl methacrylate was used as a binder in the formation of a solid waste-polymer composite. Detrick (18,19) reported that hydroquinone, present in the trace quantity of 60 ppm, served as an effective ideal inhibitor, necessitating an induction dose of roughly 1.5×10^5 rads before polymerization began. Beyond this dose, conversions varied linearly with absorbed doses initially. He also reported that oxygen served as an effective ideal retarder for both monomer and monomer-acetone polymerizations. Conversions in air were about one third the value in nitrogen and irradiations in oxygen required no induction doses to initiate polymerization. The effects of hydroquinone and oxygen are reported as independent of one another. However his studies were not carried out on the polymerization of bulk monomer but on very small samples. Thus, the effects of the inhibitor and oxygen were easily seen and his conversion curves were linear. The results of bulk polymerization may be quite different.

Therefore in the irradiation of a solid waste-monomer mixture, the presence of oxygen and inhibitor may require a larger radiation dose to produce the desired conversion of monomer than if they were removed. The inhibitor could possibly produce an induction period before polymerization began, and oxygen could reduce the polymerization rate by slowing the propagation step.

4.5 Graft Polymerization

Any polymer that has only one segmer (repeating unit) in its composition is defined as a homopolymer. If a polymer possesses more than one segmer species, it is known as a copolymer. When a monomer is irradiated in the absence of any other reactants, homopolymerization will result.

When a monomer is polymerized in the presence of an existing homopolymer, the result may be a long chain of the original polymer with chains of the polymerizing segmer attached to the original polymer. This polymer, chemically bonded to the original chain, is said to be grafted to the main chain, and the combination of the two polymers is defined as a graft polymer.

Any homopolymer formed during the polymerization which is not bonded to the original polymer can be removed either by a solvent or by mechanical means.

Of particular interest to this study is the possibility of graft polymerization of PMMA onto cellulose. Cellulose is considered structurally as an unbranched, or linear, polymer with high molecular weight. The chain structure is given in Fig. 2.

Paper fibers are manufactured from the cellulose fibers of wood or some other vegetable material. The cellulose chains are contained in smaller fibrillal, or threads, with the fibrillae arranged in several layers to form a tube a few millimeters long.

The fibers used in manufacturing most papers have approximately one thousand glucose units per cellulose chain. These fibers generally swell when placed in water. In the making of paper, the tubular fibers are mechanically beaten, flattening them into rectangular ribbons. This damage to the wall-like structures of the fibers increase the tendency of the fiber to swell in water.

Cellulose-PMMA graft polymer is composed of a cellulose chain with branch chains of PMMA attached to this backbone chain. The structure of the molecule will vary due to the branching of PMMA chains onto the cellulose backbone at random locations. A typical segment of the molecule is shown in Fig. 3. This illustrates only one segment of the cellulose backbone, and branches may originate on other segments in the same chain, the locations being random. These locations (active sites) can be produced by ionizing radiation.

The active site may be a radical produced from a molecule in the cellulose chain. The radical could be formed by radiation-induced scission of the cellulose chain, or through the production of a radical by the removal of a hydrogen atom somewhere in the cellulose chain. The resulting fiber may be in the form of a chain with a number of branches or it may appear as an element of a complicated three-dimensional network with cellulose chains joined or linked by chains of PMMA.

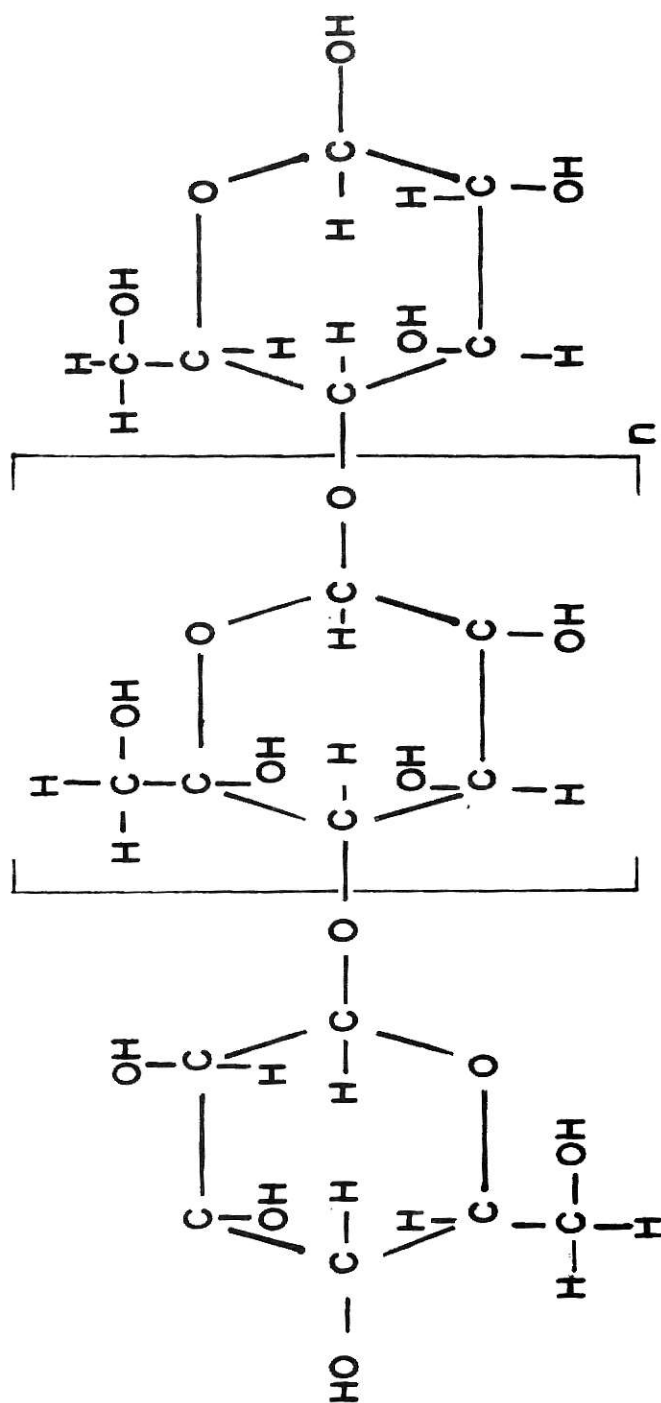


Fig.2. Chain structure of cellulose. (18)

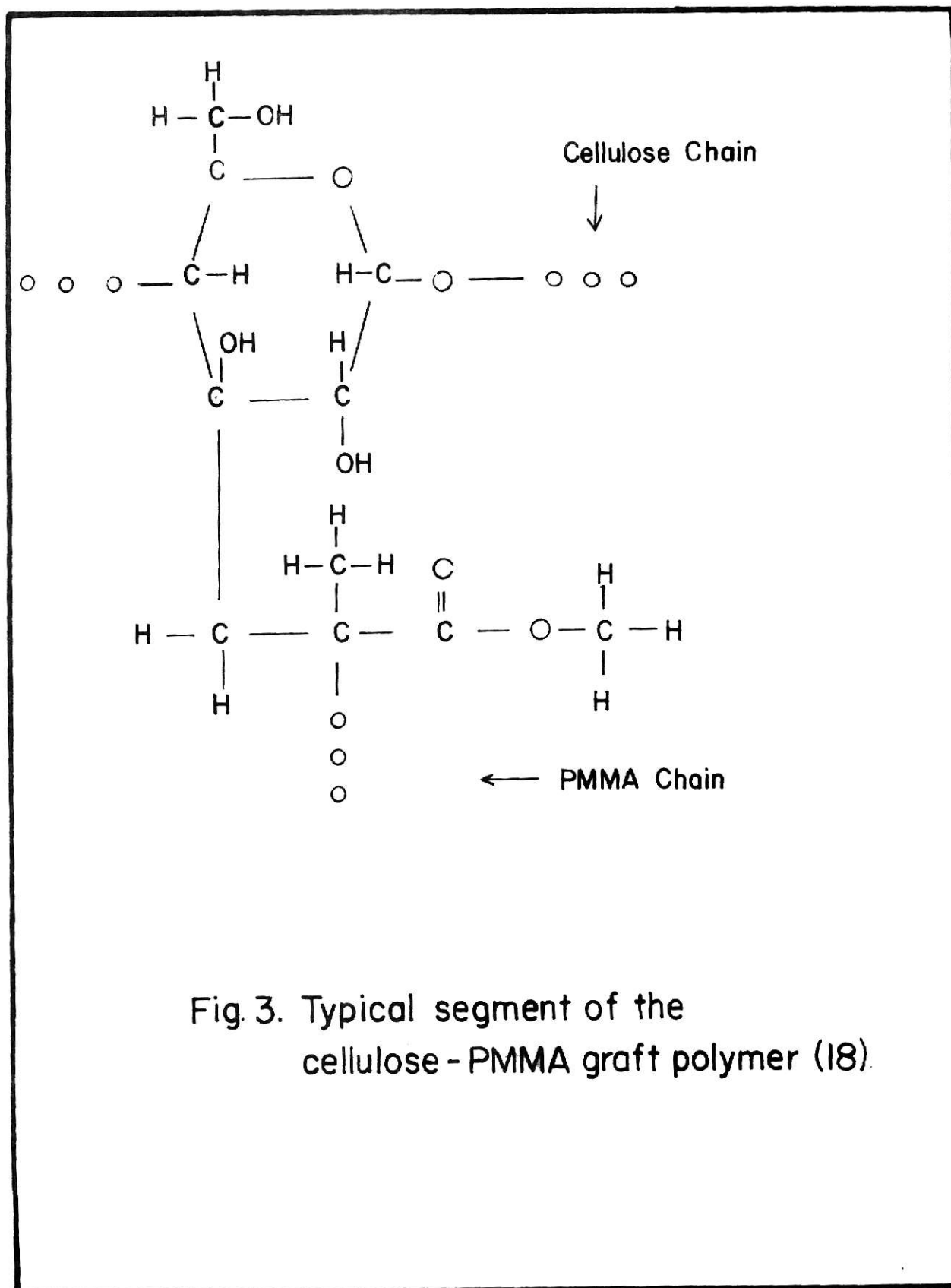


Fig. 3. Typical segment of the cellulose - PMMA graft polymer (18).

Those compounds which are initiators, inhibitors, or retarders in the homopolymerization of monomers do not necessarily produce the same effects on graft polymerization. Detrick reported that hydroquinone produced an induction period in the bulk polymerization of MMA, but when the monomer containing the inhibitor was used for grafting in paper, no induction period was found (18). Instead, the amount of graft polymerization was affected throughout the experiment. Thus hydroquinone acted more as a retarder than an inhibitor of the first type. It was felt that the explanation for the absence of the induction period may lie in preferential absorption of MMA in cellulose (compared to hydroquinone in cellulose). In such a case, grafting of PMMA would initially proceed as though no inhibitor was contained in the monomer. It is possible that the grafted PMMA chains had a greater affinity for the inhibitor contained in the monomer than does the cellulose. Thus the inhibitor had easier access to the growing PMMA and caused termination (the effect produced by retarders) after grafting had taken place.

It was also reported by Detrick that the grafting performed in air produced substantially less graft polymer than the identical operation under nitrogen (18). However, the reduction was not as large proportionally for graft polymerization under air as for bulk irradiation of MMA.

Also in the same study, Detrick found that acetone and water (simple dilutents) increased the amount of graft polymer. These dilutents were not essential to the grafting process, but demonstrated the importance of absorption of the monomer by the paper fibers. In fact, it is reported that without soaking the paper in monomer for four hours, no graft polymerization took place at all.

From this discussion it is concluded that a solid waste-polymer composite material (made by the impregnation of the waste with monomer and subsequent polymerization of the monomer to a polymer using gamma radiation) could possibly contain three different types of material. First, the solid waste material in its original form; second, homopolymer produced from the

polymerization of the monomer; and a graft or co-polymer produced by a chemical combination of the waste and polymer.

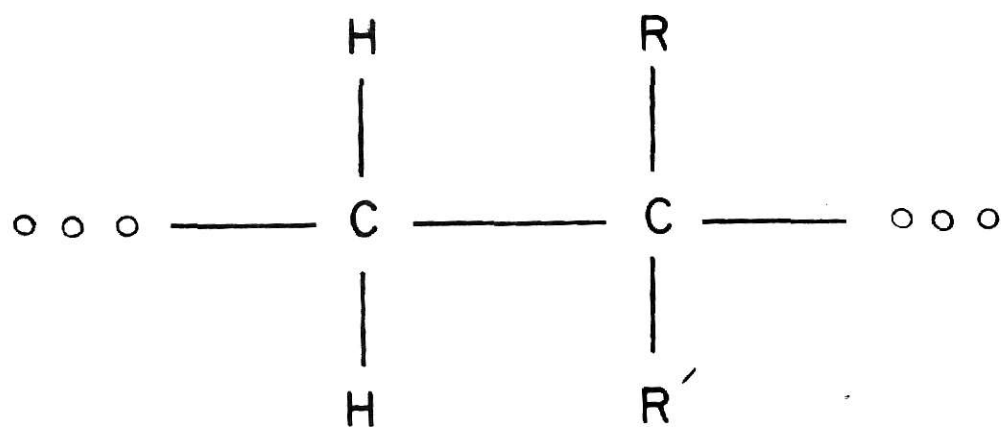
It is highly probable that graft polymerization occurs in the case where the waste contains some material that forms free radical sites (or other active sites that can initiate polymerization) upon exposure to gamma radiation. One such material is cellulose. In the absence of graft or co-polymerization, the polymer will form a matrix encasing the waste material.

It might be expected that the higher the degree of graft polymerization, the greater the strength of the composite. However, Detrick reported no apparent increase in the strength of the paper when it was grafted with PMMA (18). He formed a composite of paper and PMMA, then removed the homopolymer and tested the paper grafted with PMMA.

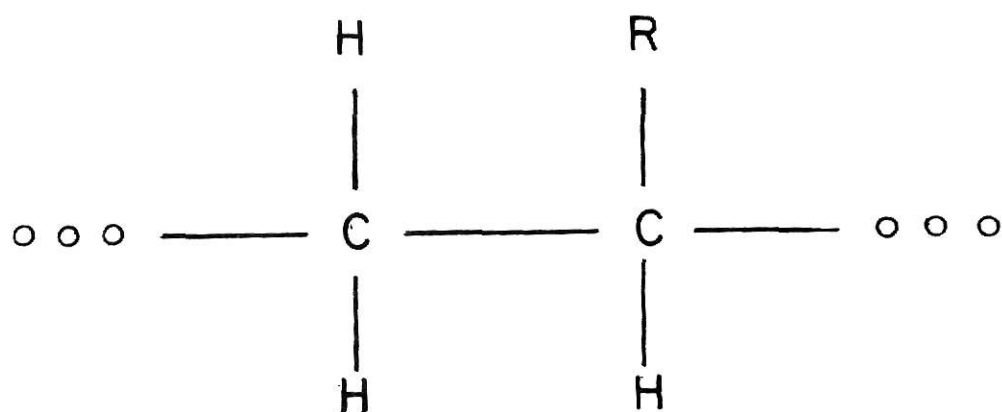
Kent et al.(14) and Bliss et al.(11) report significant improvements on the properties of wood by impregnating it with vinyl monomers. Likewise, using this method the strength of concrete has also been improved (82,83). No efforts were made to determine the degree of grafting which had taken place. Thus it is not known if the presence of the homopolymer alone is responsible for the improved qualities or if graft polymerization also has an effect on the properties of the composite formed. At this time it is impossible to discuss the importance of the degree of graft polymerization on the properties in a composite material. More information is needed on the exact nature of the bonding of the polymer to the material used as a filler.

4.6 Polymer Degradation (52)

Radiation may produce dramatic changes in the properties of polymers as a result of cleavage of main chain bonds, or crosslinking of the polymer molecules (52). Polymers react in one of two ways when subjected to radiation - they either crosslink or degrade. For vinyl-type polymers degradation usually occurs when there is a tetra-substituted carbon atom in the main-chain (see Fig. 4).



(Degrades)



(Cross links)

where R and R' represent any alkyl group.

Fig. 4. Effect of radiation on vinyl-type polymers (52).

Thus PMMA and poly(isobutene) degrade, but poly(ethylene) crosslinks. There are many exceptions to this rule and, usually, both degradation and crosslinking occur and the ratio is affected by temperature, crystallinity, stereoregularity and air.

Polymers which degrade include poly(isobutene), PMMA, poly(tetrafluoroethylene), poly(α -methyl styrene) and cellulose. Poly(styrene) degrades in air, but crosslinks in vacuum.

Oxygen also promotes degradation of polymers by the formation of the peroxy species, which prevent the permanent recombination of the geminate radical ends. Therefore in the proposed composite production process, the presence of oxygen in the irradiation atmosphere not only could retard the polymerization of the monomer, but also could increase the degradation of the polymer, lowering its average molecular weight. Most solid waste materials usually involve some type polymer which will also be subject to degradation or crosslinking.

The degradation polymer or waste could lower the strength properties of the composite. Thus if oxygen could increase this degradation it may be necessary to remove the oxygen prior to irradiation of the solid waste-monomer mixture. However, removing the oxygen will be an expensive process and the quality of the product may not be significantly improved by irradiating in an inert atmosphere. The influence of oxygen on the composite properties and on the monomer will have to be determined experimentally.

4.7 Vinyl Monomer Survey

Under investigation in this study is the recycling of solid wastes in the form of a solid waste-polymer composite.

This composite is produced by impregnating the solid waste with a monomer, then irradiating the mixture. The monomer is polymerized binding the waste material together.

The selection of monomer to be used depends mainly on the requirements of the proposed application. Since, in this study, the problem is being approached from the other direction (i.e., the composite is being formed and its properties determined and from this an application is proposed) there are other factors which should be considered. These include polymerization techniques, monomer properties and polymer properties.

The polymerization technique used in this study is the addition polymerization of a vinyl monomer initiated by radiation produced free radicals. The advantages of using gamma-radiation to initiate polymerization rather than the conventional process of using heat and a catalyst, include,

- (1) The absence of chemical catalysts permit the storage and recycle of monomer without removing the inhibitor.
- (2) Many of the monomers can be polymerized at room temperature and atmospheric pressures.
- (3) Relative large and non-uniform sections can be more rapidly and uniformly treated.

After choosing the radiation technique one must consider the properties of the monomer to be used. At room temperature, there are monomers which exist in the gaseous, liquid or solid state.

A gaseous monomer such as ethylene must be polymerized in a closed vessel capable of withstanding high pressures.

Most of the monomers used commercially are liquids. These include the acrylics, styrenes, vinyls, polyesters, and many others. These are fairly easily polymerized at room temperature and under moderate pressures.

The boiling point viscosity and dose required to polymerize the monomer should also be considered.

Solid-type monomers such as acrylamide cannot be used to impregnate compressed solid wastes. However, they could be mixed with the wastes before compression and the irradiated to produce the subsequent solid waste-polymer composite.

Another important factor in the monomer to be used is the properties of the corresponding polymers. When polymerized in the bulk, most monomers yield polymers that are either powdery, rubbery, or hard and rigid. The hardness of a polymer depends mainly on the glass transition temperature, the temperature at which a polymer loses its strength and shape. As the temperature rises above this transition temperature the mobility of the chains increases and the polymer becomes soft and its coefficient of expansion increases. Below the glass transition temperature (T_g) the mobility is zero and the polymer remains hard and glasslike.

To obtain maximum strength for a polymer composite material, a polymer with a glass transition temperature above the temperature at which the material will be used must be selected.

Although T_g of a polymer is very important, consideration must also be given to other properties such as, compressive strength, tensile strength, flexural strength, hardness, deflection temperature, flammability, water absorption and resistance to chemical attack.

Table 9 (82) gives a list of some of the more common vinyl monomers and a few of their properties.

From a study of the above factors, methyl methacrylate was chosen as the monomer to be used in this investigation for the following reasons:

- (1) MMA is a liquid with a boiling point low enough that the polymerization could be carried out at room temperature and atmospheric pressure.
- (2) MMA has a low viscosity and thus it will diffuse rapidly into the compressed solid wastes.
- (3) MMA has been successfully used to upgrade the properties of wood (11,40) and concrete (82,83).
- (4) The radiation dose required to polymerize MMA is low enough that the irradiation time is not unreasonable.

TABLE 10.* SURVEY OF MONOMER SYSTEMS FOR COMPOSITES

	Tg °F (°C)	Compressive strength, psi	Tensile strength, psi	Radiation dose for 100% con- version at 5.3 X 10 ⁵ rads/hr, Mrad	Cure time in oven at 167° F (75°C), hr; monomer +1% BzP	Monomer cost, \$/lb
Methyl methacrylate	200(95)	14,500	9,500	4.8	1.25	0.21
Styrene	200(95)	13,500	8,000	50.0	8.0	0.09
Acrylonitrile	518(270)	---	---	1.6	0.6	0.145
Styrene-acryloni- trile, 60/40	230(110) ^e	15,500	10,500	5.1	1.0	0.115
Vinyl chloride (vapor pressure, 30 psig at 68°F (20°C))	167(75)	10,500	7,000	---	---	0.082
Vinyl acetate	158(70) ^e	---	<5,000	5.1	1.0	0.14
Isobornyl methac- rylate	297(147) ^e	---	---	1.2	0.75	(0.50-1.00)
Trimethylolpropane trimethacrylate	---	---	---	0.9	0.5	0.98
Diallyl phthalate	>350(177)	22,000	6,500	58.0	8.0	---
Plaskon-941 ^a (poly- ester-styrene)	195(92) ^d	22,500	10,600	0.5	0.75	0.22
Hetron-197 ^b (poly- ester-styrene)	311(155) ^d	24,000	16,200	1.2	0.75	0.445
Epocryl U-16 ^c (epoxy- styrene)	300(148) ^d	25,000	10,200	5.1	1.5	0.40

*References (82), (83).

^aAllied Chemical Corp.^bHooker Chemical Corp., Durez Plastic Division.^cShell Chemical Co.^dPolymer softening point.

CHAPTER 5

5.0 EXPERIMENTAL

To determine the feasibility of the proposed recycling method, several exploratory experiments were conducted. A description of the equipment and supplies used in these experimental studies are given in the first part of this chapter. Then each experiment is described and its results given. Since the conclusions of one experiment lead to the following experiment, the results are discussed before going on to the next. The results of all the experimental work are summarized in the following chapter, Chapter 6.

5.1 Equipment and Supplies

A description of the equipment used in the experimental part of this study is given below.

Mechanical Shredder: A mechanical shredder was used to shred the waste paper into small irregular shaped pieces less than 1/2 in. square in size. The shredder was made by the Cumberland Engineering Company, Inc. of Providence, R.I. Its serial number was 9546 and it was marked as a "Size 1/2". It was powered by a 5 hp, 3 phase Westinghouse electric motor. The paper, cut into 2 to 3 in. squares, was placed into the hopper which fed the paper to a rotating cylinder (8 in. long, 4 in. in diameter) which had blades mounted lengthwise around its circumference.

The shredded paper was collected in a plastic bag placed below the rotating blades. Figure 5 shows the general features of the shredder.

Compression Dies: There were two different compression dies used to compress the shredded paper into plugs. The small compression die was a Carver die made of stainless steel. It had a cylinder 1.125 in. I.D. and an overall length of 3 in. The top piston had a 1.125 in. diameter and an overall length of 3.25 in. The bottom piston was 1.125 in. in diameter and 0.75 in. long. A sketch of this die is shown in Fig. 6.

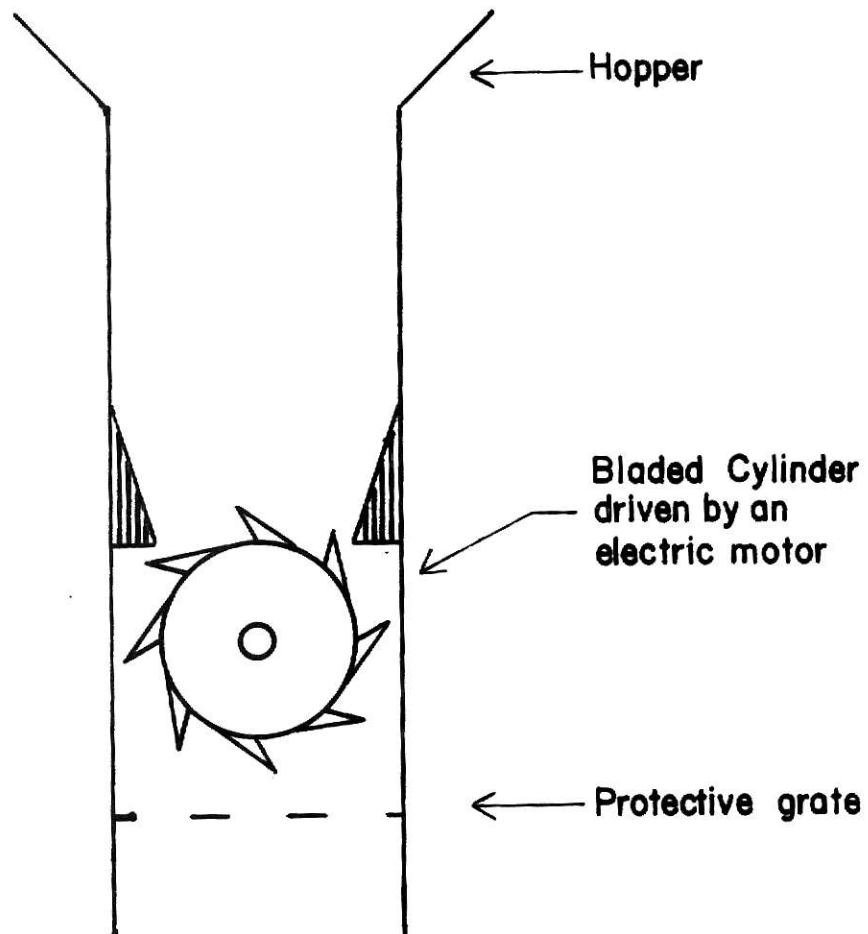


Fig. 5. General features of Mechanical Shredder used to shred paper.

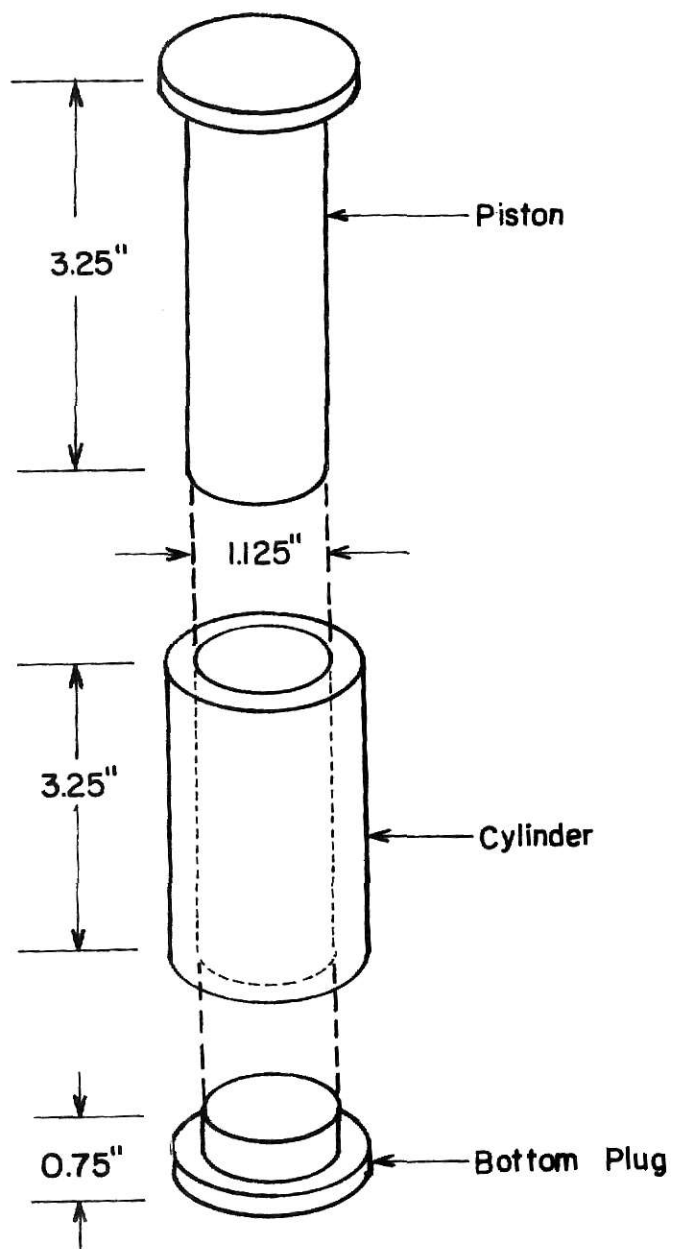


Fig. 6. Small compression die used to compress paper.

The second die used was a large compression die. It consisted of a cylinder 16.5 in. long, made from a double strength steel, 4 in. pipe used for high pressure steam lines. The pipe was bored and honed to a final I.D. of 3.10 in. and had a wall thickness of 0.13 in. Each end of the cylinder was threaded and a 4 in. I.D. pipe flange was screwed onto each end. A bottom plate of 0.5 in. thick steel was cut to an 8 in. O.D.; same as the pipe flanges on the cylinder. The bottom plug was 0.8 in. thick and 3.10 in. in diameter. The top piston consisted of a 2.5 in. thick plug, 3.10 in. in diameter connected to a steel rod 2.00 in. diameter and 16 in. long. Into the end of this rod a 0.25 in. diameter rod was attached to prevent the piston from falling through the cylinder when the paper plug was forced out. A sketch of this die is shown in Fig. 7.

Hydraulic Presses: To compress the shredded paper in the small compression die, a Carver 10 ton laboratory press was used. It was made by Freds Carver, Inc., Hydraulic Equipment, New York, N.Y. and its serial no. was 13799-26. It consisted of a hand operated hydraulic pump whose ram was attached to a bottom plate approximately 8 in. square. The ram had a 6 in. possible vertical travel. The top plate and bottom plates are mounted on two threaded 1 in. diameter rods. The height of the top plate from the bottom plate could be adjusted from 0 to 20 in. by the nuts on the threaded rods. The maximum capacity of the press is 20,000 pounds total load. To determine the pressure a pressure gauge was connected to the pump.

To compress the paper in the large die, a Southwark Emery, 300,000 pound capacity hydraulic press (serial number 50800) was used. It was made by the Baldwin-Southwark Corp., FDY and Mach. Co. Div., Philadelphia, Pa. The hydraulic pump was driven electrically and its vertical travel could be adjusted from 0 to 16 ft. The pressure readings were taken from one of three pressure gauges. These gauges had ranges of 0 to 20,000, 0 to 150,000, and 0 to 300,000 pounds respectively.

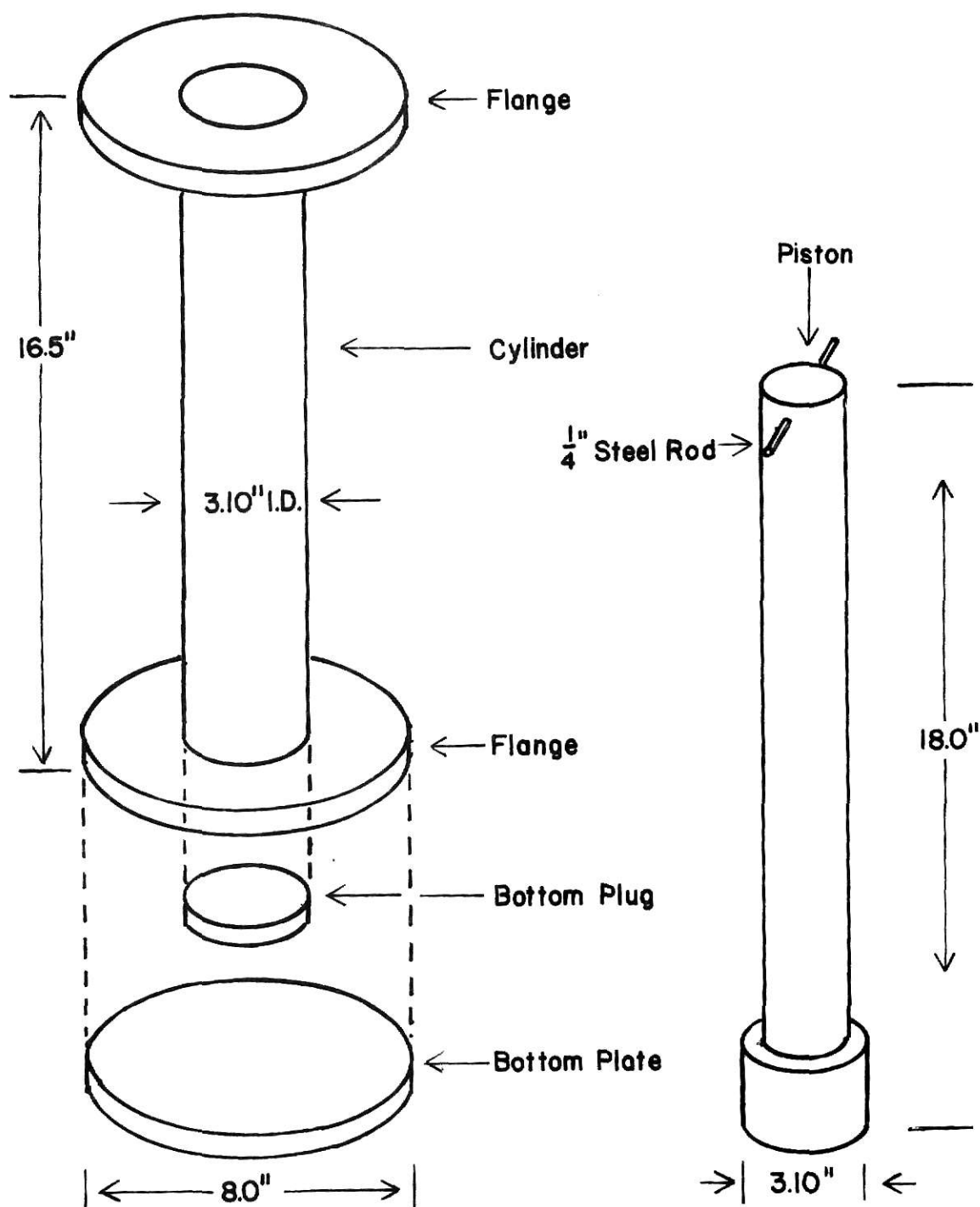


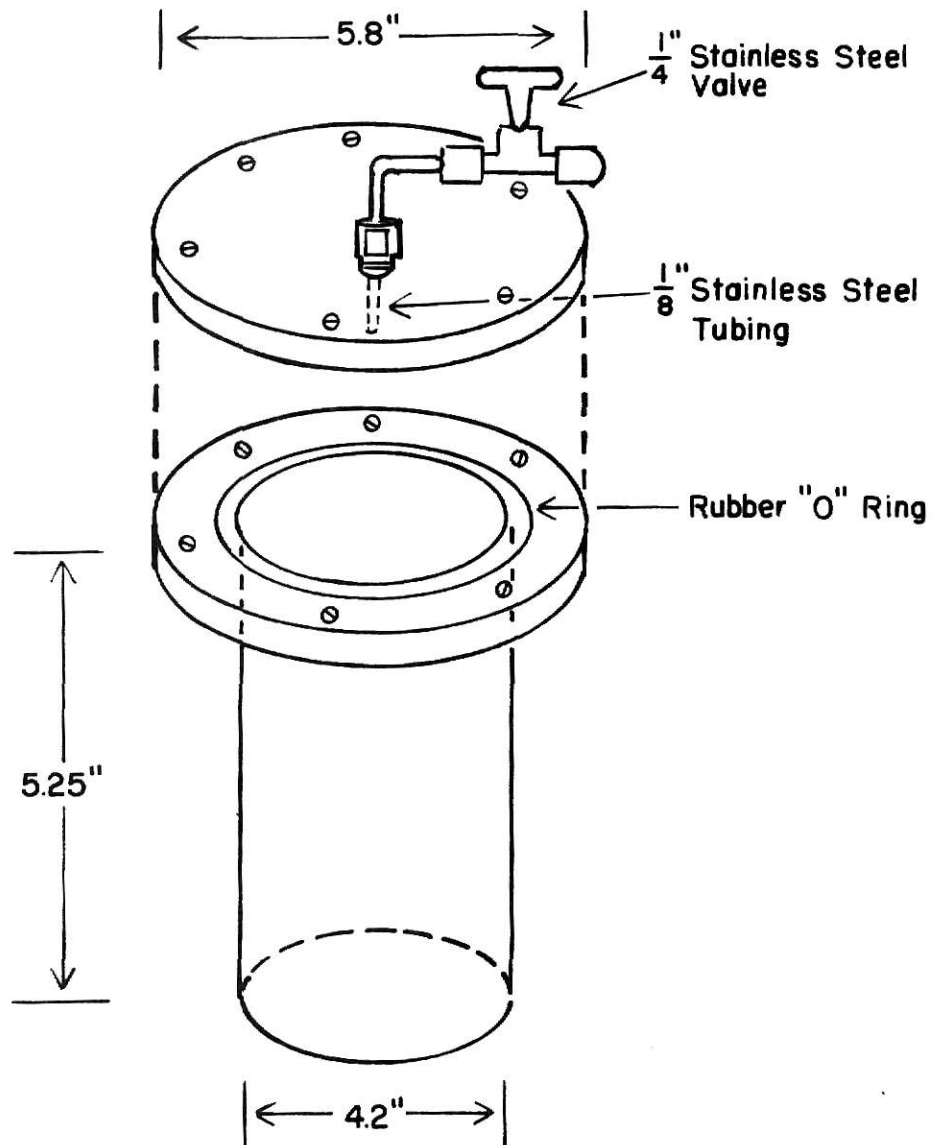
Fig. 7. Large compression die used to compress paper.

Vacuum System: To provide a vacuum, an Edwards mechanical vacuum pump (Model ED200) was used. It was manufactured by Edwards High Vacuum, Inc., 3279 Grand Island Blvd., Grand Island, New York. It had a capacity of 6.7 ft.³/min. at a pressure of 10^{-4} torr. The vacuum line was connected to the vacuum vessel by way of 1/4 in. copper tubing and brass fittings. The pressure was determined by using a thermocouple detector and an ionization vacuum gauge made by the Bendix Scientific Instruments and Equipment Div., New York, N.Y. (type GIC-1106, serial no. 2125).

Vacuum Vessel: The vacuum vessel consisted of a 5.0 in. long piece of 4.2 in. I.D. plexiglas tubing, sealed on one end by a 0.25 in. thick piece of plexiglas. The other end had a flange 0.5 in. thick and 5.8 in. O.D. Six 0.25 in. diameter holes, equally spaced around the flange allowed the top to be bolted on. Between the flange and the top, a 4.6 in. diameter O-ring was used to produce a vacuum seal. The top of the vessel was also made of 0.5 in. thick plexiglas and into it was screwed a pipe fitting. To this fitting a stainless steel screw valve was attached using 1/4 in. stainless steel tubing. On the opposite end of the pipe fitting, a 1/8 in. diameter stainless steel tube 1 in. long was fastened. This directed the incoming stream of liquid monomer into the bottle or beaker inside the vacuum vessel. A sketch of this vessel is given in Fig. 8.

Radiation Vessel: The radiation vessel was exactly like the vacuum vessel, except that the top had no inlets. It consisted of a flat piece of plexiglas containing holes for the bolts used to attach it to the vessel flange. Again an O-ring seal was used to isolate the contents from the atmosphere.

Monomer Introduction System: Monomer was placed in a 500 ml separatory funnel and the top was stoppered. Two glass tubes were put into the stopper; one glass tube extended to the bottom of the funnel, below the monomer level, and the other tube was left above the monomer level. The glass tube which extended into the monomer was connected to a compressed nitrogen gas cylinder. This way nitrogen could be bubbled through the monomer and vented to a hood. The bottom of the separatory funnel containing the



Material of construction was plexiglas.

Fig 8. Vacuum Vessel.

monomer was connected to an inlet of a three-way glass stopcock. The other inlet was attached to the nitrogen supply. A piece of 1/4 in. O.D. tygon tubing was attached to the outlet of the stopcock. The tygon tubing could then be connected to the inlet valve of the vacuum vessel. When the stopcock was opened in one direction, the vacuum vessel would be open to the monomer; and when opened in the other direction, the vacuum vessel would be connected to the nitrogen supply.

Thus, with a partial vacuum in the vacuum vessel, the desired amount of monomer (at atmospheric pressure) would be allowed into the vessel using the stainless steel valve on the vessel to control the volume of monomer introduced. At the desired time, the vacuum vessel could be returned to atmospheric pressure by turning the stopcock and admitting nitrogen. This prevented air entering the system. A sketch of this system is shown in Fig. 9.

Glove Bag: The fittings, tubing and valve on top of the vacuum vessel made its overall height too much to fit into the radiation chamber. Thus it was necessary to transfer its contents to the radiation vessel prior to irradiation. When the irradiating atmosphere was nitrogen, the transfer from one vessel to another had to be done in a closed system purged with nitrogen. A polyethylene glove bag (11 in. x 17 in.) was used for this purpose. The needed equipment was placed into the bag by an opening at the front and then the opening folded shut. A tube at the back of the bag was connected to a compressed nitrogen cylinder and a flow of nitrogen was started into the bag. When the bag became inflated, the front opening was opened slightly and a flow of nitrogen was maintained in sufficient quantity to inflate the bag and dispel the air. By leaving the bag slightly open during the preparation of the samples, the flow of nitrogen maintained a positive pressure in the bag which prevented air entering the system.

Gammacell 220: The irradiation source for this study was a Gammacell 220 Irradiation Unit made by Atomic Energy of Canada Limited. The cobalt-60

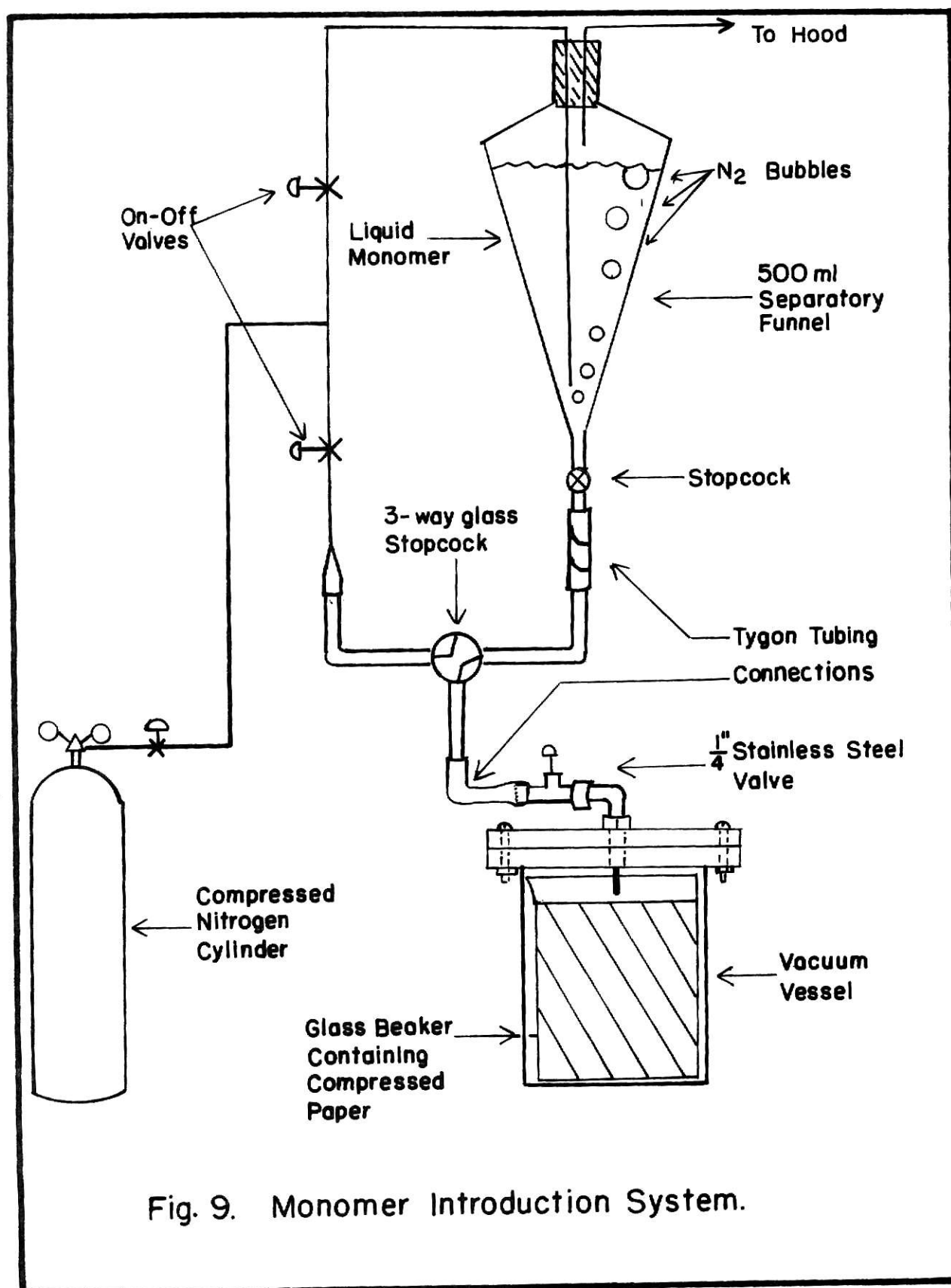


Fig. 9. Monomer Introduction System.

source consists of 12 linear source elements equally spaced in a stainless steel rack to form a radioactive cylindrical shell, $8 \frac{1}{4}$ in. between the centers of opposing elements. Each linear element is a welded stainless steel pencil (.395 in. in diameter and 8 in. long) filled with metallic cobalt.

The motor driven irradiation drawer of the assembly consists of a steel-encased lead cylinder $53 \frac{3}{4}$ in. long and $6 \frac{1}{2}$ in. in diameter. The drawer is composed of three sections, an upper section, a cylindrical sample chamber, and a lower section. The drawer is centrally located in a surrounding radiation shield, and is driven vertically through the center of source. Material to be irradiated is placed in the sample chamber and then lowered into the source. A removable door provides easy access to the sample chamber. The door is locked by a chrome-plated steel locking ring around the top of the sample chamber. The internal dimensions of the sample chamber is $8 \frac{1}{8}$ in. high and $6 \frac{1}{16}$ in. in diameter.

The unit is controlled from a panel mounted at the side of the assembly. The control panels have a chamber "Up" button, a chamber "Down" button, a digital timer with a range of 0-999 hours, minutes or seconds. A timer "In" button is used to start the timer when desired.

The irradiations in this study lasted only a few hours thus the dose rate for any one run can be assumed to be constant. However several months elapsed between several of the experiments and to compare the results the total absorbed should be used and not irradiation time alone.

To do this, a plot of the absorbed dose rate versus time was determined using the dose rate found using the Fricke dosimeter technique (15). From this the absorbed dose for MMA could be found (15). In the experimental work, the absorbed dose reported is that calculated for the monomer MMA absorption.

Supplies: The following gives the materials used in the experimental work. The monomer used was methyl methacrylate (MMA), (superior grade,

MCB no. 6683-MX1150, B.P. 100-101°C, FW 100.12), containing the inhibitor hydroquinone. The nitrogen used was "high purity" nitrogen from the Air Product Company.

The following solid wastes were collected to be used in the experimental work:

1. Used computer printout paper containing a green dye and ink printing used by the KSU computer center.
2. Newsprint.
3. Sawdust from fir lumber.
4. Cardboard.
5. Wheat straw.
6. Bagasse - shredded sugar cane stalks which is a by-product of cane sugar.
7. Dried sediment from the primary treatment of municipal sewage, collected from the local sewage plant.
8. Sludge from secondary sewage treatment.
9. Cotton cloth taken from an old white shirt.
10. Clothes lint taken from a domestic clothes dryer.
11. Human hair clippings collected from a local barber shop.

A significant amount of the experimental work in this study involved the use of used computer printout paper. The KSU computing center purchases its printout paper from Adam's Business Forms (200 Jackson, Topeka, Kansas 66612, phone 913-233-4105) or from Moore Business Forms, Inc. (4001 Huntoon, Topeka, Kansas 66612, phone 913-272-2111). They consume approximately four boxes per day. Each box contains 3700 (14.75 in. x 11 in., 3 mills thick) sheets per box.

The above distributors (Adam's and Moore Business Forms) indicated that the manufacturer of the paper they sold included the International Paper Co.; Neboosa Edwards Paper Co., Port Edwards, Wisconsin 54469; Mead Paper Co., Chillicothe, Ohio and Boise Cascade, Northstar Center, 7th and Marquette, Minneapolis, Minn. 55402.

The distributors also indicated that the computer paper was probably a No. 4 sulfite bond. Upon calling Mr. Howard Milette and Mr. Dick Uerock at Boise Cascade, it was found that the sulfite bond paper being produced consisted of the following materials:

Cellulose fibers	80%
Hardwood popular	65%
Jack pine	35%
Filler	10%
Resin	1%
Alm	1%
Moisture	5%
Surface additives	3-4%
Corn starch 75 lbs./ton of paper	
Poly acryamide .35 lbs./ton of paper	
Color dye stuffs (e.g. Blue-forlight)	

The two Boise Cascade officials also mentioned that the sulfate processing was being replaced by a different, less polluting process. Therefore the above paper composition will be subject to change. This points to one of the difficulties in planning an effective recycling method. The amount and composition of wastes are constantly changing as new and different products are introduced into the economy. Thus, a successful recycling method will have to be fairly flexible to changes in the waste composition.

5.2 Sensitivity of the Composite Process to the Type of Solid Waste Used

One important requirement of successful recycling methods, as mentioned in the second chapter, is that the residues remaining after the wastes treatment must be processed such that they can be returned to the environment without harming it. Thus if the solid waste-polymer composite process is to be used as a method of recycling, one of the first questions to be answered is what wastes can be used in this process. It was the purpose of this

experiment to find which wastes could be used to produce a composite with PMMA.

A representative solid waste from some of the major source categories (described in section 2.1) was mixed in an inert atmosphere with the monomer MMA and then subjected to gamma radiation for different period of time. After the irradiation, the samples were removed from the Gammacell and examined and a few tests were performed to determine their machinability and water absorption. A more detailed description of the procedure is given in Table 11. Most of the wastes in this table could be from more than one source and paper wastes are generated by all sources.

5.2a Procedure: The waste paper (newspaper and computer paper) was prepared in one of two ways. The layered paper samples were made by stacking together 50 paper discs (3 in. in diameter) cut from the waste paper. The shredded paper samples were prepared by shredding the paper in a Waring Blender. The waste samples were placed in glass petri dishes which were lined with aluminum foil. Plastic petri dishes were first tried but the MMA attacked the plastic. Aluminum foil was used to prevent the samples sticking to the glass. Samples 4, 5 and 6 of run 2 were prepared in the open atmosphere at room temperature. The remaining waste samples, radiation vessel, liquid monomer, and other necessary equipment were placed in the glove bag. The nitrogen was turned on and the glove bag was purged for 5 minutes then the open end was rolled up and clipped shut. With the nitrogen still on, the bag, inflated and the fritted glass tube connected to the inlet port, was submerged in the liquid monomer. The nitrogen was bubbled through the monomer for 15 minutes to remove the dissolved oxygen. Then, depending on the samples, the final preparation was carried out on the samples before mixing with the purged monomer.

The paper samples of circular sheets of paper (layered) were placed in a rack inside the glove bag. The nitrogen inlet port was connected to the bottom of the rack. This apparatus forced a stream of nitrogen up through

TABLE 11. SOLID WASTES COLLECTED TO BE USED IN PRODUCING
SOLID WASTE-PMMA COMPOSITES

Source	Solid Wastes
Urban	
Domestic	Cardboard, Newspaper, Cotton cloth
Commercial	Human hair clippings, Clothes lint
Municipal	Sediment from primary treatment at sewer plant, Sludge from secondary treatment experiment
Industrial	Sawdust from fir lumber, Used computer output paper
Agricultural	Wheat straw, Baggase
Federal	Most of the wastes above could be from a Federal source.

the sheets of paper stacked vertically in the rack. This was done to try to remove some of the trapped oxygen on the paper. The shredded paper samples were prepared by using a Waring Blender inside the glove bag. A known weight of paper was placed in the blender and then shredded. A known volume of monomer was added and then the blender was turned on again. After complete mixing, the sample was placed in the aluminum foil lined petri dish. The samples of other waste materials were placed in the petri dishes before they were put into the glove bag. These were then placed near the nitrogen inlet port, thus a stream of nitrogen passed over the open petri dishes. In each case, the samples were subjected to this purging treatment for approximately 30 minutes. After this treatment, the measured volume of monomer was added to the samples. They were then covered with aluminum foil and placed inside the plexiglas radiation vessel. The top plate was bolted into place and the reactor removed from the glove bag. The reactor was sealed in a plastic bag and placed in the Gammacell. The radiation time was either 6 or 12 hours depending on the run number.

Upon removing the samples from the plexiglas reactor after six hours of irradiation, the smell of MMA monomer was noticed. In the remainder of the runs, the irradiation time was extended to twelve hours, and the smell of the monomer was no longer detected.

During the first run, the sample chamber of the Gammacell was raised after approximately one hour of irradiation. The plexiglas reactor had turned slightly brown and it felt quite warm. The reactor was then placed back into the Gammacell for the remaining irradiation treatment. After the 6 or 12 hours of irradiation (depending on the run number), the reaction was removed and the samples taken out. At this time the reactor was at room temperature. The reactor did not crack or show any signs of a pressure build up when removing the flange. The MMA did, however, attack the inside of the plexiglas reactor and the plastic petri dishes used. The entire inside of the reactor became coated with a layer of polymerized MMA, milky white in color.

The first set of samples consisted of layered computer paper and layered newspaper all prepared in a nitrogen atmosphere. In the first run the actual (weight polymer/weight paper) ratio after irradiation is much smaller than the (weight monomer added/weight paper) ratio before the irradiation treatment. This could be due to the MMA vaporizing and then reacting with the plastic petri dishes and walls of the reactor.

The samples of the second run consisted of layered computer paper and newspaper and were subjected to an irradiation time of 12 hours. The final polymer to paper weight ratio were much closer to (weight monomer added/waste material) ratio. In this run, glass petri dishes were lined and covered with aluminum foil. This probably reduced the MMA vaporizing and reacting with the petri dishes. Three of the samples of this run were left outside the glove bag. No effort was made to remove the air from these samples before adding the degassed monomer. Other samples were put into the glove bag and purged with gaseous nitrogen to try and remove the oxygen trapped on the surface of these samples. Also a sample of pure liquid MMA was put into the reactor.

Shredded paper of both types, sawdust, and cardboard were used as samples in the third run. The irradiation time was 12 hours and all the samples were prepared inside the glove bag under a nitrogen atmosphere. No effort was made to try to compress the paper samples.

The samples of the fourth run consisted of shredded sugar cane stalks called baggase which is a by-product of cane sugar, wheat straw, layered cotton cloth, clothing lint taken from a washer and dryer, hair clippings from a local barber shop, sediment from the primary treatment process at the local sewer plant and the last sample was pure MMA monomer. All samples were prepared as a nitrogen atmosphere and irradiated for 12 hours.

After irradiation, the samples were removed and the final weight ratio and percent polymer content was determined. Each sample was qualitatively evaluated with respect to the bonding of the polymer solid waste composite. All but four samples were cut on an electric circular saw to determine the cutting

properties of the composites. The remaining four samples were composites of layered and shredded paper with high and low percentages of polymer. These were selected to be tested for lathe and drilling properties. A high speed drill was used to drill a 1/2 in. hole into each sample. Then each sample was put on a lathe. The samples were made round and then their surfaces machined flat (that is, they were turned and surfaced). Again, the samples were qualitatively rated on their machinability.

After this testing, a representative group of samples were selected and a small piece of each of these samples was cut off using a power saw. These pieces of composites were then tested for water absorption.

These small pieces were weighed, dipped in water, blotted with filter paper and weighed again. Dipping the sample into the water and blotting it with filter paper was done to find the weight of the sample which just had water absorbed on its surface. The "wet" weight was used as the basis for the percent of weight increase measurements.

After obtaining the "wet" weight, the samples were placed in plastic petri dishes and submerged in metal trays filled with distilled water. The petri dishes had to be inverted and then a weight placed on them to keep them and the samples submerged. Without the weights the samples floated to the top of the water.

The samples were removed after certain lengths of time, blotted with filter paper, weighed, then placed back into the water. Weight measurements were taken after approximately 1, 4, 16 and 72 hours of submersion.

5.2b Results: All of the waste materials tested did bond with the polymer PMMA despite the rather unsophisticated experimental procedure. This seemed to indicate that such solid waste-polymer composites are feasible. The shaping qualities and resistance to water absorption indicate that these materials have many desirable properties necessary for building materials.

In the first run the sample of layered computer paper with a final polymer to paper weight ratio of 1.52 and the newspaper sample with a final weight

ratio of 1.22 showed good bonding properties. The computer paper sample with a final weight ratio of 0.57 showed some bonding but it was not nearly as strong as the samples with a higher concentration of polymer. The other samples of layered computer paper and newspaper showed no bonding.

All of the samples from the second run exhibited good bonding qualities. Leaving the samples out in the air and not trying to remove the trapped oxygen did not seem to alter the bonding characteristics of the polymer to the paper. The purged and non-purged samples of newspaper and computer paper (with approximately the same weight polymer/weight paper ratio) showed very similar bonding qualities. However without using more sophisticated methods of testing, the exact effect of the oxygen trapped on the sample's surface could not be determined. The pure monomer sample gave a clear polymerized disc of polymer covered with a layer of white haze on the upper surface. The other samples also seemed to have a layer of white haze on their top surfaces.

The results of the third run were as follows. The cardboard sample had good bonding qualities and a marked increase in strength over regular cardboard. The final polymer to cardboard weight ratio was 1.07. The sawdust, too, showed very good bonding qualities and had a final weight ratio of 4.37. Its strength seemed to be greater than that of wood of equal thickness. The bonding qualities of the shredded paper were highly dependent on the amount of monomer added. The computer paper samples with final polymer to paper weight ratios of 0.46 and 2.98 had fair bonding qualities but very little strength. However, the shredded computer paper sample with a weight ratio of 7.25 had excellent bonding and strength properties. The shredded newspaper sample with a weight ratio of 1.11 gave fair bonding and little strength while the sample with the 5.99 ratio gave excellent bonding and strength qualities.

The first sample of run 4 consisted of bagasse. Its final polymer to bagasse weight ratio was 4.20. The top surface was rough with pieces of bagasse jutting out. The bottom surface was smooth and very shiny. Its composition seemed to be mostly pure polymer. The entire sample exhibited good bonding characteristics and a great deal of strength.

Wheat straw was the second sample and its final weight ratio was 2.00. This sample had many large voids in its interior that were visible to the eye. Pieces of the straw could be broken off fairly easily but the entire sample showed considerable strength, however, not as much as the bagasse sample.

Layers of cloth were used in the next sample, which had a final weight ratio of 2.11. The bottom and top surfaces of this sample looked very similar while in the other samples the bottom showed a much greater polymer content. This sample showed a great deal of strength and good bonding properties.

Clothing lint made up the fourth sample and had a final weight ratio of 12.24. The top surface had a fuzzy appearance while the bottom surface was smooth, shiny and composed of mostly pure monomer. This sample showed both good bonding properties and a great deal of strength.

The fifth sample was made up of hair clippings. It had a final weight ratio of 5.19. The top surface had hairs sticking out and appeared to have a mat finish with little polymer exposed. The bottom was shiny like most of the other samples.

Solid waste collected from the primary treatment of sewage gave a sample with a final weight ratio of 1.39. It had good bonding properties and showed a great deal of strength. Again its top surface looked like the solid waste and the bottom surface looked like it was pure PMMA.

The last sample was pure MMA monomer. Much of this was spilled while putting the samples in the reactor and placing it into the Gammacell. Only a small piece of the polymer was found in the petri dish after the irradiation treatment.

In each sample, the concentration of the polymer varied with the thickness of the sample. At the top of the sample there was a low polymer concentration and at the bottom surface there was almost pure polymer.

When exposed to open flame, the samples ignited and continued burning. The fire, sustained by the samples, popped and crackled like the fire of the pure PMMA polymer.

When the samples were cut into small rectangular pieces, in all but two cases, the ease of cutting seemed to be directly related to the polymer weight/solid waste weight ratio. The higher the concentration of the polymer in the sample, the harder the material was to cut. In the case of straw and cardboard, the weight ratio was fairly high, yet it was easily cut. This could be explained by the existence of a large number of voids throughout.

In most cases, the samples could be cut with the power saw without any great amount of difficulty. The saw blade did not heat up or become gummed up with polymer. The "sawdust" from these samples was fine and granular, not sticky like the sawdust from some polymers. The composite made using the sediment from the sewage plant was quite difficult to cut. Sparks were noticed as the saw blade hit small, extremely hard, particles in the composite.

Of the four samples selected to be tested for lathe and drilling properties, the samples with the low concentration drilled easily. While being turned and surfaced on the lathe, these samples showed some chipping and did not give smooth surfaces. The samples with the higher polymer concentrations caused the drill bit to heat up. Both the layered paper sample and the shredded paper sample with the higher polymer concentration exhibited good shaping qualities on the lathe. There was very little chipping and the surfaces formed were quite smooth. These results are summarized in Table 12.

The results from the water absorption test tend to indicate that the percent weight increase of water is a function of the type of solid waste material used as well as the polymer to solid waste weight ratio.

The test did show that given a certain waste material, the amount of water absorbed was a function of the polymer concentration. In the different paper samples, the ones with the higher polymer weight ratio absorbed less water than the ones with a lower weight ratio.

The percent weight increase ranged from 1.1 percent for pure PMMA to 60.0 percent for the shredded computer paper sample with a polymer weight ratio of 0.483. The lowest percent weight increase was the polymer-solid

TABLE 12. RESULTS OF IRRADIATION EXPERIMENTS

RUN NO. 1

Irradiation Time: 6 Hours (Corresponds to an absorbed dose of 8.01×10^5 rads)

All samples were prepared in a nitrogen atmosphere.

Sample No.	Waste Material	Wt. Ratio of Monomer Added/ Waste Material (before irradiation)	Wt. Ratio of Polymer/Waste Material (after irradiation)	Bonding Properties	Sawing Properties	% Weight Increase of H_2O After 3 Days
1	Layered Newspaper	1.0	0.0	None	-----	-----
2	Layered Newspaper	0.5	0.465	None	-----	-----
3	Layered Newspaper	0.2	0.019	None	-----	-----
4	Layered Newspaper	2.0	1.220	Good	Like wood	18.291
5	Layered Computer Paper	1.0	0.573	Fair	Easier than wood	36.43
6	Layered Computer Paper	0.5	0.141	None	-----	-----
7	Layered Computer Paper	0.2	0.033	None	-----	-----
8	Layered Computer Paper	2.0	1.518	Good	Harder than wood	11.584

TABLE 12. (cont'd)

RUN NO. 2

Irradiation Time: 12 Hours (Corresponds to an absorbed dose of 16.02×10^5 rads)All samples, except #4, #5, #6, were prepared in a nitrogen atmosphere. These three samples were prepared in the presence of air.

Sample No.	Waste Material	Wt. Ratio of Monomer Added/ Waste Material (before irradiation)	Wt. Ratio of Polymer/Waste Material (after irradiation)	Bonding Properties	Sawing Properties	% Weight Increase of H ₂ O After 3 Days
1	Layered Computer Paper	2.0	1.913	Good	Harder than wood	7.927
2	Layered Computer Paper	1.0	.918	Good	Like wood	19.040
3	Layered Newspaper	2.0	1.870	Good	Like wood	7.436
4	Layered Newspaper	2.0	1.867	Good	Like wood	6.581
5	Layered Computer Paper	2.0	1.918	Good	-----	-----
6	Layered Computer Paper	1.0	.882	Good	-----	-----
7	Pure Methyl Methacrylate	-----	-----	Good	Harder than wood	1.137

Samples #5 and #6 were drilled and turned on the lathe. Both showed good working properties.

TABLE 12. (cont'd)

RUN NO. 3

Irradiation Time: 12 Hours (Corresponds to an absorbed dose of 16.02×10^5 rads)

All samples were prepared in a nitrogen atmosphere.

Sample No.	Waste Material	Wt. Ratio of Monomer Added/Waste Material (before irradiation)	Wt. Ratio of Polymer/Waste Material (after irradiation)	Bonding Properties	Sawing Properties	% Weight Increase of H ₂ O After 3 Days
1	Shredded Computer Paper	Saturated	2.982	Fair	-----	-----
2	Shredded Computer Paper	1.00	0.4631	Fair	Easier than wood	59.92
3	Shredded Computer Paper	Saturated	7.246	Good	Harder than wood	3.654
4	Layered Cardboard	Saturated	1.066	Good	Easier than wood	9.057
5	Shredded Newspaper	2.00	1.105	Fair	Much easier than wood	40.212
6	Shredded Newspaper	Saturated	5.990	Good	-----	-----
7	Sawdust	Saturated	4.369	Good	Harder than wood	6.571

Samples #1 and #6 were drilled and turned on a lathe. No. 1 drilled very easily but chipped badly while being turned on the lathe. While drilling #6 the bit heated up, but this sample could be easily turned on the lathe.

TABLE 12. (cont'd)

RUN NO. 4

Irradiation Time: 12 Hours (Corresponds to an absorbed dose of 16.02×10^5 rads)

All samples were prepared in a nitrogen atmosphere.

Sample No.	Waste Material	Wt. Ratio of Monomer Added/ Waste Material (before irradiation)	Wt. Ratio of Polymer/Waste Material (after irradiation)	Bonding Properties	Sawing Properties	% Weight Increase of H_2O After 3 Days
1	Bagasse	4.748	4.202	Good	Much harder than wood	6.781
2	Wheat Straw	5.711	1.998	Fair	Easier than wood	20.465
3	Cloth	2.293	2.107	Good	Much harder than wood	6.360
4	Clothes Lint	12.581	12.238	Good	Harder than wood	13.247
5	Human Hair	5.397	5.185	Fair	Harder than wood	7.797
6	Solid Waste	1.589	1.385	Good	Much harder than wood	14.217
7	Sludge	1.367	1.008	Poor	-----	-----
8	Pure Monomer	-----	-----	Good	-----	-----

waste sample of shredded computer paper having a polymer weight ratio of 7.246. These are percent weight increases after being submerged in water for three days.

These values are still quite low compared to the percent weight increase of the different woods tested in the study of Bliss, Fan and Eckhoff (11). The values in this paper varied from a weight increase of 58 percent for untreated oak to 150 percent increase for untreated cottonwood. These values are also for a three day submersion time.

The results of the water absorption test are shown in Table 13. Some typical results are plotted in Fig. 10 for illustration and comparison.

5.2c Discussion: It is concluded that this process of making a composite can be applied to almost any solid waste. The waste from most all the major sources have been used to produce composites of substantial strength, reasonable machinability and low water absorption. Thus if this type of recycling process is applied to the treatment of solid wastes, there will be little if any residues which cannot be processed. In addition, this process might be used to recycle those residues from other recycling methods or untreated wastes which are not easily handled by other techniques.

5.3 Polymerization of MMA in the Presence of Compressed Paper

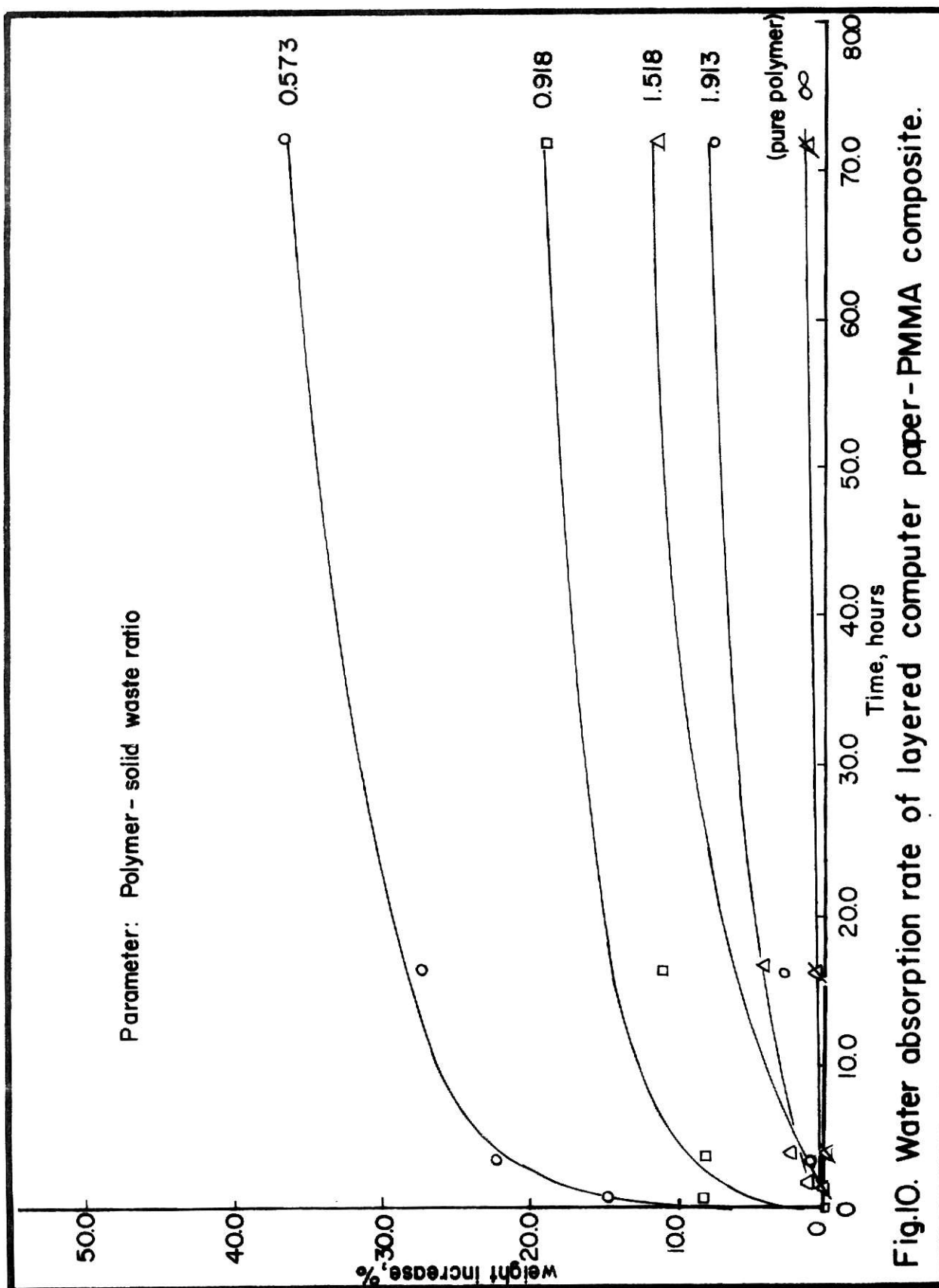
Paper was chosen as the solid waste to be used in the further investigation of the proposed recycling method. As stated earlier, it is a waste common to all major sources and, in the case of domestic trash, it constitutes 50 percent of the total wastes produced (74). The major component in paper is cellulose and the cellulose fibers are found in many other types of solid wastes. Included in these are the wastes from the lumbering industry, the pulp and paper industry and the animal and vegetation wastes of the agricultural sector. Thus, the results obtained using waste paper should apply to a great deal of the solid wastes produced. Used computer printout paper was chosen as the type of waste paper investigated because of its availability. For a description of the paper used see section 5.1 under supplies.

TABLE 13. WATER ABSORPTION TEST RESULTS

Run No.	Sample No.	Time in Hours	% Weight Increase
1	4	1.2	8.27
		3.9	9.56
		16.3	15.26
		72.2	18.29
1	5	1.1	15.06
		3.9	22.02
		16.2	27.34
		72.1	36.43
1	8	1.0	1.34
		3.8	2.70
		16.2	4.38
		72.1	11.58
2	1	1.0	1.41
		3.8	1.31
		16.2	3.06
		72.1	7.93
2	2	1.0	8.74
		3.5	8.50
		16.2	11.28
		72.1	19.04
2	3	1.0	1.94
		3.8	1.71
		16.1	4.16
		72.0	7.44
2	4	1.0	2.22
		3.8	2.19
		16.1	4.40
		72.0	6.58
2	7	1.0	- .02
		3.6	.15
		16.1	.78
		72.0	1.14
3	2	1.0	40.81
		3.8	42.83
		16.1	36.13
		72.0	59.92

TABLE 13. (cont'd)

Run No.	Sample No.	Time in Hours	% Weight Increase
3	3	1.1	.61
		3.8	1.29
		16.1	1.79
		71.9	3.65
3	4	.8	2.06
		3.8	2.39
		16.1	9.39
		71.9	9.07
3	5	.8	21.16
		3.6	18.31
		15.9	24.29
		71.8	40.21
3	7	.8	.53
		3.6	1.46
		15.9	2.83
		71.8	6.57
4	1	1.0	1.30
		3.6	.12
		15.9	2.54
		71.7	6.78
4	2	.8	1.33
		3.6	3.69
		15.9	12.00
		71.7	20.47
4	3	.9	2.20
		3.5	3.25
		15.8	4.62
		71.7	6.36
4	4	.7	.86
		3.6	8.65
		15.8	10.35
		71.6	13.25
4	5	.7	4.73
		3.4	6.54
		15.7	12.91
		71.6	7.80
4	6	.7	1.61
		3.6	4.24
		15.8	8.64
		71.6	14.22



It was desired to know how the presence of paper would affect the polymerization of MMA. Compressed paper plugs were made and soaked in the liquid MMA monomer. The MMA-paper mixture was then irradiated in nitrogen and air atmospheres for different lengths of time. The percent conversion of the monomer was determined and plotted against absorbed dose.

5.3a Procedure: The following procedure was developed to produce the compressed paper plugs used in this experiment and in the ones to follow.

1. Computer printout paper containing printed output was cut into approximately 2 in. squares, then shredded using the mechanical shredder into irregular shaped pieces $1/2$ in. square or less.
2. The bottom piston or plug was placed in the bottom of the compression die cylinder and the shredded paper was hand packed into the top of the cylinder.
3. The top piston was started into the die and then forced into the cylinder until the desired pressure was obtained using a mechanical press. The pressure was maintained at this level for 1 minute. This compacted the paper into a compressed plug.
4. The top and bottom pistons of the die were removed, and the cylinder containing the paper plug was turned upside down. The pistons were then replaced and the same pressure was again applied to the paper and held for one minute. This step was necessary to produce a paper plug of uniform density.
5. After releasing the pressure, the bottom piston was removed, and the cylinder and top piston were supported in such a way that the paper plug could be forced out the bottom of the cylinder by applying pressure to the top piston.

In this experiment the small compression die (1.125 in. diameter) and a pressure of 2500 psi was used to compress the shredded paper into 12 paper plugs.

After being measured and weighed, the compressed paper plugs were then prepared for irradiation in one of the following ways.

Method 1: The weighed paper plugs were wrapped in aluminum foil to help prevent the evaporation of monomer and placed in a weighed 4 oz. bottle having an aluminum foil lined plastic lid. The bottle (without the lid) and contents were placed into the vacuum vessel. The vessel was sealed and the inlet valve connected to the vacuum line. The vacuum pump was turned on for a certain length of time or until a certain vacuum pressure had been reached. While still under a vacuum, the inlet valve on the vacuum vessel was turned off and the vessel disconnected from the vacuum line. The inlet valve of the vessel was then connected to the monomer supply via Tygon tubing. Monomer at atmospheric pressure could then be forced into the evacuated reactor by opening the vessel inlet valve. The monomer entered the reactor through the inlet valve and stainless steel tubing and collected in the bottle containing the compressed paper plug inside the vacuum reactor. Enough monomer was introduced until the paper plug in the bottle was just submerged in a pool of monomer. Prior to its introduction, the monomer had been bubbled with nitrogen for approximately 15 min. (see Fig. 9 in section 5.1 of this thesis). After the paper plug had soaked in the monomer for six hours, the reactor was returned to atmospheric pressure by turning the 3-way stopcock valve which switched the monomer line connection to a line connected to a compressed nitrogen cylinder. The inlet valve was opened allowing nitrogen to fill the reactor until atmospheric pressure was reached. The valve on the vacuum vessel was closed and the reactor disconnected and placed in a glove bag being purged with nitrogen. Inside the nitrogen atmosphere, the reactor was opened and the bottle containing the monomer and paper was removed, the excess monomer was removed, and the lid was placed on the bottle and tightly sealed. The bottle and contents (sealed in a nitrogen atmosphere) were then ready for irradiation.

Method 2: Using this method, the paper plug was not evacuated but instead prepared in air. The paper plug was wrapped with aluminum foil and placed in a weighed bottle. Monomer was bubbled with air for 15 minutes; then enough was added to the bottle to just cover the paper plug. After soaking the paper in the pool of monomer for six hours in the open air, the excess monomer was drained off and the aluminum foil lined lid was put on and tightly secured. The samples were then ready for irradiation.

Six paper plugs were prepared by Method 1 and six by Method 2. All 12 samples were placed into the radiation chamber of the Gammacell 220 and lowered into the radiation field. After 3.1, 8.1, 11.3, 21.4, 24.1, and 29.9 hours of irradiation, one sample prepared by Method 1 and one prepared by Method 2 were removed from the Gammacell. The samples were weighed to determine if any monomer had escaped by evaporation or leakage. No appreciable weight loss was noticed.

The bottles were opened and placed in a hood to allow any unpolymerized monomer to evaporate. After 5 days in the hood, the vials were placed in the vacuum vessel and evacuated overnight to remove any last traces of unreacted monomer.

The diameter of the 4 oz. bottle neck was fairly close to the diameter of paper plug but the bottom of the bottle had a diameter much bigger than the plug. Enough monomer was poured into the bottle to cover the plug. The plug was soaked in the monomer until just prior to irradiation. Part of the excess monomer was removed. After irradiation and removing the unreacted monomer, some of the bottles had to be broken in order to remove the samples. The reason being the bottom of the sample was encased in PMMA homopolymer. All of the excess monomer may not have been removed or part of the monomer in the paper may have drained out of the paper and aluminum foil. In most cases, it is thought the presence of homopolymer was caused by not removing all the excess monomer after the soaking procedure.

In any case, the thickness of homopolymer was cut off using a hack saw. Any remaining homopolymer was removed by grinding with an electric driven

wire brush. The final weight of the aluminum foil, paper and polymer was found and from this the original weight of aluminum foil was subtracted. This gave the weight of the paper and polymer in the sample. By subtracting the original weight of paper used from the composite weight, one can get the weight of polymer in the final sample. Then the polymer percent and polymer to paper weight ratio can be found using the following equations.

$$\text{polymer percent} = \frac{\text{weight polymer}}{\text{weight of paper} + \text{weight polymer}} \quad (1)$$

$$\text{polymer to paper weight ratio} = \frac{\text{weight of polymer}}{\text{weight of paper}} \quad (2)$$

Note: In the future it is suggested that the above procedure be altered in the following way. A piece of glass tubing (36mm OD) should be cut, one for each paper plug (made using the 1.125 in. diameter compression die). The paper plug without any aluminum foil wrapping fits easily into this size of tubing. The plug can then be put into the glass tube and both placed into the 4 oz. bottle. Sufficient monomer can be added to just submerge the paper plug inside the glass tube. Both ends of the glass tube would be open, thus, the level of monomer inside the tube containing the paper plug would be the same as the monomer level in the bottle. Instead of removing any excess, sufficient monomer would be added until the paper plug was just submerged in monomer. The paper plug would then remain submerged during the soaking period and throughout irradiation. This would keep the paper saturated with monomer all during the formation of the composite. After irradiation, the glass tube would be surrounded by a thickness of homopolymer but it can now be easily removed compared to removing it from the aluminum foil wrapped sample. The amount of homopolymer between the glass tube and the paper-polymer plug is quite small. Thus by breaking off the glass tube, the final paper-polymer sample could be weighed and its polymer content and weight ratio could be found more accurately.

5.3b Results: A summary of the percent polymer and polymer to paper weight ratio value found in this experiment is given in Table 14.

One purpose of this experiment was to determine the amount of monomer polymerized in the presence of paper as a function of irradiation time. That is, assuming the paper plug was initially saturated with monomer how much of this monomer would be polymerized at a given dose. To determine the percent of this monomer that was polymerized, the following equation can be used.

$$\% \text{ conversion of monomer} = \frac{\text{weight of polymer in final sample}}{\text{weight of monomer initially in sample}} \quad (3)$$

It is difficult to determine exactly the amount of monomer initially in the sample, but if one knows the amount of polymer in a sample where 100 percent of the monomer has been polymerized, then the weight of initial monomer is equal to the weight of polymer in the final sample. That is, assuming the paper plugs were prepared the same, one has

$$\begin{array}{l} \text{weight of monomer} \\ \text{initially in sample} \end{array} = \begin{array}{l} \text{weight of polymer in the sample if} \\ 100\% \text{ of the monomer was polymerized} \end{array} \quad (4)$$

Thus equation (3) becomes,

$$\% \text{ conversion of monomer} = \frac{\text{weight of polymer in sample}}{\text{weight polymer in sample at } 100\% \text{ conversion of monomer}} \quad (5)$$

The weight polymer in a sample where 100 percent of the monomer is polymerized must now be determined. By knowing the polymer to paper weight ratio at 100 percent conversion, the weight polymer in sample at 100 percent conversion can be found using

$$\begin{array}{l} \text{weight polymer in} \\ \text{sample at 100\% con-} \\ \text{version of monomer} \end{array} = \left(\begin{array}{l} \text{polymer to paper} \\ \text{weight ratio of} \\ \text{sample at 100\% con-} \\ \text{version of monomer} \end{array} \right) \left(\begin{array}{l} \text{weight} \\ \text{paper} \\ \text{in} \\ \text{sample} \end{array} \right) \quad (6)$$

Therefore,

TABLE 14. RESULTS OF THE POLYMERIZATION OF MMA IN THE PRESENCE OF COMPRESSED PAPER

Sample No.	Irradiation Atmosphere	Irradiation Time	Absorbed Dose (rads)	Percent Polymer Content	Polymer to Paper Weight Ratio
2	Nitrogen	3.1	3.44×10^5	18.5	0.1875
5	Nitrogen	8.1	8.99×10^5	47.6	0.9072
1	Nitrogen	11.3	12.5×10^5	51.0	1.0393
3	Nitrogen	21.4	23.8×10^5	48.3	0.9334
4	Nitrogen	24.1	26.8×10^5	50.5	1.0109
6	Nitrogen	29.9	33.2×10^5	49.9	0.9942
2A	Air	3.1	3.44×10^5	4.0	0.0416
5A	Air	8.1	8.99×10^5	37.9	0.6113
1A	Air	11.3	12.5×10^5	42.5	0.7376
3A	Air	21.4	23.8×10^5	54.4	1.1921
4A	Air	24.1	26.8×10^5	47.2	0.8939
6A	Air	29.9	33.2×10^5	51.6	1.0650

$$\begin{array}{l} \text{\% conversion} \\ \text{of monomer} \end{array} = \frac{\text{weight of polymer in sample}}{\left(\begin{array}{l} \text{polymer to paper} \\ \text{weight ratio of} \\ \text{sample at 100\%} \\ \text{conversion of} \\ \text{monomer} \end{array} \right) \left(\begin{array}{l} \text{weight paper} \\ \text{in sample} \end{array} \right)} \quad (7)$$

Dividing top and bottom of the right hand side of the above equation by (weight of paper in sample), one gets

$$\begin{array}{l} \text{\% conversion} \\ \text{of monomer} \end{array} = \frac{\frac{\text{weight polymer in sample}}{\text{weight paper in sample}}}{\text{polymer to paper weight ratio of sample at 100\% conversion of monomer}} \quad (8)$$

which reduces to

$$\begin{array}{l} \text{\% conversion} \\ \text{of monomer} \\ \text{in any sample} \end{array} = \frac{\text{polymer to paper weight ratio of sample}}{\text{polymer to paper weight ratio of a sample prepared at the same pressure and 100\% of the monomer is polymerized}} \quad (9)$$

Therefore, to find the percent conversion of the monomer for the paper plugs compressed at a pressure of 2500 psi, it was necessary to find the polymer to paper weight ratio at 100 percent conversion of monomer for a paper plug made using a pressure of 2500 psi. To determine the value, the following procedure was carried out.

Four compressed paper plugs were made using the procedure described in the beginning of this section. The small die and press were used to compress paper plugs at pressures of 0 (compressed by hand), 2000, 4200 and 8200 psi.

These plugs were then prepared using Method 1 described in this section with the following modifications. Instead of 4 oz. bottles, all four plugs were wrapped with aluminum foil and put into one 400 ml beaker and then the beaker and contents put into the vacuum vessel. The vessel was evacuated for 23 hrs. to a final pressure of 60 millitorr. The monomer was introduced and the

plugs soaked for 4.5 hrs. The excess monomer was not removed but the plugs were left submerged in monomer upon putting the radiation vessel containing the beaker and plugs into the Gammacell.

From analyzing the results of the percent polymer content in the previous experiment given in Table 14, the polymer content reaches a maximum in the samples prepared by Method 1 at an irradiation time of 11.3 hours. Further irradiation produces samples with polymer content nearly equal this or less. Also in the bulk polymerization of MMA, 100 percent conversion occurs at approximately 8 hrs. Therefore by using Method 1 and an irradiation time of 10 hrs. (absorbed dose of 10.9×10^5 rads) it was assumed that the monomer would be 100 percent converted to polymer in the composites using paper compressed at 2500 psi.

After irradiation the radiation vessel was removed from the Gammacell and the beaker taken out. The four paper plugs were encased in a cylinder of homopolymer and there was no odor of monomer. Thus the monomer in the composites was assumed to be 100 percent polymerized. The paper-polymer composite plugs were separated from the homopolymer by using a hack saw to cut them free. The remaining homopolymer was removed using an electric powered wire brush. The percent polymer content and polymer to paper ratio was determined using the equations (7) and (2). A summary of these results are given in Table 15.

The polymer weight ratio value of 0.99, obtained for the paper-polymer composite using paper compressed at 2500 psi, was averaged with the values obtained from the previous experiment for those composites prepared by Method 1 and irradiated for 11.3 hours or more and with those values of the composites prepared by Method 2 and irradiated for 21.4 hours or more. This calculation is shown in Table 16. The average value was assumed to be the polymer to paper weight ratio for a composite made with paper compressed at 2500 psi and assuming 100 percent conversion of the monomer initially present in the composite.

TABLE 15. PERCENT POLYMER AND POLYMER TO PAPER WEIGHT RATIO OF THE COMPRESSED PAPER-PMMA COMPOSITES AT 100% CONVERSION OF MONOMER

Sample No.	Pressure Used to Compress Paper	Percent Polymer in Composite	Polymer to Paper Weight Ratio
1	0	77.5%	3.45
2	2,500	49.7%	0.99
3	5,000	37.5%	0.60
4	10,000	28.7%	0.40

TABLE 16. CALCULATION OF POLYMER TO PAPER WEIGHT RATIO OF THE PAPER-PMMA COMPOSITE AT 100% CONVERSION OF MONOMER USING PAPER COMPRESSED AT 2500 psi

Sample No.	Polymer to Paper Weight Ratio
1 Table 14	1.0393
3 Table 14	.9334
4 Table 14	1.0109
6 Table 14	.9942
3A Table 14	1.1921
4A Table 14	.8932
6A Table 14	1.0950
2 Table 15	<u>.9900</u>
AVERAGE =	1.0185

With this value it was then possible to determine the percent conversion of monomer in the samples discussed in Table 14. Equation (9) was used to calculate the percent conversion and the results of these are given in Table 17. In Fig. 11, the percent conversion of monomer has been plotted versus absorbed dose of the monomer.

5.3c Discussion: From this experiment it appeared that irradiations carried out in air give significantly (from 15 to 30 percent) less conversion of monomer in the paper-(compressed at 2500 psi) monomer mixture.

To achieve 100 percent conversion in these mixtures it required an absorbed dose of approximately 1.2×10^5 rads for irradiations carried out in an inert atmosphere (nitrogen) and an absorbed dose of 2.3×10^6 rads for those carried out in air. (Using the average value of polymer to paper weight ratio at 100 percent conversion of monomer given in Table 16, it was possible for some of the samples to have greater than 100 percent conversion.)

5.4 The Effect of Air and Pressure Used to Compress the Paper on the Polymer-Paper Composite Process

In the previous experiments the composites were prepared in air or in an atmosphere of nitrogen. That is, the paper and monomer were either saturated with air or the air was replaced with pure nitrogen. The following experiment was performed to determine if removing the air from the monomer or paper alone would affect the conversion of the monomer to polymer. Also, compressed paper plugs were made using a pressure of 5000 psi as opposed to 2500 psi used in the previous experiment. This was done to determine if the pressure used to compress the paper had any effect on the conversion of the monomer.

5.4a Procedure: Four compressed paper plugs were prepared using the same procedure described in section 5.3a except that a pressure of 5000 psi was used. These plugs were then prepared in one of the four following ways.

Method 1': This was the same as Method 1 described in section 5.3a except that the procedure was modified as suggested by the note in that same section. That is, the compressed paper plugs were placed in a 36mm DD glass

TABLE 17. PERCENT CONVERSION OF MONOMER FOR PAPER-PMMA COMPOSITES
USING PAPER COMPRESSED AT 2500 psi

Sample No. (From Table 14)	Irradiation Atmosphere	Absorbed Dose (rads)	Percent Conversion of Monomer
2	Nitrogen	3.44×10^5	18.4
5	Nitrogen	8.99×10^5	89.3
1	Nitrogen	12.5×10^5	102.0
3	Nitrogen	23.8×10^5	92.0
4	Nitrogen	26.8×10^5	100.0
6	Nitrogen	33.2×10^5	97.9
2A	Air	3.44×10^5	4.1
5A	Air	8.99×10^5	60.2
1A	Air	12.5×10^5	72.6
3A	Air	23.8×10^5	117.0
4A	Air	26.8×10^5	88.0
6A	Air	33.2×10^5	105.0

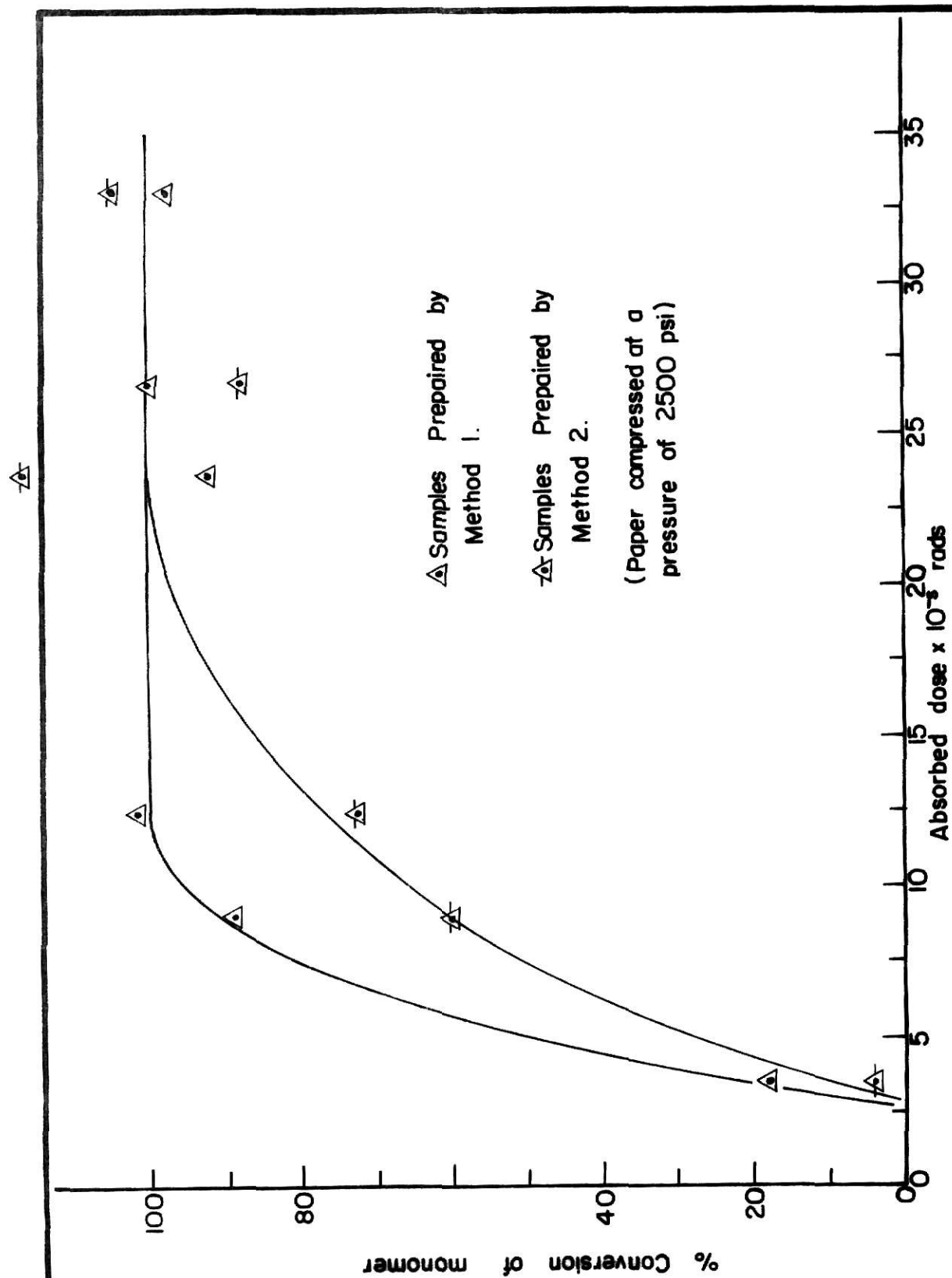


Fig. II. Conversion of Monomer using paper compressed at 2500 psi.

tube before being put in the bottles. The plug was also left submerged in a pool of monomer during soaking and irradiation.

Method 2': This was the same as Method 2 described in section 5.3a except that again the modified procedure suggested in that section was used.

Method 3: This was the same as Method 1' above except that the monomer was bubbled with air for 15 minutes instead of nitrogen prior to its introduction to the evacuated paper plug.

Method 4: This was the same as Method 2' above except that the monomer was bubbled with nitrogen for 15 minutes instead of air prior to its introduction to the paper plug prepared in air.

The prepared paper-monomer mixtures were irradiated for 8.0 hrs. which corresponded to an absorbed dose of 8.72×10^5 rads. It was hoped that this dose would give less than 100 percent conversion of the monomer (it did not in the case of the plugs compressed at a pressure of 2500 psi). In this way the effect of the different methods of preparation could be related to the percent conversion of the monomer.

After irradiation, the bottle tops were removed and the bottles placed in a hood for 3 days. For those samples prepared by Methods 1' and 3 there was solid homopolymer between the bottle wall and glass tubing surrounding the paper-polymer composite. In the samples prepared by Methods 2' and 4, the material between the bottle wall and glass tubing was not solid, but a highly viscous fluid. This indicated that the bulk monomer in those samples where the paper was not evacuated had not been completely polymerized. The irradiated samples were then taken out of the bottles and the homopolymer and glass tubing were removed from the polymer-paper composites. All four composite samples were placed in the vacuum vessel and evacuated for overnight to a final pressure of 50 millitorr. This removed all final traces of unreacted monomer.

The paper to polymer weight ratio and percent polymer values were determined for each sample using equations (1) and (2).

The percent conversion of monomer was also calculated. The paper to polymer weight ratio at 100 percent conversion of monomer was taken from Table 15. Table 16 indicated that a polymer-paper composite made using paper compressed at 5000 psi, and assuming 100 percent conversion of the monomer, should have a polymer content of 37.5 percent which correspond to a paper to polymer weight ratio of 0.600. This value was used in equation (9) to calculate the percent conversion of monomer.

5.4b Results: The results of the above calculations are given in Table 18. The results suggest that removing dissolved air from the liquid monomer was more significant than evacuating the compressed paper.

Using Method 1' gave a conversion of 81.5 percent while Method 2' gave 76.8 percent, a difference of 4.3 percent. The conversion obtained using Methods 2', 3 and 4 were almost the same. Thus it seemed that without removing the dissolved air from the liquid monomer, little was gained by evacuating the paper.

The difference of 4.3 percent at a dose of 8.72×10^5 rads using Methods 1' and 2' was very small compared to the 30 percent difference obtained in the experiment of section 5.3 for samples with paper compressed at 2500 psi and irradiated to an absorbed dose of 8.99×10^5 rads using Methods 1 and 2. These results could be due to two things: (1) the pressure used to compress the paper, or (2) the difference of leaving the paper immersed in monomer rather than pouring off the excess prior to irradiation. This problem had to be solved experimentally.

Six more paper plugs were prepared in the normal way (see section 5.3a), two at a pressure of 2500 psi, two at 5000 psi, and two at 10,000 psi. One plug at each pressure was prepared using Method 1' and the other using Method 2'. All samples were irradiated to an absorbed dose of 9.72×10^5 rads. This is slightly more than the ones previously done, but this was done to see if a greater dose gave a higher conversion for the 5000 psi plugs.

The percent polymer, polymer to paper weight ratio and conversion of monomer were determined for each sample using equations (1), (2) and (9),

TABLE 18. EFFECT OF OXYGEN ON THE PERCENT CONVERSION OF MONOMER IN THE PAPER-PMMA COMPOSITES

Sample No. ^a	Method of Preparation	Percent Polymer	Paper to Polymer Ratio	Percent Conversion of Monomer
41	Method 3	31.7	.4641	77.4
42	Method 1'	32.8	.4887	81.5
43	Method 2'	31.5	.4606	76.8
44	Method 4	31.5	.4606	76.8

^aAll samples were irradiated for 8.0 hours which corresponds to an absorbed dose of 8.99×10^5 rads.

respectively. The polymer to paper weight ratios at 100 percent conversion used in the equations for the respective paper compression pressure were taken from Table 15. The results are shown in Table 19. All samples were irradiated for 9.0 hours which corresponds to an absorbed dose of 9.72×10^5 rads.

The difference in conversion using Method 1' and Method 2' is 4.4 percent for the 2500 psi plugs, 5.3 percent for the 5000 psi plugs and 9.8 percent for the 10,000 psi plugs. All these differences are small compared to the differences in the results of the experiment of section 5.3. In that experiment the 2500 psi compressed plugs prepared by Method 1 gave from 15 to 30 percent greater conversion than the ones prepared by Method 2. This seemed to indicate that the experimental procedure of leaving the paper plugs immersed in monomer during irradiation was the reason for the small differences of conversion observed in the 5000 psi plugs presented in Table 18. That is, the procedure, as opposed to the paper compression pressure, removes the conversions' dependency on the presence of oxygen.

The 5000 psi plugs irradiated to a dose of 9.72×10^5 were expected to give the same or higher conversion of monomer than those previously irradiated at a dose of 8.72×10^5 rads. However, the plug prepared by Method 1' actually gave a 10 percent lower conversion than either of the plugs irradiated at a dose of 8.72×10^5 rads. Thus it is expected the experimental reproducibility is somewhere around 10 percent or greater.

If this is the case, then it is concluded that by leaving the paper immersed in the monomer during irradiation, the removal of air and pressure used to compress the paper have little effect on the conversion of monomer.

It was interesting, however, that all the results of those samples left immersed in monomer gave conversions between the values obtained from the 2500 psi plugs prepared in air and nitrogen of experiment 5.3 (samples were irradiated after draining off the excess monomer). It was expected that using the "immersion" technique all conversion values would be within the envelope made by the "conversions in air" and "conversions in nitrogen" curves of the experiment of section 5.3. Thus an approximate conversion curve can be

TABLE 19. THE EFFECTS OF THE PRESSURE USED TO COMPRESS THE PAPER AND THE PRESENCE OF OXYGEN ON THE CONVERSION OF MONOMER IN THE PAPER-PMMA COMPOSITES

Sample No. ^a	Method of Preparation	Pressure Used to Compress Paper (psi)	Percent Polymer Content	Paper to Polymer Weight Ratio	Percent Conversion of Monomer
71	Method 2'	2500	45.7	.8413	82.6
72	Method 1'	2500	44.4	.7984	78.2
73	Method 2'	5000	32.0	.4708	70.6
74	Method 1'	5000	33.6	.5060	75.9
75	Method 2'	10,000	24.8	.3294	84.7
76	Method 1'	10,000	22.6	.2911	74.9

^aAll samples were irradiated for 9.0 hours which corresponds to an absorbed dose of 9.72×10^5 rads.

drawn for the conversion of monomer using the "immersion" technique. This curve is shown in Fig. 12 along with the conversion curves from section 5.3.

5.4c Discussion: From the results of this experiment, it is concluded that by immersing the compressed paper in a pool of monomer during the irradiation, the conversion of the monomer is not significantly affected by the presence of oxygen nor is it a function of the pressure used to compress the paper. To give 100 percent conversion of the monomer, an absorbed dose of approximately 17.5×10^5 rads is needed.

Thus in the proposed composite process, it may not be necessary to remove the oxygen by evacuating the solid waste prior to the monomer introduction. If this is true, the economics of the process are more attractive.

The results are not conclusive and more work should be done to insure that oxygen removal is not needed and that compression pressure is not a factor in the conversion of monomer.

5.5 Testing the Physical Properties of the Composites

Another requirement for successful recycling methods is that the recycled products must have properties comparable to those competitive products on the market. To determine some of the properties of the solid waste-polymer composites relatively large samples of the material were made and tested. Again paper was chosen as the solid waste used because of its commonness and availability. MMA was used as the polymer and the samples were tested for compression and tensile strength, resistance to indentation and water absorption.

Irradiations were carried out for a sufficient length of time to insure 100 percent conversion of the monomer. All but one sample was irradiated in a nitrogen atmosphere. The remaining sample was processed in air. This was done to find out if irradiating in air would affect the properties of the final composite.

5.5a Procedure: Compressed paper plugs were made using the procedure outlined in the first part of 5.3a. The large compression die (3.1 in. diameter)

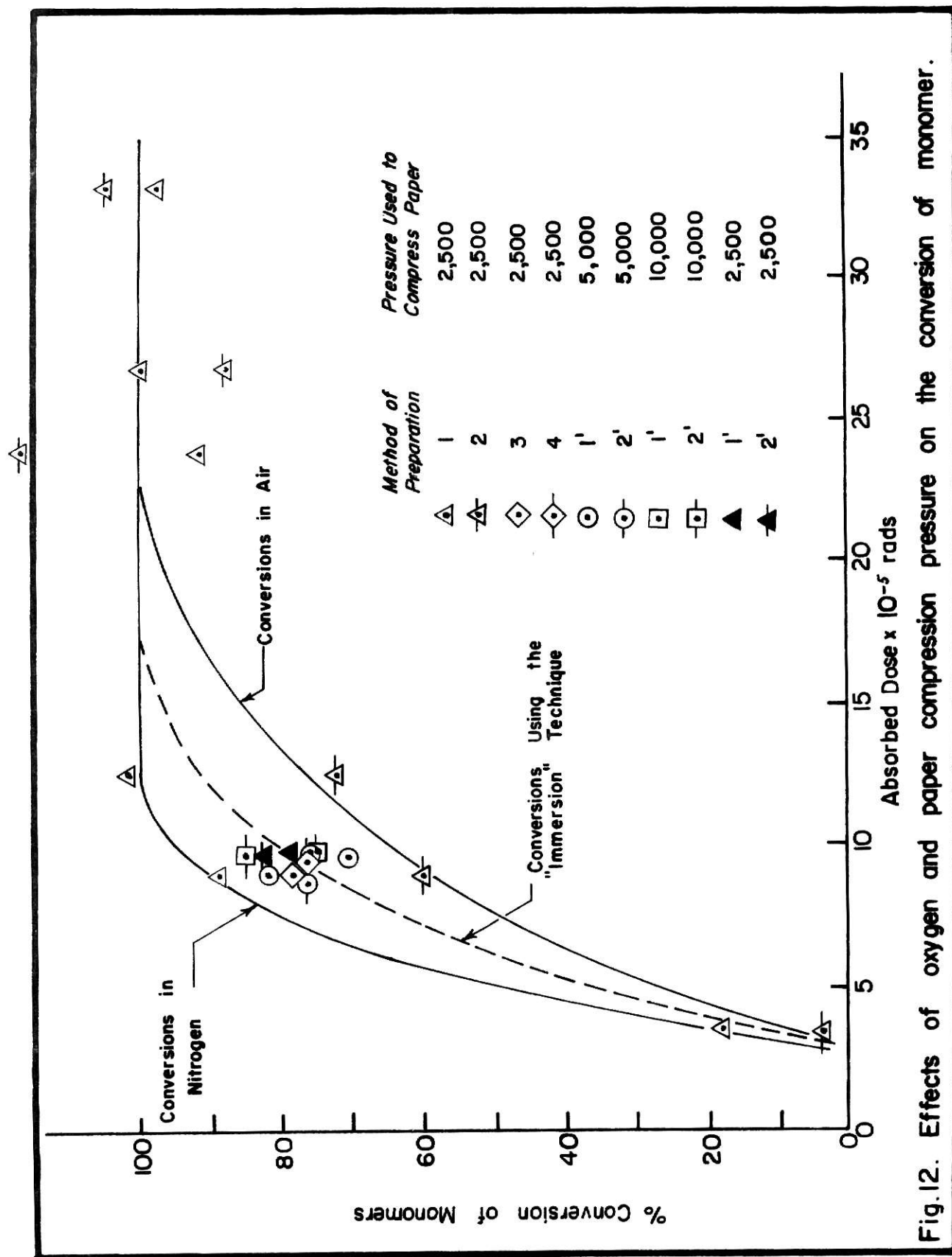


Fig.12. Effects of oxygen and paper compression pressure on the conversion of monomer.

and large press were used to make the cylindrical plugs (approximately 4 in. long and 3.1 in. diameter) at pressures of 225, 500, 10,000 psi and 4 plugs at 5000 psi.

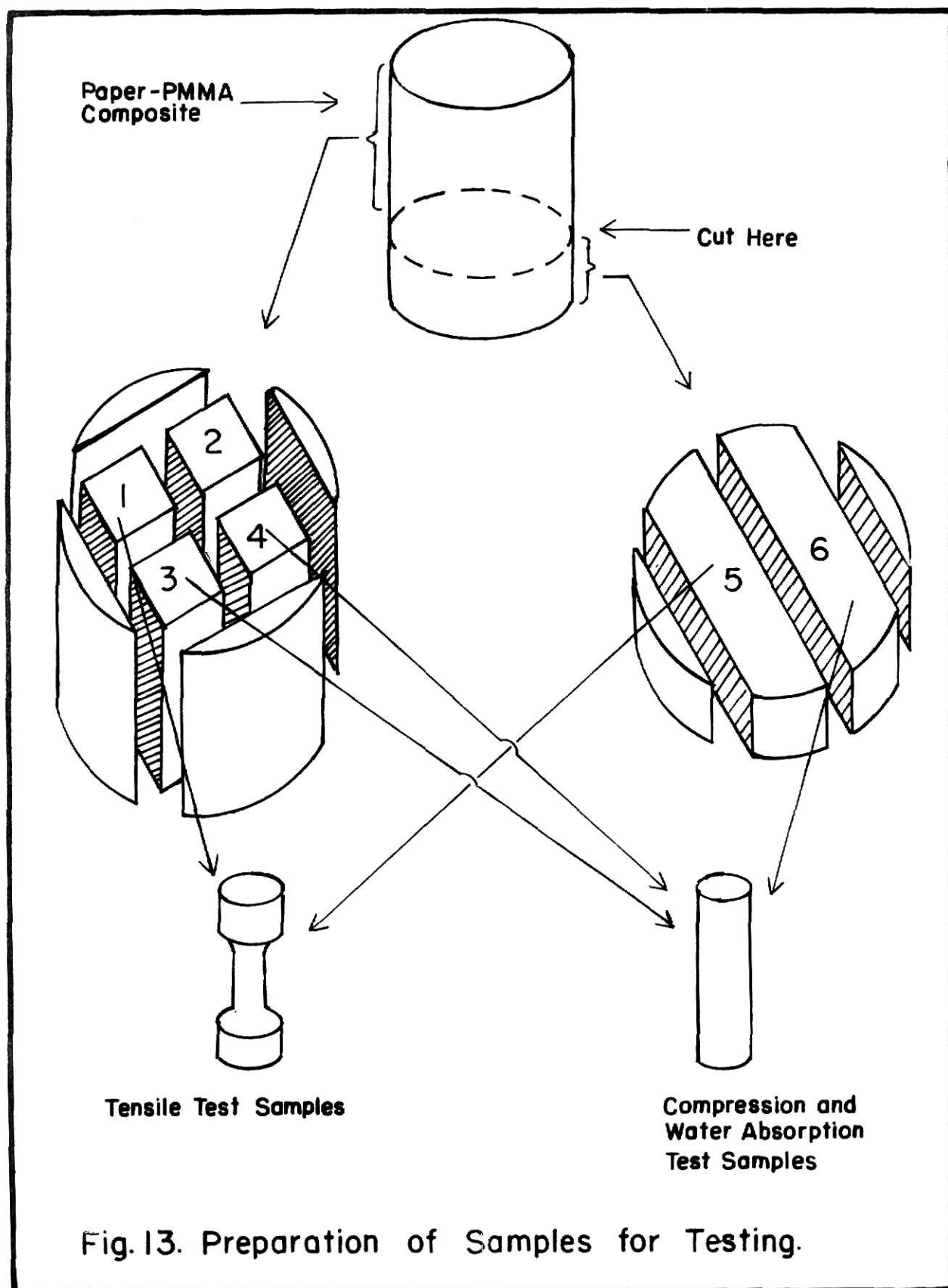
All plugs were prepared in nitrogen (Method 1') except one of the plugs compressed at 5000 psi which was prepared in air (Method 2'). A 600 ml beaker was used to hold the compressed paper plugs while being soaked in monomer and the mixture remained in the beaker during irradiation. All samples except IV were irradiated for 15 hours (corresponding to an absorbed dose of 16.4×10^5 rads). Sample IV was irradiated for 24 hours (26.2×10^5 rads). After irradiation the composite material was weighed and its percent polymer and polymer to paper weight ratio was determined using equations (1) and (2). These results are shown in Table 20.

The polymer to paper weight ratios were very close to those corresponding values in Table 15, therefore 100 percent conversion of the monomer must have occurred. The samples were prepared for testing by machining them in the following manner.

First a disc of approximately one inch thick was cut from the bottom of the composite cylinder. The top of this disc was sanded smooth and hardness readings were taken at five different locations on the smooth surface. See Appendix A section A.3 for the procedures followed to determine the hardness. The disc was then cut on a line passing through the center of the disc. Then cutting on a line one inch from and parallel to this center line, two bars of composite were produced approximately 3 in. long and having a cross section of 1 sq. in. From the top piece of the cylinder, a rectangular block was cut which had the largest possible square cross section. The cross section of this block had a diagonal length equal to the disc diameter and the block was approximately three in. thick. The block was then cut into four bars which had a cross-sectional area of 1 sq. in. and a length of approximately 3 in. These pieces were then numbered and further machined to give samples for testing. The sketch in Fig. 13 shows the numbering of the pieces and the shape of the final test samples.

TABLE 20. POLYMER CONTENT OF THE "LARGE" PAPER-PMMA COMPOSITES

Sample No.	Percent Polymer	Polymer to Paper Weight Ratio	Pressure Used to Compress Paper
I	71.7	3.534	225
II	34.2	0.520	5000
III	41.8	0.719	5000
IV	35.7	0.554	5000
V	38.3	0.622	5000
VI	65.5	1.896	500
VII	27.3	0.375	10,000



Using a metal lathe, the bars numbered "1", "2", "3", "4", "5", and "6" were then turned down to cylinders of 0.75 in. diameter. The cylinders made from the bars labeled "3", "4" and "6" were cut to lengths of 1.5 in. and their ends sanded flat and parallel. The two samples, "3" and "6", were then used to test the compressive strength of the composite in the directions both parallel and perpendicular to the direction in which the paper was compressed.

The cylinders from the bars "1" and "5" were further machined to give samples which could be tested for tensile strength in both directions. The cylinders were approximately 2.5 to 3.0 in. long and the diameter of the middle of each cylinder was reduced to 0.50 in. for a length of 1.0 in.

The cylinder from the bar marked "4" was used in the water absorption test. The bar "6" was used if "1", "3", or "4" broke during machining.

A discussion of methods used to determine the above properties is given in Appendix A. Given there are the procedures and calculations which were used to find the different properties given in the results below.

5.5b Results: The results of the above tests are summarized in Table 21.

When samples I and IV were being machined, small voids were noticed within their interior. These voids were thought to influence greatly the properties of the material. These voids were probably caused by local heating during polymerization of the monomer to vaporize. This vapor is trapped in the paper-monomer mixture, and when the monomer is completely converted, these vapor pockets leave voids in the final composite.

The local heating was caused by the heat of polymerization of MMA. When there is a great deal of monomer present, (Samples I and VI had high polymer content) the paper-monomer-polymer mixture is unable to absorb and dissipate this energy rapidly enough to prevent monomer vaporization.

When the paper was compressed to a pressure of 5000 and 10,000, these voids were no longer present. Their absence was probably due to less monomer

TABLE 21. PROPERTIES OF THE PAPER-PMMA COMPOSITES

Sam- ple No.	Pressure Used to Compress Paper (psi)	Percent PMMA	Compression Strength (psi)		Tensile Strength (psi)		Water Absorption		Hard- ness Value
			Parallel ^b	Perpendicular ^a	Parallel ^b	Perpendicular ^a	Final Percent Weight Increase	Time in Hrs. ^e	
I ^d	225	71.7	15,700	6,500	220	2,230	6.9	398	169
II ^d	5000	34.2	26,300	11,500	320	6,440	16.0	402	176
III ^d	5000	41.8	24,300	12,000	190	5,590	25.1	265	175
IV ^c	5000	35.7	19,600	7,300	140	3,590	30.0	338	146
V ^d	5000	38.3	28,700	12,800	280	7,060	17.7	384	171
VI ^d	500	65.5	9,800	9,800	80	2,890	16.5	384	131
VII ^d	10,000	27.3	20,400	10,200	210	4,290	34.0	262	174

^a Strength perpendicular to the direction in which the paper was compressed.

^b Strength parallel in the direction in which the paper was compressed.

^c Sample irradiated in an air atmosphere.

^d Samples irradiated in a nitrogen atmosphere.

^e Time in hours to reach 95% of final weight increase.

being polymerized and the large amount of paper was able to absorb the heat, keeping the temperature of the mixture low enough to prevent monomer vaporization. There was a marked improvement (no voids and better properties) in those samples prepared using a pressure of 5000 psi to compress the shredded paper as opposed to 225 psi and 500 psi. However, there was no improvement (and possibly a decrease in quality) in going from a pressure of 5000 psi to a pressure of 10,000 psi.

Also noticed during the machining of the samples, was that the paper-PMMA composites were much harder to saw, sand and turn on a lathe than was wood and it was somewhat harder to machine than the pure PMMA.

The three composite samples (II, III, and V) prepared in the same manner did show some variation in results. The range was 18 percent difference in the compression test in the direction parallel to the direction in which the paper was compressed, 11 percent in the perpendicular direction, 68 percent in the tension strength in the parallel direction, 26 percent variation in the perpendicular direction and 2 percent difference in the hardness values.

The sample prepared in air (sample IV) gave significantly lower strength values than those samples prepared at the same paper compression pressure but irradiated in a nitrogen atmosphere. In the case of compression in the direction parallel to the direction in which the paper was compressed, the results were from 23 to 46 percent better in those samples prepared in nitrogen than the one prepared in air. The range was 75 to 57 percent better for the compression strength in the direction perpendicular to the direction in which the paper was compressed, 35 to 128 percent for the tensile strength in the parallel direction, 55 to 97 percent for the tensile strength in the perpendicular direction and about 20 percent improvement in the hardness test.

Of great significance to the strength of the components is in the direction in which the force was applied compared to the direction in which the paper was compressed. In the case of compression, the components have over twice the compression strength in the direction parallel to the direction

in which the paper was compressed. However, the tensile strength in the parallel direction was extremely low and the tensile strength in the direction perpendicular to the direction in which the paper was compressed was relatively high.

The hardness (resistance to indentation) of the composite material seems to be relatively insensitive to using an air irradiation atmosphere and no difference was noticed between the samples prepared at 5000 psi and 10,000 psi. Samples I and VI did give lower values than the others and it was thought this was due to the voids giving way as the force of the indenter was applied.

From the results of the water absorption tests, it appeared that generally the amount of water absorbed and rate of absorption was directly related to the paper content of the composite (inversely proportional to the polymer content). The higher the polymer content, the less water absorbed and the longer it took for the composite to reach saturation.

Samples VII, III and IV showed a great deal of swelling during the absorption of water and they had very little strength once saturated with water. Samples II and V showed a great deal less swelling and retained some of their strength but it was significantly reduced. Samples I and VI, which had high polymer content (72 and 65 percent), showed little swelling and no apparent reduction in strength.

5.5c Discussion: To prevent voids from forming in the paper-PMMA composite it was necessary to keep the polymer content below some critical value. This critical value lay somewhere between 65 and 34 percent polymer which corresponds to using a pressure of 500 psi and 5000 psi to compress the paper, respectively.

It was also concluded that removing the oxygen from the compressed paper by evacuation, purging the monomer with nitrogen and irradiating in a nitrogen atmosphere did improve the properties of the composites. The properties obtained were from 20 to 130 percent better in the sample prepared in nitrogen than the one prepared in air. It was felt that soaking the compressed paper in

monomer and leaving it submerged during irradiation was not enough to remove the air and eliminate the significant effects that oxygen has on the process.

The total amount of water absorbed and the rate of absorption were inversely proportional to the polymer content. The more water absorbed by a composite, the greater its swelling and the weaker it became.

Thus in the proposed recycling process, it would be necessary to compact the waste to such an extent that the polymer content in the composite would be below some critical value (somewhere between 35 and 65 percent polymer). This must be done to prevent overheating in the reaction mixture and the resulting formation of voids in the composite. At any given compaction pressure, it is also necessary to remove the air from the reaction mixture in order to achieve maximum strength in the paper-PMMA composite.

To retain their strength when submerged in water, the paper-PMMA composites will have to have a high polymer content (a minimum being somewhere between 65 and 35 percent) or coated to prevent water absorption.

CHAPTER 6

6.0 CONCLUSIONS

From the experimental section of this report, the following conclusions are drawn:

- (1) Most all types of solid wastes could be used to produce composites by mixing them with MMA and subsequently irradiating the mixture.
- (2) In the radiation induced polymerization of MMA in the presence of compressed paper, the pressure used to compress the paper and the presence of oxygen in the reaction system did not significantly effect the conversion of the monomer, provided the compressed paper was allowed to be submerged in a pool of monomer prior to and during irradiation.
- (3) If the excess monomer was removed from the compressed paper-monomer mixture, then the presence of air reduced the conversion of the monomer from 15 to 35 percent for a given radiation dose.
- (4) To prevent voids from forming in the paper-PMMA composite, it was necessary to keep the polymer content below some critical value which is between 65 and 34 percent polymer. This corresponded to using pressures of 500 psi and 5000 psi to compress the paper.
- (5) To achieve maximum strength at a given compression pressure, it was necessary to remove the oxygen from the reacting mixture of monomer and paper.
- (6) The composites formed under all conditions displayed greater compressive strength in a direction parallel to the direction in which the paper was compressed and a greater tensile strength in a direction in which the paper was compressed.
- (7) The hardness of the composites seemed to be independent of polymer content and the direction in which the force was applied as long as the polymer content was such that no voids were formed. With the presence of voids, the hardness value decreased significantly.

- (8) The rate of and final amount of water absorption increased with decreasing polymer content (increased compression pressure).

The absorption of water did not appear to degrade properties of the composite with high polymer content (i.e., 65 percent or greater) while the strength of those with low polymer content (35 percent or less) were significantly reduced.

From the above conclusions derived from a preliminary analysis of the proposed recycling method, it is possible to start investigating the feasibility of the process in light of those requirements met by other successful methods. These requirements were determined from the literature review presented in Chapter 2.

(1) Residues from the recycling method: First, representative wastes from most all the major sources have been used to produce composites of substantial strength, reasonable machinability and relative low water absorption. It is then concluded that the proposed process could be applied to the treatment of all wastes and the residues which cannot be treated would be minimal.

(2) Economics of the process: It is necessary to determine the basic processing steps needed to produce the composite materials for a basis of economic studies.

It was reported that a high polymer (PMMA) content in the final composite was not desirable. In the case of high polymer content, there is a large volume of monomer that is being polymerized and heat generation causes monomer vaporization. This results in small voids left in the final composite and a degradation of their properties. Therefore, to achieve a low polymer content in the PMMA-paper composite it was necessary to compact the paper. To produce uniform compaction, the paper was shredded before compressing. By increasing the pressure used to compress the paper from 500 to 5000 psi, it was found that voids no longer existed and there was a big improvement of the strength properties. Thus the critical polymer content in the case of PMMA is somewhere between 65.5 percent (corresponding to a pressure of 500 psi) and 35 percent (5000 psi).

It is suspected that this heating effect causing voids will apply to most composites made in this manner regardless of the waste used (at least it will apply to those wastes containing large amounts of cellulose). Therefore it will probably be necessary to shred or grind those wastes treated and compress them to such an extent that the polymer content is well below 65.5 percent (when the polymer is PMMA).

Once shredded and compressed, the wastes would be ready for the addition of the monomer. The problem arises of whether or not to remove the oxygen from the reaction system. In section 5.3 it was found that the presence of oxygen in the irradiating atmosphere significantly reduced the percent conversion of the monomer if the excess monomer had been removed prior to irradiation. However, in section 5.4 the compressed paper was left submerged in a pool of monomer (MMA) during irradiation and it seemed that neither compression pressure of the paper nor the presence of oxygen had an effect on the conversion of monomer.

Another factor is the effect of oxygen on the strength of final composites. Since oxygen promotes the degradation of PMMA under the influence of radiation, the final polymer chain could be reduced, causing less strength in the composite. The results of the section 5.5 tests seem to support this.

Those samples prepared in nitrogen gave significantly better properties than the sample prepared in air. Thus it is not necessary to remove the oxygen to cut down on the absorbed dose (irradiation time) necessary to give 100 percent conversion; however, in order to obtain the maximum strength from the composites, the irradiation atmosphere will have to be void of oxygen. To remove the oxygen, it will be necessary to evacuate the compressed wastes and purge the monomer with an inert gas before they are mixed.

After the waste has become saturated with the monomer, the mixture is ready for irradiation. For the MMA-compressed paper mixture, an absorbed dose of approximately 17.5×10^5 rads was required to give 100 percent conversion of the monomer. According to the conclusions in 5.4c, this dose is

independent of the irradiation atmosphere and pressure used to compress the paper.

Now that the major steps in the process have been outlined it would be possible to begin a preliminary economic analysis. No effort has been made, as yet, to determine the cost of the process but it is suggested that one is immediately necessary as a continuance of this work.

Also in relation to the economics of the process, the radiation source will be a major item in the cost analysis. These resources require a great deal of capital investment and their availability is low. However, radiation processing is of growing importance in the chemical processing industry (31,32). Thus the sources become more available and with improved technology, the cost of radiation process will decrease making the proposed process more attractive.

(3) Properties of product: Another requirement for a successful recycling method is that the properties of the recycled product must be comparable to those virgin materials in the market where it is competing. In order to compare the properties of the composite material made and tested in the experimental part of this study to those virgin materials available, Table 22 was prepared.

As can be seen, the best composite produced has a compression strength comparable to aluminum and a tension strength equal to that of pure PMMA. The density of the material is a third greater than that of the pure PMMA but half that of aluminum. Its resistance to indentation is a great deal more than that of wood. This qualifies the composite to compete with a large number of virgin materials including wood, concrete, wood and concrete modified with polymers, pure polymers and a whole host of reinforced plastics.

(4) Market for product: Reinforced plastics (composites) seemingly have a lot going for them. They are very versatile and they have the unique properties that make them very attractive. So far, however, they have done little more than get off the ground at the market place. They are still nowhere near their commercial potential because of a lack of sophistication and competitive technology for making them and for molding them into parts.

TABLE 22. COMPARISON OF PROPERTIES OF THE PAPER-PMMA COMPOSITE WITH OTHER STANDARD MATERIALS

Material	Tensile Strength (psi)	Compression Strength (psi)	Density lbs/ft ³
Steel ^a	70,000	42,000	490
Aluminum ^a	30,000	25,000	165
Concrete ^a	400	5,000	156
Concrete - polymer (6% PMMA) ^a	1,600	20,000	165
Wood Polymer ^b	---	12,000	---
Wood (Douglas fir) ^c	---	7,400	30
Wood (Douglas fir) ^d	---	8,000	---
Pure PMMA (TC) ^e	7,000	15,000	62
Pure PMMA (TC) ^f	6,200	15,200	62
Pure PMMA (RI) ^g	10,600	17,700	62
Composite Sample (V)			
Paper-PMMA Composite			
(38% PMMA-paper compressed			
@ 5000 psi) ^h	7,000 ^l (280) ^k	28,600 ^j (12,800) ⁱ	80.5

^aProperties taken from reference (82).

^bBirch-PMMA combination, properties taken from reference (7).

^cProperties taken from reference (49), force applied parallel to grain in wood.

^dCompression strength found experimentally, force applied parallel to grain in wood.

^ePure PMMA, formed thermal catalytically, properties taken from reference (82).

^fPure PMMA, formed thermal catalytically, properties experimentally determined.

^gProperties of pure PMMA formed by radiation induced polymerization, determined experimentally.

^hComposite produced using radiation induced polymerization of MMA monomer, properties determined experimentally.

ⁱForce applied parallel to the direction in which the paper was compressed.

^jForce applied perpendicular to the direction in which the paper was compressed.

^kPulled in a direction parallel to the direction in which the paper was compressed.

^lPulled in a direction perpendicular to the direction in which the paper was compressed.

Reinforced plastics have been commercial products for more than 25 years and have established footholds in several major markets. They continue to attract attention of large companies who allocate large amounts of research funds for their improvement (58). Of most importance, they have physical and mechanical properties that place them in the big void between metals and unreinforced plastics.

In spite of their advantages, progress to date has been limited. In the U.S., domestic consumption grew at an average annual rate of 14 percent from 1959 to 1969, in 1970 it fell a drastic 12 percent (35). The growth in the sixties, however, was not limited to the U.S. Growth in consumption ranged from 10 to 35 percent abroad as well (66).

Current reinforced plastics production is about 900 million pounds per year which is nominal compared to 250 billion pounds of steel, 19 billion pounds of plastic resin and 9 billion pounds of aluminum.

There are large markets where these composite materials might penetrate to a greater extent, thus improve their demand. Their combination of high strength, light weight and good chemical resistance is particularly attractive in the transportation, construction and corrosion-resistant fields.

The construction industry alone represents a \$55 billion market where the plastic composite may compete (34). The trouble is that wood, concrete, iron, steel, gypsum and other traditional building materials have been around for a very long time. They are inexpensive, reliable, last a long time, and what is more important, the builders are familiar with them. This industry has been extremely slow to accept change. The builders need a lot of convincing before accepting anything new and changes have come about in evolutionary steps rather than dramatic, revolutionary ones.

One new development which may increase the chances of plastics becoming more important in this industry is the concept of prefabricated housing. This involves the construction of prefinished walls, exterior panels, roofs, doors, and other building components as single units. These components are then

sent to the construction site for final assembly to provide the finished housing.

This system by-passes the traditional distribution channels of building materials and make possible the use of non-traditional materials in the construction of the prefinished units (30). Articles which might involve the use of reinforced plastics (or composites) include the following (34):

- (1) Facings for walls, floors, or ceilings
- (2) Roofing shells
- (3) Doors
- (4) Interior and exterior panels
- (5) Bathroom fixtures
- (6) Duct and vents
- (7) Lighting fixtures

Of particular interest is the application of the composites as floorings. The acrylic-impregnated, radiation-cured wood have already broken into the flooring market (80). The manufacturers hope to cover heavy traffic floors such as those in office buildings, banks, gymnasiums and industrial plants. They also claim wood-plastic combinations are competitive in price with terrazzo, quarry tile, vinyl and carpeting. Sales of the wood-plastic flooring are about 7-8 million sq. ft./year. Producers see a near-term market of 50 million sq. ft./year, and double that total by 1980. It is felt that the solid waste-polymer composites could effectively compete with these wood-plastic combinations, as well as the traditional virgin materials.

This application, along with others requiring high strength and low density materials, seem to indicate that there would be a sufficient market for the large amounts of composites which could be made from solid wastes-polymer combination.

(5) Conclusion: The proposed recycling process has shown to be applicable to most types of wastes. Thus, the residues remaining from this method are few and the chance of harming the environment is low.

In the production of the composites, it is possible to achieve properties which are comparable to materials competing in very large markets. Thus the problem of the solid waste-polymer composite process is one of economics. With the volume of solid wastes skyrocketing, and the current practices of open dumping and burning becoming intolerable, in conjunction with the depletion of natural resources and advances in radiation processing, the economics of the proposed recycling method will improve with time.

CHAPTER 7

7.0 RECOMMENDATIONS

There are several areas in this study which require more experimental investigation before definite conclusions can be drawn.

One such area of question is that of the effects of oxygen and paper compression pressure. In section 5.4c it was concluded that from the results obtained, it appeared that the conversion of monomer was independent of both paper compaction pressure and the presence of oxygen. However, this should be checked by more experimental work. Samples prepared in air and in nitrogen at different compression pressures should be irradiated at different doses until 100 percent conversion of the monomer is achieved. The conversion of monomer at the different doses can then be related to the method of preparation to determine if the presence of oxygen or compaction pressure of the paper has any effect on the conversion of the monomer.

Another area of immediate interest is that of a critical polymer content in the paper-PMMA composite. It was reported in section 5.5b that those samples prepared using paper compressed at pressure of 500 psi or lower had voids in the final composites, but those made using a pressure of 5000 psi or greater did not contain these voids. It was concluded that with a high monomer content in the irradiated compressed paper-monomer mixture, the heat of polymerization was too great to be dissipated to the atmosphere or absorbed by the cellulose. Thus the temperature of the mixture rose, causing monomer vaporization. Vapor pockets were formed and trapped, causing voids in the final composites. Since samples made using a pressure of 500 psi contained voids while those prepared at 5000 psi had no voids, there probably exists some minimum pressure between these two values which is required to produce composites without voids. By preparing composites using different paper compression pressures in the 500 to 5000 psi range, the minimum pressure required (which will correspond to the "critical" polymer content in the final composite) to produce composite without voids can be found.

One other immediate need is in the area of experimental equipment. First a hood is desperately needed to vent the toxic monomer vapors. A controlled atmosphere (and possibly one which can be evacuated) glove box is needed to replace the glove bag used in this work. This would insure the removal of oxygen from the reacting mixture of paper and monomer. Finally an aluminum radiation reactor vessel is needed to replace the one made from plexiglas. The plexiglas vessel became brittle and broke easily after 100 to 150 hours of radiation exposure. One aluminum vessel has been made but its internal dimensions were too small for a 600 ml beaker (which was needed to hold the compressed paper plug-monomer mixture). If an aluminum vessel is made, it should have internal dimensions to house a 600 ml beaker and such external dimensions that it will still fit into the Gammacell 220 radiation chamber.

The following discussion presents the possible ways that this work might be extended in the future.

In Chapter 5, section 5.2, several wastes were used in making the PMMA-solid waste composites. Most of the major sources (section 2.1) were represented by these wastes. However, there were no mineral wastes used. This major category is the second largest source of solid wastes in the U.S. Similar to the mineral waste is the ash produced by the incineration of municipal and industrial wastes and in the burning of coal for the production of electricity. These mineral tailings and ash represent a large source of fairly uniform, powdered or granulated, wastes which are not subject to most recycling methods. As open dumping of these wastes become less and less desirable, there will be a great need for recycling methods in these areas. Thus the use of mineral tailings and ash in the polymer-solid waste composite process should be investigated.

Also, unless the composites themselves can be recycled after they have lost their utility, the composite process is no longer a solution to the solid waste problem but has just shifted it from the disposal of one type of waste

to another. Shavings from the machining of the composites have been saved. These, along with shredded solid waste-polymer composites should be tried as the waste used in the proposed recycling method. Other wastes that should be investigated include glass, metal and plastics.

The basic steps of the proposed recycling method has been determined (i.e., shredding, compaction, evacuation, monomer induction and irradiation). It is now possible to begin a cost analysis for the process. An estimated price per unit of composite material is needed to compare it with other materials on the market. This economic analysis should come early in the continuance of this work.

It is suggested that the possible use of other monomers be investigated. The MMA monomer is relatively expensive compared to styrene or acrylonitrile, both of which could be used instead of MMA (that is they are liquid monomers which can be polymerized by irradiation). The cost of MMA is approximately 21 cents a pound compared to 9 cents a pound for styrene and 14.5 cents a pound for acrylonitrile (82, page 78). Also, Hills (37) reported that the strength of the styrene impregnated wood was somewhat less than the PMMA-wood sample but the styrene-wood was easier to machine. Thus styrene should definitely be tried as a possibility in the polymer-solid waste composites. The problem of using styrene is that a large dose of radiation is necessary to induce polymerization. However, a mixture of acrylonitrile (40%) and styrene (60%) requires a dose similar to MMA for 100 percent conversion (see Table 10 of Chapter 4). Free radical initiators, such as carbon tetrachloride, can also be used to reduce the dose required (7,15,37,40,82,83).

The polymerization of vinyl monomers can be achieved by thermal catalytical methods as well as radiation induced. Since the radiation source will be a major cost in the proposed recycling method, the thermal catalytic method may prove to be a more acceptable way to polymerize the monomer. A good discussion of the factors to be considered in this type of process is given in reference (82), page 15. Other modifications of the process which could be investigated include mixing the shredded wastes and monomer prior

to compaction, irradiating under pressure and using different types of ionizing radiation.

Some of the physical properties of the composites have been experimentally determined (tensile and compressive strength, resistance to indentation and water absorption), but there are many more tests which could be carried out, giving an even better comparison of the composites to other materials. As mentioned in Chapter 6, one possible application of the solid waste-polymer combination is flooring materials. One particular property that would be important to this type of material is resistance to abrasion. A brief discussion on the measurement of this property is given in Appendix A, section A.3. It is suggested that a method of quantitatively measuring the abrasion resistance of the composites be developed in such a way that the "wearability" of the composites can be compared with other flooring materials.

In addition to the quantitative measurement, it is recommended that several samples of the solid wastes-polymer composites be made using different wastes, compaction pressures, irradiation atmospheres, monomers, etc. Pieces of these samples, along with commercial flooring, could then be installed in heavy traffic areas (for example, in the lobby of the library or student union or in the halls of other buildings) and a qualitative comparison made.

One other important property to flooring and other building materials is flame resistance. There are a host of flame-retardant treatments which can increase the flame resistance of the composite. It was reported in section 5.2b that the solid waste-composite samples easily ignited and continued to burn much like the pure polymer (PMMA). There are several flame-retardant additives available (85,95) which should be tried to see if they can be effectively used in the proposed composite process. These additives could possibly be dissolved in the monomer prior to its being mixed with the solid waste, which should produce a flame-resistant composite after irradiation.

NOMENCLATURE

A^*	= any molecule in an electronically excited state
A^+	= positive charged ion
$B\cdot$	= organic and inorganic free radicals
B, C	= molecular products
BzP	= benzoyl peroxide
e^-	= electron
F	= fragment of a molecule
F_i^+, F_j^-	= ionic charged molecules
$F_i\cdot, F_j\cdot$	= free radicals
M	= monomer molecule
MMA	= methyl methacrylate
PMMA	= poly(methyl methacrylate)
$P_m, P_n,$ and P_{n+m}	= "dead" polymers
Q	= binding energy of an electron
R	= any alkyl group
R'	= any alkyl group
$R\cdot$	= primary radical
RI	= radiation induced polymerization
$RM_n\cdot$	= a growing polymer chain
TC	= thermal catalytic polymerization
Tg	= glass transition temperature

ACKNOWLEDGMENTS

I would like to thank Dr. L. T. Fan, the originator of this project, for his counseling, inspiration and assistance throughout the duration of this work along with my major advisor, Dr. D. G. Retzloff.

I would like to thank Dr. J. F. Merklin of the Nuclear Engineering Department for his assistance and advice on the radiation chemistry aspects of this work and for his serving on my committee. I would also like to thank those others on the Nuclear Engineering staff who made possible my using the Gamma-cell 220.

I would like to express my appreciation to Mr. C. L. Nelson of the Industrial Engineering Department for his help in constructing some of the experimental equipment used in this work and to Mr. N. M. Johnston of the Applied Mechanics Department who assisted in developing and conducting the testing procedures used to determine the strength properties of the composites.

I would like to thank the Chemical Engineering Department for giving me financial assistance for the past two years in the form of a Graduate Research Assistantship and for the money it provided for the equipment and supplies used in the experimental work of this study.

Most of all I would like to thank my dear wife, Betty, whose patience, unwavering confidence in me, and expert typing made possible meeting all the deadlines and the completion of this work.

REFERENCES

- (1) "A National Timber Shortage by the Year 2000," Olin Magazine, No. 1, Jan. 1971.
- (2) "A Potpourri of Information Related to Disposal of Plastics Wastes," Chementator, Chem. Engr., June 28, 1971, p. 38.
- (3) Abraham, J. H., Jr., "Utilization of Waste Container Glass," Waste Age, July/Aug., 1970, p. 9.
- (4) Appell, H. R., Wender, I., Miller, R. D., "Conversion of Urban Refuse to Oil," Bureau of Mines, Solid Waste Program, Dept. of the Interior, Tech. Progress Report No. 25, May 1970.
- (5) "Applying Technology to Unmet Needs - Report on the Solid-Waste Problem," Nat'l. Comm. on Techn., Autom., and Econ. Progress, Appendix V. 5. Washington, U. S. Government Printing Office, Feb. 1966.
- (6) "Ash in Road Building," Ash at Work, II(3), 1 (1970).
- (7) Ballantine, D. S., "Use of Gamma Radiation to Produce Wood Plastic Combination," Technical Progress Review Isotopes and Radiation Technology, 2(1), 138 (1963).
- (8) Bergstrom, D. N., "Economics of Secondary Fiber Usage," Tappi, 51(4), 76A-77A (1968).
- (9) Black, R. J., et al., "The National Solid Wastes Survey - An Interim Report," Presented at 1968 Annual Meeting of the Institute for Solid Wastes of the Am. Public Works Assoc., Oct. 24, 1968.
- (10) "Blending Technology and Environment," Environ. Sci. Technol. 4(12), 1107 (1970).
- (11) Bliss, C. W., Fan, L. T., Eckhoff, N. D., "Enhancing the Properties of Indigenous Kansas Woods by Using Gamma-Ray Polymerization," Trans. Kansas Acad. Sci., 71(1), 20 (1968).
- (12) Boettcher, A. R., "Air Classification for Reclamation of Solid Wastes," Solid Waste Tech., Stanford Res. Inst., So. Calif. Lab., performed under U.S. Public Health Service Contract PH 86-68-157.
- (13) "Bureau Attacks Nation's Solid Waste," Environ. Sci. Technol., 3, 705 (1969).

- (14) Bynum, D. , Jr. , "A Partial Solution for the Solid Waste Problem," presented to Texas Section ASCE, Highway Techn. Group, May 1, 1970.
- (15) Chapiro, A. , Radiation Chemistry of Polymeric Systems, Interscience Pub. , 1962, p. 18-34, 129-131, 175-188.
- (16) "Chief of New Environmental Protection Agency Discusses Federal Role in Pollution Control," Waste Age, Jan./Feb. , 1971, p. 5.
- (17) "Converting Solid Wastes to Electricity," Environ. Sci. Technol. 4(8), 631 (1970).
- (18) Detrick, C. A. , "Exploratory Study of Radiation Induced Graft Polymerization of Methyl Methacrylate in Paper," M. S. Thesis, Univ. of Virginia (1968).
- (19) Detrick, C. A. , Kelly, J. L. , "Effects of Certain Factors on the Radiation-Induced Polymerization of Methyl Methacrylate," Ind. Eng. Chem. , 9(2), 191 (1970).
- (20) Eastlund, B. J. , Gough, W. C. , "The Fusion Torch - Closing the Cycle from Use to Reuse," USAEC, Div. of Res. , May 15, 1969.
- (21) Engdahl, R. B. , "Solid Waste Processing," BSWM Report (SW-4C), U. S. Dept. HEW, (1969).
- (22) Feldmann, H. F. , "Pipeline Gas From Solid Wastes," Presented at 69th Nat'l. Meeting of A.I.Ch.E. , Cincinnati, Ohio, May 1971.
- (23) "Fly Ash Utilization Climbing Steadily," Environ. Sci. Technol. , 4(3), 187 (1970).
- (24) "Forest Products Lab Recycle Municipal Trash for Fiber Products," Forest Products J. , 20(8), 11 (1970).
- (25) Forsberg, F. J. , "A Total Environmental View of Air, Water and Land," Waste Age, Sept./Oct. , 1970, p. 32.
- (26) Freed, V. H. , Groner, R. R. , Barbour, J. F. , "The Chemical Transformation of Solid Wastes," BSWM Res. Grant EC-00242, Presented at A.I.Ch.E. Meeting, Houston, Texas, Feb./Mar. , 1971.
- (27) Golding, B. , Polymers and Resins, Van Nostrand, Princeton, N. J. (1959).

- (28) Grinstead, R. R. , "No Desposit, No Return," Environment, 11(9) , 17 (1969).
- (29) Grinstead, R. R. , "The New Resource," Environment, 12(10) , 2 (1970).
- (30) Hallam, C. G. R. , "How Sensible is Plastics in Building? Innovation Through Industrialized Building," Plastics and Polymers, April, 1971, p. 114.
- (31) Harmer, D. E. , Ballantine, D. S. , "Radiation Processing," Chem. Eng. , April 19, 1971, p. 98.
- (32) Harmer, D. E. , Ballantine, D. S. , "Applying Radiation to Chemical Processing," Chem. Eng. , May 3, 1971, p. 91.
- (33) Herbert, W. , Flower, W. A. , "Waste Processing Complex Emphasizes Recycling," Public Works, June, 1971, p. 78.
- (34) Heylin, M. , "Plastics in Construction," Chem. Eng. News, March 29, 1971, p. 16.
- (35) Heylin, M. , "Reinforced Plastics," Chem. Eng. News, Feb. 1, 1971, p. 14.
- (36) Hickman, H. L. , Jr. , "Characteristics of Municipal Solid Wastes," Scrap Age, 26(2) , 305, Feb. , 1969.
- (37) Hills, P. R. , Barrett, R. L. , Pateman, R. J. , (United Kingdom Atomic Energy Authority, Wantage), 23-3, UNLTD Dist. , May, 1969.
- (38) Kehl, G. L. , Principles of Metallographic Laboratory Practice, Metallurgy and Metallurgical Engineering Series, McGraw Hill, 3rd ed. , 1949, p. 229.
- (39) Kennedy, S. C. , "The Disposal of Solid Wastes," J. Environmental Health, 31(2) , 149 (1968).
- (40) Kent, J. A. , Winston, A. , Boyle, Wm. , "Preparation of Wood-Plastic Combination Using Gamma-Radiation to Induce Polymerization: Effects of Gamma-Radiation on Wood," Eng. Exp. Station, W. Vir. Univ. , March, 1963.
- (41) Lawson, R. , "Management of Industrial Solid Wastes in Municipal Operations," Waste Age, Mar./April, 1970, p. 4.

- (42) Leibman, J. C., D. H. Marks, "Mathematical Analysis of Solid Waste Collection," Public Health Service Publication No. 2104, Washington, U. S. Government Printing Office, 1970, p. 196.
- (43) Leonard, J. W., "Ashes into Aggregate: The Future for Coal Wastes," West Virginia Bulletin, Feb. 1970, p. 28.
- (44) Loeher, R. C., "Pollution Implications of Animal Wastes - A Forward Oriented Review," U. S. Dept. of Interior, Fed. Water Pollution Control. Admin., July, 1968.
- (45) Ludwig, H. F., Black, R. J., "Report on the Solid Waste Problem," ASCE Proc. Paper 5909, J. Sanitary Eng. Div., 94(SA3), 355-70 (1968).
- (46) Mallan, G. M., "A Total Recycling Process for Municipal Solid Wastes," Presented at 161st ACS Nat'l. Meeting of the Div. of Ind. Eng. Chem., Los Angeles, Calif., March 1971.
- (47) Malvey, J. F., "Paper Waste Salvage Provides Profit," Plant Engineer, May 28, 1970, p. 50.
- (48) Miner, J. R., Baumann, E. R., Willrich, T. L., Hazen, T. E., "Pollution Control - Feedlot Operations," J. WPCF, March, 1970, p. 391.
- (49) Miner, D. F., Seastone, J. B., Handbook of Engineering Materials, Wiley Engineering Handbook Series, 1st ed., John Wiley and Sons, 1955, p. 3-17.
- (50) Morse, N., Roth, E. W., "Systems Analysis of Regional Solid Waste Handling," BSWM Report SW-156, U. S. Dept. HEW, Pub. Health Ser., (1970).
- (51) Newell, E. L. Jr., "The Influence of Rodents in Solid Waste Practices," Waste Age, Nov./Dec., 1970, p. 2.
- (52) O'Donnell, J. H., Sangster, D. F., Principles of Radiation Chemistry, Edward Arnold Pub. Ltd., London, 1970, p. 119.
- (53) "One System Treats Sewage Solid Wastes," Chem. Eng. News, March 23, 1970, p. 44-5.
- (54) "Papermakers Study Recycling," Chem. Eng., Dec. 14, 1970, p. 84.
- (55) "Plants Burn Garbage, Produce Steam," Environ. Sci. & Technol. 5(3), 207 (1971).

- (56) "Plastics Industry Ponders Its Recycling Problems," Chem. Eng., June 14, 1971, p. 56.
- (57) "Policies for Solid Waste Management," Ad Hoc Committee on Solid Waste Management, BSWM, SW-11C (1970).
- (58) "Polymers: Year of the Composite," Chem. and Eng. News, April 6, 1970, p. 15.
- (59) Potts, J. E., "Continuous Pyrolysis of Plastic Wastes," Presented at Nat'l. Industrial Solid Waste Management Conference, Houston, Texas, March, 1970.
- (60) Potts, J. E., "Plastic Wastes Yield to Pyrolysis," Environ. Sci. and Technol., 4(6), 473 (1970).
- (61) Prescott, J. M., "Composting Plant Converts Refuse into Organic Soil Conditioner," Chem. Engr., Nov. 6, 1967, p. 232.
- (62) Prescott, J. H., Browning, J. E., "Solid Waste Schemes Sifted," Chem. Engr., May 18, 1970, p. 80.
- (63) "Reclaiming Wastes for Profit," Environ. Sci. and Technol., 4(9), 729, (1970).
- (64) "Recycling Resources for Environmental Management," Nat'l. Assoc. of Secondary Materials Industry Inc., 7th printing, Aug., 1970.
- (65) "Refuse Can Yield Profits, Waste Technologists Say," Chem. Eng. News, April 6, 1970, p. 38.
- (66) "Reinforced Plastics Gain Ground Abroad," Chem. Eng. News, Feb. 17, 1970.
- (67) Rosen, B. H., Evans, R. G., Carabelli, P., Zaborowski, R. B., "Economic Evaluation of a Commercial Size Refuse Pyrolysis Plant," Cities Service Oil Co., March, 1970.
- (68) Senturia, S. D., Winkles, F., Wilson, D. G., Lewis, K. S., Hibberd, H., "New Sensors for the Automatic Sorting of Municipal Solid Waste," Presented at 69th Nat'l. Meeting of A.I.Ch.E., Cincinnati, Ohio, May, 1971.
- (69) Shell, G. L., Boyd, S. L., "Composting Dewatered Sewage Sludge," BSWM, U. S. Dept. HEW (1969).

- (70) Shuster, W. W. , "Production of Organic Compounds by Partial Combustion and Pyrolysis of Solid Waste Materials," Presented at Nat'l. Industrial Solid Wastes Management Conference, Houston, Texas, March, 1970.
- (71) "Solid Wastes," Environ. Sci. and Technol. , 4(5) , 384 (1970).
- (72) "Solid Waste Disposal," Chem. Engr. Deskbook, June 21 , 1971 , p. 155.
- (73) "Solid Waste Handling in Metropolitan Areas," U. S. Dept. HEW, Public Health Service Publication No. 1554, Feb. , 1964, p. 5.
- (74) "Solid Waste Management," Ad Hoc Group for Office of Science and Technology, Executive Office of the President, U.S. Gov't. Printing Office, May, 1969.
- (75) "Solid Waste: New Controls Raise Costs," Chem. Week, June 17, 1970, p. 87.
- (76) "Solid Wastes: Recycling Plastic Scraps," Chem. Eng. News, May 31, 1971, p. 7.
- (77) Solid Waste Report, Dec. 28, 1970, p. 44.
- (78) Solid Waste Report, Feb. 8, 1971, p. 17.
- (79) "Specialties; Floors Get Cobalt Cure," Chem. Week, July 14, 1971, p. 37.
- (80) Spinks, J. W. T. , Woods, R. J. , An Introduction to Radiation Chemistry, John Wiley & Sons, Inc. , 1964.
- (81) Srinivasan, V. R. , Han, Y. W. , "Isolation and Utilization of Cellulose Decomposing Bacteria," Waste Conversion for Profit, Proceedings 31st Annual Conference, Chemurgical Council, N.Y. , Oct. , 1969.
- (82) Steinberg, M. , et al. , "Concrete-Polymer Materials - First Topical Report," BNL 50134 (T-509) and USBR Gen. Rep. 41 , Dec. , 1968.
- (83) Steinberg, M. , et al. , "Concrete-Polymer Materials - Second Topical Report," BNL 50218 (T-560) and REC OCE 70-1 , Dec. , 1969.
- (84) Stephenson, J. W. , "Incineration Today and Tomorrow," Waste Age, May, 1970, p. 2.

- (85) Syska, A. D. , "Exploratory Investigation of Fire-Retardant Treatment for Particle Board," USDA Forest Service Res. Note FPL-0201, Aug. , 1969.
- (86) Thadani, N. , "The Analysis of Solid Waste Collection System," Presented at 69th Nat'l. Meeting of A.I.Ch.E. , Cincinnati, Ohio, May, 1971, p. 2.
- (87) "Tires: Disposal Problem Solved," Chem. Eng. News, June 8, 1970, p. 12.
- (88) "Turning Waste Into Feed," Chem. Week, Aug. 26, 1970, p. 24.
- (89) Vaughn, R. D. , "Reuse of Solid Wastes: A Major Solution to a Major National Problem," Waste Age, April, 1970, p. 10.
- (90) "The Garbage Block: A New Building Material," Mech. Eng. , Dec. , 1969, p. 19.
- (91) "Waste Recovery: Big Business in the 70's," Chem. Eng. News, Mar. 2, 1970, p. 14.
- (92) Weatherwax, R. E. , et al. , "A Means of Determining the Hardness of Wood and Modified Wood Over a Broad Specific Gravity Range," ASTM Bull. 153-84-89 (1948).
- (93) Williams, W. C. , "Use it/Reuse it! Political, Economic Pressures Brighten Future for Wastes," Pulp & Paper, Sept. , 1970, p. 61.
- (94) Wilson, D. G. , "Technology and the Solid Waste Problem," Dept. of Mech. Eng. , MIT, (1968).
- (95) Yamazaki, S. , "Flame Retardance of Plastics," Sekiyu to Sekiyu Kagaku 14, No. 5 (1970), Japan (English Internal. Chem. Eng. 11(2), 367 (1971)).

APPENDIX A

The following appendix describes the methods used to test the physical properties of the composites described in section 5.4.

A.1 Tensile Strength Testing

Tensile strength is one of the most commonly measured physical properties. It may be defined as the stress necessary to stretch a strip of the material being tested to its breaking point. The value representing this property is expressed in pounds per square inch of original cross-sectional area.

The actual results obtained depend upon many factors. In plastics, the tensile strength may be enhanced by incorporating relatively large amounts of filler with small amounts of plasticizer. The nature of both the filler and the plasticizer will influence the properties, and the optimum amounts of filler and plasticizer incorporated for any particular use must be determined experimentally.

Tensile strength values also may be altered by physical properties of the compounded plastic. The milling, molding, casting and laminating, and processing after fabrication may alter tensile strength. For example the strength of extruded synthetic fibers may be increased substantially by stretching or "cold drawing".

Chemical considerations, as average chain length, degree of branching or cross-linking, and the nature of chemical groups present will also affect the tensile strength. No general rule may be stated other than that the tensile strength increases with the average molecular weight, finally reaching a maximum, leveling off, then decreasing slightly. In the case of linear polymers, the tensile strengths are high because the kinked or curled macromolecular chains can stretch out and straighten. Linear molecules may also slip past each other slightly; thus, during the stretching operation, the groups responsible for secondary valence forces may become aligned and increase the

tensile strength. If a high degree of cross-linking exists in a polymeric structure, the material cannot be stretched to any extent, but the tensile strength is generally high. For example, phenol-formaldehyde resin has a high tensile strength but low elongation.

The tensile strength of the composites described in section 6.6 was determined in the following manner. A piece of the composite was machined into a cylindrical form approximately 3 in. long and 0.75 in. in diameter. The diameter of the middle of the cylinder was reduced to 0.5 in. in diameter for a length of approximately 1 in. For an idea of how the final test piece was shaped see Fig. 13 of section 5.5a.

The cylinder was made in such a way that when the pulling force was applied it was in a direction parallel to the direction in which the paper was compressed. The test sample was then placed in the jaws of a Riehler Tensile Tester (Model FS-20, Serial No. RA-26967) made by the Riehler Testing Machines, Division of Ametek Corp., East Moline, Ill. These "V" shaped jaws had ridges machined into them so that they gripped the test sample while the pulling force was applied. The pulling force was applied at a rate of 2000 psi/min. and was read on a large dial which showed the total load being applied. At the breaking point one of the needles on the dial remained at the maximum load applied while the other needle returned to the 0 point. The maximum tensile strength of the sample was then calculated by dividing the maximum load applied by the cross-sectional area of the reduced part of the test sample.

Another test sample was made from the same composite material and its tensile strength was determined in the same manner as described above except that the cylinder was made in such a way that when the pulling force was applied it was in a direction perpendicular to the direction in which the paper was compressed. Thus the tensile strength of the composite has been found in the directions both parallel and perpendicular to the direction in which the paper was compressed. The summary of the results found in this testing are summarized in Table 23.

TABLE 23. RESULTS OF TENSION TESTS

Sample No.	Reduced Diameter (in.)	Cross-sectional Area (sq. in.)	Load at Yield (lbs.)	Tensile Strength (psi)
I parallel ^a	.590	.273	59.2	216
I perpendicular ^b	.504	.199	444.0	2,228
II parallel ^a	.631	.313	98.6	315
II perpendicular ^b	.523	.215	1,384.0	6,442
III parallel ^a	.626	.308	44.0	190
III perpendicular ^b	.512	.206	1,150.0	5,585
IV parallel ^a	.618	.300	41.4	138
IV perpendicular ^b	.502	.198	709.0	3,592
V parallel ^a	.632	.314	86.6	276
V perpendicular ^b	.501	.197	1,390.0	7,062
VI parallel ^a	.616	.298	24.6	82.5
VI perpendicular ^b	.502	.198	572.0	2,890
VII parallel ^a	.630	.312	66.0	211
VII perpendicular ^b	.520	.212	910.0	4,293
10 (PMMA, RI, N ₂) ^c	.536	.226	2,375.0	10,590
11A (PMMA, RI, Air) ^d	.516	.209	>1,475.0*	>7,123
100 (PMMA, TC) ^e	.502	.198	1,225.0	6,189

^aDirection of pull is parallel to the direction in which the paper was compressed.

^bDirection of pull is perpendicular to the direction in which the paper was compressed.

^cMade by radiation induced polymerization in a nitrogen atmosphere and at an absorbed dose of 8.7×10^5 rads.

^dMade by radiation induced polymerization in an air atmosphere at an absorbed dose of 8.7×10^5 rads.

^eMade by thermal-catalytic polymerization.

*The sample did not break at the reduced diameter but broke where held by jaws; therefore the strength is probably greater than what was found.

A.2 Compressive Strength Testing

This property is allied to the tensile, but it is determined by compression rather than by stretching. The compressive strength value is the compression load in pounds at the breaking point divided by the cross-sectional area of resisting surface.

In this study, the materials to be tested were machined into cylinders .75 in. in diameter and 1.5 in. long. A Southwark-Emery Compression Tester (Serial No. 57400) made by the Baldwin-Southwark Corp., Philadelphia, Pa., was used to determine the compression strength of the sample.

The sample was placed on the machine and the load was applied at a rate of 500 lbs. per minute until the yield point was reached. The load at yield point (the load at which the sample failed) was read from one of two gages which read 0-10,000 lbs. (25 lbs/div) and 0-75,000 lbs. (100 lbs/div) respectively. To find the compression strength, in pounds per square inch, the total load at yield point was divided by the cross-sectional area of the test sample. Most samples were 0.75 in. in diameter and 1.50 in. long, however some samples were smaller. The important thing is to have the samples at least twice as long as its diameter to eliminate end effects.

The results of the compression tests are given in Table 24.

A.3 Hardness Testing

Hardness may be divided into two types: resistance to indentation and resistance to abrasion. Both vary according to the ease with which the particles of solid material can be displaced. Scratching, scarring or wearing by abrasion indicate that fine portions of the composite structure are being displaced. In practice, the effects abrasion or poor hardness are often expressed in terms of wearing quality, weathering, and permanence of gloss. The hardness value can be altered markedly by compounding and service conditions.

If hardness is considered as resistance to penetration, the resinous bodies of relatively low molecular weight and substances of the phenol-formaldehyde or urea-formaldehyde type are particularly satisfactory. If, on

TABLE 24. RESULTS OF COMPRESSION TESTS

Sample No.	Diameter (in.)	Cross-sectional Area (dia.)	Load at Yield (lbs.)	Compression Strength (psi)
I parallel ^a	.759	.452	7,120	15,736
I perpendicular ^b	.761	.455	2,955	6,497
II parallel ^a	.759	.452	11,900	26,300
II perpendicular ^b	.710	.396	4,560	11,504
III parallel ^a	.726	.414	10,050	24,277
III perpendicular ^b	.759	.452	5,410	11,957
IV parallel ^a	.763	.458	8,960	19,579
IV perpendicular ^b	.702	.387	2,820	7,286
V parallel ^a	.760	.454	13,000	28,657
V perpendicular ^b	.745	.436	5,600	12,847
VI parallel ^a	.750	.442	4,230	9,575
VI perpendicular ^b	.758	.451	4,410	9,773
VII parallel ^a	.761	.455	9,300	20,447
VII perpendicular ^b	.748	.439	4,500	10,240
12 (PMMA, RI, N ₂) ^c	.549	.236	4,180	17,676
10A (PMMA, RI, Air) ^d	.550	.238	4,120	17,321
100 (PMMA, TC) ^e	.707	.392	5,980	15,240
Wood (Douglas fir) parallel ^f	.688	.372	2,960	7,962
Wood (Douglas fir) perpendicular ^g	.687	.771	400	1,029

^aDirection of force parallel to the direction in which the paper was compressed.

^bDirection of force perpendicular to the direction in which the paper was compressed.

^cMade by radiation induced polymerization in an atmosphere of nitrogen at an absorbed dose of 8.7×10^5 rads.

^dMade by radiation induced polymerization in an atmosphere of air at an absorbed dose of 8.7×10^5 rads.

^eMade by thermal catalytic polymerization.

^fForce applied parallel to the grain of the wood.

^gForce applied perpendicular to the grain of the wood.

the other hand, hardness is thought of as resistance to scratching, the same bodies of low molecular weight are considerably poorer than those of sufficient chain length and resiliency (called elastomers). An increase in the length of the chain and an increase in the amount of crosslinkage cause an increase in this type of hardness.

According to reference (27) there are four common methods of measuring resistance to indentation. They are:

1. Shore hardness. This is an arbitrary value obtained by a gauge measurement of the resistance offered by the surface to penetration by a needle.
2. Diamond pyramid hardness. This is a value obtained by dividing the load applied to a square-based pyramidal diamond indenter by the surface area of the impression.
3. Brinell hardness. This value is obtained from the value of the force applied in pressing a standard steel ball into the surface of the material being tested, the area of the indentation, and the diameter of the ball.
4. Rockwell hardness. This value depends upon the degree of penetration of steel balls of various sizes when pressed upon the surface of the material undergoing test. Its value is obtained from the increase in depth of impression as the load is increased from a fixed minimum value to a higher value and then returned to the minimum value.

Two methods of measuring resistance to abrasion (mar resistance) are as follows (27):

1. Abraded spots are made by dropping a specific amount of abrasive (carborundum) through a tube of fixed length onto the sample which is held at an angle of 45° to the path of the abrasive. The gloss of the abraded spot is compared to the original gloss by means of a gloss meter.
2. Taber abrader. The sample is mounted on a turntable revolving at a constant rate. Abrading is done by an abrasive wheel, turning at a different fixed rate. The amount of abrasion is then determined by visual or optical means or by weight-loss measurement after a specified number of revolutions.

Abrasion resistance, brittleness, and the effects of heat play important parts in determining the particular machining operations to be used in the fabrication of polymeric substances.

A.3a Resistance to indentation: For a preliminary investigation into the hardness of the composites, it was decided that only its resistance to indentation would be measured. A Rockwell Hardness Test with certain modifications provided a method of determining the relative resistance to indentation of the composite and other materials. The method is similar to the ASTM test D143-52, also discussed in ref. (92).

The Rockwell Hardness Test is a method whereby the hardness of material can be determined by a "differential depth" measurement test. It consists of measuring the increment of depth of some kind of penetrator that is forced into the sample by a primary and secondary load. This "differential-depth" measurement method is attractive because errors due to mechanical defects of the system, (such as back lash) were eliminated as well as errors resulting from slight surface imperfections and varying qualities of contact between penetrator and surface of the specimen under test.

Each Rockwell Hardness Tester is equipped with a hardness indicating dial located directly above the shaft to which the indenter is attached. By means of a linkage system, any vertical motion of the penetrator is translated in terms of rotational motion to the large pointer of the dial.

The dial face is unscribed with 100 equal division marks, each division representing one point on the Rockwell hardness scales and an equivalent vertical motion of the indenter of .002 mm. Two sets of numerals are indicated on the dial, one set printed in red, the other in black. The red numerals are used for the standard B-scale readings, and the black for the standard C-scale readings.

The scale of the dial, with respect to motion of the pointer, is reversed so that a shallow impression when found by the indenter will indicate a high Rockwell hardness number. The dial face scale is free to move about its

normal axis by rotating the bezel of the dial. This movement permits the set point (zero) of the scale to be made coincident with the large dial pointer after the minor load of 10 kg is applied. This allows the hardness number to be read directly from the dial after the test is made. The readings of the dial is an expression of the increment of penetration due to increment in load between the minor and major loads applied.

The small pointer, located in the upper right hand quadrant of the dial face, is used to indicate full application of the minor load. The minor load is applied by means of a calibrated spring, and becomes effective when the specimen surface is brought in contact with the indenter. As the specimen is further elevated by means of the elevating screw, the indenter is forced into the specimen surface and the total load of 10 kg is applied when the small pointer becomes coincident with the red dot index mark.

For a detailed description on the principles of operation see reference (38).

The surface of the sample to be tested should be as free as possible from surface imperfections. Surface irregularities of any kind will offer unequal support to the penetrator, and thus the hardness data obtained under such conditions will be inaccurate. These surface imperfections can also be created by the hardness test itself. Therefore if a sample is to be tested more than once on the same surface, the area to be tested should be at least two diameters away from a previous penetration mark. For example, if a hardness test leaves a dent with a diameter of 1 mm, then the circumference of the next penetration dent should be at least 2 mm away from the circumference of the first dent.

The hardness readings are influenced not only the hardness of the material at the point of penetration, but also by the hardness of the material under the impression. Consequently, if a soft or hard layer is located beneath the point tested, the hardness reading will be affected. It has been found that the material tested should be at least 10 times as thick as the depth of the

penetration. For example, if in testing a material, a penetration of 0.10 mm is obtained, the sample should be at least 1.0 mm thick in order for the results to be accurate.

A Rockwell Hardness Tester made by the Wilson Mechanical Instruments Co., (N.Y., N.Y.) was used in this study. It was located in the Forge Shop classroom of the Industrial Engineering Building at K.S.U. The major load of the Tester was adjusted to 60 kg and a 1/2 in. (.491") diameter steel ball was used as an indenter. A large diameter ball was required as smaller ones penetrated the composite to too much of a depth.

The sample to be tested was placed on the plate under the steel ball ram. The "star" elevating screw is rotated by means of a capstan wheel until the sample came in contact with the steel ball. The elevating screw is rotated clockwise until the small needle on the dial was pointing at the small red dot. This gave a minor load of 10 kg, zeroing the small needle to the red dot on each sample gave the same minor load each time. Once the small needle was pointing at the red dot, the scale was zeroed by turning the face of the dial until the large needle was over the zero on the red scale (B scale). The major load lever was then tripped applying the major load to the surface of the sample via the steel ball. The number of counter clockwise revolutions made by the large needle while the major load was being applied was counted. Once the movement of the needle was almost stopped (approximately 10 sec. after the lever had been tripped), the major load was then released by turning back the lever to its original position. The large needle then moved in a clockwise direction. If the needle moved past the zero mark, 1 was subtracted from the number of counterclockwise revolutions and the net number of counterclockwise revolutions was recorded, along with the reading on the dial at which the needle finally stopped.

Since wood has been chosen as a comparison, it would be good to find its hardness and compare it to the hardness of the composite material. The trouble is that wood is much, much softer than the composite material. That

is, when the major load was being applied, the needle rotated past the zero mark twice, indicating a greater degree of penetration by the steel ball. The needle, however, only rotated past the zero mark once (and maybe not at all) when the major load was being applied. When the major load was removed the needle sometimes rotated past the zero point and sometimes it did not. Therefore in order to get value readings for all the materials tested, the following technique was used to get the relative hardness values.

The net number of counterclockwise revolutions (as mentioned above) is (the number of times the needle passed zero while making its counterclockwise movement during the application of the major load) minus (the number of times the needle passed zero while making its clockwise movement after the major load was removed).

For wood (the softest material tested) this net number of counterclockwise revolutions was one but for the composite material and the pure PMMA it was zero. Thus to have a scale to compare the wood to the composite and pure PMMA, the hardness value was determined by the following equation.

$$\text{Hardness Value} = (100 - \frac{\text{net number of counter-}}{\text{clockwise revolutions}}) \times 100 + \frac{\text{Final Reading of}}{\text{Needle on the B}} \\ \text{(red) Scale}$$

The reason for using this scale is to get some relative measurement of the hardness without getting negative hardness "values". Choosing to add the value of 100 for a net counterclockwise revolution was done because the hardness value is a reversed measurement of the increment of linear penetration. That is in the case of wood, the depth of penetration is $(200 - (\text{the dial reading})) \times .002 \text{ mm}$; in the case of the composite material and pure PMMA, the depth is $(100 - (\text{the dial reading})) \times .002 \text{ mm}$. Thus one net revolution of the needle corresponds to $100 \times .002 \text{ mm}$ of linear penetration. For example if two materials gave the same dial reading but in testing the harder material the long needle made one less counterclockwise revolution, the indenter would have made $100 \times .002 \text{ mm}$ less penetration; therefore the harder material would be given a hardness value 100 units higher than the softer material. The results of the hardness tests are given in Table 25.

TABLE 25. RESULTS OF HARDNESS TESTS

Sample No. ^a	Position	Net Number of Counter-clockwise Revolutions	Reading	Hardness Value
I	1	0	74	174
	2	0	82	182
	3	0	51	151
	4	0	69	69
	5	0	69	69
I Average				169
II	1	0	82	182
	2	0	73	173
	3	0	74	174
	4	0	74	174
	5	0	76	176
II Average				175.8
III	1	0	79	179
	2	0	73	173
	3	0	71	171
	4	0	75	175
	5	0	77	177
III Average				175
IV	1	0	59	159
	2	0	37	137
	3	0	31	131
	4	0	52	152
	5	0	50	150
IV Average				145.8
V	1	0	74	174
	2	0	76	176
	3	0	49	149
	4	0	82	182
	5	0	72	172
V Average				170.6
VI	1	0	67	167
	2	0	52	152
	3	0	47	147
	4	0	46	146
	5	1	83	83
	6	0	37	137
	7	1	83	83
VI Average				130.7

TABLE 25. (cont'd)

Sample No.	Position	Net Number of Counter-clockwise Revolutions	Reading	Hardness Value
VII	1	0	76	176
	2	0	73	173
	3	0	67	167
	4	0	78	178
	5	0	74	174
VII Average				173.6
PMMA (RI, Air) ^b	1	0	86	186
	2	0	85	185
	3	0	91	191
Average				187.3
100 PMMA (TC) ^c	1	0	93	193
	2	0	93	193
	3	0	93	193
Average				193
Wood (Douglas fir) parallel ^d	1	1	9.5	9.5
	2	1	40	40
Average				24.8
Wood (Douglas fir) perpendicular ^e	1	1	13	13
	2	1	30	30
Average				21.5

^aIn samples I through VII the force was applied in a direct parallel to the direction in which the paper was compressed.

^bMade by radiation induced polymerization in an atmosphere of air at an absorbed dose of 8.7×10^5 rads.

^cMade by thermal catalytic polymerization.

^dForce applied parallel to the grain of the wood.

^eForce applied perpendicular to the grain of the wood.

A. 4 Water Absorption Tests

The permeability of the composites materials of section 6.6 to water was determined by conducting water absorption tests. These tests were conducted to give some idea of the weatherability of the composites, or at least their reaction to submersion in water. The test samples were submerged in water for an extended period of time and their percent weight increase was determined with respect to time of submersion. Also the samples were qualitatively evaluated on their condition after submersion (i.e., was there a noticeable change in the characteristics of the composite material after long periods of exposure to water).

The procedure followed was similar to that described in section 6.2a except that samples were painted on their sides so that the absorption of water would be in only one direction.

A piece of one of the cylinders 0.75 in. diameter, approximately 1.0 in. long was painted on its sides with a black gytol paint which was impermeable to water. The end of the test piece had been sanded smooth, parallel to one another.

These test samples from each composite made was dipped in water and weighed again. Dipping the sample into the water and blotting it with filter paper was done to find the weight of the sample which just had water absorbed on its surface. The "wet" weight was used as the basis for the percent of weight increase measurements.

After obtaining the "wet" weight, the test samples were placed in glass containers filled with distilled water. These submersions were carried out at room temperature and pressure.

The samples were removed after certain lengths of time, blotted with filter paper, weighed, then placed back into the water. From these weight measurements, the percent increase was found and recorded along with the time at which they were taken.

The temperature of the water remained at 80.0°F during the entire test.

All but one sample was machined and prepared in such a fashion that the absorption of water would be in a direction parallel to the direction in which the paper was compressed. The remaining sample was prepared such that the absorption of water would be in a direction perpendicular to the direction in which the paper was compressed. Thus, it could be determined if the absorption of water was different for either case. The results of these tests are given in Table 26.

TABLE 26. RESULTS OF WATER ABSORPTION TESTS

Sample Number	(Dry Weight (gms))	Weight Increase (Wet Weight (gms)) (gms)	% Weight Increase	Time in Hours
II ^a	(7.9149)	(0.0019) ^c	(0.02) ^d	0
	(7.9168)	0.1088	1.37	24.0
		0.2111	2.66	72.0
		1.1552	14.59	384.2
		1.2650	15.98	425.7
III ^a	(7.7318)	(0.0020) ^c	(0.03) ^d	0
	(7.7338)	0.2036	2.63	24.0
		0.5520	7.18	72.0
		1.9111	24.71	384.2
		1.9425	25.12	425.7
IV ^a	(7.0515)	(0.0025) ^c	(0.04) ^d	0
	(7.0540)	0.2000	2.84	24.0
		0.5152	7.30	72.0
		2.0700	29.35	384.2
		2.1193	30.04	425.7
V ^a	(7.9695)	(0.0024) ^c	(0.03) ^d	0
	(7.9719)	0.1020	1.28	24.0
		0.3010	3.78	72.0
		1.4422	18.09	384.2
		1.5098	18.94	425.7
V ^b	(6.7614)	(0.0006) ^c	(0.01) ^d	0
	(6.7620)	0.0868	1.28	24.0
		0.3749	5.54	72.0
		1.0604	15.68	384.2
		1.1140	16.47	425.7
VI ^a	(4.9468)	(0.0055) ^c	(0.11) ^d	0
	(4.9533)	0.1139	2.30	24.0
		0.2389	4.82	72.0
		0.7714	15.57	384.2
		0.8147	16.45	425.7
VII ^a	(7.5465)	(0.0045) ^c	(0.06) ^d	0
	(7.5510)	0.4319	5.72	24.0
		1.2934	17.13	72.0
		2.4967	33.06	384.2
		2.5217	33.96	425.7

TABLE 26. (cont'd)

Sample Number		Weight Increase		% Weight Increase	Time in Hours
(Dry Weight (gms))	(Wet Weight (gms))	(gms)			
I ^e	(-----)	(-----)	(---)		0
	(-----)		1.59		32.5
			2.48		66.0
			3.38		131.7
			6.90		405.0

^aThe direction of water absorption was parallel to the direction in which the paper was compressed.

^bThe direction of water absorption was perpendicular to the direction in which the paper was compressed.

^cWeight difference between dry weight and wet weight.

^dPercent increase of wet weight to dry weight.

^eThis sample was not cylindrical in shape but irregular and none of its sides were painted.

RECYCLING OF SOLID WASTES AS SOLID WASTE-POLYMER
COMPOSITES FORMED BY RADIATION INDUCED POLYMERIZATION

by

WAYNE OTIS VANDERPOOL

B. S. , University of Colorado, 1969

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1971

ABSTRACT

From a review of current literature, the requirements met by successful solid wastes recycling methods were formulated. In light of these requirements, a preliminary investigation was carried out on a proposed-recycling method. This method involved the recycling of solid wastes in the form of solid waste-polymer composites. Solid wastes were mixed with a monomer and then the mixture was exposed to gamma radiation, which polymerized the monomer.

Various types of solid wastes were mixed with the monomer methyl methacrylate and upon irradiation all showed good bonding between the wastes and the polymer. Waste paper was shredded, compacted, evacuated, mixed with the monomer and irradiated to produce composites which were tested for tensile and compressive strength, resistance to indentation and water absorption. The parameters investigated in this process were the pressure used to compress the paper and the presence of oxygen in the radiated mixture and their effect on the properties of the paper-polymer wastes and on the conversion of the monomer to polymer.

Based on the experimental results, the properties of the composites were compared to several common materials and from this comparison, possible uses were projected.

A brief investigation into the market available for such materials led to the conclusion that the proposed recycling method is definitely feasible and the economics of the process will improve with time.