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Distr.
LIMITED

ID/WG.27/9
31 October 1968

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on the Development of the Plastics Industry in Developing Countries

Vienna, Austria, 11 - 15 November 1968

RADIATION PROCESSING IN THE PLASTICS INDUSTRY[1]

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id.68-3790

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I. INTRODUCTION

Radiation processing has been emerging as a production tool in the plastics industry. Its applications involve polymerization, graft co-polymerization, curing and modification of polymers. New products as wood-plastic combinations (WPC) have been manufactured commercially. It is intended to review the current status of radiation processing and its impact in plastic manufacture.

The radiation sources refer to both, radioisotopes and particle accelerators. In the former category, Cobalt-60, which emits electromagnetic radiation, known as gamma rays, is the most commonly used source because of its availability and reliability. Caesium-137 which is obtained from the fission products in nuclear power generation may also be considered as a suitable gamma source.

	Co-60	Cs-137
Half-life, yrs	4.6	30 ± 3
Energy, MeV	1.33,1.17	0.548
Price/Ci, $ (~100,000 Ci)	0.50	0.20 (?)

The radiation from gamma sources possesses deep penetrating power and is therefore suitable for the treatment of thick objects as well as in chemical synthesis. The merits of Cobalt-60 and Cs-137 are (i) low maintenance, (ii) low cost for replenishment and (iii) dependable and reproducible energy output. Their performances have been proven in medical products sterilization, grain irradiation and ethyl bromide synthesis. For the time being, all WPC manufacturers use Cobalt-60 as radiation source.

Accelerators are mainly electron beam accelerators of 0.5-3 MeV. They can provide high dose rate and sufficient scanning speed of electron beams and are particularly suitable for the continuous treatment of thin sheets of plastics, textiles and surface coatings.

The radiation source provides the necessary energy to initiate chemical reaction in a given system, but its selection is very much dependent on the purpose and materials to be treated. The geometry of the source and the objects should be arranged in such a way as to permit uniformity of dose and to suit the characteristic feature in the polymerization.

In comparison to conventional catalyst-initiated polymerization systems, radiation-induced polymerization takes place without the fear of catalyst residues in the polymer. The products may show superior electrical properties and thermal stability. Some polymerization reactions can be initiated with the aid of radiation, while with ordinary catalysts they fail to take place due to the presence of inhibitors. For this reason, radiation processing opens a new horizon in the plastics industry.

For economic considerations, the feasibility of a radiation process should be viewed from the following factors:

1. Cost of source and its installation;
2. Source replacement;
3. Amortization;
4. Installation maintenance;
5. Load factor;
6. Production rate from a given output of energy.

The last factor is directly related to the process. It is known that for one watt of energy the number of kilograms of material produced is equivalent to 0.373×10^{-6} (G) (M), where M refers to the molecular weight of the product, and G is the number of radicals produced by 100 eV of energy. For the production of polymers through chain reactions, a G-value around 10 will be promising. Fortunately, most monomer systems have high G-values to warrant their exploitation in radiation processing.

It should be emphasized that the total dose requirement has a direct bearing to the plant capacity, the higher the required dosage, the lower the plant output and the higher the cost of production. The selection of an optimal dose rate is therefore a problem including both engineering and economic considerations.

II. WOOD-PLASTIC COMBINATIONS

There are three WPC manufacturers in the U.S.A. and one in France, all using methyl methacrylate. In England Joseph Rodgers & Sons has recently planned the marketing of WPC using a mixture of styrene and acrylonitrile.

Company	Year	Product	Use
American Novawood Co.	1966	Cammapar	flooring
Lockheed-Georgia Co.	1966	Lockwood	product evaluation
Nuclear Materials and Equipment Corporation	1968	Perma Grain	flooring
Joseph Rodgers & Sons	1968	Manhattan-??	cutlery handles

The treated wood is superior to the natural wood in the following aspects: static bending; shear hardness; dimensional stability; compressive strength; weatherability; decay resistance and abrasion resistance. In some cases, flame retardency of WPC is a possibility if a proper monomer is selected. The machinability and nailability of WPC, however, is no better than that of natural wood. In comparison to plastics, WPC excels in most mechanical properties, and has a better thermal resistance. Potential applications can be exploited in construction, furniture, and specialities. It has been evaluated by Vitro Engineering Company that the selling price of WPC using MMA is $1.50/bd.ft., and is much higher than the price of ordinary wood ($0.35/bd.ft.).

The cost reduction efforts should be emphasized on the use of lower unit cost monomers, and to reduce monomer content and dosage. The product improvement should be sought through the uniformity of treatment and the relationship between physical properties and the end-uses. Since both homopolymerization and graft polymerization are involved in WPC manufacture, the effect of extend of grafting on the physical properties should also be investigated.

The improvement of the quality of wood through impregnation has led to the development of a broad class of impregnated fibrous materials. Bagasse board, bamboo, and jute have been successfully treated by radiation-induced polymerization with vinyl monomers. The finished products possess good dimensional stability, insect and fungus resistance and reinforced mechanical strength. Such treatment will convert some abundant low-cost fibrous stock into useful construction materials as in prefabricated housing. With the choice of a low cost monomer system, the product can compete with natural wood price-wise. The success of such an attempt will mean a new market of monomer, and for the tropical region inexpensive and readily assembled building material that will resist deformation and natural decay.

The following table shows the operating cost and the plant investment in WPC manufacture.

ESTIMATED PLANT INVESTMENT AND OPERATING COSTS FOR WOOD-PLASTIC COMBINATIONS*

Production: 2,500 lb/hr, 8,000 hr/year operation or 9,000 t/yr

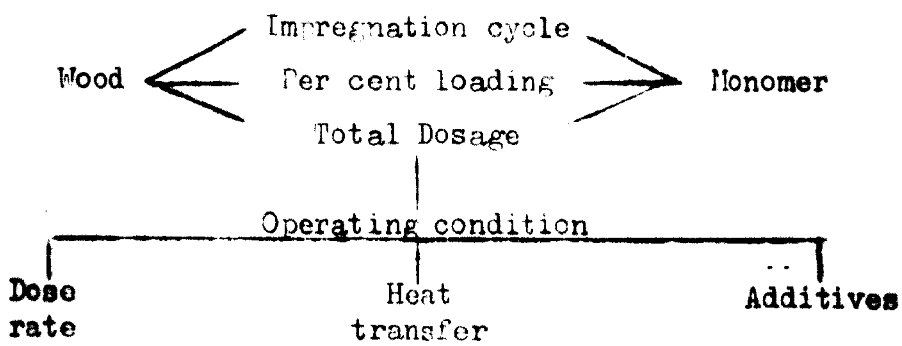
A. Plant Investment	Cost $
Impregnator and Accessories	146,000
Cobalt-60 source, 1 Mc at $0.50/Ci	500,000
Irradiator	127,000
Building and Land	285,000
Plant Utilities	105,000
Engineering and Construction Fees	244,000
Total Fixed Capital	1,407,000
B. Annual Operating Cost	
Depreciation	140,000
Replacement of Source, 12.5% per year	63,000
Direct Labour	110,000
Maintenance, Operating Supplies and Utilities	42,000
Factory Overhead	110,000
General Expenses	140,000
Total Cost	605,000
Cost per ton of product:	$ 67,-

* Based on A. D. Little Inc. and Vitro Engineering Company figures

E. Rotkirch in the Scandinavian Symposium on WPC, Helsinki, May 1968, gave the following estimates:

Plant Capacity, t/yr	Capital Investment, $	Operating Cost, $/ton
10,000	1,310,000	50.2
100,000	5,000,000	18.7

In practice, the manufacturing cost is influenced by the selection of wood species, monomer system and operating conditions. The interaction of factors can be sketched as below:



Even under the same conditions, the variation of throughput with the type of monomer and the related total dosage will effect the production cost significantly as shown in the following table based on a polymer content of 25% in the product:

Monomer	Dosage, Mrad	Relative throughput	Cost per kg of product, $			
			Impregnation	Irradiation	Monomer	Total
Vinyl acetate	0.5	1	0.03	0.03	0.08	0.14
Vinyl chloride	0.6	0.83	0.02	0.03	0.05	0.10
Methyl methacrylate	1.5	0.33	0.03	0.07	0.16	0.26

III. GRAFT COPOLYMERIZATION

WPC is one example where the monomer molecules are linked to cellulose. The grafting technique has been used to improve the properties of textiles and plastic films. Recently the Brookhaven National Laboratory has reported the research on plastic impregnated concrete that has improved compression strength by a factor of 2.4 and reduced permeability by 98%. In general, the grafting can be done by either of the following methods:

1. Irradiation of polymer in the presence of a monomer;
2. Pre-irradiation of polymer alone followed by grafting with a monomer;
3. Irradiation of swollen polymer-monomer systems.

A number of research activities was reported in the use of monomer vapours. Hopefully, vapour-phase copolymerization should ease the control of the extent of grafting, and should be a very nice combination with method (2) from the viewpoint of material handling. However, the technique has not reached the stage for practical applications.

There is a vast number of reports on the radiation grafting of different kinds of plastics with every conceivable monomer. The major effort is to alter the characteristics of the polymer in desired directions. Polyethylene films can be modified to improve scuff resistance, printability, adhesion and permeability. In textiles, grafting improves the soil release and crease resistance of polyester-cotton blends. Using accelerators, Deering Milliken Inc. and Burlington Industries respectively commercialize the treatment of fabrics with suitable vinyl monomers. Other improvements have been sought including washability, dye retention, and antistatic properties.

IV. CURING OF UNSATURATED POLYESTERS

Electron beam curing of styrene-polyester resins has been on the threshold of commercial success. Distinctive advantages over conventional practice are summarized in the following:

1. Instantaneous curing in air at ambient temperature;
2. Simplification of handling and storage of polyester because no catalyst is required;
3. Less floor space required for continuous processing;
4. Continuous coating of polyester on heat-sensitive substrates without damage to the base materials.

Coating equipment is available to treat 4 ft width board at speeds up to 100 linear ft/min. Several major paint companies have produced paint formulations that cure to an excellent finish with a small dose of radiation. The new curing method will open up new fields of polyester paints, which do not require solvent in application. Previously the main objections to the use of polyester paints have been difficult in curing, the limited shelf-life and the assurance of "tack-free" surfaces. Radiation curing will eliminate all these troubles. Another group of coatings based on acrylics has also been developed successfully for marketing.

With powerful accelerators in the range of 1.5-3 MeV, it is possible to cure glass fibre reinforced wet-lay-up laminates, prepregs and even moulding compounds. The radiation-cured materials can compete with hot-press cured materials with regard to mechanical properties as well as to cost. With a total dose of 5 Mrad, the cost based on semi-commercial production is around four cents per kg of the product. However, more engineering effort in the development of accelerators is necessary as to permit the curing of objects with complicated geometrical shapes.

V. MODIFICATION OF POLYMER STRUCTURES

The direct modification of the structure of polymers should be regarded as the earliest commercial application of radiation. The General Electric Company introduced irradiated polyethylene tape more than a decade ago. Cryovac L, a food-wrapping material from W. R. Grace, is produced by irradiation of polyethylene film. A number of companies irradiated polyethylene insulations used in wire and cable coverings. Both Toyo Rayon Company and Sekisui Chemical Company in Japan have succeeded in the manufacture of foamed polyethylene through radiation-induced cross-linking of the polymer in the presence of blowing agent. Some heat shrinkable polyethylene tubing, bags and films are also in production by Sumitomo Company. Irradiated polyethylene shows a higher tensile strength, better resistance to solvent, heat and aging. As an insulating material it is almost immune to stress cracking, which has been a major defect of ordinary polyethylene in wire and cable covering.

It has been revealed that the Union Carbide Corporation has a plan of installing 100,000 curies of cobalt-60 to alter the molecular weight and the viscosity of polyethylene oxide. Another interesting application is shown in the cross-linking of natural rubber latex when it is irradiated with 13 Mrad to form films of excellent mechanical properties.

Despite the fact that excessive irradiation will cause the breakdown or deterioration of polymeric materials, it is safe to quote from the success of irradiated polyethylene that a suitable dosage, in the range of 4-40 Mrad, will favourably modify the properties of polymers. The modification is usually achieved by the post-irradiation of manufactured goods. Radiation energy emitted from accelerators initiates the formation of free radicals and these radicals on recombination lead to cross-linking. Such treatment may introduce some special applications in the plastic industry, particularly in improving the thermal and solvent resistance of thermoplastics.

VI. CONCLUSIONS

In the search of a new technology for the plastics industry, radiation processing has a promising future. From their initial successes in the chemical industry, plastics processing and medical products sterilisation, radiation processing plants are safe and easy to operate. More engineering and technological development programmes are underway in advanced countries to refine the scale-up of processes and to lower the investment cost of new plants.

In the promotion of a sophisticated technology, the situation in developing countries is in general somewhat different from the patterns shown in advanced countries. Some factors are in common, but more pronounced in developing countries. There is a time lapse which is unavoidable from concept to full scale production, and additional time and effort will [illegible] be needed to adapt the technology to local environment in developing countries. It is more critical in the lack of enough well-trained engineers and technical people to carry on the programme when an integrated approach is desirable. A successful project always calls for a broad spectrum of activities from process development to product engineering. Radiation processing can not be an exception and should require more effort to change the fears and doubts in decisions. Even in the U.S.A. it took four years for [illegible] to settle down the controversy and finally to become a new commercial field.

The contributions of radiation processing, in cross-linking of polyethylene, in curing of polyester resins and in impregnated fibrous materials, are within the reach of developing countries. The success of the attempt will depend on the enthusiasm of the countries concerned and on a sound development scheme including training and [illegible]. In view of the limited resources in these countries, the endeavour of international organisations may provide the necessary technical assistance and promote regional co-ordinated effort to facilitate the [illegible]. In concluding the remarks we may outline the ways and means for the development of radiation processing of impregnated fibre board in developing countries as an example:

1. [illegible]

   (a) [illegible]
   (b) [illegible]
   (c) [illegible]
   (d) [illegible]

2. [illegible]

   (i) [illegible]
   (ii) [illegible]
   (iii) [illegible]

[illegible]

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