Radiation processing is now a useful production tool in industry. Every year raw material worth several hundred million dollars is irradiated and converted to newer and better products. This review article is based on a paper presented at Nuclex '69 (Basle, Switzerland, October) on behalf of the Agency by H.C. Yuan, F. Antoni and C.K. Beswick, and summarizes industrial aspects in radiosterilization of medical supplies and polymer processing. Dr. Antoni is now working at the Frédéric Joliot-Curie National Institute for Radiobiology and Radiohygiene, Budapest, Hungary.

Some products for which the wood plastic radiation treatment is suitable. They include sports goods, tool handles, flooring, tool handles and furniture dowelling. Photo: USAEC
The radiation sources referred to in this article are both radioisotopes and particle accelerators. In the former category cobalt-60 is the most commonly used gamma 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. The merits of cobalt-60 and caesium-137 in industrial processing are low maintenance, low cost for replenishment, reproducible energy output, and deep penetration for the treatment of thick objects. Performances of cobalt-60 have been proved in radiosterilization, woodplastics and chemical synthesis.

Accelerators are mainly electron beam accelerators of 0.3-3 MeV. They can provide high dose rates and sufficient scanning speeds of electron beams and are particularly suitable for the continuous treatment of thin sheets of plastics, textiles and surface coatings. The choice of the radiation source is therefore dependent on the purpose and materials to be treated, and it is highly desirable to take into account the uniformity of dose and the characteristics of the process.

Radiosterilization

Modern radiosterilization plants are highly efficient installations for sterilizing disposable articles and many surgical appliances. The sterilization is particularly suitable for articles made from plastics or items of biological origin such as sutures which are difficult to sterilize by thermal or chemical methods. The irradiation of prepacked items in hermetically sealed cartons permits the ready use of the sterilized articles. In fact, radiosterilization has brought the use of disposable syringes to the medical profession.
A particular feature of well-designed irradiators is the extreme safety precautions against any possible accidents. Many sensing devices can detect any abnormalities in ventilation, temperature, power failure and earthquakes, and feed the information to the control console to guarantee safety. Interlock systems are incorporated to avoid accidental exposure to radiation. The automatic conveyor system handles the packages in a manner to ensure uniform irradiation inside the package with a maximum to minimum dose ratio of not more than 1.2.

Plant capacity ranges from 100,000 to 1,500,000 curies of cobalt-60 for the sterilization of 50,000 to 1,000,000 cu.ft. of products. The cost for sterilization is of the order of US $0.20-1.00 per cu.ft. depending upon the volume of products.

With the growing acceptance of radiosterilization the preparation of a Code of Practice was proposed in a Panel on Gamma and Electron Irradiation in Copenhagen, 1964. The Code was drafted in 1966 under the auspices of the International Atomic Energy Agency and discussed in principle in the IAEA's Symposium on Radiosterilization of Medical Products in Budapest, 1967. The proposed code emphasized that the efficiency of radiosterilization is dependent on the number and types of contaminating organisms and also upon the environmental conditions of the facilities. Thus, in practice, the microbiological standards must be met through proper dosimetry control and a comparison of the bacteria count before and after irradiation. The recommended dosage should be considered on the articles to be sterilized, the evidence of contamination of the items, and the margin of safety required in the end-use.

Current practice of radiosterilization has been extended to industrial enzyme preparations and possibly to a few vaccines.

Impregnated Fibrous Materials

Impregnation of wood with monomer followed by irradiation leads to wood-plastic combinations (WPC). A large fraction of the monomer molecules is polymerized in situ to fill the cells of wood. To a small extent grafting copolymerization of the monomer on to cellulose takes place during irradiation and this copolymerization depends very much on the swelling condition of the fibres.

There are four WPC manufacturers in the U.S.A. and one in France, all using methyl methacrylate. In England one firm, has recently planned the marketing of WPC using a mixture of styrene and acrylonitrile. Flooring and cutlery handles are included in the products, but others are being evaluated.

The treated wood is superior to the natural wood in: static bending, shear hardness, dimensional stability, compressive strength, weatherability, decay resistance and abrasion resistance. In some cases, flame retardancy of WPC is a possibility if a proper monomer is selected. The machinability and nailability of WPC, however, is not better than that of natural wood. In comparison to plastics, WPC excels in most mechanical properties, and has a better thermal resistance. Potential applications are in construction, furniture, and specialities. An evaluation has shown that the selling price of WPC using methyl methacrylate is
$1.50/bd.ft, which is much higher than the price of ordinary wood ($0.35/bd.ft.). In practice, the manufacturing cost is influenced by the selection of wood species, monomer system and operating conditions. The interaction of these factors can be shown as below:

![Diagram](image)

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

Cost reduction efforts should be related to the use of lower unit cost monomers, and the reduction of monomer content and dosage. Product improvement should be sought through 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 extent of grafting on the physical properties should also be investigated.

Table I. Variation of processing cost with monomer.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Dosage Mrad</th>
<th>Relative throughput</th>
<th>Cost per kg of product, $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate</td>
<td>0.5</td>
<td>1</td>
<td>0.03 0.03 0.08 0.14</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>0.6</td>
<td>0.83</td>
<td>0.02 0.03 0.05 0.10</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>1.5</td>
<td>0.33</td>
<td>0.03 0.07 0.16 0.26</td>
</tr>
</tbody>
</table>

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 construction materials useful for such purposes as prefabricated housing. With the choice of a low cost monomer system, the product can compete in price with natural wood. The success of such an attempt will mean a new market for monomers; for tropical regions it could result in inexpensive and readily assembled building material that will resist deformation and natural decay.
Stronger concrete

Following the commercial development of WPC a similar impregnation and irradiation technique has been applied to study concrete-polymer materials at Brookhaven National Laboratory. Concrete-polymer combinations containing 6.7% of polymethyl methacrylate have shown excellent mechanical properties and corrosion resistance (see Table II):

Table II. Improvement of concrete polymer combinations

<table>
<thead>
<tr>
<th>Properties</th>
<th>% Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression strength, psi</td>
<td>20255</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>1627</td>
</tr>
<tr>
<td>Modulus of elasticity, psi</td>
<td>6.3×10⁶</td>
</tr>
<tr>
<td>Modulus of rupture, psi</td>
<td>2637</td>
</tr>
<tr>
<td>Freeze-thaw resistance, wt. loss</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

This material will find construction applications in areas where extreme service conditions will be encountered.

Curing paint and coatings

Electron beam curing of unsaturated polyester and acrylics 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 paints because no catalyst is required;
3. Less floor space required for continuous processing;
4. Continuous coating on heat-sensitive substrates without damage to the base materials;
5. Prevention of pollution because monomer release is minimized.

Accelerators in the range of 300 — 500 KeV are used to treat 4 ft wide board at speeds up to 80 linear ft/min. The thickness of coating should not exceed 10 mils.

Several major paint companies have produced paint formulations that cure to an excellent finish with a dose of 6 — 12 Mrad. The new curing method will open up new fields for polyester paints, which do not require solvent in application. Previously the main objections to the use of polyester paints have been difficulty 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. Radiation curing in the future will probably extend to urethanes and epoxies.

Linear accelerator (CIRCE 10) for industrial irradiation. Photo: Compagnie Générale de Télégraphie Sans Fil, France.
With powerful accelerators in the range of 1.5-3 MeV, it is also possible to cure glass fibre reinforced wet-lay-up laminates, prepregs and even molding compounds. The radiation-cured materials can compete with hot-press cured materials in mechanical properties as well as cost. With a total dose of 5 Mrad, the cost based on semi-commercial production is around four cents per kg for the product. However, more engineering effort in the development of accelerators is necessary to permit the curing of objects with complicated geometrical shapes.

New properties for textiles

After a decade of intensive research effort, radiation curing of textiles has reached the stage of commercial production. Radiation energy promotes the grafting of a chosen vinyl monomer to the cellulose in such a manner as to prevent the shrinkage and wrinkling of cotton while still retaining the comfort of natural fibres.

The radiation curing system is based on the addition of multifunctional vinyl monomer to the cellulose. In fact, the whole process takes place in two successive steps and can proceed by either route (a) or (b);

(a) Chemical grafting of the monomer to the cellulose followed by cross-linkage under the influence of ionizing radiation.

(b) Radiation-induced grafting of the vinyl monomer to cellulose followed by acid-catalyzed cross-linkage.

The curing raises the crease recovery angles, both wet and dry, and sets creases permanently. The use of radiation does not bring any significant drop in tensile, tear or abrasion strength of the treated fibres.

Natural cotton can be made more resistant to water after resin finishing and it is possible to facilitate the release of oily stains and to reduce wetting. Since the sorption and permeability of moisture is important to the comfort and wear properties of a textile, it is unnecessary to load the cellulose with excessive polymers that may even cause the disruption of the texture of the fibre. Preferably and also economically a small amount of monomer cross-linked to the fibre will retain the permeability and sorption of moisture or "breathing" properties of cotton. Good resistance to weathering, mildew and rot has been achieved through such a treatment.

It is essential that the resin-finished textile will not irritate human skin, accumulate electrostatic charges and affect dyeability. Thus far methylol acrylamide has been proven to be a versatile monomer in commercial application.

For commercial production electron accelerators can deliver a large dose in the order of several megarads per second and can process fabrics at a speed of 30-40 meters per minute. The accelerator can easily be incorporated in the production lines of textile mills, the cost of its operation being less than one cent per meter of fabrics.

Radiation processing takes place at room temperature, permits immediate start-up and greatly reduces fumes and odours that usually accompany operations at high temperature. Another advantage of working at room temperature is to reduce damage to textiles and fire hazards to a minimum.

Two different routes to durable press fabrics are known. Both processes use an emulsion of methylol acrylamide with the addition of...
zine salt, which helps to swell the cellulose for easier and faster diffusion of monomer molecules into the fibres.

For synthetic fibres, grafting with a suitable monomer system can improve the dyeability and electrostatic behaviour of the fibre. The trend in radiation grafting of different fibres indicates that both surface characteristics and crystallinity of the fibre play a significant role in the formation of grafting polymer. For better results a high frequency of short graft side chains is superior to a low frequency of long side chains and the formation of homopolymers should be avoided as much as possible.

Modification of plastics

The direct modification of the structure of polymers should be regarded as the earliest commercial application of radiation. Crosslinking of thermoplastics is usually achieved by post-irradiation of extruded products. Radiation energy emitted from accelerators initiates the formation of free radicals in the polymers and these radicals on recombination lead to cross-linking which improves the thermal and solvent resistance of the polymer.

An American company introduced irradiated polyethylene tape more than a decade ago. In wire and cable covering, irradiated polyethylene
is almost immune to stress cracking and can be used in continuous service up to 130°C. Insulation properties can also be improved.

The memory effect or heat-shrinkable property of irradiated polyethylene has been applied to the production of Cryovac L. Low or medium density polyethylene is extruded to form tubing, which is squeezed to a flat tape of 20-mils thickness. Irradiation with 500 keV to 2 MeV electrons followed by blowing and stretching gives a film suitable for food-wrapping and other packaging purposes. Heat shrinkable polyethylene tubing and bags with better impact and tensile strength are also entering commercial production.

Polyethylene foam is another product derived from the irradiation of low density polyethylene with a dose of 10 Mrad in the presence of a blowing agent. The foam has a density varying from 0.035 to 0.11 g/cm and a resilience of 53% for the lightest foam. As a heat insulation material polyethylene foam has a very low thermal conductivity and can be used for low temperature insulation down to -70°C. Using a similar technique, polymethyl methacrylate foam is also in production. The main advantage of the radiation method is to prevent deformation of the polymer due to flow when the foam formation is carried out at elevated temperature.

Cross-linking of natural rubber latex requires a dose of 13 Mrad. The use of sensitizers such as chloroform or carbon tetrachloride can reduce the dosage considerably. The technique gives film of excellent mechanical properties and may find applications in the vulcanization of thin articles.

Improving backbone polymers

The objective of radiation-induced graft copolymerization of plastics with a suitable monomer system is to improve the properties of backbone polymers for better performance. Polyethylene and polyvinyl chloride are among the most common plastics under investigation.

The grafting of gaseous butadiene on to polyvinyl chloride has been successfully studied in Japan. The PVC in powder form is irradiated with butadiene in an inner source-type cylindrical vessel containing 6000 curies of cobalt-60. The major improvement is the increase of impact strength to 130 kg-cm/cm for the polymer with 8-25% grafting. This high impact is a 50-fold increase over ordinary PVC. Grafting of polyethylene with butadiene can improve the chemical reactivity and mechanical flexibility.

The radiochemical grafting technique is used in the preparation of ion exchange resins and membranes. Potential applications are in chemical processing and water desalination.

Polymerization in Unusual Systems

High energy radiation is the only applicable method of initiating solid-state polymerization through either free radical, cationic or anionic mechanisms. An increasing degree of control of steric or crystalline structures of polymer molecules would be expected in solid-state polymerization.
The post-polymerization of preirradiated highly purified trioxane has reached the pilot plant stage in Japan. It has been estimated that the irradiation cost is in the order of 1 cent/kg of product, assuming a saturation yield of 65% and a production capacity of 8,000 tons/year.

Radiation-induced polymerization under high pressure has been pursued in the polymerization of ethylene and its copolymerization with other monomers. Several pilot plants have been built for process development on polyethylene.

Industrial applications of the radiation process, however, will depend on its competition with conventional technology, which has been well established and commercialized for more than twenty years.

General

There is no doubt that radiosterilization has established its status in commercial production. As more experience is accumulated, the installation cost of the plant might be lowered.

In the application of radiation processing to the plastics industry, the problem is of both an economic and engineering nature.

Economic considerations influencing the feasibility of a radiation process are:
- Cost of source and its installation
- Source replacement
- Amortization
- Maintenance
- Load factor
- Production rate from a given output of energy.

The last is directly related to the process.

Total dose is closely related to the plant throughput, the following figures on the various processing costs with accelerators showing the trend:

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Dose, Mrad</th>
<th>Cost, US cents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textiles</td>
<td>yard</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Surface coating</td>
<td>sq. ft.</td>
<td>6—12</td>
<td>0.12—0.17</td>
</tr>
<tr>
<td></td>
<td>lb</td>
<td>20</td>
<td>0.6—0.9</td>
</tr>
<tr>
<td>Polyethylene film</td>
<td>lb</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Polyethylene foam</td>
<td>lb</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Polyethylene shrinkable tubing</td>
<td>lb</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>

The selection of an optimal dose rate for a given process, however, involves technological investigation of the relevant parameters. Almost invariably the processing is exothermic in nature and the effect of either mixing or diffusion has been noticed in many processes.

The principle in general is in line with conventional methods, but the situation is more complicated so far as distribution of radiation flux and the coupling influence on the rate of changes are concerned.

For processes with large amount of heat of polymerization in the bulk phase, the stability of the reactor and its control should not be overlooked.
It is apparent that a well-planned systems approach will be the answer to the complicated nature of radiation chemical processing and more efforts in engineering development will enhance the future of industrial radiation processing.

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