NUKLEONIKA 2006;51(Supplement 1):S129–S132

PROCEEDINGS

Radiation processing of polymers and semiconductors at the Institute of Nuclear Chemistry and Technology

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Abstract R&D studies in the field of radiation technology in Poland are mostly concentrated at the Institute of Nuclear Chemistry and Technology (INCT). The results of the INCT works on polymer and semiconductor modification have been implemented in various branches of national economy, particularly in industry and medicine. Radiation technology for polymer modification was implemented in the middle of the 1970-ties. Among others, the processes of irradiation and heat shrinkable products expansion have been developed. The transfer of this technology to Polish industry was performed in the middle of the 1980-ties. The present study aims at the formulation of new PE composites better suited to new generation of heat shrinkable products, for example, a new generation of hot-melt adhesives has been developed to meet specific requirements of customers. Modified polypropylene was used for the production of medical devices sterilized by radiation, especially disposable syringes, to overcome the low radiation resistance of the basic material. Modified polypropylene (PP-M) has been formulated at the INCT to provide material suitable for medical application and radiation sterilization process. Modification of semiconductor devices by EB was applied on an industrial scale since 1978 when the INCT and the LAMINA semiconductor factory successfully adopted that technology to improve specific semiconductor devices. This activity is continued on commercial basis where the INCT facilities served to contract irradiation of certain semiconductor devices according to the manufacturing program of the Polish factory and customers from abroad.

Key words electron beam accelerators • radiation processing

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Received: 12 December 2005
Accepted: 15 May 2006

Introduction

Electron beam (EB) process has been successfully applied for modification of gas, liquid and solid phase of the matter. The process requires certain electron energy, and the beam power level depends on specific demands of applied technology. The advantages of radiation process provide the unique capability for material modifications, its high efficiency and possibility to transfer high amount of energy directly into the irradiated object. Whereas the disadvantage is mostly related to high investment cost of an accelerator, it may be effectively overcome in the future as a result of high power accelerators and accelerator technology development.

The first electron accelerator applied in the field of radiation chemistry and radiation processing was installed in Poland in 1971 when a multipurpose facility was completed the INCT in Warsaw [9]. Since then, 15 electron accelerators have been installed in Poland as laboratory instruments (3), pilot plant installations (6) and industrial facilities (6). Four accelerators with a total beam power over 1000 kW were installed at an industrial demonstration facility for flue gas treatment in a power station in Szczecin, harbor city located in northwestern part of Poland [3]. It should be noticed

that nine electron accelerators for radiation processing have been installed at the INCT up to now [10]:
– LAE 13/9, with energy up to 13 MeV, beam power 9 kW and scan 60 cm for multipurpose use and for R&D application,
– ILU-6, with energy up to 2 MeV, beam power 20 kW and frequency 127 MHz, used as a pilot plant facility,
– ELV-3 two units 0.7 MeV, 50 kW both installed in a pilot plant for flue gas treatment,
– AS-2000 electrostatic accelerator with energy adjusted in the range 0.1–2 MeV and beam current up to 100 μA,
– PILOT (linac) with energy 10 MeV and beam power 1 kW in a pilot facility for food processing,
– Elektronika 10/10 with electron energy 10 MeV, 10 kW for food product treatment,
– Elektronika 10/10 with electron energy 10 MeV and beam power up to 15 kW for radiation sterilization,
– LAE 10 with electron energy 10 MeV and pulse duration 10 ns for research study in radiation chemistry (pulse radiolysis experiments).

Radiation processing of polymers

Radiation technology for polymer modification was successfully implemented in industry in many countries since the first EB industrial application in the middle of the 1950-ties. The cross-linking of polymers can be performed efficiently in an electron beam facility during continuous irradiation process. The chemical and physical structures of cross-linked material are changed and, at the same time, some desired properties can be obtained. This creates a possibility of different applications of final product. Pure thermoplastic cross-linking is limited to the polyethylene (PE) and its ethylene copolymers (e.g. EVA) as well as the ethylene-propylene rubber (EPR) and the ethylene-propylene dien rubber (EPDM). The advantages of EB technology in respect to other methods are connected to lower energy consumption, not limited by compounds (EB process can easily be applied to EPDM, PVC and other materials), less factory space needed, higher cross-linking speed and better process control.

Heat shrinkable tubes and tapes are useful products which can solve a lot of industrial and workshop problems. These products have found various applications as insulation of electric wires, protection in heavy environmental conditions (chemical, biological and atmospheric corrosion), marking and many others. The cross-linking of polyethylene and its copolymers by means of high energy electrons irradiation induces a permanent memory effect. Such irradiated polymers are non melting, exhibiting perfect elasticity above their crystalline melting point. Supplied in oriented form, the application of heat will shrink this material to its original dimension, the phenomenon referred to as elastic memory. Thermomeltable glue is added to certain products and specific application.

The manufacturing process of heat shrinkable products consists of three major steps: extrusion, irradiation and expansion (orientation). The extrusion process is performed with typical equipment for polymer processing with specific parameters like material thickness, tubes diameter or tapes width. The irradiation process can be performed as a continuous process or as a unit operation. The unit operation is sometime the only solution for specific type of products. This is related to big size tubes with certain wall thickness and length usually less than 1 m. These products are not so elastic. Electrons with a certain energy should be able to penetrate the full material volume. On the other hand, low diameter tubes may require unit operation process due to limited speed of rewinding caused by limited mechanical properties. The drums with tubes are used during irradiation and expansion processes. The expansion (orientation) processes are performed by technological equipment specific for certain producers. The construction of every apparatus depends on the applied method and size of the products. Several passes in one machine is used to increase the productivity.

Heat shrinkable products made of cross-linked PE are produced on an industrial scale in Poland. The heat shrinkable tubes technology was initiated at the INCT in the 1970-ties [8]. Degree of cross-linking PE is kept at a level of 60%. Special attention is paid to achieving the maximum steadiness of the cross-linking degree through the tube section. Tubes cross-linking process should be characterized by a high stability of electron beam parameters and stable speed of tube movement during irradiation process.

The expanding machine that is the most crucial part of the technology has been developed. Several types of tube expansion and extruding devices were constructed in the Energokabel R&D Office with INCT cooperation. The features of these machines are: original design, simple operation and reliability. The equipment for tube expanding was exported to many countries among them to Germany (1982/83), Switzerland (1983), Yugoslavia (1989), Romania (1990), Malaysia and Iran (1998). The technology transfer to industry was performed in the middle of the 1980-ties. The license on heat shrinkable tube manufacturing was introduced to the Technical Equipment Factory (RADPOL) located at Człuchów, where the production on an industrial scale was initiated. The electron accelerator and other equipment (extruders, expansion machines) were installed in this factory.

The heat shrinkable tapes technology was initiated at the INCT in the 1980-ties [5]. The regular, flexible and flame resistant tapes and tapes with heat-melt adhesive and butyl rubber material of various thicknesses are being developed since then and are being produced on a pilot plant scale. The wide assortment of the heat shrinkable tapes with different thickness (0.5–3 mm) and width (25–700 mm) has been manufactured at the INCT. Heat-shrinkable tapes covered with hot-melt adhesive are especially useful to seal joints preinsulated pipes. Necessary technological lines for tapes irradiation and expansion have been designed and built at the INCT.

A study on the formulation of new PE composites better suited to new generation of heat shrinkable products has been started at the INCT. The assortment of weldable tapes covered by hot-melt adhesive has been elaborated. PE composites have to meet the following requirements: cross-linking at a minimum level of pure PE, better mechanical properties than pure PE, higher surface free energy than that obtained with pure PE. Low density polyethylene (LDPE) has been modified by the use of partially miscible more polar additives. New generation of hot-melt adhesives has been developed to meet specific requirements of customers [6, 7].

Polymers suitable for radiation sterilization

Radiation sterilization with electron beam application has been introduced in Poland by the INCT in the early 1970-ties. This was proceeded with research works and testing of radiation tolerance of different plastic materials, microbiological studies on sterilization effectiveness, elaboration of dosimetry systems for routine dose and dose-depth determination. The research and commercial irradiation was made using a linear electron accelerator which was installed in 1971. The detailed research programme was performed in the period 1973–1977 and allowed to develop methods and procedures and to evaluate suitable materials for industrial application of the process. The commercial radiation sterilization started in 1974. Dedicated electron beam facility for radiation sterilization of single-use medical devices was designed and introduced into operation at the INCT in 1993 [11]. Its total capacity is up to 100 million medical devices sterilized within one year.

The INCT does not only concentrate on the implementation of the sterilization process itself, but also wants to introduce some results from research into practice, among others is an investigation on polypropylene (PP). This polymer is commonly used for manufacturing disposable medical devices. However, common medical devices made of PP are not suitable for radiation sterilization because of chain scission of PP that is caused by irradiation and leads to undesirable changes in polymer properties. There are two stages of degradation: loss of integrity during irradiation as a consequence of direct scission and post-irradiation effect which results from reactions of residual radicals. There are several ways to improve radiation tolerance of polypropylene. This can be done by:
- controlling the crystallization process which results in a smaller content of crystalline phase and a smaller average diameter of crystallite,
- narrowing molecular-weight distribution, high molecular weight and isotacticity,
- copolymerization with other polymers, for example, with ethylene since ethylene/propylene copolymers are stable up to 50 kGy,
- addition of polymers or low molecular compounds (stabilizers) containing aromatic groups (e.g. phenolic and amine antioxidants) or addition of elastomers containing double bonds,
- polymer orientation.

Modified polypropylene was used for the production of medical devices sterilized by radiation, especially disposable syringes, to enhance radiation resistance of the basic material. Modified polypropylene (PP-M) has been formulated at the INCT to provide material suitable for medical application and radiation sterilization process [1, 2]. The main component is polypropylene MALEN P-J603, produced in Poland, with melt flow index MFR = 8.58 g/10 min (230°C/2.16 kg). Homo-polymer PP contains typical antioxidant and sliding agent which diminishes sliding force between the piston and the frame (in two element syringes) according to ISO standard. PP and all other components of PP-M fulfill the requirements of European Pharmacopoeia and international regulations. Disposable syringes made of this material have obtained positive remarks from medical experts. This material is also being used for manufacturing of different product treated by radiation.

Investigations of radiation resistant polypropylene have been performed to establish the effect of low dose irradiation on radical processes in the polypropylene stabilized by hindered-amine light stabilizers (HALS) and in blends with radiation resistant elastomer (styrene-butadiene-styrene triblock copolymer).

Hydrogel materials production has taken place in Poland. Combined effect of cross-linking and sterilization by ionizing radiation is applied for the production of the hydrogel. Often hydrogels are based on water-soluble hydrophilic polymers such as poly(vinylpyrrolidone) (PVP) and poly(acrylamide). Natural polymers such as: agar-agar and gelatin are also used. Scientists from the Technical University of Lódź are the inventors of original technology of hydrogel production. Technology is patented in Poland and abroad. Hydrogels made in Poland on an industrial scale are used as “wet” wound care products. Around 500,000 pieces of hydrogel wound dressing were irradiated at the INCT until now. Clinical use of gel dressings showed that:
- already after first exchanges of the dressings, the burning pain ceases, giving feeling of “soothing” to the injured person,
- during change of the dressing, contamination, discharges, fibrin and necrosis tissues are removed, leaving non-damaged granulation,
- exchange of the dressing is painless,
- the dressing protects the wound well against drying and external infection,
- the dressing prevents from overgrown scars.

Semiconductors modification

Electron beam modification of silicon devices is based on the minority carrier lifetime decreasing after radiation treatment. To obtain suitable conditions for such process, numbers of defects are created in silicone crystal by high energy electrons. Certain irradiation conditions should be followed to reach a compromise due to carriers lifetime decreasing that leads to faster switching properties and, at the same time, reduces the load current level. It should be mentioned that the defects created in silicone matrix are stable over a period of 40 years when the temperature of the silicon device does not exceed 125°C.

The radiation method offered an alternative to traditional technique of high temperature gold or platinum diffusion into semiconductor crystals. EB technology helped to solve the common diffusion problems, like non-uniform deep distribution and higher leakage currents. The major advantages of high energy electrons come from the ability to penetrate deeply into the matter. The uniform distribution of recombination centers is created. The devices switching time can be tailored according to user needs even in finished or encapsulated power devices.

EB processed fast switching power thyristors, triacs and diodes have been used in the growing number of applications, for which the long-term stability and efficiency of energy saving semiconductors components is important and must be guaranteed at competitive prices. The uninterrupted power supplies for data processing centers and hospital reanimation equipment are such examples, followed by many other applications in metallurgy, mining, transport, household applications and other areas. EB technology does not involve in the increased investment, except the electron beam utilization cost. It can be quickly recovered due to the major improvement and simplification of the device manufacturing process.

The EB modification of the semiconductors devices was applied on an industrial scale since 1978 where the INCT and the LAMINA semiconductor factory successfully adopted this technology for specific semiconductor devices [4]. Electrical energy saving due to EB modified semiconductors applied in Polish industry was estimated to be 32 GWh per year. It reduced requirements for installed power of electrical generators in a power station by more than 200 MW. This activity is continued on commercial basis where the INCT facility is being used as contract irradiation services for certain semiconductor devices according to the manufacturing program of the LAMINA factory and customers from abroad.

Conclusions

The heat shrinkable tubes and tapes technologies, polypropylene modified to overcome low radiation resistance of the basic material, EB processed fast switching power thyristors, triacs and diodes are the best examples of R&D activity performed at the INCT. The results of the INCT works on polymers and semiconductors modification have been successfully implemented in industry and medicine. Nowadays, with its nine electron accelerators (covering electron energy range 0.1–10 MeV) in operation and with the staff experienced in the field of electron beam application, the INCT is one of the most advanced centers of science and radiation processing. Recently, the INCT has started research on using radiation methods for modifications and sterilization polymers for medical applications, especially as scaffolds in tissue engineering and those applied in nanotechnology.

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