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Electron beam accelerators—trends in radiation processing technology for industrial and environmental applications in Latin America and the Caribbean

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ABSTRACT

The radiation processing technology for industrial and environmental applications has been developed and used worldwide. In Latin America and the Caribbean and particularly in Brazil there are 24 and 16 industrial electron beam accelerators (EBA) respectively with energy from 200 keV to 10 MeV, operating in private companies and governmental institutions to enhance the physical and chemical properties of materials. However, there are more than 1500 high-current electron beam accelerators in commercial use throughout the world. The major needs and end-use markets for these electron beam (EB) units are R and D, wire and electric cables, heat shrinkable tubes and films, PE foams, tires, components, semiconductors and multilayer packaging films. Nowadays, the emerging opportunities in Latin America and the Caribbean are paints, adhesives and coatings cure in order to eliminate VOCs and for less energy use than thermal process; disinfestations of seeds; and films and multilayer packaging irradiation. For low-energy EBA (from 150 keV to 300 keV). For mid-energy EBA (from 300 keV to 5 MeV), they are flue gas treatment (SO_2 and NO_X removal); composite and nanocomposite materials; biodegradable composites based on biorenewable resources; human tissue sterilization; carbon and silicon carbide fibers irradiation; irradiated grafting ion-exchange membranes for fuel cells application; electrocatalysts nanoparticles production; and natural polymers irradiation and biodegradable blends production. For high-energy EBA (from 5 MeV to 10 MeV), they are sterilization of medical, pharmaceutical and biological products; gemstone enhancement; treatment of industrial and domestic effluents and sludge; preservation and disinfestations of foods and agricultural products; soil disinfestations; lignocellulosic material irradiation as a pretreatment to produce ethanol biofuel; decontamination of pesticide packing; solid residues remediation; organic compounds removal from wastewater; and treatment of effluent from petroleum production units and liquid irradiation process to treat vessel water ballast. On the other hand, there is a growing need of mobile EB facilities for different applications in South America.

1. Introduction

The industrial uses of electron beam accelerators started in the late 1950s, with the crosslinking of polyethylene wire insulation. Nowadays, the number of electron accelerators in use for various radiation processing applications exceeds 1500. These accelerators are used mainly in plastics, automotive, wire and electric cables, semiconductors, health care, aerospace and environmental industries, as well as numerous research and development facilities around the world (IAEA, 2002). In Latin America and the Caribbean, particularly in Brazil, there are 24 and 16 industrial electron beam accelerators, respectively, with energy from 200 keV to 10 MeV, operating in private companies and governmental institutions to enhance the physical and chemical properties of materials (IAEA, 2011). These electron accelerators for radiation processing are presented in Tables 1 and 2.

2. Needed technologies

The current use of the electron beam accelerators in radiation processing technology for industrial applications shows that

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Table 1
Industrial electron beam accelerators with energy from 200 keV to 10 MeV operating in Latin America and the Caribbean.

Country	Organization	City	Units	Products	Additional Information
Brazil	IPEN-CNEN/SP	Sao Paulo	2	*R and D*: wastewater treatment, polymer modification, shrink tube and film, surface curing, food irradiation	Radiation Dynamics, Inc. (RDI), JOB 188, 37.5 kW, 1.5 MeV, roller bed conveyor (batch), pilot plant for wastewater treatment (30 L/min)
				Commercial: wire and electric cables, semiconductors, sterilization of medical and pharmaceutical devices, PE foam sheets	RDI, JOB 307, 97.5 kW, 1.5 MeV, continuous treatment system (300 m/min)
Ecuador	Escuela Politecnica Nacional	Quito	1	*R and D*: food irradiation,wires and electric cables	ELU-6U, 6-10 MeV
Mexico	Comision Nacional de Seguridad Nuclear y Salvaguardias	Tijuana	2	Polymer modifications (plastics and rubber)	RDI Dynamitron 300/46/1220, 3 MeV
	ICU Medical S.A.	Ensenada	1	Sterilization of medical devices,polymer modifications	Precision Scan, SB108, 10 MeV
	Cryovac	México City	1	Fresh food packaging	Nissin High Voltage, 2SP500, 500 keV
Costa Rica	BeamOne SRL	Alajuela	1	Sterilization of medical and pharmaceutical devices	Titan Corporation,10 kW, 10 MeV
Dominican Republic	FENWAL International Inc. (BAXTER)	Haina	2	Sterilization of medical and pharmaceutical devices	Titan Corporation, TB-10/15, 10 MeV, 1.44 mA EL Surbeam/Varian,SB-1/5, 650 keV, 0.094 mA

Table 2
Industrial electron beam accelerators with energy from 200 keV to 10 MeV operating in Brazil.

Company	Manufacturer	Model	Energy (keV)	Current (mA)	Applications
IPEN-CNEN/SP and Cofibam	Radiation Dynamics, Inc.	JOB 188 JOB 307	1500	25 60	*R and D* and crosslinking
Antilhas Embalagens	Energy Sciences, Inc.	EZCure I	110	500	Curing
Bridgestone–Firestone	Energy Sciences, Inc.	EC/300—1 and 2	300	500	Crosslinking
CryovacBrasil	Cryovac	ECLU—1,2,3 and 4	500	30	Crosslinking
Unipac Embalagens	Energy Sciences, Inc.	CB200/060/070	210	168	Curing
Curwood Itap	RPC Industries	Broad Beam—1 and 2	300	600	Curing
Acome do Brasil	Acome/Radiation Dynamics, Inc.	DPC 1000	550	66	Crosslinking of wire and electric cables
Prysmian	Radiation Dynamics Inc.	JOB 308	1500	60	Crosslinking of wire and electric cables
Aceletron	Titan Corporation/EL Surebeam	LINAC—1 and 2	10,000	1.8	Food irradiation, gemstone enhancement, radiosterilization of medical disables, cosmetics, polymer modification

polymers dominate the industry. While these technologies are well established in the industrialized countries, they are also needed in Latin America and the Caribbean where their introduction and expansion would require assistance for technology transfer and financial support from the industrialized countries and international aid agencies. The established and needed technologies include the following (IAEA, 2008):

- Crosslinking of selected thermoplastics for enhancing their performance, through improvements in their mechanical and/or surface properties, electrical conductance and resistance, thermal stability, and imparting heat-shrink properties, including wire and cable insulation, multilayer packaging films, plastics tubing and foam sheets.
- Radiation vulcanization of elastomers, in addition to automobile tires.
- Radiation modification of semiconductors devices.
- Radiation sterilization of medical devices, cosmetics and pharmaceutical products. and
- Decontamination of packaging for foods and pharmaceutical raw materials.

3. Emerging technologies

The success of the emerging technologies will be a function of not only the products development and marketing, but also the coordinated research effort. Any reduction in time and effort achieved through collaboration between industry, university and research institute could lead to faster and more economical commercialization. In most of the following emerging technologies in Latin America and the Caribbean, application of electron beam accelerators with different energies for radiation processing, continued research and development would be needed to bring them to the maturity level that is required needed to secure both the markets, and the required investment of capital, for their commercialization (IAEA, 2002, 2008):

- Low-energy (from 150 keV to 300 keV)—paints and varnishes for graphic arts, electronic circuits, optical fibers, adhesives for plastics and inks, and coatings for CDs, DVDs and wood finishes cure; disinfestations of seeds; films and multilayer packaging irradiation.
- Mid-energy (from 300 keV to 5 MeV)—flue gas treatment; composite, nanocomposite materials and biodegradable composites based on biorenewable resources irradiation; human tissue sterilization; carbon and silicon carbide fibers modification; irradiated grafting ion-exchange membranes for fuel cells application; electrocatalysts nanoparticles production; and natural polymers irradiation and biodegradable blends production. and
- High-energy (from 5 MeV to 10 MeV)—sterilization of medical, pharmaceutical and biological products; gemstone enhancement; treatment of industrial and domestic effluents and sludge; preservation and disinfestations of foods and agricultural products; soil disinfestations; lignocellulosic material irradiation as a

pretreatment to produce ethanol biofuel; decontamination of pesticide packing; solid residues remediation; organic compounds removal from wastewater; and treatment of effluent from petroleum production units and liquid irradiation process to treat vessel water ballast.

3.1. Radiation curing of composite materials, inks, coating and adhesives

Electron-beam (EB) curing has several advantages over conventional thermal curing methods: improved parts and material handling; ability to combine various materials and functions in a single operation, utilizing lower cost tooling; reduced cure times; energy savings, efficiency and environmental friendly. There are low-energy electron beam accelerators manufactured by PCT Engineered Systems, LLC and by Energy Sciences, Inc. (ESI). The EB curing of composites has several advantages compared with conventional thermal processing. Curing at ambient temperature allows greater control of part dimensions and eliminates internal stresses that otherwise occur during cooling, which can reduce material strength and durability. Curing time is significantly shorter, and the resins (which are not designed to cure thermally) are more stable and thus have longer shelf life. In addition, the EB process has environmental advantages in that the emission of volatile components is greatly reduced. This technology has been used in an aerospace application, in multi-layer tubes and is under investigation in numerous other areas, such as structural parts for use as automotive panels, and for electro-optical devices, healthcare products, and in many other areas (Machado et al., 2005).

The faster curing times of radiation curing technology allied to the increase of production cycles (three times or higher) is an alternative for the current peroxide system cure used in the composites market. In South America it is still under development at some main composite producers. It demands investments in new equipments (lamps and ovens). However, it will be an interesting trend for the future due to the regulations regarding styrene emissions. The UV and EB energy saving curing technologies can be applied to processes like hand lay-up, spray-up, filament winding, gel coats and some applications in pultrusion, replacing thermal curing practices. The search for lower styrene emissions is one of the main concerns for the composite producers, mainly for safety, health and environmental reasons. Also, the final physical properties of the finished composite are enhanced, showing greater hardness and gloss. Market has become global. South America is a part of this global market in spite of its economic situation. Therefore, all new developments will affect significantly the use of UV and EB technologies (Machado et al., 2007).

3.2. Renewable energy by irradiation of lignocellulosic material for ethanol production

The main purpose is the cleavage of lignocellulosic material from sugarcane bagasse using ionizing radiation from an industrial electron beam accelerator, in order to make the cellulose hydrolysis and the fermentation of their sugars to ethanol for biofuel production easier. The media value obtained of studied sugarcane bagasse were 41.9% of cellulose, 31.3% of hemicelluloses, 19.5% of lignin, 6.3% of soluble, and 1.0% of ash. These samples have about 50% of humidity and the ionizing radiation does not change this parameter, which is a positive point for combination with enzymatic or chemical hydrolysis. The main challenge is to obtain the desirable effects by applying doses as low as possible to hydrolyies the polysaccharides, and at the same time to avoid the glucose loss due to uncontrolled degradation of cellulose and hemicelluloses (Duarte et al., 2010).

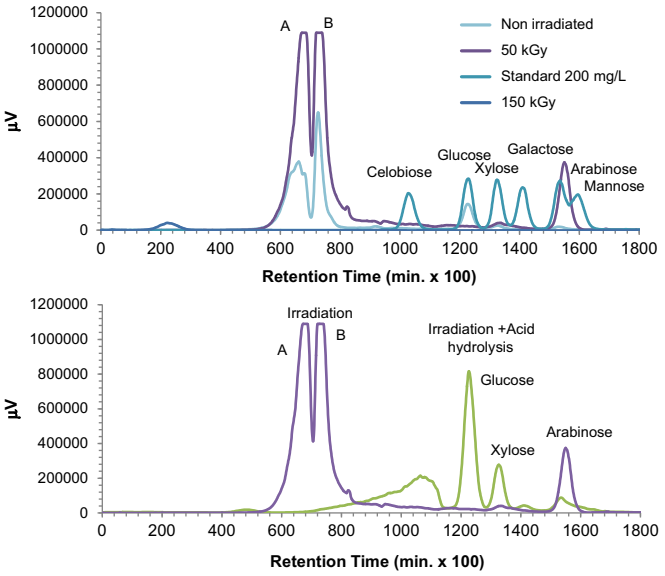

Fig. 1. Sugars decomposition after EB-irradiation (50 kGy) of sugarcane bagasse (SCB).

Structure and composition modifications in sugarcane bagasse were demonstrated with absorbed doses from 5 kGy to 150 kGy. The lignin was not degraded completely, but the cellulose was cleaved forming oligosaccharides. The acid hydrolysis of the hot extract showed that the partial degradation of cellulose and hemicelluloses formed cello-oligosaccharides from glucanases and xylanases (Fig. 1). The radiation processing converts 0.5% of the cellulose at 20 kGy and 2% of the hemicelluloses at 70 kGy, the major part remaining as oligosaccharides. About 99% of cellulose and hemicelluloses are converted to oligosaccharides with 70 kGy (Ribeiro et al., 2010). The ongoing studies in this subject are the combination of pretreatment technologies and the enzymatic hydrolysis.

3.3. Carbon and silicon carbide fiber modification

Composite materials are systems composed of two or more constituents differing in form and/or material composition that are essentially immiscible with each other. Polymeric composites are made of an organic matrix and a reinforcement material. Advanced composite materials are made from carbon fibers embedded in epoxy matrix. These materials are used in structural applications working under high mechanical loads.

An important factor to assure the good mechanical performance of the carbon fiber based composite material is the adhesion properties between the carbon fiber surface and the epoxy matrix. Commercial carbon fibers have a sizing material on their surfaces in order to protect the filaments and also to improve their adhesion to the polymeric matrix.

The modifications induced by EB irradiation promote changes on the fiber surface, resulting in a better adhesion between the carbon fibers and the epoxy matrix used to prepare test specimens. This effect was an important factor that improved the mechanical performance of the composite obtained from these materials. The improvement obtained was similar in the range of applied doses, from 50 kGy to 300 kGy, as shown in Fig. 2. This mechanical improvement was observed only for the composite prepared from irradiated carbon fibers, and not for the application

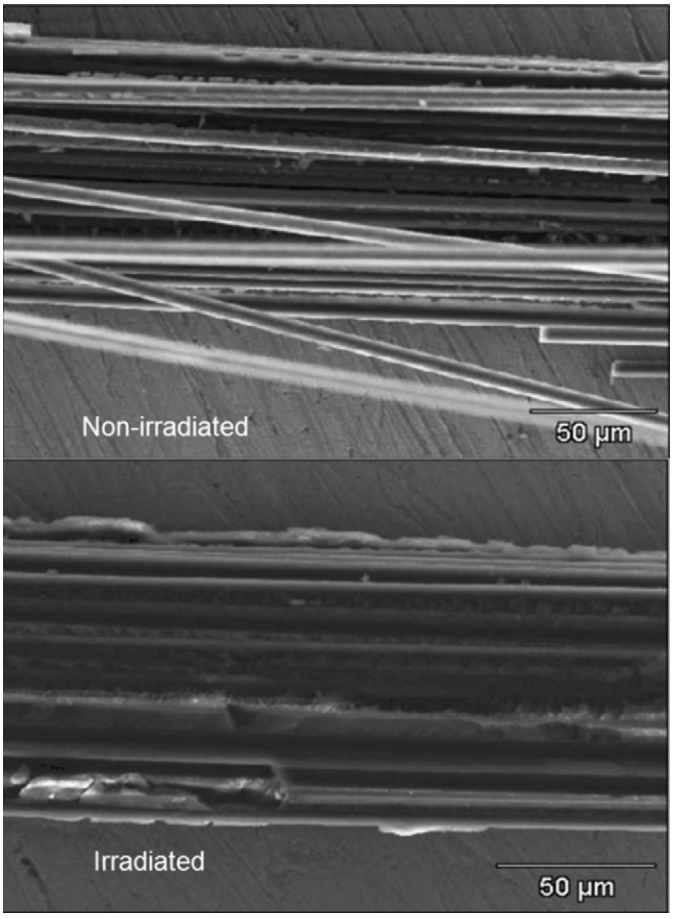

Fig. 2. Carbon fibers (12 k) non-irradiated and irradiated by EB (50–300 kGy).

of EB radiation on resin-impregnated composite. This behavior was observed for 6 k and 12 k commercial carbon fibers, independent of the differences in the sizing materials and the number of filaments per roving (Giovedi et al., 2005; Pino et al., 2007).

3.4. Fuel cell membranes

Grafting is a powerful surfacing modification process to produce new polymeric materials with an intimately molecular interaction, not present in simple processes like adhesion, traditional blending and copolymerization. Grafting process by ionizing radiation has been more attractive lately due to the fast free radicals production without chemical intermediates, like initiators. These chemicals often need long time periods to react and have high toxicity. Therefore, grafting by ionizing radiation applying EB is environmentally practicable to develop novel absorbents and membranes.

The irradiation grafting of dimethylaminoethyl methacrylate (DMAEMA) monomer and heparin onto polyvinyl chloride (PVC) flexible film surface can be applied to prevent thromboembolism when packaging blood in blood banks. Also, modification of polymeric matrix by grafting copolymerization can be used as a base material to improve several chemical syntheses (Augusto et al., 2010). The diffusional effects derived from ion exchange and other mass transport agents are studied in polymeric substrates irradiated and modified by monomer insertion or grafting, considering the measurements of its surfacial, mechanical, thermal and chemical properties.

Grafting modified membranes can be applied at ion exchange membrane for PEM-FC (proton exchange membrane or polymer electrolyte membrane fuel cells) (Muto et al., 2005). The investigation of the fluorinated and perfluorinated polymeric films styrene grafted by EB had promising results when the mutual irradiation was performed under warming and vacuum conditions. The simultaneous and pre-irradiation grafting methods under vacuum or inert gas conditions will be achieved using a stainless steel chamber. It is sealed with screws that are pressing an o-ring in the top cap, which has a titanium foil window. The titanium window allows penetration of the electron beam.

The PVDF films obtained by vapor phase during mutual grafting irradiation with about 15% of styrene, allow high percentage of water uptake when this copolymer is sulfonated. These results indicate that mutual styrene grafting can be performed with an industrial EB accelerator as a fast alternative to produce ionomers that can compete with commercial Nafion® films. The vapor phase grafting mechanism is an interesting copolymerization method where active species generation and diffusion play a role (Ra et al., 2011).

The ion tracked styrene-g-PVDF films (material developed in Argentina collaboration work) were sulfonated in our laboratory and we could evaluate the percentage of water uptake, ion-exchange capacity (IEC) and tensile strength maximum as a mechanical property; these films shown an intense water uptake due to the micrometric–nanometric pores obtained by tracking of swift heavy ions (a nuclear process). Some properties of these films were compared to Nafion®, then, this new ionomer material could be used in processes that require a high water uptake. The electrochemical *I–V* behavior of ion tracked films was analyzed by polarization curves, and we observed the charge transfer region at higher potentials, that is an electrochemical characteristic of Nafion® films when they are immersed in high acidic media.

3.5. Electrocatalysts nanoparticles

Fuel cells convert chemical energy directly into electrical energy with high efficiency and less emission of pollutants and are extremely attractive as power sources for mobile, stationary and portable applications. In the proton exchange membrane fuel cell (PEMFC) the anodic oxidation of hydrogen and the cathodic reduction of oxygen should be catalyzed to occur at adequate rates at low temperatures. PtRu carbon-supported nanoparticles are the best electrocatalysts for anodic and cathodic reactions. However, the use of hydrogen as a combustible continues to be a problem especially for mobile and portable applications. Therefore, there has been an increasing interest in using alcohols directly as combustibles (Direct Alcohol Fuel Cell—DAFC). Methanol has been considered the most promising combustible and carbon-supported PtRu nanoparticles (PtRu/C) the best electrocatalyst.

PtRu/C electrocatalysts, carbon-supported PtRu nanoparticles, as shown in Fig. 3, were prepared subjecting water/ethylene glycol mixtures containing Pt (IV) and Ru (III) ions with a nominal Pt:Ru atomic ratio of 50:50 and the carbon support to electron beam irradiation. The electrocatalysts nanoparticles characterized by energy dispersive X ray analysis (EDX), X ray diffraction (XRD) and the PtRu/C electrocatalysts have shown the typical FCC structure of platinum–ruthenium alloys. Thereafter, the electrocatalytic activity was tested, for methanol electro-oxidation aiming fuel cell application, using cyclic voltammetry and chronoamperometry. The obtained PtRu/C electrocatalysts have shown superior performance for methanol electro-oxidation at room temperature compared to commercial PtRu/C electrocatalyst. PtRu/C electrocatalysts have been prepared in a single step subjecting water/ethylene glycol solutions containing Pt(IV) and Ru(III) ions and the carbon support to electron beam radiation at room temperature with stirring (Silva et al., 2007).

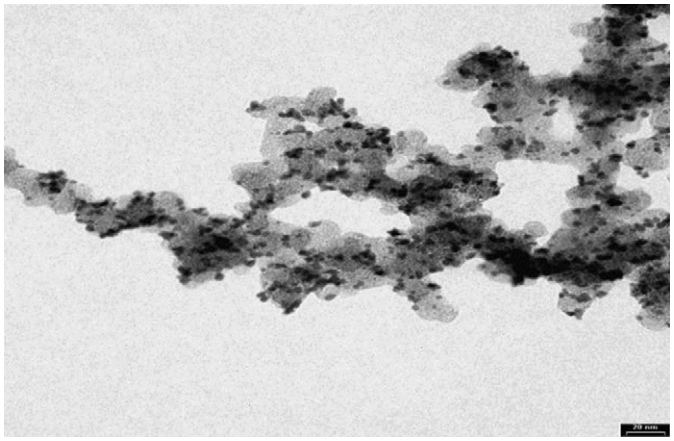

Fig. 3. PtRu/C electrocatalyst irradiation for Direct Methanol Fuel Cell (DMFC).

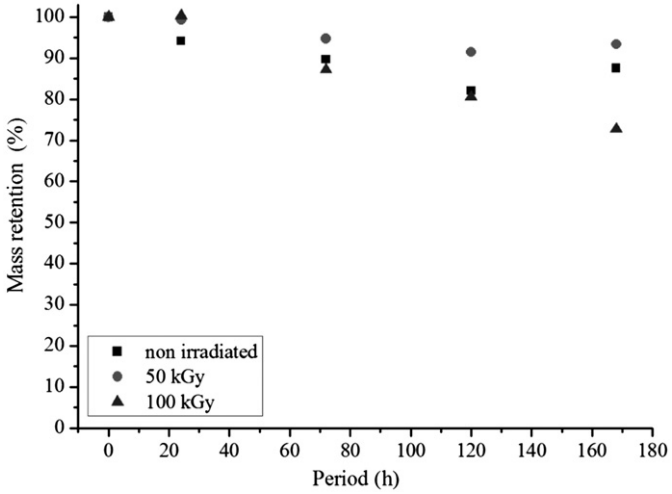

Fig. 4. Retention of mass of non-irradiated and EB irradiated 10% coconut fiber composite after digestion by enzymatic method.

3.6. Biodegradable composites based on biorenewable resources

The problem of environmental pollution caused by plastic waste can be solved by the development of biodegradable polymeric materials. Poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) have been receiving much attention lately due to their biodegradability in the human body as well as in the soil, biocompatibility, environmentally friendly characteristics and non-toxicity. Moreover, both polymers PLLA and PCL can be used in biomedical applications, which require a proper sterilization process. However, polymeric structural changes such as scission and crosslinking are induced by radiation processing of polymers.

Studies were done with blends and composites based on two commercial polymers: poly (ε-caprolactone), PCL, and poly (L-lactic acid), PLLA, a coconut fiber. Pellets were prepared at National Institute of Advanced Industrial Science and Technology—AIST, Research Institute for Sustainable Chemical Innovation, Japan. Sheets from twin screw extruded pellets were prepared using a Tokyo Ikeda hot press machine from Japan Atomic Energy Agency—JAEA, Takasaki, Japan. Samples were irradiated with an electron beam using a Dynamitron ($E=1.5$ MeV) at IPEN-CNEN/SP with doses from 50 kGy to 1000 kGy, 22.37 kGy/s, and at JAEA with radiation doses ranging from 10 kGy to 500 kGy, at a dose rate of 0.6 kGy/s. The non-irradiated and irradiated samples were studied using several analytical techniques and characterization assays that allowed understanding of their properties in order to enable their application as precursors in medical and surgical devices (Kodama et al., 2009).

Even though mechanical properties did not improve by adding coconut fiber, neither with an increase in radiation dose, the variation observed will not significantly affect artifact use. Considering the biomedical application, *in vitro* tests of unirradiated and EB irradiated samples with 20 kGy, extract of samples showed that less than 10% of cells died, indicating that the materials studied can be used as a biomaterial. Biodegradability results indicated that the materials studied suffered elevated degradation in the presence of enzymes and were not negatively affected by radiation processing, as shown in Fig. 4.

3.7. Nanocomposites for enhancing their functionality and utility

Carbon nanofibers are being thoroughly investigated for use in polymer matrix composites because they are less expensive than carbon nanotubes while still providing attractive mechanical, electrical, and thermal properties. The major issue in using carbon nanofibers in composites is the ability to disperse them homogeneously into the polymeric matrix. Van der Waals forces strongly hold the nanofibers together as bundles or agglomerates leading to bad dispersion and, consequently, weak interfacial bonding that limits the performance of polymer nanocomposites. The enhancement of the dispersion of carbon nanofibers in polymer matrices depends on the surface treatment, referred to as functionalization.

A radiation based process is recommended as an alternative, environmental friendly method to functionalize carbon nanofiber compared to the current wet chemical techniques. The radiation process relies on displacement of atoms of carbon from their equilibrium positions due to electronic excitation and direct collisions of high energy electrons with nuclei (via electron beam process) and/or grafting of polymer chains onto carbon nanofiber surfaces (via gamma radiation and electron beam). Carbon nanofibers are grafted with organic functional groups through electron beam and gamma radiation. Functional groups are provided from polymers and monomers such as methyl methacrylate, styrene, polyethylene glycol, acrylic acid and epoxy, which are deposited on and covalently bonded to the carbon nanofiber surface. Nanocomposites are produced with these functionalized carbon nanofibers. Several analytical techniques are used to evaluate this process and assess the impact on morphology, mechanical, electrical and thermal properties of the nanocomposites. The market opportunities for the products manufactured with these functionalized carbon nanofibers may include catalysts for fuel cells, sensors, microelectronic devices, ballistic protection, scratch and abrasion resistant coatings, thermal management, antistatic material, EMI shielding, conductive plastics, structural and thermal conductive materials (Evora et al., 2010).

4. Conclusions

There is a growing use of low-energy electron beam accelerators (EBA) for the curing of inks, coating and adhesives for the elimination of volatile organic compounds (environmentally friendly), and in energy savings and efficiency. Lower cost and low energy EBA are commercially available. There is a growing need for mobile facilities in different applications, such as, industrial wastewater treatment and seed disinfestation in South America.

There is an increasing diversity of products and processes that require high and mid-energy EBA for food irradiation, sterilization of disposable medical, pharmaceutical and cosmetic devices, crosslinking of wire and electric cables, multilayer packaging films, heat shrinkable tubes and films, tires and components,

composite and nanocomposite materials, biodegradable composites based on biorenewable resources, carbon and silicon carbide fibers modification, lignocellulosic and natural polymers irradiation, semiconductor modification, gemstone enhancement, grafting, electrocatalysts nanoparticles production, solid residues remediation, wastewater and flue gas treatments. There is a need of improvements in the reliability of medium and high energy EBA, with regard to window life time, power supply and cathode.

The future of the electron beam application for flue gas treatment depends on technical developments to make the radiation technology very competitive for environmental applications. Due to this fact it is necessary to establish new applications for the EBA process in petrochemical complexes, incinerators and mines, to carry out R and D works in EBA systems and power supplies (capacity) supported by IAEA, including interregional projects, to promote fertilizer marketing for the valuable collected fertilizer (by-products), and to reach reliability, decreasing the power consumption and capital cost, optimizing the engineering technology and equipment to improve stability of the installation.

Improved efficiency, with reduction in time and required dose, and effort achieved though collaboration between industry, university and research institute could lead to faster and more economical commercialization. Closer contacts with the polymer industries may open up new opportunities for radiation processing by EBA.

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