Application of Electron Beam in Development of Environment-friendly Cable

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Abstract

An overview of the radiation crosslinking technology and its application in development of environment-friendly cable which is not only contains no halogens and brominated flame retardants but also has improved fire safety is presented in this paper. The process of radiation crosslinking changes polymer from a series of separate polymer chains into a single interwoven molecule. This change improves heat resistance and mechanical properties, so the developer can design the material with higher filler loading. Environment-friendly cable can be assessed by chemical analysis of toxic materials and by testing of fire hazards such as flame propagation, smoke and toxic gas emission.

1. Introduction

Electron beam facilities have been used for many industrial applications such as crosslinking of wire and cables. By crosslinking of the polymers, a three-dimensional network of chemical bonds is formed between polymer chains, enhancing the heat resistance and mechanical properties.[1)]

In recent years, concerns have been widely issued about the environmental hazards of polyvinyl chloride (PVC) and brominated flame retardants (BFRs) incorporated polyolefins which are used for insulation and jacketing of wire and cables. Especially, during incineration processes, these materials are believed to contribute to highly toxic dioxin emissions. Furthermore, lead stabilizers in PVC can cause environmental pollution and phthalates used as plasticizers for PVC are suspected as the endocrine disrupting chemicals. Also, there is no doubt that toxic gas and smoke emitted during the combustion process of halogen containing cables is the major cause of injuries and fatalities in fires. As a consequence, the development of environment-friendly cables is mainly driven not only by environmental issues, but also by the increasing awareness about fire safety of consumers.[2~3)]

Research and development for environment-friendly cables has been actively done mainly in Japan and Europe. Till these days, its applications are limited to particular industrial area according to the needs of customers. But recently, the European Community (EC) adopted the directives on 'End of Life Vehicles (ELV)', 'Waste Electrical and Electronic Equipment (WEEE)' and 'Restriction of the use of Hazardous Substances (RoHS)'. Those directives specify the recycle ratio, hazardous material and effectuation schedule for the product and packaging material for vehicles, electrical and electronic equipment. Thus, it is forecasted that the replacement to environment-friendly cables is expanded and accelerated.[4~5]

Environment-friendly cables are formed by removing halogens such as PVC and brominated flame retardants as well as heavy metal additives from cable materials. Halogen free flame retardancy (HFFR) is commonly achieved by the addition of inorganic fillers, typically aluminum hydroxide (ATH) or magnesium hydroxide (MDH) into the polyolefin matrix. Although these fillers are essentially non-toxic, the high loading level is required for adequate flame retardancy. This often leads to a marked deterioration of other critical polymer characteristics such as mechanical and physical properties. Crosslinking of polymer matrix by electron beam irradiation, so called 'radiation crosslinking', is one of the breakthroughs to solve the drawbacks of the halogen free flame retardant systems. After crosslinking, since the polymer molecules are chemically linked to each other and no longer able to move at random, mechanical properties like tensile strength and abrasion resistance can be improved.[6]

The purpose of this paper is to give an overview of the radiation crosslinking technology and its application for development of environment-friendly cable. In addition, the effects of radiation crosslinking in HFFR insulations on thermal and mechanical properties are investigated.

2. Application of Electron Beam in Wire and Cable Industry

2.1 Crosslinking of Polymers

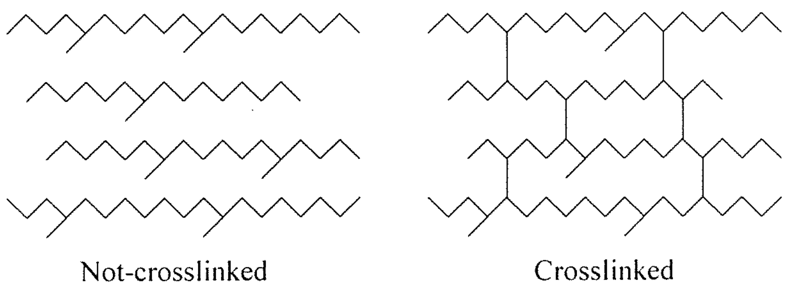

Fig.1. Not-crosslinked and crosslinked polymer structures.

The crosslinking of polymers refers to the modification of polymer properties by inducing chemical links between individual macromolecules as shown in Fig. 1. There are three different methods such as peroxide crosslinking, silane crosslinking and radiation crosslinking are available for crosslinking of polymeric materials.

Firstly, peroxide crosslinking is brought by the presence of an added chemical additive like peroxide. Under the influence of heat, the peroxide breaks up into reactive species and those interlink two neighboring molecules. The reactions usually occur in the melt, which ensures randomization of the location of the crosslink junctions in the network. In this method, the extent of crosslinking is controlled by the amount of peroxide. Secondly, silane crosslinking takes place in three steps. At first step, reactive vinylsilane groups are grafted onto the backbone of polymer at random locations, the reaction being carried in the melts. At next, the grafted polymer is exposed to moisture, which hydrolyzed the silane groups. Finally, the hydrolyzed silane groups on adjacent molecules condense to form intermolecular links. In this process, the degree of crosslinking is determined by the number of vinylsilane units grafted along the time of exposure to moisture. Thirdly, crosslinking by irradiation results from dissipation of the energy carried by fast electrons penetrating into the polymer matrix. When high-velocity electrons are absorbed in polymer, the energy is transferred to bound electrons in atoms and molecules, causing them to be in higher states of excitation. Ions and radicals are formed which initiate chemical reactions within the irradiated polymeric material.[7] Crosslinking reaction during irradiation is depicted in Fig. 2

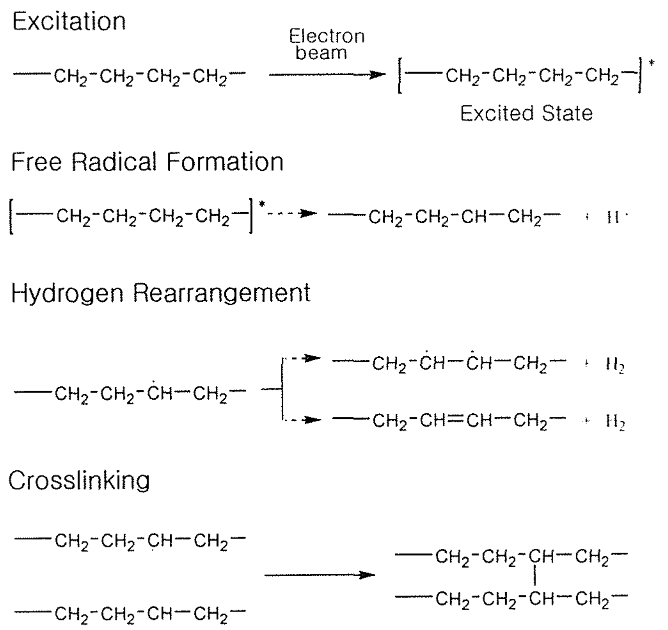

Fig. 2. Reaction mechanism of radiation crosslinking.

The crosslinking process changes polymeric material from a series of polymer chains into a single interwoven molecule. This change improves heat resistance, environmental stress crack resistance and gives higher tensile strength which allows compounds to incorporate higher filler loading. A power cable with XLPE (crosslinked polyethylene) insulation can operate at conductor temperatures of 90℃, while the thermoplastic polyethylene (not-corsslinked polyethylene) insulated cable can not operates at 90℃. Since conductor temperature is proportional to the amount of current sent through the cable, more power can be sent through an XLPE cable than through a not-crosslinked cable of the same dimension.

2.2 Elecron Beam Facility for Crosslinking of Wire and Cable

There are two kinds of ionizing radiation source for radiation processing in industry. Those are the radiation from cobalt-60 and from electron beam. Although the gamma radiation from cobalt-60 has a mean penetration distance of 0.25m of unit specific gravity, its low dose rate makes it unsuitable for radiation crosslinking. Also, the long time exposure to gamma irradiation in air will lead to polymer oxidation. The cost effective radiation source of high current, high power electron beam system is used in wire and cable industry. That offers high dose rates and thus short irradiation times.[1] Fig. 3 shows a schematic of wire processing facility.

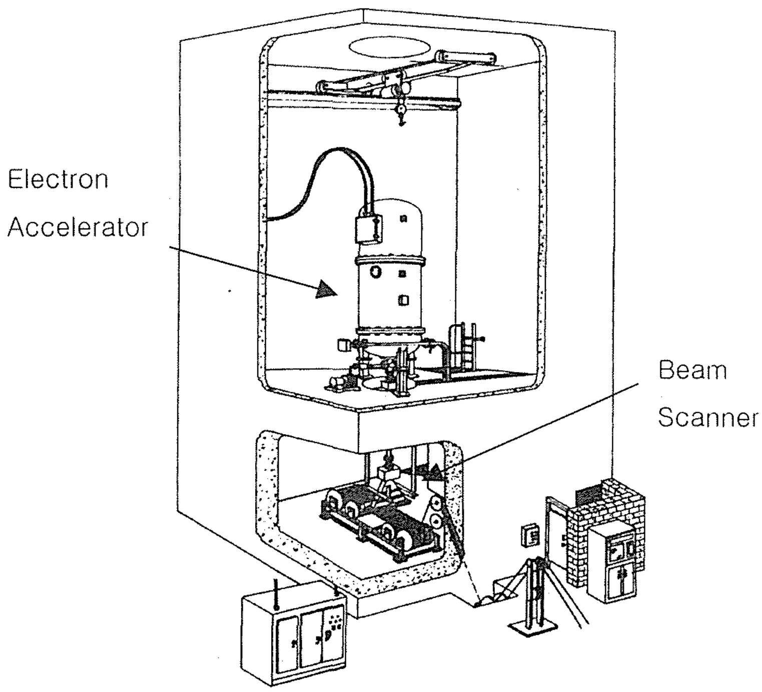

Fig. 3. Electron beam wire processing facility.

Radiation crosslinking of wire and cable requires medium accelerating voltages of 0.5 to 3 MeV. The depth of penetration of the electrons is governed by the accelerating voltage. Thus the selection of an electron accelerator of appropriate beam energy is important, since it defines the maximum thickness of the wire and cable insulation that can be effectively crosslinked by the penetrating electrons. Above 1MeV, the penetration depth of electrons into material is almost nearly proportion to their energy. Thus, 2MeV electons penetrate water to a depth of 11mm, while 1MeV electrons penetrate to 5.5mm. While, below 1MeV, the proportionality factor is no longer a constant and electron penetration depth drops off fasters than their energy. Also, the penetration is inversely proportional to the specific gravity of the material being irradiated. For example, a 100μm aluminum sheet (specific gavity = 2.7) is equivalent to 270μm of water.

3. Development of Environment-friendly Cables

3.1 Environment-friendly Cables

There are three different approaches to make an environment-friendly materials for wire and cables: (1) lead free PVC, (2) dioxin free brominated flame retardant polyolefin(PO), (3) HFFR PO.

When PVC is processed at high temperature without a stabilizer, it is degraded by dehydrochlorination and chain scission. Free hydrogen chloride (HCl) evolves and discoloration of the resin occurs along with important degradation in physical and chemical properties. Lead stabilizers are commonly used for PVC because they are characterized by outstanding electrical properties as well as thermal stability. At present, lead stabilizer is being replaced by lead free stabilizers which made of plurality of metallic soaps such as Ca/Zn, Ba/Zn and hydrotalcite.[8)]

Regarding the incineration of plastics filled with several BFRs, there is a concern about the possible emission of dioxin and furans. BFRs comprise a diverse group of chemical classes, which are used or have been used in array of commercial and industrial applications for the purpose of fire prevention. The accumulation of several classes of BFRs in the environment has become increasingly evident. Recently, the EC proposed to restrict the use of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs). In the meantime, dioxin free BFRs are introduced to replace the decabrominated diphenyl ether (deca-BDE) which is a major flame retardant in the cable industry. Fig. 4 represents the structural formulas of dioxin, furans and two BFRs.[9)]

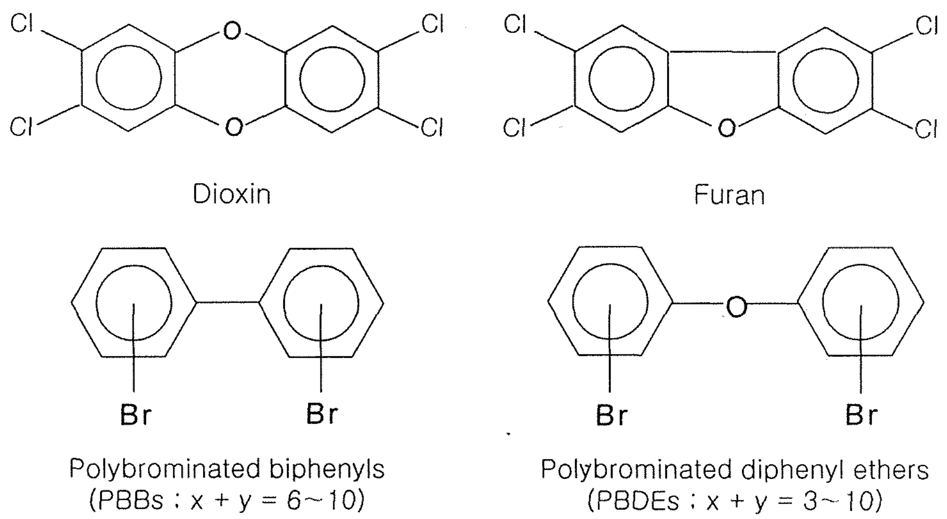

Fig. 4. Structural formulas of dioxin, furan and two BFRs (PBBs, PBDEs).

Unlike "lead free PVC" and "dioxin free PO", HFFR PO exhibits not only flame retardant property but also low smoke and low toxic gas emissions during combustion. HFFR PO mainly consists of blends of polyethylene and ethylene copolymers such as ethylene vinylacetate and ethylene ethylacrylate. The majority of HFFR PO incorporates ATH and MDH as a flame retardant. The flame retardation mechanism of ATH is based on its thermal decomposition between 200~400℃. During this energy consuming endothermic reaction process, ATH releases its chemically bonded water, while the corresponding aluminum oxide remains as char residue. Consequently, heat energy is removed from the burning zone and generated steam cools the compound surface. The atmosphere directly surrounding the compound surface is diluted by lowering the oxygen content and the concentration of burnable gases which come from thermal decomposition of the polymer matrix. The aluminum oxide layer provides a protective layer on the surface of the burning material, preventing oxygen and heat reaching it.[6]

Table 1. Applications of HFFR PO compounds.

Application		Not-crosslinked	Crosslinked		
			Radiation	Peroxide	Silane
Electronics	Consumer Electronics	○	○		
	Electrical Appliances	○	○		
Transportations	Automotive	○	○		
	Rail Transport	○	○	○	
	Marine & Offshore	○	○	○	○
Building and Construction		○		○	○
Power transmission and distribution		○		○	○
Communications		○			

HFFR PO are applicable to a wide variety of applications including electronics, transportation, construction, communications and power transmission as shown in Table 1.

The radiation crosslinking method is most productive for small-sized and thin wall wires. Thus, HFFR wires used for electronics and automotives have been produced by the radiation crosslinking method. The advantage offered by electron crosslinking is that products can be crosslinked in their final solid form. This gives great flexibility in extrusion of wire and cable materials. The degree of crosslinking is controlled by the electron dosage, which is usually expressed in megarads. With radiation crosslinking, the molecular weights of the matrix polymers can be better controlled.

A photograph of the HFFR PO insulated wires for electronics is show in Fig. 5.

Fig. 5. A photograph of HFFR wires used for electronics and automotives.

3.2 Effects of Electron Beam Crosslinking on Properties

Radiation induces the ionization of the polymer and creates free radicals on carbon atoms. These are ready to give direct covalent bonding between the chains of polymer. Thus, the crosslinking process changes a linear network into a three-dimensional one. Consequently, it gives a significant improvement in their mechanical behavior with temperature.

Fig. 6 shows the effect of radiation crosslinking on stress-strain behavior of HFFR insulation at ambient temperature. In this figure, the labels which read R00, R20, R40 and R60 represent the cases when the radiation dosages are 0mA (not-crosslinked), 20mA, 40mA and 60mA respectively. From this figure, it can be informed that when the radiation dosage getting higher, the yield strength, ultimate tensile strength and toughness are also getting higher, while the elongation at break somewhat lowers. This behavior comes from the fact that the higher radiation dosage, the higher crosslinking density.

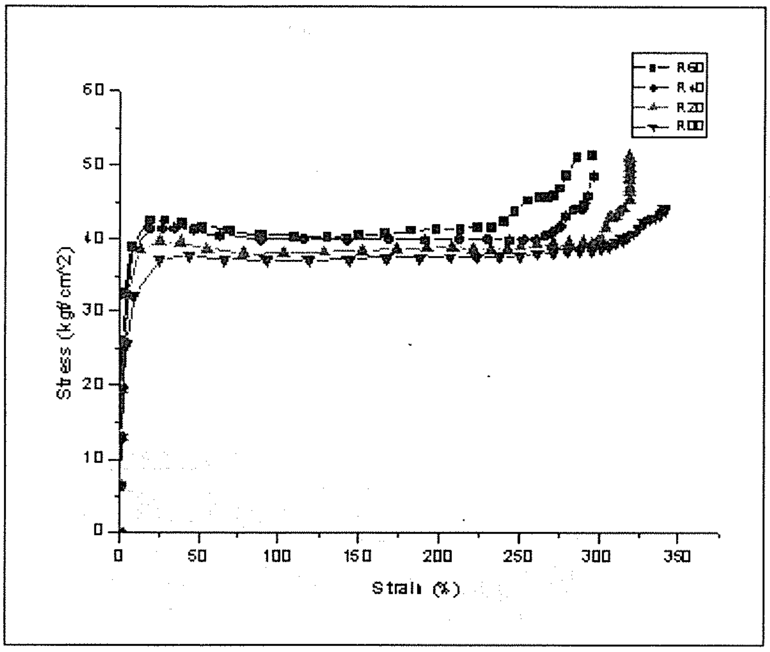

Fig. 6. Effect of radiation crosslinking on stress-strain behavior of HFFR insulation at ambient temperature.

At elevated temperature, the effect of radiation crosslinking is even more dramatic than that at ambient temperature. Fig. 7 shows the effect of radiation dosage on stress-strain behavior of HFFR insulation at elevated temperature, say 120℃. In this figure, R00T120 label means 0mA of radiation dosage (that is, not-crosslinked) and R20T120, R40T120, R60T120 stand for the case of 20mA, 40mA and 60mA respectively. Just like the result shown in Fig. 6, as the irradiation dosage increases, the yield strength, ultimate tensile strength and toughness of HFFR insulations are getting higher with slight decrease of elongation at break. Comparing the ultimate tensile strength, the result at ambient temperature shown in Fig. 6 tells that the ultimate tensile strength of 60mA case increased about 20% more than that of not-crosslinked case, while at elevated temperature, there is about 400% increase. Such a high increase in mechanical properties at elevated temperature ensures its superior high temperature stability.

From Fig. 6 and Fig. 7, it can be concluded that the radiation crosslinking of HFFR insulation improves its mechanical properties. In addition, the effect of radiation is more evident at high temperature.

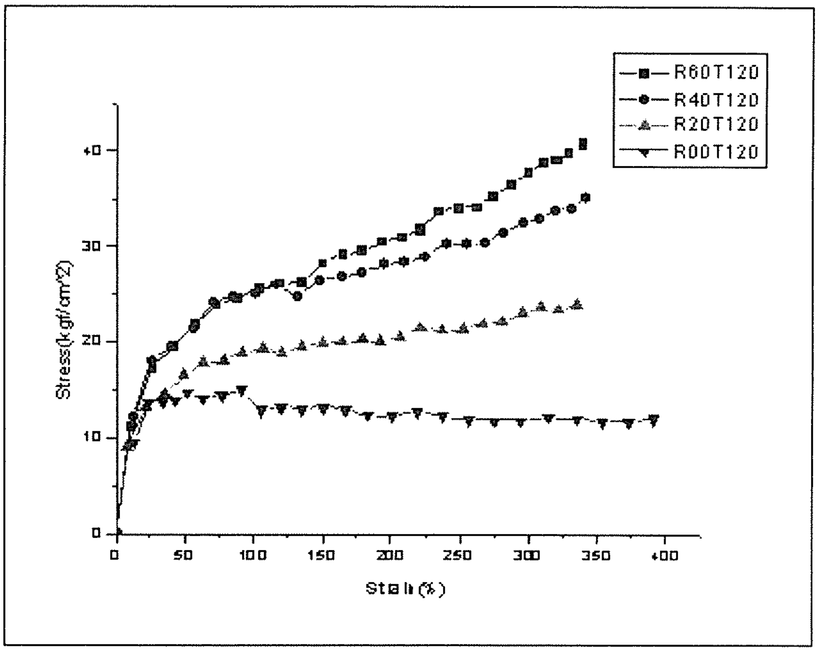

Fig. 7. Effect of radiation crosslinking on stress-strain behavior of HFFR insulation at elevated temperature.

3.3 Evaluation of Environment-friendly Cables

Environmental hazard of wire and cables is usually assessed by analysis of toxic materials and fire tests.

Toxic materials including heavy metals and halogens can be analyzed by XRF (X-ray fluorescence spectrometer) and ICP-AES (inductively coupled plasma-Atomic emission spectrometer). These analyses are applied to polymer samples used for insulation and jacket in the cable.

Fire hazard assessment involves four basic principals which require performance measurement as follows:

1) Fire Retardancy and Propagation
2) Smoke Generation Characteristics
3) Corrosivity
4) Toxicity

The fire retardancy and propagation is tested by prescriptive standards such as single and bunched vertical burning. Especially these tests concern fire propagation on a pass/fail basis. UL VW-1 (UL1581, section 1080) as shown in Fig. 8 is a representative test methods for wire and cable.

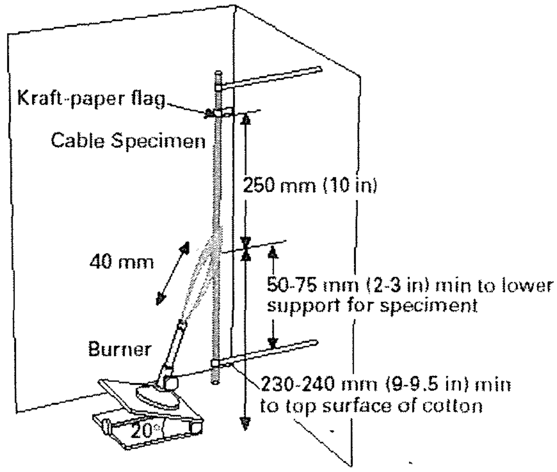

Fig. 8. UL 1581, section 1080 flame test method (VW-1).

In a fire situation, smoke obscures visibility thus impeding the escape of people. Smoke obscuration is mostly assessed in materials tests, particularly the NBS smoke chamber like ASTM E662. Low smoke cables are qualified by the 3 meter cube test (IEC 61034) as shown in Fig. 9.

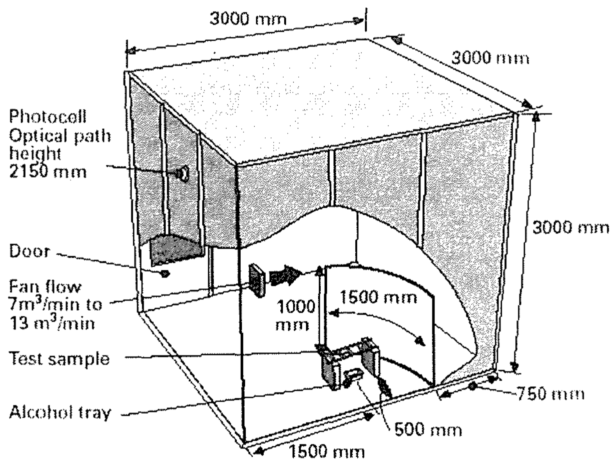

Fig. 9. 3 meter Cube Smoke Test Method (IEC 61034).

Acid gases combine with water to cause metal corrosion. Currently, acid gases were believed to be the only reason of corrosion. Thus, corrosive potential of smoke was determined based only on acid gas emission rankings after material combustion in a hot tube furnace under an air flow. Water soluble effluents were captured and the solutions titrated for acid gas content (HCl, HBr, HF), acidity (pH) and conductivity (IEC 754).

There is no doubt that the inhalation of toxic products formed during the combustion process is a major cause of injuries and fatalities occurring in fires. The UK Navy requires cable materials to meet NES 713: a small burner is used on cable materials, and concentrations of a set of 12 combustion gases are measured with Draeger tube. Concentrations are then divided by pre-specified NES 713 toxicity indices to obtain an overall index, which is better as it gets lower.

4. Conclusion

In this paper, it is presented that the status and role of the electron beam radiation technique in wire and cable industry. The radiation crosslinking is a crucial way to improve mechnical properties and thermal properties of insulation and sheath material especially for environment-friendly wire and cable. In addition, the trend in development of environment-friendly cable and test methods for fire performance of wire and cable are also explained. In conclusion, it is global trend to make wire and cable to be environment-friendly cable. Thus, the radiation crosslinking of wire and cable will be a prevailing crosslinking method for the future.

References

1. A. Bhattacharya, progress in polymer science, **25**, 371, 2000
2. K. Moriuchi, et al., SEI Technical Review, **54**, 81, 2002
3. H. Kimura, et al., Hitachi Cable Review, **20**, 79, 2001
4. European Union, "Directive on Waste Electric and Electronic Equipment", Official journal of the European Union, L37/24, 2003
5. European Union, "Directive on Restriction of the use of certain hazard in Electric and Electronic Equipment", Official journal of the European Union, L37/19, 2003
6. J. Troitzsch, "Plastics Flammability Handbook", Hanser Pubrishers, New York, 45, 1983
7. S. Venkatraman, Advances in Polymer Technology, **9**, No.3, 265, 1089
8. H. Zweifel, "Plastic Additives Handbook", 426, 2000
9. H. Hakk and R. J. Letcher, Environmental International, **29**, 801, 2003