ABSTRACT

The effects of electron beam (EB) irradiation on dielectric breakdown voltage (BDV) and insulation resistance ($\rho_I$) changes of poly(ethylene-co-tetrafluoroethylene) (ETFE) insulated electric wire were investigated. Electric wire was prepared by extruding pristine ETFE. The samples were irradiated in air at room temperature by a universal EB accelerator by doses ranging from 1 to 20 Mrad. The thermal behaviour of extruded samples has been also investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). When the ETFE insulated wire was exposed to EB irradiation, BDV and $\rho_I$ were decreased gradually with irradiation dose. As the irradiation dose increased, the char formation and size of breakdown point were decreased significantly (above 10 Mrad). In TGA study, the thermal stability of EB-irradiated ETFE samples decreased significantly with radiation dose. For ETFE-20 the TGA traces showed a shift of the weight loss towards lower temperature with stabilization of 50°C lower than pristine ETFE. DSC Melting temperature ($T_m$) and crystallization temperature ($T_c$) of EB-irradiated ETFE tended to decrease as the irradiation dose increased. The crystallinity ($\chi$) was slightly increased up to 5 Mrad irradiation dose and decreased significantly with irradiation dose above 5 Mrad. An increase in $\chi$ values occurred due to chain scission in the amorphous region, which led to crystallite perfection. The chain scission process created shorter polymer chain links which became easier to fit into a localized crystalline domain. At higher EB irradiation dose, the crystalline structure tended to be destroyed which led to decreases in $T_m$ and $T_c$. After EB irradiation, the tensile properties and scrape abrasion resistance of ETFE were also decreased with respect to pristine ETFE.

INTRODUCTION

The effects of high-energy irradiation on polymers can lead to changes in their properties, and their interaction with high-energy electrons is a complex and random process [1]. The changes resulting from irradiation are mainly a consequence of electron absorption followed by bond cleavage to give radicals, radical recombination leading to the formation of cross-links and end-links or disproportionation to give chain scission and gas evolution, mainly by radical recombination [2,3]. The final result depends on the nature of the material, on the dosage, dosage rate and the radiation energy. Thus, there are many ways to exploit these processes technologically, such as
cross-linking [4-7] and surface modification [8-10].

Poly(ethylene-co-tetrafluoroethylene) (ETFE) copolymers occupy a special position among fluoropolymers as they are contain alternating structural units of polyethylene and poly(tetrafluoroethylene) which are conferred with a unique combination of properties imparted from both hydrocarbon and fluorocarbon polymers [5]. They are commonly used in nuclear industry for tie or cable wraps, and in the aviation industry as coating materials. Another key use of ETFE is for the covering of electrical wiring used in high stress, low fume toxicity and high reliability applications. ETFE is frequently used as wire insulation either in its natural state [11] or cross-linked for improved physical properties [12-15]. Electron beam (EB) cross-linked ETFE wire is widely used in aircraft airframes. Electrically insulated wires are often used in environments in which the physical, mechanical, electrical and thermal properties of the insulation are put to test by extreme conditions. The ETFE insulation is thinner and lighter than the materials used for comparable wires. It can be used at temperatures up to 200°C and will withstand temperature as low as -65°C [14]. This is because ETFE copolymers have excellent mechanical toughness, chemical resistance and electrical properties [10]. In addition, ETFE exhibits a high-energy radiation resistance and can withstand moderately high temperatures for a long period of time.

Wolf et al. have studied the thermal oxidative degradation of a semi-crystalline thermoplastic polymer and ETFE used for electrical insulation as a function of irradiation, temperature and its contact with a metal surface [16]. They found that the rate of thermal degradation is a strong function of the total radiation dose regardless of its conductor element. A spectroscopic evaluation of a commercial wire insulation based on a cross-linked ETFE was also conducted by Morelli et al. to determine the chemical changes taking place during thermal aging. These studies have provided insight into the roles of the various additives, such as triallylisocyanurate and antimony oxide, in the formulated cross-linked ETFE insulation [17]. However, research works on the effect of electron-beam irradiation on ETFE insulated wire and its consequent radiation induced changes on the insulation properties are scarce despite their extensive use [11-17]. As in the case of many other polymeric materials, ionizing radiation has various effects on fluoropolymers and fluorinated polymers [3-6]. The absorbed dose distribution depends on the thickness, density and atomic composition of the insulation as well as the diameter and composition of the metallic conductor. Because of the cylindrical geometry and the shielding and backscattering effects of the conductor, accurate calculations of the dose distribution are not simple [15]. In this study, the effects of electron beam (EB) irradiation on ETFE insulated electric wire were studied. Insulations are commonly used as a flexible polymer coating on electric wire. The service life of an electric wire is determined by the condition of the insulating material [18,19]. An electric wire was prepared by extruding pristine ETFE and EB-irradiated at doses ranging from 1 to 20 Mrad. The microstructure, electrical, mechanical and thermal properties of EB-irradiated wire were evaluated.

**EXPERIMENTAL**

**Materials**

ETFE resin (Neoflon EP512, Daikin Industries, Tokyo, Japan) was used as received. The resin was pre-dried in a convection oven for at least 12 h at 100°C to remove any moisture from the pellets before processing. The characteristics of the resin used in this study are summarized in Table 1.

**Extrusion of Electric Wire**

The electric wire was composed of a conductor and

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<table>
<thead>
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<th>Table 1. ETFE Specifications.</th>
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<tr>
<td>Material</td>
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<tr>
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<tr>
<td>ETFE</td>
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an insulation layer. The insulation layer was applied to the annealed copper conductor by extrusion with ETFE resin (thickness: 1 mm). ETFE pellets were dried in a hopper equipped with a dehumidifying dryer at least 24 h at 100°C to remove any moisture from the pellets before extruding. The wire sample was extruded (temperature setting of rear zone: 280°C, second zone: 295°C, forward zone: 305°C, adapter: 320°C and die: 340°C) at a speed of 200 rpm using a single screw extruder (TE4001, Dong Bang Engineering, Ansan, Korea) equipped with 40 mm of diameter screw. Extruded samples were quenched by passage through a water-cooling zone at a rate of 50 m/min.

**Electron Beam Irradiation of Electric Wire**

Electron beam irradiation of extruded wire was carried out using an EB accelerator (ELV 4, EB Tech Co., Daejeon, Korea). The samples were placed on a tray of a conveyer and irradiated in air at room temperature. The conveyer speed was kept constant at 1 m/min. The applied irradiation dose was varied from 1 to 20 Mrad by increasing the number of passes. The doses were verified using cellulose triacetate (CTA) dosimeter film based on ISO/ASTM51650 [20]. The specifications of the ELV-4 are presented in Table 2.

**Characterization**

Insulation resistance ($\rho_I$) of samples was measured by a megohmmeter (TeraOhm 5kV, Metrel, USA) according to ASTM D 257 [21]. The charge time was 30 s, and the current stress of the measurements was 500 V at 20°C ± 1°C.

Scanning electron microscopy (SEM) observations of the samples were performed on a Hitachi S-4300 model (Tokyo, Japan). The fractured surfaces of the composites were prepared by using cryogenic fracturing in liquid nitrogen followed by a coating with platinum in an SPI sputter coater. The morphology was determined using an accelerating voltage of 15 kV.

The Fourier transform infrared (FTIR) absorption spectra of the EB-irradiated samples were measured with a Perkin Elmer infrared spectrometer (Spectrum 2000, Shelton, CT) in KBr pellets. The spectra were measured in the wavenumber range from 4000 to 400 cm$^{-1}$ and analyzed using a commercial software.

The surface appearance of samples was measured with a video microscope (Inf-500TM, charge-coupled device (CCD) video microscope, Moritex Corp., Tokyo, Japan) with a PC that contained video capture software (i-Solution Lite, Image & Microscope Technology, Daejeon, Korea).

Thermal properties of the specimen were determined by DSC (differential scanning calorimetry) (Perkin Elmer DSC 7, Norwalk, CT). The thermal history of the samples was removed by scanning to 300°C with the heating rate of 20°C/min. After cooling down the specimen to room temperature at the rate of -5°C/min, it was re-heated at 20°C to 300°C with the heating rate of 20°C/min and the DSC curves were obtained. The heat of melting and the heat of crystallization were calculated from the areas under the melting and cooling peaks, respectively. The degree of crystallinity ($\chi$) was calculated using the following equation [5]:

$$\chi(\%) = \left( \frac{\Delta H_m}{\Delta H_{m100}} \right) \times 100$$  \hspace{1cm} (1)

where, $\Delta H_m$ is the heat of melting of ETFE films and it is proportional to the area under the melting peak and $\Delta H_{m100}$ is the heat of melting of 100% crystalline ETFE polymer, which equals 113.4 J/g [4].

Thermal stability of samples was determined by thermogravimetry (TGA Q50, TA instrument, USA). The TG curves were obtained under N$_2$ atmosphere at a flow rate of 4 mL/min and a scanning from 20°C to 800°C with the heating rate of 20°C/min.

**Table 2. Specifications of the ELV-4 EB accelerator.**

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>EB power (kW)</th>
<th>Non-uniformity of current density (%)</th>
<th>Input voltage (V)</th>
</tr>
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<tr>
<td>0.8~1.5</td>
<td>50</td>
<td>&lt; 10</td>
<td>220/380</td>
</tr>
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Tensile Test Procedure
Tube type specimens for mechanical tests were prepared in accordance with IEC 60811-1-1 [22] specification. The sample of wire was cut into pieces approximately 100 mm long and the conductor was removed by careful rolling of the wire under low mechanical force. The test specimens were preconditioned to 20% relative humidity and 20 ± 1°C in order to standardize test conditions. Tensile properties of the samples were determined with a universal test machine (UTM, Model DECMC00, Dawha Test Machine, Korea) at a cross-head speed of 250 mm/min. The mean value of at least five specimens of each sample was taken, although the specimens that broke in an unusual manner were disregarded.

Scrape Abrasion Resistance Test
Scrape abrasion resistance was measured using an Abrasion Tester (Core Tech, Korea). The test pieces were 750 mm of extruded wire in length and they were prepared by EB irradiation. The travel distance of specimen was 10 mm at a speed of 60 cycles per minute and the test loads were 5 N and 10 N. The abrasive used was a needle (material: tungsten carbide, diameter: 4.5 mm, knife: 4.5 mm × 1 mm). Each specimen underwent five tests and was moved about 100 mm between each test and turned at an angle of 90°, always in the same direction. A wire sample was fixed to the sample holder and 24 V direct current (DC) voltage was applied between abrasive and wire conductor. When electric contact occurred between abrasive and conductor, test equipment stopped running and the cycles at breakdown were automatically counted.

Flexibility Test
A straight piece of 300 mm wire was carefully wound in 10 continuous adjacent turns around a polished mandrel of 60 mm diameter. The specimen was placed into an oven with forced air circulation at room temperature or 240°C for 30 min. After removal from the oven, the specimen was allowed to cool to room temperature. After cooling the thermally aged wire was straightened and was examined for cracks under a video microscope.

Breakdown Voltage Measurement
The measurements of breakdown voltage (BDV) were carried out at 60 Hz alternating current (AC) voltage by using a high voltage tester (SM-40PT08, Sungmin Instruments, Korea) with a rate of 0.5 kV/s in air. The test sample consisted of copper conductor (diameter of 2 mm) and outer insulator (insulation thickness of 1 mm). Before conducting the BDV test, an aluminium foil was wrapped around the outer surface of the wire. An AC voltage was applied between the aluminium wrap and the wire conductor and a dielectric BDV was measured. Ten samples were tested and the average voltage was calculated.

RESULTS AND DISCUSSION
BDV and ρ_1 Changes of Extruded Wire after EB Irradiation
The ETFE insulated wire was subjected to EB irradiation (1 to 20 Mrad) and the BDV measurement results of the EB-irradiated samples are summarized in Table 3 (left part). The abbreviation of the sample code in Table 3, ETFE-01, for example, means that

<table>
<thead>
<tr>
<th>Sample code</th>
<th>EB irradiation</th>
<th>Thermal aging at 240°C for 30 min</th>
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<tr>
<td></td>
<td>Flexibility</td>
<td>BDV (kV)</td>
</tr>
<tr>
<td>ETFE</td>
<td>No crack</td>
<td>21.6 ± 0.6</td>
</tr>
<tr>
<td>ETFE-01</td>
<td>No crack</td>
<td>21.3 ± 0.6</td>
</tr>
<tr>
<td>ETFE-05</td>
<td>No crack</td>
<td>20.9 ± 1.1</td>
</tr>
<tr>
<td>ETFE-10</td>
<td>No crack</td>
<td>20.5 ± 1.4</td>
</tr>
<tr>
<td>ETFE-15</td>
<td>No crack</td>
<td>18.7 ± 0.5</td>
</tr>
<tr>
<td>ETFE-20</td>
<td>No crack</td>
<td>16.8 ± 1.9</td>
</tr>
</tbody>
</table>
the ETFE insulated wire was EB-irradiated at 1 Mrad. The BDV of ETFE-01, ETFE-05 and ETFE-10 were slightly changed compared with pristine ETFE. In sharp contrast BDV of ETFE-15 and ETFE-20 were decreased significantly. Approximately 13% and 22% decreases were observed in BDV of 18.7 and 16.8 kV, respectively. The dielectric breakdown causes a high-temperature arc to propagate through a dielectric medium and these can lead to ignition of the medium or of the surrounding objects. Figure 1 demonstrates the breakdown points after dielectric breakdown test. As the irradiation dose increased, the char formation and size of breakdown point were decreased significantly (above 10 Mrad). This means that the breakdown of EB-irradiated wire is determined by the electrical field at the tip of the defect.

**Figure 1.** Images of the breakdown points after dielectric breakdown test (200x).
After EB irradiation, the changing $\rho_I$ of wire samples also shows the same behaviour (Figure 2). $\rho_I$ is the resistance to current leakage through and over the surface of the material. It is found that by measuring the direct current or voltage drop across an electrical insulating material its resistance may be determined by the application of Ohm's law and it is typically expressed in M$\Omega$. The microstructural defects such as voids, cracks, delaminations and impurities are associated with variations of $\rho_I$.

Figure 3 represents SEM micrographs of the fractured surface of the extruded ETFE insulation before and after EB irradiation. The pristine ETFE shows a single phase with clear brittle fracture behaviour. After irradiation at 5 Mrad, the fractured surface did not show any morphological change.
compared with pristine ETFE. In the micrographs taken on the surface of 15 and 20 Mrad irradiated specimens, the wave texture was disappeared and many voids were found.

As shown in Scheme I, the radiation induced chemical changes in polymers including chain cross-linking, chain scission and creation of small molecular products, structural and morphological changes [5,9]. When voids are present in solid dielectrics and the electrical field is sufficiently high, the air or other gases inside the voids ionizes and creates breakdown pulses across the voids. These pulses are referred to as discharges. Most solid-dielectric insulations degrade under the presence of partial discharge and lead to premature failure of the insulation. These discharges result in an increase in current flow through the insulation between the conductor and ground and a consequent reduction in the amount of current which is able to be transmitted through the conductor. This failing process increases the dielectric absorption current taken by the insulation, and megohmmeter shows a decrease in $\rho_I$ with increasing voids in insulation by EB irradiation.

**Scheme I.** Schematic representation of mechanism of EB irradiation induced reactions in ETFE.

Thermal Stability of ETFE Insulated Wire after EB Irradiation

Table 3 (2 columns in the right) shows the result of flexibility test and dielectric BDV of EB-irradiated wires after thermal aging at 240°C for 30 min. After flexibility test at 240°C for 30 min, extruded- and EB-irradiated wire did not show insulation crack phenomenon. The BDV of pristine ETFE was not significantly changed after thermal aging. In general, continuous maximum temperature rating of ETFE insulated wire is 155°C. It withstands temperature up to 180°C for 168 continuous hours [23] and it goes under thermal aging at 240°C with no cracks detected after exposure for 30 min [24]. In sharp contrast, when the EB-irradiated wire has been exposed to thermal aging at 240°C for 30 min, the BDV reduction is more significant (Table 3). The BDV reductions are 12.6, 17.2, 21.9, 24.2 and 34.9% as in the order given for ETFE-01, ETFE-05, ETFE-10, ETFE-15 and ETFE-20 with respect to that of corresponding un-irradiated thermally aged sample. The thermal aging is manifested in two ways of forming polymer radicals [25] and microvoids [26] in the material. This leads to formation of defects of extruded layer and lowering the BDV of wire samples significantly [19].

Figure 4 demonstrates the surface images of EB-irradiated wire before and after thermal aging at 240°C for 30 min. The surface of the EB-irradiated samples shows increased scratching with the irradiation dose. In sharp contrast, after thermal aging of the EB-irradiated samples the number and the size of the black spots on the surface of insulation were increased as the irradiation dose increased. The
accelerated aging at higher temperature is caused by an increasing thermal degradation of an organic material. Structural changes in ETFE that accompany the formation of surface defects by the EB irradiation can cause significant reduction in thermal oxidation resistance of insulation.

TGA Measurements were also conducted on EB-irradiated samples to elucidate their thermal degradation behaviours. Some typical weight-loss curves as a function of temperature are shown in Figure 5. The weight loss of fluoropolymers is associated with evolution of small molecules initially beginning with water and then low molecular weight oligomers and finally HF. It is observed that the partially fluorinated ETFE is stable up to 450°C and shows one step of weight loss. In contrast, the thermal stability of EB-irradiated ETFE samples decreases significantly with increasing radiation dose. For ETFE-20 the TGA traces show a significant shift of the weight loss towards lower temperature with stabilization of 50°C lower than pristine ETFE. As listed in Table 4, it can be seen that the pristine ETFE exhibits a higher thermal-oxidative stability in terms of $T_{5\%}$ (a mass loss of 5% occurs during degradation) with
Figure 5. TGA Thermograms of the EB-irradiated ETFE samples.

respect to that of EB-irradiated samples. Meanwhile, the residues at 500°C are 84.9, 82.6, 63.7, 57.3, 54.6 and 49.5% for ETFE, ETFE-01, ETFE-05, ETFE-10, ETFE-15, and ETFE-20, for the above given order, which confirms that the EB irradiation facilitates thermal degradation. These findings are in good agreement with the result of the BDV reduction listed in Table 3.

After thermal aging, it is also found that the copper conductor of EB-irradiated wire changed into yellowish colour (Figure 6). This suggested that EB irradiation could promote dehydrogenation of ETFE at a lower temperature compared to pristine ETFE. Copper oxidizes slowly in air, corroding to produce a brown or green patina. At higher temperatures the process is much faster and produces mainly black copper oxide (Figure 6a). The oxide can be reduced by hydrogen gas (H$_2$), which is a moderately strong reducing agent, producing a shiny, clean copper surface.

Equations for the reactions are:
\[
2Cu (s) + 1/2O_2 (g) \rightarrow 2CuO (s) \\
CuO (s) + H_2 (g) \rightarrow Cu (s) + H_2O (g)
\]

Figure 7 shows FTIR spectra of pristine and EB-irradiated ETFE samples. After EB irradiation, small adjacent bands at 1741 and 1654 cm$^{-1}$ can be identified and their amplitudes increase with increasing irradiation dose. These two bands are assigned for -C=O and -C=C- groups, respectively [5]. Moreover, the intensity of the band at 2985 cm$^{-1}$ decreases with increasing irradiation dose, which could be an indication of cleavage of C-H bonds.

### Mechanical and Thermal Properties Changes after EB Irradiation

Table 5 summarizes the effect of EB irradiation on the tensile properties of ETFE copolymer. It is noteworthy that tensile strength of EB-irradiated samples was slightly decreased upon irradiation. In sharp contrast, the elongation-at-break of EB-irradiated samples was decreased gradually with irradiation dose. In case of ETFE-20, an approximately 57% decrease in the elongation-at-break of 210% was observed relative to that of pristine ETFE. The decreased tensile properties of the EB-irradiated samples might be explained by the scission of macromolecular chains induced by EB irradiation [3]. It can be also found that there is a
Figure 6. Surface images of EB-irradiated conductor samples before and after thermal aging at 240°C for 30 min (300x).
decreasing trend in scrape abrasion resistance with increase in irradiation dose compared to un-irradiated wire (Figure 8). As scrape abrasion resistance basically depends on the hardness of a material, this may indicate that EB irradiation also results in reduction of surface hardness.

The results of DSC thermal properties of EB-irradiated samples are summarized in Table 6. Melting temperature ($T_m$) and crystallization temperature ($T_c$) of EB-irradiated ETFE tend to decrease as the irradiation dose increases. In general, it is accepted that the effect of irradiation, either electron beam or gamma rays, on the crystalline region causes some imperfections. Meanwhile, $\chi$ was slightly increased up to 5 Mrad and decreased significantly with irradiation dose above 5 Mrad. The polymer melting behaviour and crystallinity were influenced by radiation processing [4, 5]. An increase in $\chi$ values occurs due to chain scission in the amorphous region, which leads to crystallite perfection. The chain scission process creates shorter polymer chain links which become easier to fit into a localized crystalline domain. At higher EB irradiation dose, the crystalline structure tends to be destroyed which leads to decreases in $T_m$ and $T_c$.

**CONCLUSION**

Pristine ETFE resin was extruded as an electric wire...
and the EB irradiation effects on the microstructure, electrical, mechanical and thermal properties of extruded wire were investigated. When the ETFE insulated wire was exposed to EB irradiation, BDV and $\rho_I$ were decreased gradually with increased EB irradiation dose. This was due to EB irradiation induced chemical changes in polymers creating weak pathways and they reduced $\rho_I$ and accelerated dielectric breakdown. SEM Observation confirmed that the original wave texture was disappeared and many voids were emerged at the fracture surface of ETFE-15 and ETFE-20. TGA Traces showed that the thermal stability of EB-irradiated ETFE samples decreased significantly compared with pristine ETFE. After EB irradiation the tensile properties and scrape abrasion resistance of the extruded wire samples also decreased with irradiation dose. The reduction of thermal stability and mechanical properties was considered to be due to macromolecular chain scission induced by EB irradiation. FTIR Spectral analysis showed that in EB-irradiated samples, the formation of $\text{-C=O}$ and $\text{-C=C-}$ groups can be identified and their amplitude is increased with irradiation dose. Moreover, the intensity of the band at 2985 cm$^{-1}$ is decreased with increasing irradiation dose, which could be an indication of cleavage of C-H bonds. After thermal aging the colour of copper conductor of EB-irradiated wires was turned yellowish. It can be explained that EB irradiation could promote dehydrogenation of ETFE at a lower temperature compared with pristine ETFE. After EB irradiation, the $T_m$ and $T_c$ of ETFE fall gradually with irradiation dose, whereas $\chi$ is slightly increased up to 5 Mrad and it is decreased significantly thereafter. Upon EB irradiation in the presence of a copper conductor, ETFE is prone to reactions such as chain scission, formation of unsaturated bonds and oxidation, resulting in less crystalline perfection and consequently lower $T_m$ and $T_c$.

REFERENCES


