Electrical Conductivity Enhancement of PTFE (Teflon) Induced by Homogeneous Low Voltage Electron Beam Irradiation (HLEBI)

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Electrical conductivity (σ) enhancement, control, aging stability, and linear relation between σ and reciprocal temperature (1/T) in PTFE (Teflon) had been examined by homogeneous low potential electron beam irradiation (HLEBI). Irradiations up to 0.432 MGy were found to raise the σ of PTFE more than two orders of magnitude. In addition, control of electron movement or Fermi level by HLEBI on polymers seems possible since at low HLEBI levels up to 0.216 MGy, a strong dependence on σ was observed. Aging stability investigation showed the saturated conductivities at 10⁷ σ (2.5 × 10⁻¹⁰ and 3.6 × 10⁻¹³ S m⁻¹) obtained at EB doses of 0.0432 and 0.432 MGy, respectively were approximately 4.9 and 70.6 times higher than that of untreated PTFE (5.1 × 10⁻¹⁷ S m⁻¹). Although the aging initially reduced the σ of irradiated samples, σ was remarkably higher than the untreated. For example, the lower dose 0.0432 MGy samples decayed significantly, but its σ value (2.5 × 10⁻¹⁵ S m⁻¹) was still about 490% above untreated condition at 5.1 × 10⁻¹⁷ S m⁻¹. ESR (electron spin resonance) measurements showed aging for 10⁶ s only slightly reduced the peak intensity of irradiated PTFE. This indicated the charge carriers generated did not easily decay. Results agree with the literature where PTFE was irradiated with VUV and radicals such as CF₃⁺ did not substantially decay with aging. Since the slopes of linear relationships between logarithmic electrical conductivity (ln σ) and reciprocal temperature (1/T) of all PTFE samples irradiated were approximately equal to that before treatment from 303 to 375 K, HLEBI didn’t convert the system. The small irradiation dose of 0.0432 MGy raised the electrical conductivity at room temperature. At higher temperatures above ∼375 K, the 0.0432 and 0.432 MGy-HLEBI generated drops in conductivity σ. When unstable dangling bonds with isolated radicals at terminated sites are assumed to be formed in irradiated PTFE, the σ recovery by heating to 424 K as well as high σ of irradiated PTFE could be explained. HLEBI probably generated dangling bonds in the form of radicals acting as acceptors to carry charge. Since a chemical dopant was not needed to act as a charge carrier, HLEBI could probably be an attractive method to attain homogeneous doping of organic films. [doi:10.2320/matertrans.M2011273]

1. Introduction

Electro-conductive materials have been applied for industrial trials. Indium-tin-oxide (ITO)¹) is an electro-conductive ceramic exhibiting 10⁻¹⁵Ωm resistivity, which has been commercially utilized for transparent electrodes in liquid-crystal displays. On the other hand, an electro-conductive polymer is transparent poly(3,4-ethylenedioxythiophene) (PEDOT)³) which exhibits high electrical conductivity of 4.0 × 10⁻⁴·6.0 × 10⁻⁵ S/m. However, there are two serious problems. One is the price of PEDOT (1,520 yen/mL: Sigma-Aldrich Japan, Tokyo) is several times higher than that of ITO (The price of Indium is 660 yen/g: The Nilaco Corporation, Tokyo). Another is instability and lack of reproducibility of both electrical and mechanical properties. If these problems are solved, the flexible and transparent electro-conductive polymers can be utilized as low-cost flexible integrated circuits printed by ink jet.

The treatment of electron beam irradiation was employed. Two general types are high-voltage and low-voltage. The high voltage electron beam irradiation (EBI) is classified as having greater than one MeV (one MeV-class) and easily induces radiation damage:¹¹) its strength typically weakens materials. However, homogeneous EBI with extremely low voltage (HLEBI) on the order of 0.10 MeV (0.10-MeV-class) simply charges materials hence has been a good tool for enhancing hardening, elasticity, ductility and strength of ceramics, polymers and their composites.⁴⁻⁶) The action of the HLEBI often cuts weak covalent chemical bonds resulting in the generation of dangling bonds. Between the terminated atoms of the dangling bonds in the molecular structure therefore, repulsive force probably occurs between the outer shell electrons. As the local repulsive force probably relaxes the deformed strain with internal compressive stress,⁵⁻⁹) effects of HLEBI enhancing hardening, elasticity, ductility and strength can be expected and is well-documented for ceramics, polymers and their composites.¹⁻⁶)

Similarly, this work predicts electrical conductivity of conventional polymers can be raised approximately 2 orders of magnitude at low cost utilizing the 0.10 MeV-class HLEBI. Treatments were carried out to obtain the optimum absorbed dose. The polymer under study is polytetrafluoroethylene, PTFE (Teflon), illustrated in Fig. 1, being a powerful insulator with high heat resistance and having excellent tribology even at high temperature.

In PTFE, Ono et al. found irradiations of VUV generated mainly CF₃⁺ radicals,⁷) while Oshima et al. measured ESR spectra of PTFE degraded by ⁶⁰Co γ-ray irradiation reporting the presence of the alkyl radical (–CF₂–C–CF₂–) and the chain end radical (–CF₂–CF₂–).⁸) Hence, it is strongly expected these radicals along with CF₃⁺ are present in PTFE film for the electron beam irradiation. When PTFE is irradiated with HLEBI, the irradiation cuts the weak covalent bonds between monomers and forms dangling bonds with isolated atoms (Fig. 1(b)) and may generate free radicals. The dangling bonds may act as acceptors, or holes in a semiconductor attracting electrons from neighboring bonds. An electron will jump to repair the unpaired bond hence creating another hole. The process will repeat itself
generating current as in a p-type semiconductor. Since a chemical dopant is not needed to act as a charge carrier, HLEBI can be an attractive method to attain homogeneous doping of organic films. In addition, varying EB dose may make it possible to control the Fermi level which may have applications for semiconductors.

In glasses, HLEBI creates dangling bonds and increases mean atomic distance $r_D$ between neighboring atoms and decreases the coordination number, $N_D$. With the high electronegativity of F, the extra space created may assist charge carriers to flow more freely through the medium increasing electrical conductivity of PTFE. HLEBI has been, thus, expected to be a low cost method to enhance the electrical conductivity by dangling bond formation via the high density of electrons carrying the electric charges within the PTFE matrix.

The purpose of the present work is to control effects of HLEBI on the electrical conductivity of PTFE. Furthermore, the stability of the conductivity enhancement, i.e. the effect of aging has been evaluated.

2. Experimental Procedure

2.1 Sample and its electrical resistivity measurement

Samples were cut to $100 \times 100 \times 0.05$ mm in size from PTFE sheet 50 µm in thickness (Skived tape, Chukoh Chemical Industries, Ltd. Tokyo). With its high insulating properties, the electrical resistivity of PTFE could not be measured by using a standard DC four-probe method. Therefore, volume electrical conductivity measurements were taken with a universal electron meter (MMAII-17A, Kawaguchi Electric Works, Tokyo) at room temperature in air. Electrical conductivity measurements were taken intermittently up to 3 ks. Samples were subsequently aged further and conductivity measurements were taken intermittently up to $10^6$ s at 292.7 ± 3.3 K under Ar atmosphere.

2.2 Electron beam irradiation (HLEBI)

Sheet electron beam irradiation with low energy was homogeneously performed using an electron-curtain processor illustrated in Fig. 3 (Type CB175/15/180L, Energy Science Inc., Woburn, MA). After samples were cut to $100 \times 100 \times 0.05$ mm size, they were irradiated with the electron beam through a titanium thin film window attached to a vacuum chamber, 240 mm in diameter. A tungsten filament in a vacuum was used to generate the electron beam at a low energy with acceleration potential, $V$ of 170 kV and irradiating current density, $I$ of 0.089 A m$^{-2}$. Although electron beam generation was done in a vacuum, the irradiated sample was kept under protective N$_2$ gas at 1 atm pressure maintaining a residual concentration of oxygen below 400 ppm to prevent oxidation. The distance between sample and window was 35 mm. The N$_2$ gas flow rate was 1.5 L s$^{-1}$ at 0.1 MPa N$_2$ gas pressure. Samples were
placed in an aluminum plate holder (0.15 m \times 0.15 m) and transported on a conveyor at a speed of 10.0 m/min. The sheet electron beam irradiation was applied intermittently. One sweep going one way was 0.0423 MGy (kJ g\textsuperscript{-1}) for the short time of 0.23 s to avoid excess heating of the sample: the sample surface temperature remained below 323 K just after irradiation. Repetitive applications were applied to achieve the desired HLEBI dose to both side surfaces. The gap interval between sweeps was 30 s. The resulting EB dosage, \( D \) (MGy) was proportional to the yield value determined from the irradiation current, \( I \) (mA), conveyor speed, \( S \) (m/min), and number of irradiation sweeps (\( N \)) by the following equation.

\[
D = 0.216(I/S)N
\]

The yield value was calibrated by FWT nylon dosimeters (FWT-60-00: Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117, USA) and irradiation reader (FWT-92D: Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117, USA).

### 2.3 ESR analysis

To obtain more precise information on atomic-scale structural changes in the PTFE, the density of the dangling bonds was obtained using an electron spin resonance spectrometer (ESR, JES-FA200, JEOL Ltd. Tokyo).\textsuperscript{6,9} ESR is utilized to detect unpaired electrons by their spins (\( m_s = +/− 1/2 \)) since electrons have a magnetic moment and spin quantum number. The unpaired electrons’ magnetic moments either align themselves parallel or anti-parallel to an induced magnetic field producing a peak at a particular magnetic field, \( B \). The microwave frequency range used in the ESR analysis was the X-band at 9.45 ± 0.05 GHz with a field modulation of 100 kHz. The microwave power was 1 mW. The magnetic field was varied from 317 to 327 mT. The electron spin density was calculated using a Mn\textsuperscript{2+} standard sample. Only ESR spectra, instead of spin densities, were given.

### 3. Results

#### 3.1 HLEBI induced high electrical conductivity of PTFE sheet

Figure 4 shows effect of EB dose (\( D/MGY \)) on electrical conductivity (\( \sigma/\text{S}\text{-m}^{-1} \)) of PTFE. HLEBI to 0.216MGy enhances the electrical conductivity over 2 orders of magnitude from \( 5.1 \times 10^{-15} \) to \( 1.7 +/− 0.8 \times 10^{-14}\text{S}\text{-m}^{-1} \). Moreover, the \( \sigma \) values (\( 1.7 +/− 0.8 \times 10^{-14} \) and \( 6.1 \times 10^{-15}\text{S}\text{-m}^{-1} \)) of PTFE treated by HLEBI with 0.216 and 1.296MGy are about 333 and 120 times higher than that of untreated PTFE (\( 5.1 \times 10^{-17}\text{S}\text{-m}^{-1} \)), respectively.

Figure 4 suggests control of electron movement, or Fermi level by HLEBI seems possible. At low HLEBI levels, \( \sigma \) shows a strong dependence up to 0.216 MGy after which \( \sigma \) is approximately constant up to 1.296MGy.

#### 3.2 Dangling bond formation

Conventional X-ray diffraction patterns of the PTFE were obtained before and after HLEBI. However, remarkable differences were not observed.

On the other hand, Fig. 5 shows HLEBI produces detectable ESR signals in the PTFE: as irradiation dose is increased from 0.0432 to 0.432MGy, the signal intensity increases and the signal peak is sharpened showing an increase in unpaired electrons, which are probably dangling bonds.\textsuperscript{5,6,9}

HLEBI often cuts the weak covalent atomic bonds between monomers generating dangling bonds of the terminated atoms in PTFE, resulting in a high density state of outer shell electrons. These dangling bonds may be in the form of radicals. ESR signals are similar in shape and magnetic field value (\( B \)). Thus, it is possible one type of dangling bond is observed in the irradiated PTFE. In contrast, a signal is not found in the untreated samples. This is because ESR is utilized to detect unpaired electrons by their spins (\( m_s = +/− 1/2 \)). The ESR field is examined in the \( B \) range of 317 to 327 mT before and after HLEBI. Note Fig. 5 shows for the small dose 0.0432MGy irradiated samples, a small ESR peak was detected. The two small peaks in the extreme right and left fields of Fig. 5 are from the Mn\textsuperscript{2+} standard sample.

ESR peaks are observed for all irradiated PTFE samples whose inflection points (arrows) occur at \( \sim 320.5 \) and \( \sim 320.6 \text{mT} \) for 0.216 and 0.432MGy irradiations, respectively. The inflection points appear to shift to a slightly higher \( B \) as the HLEBI dose is increased.
4. Discussion

4.1 Aging effects

To investigate aging stability, Fig. 6 is a log10-log10 plot of effects of aging time (s) on electrical conductivity (\(\sigma\)) of EB irradiated PTFE samples at room temperature (292.7 ± 3.3 K) under Ar atmosphere. The zero point is defined as just after EB irradiation and the first measurement time is determined to be 3 ks.

The saturated electrical conductivity will be defined as \(\sigma_o\), since the \(\sigma\) at aging time of \(10^5\) s is almost saturated (right side of Fig. 6). Note, \(\sigma_i (2.5 \times 10^{-16} \text{ and } 3.6 \times 10^{-15} \text{ S m}^{-1})\) obtained at EB doses of 0.0432 and 0.432 MGy, respectively are approximately 4.9 and 70.6 times higher than \(\sigma\) of untreated PTFE (5.1 \times 10^{-17} \text{ S m}^{-1}). Although the aging initially reduces the \(\sigma\) of irradiated samples, \(\sigma_i\) are remarkably higher than the untreated. For example, the lower dose 0.0432 MGy samples decrease the \(\sigma\) significantly, but \(\sigma_i\) value (2.5 \times 10^{-16} \text{ S m}^{-1}) is still about 490% above untreated condition at 5.1 \times 10^{-17} \text{ S m}^{-1}. This indicates that the electrical carriers generated by HLEBI retain for the long term of \(10^5\) s. To illustrate the retainment of charge during aging, the retained conductivity ratio (\(R_c\)) is defined here as:

\[
R_c = (\sigma_i - \sigma_o)/(\sigma_i - \sigma_o)
\]

where \(\sigma_o\) is electrical conductivity (\(\sigma\)) of the untreated samples. The \(\sigma_i\) is \(\sigma\) of irradiated samples measured at 3 ks.

Hence, \(R_c\) are 0.056 and 0.169 for the lower dose 0.0432 and higher dose 0.432 MGy irradiated samples, respectively. Therefore, \(\sigma_i\) is more stable through time for the higher 0.432 MGy condition.

Note Fig. 6 shows using half the dose at 0.216 MGy exhibits the same \(\sigma_i\) value as the 0.432 MGy. This could be due to less variance in \(\sigma_i\) as EB dose is increased so lower doses can be used for cost considerations.

The ESR signal intensities or relative peak heights (I) are also reduced with aging time. Figure 7 illustrates the ESR signals of the small dose of 0.0432 (fine lines) and large dose of 0.432 (thick lines) MGy-irradiated PTFE at the 3 ks (intensity = \(I_f\); solid lines) and after aging \(10^5\) s (intensity = \(I_a\); broken lines) at 292.7 ± 3.3 K under Ar atmosphere. Since no ESR-signal can be observed in untreated PTFE (see Fig. 5), it is evident that HLEBI generates the signal intensity from dangling bond formation (see Fig. 7). Although aging for the long-term \(10^5\) s (saturation point) slightly reduces the signal intensity of ESR peak compared to that of 3 ks, the high intensity is still observed.

To illustrate the retainment of dangling bond density during aging, the retained density ratio (\(R_d\)) is defined here as:

\[
R_d = (I_f - I_o)/(I_f - I_o)
\]

As no ESR-signal can be observed in untreated PTFE, \(I_o = 0\). Hence, \(R_d\) are 0.91 and 0.93 for the small dose of 0.0432 (fine lines) and large dose of 0.432 (thick lines) MGy irradiated samples, respectively. This indicates the dangling bonds generated exhibit aging stability: they do not easily decay and are not easily annihilated with aging.

This result can probably be attributed to the density of residual dangling bonds with charge carriers in the form of free radicals such as \(\text{CF}^+\) (\(-\text{CF}_2\)–\(-\text{CF}_2\)–) or \((-\text{CF}_2\)–\(-\text{CF}_2\)–\(-\text{CF}_2\)–) \(8\). It is reported these radicals have a long lifetime and do not decay easily in PTFE. \(8\) The increased conductivity is probably due to dangling bonds acting as acceptors, or holes in a semiconductor attracting electrons from neighboring bonds. An electron will jump to repair the unpaired bond hence creating another hole. The process probably repeats itself generating current as in a p-type semiconductor. With this, the high retained conductivity ratio (\(R_c = 0.169\) of PTFE samples irradiated at large dose of 0.432 MGy (see Fig. 6) can be explained.

4.2 Electrical conductivity enhancement by HLEBI

When \(E_A\), \(\sigma_0\) and \(k\) are the activation energy, \(\sigma\) at infinity temperature and Boltzman constant, the electrical conductivity (\(\sigma\)) of a semiconductor as function of temperature (\(T\)) has often been expressed by the equation \(12\)–\(14\):

\[
\sigma = \sigma_0 \exp(-E_A/kT)
\]
5. Conclusions

Electrical conductivity enhancement of PTFE (Teflon) induced by homogeneous low potential electron beam irradiation (HLEBI) was investigated.

(1) EB irradiations up to 0.432 MGY were found to raise the electrical conductivity ($\sigma$) of PTFE more than 2 orders of magnitude higher than that before irradiation.

(2) Since a strong dependence of $\sigma$ on HLEBI up to 0.216 MGY was observed, control of electron movement or Fermi level by HLEBI seems possible for polymers.

(3) HLEBI produced detectable ESR signals in the PTFE: as irradiation dose was increased from 0.0432 to 0.432 MGY, the signal intensity increased and the signal peak was sharpened indicating an increase in unpaired electrons, which were probably dangling bonds. HLEBI often cuts the weak covalent atomic bonds between monomers generating dangling bonds of the terminated atoms in PTFE, resulting in a high density state of outer shell electrons. These dangling bonds were probably in the form of radicals. ESR signals were similar in shape and magnetic field value. Thus, it is possible one type of dangling bond was observed in the irradiated PTFE. In contrast, a signal was not found in the untreated samples.

(4) Aging stability investigation showed the saturated conductivities at $10^6$ s ($\sigma_i$) (2.5 x 10^{-16} and 3.6 x 10^{-15} S m^{-1}) obtained at EB doses of 0.0432 and 0.432 MGY, respectively, were approximately 4.9 and 70.6 times higher than $\sigma$ of untreated PTFE (5.1 x 10^{-17} S m^{-1}). Although the aging initially reduced the $\sigma$ of irradiated samples, $\sigma_i$ were remarkably higher than the untreated. For example, the lower dose 0.0432 MGY samples decayed significantly with retained conductivity ratio ($R_\sigma$) of 0.056 and 0.169 for 0.0432 and 0.432 MGY irradiated samples, respectively. However, the $\sigma_i$ value of the 0.0432 MGY irradiated samples was still about 490% above untreated condition at 5.1 x 10^{-17} S m^{-1}. This indicates that the electrical carriers generated by HLEBI retained for the long term of $10^6$ s.

(5) Since no ESR-signal could be observed in untreated PTFE, it was evident that HLEBI generated the signal intensity from dangling bond formation. Although aging for the long-term $10^6$ s (saturation point) slightly reduced the signal intensity of ESR peak compared to that of 3 ks, the high intensity was still observed. The retained density ratios ($R_d$) were 0.91 and 0.93 for the small dose of 0.0432 and large dose of 0.432 MGY irradiated samples, respectively, following the trend of $\sigma_i$. This indicated the dangling bonds generated exhibited aging stability: they did not easily decay and were not easily annihilated with aging.

(6) The linear relationships between logarithmic electrical conductivity ($\ln(\sigma)$) and reciprocal temperature ($1/T$) were obtained by experiment. Since the slopes of all PTFE samples irradiated were approximately equal to that before treatment from 303 to 375 K, the plots exhibited the same slope independent of irradiation dose and aging time. Thus, HLEBI didn’t convert the $\sigma$ system.

At temperatures from 375 to 424 K, $\sigma$ decreased deviating from linearity for the 0.0432 and 0.432 MGY irradiated samples independent of aging time. This drop was not observed in the untreated samples. The drops are probably caused by the annihilation of residual electrical carrier related to dangling bonds and isolated radicals in the matrix.
HLEBI probably generated dangling bonds in the form of radicals acting as acceptors to carry charge. Since a chemical dopant was not needed to act as a charge carrier, HLEBI could be an attractive method to attain homogeneous doping of organic films.

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