Electron beam processed polymers with multi-properties

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This paper mainly describes that surface density changes in dangling bonds caused the multi-properties of polymers irradiated by electron beam (EB). The irradiated polymers with high wettability, mist resistance, sterilization and high hardness have been successfully developed. EB irradiation decreases the water contact angle of polymers, because dangling bond formation generally attracts the poling of water molecules. Scattering of light reflection of fine sessile drops of water usually causes the misting. The extremely thin film of water is formed by wettability enhancement induced by EB irradiation. Thus, the electron beam irradiation prevents the misting. On the other hand, the hardening has been generated by EB irradiation.

Keywords: electron beam, polymer, wet, misting, strength, irradiation

I. INTRODUCTION

In order to obtain multi-properties, such as mist resistance, wettability and high strength, the surface physical properties with atom activation should be controlled by high power treatments. Electron beam (EB) irradiation is an excellent tool to control surface physical properties related to dangling bond, charging and absorption impurity atoms.

One of proposed countermeasures to the present serious problems caused by misting borrows from the ability of the human eye to recover against blurring. A tear film in the eye is a key factor in achieving clear vision. Thus, we have tried to enhance wettability with commercially achievable safe by using convenient irradiation apparatus.

On the other hand, plasma ion irradiation has increased wettability. However, the effects on properties are not reproducible, because plasma ion irradiation generally retains residual impurities in samples. In contrast, EB irradiation increases wettability, while eliminating residual impurity atoms. The mist resistant dentist’s mirror, sapphire lens, and diamond window have been made possible by a sheet electron beam irradiation [SEBI] treatment with sterilization, in which the effective exposure time was varied from a few minutes to a few hours. Namely, EB irradiation has been applicable to mist resistance treatment with sterilization.

In addition, EB irradiation is also useful to enhance surface strength of polymers because of network structure relaxation related to dangling bond. To control smart properties such as sterilization, wettability, mist resistance and strength for polymers; electron beam (EB) irradiation is presently being developed. EB irradiation homogeneously activates surface atoms, breaks chemical bonds and migrates mobile atoms in a surface layer up to 0.1-0.4 mm in depth (see eq. 2 in Methods) for light weight materials. It also relax the residual stress and
strain of inter-molecular and interatomic bonding in polymer structure, possibly allowing us to control the surface properties.

Changes in dangling bond density and charging should simultaneously contribute to the surface properties, such as wettability, high resistance to misting, sterilization and strength of glassy materials irradiated by electron beam. Therefore, we have undertaken the present study to investigate the possible beneficial effects of electron beam irradiation on the multi-properties of the surface layer in polymers.

II. EXPERIMENTAL

Polyethylene terephthalate (PET), acrylic resin (MMA) and polycarbonate (PC) were used as samples. The sample size was 20 mm x 20 mm x 5 mm, respectively. The sheets were homogeneously irradiated using an electron - curtain processor (Type CB2215/15180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd. Tokyo). The specimen was irradiated by the electron beam through a titanium thin film window attached to the vacuum chamber (240 mm in diameter). A tungsten filament in vacuum generated the electron beam using an acceleration potential of 170 kV and an irradiating current of 4.0 mA. In order to prevent oxidation, samples were kept under the protection of one atmospheric pressure of nitrogen gas having a residual concentration of oxygen below 400 ppm. Each dose of EB irradiation was only applied for a short time (0.23 s) to avoid excessive heating of the sample. The temperature of the surface of the sample was below 323 K just after irradiation. The sample was transported on a conveyor at a speed of 9.56 m/min. The dosage was proportional to the yield value determined from the irradiation current (I, mA), the conveyor speed (S, m/min), and number of irradiations (N) according to the following equation:

\[ \text{Dosage(MGy)} = 0.216 \times (I \times S \times N) \quad (1) \]

Irradiation dose was corrected by using RCD nylon radiometer film (Far West Technology, Inc., CA, USA). The distance between sample surface and window surface was 35 mm. The average irradiation depth (Dth, μm), calculated by sample density (ρ, kg/m³) and irradiation potential (V, kV), was expressed by a following equation.

\[ \text{Dth} \times \rho = 66.7 \times V^{0.6} \quad (2) \]

If the measured density was 1.3 x 10³ kg/m³ for the glassy sample, the EB-irradiation depth should be 0.15 mm. The energy of the incident electrons was reduced from 170 keV to 128 keV due to the nitrogen atmosphere and the titanium window of 10 μm in thickness.

To obtain more precise information on structural changes in the glass at the atomic scale, the density of dangling bonds in a sample was obtained using an electron spin resonance spectrometer (ESR, SA2000, JEOL, Tokyo). The microwave frequency range used in the ESR analysis was the X-band of 9.45 ± 0.05 GHz, with a field modulation of 100 kHz. The spin density was calculated using a Mn²⁺ standard sample. ESR signals attributable to dangling bonds were observed.

To measure the rate of mist removal, fine droplets were blown onto the surface at an approximate rate of 6 x 10⁻⁴ m³/s at 310 K under atmospheric pressure. The distribution of the radii of the fine drops on the diamond surface immediately after completion of the blowing was determined by means of a microscope and a videotape recorder. The time to clear vision (τc) was measured by using a videotape recorder. The starting point for measuring mist removal was considered to be just after the completion of blowing for 3 s under saturated vapor pressure. The minimum detectable time to clear vision was 0.2 s.

III. RESULTS AND DISCUSSION

III-A EB processed physical properties

Fig. 1 shows the FT-IR spectra before and after EB-irradiation, which decreased the peaks heights of FT-IR spectra. Polymer was resolved by EB-irradiation. On the other hand, it was possible to detect dangling bonds generated by the EB irradiation. A ESR signal was observed in irradiated polymers corresponding to dangling bonds, as shown
in Fig. 2. The dangling bonds strongly attract poling molecules. Since water molecules show poling, EB-irradiation probably affects the wettability. Thus, water contact angle should be small on the surface of irradiated polymers.

dangling bond formation mainly caused the EB effects.

![Intensity vs Wavelength](image1)

**Fig. 1.** FT-IR spectra before and after EB-irradiation.

![Polyethylene terephthalate (PET)](image2)

**Fig. 2.** ESR spectra before and after EB-irradiation.

**III-B. Wettability and Mist resistance**

Dangling bond formation\(^9,10\) caused adsorption\(^11\) of poled molecules. Since water molecules show poling, the water contact angle should be small on the surface of polymers irradiated by electron beam.

Fig. 3 shows relationship between EB irradiation dose and water-contact angle. The EB irradiation decreased the contact angle of water sessile drop on polymers. Fig. 4 shows relationship between EB irradiation dose and the time to clear vision. The EB irradiation decreased the clear time. It shows that EB irradiation enhanced the mist resistance of polymer.

Based on results of effective dose of electron beam, Fig. 3. Relationship between EB irradiation dose and water-contact angle.

![Contact angle vs Irradiation dose](image3)

**Fig. 4.** Relationship between EB irradiation dose and time to clear vision.

**III-C. Hardness**

The EB treatment strengthened inorganic materials, such as hydroxyl apatite ceramics applied for soda glass\(^12\) and glass fiber.\(^13\) Furthermore, high ductility was observed for resin irradiated by electron beam.\(^8\) If it should break the tightly bonded molecule, it relax the loading strain in the tightly bonded polymer structure, probably allowing us to control the ductility.

On the other hand, if the relaxation of
intermolecules bonding force enhanced the adhesive force of polymer, EB-irradiation should enhance the hardness. Fig. 5 shows Hv hardness change against EB-irradiation dose. The Vickers hardness of polycarbonate sample was increased by the low electron dose.

![Graph showing Hv hardness change](image)

Fig. 5. Hv hardness change against EB-irradiation dose.

The excess irradiation dose decreased the Vickers hardness of polycarbonate sample.

On the other hand, effects of EB-irradiation on Vickers Hardness were not observed for Acrylic resin and Polyethylene terephthalate samples.

**V. CONCLUSION**

Based on surface physical properties of dangling bond, the EB irradiated polymers with multi-properties of wettability, mist resistance and hardness were developed. The electron beam irradiation decreased the contact angle of water and prevents the misting.

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