Effects of Homogeneous Low Voltage Electron Beam Irradiation on Adhesive Strength of Polycarbonate (PC) Sheet Covered with Nylon6 Film

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The effects of homogeneous low voltage electron beam irradiation (HLEBI) on the adhesive strength of different polymers without glue but with sterilization were investigated. HLEBI at more than 0.043 MGy generated adhesive force and enhanced fracture strain at the interface in polycarbonate (PC) composites covered with nylon6 film. HLEBI at less than 0.130 MGy increased the elasticity ($d\sigma/d\varepsilon$) and fracture stress of the composites. Although it was far below that of commercial pure metal, the elasticity (2 GPa) of composites irradiated from 0.130 to 0.216 MGy was very close to that of nylon6. HLEBI from 0.216 to 0.432 MGy increased the fracture strain of the composites, whereas it decreased elasticity ($d\sigma/d\varepsilon$). Based on the results, HLEBI from 0.130 to 0.432 MGy apparently maintained the high fracture strength of the composites. To investigate the influence of EB irradiation on adhesive strength, electron spin resonance (ESR) signals related to dangling bonds were observed. Since HLEBI generated dangling bonds in both PC and nylon6, the dangling bonds probably served as reactive and bonding sites for each polymer at the interface. Results indicated that HLEBI enhanced the adhesive strength of the composites, therefore, it was concluded that HLEBI was probably a useful tool for quickly joining the different polymers. [doi:10.2320/matertrans.MRA2008489]

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1. Introduction

Composite polymers have been prepared for biomedical applications by joining them with heating and glue.^{1,2)} However, these methods often degrade the adhesive strength and chemical properties, thereby affecting human health.³⁾ Development of rapid adhesion without heating and glue would solve this problems.

Homogeneous low voltage electron beam irradiation (HLEBI) improves the mist resistance and wetting of inorganic materials.⁴⁻⁶⁾ This improvement is mainly caused by the irradiation with the formation of dangling bonds. Dangling bonds have also been formed in polymers.⁷⁾ Dangling bonds enhance surface energy, which is probably a tool for joining the different polymers.⁸⁾ Thus, rapid and safe adhesion between different polymers may be possible by using HLEBI.

Since polycarbonate (PC) exhibits high transparency, light weight and high impact resistivity, this structural polymer can be applied to helmets, compact disc and machine parts, as well as biomedical transparent apparatuses for artificial dentition. The influence of HLEBI on the tensile strength of PC was studied. The results indicated that HLEBI increased tensile strength.⁹⁾

Since nylon exhibits wear resistance, as well as high strength and fracture toughness, it can be applied to biomedical thread (suture) and artificial tendons. The development of rapid and safe adhesion method between nylon film and PC sheet would allow many biomedical applications.¹⁰⁾

In addition, sterilizing with HLEBI requires a few seconds, whereas sterilizing with ultraviolet light irradiation requires a few hours.^{11,12)} Thus, HLEBI is expected to be a useful tool for gluing different polymers while sterilizing them for biomedical applications.

Fig. 1 Schematic diagram of composites loaded to 0.27 MPa during irradiation.

Therefore, this study investigated the effects of HLEBI on adhesive strength at the interface between nylon6 film and PC sheet.

2. Experiment Procedure

2.1 Homogeneous irradiation of electron beam

Composites sheets were constructed with nylon film (10 mm × 10 mm × 0.025 mm, EMBLEM, YUNITIKA Co. Ltd. Japan) and polycarbonate (PC; $[-O-R-O-CO-]_n$) (10 mm × 10 mm × 2 mm, Rekisan sheet, General Electric, Co., Ltd., US). Both stainless steel springs and 0.015 mm thick nylon6 supporting film, which loaded the compressive stress (0.27 MPa) at interface, to reproducibly connect each polymer surface (Fig. 1). When the compressive stress of more than 0.27 MPa was loaded for more than 1 h, a high reproducibility of joint strength was obtained.

Since no adhesive force was observed at the interface between the supporting film and the nylon film in the composites, it was easy to remove the supporting film after irradiation. The specimen at the outer surface of the nylon film was homogeneously irradiated by an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co., Ltd., Tokyo).^{3,11-13)} The specimen was homogeneously irradiated with an electron beam through a titanium window attached to

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Fig. 2 Schematic drawing of a sample.

a 240 mm-diameter vacuum chamber. A tungsten filament in a vacuum was used to generate the electron beam with an electrical voltage of 170 kV and an irradiating current of 2.0 mA. To prevent oxidation, the samples were kept in a nitrogen atmosphere of 0.1 MPa with a residual oxygen concentration of less than 400 ppm. The flow rate of the nitrogen gas was 1.5 L/s.

2.2 Tensile test

Composite samples were prepared for the tensile test to evaluate the influence of HLEBI on elasticity, fracture strength and its strain (Fig. 2). Stainless steel rods (SUS304, JIS 4318, TAIHOH Co., Ltd., Japan) joined to the both surface sides of composites sample by adhesive paset (SUPER X, Cemendine Co., Ltd., Japan). The tensile test was performed using an Instron tensile tester, with a strain rate of 1 mm/min.

2.3 Electron spin resonance (ESR) measurement

The density of the dangling bonds was measured by means of electron spin resonance (ESR) spectrometer (JES-FA2000, Nippon Denshi Ltd., Tokyo) to obtain more precise information on atomic-scale structural changes in the polymers.^{14,15)} The microwave frequency used in the ESR analysis was in 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 318.7 to 328.7 mT. The spin density was calculated by using a Mn^{2+} standard sample. Only ESR spectra (instead of spin densities) were given. The density of the dangling bonds was estimated based on the standard calibration material [4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL, 089-04191, Wako Pure Chemical Industries Ltd., Tokyo)] and Mn^{2+} in the MnO by double integration of the intensity of the ESR signal.⁶⁾

3. Results

3.1 Adhesive strength of irradiated composites

Composites constructed with PC sheet and nylon6 film must be prepared by irradiation. The joint strength of untreated composites specimens, which are constructed with PC and nylon6, cannot be measured. HLEBI homogeneously joins the PC sheet with the nylon6 film at the interface. Figure 3 depicts the stress-strain curves of the PC-nylon6 composites irradiated at doses from 0.043 to 0.432 MGy. HLEBI at less than 0.216 MGy increased the fracture stress of the composites. The greatest fracture stress was found in the

Fig. 3 Stress-strain curve of an irradiated sample of joined nylon film and PC sheet.

Fig. 4 Relationship between elasticity ($d\sigma/d\epsilon$) and strain of composites constructed with nylon film and PC sheet irradiated by each dose of HLEBI.

composites irradiated at 0.216 MGy; additional irradiation at 0.432 MGy slightly decreased the fracture stress.

HLEBI from 0.216 to 0.432 MGy increased the fracture strain. The greatest fracture strain was found in composites irradiated at 0.432 MGy.

3.2 Elasticity enhancement of composites treated by HLEBI

Deformation resistivity was defined as the slope ($d\sigma/d\epsilon$) of the stress-strain curve (Fig. 3). Although there was no adhesive force related to the deformation resistivity ($d\sigma/d\epsilon$) in the composites before irradiation, HLEBI generated adhesive force with deformation resistivity ($d\sigma/d\epsilon$). Figure 4 plots changes in the deformation resistivity ($d\sigma/d\epsilon$) of the composites against strain during deformation. The deformation decreased the $d\sigma/d\epsilon$ values. HLEBI from 0.130 to 0.216 MGy indicated a higher $d\sigma/d\epsilon$ than that irradiated at 0.043 MGy. HLEBI from 0.043 to 0.216 MGy indicated a sharp strain-dependent $d\sigma/d\epsilon$.

When the strain (ϵ) exceeded 1.5×10^{-3} , $d\sigma/d\epsilon$ of the composites irradiated at 0.432 MGy was higher than the other experimental values obtained. However, the composites irradiated at 0.432 MGy indicated the lowest initial $d\sigma/d\epsilon$ ($(d\sigma/d\epsilon)^0$) in the irradiated composites.

Fig. 5 Stress-strain curves of nylon6 film and PC sheet with and without HLEBI.

Fig. 6 Relationship between elasticity ($d\sigma/d\varepsilon$) and strain of PC sheet and Nylon6 film irradiated by each dose of HLEBI.

3.3 Influence of HLEBI on tensile strength of nylon6 and PC

Figures 5 and 6 illustrate tensile stress-strain curves and strain dependent deformation resistivity ($d\sigma/d\varepsilon$) of nylon6 and PC with and without HLEBI. Although HLEBI decreased the fracture strain (Fig. 5), it enhanced the deformation resistivity (Fig. 6) of nylon6. Thus, HLEBI decreased the fracture stress of nylon6 (Fig. 5).

However, HLEBI at less than 0.216 MGy slightly decreased the fracture strain (Fig. 5) as well as the deformation resistivity ($d\sigma/d\varepsilon$) of PC (Fig. 6). Thus, HLEBI decreased the fracture stress of PC (Fig. 5).

Additional irradiation from 0.216 to 0.432 MGy enhanced deformation resistivity (Fig. 6), but decreased fracture strain (Fig. 5). Thus, additional irradiation slightly enhanced the fracture stress of PC (Fig. 5).

3.4 ESR signal

Figure 7 depicts the ESR signals of PC and nylon6 with and without irradiation. ESR signals could not be detected in the untreated sample, but ESR signals were observed in the irradiated samples of PC and nylon6, indicating dangling bonds. HLEBI at 0.216 MJ/kg (MGy) enhanced the intensity of the ESR signals, suggesting that dangling bonds were formed in the PC and nylon6. Furthermore, additional irradiation from 0.216 to 0.432 MJ/kg (MGy) enhances the intensity of the ESR signal related to the additional densities of dangling bonds in the polycarbonate (PC) and nylon6.

4. Discussion

4.1 Adhesive strength induced by HLEBI

The initial $d\sigma/d\varepsilon$ value ($(d\sigma/d\varepsilon)^0$) was determined in

Fig. 7 ESR signals from (a) PC and (b) nylon6 with and without HLEBI (0.216 and 0.432 MGy).

Fig. 8 Changes in elasticity ($(d\sigma/d\varepsilon)^0$) of composites constructed with nylon film and PC sheet for each EB irradiation dose, together with nylon film and PC sheet.

order to evaluate the elasticity, when the strain was zero. Figure 8 plots changes in the elasticity ($(d\sigma/d\varepsilon)^0$) of composites constructed with nylon film and PC sheet against the dose of HLEBI, together with nylon film and PC sheet.

HLEBI at less than 0.043 MGy generated the adhesive force at the interface in the composites. HLEBI at less than 0.130 MGy increased $(d\sigma/d\varepsilon)^0$, (i.e., the elasticity of composites of nylon6 and PC, whereas additional HLEBI at more than 0.130 MGy decreased elasticity.

The elasticity of composites irradiated from 0.043 to 0.216 MGy exceeded that of PC. The elasticity of commercial pure metals was 75.7 GPa for aluminum, 136 GPa for copper, 60 GPa for tin, 44.3 GPa for magnesium and 15 GPa for lead.¹⁶⁾ Although it was far below that (15 GPa) of pure lead,¹⁶⁾ the elasticity (2 GPa) of composites irradiated from 0.130 to 0.216 MGy was very close to that of nylon6.

Figure 9 depicts changes in the fracture strain of composites constructed with nylon film and PC sheet for each EB irradiation dose, together with nylon6 film and PC sheet. HLEBI at less than 0.043 MGy generated the adhesive fracture strain of the composites, although HLEBI from 0.043 to 0.216 MGy slightly decreased the adhesive fracture strain.

Additional HLEBI at more than 0.216 MGy increased fracture strain. Although this ε_f value was far below those of

Fig. 9 Changes in the fracture strain of composites constructed with nylon6 film and PC sheet for each EB irradiation dose, together with nylon film and PC sheet.

Fig. 10 Changes in the fracture stress of composites constructed with nylon6 film and PC sheet for each EB irradiation dose, together with nylon film and PC sheet.

PC and nylon6, 0.432 MGy- HLEBI yielded the maximum value of the fracture strain (ϵ_f) of the composites, confirming that HLEBI at 0.432 MGy was the appropriate condition to prepare the ductile composites constructed with nylon6 film and PC sheet.

Figure 10 plots changes in fracture stress (σ_f) of composites constructed with nylon film and PC sheet for each EB irradiation dose, together with nylon film and PC sheet. HLEBI at less than 0.043 MGy generated adhesive force, related to the fracture stress of the composites. Although the σ_f values of the composites were far below those of both nylon6 and PC, high fracture stress was found in the composites irradiated from 0.130 to 0.432 MGy.

Since HLEBI at 0.432 MGy decreased the elasticity ($d\sigma/d\epsilon$) and increased the fracture strain of the composites, HLEBI from 0.130 to 0.432 MGy apparently maintained the high fracture stress of the composites.

Therefore, it was confirmed that HLEBI from 0.130 to 0.432 MGy was the optimum condition to maintain the high adhesive fracture strain to prevent crack propagation of composites constructed with nylon6 film and PC sheets.

4.2 Influence of dangling bond formation induced by irradiation on mechanical properties

ESR signals (Fig. 7), indicated that HLEBI enhanced the density of dangling bonds in PC and nylon6. The density of dangling bonds at 0.216 MGy was 1.68×10^{13} Spin·mm⁻³ in nylon6 and 1.68×10^{13} Spin·mm⁻³ in PC sheet. Nylon6 film was generated dangling bonds by HLEBI. Since the air gap had not existed between nylon6 film and PC sheet, the adhesion stress at the composite interface was detected. On the other hand, since the air gap has been exists between the support film and sample, the adhesion between nylon6 support film and specimen did not occur.

If the enhanced dangling bonds induced by HLEBI less than 0.216 MGy acted as bonding sites at the interface between PC and nylon6, the maximum fracture strain (Fig. 9) and fracture stress (Fig. 10) were found in the composites irradiated at 0.216 MGy.

The density of dangling bonds at 0.432 MGy was 2.38×10^{13} Spin·mm⁻³ in nylon6 and 2.88×10^{15} Spin·mm⁻³ in PC. If additional dangling bonds induced by HLEBI from 0.213 to 0.432 MGy acted as crack origins and propagation sites at the interface between PC and nylon6, HLEBI from 0.216 to 0.432 MGy decreased the fracture strain (Fig. 9) and fracture stress (Fig. 10).

HLEBI of less than 0.432 MGy always enhanced elasticity (Fig. 8). If HLEBI partially broke the polymer and relaxed the residual stress, the potential curve of the mean correlation distance among the atoms in the molecules would probably become sharp. Therefore, it was assumed that HLEBI enhanced elasticity.

4.3 Discussion of irradiation depth in polymer

Christenhusz and Reimer¹³⁾ evaluated the depth of penetration of EB irradiation of less than 200 kV electrical potential by measuring the Joule heat generated in copper films.¹³⁾ Based on density (ρ : kg/m³) and potential drop (ΔV : kV), penetration depth (D_{th} : m) was given by

$$D_{th} = 66.7 \Delta V^{5/3} / \rho. \quad (1)$$

The potential at the surface sample (V_s) was expressed by the following equation.¹³⁾

$$V_s = V_o - \Delta V \quad (2)$$

Based on the assumption of Christenhusz and Reimer,¹³⁾ the potential drop (ΔV) was caused by the loss of irradiation energy of the electron beam from the initial potential at the filament surface of the electron beam gun (V_o) to the potential at the surface sample (V_s). The potential drop (ΔV) was expressed by the following equation.¹³⁾

$$\Delta V = \tau \cdot V_o / S \quad (3)$$

Here, τ was thickness and S was mass thickness of the Ti sheet and nitrogen gas.

The electrical potential (128 keV) was estimated from the electrical potential (170 keV), the thickness [10.0×10^{-5} mm (10 μ m)] of the titanium window [$\rho = 4540$ kg/m³ (4.54 g/cm³)], and the distance (30 mm) in the nitrogen gas atmosphere ($\rho = 1.13$ kg/m³) between the surface of the sample and the window. Since the electrical potential was 128 keV, equation (1) predicted that the penetration depth

(D_{th} : m), estimated by Christenhusz and Reimer,¹³⁾ should be 190 μm for nylon6 and 157 μm for PC, when the densities (ρ) were 1140 for nylon6 and 1380 kg/m^3 for PC.

The penetration depth (Libby assumption¹⁷⁾) of EB irradiation related to mass thickness (S : mg/cm^2) and irradiation voltage (V_s/kV), was expressed by

$$S = 1/150 \times \Delta V^{5/3}. \quad (4)$$

The estimated mass thickness was 34.8 mg/cm^2 , when the initial irradiation voltage was 170 keV. Since the mass thickness of the Ti foil (1.78 mg/cm^2) and N_2 gas (0.15 mg/cm^2) reduced the penetration depth of HLEBI, the mass thickness (S) of the polymer sample was 32.9 mg/cm^2 .

In addition, based on the Libby assumption,¹⁷⁾ the electrical potential of the sample surface was expressed by

$$\Delta V = (150 \times S)^{3/5}. \quad (5)$$

Furthermore, the penetration depths of nylon6 (289 μm) and acryl acid resin (238 μm) were obtained by the assumptions of Libby.¹⁷⁾

The sample was positioned in an aluminum plate holder (0.15 m $\times$ 0.15 m) and transported on a conveyor at a speed of 9.56 m/min. Because the minimum dose of HLEBI was 43.2 J/g ($1.13 \times 10^{13} \text{ e m}^{-2} = 43.2 \text{ kGy}$), each burst of irradiation was performed for a short time (0.23 s) at 0.0432 MGy to avoid excessive heating of the sample. As a result, the temperature of the sample surface remained below 323 K just after irradiation. Both surfaces of the samples were repeatedly irradiated to increase the total irradiation dose. The interval between the end of one period of irradiation and the start of the next was 30 s. The dosage was proportional to the yield determined from the irradiation current, the conveyor speed and number of irradiations.

The yield was calibrated using Radio chromic nylon film (FWT-60-00: FAR WEST TECHNOLOGY Inc., Goleta, CA, USA) and dose-meters (FWT-92D: FAR WEST TECHNOLOGY Inc., Goleta, CA, USA).

The electron number density (Gy) was expressed by the following equation in metals.¹⁸⁾

$$Ng = DE/Cg \quad (6)$$

where, Ng (em^{-2}) was the irradiation dose, DE (Sv/s) was the dose equivalent, and Cg ((Sv/s)/(e/(m^2s))) was transferred coefficient of particle flux per dose equivalent [0.1649×10^{-13}].¹⁸⁾

Since the irradiated depth of nylon6 of supporting film (15 μm thickness) and adhesive film (25 μm thickness) in the composites was 40 μm , the adhesive interface was perfectly irradiated. In addition, the irradiated thickness of PC exceeded 10% of the sample thickness (2.0 mm) of the PC in the composites.

5. Conclusion

The effects of homogeneous low voltage electron beam irradiation (HLEBI) on the adhesive strength at the interface in PC composites covered with nylon6 film without glue were investigated.

(1) HLEBI at more than 0.043 MGy generated the adhesive force and increased the fracture strain.

(2) HLEBI at less than 0.130 MGy increased the elasticity ($d\sigma/d\varepsilon$) and fracture stress of the composites.

(3) The elasticity (2 GPa) of composites irradiated from 0.130 to 0.216 MGy was very close to that of nylon6, although it was far below that of commercial pure lead.

(4) HLEBI from 0.216 to 0.432 MGy decreased the elasticity ($d\sigma/d\varepsilon$) of the composites, but increased the fracture strain. Based on the results, HLEBI from 0.130 to 0.432 MGy apparently maintained the high fracture strength of the composites.

(5) ESR signals related to dangling bonds were observed to analyze the influence of HLEBI on adhesive strength. The dangling bonds that HLEBI generated in PC and nylon6 probably acted as reactive and bonding sites for each polymer at the interface.

These results indicated that HLEBI enhanced the adhesive strength of the composites. Since the adhesive force was probably obtained between any polymers that HLEBI formed dangling bonds, HLEBI should be one of adhesive technology of wide application. As a conclusion, it was concluded that HLEBI might be a useful tool for quickly joining the different polymers, as well as sterilizing.

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