Creation of Adhesive Force between Laminated Sheets of Polytetrafluoroethylene (PTFE) and Polyethylene (PE) by Homogeneous Low Energy Electron Beam Irradiation Prior to Hot-Press for Bio-Adaptable Application

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Bio-adaptable 2-layer polytetrafluoroethylene/polyethylene (PTFE/PE) laminated sheets were prepared by a new adhesion method, a double-step treatment consisting of applying low dose (<0.43 MGy) homogeneous low energy electron beam irradiation (HLEBI) to the 2-layer assembly where the HLEBI penetrates through the PTFE and PE layers, respectively, prior to hot-press under 5 MPa and 433 K. Although the adhesion of the PTFE/PE sheets cannot be observed without the new double-step treatment, bonding forces were created as evidenced by the mean adhesive forces of peeling resistance (Fp). The adhesion cannot be observed without HLEBI. On the other hand, application of a small dose of HLEBI (less than 0.43 MGy) prior to hot-press irradiation enhances the Fp at each Pp. The maximum Fp values at each Pp (0.06, 0.50 and 0.94) of the laminated sheet irradiated at 0.13, 0.13, and 0.22 MGy are 5.44, 10.7, and 19.7 Nm−1, respectively. Based on the 3-parameter Weibull equation, the lowest Fp value at each Pp of zero (Fp) could be estimated. An increasing trend in Fp occurs by the double-step treatment applying HLEBI up to 0.43 MGy reaching a maximum at 2.66 Nm−1, improving the safety level without radiation damage of PTFE/PE. It was more than 6 times higher than that of PTFE/Polyurethane (PU) (0.4 Nm−1). When HLEBI cuts the chemical bonds and generates dangling bonds without bonding electrons in PTFE and PE, the created adhesion between the laminated sheets can be explained. Based on X-ray photoelectron spectrometer (XPS) surface analysis of the PTFE/PE laminated sheets after the peeling tests, fluorine (F) was detected on the PE peeled surface, indicating both strong chemical and intermolecular bonds generated by the double-step treatment. For these reasons, double-step treatment is a useful method for quick lamination of PTFE and PE with sterilization without the use of glue.

Keywords: polytetrafluoroethylene, polyethylene, adhesive force, electron beam, peeling resistance

1. Introduction

Composite polymers have been prepared for numerous biomedical applications by laminating 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 remedy this. To solve the problem, the development of rapid and safe adhesion method between Polytetrafluoroethylene (PTFE) and Polyethylene (PE) sheets has been expected. PTFE exhibits high wear resistance as well as high strength and fracture toughness. It can be applied to artificial blood vessels.4) PE exhibits high wear resistance and high strength as well as transparency.5) It can be applied to artificial lunge.

Homogeneous low energy electron beam irradiation (HLEBI) improves the mist resistance and wetting of inorganic materials,6) and increases polymer adhering to glass fibers raising impact strength in GFRP.7) Improvements are mainly caused by the irradiation with the formation of dangling bonds in polymers.8) Dangling bonds enhance surface energy, which is probably the mechanism for joining the different polymers.9) Thus, rapid and safe adhesion between different polymers by using HLEBI can be expected.

In addition, treatment time of HLEBI-sterilization is only a few seconds, although sterilizing with ultraviolet light irradiation requires a few hours.10,11) Thus, HLEBI is expected to be an excellent method for not only gluing different polymers without volatilization, but also simultaneously sterilizing them for biomedical applications. The double-step treatment with hot-press after HLEBI is a useful method to activate the surface to enhance the adhesive force. Therefore, the effects of HLEBI prior to hot-press lamination on the adhesive force of peeling resistance of bio-adaptable and high strength PTFE/PE laminated sheets of PTFE and PE have been investigated.

2. Experimental Procedure

2.1 Preparation of PTFE/PE laminated film

Figure 1 shows constitutional formula of (a) PTFE and (b) PE. Composite sheets were constructed with PTFE (10 mm × 40 mm × 0.050 mm, Skived tape MSF-100, Chukoh chemical industries Co. Ltd., Japan) and PE (10 mm × 40 mm × 0.080 mm, High-star PF 100, Star plastic Industry Inc., Japan). The glass transition temperatures (Tg) of PTFE and PE are 399 and 183–194 K, respectively.12)

2.2 Homogeneous irradiation of electron beam

As illustrated in Fig. 2, a jig constructed of a central stainless steel spring between two urethane rubber supporting bases is employed. The 2-layer laminate sample is assembled...
on the jig: one 0.05 mm thick PTFE layer, followed by one 0.08 mm thick PE layer, on top of which is placed a 0.015 mm thick supporting film. Since the HLEBI first penetrates the PE layer, followed by the PTFE layer we refer to the samples as PTFE/PE.

To obtain high reproducibility of peeling strength results, compressive stress of more than 80 kPa was loaded for more than 1.0 h.[3,13,14] Since no peeling force was observed at the interface between the back surface of PTFE or PE layer and the nylon 6 supporting film and in the jig, it was easy to remove the supporting film after irradiation. The sample at the outer surface of the nylon film was homogeneously irradiated in the jig (Fig. 2) by an electron-curtain processor (Type CBI75/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co., Ltd., Tokyo).[3,10,13–16] The samples were homogeneously irradiated with an electron beam through a titanium window attached to a 24 cm-diameter vacuum chamber. A tungsten filament in a vacuum was used to generate the electron beam with an electric voltage of 0.17 MeV and an irradiating current of 2.0 mA. To prevent oxidation, the samples were kept in a nitrogen atmosphere of 0.10 MPa with a residual oxygen concentration of less than 0.040%. The flow rate of the nitrogen gas was 1.5 L/s.

Given the densities ($\rho$) are 2.1 g·cm$^{-3}$ for PTFE and 0.863 g·cm$^{-3}$ for PE, the penetration depth ($D_{th}$) values of 0.105 mm for PTFE and 0.229 mm for PE were estimated by assumptions of Christenhusz and Reimer, respectively.[17] In addition, the $D_{th}$ values of PTFE (0.152 mm) and PE (0.34 mm) were also calculated by the assumptions of Libby.[18] Namely, the effective depth of homogeneous irradiation is 0.223 ± 0.118 mm. Consequently, since the irradiated thickness of laminated composites with PTFE film (50 µm thickness) and PE film (80 µm thickness) was 130 µm, the adhesive interface is perfectly irradiated throughout their thicknesses.

PTFE/PE composite film lamination was subsequently performed by the uni-directional hot-press at 433 K for 3.0 min under 5 MPa atmosphere after HLEBI.

### 2.3 T-peeling test

Composite samples after removing the 15 µm thick nylon 6 supporting film were prepared for the T-peeling test to evaluate the influence of HLEBI on the mean adhesive force of peeling resistance ($F_p$). The peeling adhesive force ($F_p$) and its peeling distance ($d_p$) were obtained by the peeling test, which was performed by using a micro-load tensile tester (F-S Master-1K-2N, IMADA Co. Ltd., Japan) with a strain rate of 10 mm/min.[15,16] Since the unit of the $F_p$ is Nm$^{-1}$, the $\sigma F_p$ is used instead of the adhesive strength, whose units should be Nm$^{-2}$. The sample condition of tensile test is as follows.

1. The vertical length from the peeling contact point to the end of the sample was 5 mm.
2. The $F_p$ is determined by using micro-load tensile tester. The $\sigma F_p$ is estimated by the peeling load and experimental peeling width and length of 10 and 30 mm, respectively. The initial distance before peeling ($d_i$) is defined at the start point of peeling force, which corresponds to the start point of the first relaxation. The $d_i$ value is ~1 mm.

### 2.4 Peeling probability

The accumulated probability ($P$) of Median Rank method[19] is one of convenient ways to analyze the mechanical probabilities of adhesive strength[13,14] adhesive peeling resistance[15] and elasticity,[20] as well as strength and impact value on fracture.[8,21–26] This method is useful to evaluate the effects of process, precisely. Evaluating the peeling probability ($P_p$) is also the convenient method of quantitative analyzing experiment values relating to peeling resistance.[15] It is expressed by the following equation.

$$P_p = (I - 0.3)/(n + 0.4)$$

Here, $n$ and $I$ are the total number of samples ($n = 11$) and order of peeling of each sample (0 ≤ $I$ ≤ 11), respectively. When the $I$ values were 1, 6, and 11, the $P_p$ values were 0.06, 0.50 and 0.94, respectively.

### 2.5 Electron spin resonance measurement

Dangling bond density was measured by electron spin resonance spectrometer (ESR: JES-FA200, JEOL Ltd., Tokyo) to obtain more precise information on atomic-scale structural changes in the polymers.[8,13–15] The microwave frequency used in the ESR analysis was in the X-band at 9.45 ± 0.05 GHz with a field modulation of 0.10 MHz. The microwave power was 1.0 mW. The magnetic field was varied from 317.0 to 327.0 mT.

### 2.6 The lowest adhesive force

In order to estimate the statistical adhesive force at extremely low peeling probability ($P_p$) value precisely, the lowest mean adhesive force of peeling resistance ($\sigma F_p$) value at $P_p$ of zero ($F_0$) for safety design is assumed to be attained from the adaptable relationship of the 3-parameter Weibull equation iterating to the high correlation coefficient ($F$). The $F_0$ depends on the risk of rupture ($\sigma F_p = F_0/F_{III}$).[15–16,20–28]

$$F_p = 1 - \exp[-(\sigma F_p - F_0)/F_{III}^\alpha]$$

In predicting the required $\sigma F_p$ of new structural materials, coefficient ($\alpha$) and constant ($F_{III}$) are the key parameters. The $F_{III}$ value is the $\sigma F_p$ value, when the term $\ln[-\ln(1 - P_p)]$ is zero. When $P_p = 0$, the $\sigma F_p$ value is defined as the $F_0$.

### 3. Results

Not only HLEBI, but also hot pressing cannot create adhesion of PTFE/PE. Although the adhesion of the laminated PTFE/PE without our double-step treatment: applying HLEBI prior to hot-press, has never been observed.
in the literature, the adhesive load of peeling resistance of the PTFE/PE sheets constructed with PTFE and PE by HLEBI before lamination has been successfully developed and measured. Figure 3 depicts the peeling adhesive force ($F_p$)–peeling distance ($d_p$) curves of the PTFE/PE laminated sheets hot-pressed at 433 K for 3.0 min under 5 MPa after HLEBI at 0.43 MGy at mean $P_p$. When the mean adhesive force of peeling resistance ($\bar{F}_p$) is defined from 10 to 30 mm, $\bar{F}_p$ values of PTFE/PE with double-step treatment is defined and firstly detected, quantitatively. Figure 4 plots the relationships between $\bar{F}_p$ and the peeling probability ($P_p$) of PTFE/PE laminated sheets hot-pressed at 433 K after HLEBI at each dose. The $\bar{F}_p$ values of PTFE/PE with double-step treatment of hot-press after HLEBI are always found, although adhesion between PTFE and PE cannot be observed by the simple hot-press followed by HLEBI. The maximum $\bar{F}_p$ values at low ($<0.4$), middle (from 0.4 to 0.7) and high $P_p$ ($>0.9$) are found at of PTFE/PE laminated sheets irradiated at 0.43, 0.13 and 0.22 MGy, respectively.

![Fig. 3 Peeling adhesive force ($F_p$)–peeling distance ($d_p$) curves of PTFE/PE laminated sheets hot-pressed at 433 K for 3.0 min under 5 MPa after HLEBI at 0.43 MGy at mean $P_p$.](image)

![Fig. 4 Relationships between mean adhesive forces of peeling resistance ($\bar{F}_p$) and peeling probability ($P_p$) of PTFE/PE laminated sheets hot-pressed at 433 K after HLEBI.](image)

Figure 5 depicts the changes in $\bar{F}_p$ (Nm$^{-1}$) at each $P_p$ of 0.06 and 0.50 of PTFE/PE laminated sheets hot-pressed at 433 K against dose of HLEBI, together with the lowest adhesive force ($\varnothing: F_s = \bar{F}_p$ at $P_p = 0$).

The $\bar{F}_p$ at each $P_p$ is perfectly zero without HLEBI. Namely, the adhesion cannot be observed without HLEBI. On the other hand, applying a small dose of HLEBI less than 0.43 MGy prior to hot-press lamination enhances the $\bar{F}_p$ at each $P_p$. The maximum $\bar{F}_p$ values at each $P_p$ (0.06, 0.50 and 0.94) of the laminated sheet irradiated at 0.13, 0.13 and 0.22 MGy are 5.44, 10.7 and 19.7 Nm$^{-1}$, respectively. On the other hands, since radiation damage decays the polymers with the higher dose of 0.65 MGy HLEBI, the fracture occurs instead of peeling. Thus, the $\bar{F}_p$ cannot be detected.

4. Discussion

4.1 The lowest adhesive force

Figure 6(a) plots changes in correlation coefficient ($f$) with respect to the potential $F_s$ value ($\bar{F}_s$) estimated from eq. (2). The $\bar{F}_s$ value is the $\bar{F}_p$ value at the maximum $F$ value.

Figure 6(b) illustrates the linear relationships between $\ln(\bar{F}_p - F_s)$ and $\ln[-\ln(1 - P_p)]$ for PTFE/PE laminated sheets hot-pressed at 433 K after HLEBI. The values of $F_{III}$ and $m$ are determined by the least-squares method. The $m$ value is estimated by the slope of the relationship when $\bar{F}_s = F_s$.

In addition, Fig. 5 shows HLEBI up to 0.43 MGy of the 2-layer assembled PTFE/PE prior to hot-press lamination apparently improves the $F_s$ value. Here, the $F_s$ are always lower than the experimental $\bar{F}_p$ values at $P_p = 0.06$ and 0.50.

The maximum $F_s$ value occurs at 0.43 MGy at 2.66 Nm$^{-1}$, which is always lower than that of the experimental $\bar{F}_p$. Consequently, the 0.43 MGy-HLEBI applied to the 2-layer assembled PTFE/PE prior to hot-press lamination improves the safety level.

![Fig. 5 Changes in mean adhesive forces of peeling resistance ($\bar{F}_p$) at each peeling probability ($P_p$) of 0.06 and 0.50 of PTFE/PE laminated sheets hot-pressed at 433 K against dose of HLEBI, together with the lowest adhesive force ($\varnothing: F_s = \bar{F}_p$ at $P_p = 0$).](image)
4.2 Adhesion with dangling bond formation

Although remarkable ESR signals could not be detected in either the untreated PTFE or PE, ESR signals, indicating dangling bond formation, in fact have been observed in PTFE and PE films treated by HLEBI.\(^{15}\)

When HLEBI cuts the chemical bonds and generates dangling bonds with nonbonding electrons in PTFE and PE polymers, the electrons probably induce the chemical bonding and intermolecular coulomb attractive forces. The mean adhesive force of peeling resistance (\(\sigma_{F_p}\)) created between the PTFE/PE sheets by the double-step treatment applying HLEBI prior to hot-press lamination can therefore be explained.

As shown in Fig. 1, the PTFE is composed of elements F and C, whereas the PE is composed of C and H. Figure 7 illustrates (a) fluorine (1s) signal and (b) carbon (1s) signal from the peeled PE surface by X-ray photoelectron spectrometer (XPS: Quantum 2000, ULVAC Co., JAPAN) surface analysis of PTFE/PE laminated films with and without the double-step treatment applying HLEBI. Based on the results of XPS surface analysis for PTFE/PE laminated sheets after the double-step treatment, fluorine is also found in the PE side peeled surface after HLEBI (see Fig. 7(a)). No signals can be observed in the samples untreated or those simply treated by HLEBI or hot-press. Thus, the adhesion by double-step treatment induces mass transport at the interface of the PTFE/PE layered structure, when both strong chemical and molecular bonds probably occur between the polymer sheets.

From the double-step treatment applying 0.04 MGy-HLEBI, electrons probably induce polarization at terminated atoms of the PTFE and PE at the adhesive interface creating adhesion. At increased dose of 0.13 MGy, the dangling bond density appears to be at or near the optimum for maximum adhesive force.

On the other hand, carefulness must be considered in design since higher dangling bond densities occur from the double-step treatment applying HLEBI doses greater than 0.22 MGy acting as crack origins and propagation sites at the laminated interface between PTFE and PE, degrading the polymers and reducing \(\sigma_{F_p}\) (see Fig. 5). Therefore, with
4.3 Stronger adhesion of PTFE/PE than PTFE/PU

The maximum values (2.66, 5.44, 10.7 and 19.7 Nm⁻¹ at each $P_p$ of zero, 0.06, 0.50 and 0.94) of PTFE/PE irradiated at 0.43, 0.13, 0.13 and 0.22 MGy are about 7, 13, 14 and 3.4 times higher than that of PTFE/Polyurethane (PU) (0.38, 0.42, 0.78 and 5.8 Nm⁻¹ at 0.43, 0.43, 0.65 and 0.30 MGy), respectively.¹⁰

Based on the XPS results for PTFE/PU¹⁶) laminated sheets, no signals can be observed in the samples untreated or those simply treated by HLEBI or hot-press, as same as PTFE/PE (see Fig. 7(a)). Fluorine is also found in the PU side peeled surface of PTFE/PU after the double-step treatment. The XPS peak intensity of fluorine (1s) of the PE side is 25% higher than that of the PU side, although the carbon (1s) intensity reduction ratio of PE before and after double-step treatment is approximately equal to that of PU.¹⁵

Since the trapping numbers of PTFE polymers of PE side is larger than that of PU side, the number ratio of mass transport molecules at the interface of the PTFE/PE layered structure is probably much higher than that of PTFE/PU, resulting in strong adhesion of PTFE/PE layered structure rather than the PTFE/PU. This is the first reason with partially experimental evidence.

In addition, another possible explanation can be suggested. Although the structure of PU polymer constructed with carbon, hydrogen, oxygen and nitrogen atoms is complex, PE (–[C₂H₂]ₙ–) as well as PTFE (–[C₂F₂]ₙ–) exhibits simple structure. When the dangling bonds form at substitutional sites of H and F atoms in PE and PU polymers irradiated by electron beam, the both mean interatomic distance of C–C bonds in principal chains with dangling bonds at PTFE and PE sides at adhesive interface probably become getting nearly equal to each other. The reaction probability of bonding sites at PTFE/PE interface should be much higher than that of PTFE/PU. Based on the XPS intensity of mass transport of PTFE polymers to PE (see Fig. 7(a)) and PU sides,¹⁶) it should be the second possible explanation of the stronger adhesive force of PTFE/PE than PTFE/PU.

The C–H, C–O and CF₂ signals in Fig. 7(b) explained as follows. The double-step treatment applying increased HLEBI dose generates CF₂ signal, whereas it annihilates the C–O signal. The large shift of big C–H signal before and after the double step treatment cannot be obtained within experimental errors, although the double step treatment slightly decreases the binding energy of top of C–H signal.

5. Conclusion

The adhesion of 2-layer laminated polytetrafluoroethylene/polyethylene (PTFE/PE) sheets without our double-step treatment with hot-press after homogeneous low energy electron beam irradiation (HLEBI) has never been observed in the literature. However, strong adhesion of the PTFE/PE was created from the new double-step treatment applying low dose ≤0.43 MGy homogeneous HLEBI of the 2-layer assembled PTFE/PE prior to hot-press lamination under 5 MPa and 433 K.

(1) The double-step treatment applying HLEBI from 0.04 to 0.43 MGy enhanced the mean adhesive force of peeling resistance ($F_p$), although no adhesion occurs and the $F_p$ value was perfectly zero for the samples untreated or those simply treated by HLEBI or hot-press. The double-step treatment applying increased HLEBI dose from 0.04 to 0.13 MGy enhanced the $F_p$ at all peeling probabilities. The adhesion cannot be observed without HLEBI. On the other hand, applying a small dose of HLEBI less than 0.43 MGy prior to hot-press lamination enhances the $F_p$ at each $P_p$. The maximum $F_p$ values at each $P_p$ (0.06, 0.50 and 0.94) of the laminated sheet irradiated at 0.13, 0.13 and 0.22 MGy are 5.44, 10.7 and 19.7 Nm⁻¹, respectively.

(2) Based on the 3-parameter Weibull equation, the lowest $F_p$ value at peeling probability ($P_p$) of zero ($F_c$) could be estimated. The double-step treatment applying HLEBI up to 0.43 MGy apparently improved the $F_c$. The maximum $F_c$ value of the PTFE/PE laminated sheets with hot-press after 0.43 MGy-irradiation dose was 2.66 Nm⁻¹. Consequently, the double-step treatment of applying 0.43 MGy-HLEBI before lamination assembly improved the safety level.

(3) Based on the results of XPS surface analysis for PTFE/PE laminated sheets after the peeling test, fluorine was detected on the peeled PE surface after the double-step treatment. Thus, the adhesion by double-step treatment induced mass transport at the interface of the PTFE/PE layered structure, resulting in strong chemical bonding between the polymer sheets.

(4) The maximum peeling adhesive force $F_p$ value at $P_p$ (zero, 0.06 and 0.50) of the laminated sheet irradiated at 0.43, 0.43 and 0.13 MGy were 2.66, 8.86 and 10.7 Nm⁻¹, respectively. However, the higher dose of the double-step treatment applying 0.13 MGy HLEBI apparently reduced the $F_p$ at low $P_p = 0$ and 0.06. Therefore, with careful consideration to dose level, the double-step treatment applying HLEBI proves a useful method for quick lamination of PTFE and PE with sterilization without the use of glue.

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REFERENCES

1) M. Kobayashi: Plastics 41 (1990) 84–89.