High Adhesive Force between Laminated Sheets of Titanium and Polyurethane Improved by Homogeneous Low Energy Electron Beam Irradiation Prior to Hot-Press

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2-layer Titanium/Polyurethane (Ti/PU) 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) prior to hot-press under 5 MPa and 413 K. Although the weak hot-press adhesion of the Ti/PU was observed without HLEBI, the new adhesion raised the bonding forces as evidenced by the mean adhesive forces of peeling resistance (${}^{\circ}F_p$). Based on the 3-parameter Weibull equation, the lowest ${}^{\circ}F_p$ value at peeling probability (P_p) of zero (F_s) could be estimated. An increasing trend in F_s occurred by the double-step treatment applying HLEBI up to 0.22 MGy reaching a maximum at 123 Nm⁻¹, improving the safety level without radiation damage. XPS (X-Ray Photoelectron Spectroscopy) observations of the peeled 0.22 MGy irradiated Ti revealed generation of a TiO₂ peak at 530.6 eV possibly explaining the increased adhesion. The residual PU deposition is apparently found to be retained on the Ti sheet by inter-matrix fracture of PU further into the thickness. This can be explained by the adhesion force between Ti/PU being stronger than the cohesive force of PU polymer itself. [doi:10.2320/matertrans.MBW201513]

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1. Introduction

Titanium (Ti) with a high durability and specific strength is utilized for not only the heat exchanger and building materials because of its high corrosion resistance by passivation to an acid and water at room temperature instead of expensive platinum and gold with strong corrosion resistance, but also the medical artificial bone with its biocompatibility. Its passive film with photo catalyzer also has been applied to self-cleaning roofs and walls of architectures with wetting molecule decomposition and sterilization.

Polyurethane (PU) is one of the most versatile materials in the world today. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances, to thermoplastic pure PU used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors.¹⁾ The Titanium/Polyurethane (Ti/PU) adhesion method is important technology to be utilized for biomedical application. However, no one has been reported. The Ti/PU adhesion by both hot-press and its strengthening method treated by homogeneous low energy electron beam irradiation (HLEBI) prior to hot-press has been found. HLEBI improves the mist resistance and wetting of inorganic materials,²⁾ and increases polymer adhering to glass fibers raising impact strength in GFRP³⁾ Improvements are mainly caused by the irradiation with the formation of dangling bonds at terminated atoms in polymers.⁴⁾ Dangling bonds enhance surface energy, which is probably the mechanism for joining the different polymers.⁵⁾ When free electrons at Ti surface act as bonding electrons like dangling bonds in polymers, rapid and strong adhesion of Ti/PU by using HLEBI prior to hot-press can be expected. Therefore, the effects of HLEBI prior to hot-press lamination on the

adhesive force of peeling resistance of bio-adaptable and high specific strength Ti/PU laminated sheets of Ti and PU have been investigated.

2. Experimental Procedure

2.1 Preparation of Ti/PU laminated sheets

Composite sheets were constructed with titanium (Ti, 10 mm × 40 mm × 0.02 mm, Nilaco Co., Ltd.) and polyurethane (PU, 10 mm × 40 mm × 0.075 mm). Pure PU film was prepared by a simple solution cast method.⁶⁻¹⁰⁾ One gram of PU granules (Noveon Estane 58888 NAT021, Lubrizol Corporation, Wickliffe, OH, USA) was dissolved in approximately 20 mL of N,N-dimethylformamide (DMF) at 358 K for 45 min. The solution was poured onto a glass plate and dried at 328 K at atmospheric pressure for one day. The obtained films were removed from the plate with ethanol. Subsequently, they were placed in a ventilated oven at 403 K for 4 h in order to eliminate residual solvent. The thicknesses of the films were about 0.075 mm. The glass transition temperatures (T_g) of PU is 228 K.⁷⁾

2.2 Homogeneous low energy electron beam irradiation (HLEBI)

The 2-layer laminate sample is assembled on the jig: one 0.02 mm thick Ti layer, followed by one 0.075 mm thick PU layer, on top of which is placed a 0.015 mm thick nylon 6 supporting film. Since the HLEBI first penetrates the PU layer, followed by the Ti layer we refer to the samples as Ti/PU.

To obtain high reproducibility of peeling strength results, compressive stress of more than 80 kPa was loaded for more 1.0 h. Since no peeling force was observed at the interface between the back surface of Ti or PU layer and the nylon 6 supporting film and in the jig, it was easy to remove the supporting film after HLEBI. The sample at the outer surface of the nylon film was homogeneously irradiated in the jig

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by an electron-curtain processor (Type CB250/30/20 mA, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd. Tokyo).^{8–10} The sample was homogeneously irradiated with the sheet HLEBI with low energy through a titanium thin film window attached to a 550 mm diameter vacuum chamber. A tungsten filament in a vacuum is used to generate the electron beam at a low energy (acceleration potential, V: kV), of 170 keV and irradiating current density (I , A/m) of 0.0131 A/m.

Although the sheet electron beam generation is in a vacuum, the irradiated sample has been kept under protective nitrogen at atmospheric pressure. The distance between sample and window is 25 mm. To prevent oxidation, the samples are kept in a protective atmosphere of nitrogen gas with a residual concentration of oxygen below 300 ppm. The flow rate of nitrogen gas is 1.5 L/s at 0.1 MPa nitrogen gas pressure.

Given the densities (ρ) are $4.54 \text{ g}\cdot\text{cm}^{-3}$ for Ti and $1.13 \text{ g}\cdot\text{cm}^{-3}$ for PU, the penetration depth (D_{th}) values of 0.020 mm for Ti and 0.192 mm for PU were estimated by assumptions of Christenhusz and Reimer, respectively.¹¹ The experimental penetration depth values of metals and ceramics were approximately equal to that of the estimated value, whereas the experimental values of polymers were generally deeper than that of calculated one. Furthermore, the D_{th} values of Ti (0.077 mm) and PU (0.291 mm) were also calculated by the assumptions of Libby.¹² The experimental penetration depth of polymers were probably equal to and deeper than that of these calculated values. Consequently, since the irradiated thickness of laminated composites with Ti film (20 μm thickness) and PU film (75 μm thickness) were 95 μm , the adhesive interface is irradiated throughout their thicknesses.

Ti/PU composite film lamination was subsequently performed by the uni-directional hot-press at 413 K for 3.0 min under 5 MPa atmosphere after HLEBI.

2.3 T-peeling test

Composite samples after removing the 0.015 mm 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 (${}^{\circ}F_p$). 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.^{9,10} Since the unit of the F_p is Nm^{-1} , the ${}^{\circ}F_p$ is used instead of the adhesive strength, whose units should be Nm^{-1} . 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 ${}^{\circ}F_p$ 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 meth-

od¹³ is one of convenient ways to analyze the mechanical probabilities of adhesive strength,^{14,15} adhesive peeling resistance¹⁶ and elasticity,¹⁷ as well as strength and impact value on fracture.¹⁸ 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.¹⁶ It is expressed by the following equation.

$$P_p = (I - 0.3)/(n + 0.4) \quad (1)$$

Here, n and I are the total number of samples ($n = 11$) and order of peeling of each sample ($0 \leq I \leq 11$), 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 X-ray photoelectron spectrometer (XPS) measurements

X-ray photoelectron spectrometer (XPS: Quantum 2000, ULVAC Co., JAPAN)¹⁶ was used for surface analysis of peeled 0.22 MGy HLEBI Ti and unassembled untreated Ti. Both Ti and PU contain elements C, H, N, Ti and O. Narrow scans for the C (1s) and O (1s) signals from the Ti surfaces were detected by the XPS.

3. Results

The hot pressing can create the weak adhesion force of Ti/PU without HLEBI, whereas a single process of HLEBI cannot create adhesion of Ti/PU. Although the adhesion of the laminated Ti/PU without our double-step treatment: applying HLEBI prior to hot-press has not been observed, the large adhesive load of peeling resistance of the Ti/PU sheets constructed with Ti and PU by HLEBI prior to hot-press has been successfully developed and measured.

Figure 1 shows a comparison of peeling load, L_p (N) vs. peeling distance, d_p (mm) curves between HLEBI at 0.22 MGy and untreated Ti/PU laminated sheets at medium accumulative probability of peeling force, ($P_p = 0.50$). When the ${}^{\circ}F_p$ is the mean peeling load for effective peeling distance from 10 to 30 mm, ${}^{\circ}F_p$ values of Ti/PU are determined.

Fig. 1 Peeling load (L_p)-peeling distance (d_p) curves of Ti/PU laminated sheets before and after 0.22 MGy-HLEBI at medium P_p of 0.50.

Fig. 2 Relationships between $^{\circ}F_p$ and P_p of Ti/PU laminated sheets untreated and HLEBI-treated, together with the calculated $^{\circ}F_s$ value at $P_p = \text{zero}$ (F_s).

Fig. 3 Changes in experimental $^{\circ}F_p$ at each P_p of 0, 0.06, 0.50 and 0.94 of Ti/PU laminated sheets against dose of HLEBI.

Figure 2 plots the relationships between $^{\circ}F_p$ and the P_p of the Ti/PU laminated sheets with and without HLEBI at each dose from 0.04 to 0.43 MGy prior to hot-pressed at 413 K. Although adhesion between Ti and PU cannot be observed by HLEBI without hot-press, the $^{\circ}F_p$ values of Ti/PU with double-step treatment of HLEBI from 0.04 to 0.43 MGy prior to hot-press are mostly higher than that without HLEBI prior to hot-press.

Figure 3 shows the mean $^{\circ}F_p$ for low-, medium- and high- P_p of 0.06, 0.50 and 0.94 against HLEBI occurs in the 0.22 MGy-HLEBI samples at 125.7, 160.5 and 289.4 Nm^{-1} , respectively. The $^{\circ}F_p$ at low- and medium- and high- P_p of 0.06, 0.50 and 0.94 were 125.7, 160.5 and 289.4 Nm^{-1} , respectively, which were more than 6.5, 3.5 and 2.8 times larger than 19.4, 46.4 and 101.9 Nm^{-1} before treatment. All $^{\circ}F_p$ values of Ti/PU laminated sheets with 0.04 to 0.43 MGy apparently exceed all corresponding values of untreated samples. Thus, adhesion of Ti/PU laminated sheets with 0.04 to 0.43 MGy-HLEBI deems effective.

4. Discussion

4.1 The adhesive force compared with references

Figure 4 plots the relationships between $^{\circ}F_p$ and the P_p of

Fig. 4 Relationships between $^{\circ}F_p$ and P_p of Ti/PU laminated sheets untreated and HLEBI-treated at 0.22 MGy, together with practical references.

the Ti/PU laminated sheets with and without HLEBI at 0.22 MGy prior to hot-pressed at 413 K, together with practical references. The $^{\circ}F_p$ values of Ti/PU with double-step treatment of HLEBI at 0.22 MGy prior to hot-press are apparently higher than that of the commercially used Gummed cloth tape roll and approximately equal to that of both Scotch tape/Ti and Gummed cloth tape/Ti laminations.

4.2 The statistically lowest adhesive force

In order to obtain the statistically lowest peeling stress for safety design, the lowest $^{\circ}F_p$ value at $P_p = 0$ (F_s) is assumed to be attained from the adaptable relationship of the 3-parameter Weibull equation iterating to the high correlation coefficient (F). The P_p depends on the risk of rupture ($[(^{\circ}F_p - F_s)/F_{III}]^{8-10}$).

$$P_p = 1 - \exp[-((^{\circ}F_p - F_s)/F_{III})^m] \quad (2)$$

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

Figure 5 plots the iteration to obtain the F with respect to the potential adhesive force of peeling $^{\circ}F_s$ value ($^{\circ}F_s$) estimated from the logarithmic form.

Figure 6 illustrates the linear relationships between $\ln(^{\circ}F_p - F_s)$ and $\ln[-\ln(1 - P_p)]$. The values of F_{III} and m are determined by the least-squares best fit method. The m value is estimated by the slope of the relationship when $^{\circ}F_s = F_s$. Figure 3 shows F_s is always lower than the experimental $^{\circ}F_p$ value. The HLEBI from 0.04 to 0.43 MGy improves the F_s values of the Ti/PU laminated sheets over that of the untreated. The 0.22 MGy-HLEBI apparently enhances the F_s from 4.2 $\text{N}\cdot\text{m}^{-1}$ for the untreated to 123 $\text{N}\cdot\text{m}^{-1}$, as well as at low P_p of 0.06 (the lowest experimental $^{\circ}F_p$ from 19.4 for the untreated to 125.6 $\text{N}\cdot\text{m}^{-1}$). Consequently, HLEBI enhances the safety level (reliability) of Ti/PU laminated sheets. This indicates HLEBI induced adhesion can be applied to practical articles with sterilization without volatilization, when the adhesive force of peeling resistivity is less than 123 $\text{N}\cdot\text{m}^{-1}$.

Fig. 5 Changes in f against the potential $^{\circ}F_s$ value ($^{\circ}F_s$) for Ti/PU laminated sheets untreated and HLEBI-treated.

Fig. 6 Liner relationships between $\ln(^{\circ}F_p - F_s)$ and $\ln[-\ln(1 - P_p)]$ for Ti/PU laminated sheets untreated and HLEBI-treated.

4.3 X-ray photoelectron spectrometry (XPS) of Ti surface

When HLEBI cuts the chemical bonds and generates dangling bonds with nonbonding electrons in PU polymer, the electrons probably induce the chemical bonding. The $^{\circ}F_p$ created between the Ti/PU sheets by the double-step treatment applying HLEBI prior to hot-press lamination can therefore be explained. The PU is composed of hydrogen (H), carbon (C), nitrogen (N) and oxygen (O).

Figure 7 and Fig. 8 show X-ray photoelectron spectrometry (XPS) of carbon (C 1s) and oxygen (O 1s) signals of the peeled surface of Ti/PU laminated sheet with and without 0.22 MGy HLEBI. Results indicate the HLEBI acts to produce adhesion in the Ti/PU laminated sheet where fracture generally occurred near the peeled Ti/PU interface.

In Fig. 7 the XPS narrow scan of carbon (C 1s) of the peeled 0.22 MGy sample shows peaks at ~ 284 eV corresponding with the C 1s in C-H groups. In order to calibrate the results in detail, XPS signals of C 1s have been obtained for PU with and without HLEBI (Solid and Broken lines in Fig. 7). Since the lamination increase the concentrations of

Fig. 7 Carbon (1s) signal in Ti side of XPS analysis of Ti/PU laminated sheets with and without HLEBI.

Fig. 8 Oxygen (1s) signal in Ti side of XPS analysis of Ti/PU laminated sheets with and without HLEBI.

carbon, it probably attributes to weak adhesion force of the Ti/PU lamination untreated, as shown in Figs. 2 and 3. The highest signal intensity of C-H, C-C and C=C groups for 0.22 MGy sample is gotten. Since chemical bonds of C-C and C=C cannot be found in PU structure, C-H bonds of PU on Ti sheet should exist. Thus, the fracture propagates at inside of PU.

Since HLEBI enhances the XPS signal of C-H group and increases the number of C-H bonds of PU on Ti, the adhesion force at Ti/PU interface is probably getting higher than that of cohesive force of PU inside.

The intermolecular hydrogen bonding (~ 20 kJ/mol)¹⁹⁾ between oxygen atoms in passive film of Ti and hydrogen atoms in PU should always contribute the adhesion force at interface.

In order to calibrate the results in detail, XPS signals of O (1s) in O-H and TiO₂ groups have been obtained for Ti/PU with and without HLEBI (Solid and Broken lines in Fig. 8). The low intensity of O (1s) in O-H and TiO₂ signals for Ti/PU untreated is gotten, whereas HLEBI boosts the both of them. Since HLEBI often cuts the chemical bonds in the PU and Ti passive film, it easily forms the O-H and TiO₂ bonds near interface, as shown in Fig. 8. Thus, increasing number

of hydrogen bonding probably induces the adhesive force between the Ti passive film and PU.

In addition, when HLEBI cuts and activates the Ti atoms in passive films and the C=O bonds in PU, Ti–O interatomic chemical bonding at interface probably contributes to increasing the adhesion force between Ti and PU, as shown in Fig. 3.

Since 0.22 MGy-HLEBI remarkably enhances the intensity, it remarkably enhances the oxygen concentration at PU interface. Since HLEBI activates the terminated polymer atoms, oxygen atoms from atmospheric molecules are attracted to surface, and then contaminate the polymers. It shows that the lamination simply increase the oxygen concentration because of oxygen contamination effects from atmospheric molecules, as shown in Fig. 8. The contamination probably attributes to weak adhesion force of the Ti/PU lamination untreated, as shown in Figs. 2 and 3.

On the other hand, carefulness must be considered in design since higher dangling bond densities occur from the double-step treatment applying HLEBI doses more than 0.22 MGy acting as crack origins and propagation sites at the laminated interface between Ti and PU, degrading the polymers and reducing $^{\circ}F_p$ (see Fig. 3). Therefore, with cautious consideration to dose level, the double-step treatment applying HLEBI prior to hot-press proves a useful method for quick lamination of Ti and PU without the use of glue.

5. Conclusion

2-layer Titanium/Polyurethane (Ti/PU) laminated sheets were prepared by a new adhesion method, a double-step treatment consisting of applying low dose (≤ 0.43 MGy) of homogeneous low energy electron beam irradiation (HLEBI) prior to hot-press under 5 MPa at 413 K. Although the weak adhesion of 2-layer Ti/PU laminated sheets without our double-step treatment with hot-press after HLEBI had been observed, the strong adhesion of the Ti/PU was found from the new double-step treatment applying low dose ≤ 43 MGy-HLEBI of the 2-layer assembled Ti/PU prior to hot-press lamination under 5 MPa at 413 K.

- (1) The double-step treatment applying increased HLEBI dose from 0.04 to 0.43 MGy prior to hot-press enhanced the mean adhesive forces of peeling resistance ($^{\circ}F_p$) at peeling probability (P_p) of 0, 0.06, 0.50 and 0.94. The $^{\circ}F_p$ values of Ti/PU with double-step treatment of HLEBI at 0.22 MGy prior to hot-press are apparently higher than that of peeling resistance of the commercially used Gummed cloth tape roll and approximately equal to that of both Scotch tape/Ti and Gummed cloth tape/Ti laminations.
- (2) Based on the 3-parameter Weibull equation, the lowest $^{\circ}F_p$ value at the lowest P_p of zero (F_s) could be estimated. The double-step treatment applying HLEBI up to 0.22 MGy prior to hot-press apparently improved the F_s . The maximum F_s value of the Ti/PU laminated sheets with hot-press after 0.22 MGy-HLEBI dose was 123 Nm^{-1} . Consequently, the double-step treatment of applying 0.22 MGy-HLEBI prior to hot-press improved the safety level.
- (3) The maximum peeling adhesive force $^{\circ}F_p$ value at high

and low P_p (0, 0.06 and 0.94) of the laminated sheets irradiated at 0.22 MGy were 123, 125.8, 160.5 and 289.4 Nm^{-1} , respectively. However, the higher dose of the double-step treatment applying more than 0.30 MGy HLEBI apparently reduced the $^{\circ}F_p$ at each P_p . Therefore, with careful consideration to dose level, the double-step treatment applying HLEBI prior to hot-press proves a useful method for strong and quick lamination of Ti and PU with sterilization without the use of glue.

- (4) Based on the results of XPS surface analysis for Ti/PU laminated sheets after the peeling test, oxygen atoms were detected on the peeled Ti surface after the double-step treatment, resulting in strong chemical bonding at interface.
- (5) HLEBI up to 0.22 MGy reaching a maximum at 123 Nm^{-1} , improving the safety level without radiation damages. When HLEBI cuts the chemical bonds in PU polymer and generates terminated atoms with dangling bonds, they probably induce the chemical and hydrogen bonding. Therefore, increasing adhesion force between the laminated sheets can be explained.

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