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

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2-layer aluminum/polyurethane (Al/PU) laminated sheets were prepared by a new adhesion method, a double-step treatment consisting of: (1) applying low dose ≤0.43 MGy homogeneous low energy electron beam irradiation (HLEBI) to the 2-layer assembly where the HLEBI penetrates through the Al and PU layers, respectively, prior to (2) hot-press under 5 MPa and 403 K. Although the adhesion of the Al/PU sheets cannot be observed without the new double-step treatment, bonding forces were created as evidenced by the mean adhesive forces of peeling PU, the created adhesion between the laminated sheets can be explained.

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1. Introduction

Aluminum exhibits the high electric conductivity, shiny silver color and light specific weight, as well as high corrosion resistance due to passivation. Structural components made from aluminum and its alloys are utilized for the structural and electric articles. 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.

Homogeneous low energy electron beam irradiation (HLEBI) improves the mist resistance and wetting of inorganic materials, and increases polymer adhering to glass fibers raising impact strength in GFRP. Improvements are mainly caused by the irradiation with the formation of dangling bonds in polymers. Dangling bonds enhance surface energy, which is probably the mechanism for joining the different polymers. Thus, rapid and safe adhesion between different polymers by using HLEBI 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 strength aluminum/polyurethane (Al/PU) laminated sheets of PU and Al have been investigated.

2. Experimental Procedure

2.1 Preparation of Al/PU laminated film

Composite sheets were constructed with PU (10 mm × 40 mm × 0.120 mm) and Al (10 mm × 40 mm × 0.011 mm, Toyo Aluminium Ekco Products Co., Ltd., Japan). Pure PU film was prepared by a simple solution cast method. One gram of PU granules (Noveon Estate 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 120 μm. The glass transition temperatures (Tg) of PU is 228 K.

2.2 Homogeneous irradiation of electron beam

As illustrated in Fig. 1, 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 0.120 mm thick PU layer, followed by one 0.011 mm thick Al layer, on top of which is placed a 0.015 mm thick supporting Nylon film. Since the HLEBI first penetrates the PU layer, followed by the Al layer we refer to the samples as Al/PU.

To obtain high reproducibility of peeling strength results, compressive stress of more than 80 kPa was loaded for more
than 1.0 h. Since no peeling force was observed at the interface between the back surface of Al or PU 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. 1) by an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co., Ltd., Tokyo). 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 initial distance before peeling (d) was 5 mm. The peeling resistance of the Al/PU laminated sheets hot-pressed at 403 K for 3.0 min under 5 MPa after HLEBI at 0.22 MGy at Pp of 0.94.

Al/PU composite film lamination was subsequently performed by the uni-directional hot-press at 403 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 (Fp). The peeling adhesive force (Fp) and its peeling distance (dp) 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. Since the unit of the Fp is N m⁻¹, the Fp is used instead of the adhesive strength, whose units should be N m⁻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 Fp is determined by using micro-load tensile tester. The Fp is estimated by the peeling load and experimental peeling width and length of 10 and 35 mm, respectively. The initial distance before peeling (d) is defined at the start point of peeling force, which corresponds to the start point of the first relaxation. The d value is ~1 mm.

### 3. Results

Although the adhesion of the laminated Al/PU 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 Al/PU sheets constructed with Al and PU by HLEBI before lamination has been successfully developed and measured. Figure 2 depicts the peeling adhesive force (Fp) - peeling distance (dp) curves of the Al/PU laminated sheets hot-pressed at 403 K for 3.0 min under 5 MPa after HLEBI at 0.22 MGy at Pp of 0.94. When the mean adhesive force of peeling resistance (Fp) is defined from 10 to 30 mm, Fp values of Al/PU with double-step treatment is defined.

Figure 3 plots the relationships between mean adhesive forces of peeling resistance (Fp) and peeling probability (Pp) of Al/PU laminated sheets hot-pressed at 403 K after HLEBI.

Al/PU laminated sheets hot-pressed at 403 K for 3.0 min under 5 MPa after HLEBI at 0.22 MGy at Pp of 0.94. When the mean adhesive force of peeling resistance (Fp) is defined from 10 to 30 mm, Fp values of Al/PU with double-step treatment is defined.

Figure 4 depicts the changes in Fp (Nm⁻¹) at each Pp of 0.06 and 0.50 of Al/PU laminated sheets hot-pressed at 403 K against HLEBI dose, together with the lowest adhesive force (Fp = Fp at Pp = 0). The Fp at each Pp 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 0.22 MGy prior to hot-press lamination enhances the $F_p$ at each $P_p$. The maximum $F_p$ value at $P_p$ (0.06 and 0.50) of the laminated sheet irradiated at 0.13 and 0.22 MGy are 18.6 and 34.0 Nm$^{-1}$, respectively. However, the higher dose of 0.30 MGy HLEBI apparently reduces the $F_p$ at $P_p$ = 0.06 and 0.50.

4. Discussion

4.1 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 ($F_p$) value at $P_p$ of zero ($F_s$) 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 $P_p$ depends on the risk of rupture ($F_p - F_s$).

$$P_p = 1 - \exp\left(-\left(F_p - F_s\right)/F_m\right)$$

In predicting the required $F_p$ of new structural materials, coefficient ($m$) and constant ($F_m$) are the key parameters. The $F_m$ value is the $F_p$ value at $P_p$ of 0.63, when the term $\ln(-\ln(1 - P_p))$ is zero.

When $P_p = 0$, the $F_p$ value is defined as the $F_s$. Figure 5(a) plots changes in correlation coefficient ($F$) with respect to the potential $F_p$ value ($F_s$) estimated from eq. (1). The $F_s$ value is the $F_p$ value at the maximum $F$ value.

In addition, Fig. 4 shows HLEBI up to 0.22 MGy of the 2-layer assembled Al/PU prior to hot-press lamination apparently improves the $F_s$ value. Here, the $F_s$ are always lower than the experimental $F_p$ values at $P_p$ = 0.06 and 0.50.

The maximum $F_s$ value occurs at 0.22 MGy at 16.7 Nm$^{-1}$, which is always lower than that of the experimental $F_p$. Consequently, the 0.22 MGy-HLEBI applied to the 2-layer assembled Al/PU prior to hot-press lamination improves the safety level.

4.2 Influence of dangling bond formation on mechanical properties

Although remarkable ESR signals could not be detected in either the untreated PU, ESR signals, indicating dangling bond formation, in fact have been observed in PU film treated by HLEBI.

When HLEBI cuts the chemical bonds and generates dangling bonds with nonbonding electrons in PU polymer, 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 Al/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 6 illustrates carbon (1s) signal from the peeled Al surface by X-ray photoelectron spectrometer (XPS: Quantum 2000, ULVAC Co., JAPAN) surface analysis of Al/PU laminated films with and without the double-step treatment applying HLEBI. Based on the results of XPS surface analysis for Al/PU laminated sheets after the double-step treatment, carbon is found in the Al side peeled surface after HLEBI (see Fig. 6). Small signal 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 Al/PU layered structure, resulting in strong chemical bonding between the Al and PU sheets.

From the double-step treatment applying 0.043 to 0.22 MGy-HLEBI, electrons probably induce polarization at terminated atoms of the Al and PU at the adhesive interface creating adhesion. At increased dose of 0.22 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 0.30 MGy acting as crack origins and propagation sites at the laminated interface between Al and PU, degrading the polymers and reducing \(\sigma F_p\) (see Fig. 4). Therefore, with cautious consideration to dose level, the double-step treatment applying HLEBI proves a useful method for quick lamination of Al and PU without the use of glue.

5. Conclusion

The adhesion of 2-layer laminated Al/PU 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 Al/PU was created from the new double-step treatment applying low dose \(\leq 0.43\) MGy homogeneous HLEBI of the 2-layer assembled Al/PU prior to hot-press lamination under 5 MPa and 403 K.

1) The double-step treatment applying HLEBI from 0.043 to 0.22 MGy enhanced the mean adhesive force of peeling resistance \((\sigma F_p)\), although no adhesion occurs and the \(\sigma F_p\) 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 0.043 to 0.22 MGy enhanced the \(\sigma F_p\) at all peeling probabilities. Based on the 3-parameter Weibull equation, the lowest \(\sigma F_p\) value at peeling probability \((P_p)\) of zero \((F_p)\) could be estimated. The double-step treatment applying HLEBI up to 0.22 MGy apparently improved the \(F_p\). The maximum \(F_p\) value of the Al/PU laminated sheets with hot-press after 0.22 MGy - irradiation dose was 34.0 Nm\(^{-1}\). Consequently, the double-step treatment of applying 0.22 MGy-HLEBI before lamination assembly improved the safety level.

2) Based on the 3-parameter Weibull equation, the lowest \(\sigma F_p\) value at \(P_p\) of zero \((F_p)\) could be estimated. An increasing trend in \(F_p\) occurs by the double-step treatment applying HLEBI up to 0.22 MGy reaching a maximum at 34.0 Nm\(^{-1}\), improving the safety level.

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

4) The maximum peeling adhesive force \(\sigma F_p\) at \(P_p\) (zero, 0.06 and 0.50) of the laminated sheet irradiated at 0.22, 0.13 and 0.22 MGy were 16.7, 18.6 and 34.0 Nm\(^{-1}\), respectively. However, the higher dose of the double-step treatment applying 0.30 MGy HLEBI apparently reduced the \(\sigma F_p\) 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 Al and PU with sterilization without the use of glue.

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REFERENCES