Effects of Homogeneous Low Energy Electron Beam Irradiation (HLEBI) on Adhesive Force of Peeling Resistance of Laminated Sheet with Polyethylene (PE) and Austenitic 18-8 Stainless Steels

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2-layer laminated sheets (PE/18-8) with Polyethylene (PE) and austenitic 18-8 stainless steels (18-8) 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 343 K. Although the weak hot-press adhesion of the PE/18-8 was observed without HLEBI, the new adhesion raised the bonding forces as evidenced by the mean adhesive forces of peeling resistance ($F_p$). Based on the 3-parameter Weibull equation, the lowest $F_p$ value at peeling probability ($P_p$) of zero ($F_0$) could be estimated. An increasing trend in $F_p$ occurred by the double-step treatment applying HLEBI up to 0.30 MGy reaching a maximum at 0.85 N m$^{-1}$, improving the safety level without radiation damage. When HLEBI cut the chemical bonds in PE polymer and generated terminated atoms with dangling bonds, they probably induced the chemical bonding. Therefore, increasing adhesion force between the laminated sheets could be explained.

1. Introduction

Techniques to increase the strength of metal/composite joints are highly sought after. Polyethylene (PE) exhibits high wear resistance and high strength as well as transparency.1) Austenite stainless steel (18-8) for structural applications has been widely utilized in the aerospace, automotive and shipbuilding industries, along with various day-to-day items.

The adhesion method to prepare 2-layer laminated sheets (PE/18-8) with PE and 18-8 is important technology to be utilized for biomedical application. However no one has been probably reported in international journals. The CFRP/18-8 adhesion treated by homogeneous low energy electron beam irradiation (HLEBI) prior to hot-press has been found.2) HLEBI improves the mist resistance and wetting of inorganic materials,3) and increases polymer adhering to glass fibers raising impact strength in GFRP.4)

Applying surface treatment of low dose of electron beam (EB) irradiation on the order of 0.01 to 1 MGy has been gaining momentum as a successful method to adhere polymeric materials without the use of adhesive. Polyimide/polytetrafluoroethylene (PI/PTFE) layered films have been successfully fabricated by homogeneous low energy electron beam irradiation (HLEBI);5) while applying 0.50 MGy EB dose increased adhesive bond strength between PET films and acrylic adhesive.6) HLEBI has been found to increase adhesive mechanical properties of polymer-polymer joints for biomedical applications of PDMS (polydimethylsiloxane)/PTFE,7) PDMS/PP (polypropylene),8) and create strong adhesion in the difficult to bond PTFE/PE (polyethylene).9)

Improvements are mainly caused by the irradiation with the formation of dangling bonds at terminated atoms in polymers.10) Dangling bonds enhance surface energy, which is probably the mechanism for joining the different polymers.11) When free electrons on PE and 18-8 surface act as bonding electrons like dangling bonds in polymer, rapid and strong adhesion of PE/18-8 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 strength PE/18-8 laminated sheets of PE/18-8 have been investigated.

2. Experimental Procedure

2.1 Preparation of PE/18-8 laminated sheets

Composite sheets were constructed with 18-8 (10 mm × 40 mm × 0.02 mm, Nilaco Co., Ltd.) and PE (10 mm × 40 mm × 0.08 mm, High-star PE 100, Star plastic Industry Inc., Japan). The glass transition temperatures ($T_g$) of PE is 183–194 K.12)

2.2 Homogeneous low energy electron beam irradiation (HLEBI)

The PE/18-8 laminated sheets was irradiated by using an electron-curtain processor (Type CB250/15/10 mA, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd. Tokyo).13-22) The specimen was homogeneously irradiated with the sheet HLEBI with low energy through a titanium thin film window attached to a 240 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 kV and irradiating current density ($I$, A/m$^2$) of 0.089 A/m$^2$.

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 35 mm. To prevent oxidation, the samples are kept in a protective atmosphere of nitrogen gas

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with a residual concentration of oxygen below 400 ppm. The flow rate of nitrogen gas is 1.5 L/s at 0.1 MPa nitrogen gas pressure.

The absorbed dose is controlled by the integrated irradiation time in each of the samples. Here, absorbed dose is corrected from irradiation dose by using an FWT nylon dosimeter of RCD radiometer film (FWT-60-00: Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117, USA) with an irradiation reader (FWT-92D: Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117, USA). The absorbed dose corresponded to irradiation dose is 0.0432 MGy at each irradiation, which is applied for only a short time (0.23 s) to avoid excessive heating of the sample; the temperature of the sample surface remains below 323 K just after irradiation. The sample in the aluminum plate holder (0.15 m × 0.15 m) is transported on a conveyor at a speed of 9.56 m/min. The sheet HLEBI is applied intermittently. Repeated irradiations to both side surfaces of the holder (0.15 m) is transported on a conveyor at a speed of 9.56 m/min, and number of irradiations (N) are determined, the irradiated dosage is proportional to the yield value from the irradiation current (I, mA), the conveyor speed (S, m/min) and number of irradiations (N).

Based on the density (ρ: kg/m³) and irradiation voltage at the specimen surface (V: kV), the penetration depth (D₀: m) of HLEBI is expressed by the following equation.23)

\[ D₀ = 66.7V^{5/3}/ρ \]  

Specimen surface electrical potential (V) was mainly reduced going through the Ti window (ΔVₜι) and N₂ gas atmosphere (ΔV₂ₙ). 

\[ V = 170 \text{ keV} − ΔVₜι − ΔV₂ₙ \]  

(2)

Based on eq. (2), the dropped potential values, ΔVₜι and ΔV₂ₙ are estimated from the acceleration potential (170 keV), the 10 µm thickness (Tₜι) of the titanium window (density: 4540 kg m⁻³), and the 35 mm distance between the sample and the window (T₂ₙ) in the N₂ gas atmosphere (density: ρ₂ₙ = 1.13 kg m⁻³). 

\[ Vₜι = (Tₜι/D₀ₜι) \times 170 \text{ keV} \]

\[ = Tₜιρ₀ₜι/[66.7 \times (170 \text{ keV})^{2/3}] \]

\[ = (10^{-5} \text{ m}) \times (4540 \text{ kg m}^{-3})/[66.7 \times (170 \text{ keV})^{2/3}] \]

\[ = 22.2 \text{ keV} \]  

(3)

\[ ΔV₂ₙ = (T₂ₙ/D₀₂ₙ) \times Vₜι \]

\[ = T₂ₙρ₂ₙ/[66.7 \times (Vₜι)^{2/3}] \]

\[ = (35 \times 10^{-3} \text{ m}) \times (1.13 \text{ kg m}^{-3})/[66.7 \times (170 \text{ keV})^{2/3}] \]  

(4)

Since the dropped potential values are 22.2 and 18.2 keV, the specimen surface electrical potential, V is 129.6 keV as follows.

\[ V = 170 \text{ keV} − 22.2 \text{ keV} − 18.2 \text{ keV} = 129.6 \text{ keV} \]  

(5)

Given typical density of PE is 863 kg m⁻³, the HLEBI depth into the PE film estimated from eq. (1) is D₀ = 229 µm, more than four times larger than the PE thickness of 80 µm, hence the HLEBI penetrated through the entire thickness.

### 2.3 90°-peeling test

Composite samples after hot-press under 5 MPa at 343 K were prepared for the 90°-peeling test to evaluate the influence of HLEBI on the mean adhesive force of peeling resistance (F_p), as shown in Fig. 1. Peeling load (L_p) vs. peeling distance (d_p) curves were obtained by using a micro-load tensile tester (F-S Master-1K-2N, IMADA Co. Ltd., Japan) with a strain rate of 10 mm/min.7) Since the unit of the F_p was N m⁻¹, the F_p was used instead of the adhesive strength, whose units should be N m⁻². The sample condition of tensile test was as follows:

1. The vertical length from the peeling contact point to the end of the sample was 5 mm.

2. The F_p was determined by using micro-load tensile tester. The F_p was estimated by the peeling load and experimental peeling width and length of 10 and 35 mm, respectively. The initial distance before peeling (d_i) was 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 is one of convenient ways to analyze the mechanical probabilities of adhesive strength,25,26) adhesive peeling resistance7) and elasticity,27) as well as strength and impact value on fracture.28-34) 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.7) It is expressed by the following equation.

\[ P_p = (I − 0.3)/(n + 0.4) \]  

(6)

Here, n and I are the total number of samples (n = 11) and order of peeling of each sample (0 ≤ I ≤ 11), respectively. While 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)7) was used for surface analysis of peeled 0.30 MGy HLEBI 18-8 stainless and PE. Both 18-8 stainless and PE contain elements C and O. Narrow scans for the C (1s) and O (1s) signals from the PE and 18-8 surfaces were detected by the XPS.
3. Results

3.1 Peeling load \( (L_p) \)-Peeling distance \( (d_p) \) curve

Figure 2 shows a comparison of \( L_p \) (N) vs. peeling distance, \( d_p \) (mm) curves between HLEBI and untreated PE/18-8 joint at median accumulative probability of peeling force, \( P_p = 0.50 \). Although without HLEBI a large adhesive load of peeling resistance in the PE/18-8 could not be obtained, by applying HLEBI at 0.30 MGy the peeling load, \( L_p \) is significantly increased (~1.9 N) over the low value of the untreated (~0.20 N). The 0.30 MGy-HLEBI therefore laminates the PE with the 18-8 stainless, generating the higher peeling resistance. Based on the optical scale observation, the fracture can be seen to always occur at the interface.

3.2 Adhesive force of peeling (\( F_p \)) as a function of accumulative probability of peeling force (\( P_p \))

Figure 3 plots the relationships between the adhesive force of peeling resistance (\( F_p \)) and peeling probability (\( P_p \)) of the PE/18-8 laminated sheets for the untreated and HLEBI-treated. Applying 0.30 MGy HLEBI gives the highest \( F_p \) values at low \( P_p \) < 0.4. Figure 4 shows the maximum \( F_p \) for low- and median- \( P_p \) of 0.06 and 0.50 against absorbed dose in the 0.30 MGy-HLEBI samples at 0.9 and 3.3 N m\(^{-1}\), respectively. They were up to 0.9 and 3.3 N m\(^{-1}\) larger than 0 and 0 N m\(^{-1}\) before treatment. All \( F_p \) values of PE/18-8 laminated sheets with small dose of 0.04 to 0.43 MGy apparently exceed all corresponding values of untreated samples. Thus, adhesion of PE/18-8 laminated sheets with small dose from 0.04 to 0.43 MGy-HLEBI deems effective.

4. Discussion

4.1 The statistically lowest adhesive force

In order to obtain the statistically lowest peeling stress for safety design, the lowest \( F_p \) value at \( P_p = 0 \) \( (F_\text{m}) \) 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 \( (\ln F_p - F_\text{m})/F_\text{III} \). \(^{7,27,31-36}\)

\[
P_p = 1 - \exp[-(\ln F_p - F_\text{m})/F_\text{III}^m]
\]

(7)

The \( F_\text{III} \) value is the \( F_p \) value, when the term \( \ln[-\ln(1 - P_p)] \) is zero. When \( P_p = 0 \), the required \( F_p \) value to evaluate new structural materials is defined as the \( F_p \). In predicting the \( F_p \), coefficient \( (m) \) and constant \( (F_\text{III}) \) are the key parameters. Figure 5 plots the iteration to obtain the highest correlation coefficient \( (F) \) with respect to the potential adhesive force of peeling \( F_p \) value \( (F_p) \) estimated from the logarithmic form.

Figure 6 illustrates the linear relationships between \( \ln (\ln F_p - F_\text{s}) \) and \( \ln [-\ln (1 - P_p)] \). The values of \( F_\text{III} \) and \( m \) are determined by the least-squares best fit method. The \( m \) value is estimated by the slope of the relationship when \( F_p = F_\text{m} \). The constant values of \( m \), \( F_\text{III} \) and \( F_\text{s} \) are summarized in Table 1.

Figure 4 shows \( F_p \) is always lower than the experimental \( F_p \) value. The HLEBI from 0.04 and 0.22 to 0.43 MGy improves the \( F_p \) values of the PE/18-8 laminated sheets over that of the untreated. The 0.30 MGy-HLEBI apparently enhances the \( F_p \) from 0 N m\(^{-1}\) for the untreated to 0.8 N m\(^{-1}\), as well as at low \( P_p \) of 0.06 (the lowest experimental
HLEBI enhances the safety level (reliability) of PE/18-8 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 0.8 \text{ Nm}^{-1}.

### 4.2 X-ray photoelectron spectrometry (XPS) of PE surface

Figure 7 and Figure 8 show fracture surface analysis by X-ray photoelectron spectrometry (XPS) of carbon (C (1s)) and oxygen (O (1s)) signals of the peeled surface of PE/18-8 laminated sheet with and without 0.30 MGy HLEBI. Results indicate the HLEBI acts to produce adhesion in the PE/18-8 lamination joint where fracture generally occurred near the peeled PE/18-8 interface.

In Fig. 7 the XPS narrow scan of carbon (C (1s)) of the peeled 0.30 MGy sample shows peaks at ~284 eV corresponding with the C (1s) in C-C groups. In order to calibrate the results in detail, XPS signals of C (1s) have been obtained for PE/18-8 with and without HLEBI (Solid and Broken lines in Fig. 7). The highest intensity of C-C signal for 0.30 MGy sample is gotten. HLEBI increases the carbon ratio of PE to 18-8 stainless.

In order to calibrate the results in detail, XPS signals of O (1s) in the peeled 0.30 MGy sample shows peaks at ~530 eV corresponding with the O (1s) in O=C-O groups. In order to calibrate the results in detail, XPS signals of O (1s) have been obtained for PE with and without HLEBI (Solid and Broken lines in Fig. 8). The lowest intensity of O (1s) in O=C-O signals for untreated PE/18-8 is gotten. Since 0.30 MGy-HLEBI remarkably enhances the oxygen concentration at PE interface. Since HLEBI activates the

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**Table 1** Constant values of \( m \), \( F_{III} \) and \( F_{s} \) are summarized.

<table>
<thead>
<tr>
<th>HLEBI</th>
<th>( m )</th>
<th>( F_{III} )</th>
<th>( F_{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.45</td>
<td>44.12</td>
<td>0.38</td>
</tr>
<tr>
<td>0.13</td>
<td>0.51</td>
<td>31.61</td>
<td>0.1</td>
</tr>
<tr>
<td>0.22</td>
<td>1.29</td>
<td>3.73</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>0.58</td>
<td>29.55</td>
<td>0.8</td>
</tr>
<tr>
<td>0.43</td>
<td>0.42</td>
<td>42.61</td>
<td>0.27</td>
</tr>
</tbody>
</table>
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 PE/18-8 laminated interface between PE and 18-8 stainless, degrading 0.30 MGy acting as crack origins and propagation sites at the laminated interface between PE and 18-8 stainless, degrading the polymers and reducing \( \gamma F_p \) (see Fig. 4). 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 PE and 18-8 stainless without the use of glue.

5. Conclusions

2-layer Polyethylene (PE)/austenitic 18-8 stainless steels (PE/18-8) laminated sheets were prepared by a new adhesion method, a double-step treatment consisting of applying low dose (\( \leq 0.43 \text{ MGy} \)) of homogeneous low energy electron beam irradiation (HLEBI) prior to hot-press under 5 MPa at 343 K. Although the weak adhesion of 2-layer laminated PE/18-8 sheets without our double-step treatment with hot-press after HLEBI had been observed, the strong adhesion of the PE/18-8 was found from the new double-step treatment applying low dose \( \leq 0.43 \text{ MGy-HLEBI} \) of the 2-layer assembled PE/18-8 prior to hot-press lamination under 5 MPa at 343 K.

(1) The double-step treatment applying increased HLEBI dose from 0.04 to 0.43 MGy prior to hot-press enhanced the adhesive force of peeling resistance (\( \gamma F_p \)) at peeling probability (\( P_f \)) of 0.06 and 0.50.

(2) Based on the 3-parameter Weibull equation, the lowest \( \gamma F_p \) value at the lowest \( P_f \) of zero (\( F_a \)) could be estimated. The double-step treatment applying HLEBI up to 0.30 MGy prior to hot-press apparently improved the \( F_a \). The maximum \( F_a \) value of the PE/18-8 laminated sheets with hot-press after 0.30 MGy-HLEBI dose was 0.8 N m\(^{-1}\). Consequently, the double-step treatment of applying 0.30 MGy-HLEBI prior to hot press improved the safety level.

(3) The maximum peeling adhesive force \( \gamma F_p \) value at low \( P_f \) (zero and 0.06) of the laminated sheet irradiated at 0.30 MGy were 0.8 and 0.9 N m\(^{-1}\), respectively. However, the higher dose of the double-step treatment applying more than 0.43 MGy HLEBI apparently reduced the \( \gamma F_p \) at each \( P_f \). 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 PE and 18-8 stainless with sterilization without the use of glue.

(4) Based on the results of XPS surface analysis for PE/18-8 laminated sheets after the peeling test, carbon 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 PE/18-8 layered structure, resulting in strong chemical bonding at interface.

(5) HLEBI up to 0.30 MGy reaching a maximum at 0.8 N m\(^{-1}\), improving the safety level without radiation damages. When HLEBI cuts the chemical bonds in PE and generates terminated atoms with dangling bonds, they probably induce the chemical bonding. Therefore, increasing adhesion force between the laminated sheets can be explained.

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