Adhesive Resistance to Peeling Force of PTFE/PDMS Laminated Sheet Assisted by Homogeneous Low Voltage Electron Beam Irradiation at 77 K

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The effects of homogeneous low voltage electron beam irradiation (HLEBI) under liquid nitrogen on the adhesive force of peeling (${}^{\circ}F_p$) at accumulative probability of peeling (P_p) of laminated PTFE/PDMS sheets of polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS) at 77 K were investigated without glue. ${}^{\circ}F_p$ values at each P_p of PTFE/PDMS laminated sheets irradiated of 0.04 to 0.43 MGy at both 77 and 298 K exceed the corresponding values of the untreated samples. Although 298 K-HLEBI with 0.04 MGy improves ${}^{\circ}F_p$ value at low P_p (0.06), 77 K-HLEBI didn't improve it. On the contrary, the 77 K-HLEBI with 0.22 MGy apparently enhanced the ${}^{\circ}F_p$ at low- P_p of 0.06. It is higher than that of 298 K-HLEBI with 0.22 MGy. Furthermore, the operation dose range at high ${}^{\circ}F_p$ value of more than 1.5 N m^{-1} at low P_p (0.06) at 77 K, indicator of high industrial reliability of production process, was 0.33 MGy, which was more than 3.7 times broader than that at 298 K. Based on the 3-parameter Weibull equation, the lowest ${}^{\circ}F_p$ value at P_p of zero (F_s) could be estimated. The 0.22 MGy-HLEBI at 77 K apparently improves the F_s , which was higher than that of 0.22 MGy-HLEBI at 298 K. Decreasing the irradiation temperature from 298 to 77 K controlled the rapid adhesion and rapid decay of adhesion at low- P_p , which were mainly caused by the low forming ability of dangling bonds induced by strong apparent bonding force, which is related to decreasing atoms vibration energy. Since the 0.22 MGy-HLEBI at 77 K controlled the recovery of dangling bonds and generated the chemical bonds, the strong adhesive force of PTFE/PDMS treated by 0.22 MGy-HLEBI at 77 K could be explained. Therefore, HLEBI under liquid nitrogen was useful tool for quick strong PTFE/PDMS lamination with sterilization for bio-adaptable application. [doi:10.2320/matertrans.MAW201416]

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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 Polydimethylsiloxane (PDMS) 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⁾ PDMS exhibits high transparency and bio-adaptability and has been mainly applied to contact lenze.⁵⁾ In addition, since the PDMS also shows self-adhesive,³⁾ it can be expected to apply to wrapping the bio-medical sensors.

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⁾ Although the large irradiation dose of HLEBI apparently decays as usual radiation damage, small dose often improves the strength of the polymers of polycarbonate and epoxy resin.^{8,9)} HLEBI cut the chemical bonds and generated active terminated atoms with dangling bonds in polymers.¹⁰⁾ Dangling bonds enhance surface energy, which is probably caused by chemical bonds for joining the different polymers for PTFE/PDMS at weak-linked polymers near the PTFE/PDMS interface.¹⁰⁾

In addition, treatment time of HLEBI-sterilization is only a few seconds, although sterilizing with ultraviolet light

irradiation requires a few hours.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.

In order to enhance the HLEBI effects on adhesive force, the heating by hot-press after HLEBI was also used to succeed in additive improvement in adhesive force for PTFE/PU and Al/PU.^{12,13)}

On the other hand, the cooling is also useful tool to improve the adhesive force. The annihilation of active terminated atoms with dangling bonds generally induces partly occurs at room temperature because of heating recovery. When HLEBI is performed at low temperature, it may control the annihilation and may enhance the probability of the chemical bonds at each weak-linked polymer. It also improves the adhesive force.

Therefore, the effects of HLEBI at 77 K on peeling resistance of laminated sheet of PTFE and PDMS have been investigated.

2. Experimental Procedure

2.1 Preparation of PTFE/PDMS laminated film

Composite sheets were constructed with PTFE (10 mm × 40 mm × 0.050 mm, Skived tape MSF-100, Chukoh chemical industries Co. Ltd., Japan) and PDMS (10 mm × 40 mm × 0.070 mm, DOW CORNING TORAY SILPOT 184 W/C, Dow Corning Toray Co. Ltd., Japan). Although the PDMS films had been formed by solvent casting method of the spin coating, the PDMS films were prepared by solvent casting method of Doctor Blade with high productivity.¹⁴⁾ The glass transition temperatures (T_g) of PTFE and PDMS are 399 and 150 K, respectively.¹⁵⁾

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Fig. 1 Schematic diagram of PTFE/PDMS laminated sheet loaded to 80 kPa during irradiation.

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 was assembled on the jig: one 0.05 mm thick PTFE layer, followed by one 0.07 mm thick PDMS layer, on top of which was placed a 0.015 mm thick supporting film. Since the HLEBI first penetrated the PDMS layer, followed by the PTFE layer we referred to the samples as PTFE/PDMS.

To obtain high reproducibility of peeling strength results, compressive stress of more than 80 kPa was loaded for more than 1.0 h.^{10,12,13} Since no peeling force was observed at the interface between the back surface of PTFE or PDMS 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).^{10,12,13,16} The samples are treated at low temperature of 77 K and room temperature of 298 K on Al block with and without dipping liquid nitrogen in Al plate. The level of liquid nitrogen is approximately at the interface between sample and Al block to maintain the constants of irradiation potential and dose because of protecting the liquid covering. The samples were homogeneously irradiated with an electron beam through a titanium window attached to a 0.24 m-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 m³/Ms (L/s).

Given the densities (ρ) were 2.1 Mg·m⁻³ (g·cm⁻³) for PTFE and 0.97 Mg·m⁻³ (g·cm⁻³) for PDMS, the penetration depth (D_{th}) values of 0.105 mm for PTFE and 0.256 mm for PDMS were estimated by assumptions of Christenhusz and Reimer, respectively.¹⁷ In addition, the D_{th} values of PTFE (0.152 mm) and PDMS (0.38 mm) were also calculated by the assumptions of Libby.¹⁸ Namely, the effective depth of homogeneous irradiation was 0.317 ± 0.061 mm. Consequently, since the irradiated thickness of laminated composites with PTFE film (50 μ m thickness) and PDMS film (70 μ m thickness) was 120 μ m, the adhesive interface is perfectly irradiated throughout their thicknesses.

2.3 T-peeling test

Composite samples after removing the 15 μ m 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.^{10,12,13} Since the unit of the F_p was N m⁻¹, the ${}^{\circ}F_p$ 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 ${}^{\circ}F_p$ was estimated by the peeling load and experimental peeling width and length of 10 and 30 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 Electron spin resonance (ESR) and X-ray photoelectron spectrometer (XPS) measurements

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.^{7,10,19} 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.

The PTFE is composed of elements F and C, whereas the PDMS is composed of C, H, Si and O. Fluorine (1s) signals from the peeled PDMS surface, carbon (1s), silicon (2p) and oxygen (1s) signals from the peeled PTFE were detected by X-ray photoelectron spectrometer (XPS: Quantum 2000, ULVAC Co., JAPAN)¹⁰ surface analysis of PTFE/PDMS laminated films with and without applying HLEBI at 77 and 298 K.

3. Results

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

Although the large adhesive load of peeling resistance has never been measured before irradiation, the laminated sheets constructed with PTFE and PDMS have been prepared before and after room and low temperature HLEBI. HLEBI under 77 and 298 K laminates the PTFE with the PDMS films. Figure 2 depicts the peeling load (L_p) - peeling distance (d_p) curves of the PTFE/PDMS laminated sheets before and after room and low temperature HLEBI at 0.22 MGy. When the mean adhesive force of peeling resistance (${}^{\circ}F_p$) is defined from 10 to 30 mm, ${}^{\circ}F_p$ values of PTFE/PDMS before and after HLEBI under 77 and 298 K are defined and firstly detected, quantitatively.

3.2 Mean adhesive force of peeling resistance (${}^{\circ}F_p$)

The accumulated probability (P) of Median Rank method²⁰ is one of convenient ways to analyze the mechanical probabilities of adhesive strength,¹⁶ adhesive peeling resistance¹⁰ and elasticity,²¹ as well as strength and impact

Fig. 2 Peeling load (L_p) - peeling distance (d_p) curves of PTFE/PDMS laminated sheets after 0.22 MGy-HLEBI at 77 and 298 K at P_p of 0.50.

value on fracture.^{7,22-25}) This method is useful to evaluate the effects of process, precisely. Evaluating the accumulative probability of peeling (P_p) is also the convenient method of quantitative analyzing experiment values relating to peeling resistance.¹⁰) 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 are 1, 6, and 11, the P_p values are 0.06, 0.50 and 0.94, respectively.

Although the large dose of HLEBI apparently decays as usual radiation damage, small dose from 0.04 to 0.43 MGy improves the ${}^{\circ}F_p$ values of the PTFE/PDMS laminated sheets. Figure 3 plots the relationships between ${}^{\circ}F_p$ and the P_p of PTFE/PDMS laminated sheets before and after HLEBI

under (a) low and (b) room temperatures, together with the lowest adhesive force estimated ($\odot$: $F_s = {}^{\circ}F_p$ at $P_p = 0$). Small ${}^{\circ}F_p$ values of PTFE/PDMS laminated sheets untreated at room temperature of 298 K can be obtained, although adhesion cannot be detected for untreated samples at 77 K. ${}^{\circ}F_p$ values at each P_p of PTFE/PDMS laminated sheets irradiated of 0.04 to 0.43 MGy at 77 and 298 K always exceed the corresponding values of the untreated samples.

Figure 4 depicts the changes in ${}^{\circ}F_p$ (N m^{-1}) at each P_p of 0.06 and 0.50 of PTFE/PDMS laminated sheets before and after HLEBI under (a) low and (b) room temperatures, together with the lowest adhesive force estimated ($\odot$: $F_s = {}^{\circ}F_p$ at $P_p = 0$). HLEBI with small irradiation dose of 0.04 MGy at both 77 and 297 K improves ${}^{\circ}F_p$ values (4.68 and 4.89 N m^{-1}) at mid- P_p (0.50), respectively. The ${}^{\circ}F_p$ values at low- P_p (0.06) is zero N m^{-1} for small dose of 0.04 MGy at 77 K, although 0.04 MGy-HLEBI at 298 K also enhances the ${}^{\circ}F_p$ values up to 3.00 N m^{-1} at low- P_p (0.06). Namely, although 298 K-HLEBI with 0.04 MGy improves ${}^{\circ}F_p$ value at low P_p (0.06), 77 K-HLEBI didn't improve it. Decreasing the irradiation temperature controls the rapid adhesion.

On the contrary, the 77 K-HLEBI with 0.22 MGy apparently enhanced the ${}^{\circ}F_p$ at low- P_p of 0.06. It is higher than that of 298 K-HLEBI with 0.22 MGy. The ${}^{\circ}F_p$ value (2.98 and 4.84 N m^{-1}) at low and mid- P_p (0.06 and 0.50) of 0.22 MGy-HLEBI at 77 K under liquid nitrogen was more than 2.4 and 1.2 times larger than that (1.26 and 4.10 N m^{-1}) at room temperature of 298 K.

Furthermore, the operation dose range at high ${}^{\circ}F_p$ value of more than 1.5 N m^{-1} at low P_p (0.06) at 77 K under liquid nitrogen was 0.30 MGy from 0.13 to 0.43 MGy. The dose range is more than 3.7 times broader than that (0.13 MGy) from 0.04 to 0.13 MGy at room temperature of 298 K. The 0.22 MGy HLEBI process at 77 K with the large dose range (0.30 MGy) enhances the high industrial reliability of production process.

Fig. 3 Relationships between ${}^{\circ}F_p$ and the accumulative probability of peeling (P_p) of PTFE/PDMS laminated sheets untreated and treated by HLEBI at (a) low and (b) room temperatures, together with the lowest adhesive force estimated ($\odot$: $F_s = {}^{\circ}F_p$ at $P_p = 0$).

Fig. 4 Changes in $^{\circ}F_p$ at each P_p of 0.06 and 0.50 of PTFE/PDMS laminated sheets untreated and treated by HLEBI under (a) low and (b) room temperatures HLEBI, together with the lowest adhesive force ($\odot$: $F_s = ^{\circ}F_p$ at $P_p = 0$).

4. Discussion

4.1 The lowest adhesive force

In order to obtain the safety design, the lowest $^{\circ}F_p$ value at P_p of zero (F_s) assumes 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 ($[^{\circ}F_p - F_s]/F_{III}$).^{10,21-26)}

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

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. Figures 5 (a) and (b) plots changes in correlation coefficient (f) with respect to the potential $^{\circ}F_s$ value ($^{\circ}F_s$) estimated from eq. (2). The $^{\circ}F_s$ value is the $^{\circ}F_s$ value at the maximum F value. Figure 5 (c) and (d) illustrates the linear relationships between $\ln(^{\circ}F_p - F_s)$ and $\ln[-\ln(1 - P_p)]$ for PTFE/PDMS laminated sheets before and after low and room temperature 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 $^{\circ}F_s = F_s$.

Figure 4 also depicts the changes in the lowest adhesive force ($\odot$: $F_s = ^{\circ}F_p$ at $P_p = 0$), together with $^{\circ}F_p$ (Nm^{-1}) at each P_p of 0.06 and 0.50 of PTFE/PDMS laminated sheets before and after HLEBI under (a) low and (b) room temperatures, respectively. The estimated $^{\circ}F_p$ value (2.85 Nm^{-1}) at zero of P_p of 0.22 MGy-HLEBI at 77 K under liquid nitrogen, which is slightly smaller than the experimental one (2.98 Nm^{-1}) at small P_p (0.06), is remarkably higher than estimated $^{\circ}F_p$ value at room temperature of 298 K. The 0.22 MGy-HLEBI under liquid nitrogen apparently improves the safety adhesive force.

4.2 Adhesion with dangling bond formation

Although the large dose of HLEBI apparently decays as usual radiation damage, small dose from 0.04 to 0.43 MGy improves the $^{\circ}F_p$ values of the PTFE/PDMS laminated sheets. Although remarkable electron spin resonance (ESR) signals, indicating dangling bond formation, could not be detected in either the untreated PTFE or PDMS, the ESR signals of PTFE treated by 298 K-HLEBI could be detected.¹⁰⁾ Increasing the density of active terminated atoms with dangling bonds enlarges the free volume in polymers.²⁷⁾ Since HLEBI up to 0.43 MGy enhances the intensity of the ESR signals in the PTFE, it gradually enhances the density of dangling bonds. On the other hand, HLEBI up to 0.04 MGy slightly enhances the intensity in the PDMS.¹⁰⁾ Since the glass transition temperature (T_g) of PDMS is below room temperature, the recovery easily occurs, resulting in weak in PDMS.

Although the recovery partly occurs at room temperature, HLEBI cut the chemical bonds and generated active terminated atoms with dangling bonds in PTFE and PDMS polymers. It is possible to induce the chemical bonding at not only interface, but also cross-linked polymers. The annihilation of active terminated atoms with dangling bonds of polymers generally induces partly occurs at room temperature by heating recovery. When HLEBI is performed at low temperature, it probably controls the annihilation and enhances the probability of the chemical bonds at each cross-linked polymer. Thus, it also improves the adhesive force.

4.3 Concepts of chemical bonds between terminated groups of cross-linked PTFE and PDMS polymers with dangling bonds

Figure 6 illustrates the constitutional formula of chemical bonds of $[\text{PTFE}]_n$ - $[\text{PDMS}]_m$ and $[\text{PDMS}]_m$ - $[\text{PTFE}]_n$ of cross-linking zone of PTFE/PDMS laminated composites sheet.

Fig. 5 Changes in correlation coefficient (f) of eq. (2) against the potential value ($^{\circ}F_s$) ((a), (b)), and liner relationships between $\ln(^{\circ}F_p - F_s)$ and $\ln[-\ln(1 - P_p)]$ ((c), (d)) for PTFE/PDMS laminated sheets untreated and treated by HLEBI at 77 ((a), (c)) and 298 K ((b), (d)).

Fig. 6 Constitutional formula of chemical bonds of $[\text{PTFE}]_n\text{--}[\text{PDMS}]_m$ and $[\text{PDMS}]_m\text{--}[\text{PTFE}]_n$ of cross-linking zone of PTFE/PDMS laminated composites sheet.

When the cross-linking occurs at interface between PTFE and PDMS samples, chemical atomic bonds between active terminated silicon (or oxygen) atom in cross-linked PDMS polymers and active terminated carbon atom in cross-linked PTFE polymers probably attribute to the HLEBI-adhesion.

4.4 Effects of decreasing the irradiation temperature on adhesive force and density of dangling bonds evaluated by ESR

Figure 7 shows ESR signals related to dangling bonds of peeled PTFE and PDMS sheets before and after HLEBI with 0.04 and 0.22 MGy at 77 and 298 K, respectively. Increasing HLEBI dose enhances the intensity of ESR signal of PTFE. Dangling bonds relate to the interatomic bonding strongly related to atoms vibration energy. Thus, Since ESR intensity

of PTFE irradiated at 298 K is higher than that at 77 K, decreasing irradiation temperature from 298 to 77 K suppresses the formation of dangling bonds for PTFE polymers.

When the experimental adhesive force at low P_p of 0.06 is extremely low near zero (see Fig. 4), when remarkable ESR signals cannot be observed, as shown in Fig. 7(a) and (b).

On the other hand, as the adhesion decay occurs at 298 K-0.22 MGy, radiation damage apparently occurs at its ESR intensity of the PTFE.

Since the highest value of adhesive force at low P_p of 0.06 is found at 298 K-0.04 MGy and 77 K-0.22 MGy, the density of dangling bonds is optimum to improve the adhesion force, as shown in Fig. 7(a) and (b).

ESR signals can be detected for PDMS treated by HLEBI at 298 K, although ESR signals cannot be mostly observed at 77 K. Decreasing the irradiation temperature from 298 to 77 K apparently suppresses the formation of dangling bonds for PDMS polymers, resulting in delay of the radiation damage.

As shown in Fig. 4, decreasing the irradiation temperature from 298 to 77 K suppresses the not only rapid adhesion ($^{\circ}F_p$) from zero to 3.00 Nm^{-1} , but also rapid decay of adhesion ($^{\circ}F_p$) from 3.00 to less than 1.0 Nm^{-1} at low- P_p of 0.06. Controlling both rapid adhesion and rapid decay of adhesion is mainly caused by suppressing the formation of dangling

Fig. 7 ESR signals of peeled PTFE and PDMS sheets before and after HLEBI with 0.04 and 0.22 MGy at 77 and 298 K.

bonds induced by strong apparent bonding force, which is related to decreasing atoms vibration energy by decreasing the irradiation temperature.

4.5 Chemical bonds of cross-linking evaluated by XPS

As shown in Fig. 6, the PTFE is composed of elements of F and C, whereas the PDMS is composed of elements of C, H, Si and O. Figure 8(a) illustrates fluorine (1s) signals from

the peeled PDMS surface by XPS surface analysis of PTFE/PDMS laminated films with and without applying 0.22 MGy-HLEBI at 77 and 298 K, when the low P_p value is 0.06.

Based on the results of XPS surface analysis for PTFE/PDMS laminated sheets after 0.22 MGy-HLEBI under 77 and 298 K, fluorine is found in the PDMS side peeled surface. No signals can be observed in the samples untreated and treated by 0.04 MGy-HLEBI at 77 K. On the contrary, the XPS signals observed exhibits that the peeling test cuts the cross-linked parts of PTFE molecules including the element F on the PDMS side in the laminated composites sheets treated by 0.04 MGy at 298 K and 0.22 MGy at 77 and 298 K.

The XPS signal intensity of PTFE/PDMS treated by 0.22 MGy-HLEBI at 298 K is much higher than that by 0.22 MGy-HLEBI at 77 K. The residual amount of PTFE molecules of PTFE/PDMS treated by 0.22 MGy-HLEBI at 298 K is much larger than that by 0.22 MGy-HLEBI at 77 K. Since the $^{\circ}F_p$ value (2.98 N m^{-1}) at low P_p (0.06) of 0.22 MGy-HLEBI at 77 K under liquid nitrogen was more than 2.4 times larger than that (1.26 N m^{-1}) at room temperature of 298 K, the radiation damage of PTFE molecules of PTFE/PDMS treated by 0.22 MGy-HLEBI at 77 K should be smaller than that by 0.22 MGy-HLEBI at 298 K.

Since the adhesive chemical bonding at cross-linking zone near PTFE/PDMS interface is probably lower than the fracture strength between cross-linked PTFE molecules and residual PTFE molecules in PTFE sheet, it can be explained that the high $^{\circ}F_p$ value can be detected of laminated composites sheet treated by 0.04 MGy-HLEBI at 298 K and 0.22 MGy-HLEBI at 77 K.

The strength of PTFE polymers are generally much stronger than that of PDMS. Thus, the dominant factors to adhesion should be the strength of PTFE polymers, rather than that of PDMS. Although the contribution of cross linked PDMS polymers is not so large, the influence of PDMS cross linked polymer on adhesion is investigated. Figure 8(b) illustrates silicon (2p) signals from the peeled PTFE surface by XPS surface analysis of PTFE/PDMS laminated films

Fig. 8 Fluorine (1s) and silicon (2p) signals on PDMS and PTFE sides from XPS analysis PTFE/PDMS laminated sheets untreated and treated by 0.04 and 0.22 MGy-HLEBI at low (77 K) and room temperatures (298 K), respectively.

treated by 0.22 MGy-HLEBI at 77 and 298 K, when the low P_p value is 0.06. The XPS signals observed exhibit that the peeling test cuts the cross-linked parts of PDMS molecules including the element Si on the PTFE side in the all laminated composites sheets treated by HLEBI at 77 and 298 K.

The XPS signal intensity of PTFE/PDMS treated by 0.22 MGy-HLEBI at 77 K exhibits the highest value, which is 1.25 and 2.5 times higher than that of both 0.04 MGy-HLEBI at 77 and 298 K and 0.22 MGy at 298 K. The XPS signal intensity related to residual amount of PDMS molecules with Si of PTFE/PDMS treated by 0.22 MGy-HLEBI at 77 K is 1.25 higher than that by 0.04 MGy-HLEBI at 298 K. On the contrary, the XPS signal of element F of PTFE molecules in PDMS side in PTFE/PDMS treated by 0.04 MGy-HLEBI at 298 K is about 4 times higher than that by 0.22 MGy-HLEBI at 77 K, as shown in Fig. 8(a). Although the $^{\circ}F_p$ value (2.98 N m^{-1}) at low P_p (0.06) of 0.22 MGy-HLEBI at 77 K and 0.04 MGy-HLEBI at 298 K are same to each other, we conclude that the dominant factor of one is different from another.

On the other hand, the XPS signal intensity of Si in PTFE side of PTFE/PDMS treated by 0.04 MGy at 298 K is about 60% of that by 0.22 MGy at 77 K, whereas its intensity of F in strong PTFE molecules in PDMS is too small. Thus, the lowest adhesion force can be explained.

In addition, since the XPS signal intensity of Si in PTFE side of PTFE/PDMS treated by 0.22 MGy at 298 K is about 30% of that by 0.22 MGy at 77 K, the decreasing adhesion force can be explained, as shown in Fig. 4.

4.6 Principle of HLEBI adhesion of PTFE/PDMS

It is possible that HLEBI cuts the chemical bonds of atoms in monomers, as well as that between monomers.

When HLEBI cuts molecules in both polymers and forms the terminated atoms of $-\text{CH}_3$, $-\text{H}$ and $-\text{F}$ with dangling bonds, it cannot attribute to the chemical bond site between cross-linked different molecules.

When HLEBI cuts molecules in both polymers and forms the terminated atoms of $[\text{PTFE}]_n\text{-CF}_2$ -, $-\text{O-}[\text{PDMS}]_m$ and $-\text{Si}(\text{CH}_3)_2\text{-}[\text{PDMS}]_m$ with dangling bonds, it is possible to form the bonding modes of $[\text{PTFE}]_n\text{-CF}_2\text{-}[\text{PDMS}]_m$, $[\text{PTFE}]_n\text{-O-}[\text{PDMS}]_m$ and $[\text{PTFE}]_n\text{-Si}(\text{CH}_3)_2\text{-}[\text{PDMS}]_m$ between cross-linked PTFE and PDMS polymers.

Although the dominant factor of precise bonding mode for adhesion cannot confirmed, chemical bonds between cross-linked PTFE and PDMS polymers should attribute to the HLEBI-adhesion.

5. Conclusion

The effects of homogeneous low voltage electron beam irradiation (HLEBI) at 77 K with sterilization on the adhesive force of peeling ($^{\circ}F_p$) of laminated PTFE/PDMS sheets constructed with polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS) were investigated without glue.

- (1) The relationships between $^{\circ}F_p$ and the accumulative probability of peeling (P_p) of PTFE/PDMS laminated sheets before and after HLEBI under low and room temperatures were obtained. $^{\circ}F_p$ values at each P_p of

PTFE/PDMS laminated sheets irradiated of 0.04 to 0.43 MGy at both 77 and 298 K exceed the corresponding values of the untreated samples. Although 298 K-HLEBI with 0.04 MGy improves $^{\circ}F_p$ value at low P_p (0.06), 77 K-HLEBI didn't improve it. On the contrary, the 77 K-HLEBI with 0.22 MGy apparently enhanced the $^{\circ}F_p$ at low- P_p of 0.06. It is higher than that of 298 K-HLEBI with 0.22 MGy.

- (2) The operation dose range at high $^{\circ}F_p$ value of more than 1.5 N m^{-1} at low P_p (0.06) at 77 K was 0.30 MGy from 0.13 to 0.43 MGy. It was more than 3.7 times broader than that (0.13 MGy) from 0.04 to 0.13 MGy at 298 K. It enhances the high industrial reliability of production process.
- (3) Based on the 3-parameter Weibull equation, the lowest $^{\circ}F_p$ value at P_p of zero (F_s) could be estimated. The 0.22 MGy-HLEBI at 77 K apparently improves the safety adhesive force, which is higher than that 0.22 MGy-HLEBI at 298 K.
- (4) The X-ray photoelectron spectrometer (XPS) signal intensity of the element F on the PDMS side in PTFE/PDMS treated by 0.22 MGy-HLEBI at 298 K is much higher than that by 0.22 MGy-HLEBI at 77 K. Since the $^{\circ}F_p$ value (2.98 N m^{-1}) at low P_p (0.06) of 0.22 MGy-HLEBI at 77 K under liquid nitrogen was more than 2.4 times larger than that (1.26 N m^{-1}) at room temperature of 298 K, the radiation damage of PTFE molecules of PTFE/PDMS treated by 0.22 MGy-HLEBI at 77 K should be smaller than that by 0.22 MGy-HLEBI at 298 K.
- (5) Since the adhesive chemical bonding at cross-linking zone near PTFE/PDMS interface is probably lower than the fracture strength between cross-linked PTFE molecules and residual PTFE molecules in PTFE sheet, it can be explained that the high $^{\circ}F_p$ value can be detected of laminated composites sheet treated by 0.04 MGy-HLEBI at 298 K and 0.22 MGy-HLEBI at 77 K.
- (6) Based on the silicon (2p) signals from the peeled PTFE surface by XPS surface analysis of PTFE/PDMS laminated films with and without applying 0.22 MGy-HLEBI at 77 and 298 K, the XPS signal intensity related to residual amount of PDMS molecules of PTFE/PDMS treated by 0.22 MGy-HLEBI at 77 K is 1.25 higher than that by 0.04 MGy-HLEBI at 298 K. On the contrary, the XPS signal of element F of PTFE molecules in PDMS side in PTFE/PDMS treated by 0.04 MGy-HLEBI at 298 K is about 4 times higher than that by 0.22 MGy-HLEBI at 77 K. Although the $^{\circ}F_p$ value (2.98 N m^{-1}) at low P_p (0.06) of 0.22 MGy-HLEBI at 77 K and 0.04 MGy-HLEBI at 298 K are same to each other, we conclude that the dominant factor of one is different from another.

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