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Peeling Force of Fluororesin/PDMS Laminated Sheet Assisted by Homogeneous EB-Irradiation under High Temperature of 363 K

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Summary: *The effects of homogeneous low voltage electron beam irradiation (HLEBI) under high temperature of 363 K on the adhesive force of peeling (^oF_p) at accumulative probability of peeling (P_p) of laminated PTFE/PDMS sheets of polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS) were investigated without glue. ^oF_p values at mid-P_p of PTFE/PDMS laminated sheets irradiated of 0.04 MGy at 363 and 298 K exceeded the corresponding values of the untreated samples. The ^oF_p value of 0.22 MGy-HLEBI at mid-P_p (0.50) was more than 12% and 18% larger than that (4.31 and 4.10 Nm^{-1}) of the untreated samples at high and room temperatures of 363 and 298 K, respectively. Increasing the irradiation temperature from 298 to 363 K improved the rapid adhesion and rapid decay of adhesion at mid-P_p. They were mainly caused by the enhancement of cross-linking with each polymerat their interface induced by increasing atoms vibration energy. Since the 0.04 MGy-HLEBI at 363 K simultaneously generated the chemical bonds at terminated atoms with dangling bonds, the strong adhesive force of PTFE/PDMS treated by 0.04 MGy-HLEBI at 363 K could be explained. Therefore, HLEBI at high temperature of 363 K was useful tool for quick strong PTFE/PDMS lamination with sterilization for bio-adaptable application.*

1 INTRODUCTION

Composite polymers have been prepared for numerous biomedical applications by laminating them with heating and glue [1,2], although 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 lens [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 cross-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 condition 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 [14]. When HLEBI is performed at low temperature, it may control the annihilation and may enhance the probability of the chemical bonds at each cross-linked polymer. It also improves the adhesive force. On the other hand, the effects of HLEBI at room and low temperatures of 298 and 77 K on peeling resistance of laminated sheet of PTFE and PDMS with sterilization for bio-adaptable application have been investigated [15,16]. When the atom vibration improves the cross-linking condition, the high temperature HLEBI can be expected to enhance the adhesive force. When HLEBI cut the chemical bonds and generated terminated atoms with dangling bonds in PTFE and PDMS polymers, it activated the cross-linking zone at their interface. It was possible to induce the chemical bonding and intermolecular attractive force between each different polymer. When high temperature HLEBI enhances the sites of intermolecular chemical bonds, the quick and strong adhesive force under high temperature is expected. Therefore, the purpose of the present work is to perform the HLEBI under heating at high temperature of 363 K.

2 EXPERIMENTAL PROCEDURE

2.1 PREPARATION OF PTFE/PDMS LAMINATED FILM

Composite sheets were constructed with PTFE (10mm x 40mm x 0.050mm, Skived tape MSF-100, Chukoh chemical industries Co. Ltd., Japan) and PDMS (10mm x 40mm x 0.070mm, 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. [15,16] The glass transition temperatures (T_g) of PTFE and PDMS are 399 and 150K, respectively.[15,16,17]

2.2 HOMOGENEOUS IRRADIATION OF ELECTRON BEAM

As illustrated in Fig. 1, a jig constructed of a central stainless steel spring between two Al supporting bases is employed. The 2-layer laminate sample was assembled on the jig: one 0.05 mm thick PTFE layer, followed by one 0.07mm 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 refereed to the samples as PTFE/PDMS. To obtain high reproducibility of peeling strength results, compressive stress of more than 80kPa was loaded

for more than 1.0h.[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).[10,12,13,18] The samples are treated by HLEBI at high temperature (363 K) and room temperature (298 K) using by heat gun. 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 0.10MPa with a residual oxygen concentration of less than 0.040%. The flow rate of the nitrogen gas was 1.5 m^3/Ms (L/s). Given the densities (μ) were 2.1 $Mg \cdot m^{-3}$ ($g \cdot cm^{-3}$) for PTFE and 0.97 $Mg \cdot m^{-3}$ ($g \cdot cm^{-3}$) 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.[19] In addition, the D_{th} values of PTFE (0.152 mm) and PDMS (0.38 mm) were also calculated by the assumptions of Libby.[20] 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 μm thickness) and PDMS film (70 μm thickness) was 120 μm, the adhesive interface is perfectly irradiated throughout their thicknesses.

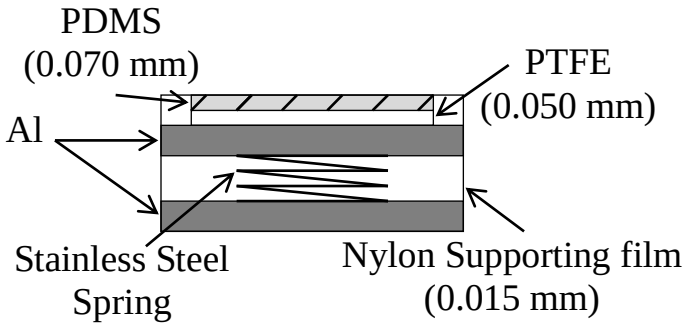

Figure 1: Schematic diagram of PTFE/PDMS laminated sheet loaded to 80 kPa during irradiation.

2.3 T-PEELING TEST

Composite samples after removing the 15μm 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 (^oF_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 10mm/min.[10,12,13] Since the unit of the F_p was Nm^{-1}, the ^oF_p was used instead of the adhesive strength, whose units should be Nm^{-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 ^oF_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, [10,21] 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 1.0mW. 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 363, 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 high, low and room temperature HLEBI. HLEBI under 363 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 high temperature HLEBI at 0.04 MGy. When the mean adhesive force of peeling resistance (^oF_p) is defined from 10 to 30 mm, ^oF_p values of PTFE/PDMS before and after HLEBI under 363 K are defined and firstly detected, quantitatively.

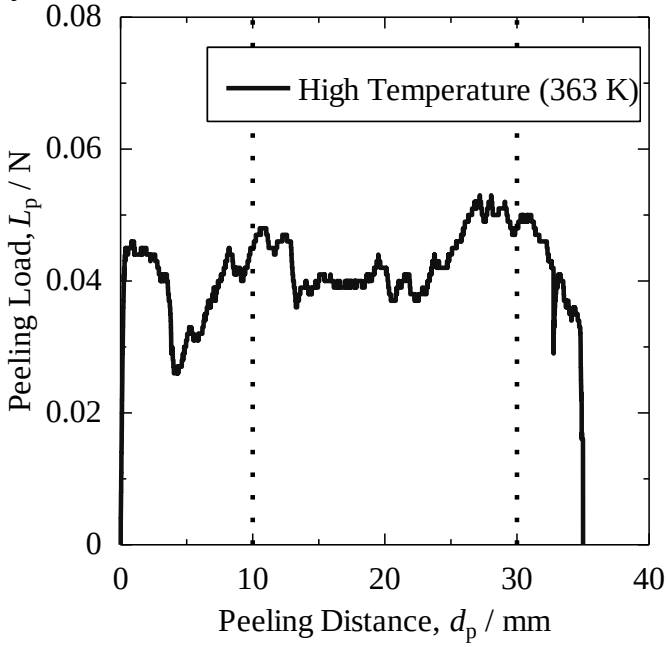

Figure 2: Peeling load (L_p) - peeling distance (d_p) curves of PTFE/PDMS laminated sheets after 0.04 MGy-HLEBI at 363 K at P_p of 0.50.

3.2 MEAN ADHESIVE FORCE OF PEELING RESISTANCE ($^{O}F_{P}$)

The accumulated probability (P) of Median Rank method [22] is one of convenient ways to analyze the mechanical probabilities of adhesive strength [18], adhesive peeling resistance [10] and elasticity [23], as well as strength and impact value on fracture [7, 24-27]. 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.

$$P_p = (I\text{-}0.3)/(n\text{+}0.4) \qquad (1)$$

Here, n and I are the total number of samples (n = 11) and order of peeling of each sample ($0 \leqq I \leqq 11$), 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 0.43MGy improves the $^{o}F_p$ values of the PTFE/PDMS laminated sheets. Figure 3 depicts the changes in $^{o}F_p$ (Nm^{-1}) at each P_p of 0.50 of PTFE/PDMS laminated sheets before and after HLEBI under high, low and room temperatures. HLEBI with small irradiation dose of 0.04MGy at each 363 K improves $^{o}F_p$ values at mid-P_p (0.50), respectively. $^{o}F_p$ values at mid-P_p of PTFE/PDMS laminated sheets irradiated of 0.04 MGy at 363 exceeded the corresponding values of the untreated samples. The $^{o}F_p$ value of 0.22 MGy-HLEBI at mid-P_p (0.50) was more than 12% larger than that (4.31 Nm^{-1}) of the untreated samples at high temperatures of 363 K, respectively. Increasing the irradiation temperature from 298 to 363 K improved the rapid adhesion and rapid decay of adhesion at mid-P_p.

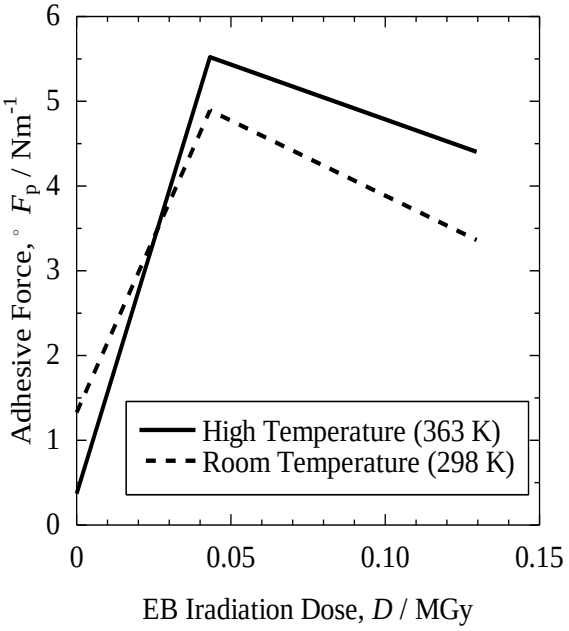

Figure 3: Changes in $^{o}F_p$ at each temperature of PTFE/PDMS laminated sheets untreated and treated by HLEBI at room temperature [14] and high teperature of 363 K.

4 DISCUSSION

4.1 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 $-CH_3$, -H and -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 [PTFE]n-CF_2-, -O-$[PDMS]_m$ and -Si(-CH_3)$_2$-$[PDMS]_m$) with dangling bonds, it is possible to form the bonding modes of $[PTFE]_n$-CF_2-$[PDMS]_m$, $[PTFE]_n$-O-$[PDMS]_m$ and $[PTFE]_n$-Si(-CH_3)$_2$-$[PDMS]_m$ 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.

4.2 Chemical bonds of cross-linking evaluated by XPS

The PTFE is composed of elements of F and C, whereas the PDMS is composed of elements of C, H, Si and O. Figure 4 illustrates fluorine (1s) signals from the peeled PDMS surface by XPS surface analysis of PTFE/PDMS laminated films with and without applying 0.04 MGy-HLEBI at 363 and 298 K, when the mid P_p value is 0.50.

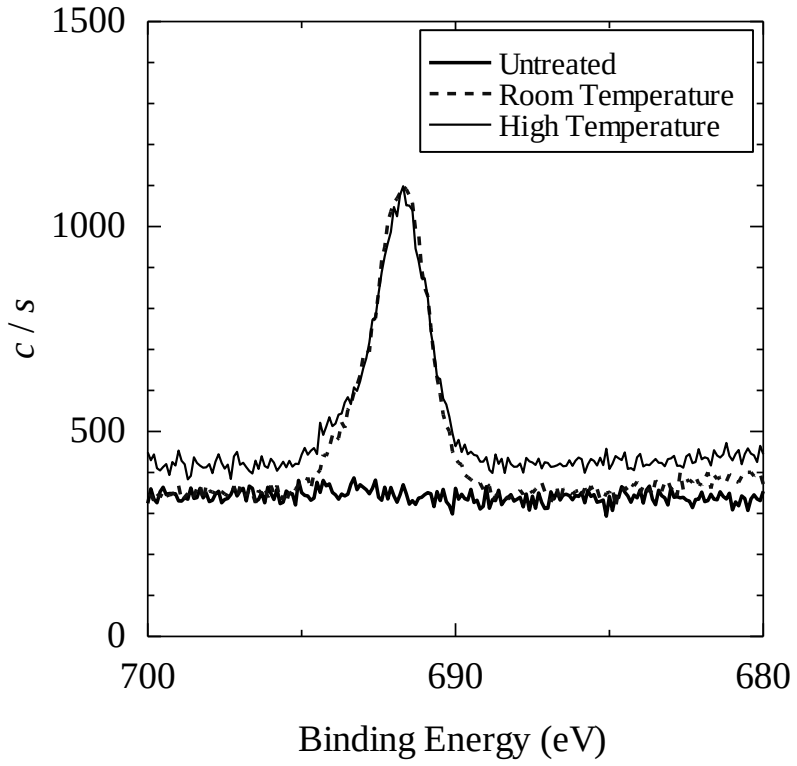

Figure 5: Fluorine (1s) signals on PDMS sides from XPS analysis PTFE/PDMS laminated sheets untreated and treated by 0.04 MGy-HLEBI at high (363 K) and room temperatures (298 K [14]), respectively.

Based on the results of XPS surface analysis for PTFE/PDMS laminated sheets after 0.04 MGy-HLEBI under 363 and 298 K, fluorine is found in the PDMS side peeled surface. 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 363 and 298 K. The XPS signal intensity of PTFE/PDMS treated by 0.04 MGy-HLEBI at 363 K is equal to that by 0.04 MGy-HLEBI at 298 K. The strength of PTFE polymers is generally much stronger than that of PDMS. Since the adhesive chemical bonding at cross-linking zone near PTFE/PDMS interface is probably higher than the cohesive force between cross-linked PTFE molecules and residual PTFE molecules in PTFE sheet, it can be explained that the high ${}^{o}F_{p}$ value can be detected of laminated composites sheet treated by 0.04 MGy-HLEBI at 363 K. Although the contribution of cross linked PDMS polymers is not so large, the influence of PDMS cross linked polymer on adhesion is investigated.

4.3 ADHESION WITH DANGLING BOND FORMATION

Although the large dose of HLEBI apparently decays as usual radiation damage, small dose from 0.04 to 0.43MGy improves the ${}^{o}F_{p}$ 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 297K-HLEBIcouldbedetected. [10] Increasing the density of active terminated atoms with dangling bonds enlarges the free volume in polymers. [28] Since HLEBI up to 0.43MGy 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 0.04MGy 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. Increasing the irradiation temperature from 298 to 363 K improved the rapid adhesion and rapid decay of adhesion at mid-P_p. They were mainly caused by the enhancement of cross-linking with each polymerat their interface induced by increasing atoms vibration energy. Since the 0.04 MGy-HLEBI at 363 K simultaneously generated the chemical bonds at terminated atoms with dangling bonds, the strong adhesive force of PTFE/PDMS treated by 0.04 MGy-HLEBI at 363 K could be explained. Therefore, HLEBI at high temperature of 363 K was useful tool for quick strong PTFE/PDMS lamination with sterilization for bio-adaptable application.

5 CONCLUSION

The effects of homogeneous low voltage electron beam irradiation (HLEBI) under high temperature of 363 K on the adhesive force of peeling (${}^{o}F_{p}$) at accumulative probability of peeling (P_p) of laminated PTFE/PDMS sheets of polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS) were investigated without glue.

(1)${}^{o}F_{p}$ values at mid-P_p of PTFE/PDMS laminated sheets irradiated of 0.04 MGy at 363 and 298 K exceeded the corresponding values of the untreated samples. The ${}^{o}F_{p}$ value of 0.22 MGy-HLEBI at mid-P_p (0.50) was more than 12% and 18% larger than that (4.31 and 4.10 Nm^{-1}) of the untreated samples at high and room temperatures of 363 and 298 K, respectively. Increasing the irradiation temperature from 298 to 363 K improved the rapid adhesion and rapid decay of adhesion at mid-P_p.

(2)They were mainly caused by the enhancement of cross-linking with each polymerat their interface induced by increasing atoms vibration energy. Since the 0.04 MGy-HLEBI at 363 K simultaneously generated the chemical bonds at terminated atoms with dangling bonds, the strong adhesive force of PTFE/PDMS treated by 0.04 MGy-HLEBI at 363 K could be explained.

(3) The X-ray photoelectron spectrometer (XPS) signal 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 363 and 298 K. The XPS signal intensity of PTFE/PDMS treated by 0.04 MGy-HLEBI under 363 K is equal to that by 0.04 MGy-HLEBI under 298 K.

Therefore, HLEBI at high temperature of 363 K was useful tool for quick strong PTFE/PDMS lamination with sterilization for bio-adaptable application.

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