Effects of Electron Beam Irradiation on Impact Value of Carbon Fiber Reinforced Thermoplastic Polyetheretherketone

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Homogeneous low voltage electron beam irradiation (HLEBI) improves the Charpy impact value (a_{uc}) of composites sheets of carbon fiber reinforced thermoplastic polyetheretherketone (CFRTP) with 2 mm thickness, although the irradiated depth estimated is $177 \pm 32 \mu\text{m}$ at their both sides surface. The a_{uc} values at low fracture probability (P_f) of 0.13 for CFRTP irradiated at 0.43 MGy (kJg^{-1}) is 78 kJm^{-2} , which is 56% higher than that (50 kJm^{-2}) for CFRTP before irradiation. Although the lowest impact values (a_s) estimated by three parameters Weibull equation is zero for CFRTP before irradiation, HLEBI enhances the a_s value. The highest a_s value is more than 55 kJm^{-2} for CFRTP irradiated from 0.43 to 0.65 MGy. Thus, HLEBI remarkably enhances the a_s value, as well as the a_{uc} value at low P_f value. Since HLEBI enhances the Weibull coefficient (n), it also enhances the reproducibility of CFRTP samples. The maximum n value is found at 0.43 MGy of HLEBI dose. The interfacial friction force, as well as the strengthening of both carbon fiber and polyetheretherketone probably contributes the HLEBI effects to enhance the a_s value of CFRTP, as well as enhancement of reproducibility. [doi:10.2320/matertrans.M2009210]

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1. Introduction

Carbon fiber reinforced polymers [CFRP], which are typical composite materials, and have been applied as light structural materials with high strength.^{1,2)} The further strengthening has been always expected to develop high-speed transports with small energy consumption. Although influences of electron beam (EB) irradiation with high energy on the fracture toughness of carbon cross of carbon fibers in thermo-hardened epoxy resin matrix (thermo-hardened CFRP) have been often reported,³⁾ no one has succeeded the strengthening of CFRP irradiated by electron beam.

On the other hand, the homogeneous low voltage electron beam irradiation (HLEBI) often induces not only the hardening, high wear resistance and sterilization for practical use of polymer, but also the mist resistance.⁴⁻⁶⁾ In addition, the irradiation has improved not only the bending fracture strain of carbon fiber,^{7,8)} but also the deformation resistivity, strength and fracture strain on static tensile test.⁹⁾ In our recent research, it has succeeded that the EB-irradiation also enhances the fracture stress and fracture strain of static bending test of thermo-hardened CFRP.¹⁰⁾ Furthermore, the improvement of impact value of thermo-hardened CFRP by EB-irradiation has been also reported to apply to high-speed transports.¹¹⁾

Carbon fiber reinforced thermoplastic polymers (CFRTP), already applied for automobile bumper and IC substrate, can be easily produced with high productivity for mass production at various forming process. However, it is serious problem that high viscosity of thermoplastic polymer with low wetting to carbon fiber induces the low strength of CFRTP. HLEBI often enhances the deformation resistivity (elasticity) of polymer¹²⁾ and carbon fiber.⁷⁻⁹⁾ In addition,

Fig. 1 Rational formula of Polyetheretherketone (PEEK).

it is also possible to enhance the interface strength induced by surface activation, which is generated by charging and dangling bond formation.

Since the interfacial area of carbon fiber with $6 \mu\text{m}$ diameter is extremely large, the enhancement of friction force induces the strength of CFRP. In order to enhance the interfacial friction force, the HLEBI to interface in CFRTP is probably effective. Polyetheretherketone (PEEK), which monomer is mainly constructed with three six-membered rings (see Fig. 1), is one of typical thermoplastic super-engineering polymer with high resistance to heat, wear and reaction.¹³⁾ Thus, it is generally applied to interior and upholstery of cabin in airplane and automobile. Therefore, the purpose of the present work is to investigate effects of HLEBI on impact value of CFRTP constructed with polyetheretherketone and carbon fiber.

2. Experimental Procedure

2.1 CFRTP sample preparation

The CFRTP sample, which volume is 1600 mm^3 , has been constructed with the bundle of carbon fiber (Diameter = $6 \mu\text{m}$, T800HB, Toray Industries, Inc.) and thermoplastic polymer (Polyetheretherketone; APTIV 2000-025, Victrex plc) matrix. Volume fractions of carbon fiber and polymer matrix are 52.6 and 47.4 vol%, respectively.

Making composites is performed under 2.0 MPa Ar-H₂ gas atmosphere at 350°C for 10 min.

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Since the bundle direction is a longitudinal direction, the high unidirectional strength can be expected. To evaluate the dynamic fracture toughness, the impact tests of the CFRP with and without the irradiation are measured using a standard impact test machine (Shimadzu Corporation No. 51735).

2.2 Impact test

In order to evaluate the impact fracture toughness, the Charpy impact values of the CFRTPs with and without HLEBI were measured using a standard impact fracture energy measurement system (Shimadzu Corporation No. 51735) (JIS K 7077).^{11,14} The CFRTP sample, which sizes are 80 mm length, 10 mm width and 2.0 mm thickness. The impact fracture energy (E) was expressed by the following equation.^{11,14}

$$E = WR[(\cos \beta - \cos \alpha) - (\cos \alpha' - \cos \alpha)(\alpha + \beta)/(\alpha - \alpha')] \quad (1)$$

Here, E , W , R , β , α and α' were impact fracture energy (kJ), hammer mass (kg), length (m) of hammer weight point from rolling center, start angle before impact, the maximum angle after impact and the maximum angle of the blank test, respectively. The Charpy impact value (a_{uc} : kJm⁻²) was expressed by the following equation.

$$a_{uc} = E/(bt) \quad (2)$$

Here, E , b ($= 10 \pm 0.2$ mm) and t ($= 2.00 \pm 0.15$ mm) were impact fracture energy (J), sample width (mm) and span distance (sample thickness, mm), respectively. The distance between supporting points was 40 mm.

2.3 Condition of EB-irradiation

Sheet electron beam irradiation with low energy has been homogeneously performed using an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA).⁴⁻¹² The specimen is machined from the sheet heat-treated for making composites and is homogeneously irradiated with the electron beam through a titanium thin film window attached to the vacuum chamber, 240 mm in diameter. Since HLEBI treated after forming interface between carbon fiber and PEEK matrix, improvement of adhesive force can be expected. A tungsten filament in vacuum is used to generate the electron beam at a low energy (acceleration potential, V : kV), of 170 kV and irradiating current density (J : Am⁻²) of 0.089 Am⁻². Although electron beam generation has been in vacuum, the irradiated sample has been kept under protective nitrogen at atmospheric pressure. The distance between sample and window has been 35 mm. To prevent oxidation, the samples are kept in a protective one atmosphere of nitrogen gas with a residual concentration of oxygen of below 400 ppm. The flow rate of the nitrogen gas is 1.5 Ls⁻¹ at 0.1 MPa of nitrogen gas pressure. Each irradiation dose (0.043 MGy (kJg⁻¹)) 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 $\times$ 0.15 m) is transported on a conveyor at a speed of 9.56 m·min⁻¹. The sheet electron beam irradiation has been applied intermittently. Repeated

irradiations to both side surfaces of samples are used to increase the total dose of irradiation. The interval between the end of one period of irradiation and the start of the next operation is 30 s. When the irradiation current (I : mA), the conveyor speed (S : m·min⁻¹) and number of irradiations (N) are determined, the irradiated dose (D : MGy) is expressed by a following equation.¹⁵

$$D = 0.216(I/S)N \quad (3)$$

The irradiation dose has been controlled by the integrated irradiation time in each of the samples. Here, irradiation dose has been corrected by using FWT nylon dosimeter of RCD radiometer film (FWT-60-00: Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117, USA) with irradiation reader (FWT-92D: Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117, USA). The dose is 0.0432 MGy at each irradiation.

2.4 Evaluation of dangling bonds

To obtain more precise information on atomic-scale structural changes in the CFRTP, the density of the dangling bonds was obtained using an electron spin resonance spectrometer (ESR, JES-FA200, Nippon Denshi Ltd. Tokyo).⁹ The microwave frequency range used in the ESR analysis was the X-band at 9.45 ± 0.05 GHz with a field modulation of 100 kHz. The microwave power was 1 mW. The magnetic field was varied from 318.7 to 328.7 mT. The spin density was calculated using a Mn²⁺ standard sample. Only ESR spectra, instead of spin densities, were given.

3. Results

3.1 Effects of HLEBI on impact value

Evaluating the probability of fracture (P_f) is a convenient method of quantitative analyzing experiment values relating to fracture. P_f is expressed by the following equation, which is a generalized form of the median rank method:¹⁶

$$P_f = (i - 0.3)/(N_s + 0.4) \quad (4)$$

where N_s and i are the total number of samples ($N_s = 11$) and the order of fracture of each sample, respectively. Here, the order of fracture is the aligned number of fractured samples from low to high impact value. When the i values are 2, 6, and 10, the P_f values are 0.13, 0.50, and 0.85, respectively.

Figure 2 shows changes in impact value (a_{uc}) of CFRTP against P_f value at each dose of HLEBI.

Remarkable effects of HLEBI on a_{uc} value of CFRTP have been obtained at low P_f value of less than 0.2. The direct irradiation of more than 0.12 MGy remarkably enhances the a_{uc} value of the CFRTP at low P_f value of less than 0.2.

Figure 3 shows changes in a_{uc} value of CFRTP against dose of HLEBI at each P_f value. The irradiation less than 0.12 MGy and more than 0.65 MGy enhances the a_{uc} value of the CFRTP at high P_f value of 0.85. The irradiation less than 0.22 MGy slightly enhances the a_{uc} value of the CFRTP at mid P_f value of 0.50.

Although the irradiation doesn't tremendously increase the a_{uc} value at high P_f value, remarkable effects of HLEBI from 0.12 to 0.86 MGy on a_{uc} value of CFRTP have been obtained at low P_f value of 0.13. The irradiation less than

Fig. 2 Relationships between Charpy impact value (a_{uc}) of carbon fiber reinforced thermoplastic PEEK (CFRTP) and fracture probability (P_f) at each electron beam irradiation.

Fig. 3 Changes in experimental impact values (a_{uc}) at each fracture probability ($P_f = 0.13, 0.50, 0.63 (a_{III})$ and 0.85) of carbon fiber reinforced thermoplastic PEEK (CFRTP) plotted against the EB irradiation dose.

0.43 MGy apparently enhances the a_{uc} value of the CFRTP at low P_f value of 0.13. 0.43 MGy HLEBI enhances the a_{uc} value from 50 to 78 kJm⁻². The a_{uc} value of CFRTP irradiated at 0.43 MGy is about 60% higher than that without irradiation at low P_f value of 0.13.

3.2 Dangling bond formation

From the conventional X-ray diffraction patterns of the carbon fiber before and after the EB irradiation, remarkable difference cannot be observed. On the other hand, EB irradiation in fact produces detectable dangling bonds.⁷⁻⁹⁾ To discuss the influences of electron beam irradiation on the Charpy impact values, ESR signals related to dangling bonds have been observed.

Fig. 4 ESR signals of PEEK before and after EB irradiation.

Fig. 5 ESR signals of carbon fibers before and after EB irradiation.

Figure 4 shows the ESR signals at 322.8 mT of PEEK with and without EB irradiation. ESR signals are observed for the PEEK samples before and after irradiation corresponding to dangling bonds (see Fig. 4). As shown in Fig. 4, the electron beam irradiation at 0.43 MGy increases the intensity of ESR signal, which exhibits to generate the dangling bonds in PEEK.

Figure 5 shows the ESR signals at 322.4 mT of carbon fiber with and without EB irradiation. A sharp ESR signal, corresponding to dangling bonds, is detected in the carbon fiber before irradiation (see Fig. 5). EB-irradiation decreases the height of sharp ESR signal of carbon fiber.

Fig. 6 Weibull plots of CFRTP irradiated by electron beam at each dose.

Fig. 7 Changes in Weibull coefficient (n) of CFRTP against the EB irradiation dose.

4. Discussion

4.1 Influence of HLEBI on Weibull coefficient (n) of impact value of CFRTP

The Weibull coefficient (n) is one of standard and traditional factors to compare with many other structural materials.¹⁷⁾ When a_{uc} and a_0 are measured Charpy impact value and constant, P_f as a function of the risk of rupture (a_{uc}/a_0) is expressed by the following equation.¹⁷⁾

$$P_f = 1 - \exp[-(a_{uc}/a_0)^n] \quad (5)$$

The linear relationship can be obtained as the following equation.

$$\ln(-\ln(1 - P_f)) = n \ln a_{uc} - n \ln a_0 \quad (6)$$

Figure 6 shows Weibull plots of CFRTP irradiated by the electron beam at each dose. The n value corresponds to the slopes of the relationships of Weibull plots.

Figure 7 shows the change in n value against EB irradiation dose. The EB irradiation enhances the n value.

The highest n value of CFRTP is obtained at 0.43 MGy. EB irradiation from 0.13 to 0.86 MGy apparently enhances the reliability related to n value of impact value of CFRTP.

As a results, HLEBI enhances the reproducibility with decreasing the experimental errors.

4.2 Effects of HLEBI on the lowest impact value

On the other hand, since the experimental impact values at less than 0.2 of low P_f value have been largely deviated from the linear relationship (see Fig. 6), the practical impact value at low P_f value cannot be estimated.

If the statistic equation is assumed to be applicable to the measured a_{uc} value, the P_f value depends on the risk of rupture ($[a_{uc} - a_s]/a_{III}$).^{18,19)}

$$P_f = 1 - \exp[-([a_{uc} - a_s]/a_{III})^m] \quad (7)$$

In predicting the required impact value of the new structural materials, the lowest impact value (a_s), the coefficient (m) and constant (a_{III}) are key parameters. The

Fig. 8 Changes in correlation coefficient (F) of eq. (7) against the potential a_s value ($^{\circ}a_s$). The lowest impact value (a_s) was determined at the maximum F value.

a_{III} is the a_{uc} value at 0.632 of P_f , when the term ($\ln[-\ln(1 - P_f)]$) is zero. A change in the a_{III} value with respect to EB irradiation dose is also shown in Fig. 3. The a_{III} values of EB irradiated CFRTP are slightly less than that before treatment.

As the P_f value is equal to zero, the a_{uc} value is defined as the a_s value. When a correlation coefficient (F) of eq. (7) shows the maximum value, the potential ($^{\circ}a_s$) value can be determined to be as the lowest impact value (a_s) applied. Figure 8 shows changes in the F value with respect to the $^{\circ}a_s$ value. Since the F value is from 0.94 to 0.99 in Fig. 8, the relationships in Fig. 9 exhibit the high linearity.

Figure 10 shows variations of the a_s value against EB irradiation dose, together with the experimental a_{uc} value at

Fig. 9 Linear relationships between $\ln(a_{uc} - a_s)$ and $\ln[-\ln(1 - P_f)]$ for CFRTF irradiated by electron beam at each dosage.

Fig. 10 Changes in experimental impact values (a_{uc}) at low P_f of 0.13 (○) and the lowest impact values (●: $a_s = a_{uc}$ at $P_f = 0$) plotted against the EB irradiation dose.

the low P_f value of 0.13 for each sample. Since the a_s is the a_{uc} value at the lowest P_f value of 0, it is always lower than the experimental a_{uc} value at low P_f value of 0.13. Although the a_s value is zero for CFRTF before irradiation, HLEBI enhances the a_s value. HLEBI from 0.13 to 0.86 MGy, which exhibits the high a_s value of more than 30 kJ m^{-2} , enhances the a_s value. Furthermore, the highest a_s value is more than 55 kJ m^{-2} for CFRTF irradiated from 0.43 to 0.65 MGy.

4.3 Effects of dangling bonds induced by HIEBL on impact value improvement of CFRTF constructed with carbon fiber, PEEK and their interface

Improvement of the impact value of CFRTF by HLEBI probably depends on strengthening carbon fiber, ductility enhancement of polymer matrix and enhancement of interfacial friction.

Based on the ESR signals of carbon fiber in Fig. 5, dangling bonds have been observed in carbon fiber before treatment. Based on the standard calibration material TEMPOL (2,2,6,6-tetramethyl-4-piperidinol-1-oxyl) and Mn^{2+} in the MnO, the density of dangling bonds is estimated by the double integrated intensity of ESR signal.⁷⁻⁹⁾

Dangling bonds generally exist in carbon fiber before irradiation. Based on the ESR signals in Fig. 5, the densities of dangling bonds of carbon fibers before and after 0.43 MGy irradiation are 1.15×10^{18} and $7.76 \times 10^{17} \text{ spins m}^{-3}$, respectively. Dangling bonds generally exist in carbon fiber before irradiation. HLEBI often decreases the density of dangling bonds. Annihilation of dangling bonds has often enhanced the tensile fracture stress and fracture strain of bending tests.⁷⁻⁹⁾

HLEBI annihilates dangling bonds in the hexagonal atomic structure of graphite,^{8,9)} it probably prevents the generation of cracks and often enhances the elasticity, resulting in ductility enhancement and strengthening of the carbon fiber.^{8,9)}

In addition, HLEBI often enhances the ductility and strengthening of the polymer matrix.¹⁰⁾ Based on the ESR signals of PEEK in Fig. 4, dangling bonds have been also observed in PEEK before treatment. Based on the ESR signals in Fig. 4, the densities of dangling bonds of PEEK samples before and after 0.43 MGy irradiation are 1.23×10^{13} and $3.81 \times 10^{13} \text{ spins m}^{-3}$, respectively. HLEBI increases the density of dangling bonds (see Fig. 4). When HIEBL cuts the weak chemical bonds of PEEK, the repulsive force between terminated atoms with dangling bonds occurs, resulting in generating volume expansion at dangling bonds. The expansion induced by HIEBL generates the compressive stress in PEEK matrix, which prevents to generate and propagate the crack in PEEK matrix.

When the compressive stress induced by HIEBL also enhances the friction force at interface between carbon fiber and PEEK, it prevents to pull out the carbon fiber from the PEEK matrix.

Based on both effects of compressive stress, HIEBL enhances the impact values of CFRTF. The interfacial friction force, as well as the strengthening of both carbon fiber and polyetheretherketone probably contributes the HLEBI effects to enhance the a_s value of CFRTF, as well as reproducibly enhancement with decreasing the experimental errors.

On the other hand, additional EB irradiation of more than 0.86 MGy apparently decreases the impact value at low P_f value, as shown in Figs. 2 and 3. Since the additional irradiation easily breaks the chemical bonds of PEEK polymer and carbon fiber, it probably not only generates many crack origins, but also links cracks with crack propagation. The decay of impact values of CFRTF irradiated at 0.86 MGy can be explained by the excess formation of dangling bonds.

4.4 Penetration depth of electron supplied from HLEBI system in CFRTF

Penetration depth of electron beam is one of serious problem to dominate the productivity and CFRTF thickness to apply the practical use. Based on the density (ρ : kg m^{-3})

Fig. 11 Change in penetration depth against sample density.

and irradiation voltage (V : kV), the EB-irradiation depth (D_{th} : m) is expressed by the following equation.¹⁵⁾

$$D_{th} = 66.7V^{5/3}/\rho \quad (8)$$

$$\log D_{th} = \log 66.7 + 5/3 \log V - \log \rho \quad (9)$$

The surface electrical potential (128 keV) is estimated from the electrical potential (170 keV), the 10 μm thickness of the titanium (density: 4540 kgm^{-3}) window and the 30 mm distance between the sample and the window in the nitrogen gas atmosphere (density: 1.13 kgm^{-3}). Since the measured density of the CFRTTP sample is 1546 kgm^{-3} (1.546 kgL^{-1}), the EB-irradiation depth estimated from eq. (9) is 1.45×10^{-4} m (145 μm). Figure 11 shows density dependent effective depth of EB-irradiation for carbon fiber (1810 kgm^{-3}), PEEK (1260 kgm^{-3}) and CFRTTP, in which the volume fraction of carbon fiber in PEEK is 52.6 vol%. By using the relation and density, effective depth of EB-irradiation for carbon fiber, PEEK and CFRTTP are 123, 177 and 145 μm . Since the effective depth of the sheet electron beam irradiation is 0.29 mm in the CFRTTP, the irradiated depth from each sample surface is 14.5% of the CFRTTP sample thickness of 2.0 mm.

On the other hand, the HLEBI depth (D_{th} : m), related to the mass thickness (l_0 : gm^{-2}) and irradiation voltage (E : kV), is also expressed by the following equation suggested by Libby.²⁰⁾

$$l_0 = E^{5/3}/15 \quad (10)$$

The estimated mass thickness is 348 gm^{-2} , when initial irradiation voltage is 170 keV. Since the mass thickness values of Ti foil (17.8 gm^{-2}) and N_2 gas (1.50 gm^{-2}) reduce the EB-irradiation depth, the mass thickness of CFRTTP sample is 323 gm^{-2} . In addition, the irradiation voltage on sample surface is expressed by the following equation.

$$E = (15l_0)^{3/5} \quad (11)$$

Namely, the EB-irradiation depth of CFRTTP is obtained by assumptions of Christenhusz and Reimer (see eq. (9)),¹⁵⁾ and Libby.²⁰⁾ Effective depth of EB-irradiation for carbon fiber, PEEK and CFRTTP are 123, 177 and 145 μm by using the

Fig. 12 Photograph of fractured CFRTTP before and after irradiation.

assumption of Christenhusz and Reimer (see eq. (9)), and are 178, 257 and 209 μm by using the assumption of and Libby.²⁰⁾

Although the irradiated depth estimated is $177 \pm 32 \mu\text{m}$ at both sides surface of composite sheet with 2 mm thickness, we conclude that the HLEBI improves the impact value of CFRTTP.

Based on the results of impact fracture of CFRP at each P_f value,¹¹⁾ the interfacial fracture between fiber and matrix as well as bending fracture at the impact point occurs at high P_f value, whereas the bending fracture mainly occurs at low P_f value. Figure 12 shows photographs of fractured CFRTTP samples before and after irradiation. Although the interfacial fracture with fiber pull-out as well as bending fracture apparently occurs of the fractured fuzzy CFRTTP samples at high P_f value of 0.5, the simple bending fracture mainly occurs of irradiated CFRTTP with the highest a_{uc} value at low P_f values of 0.13. Since HLEBI prevents to fracture at the interface and enhances the a_{uc} value at low P_f value, we conclude that HLEBI probably enhances the resistance to interfacial fracture as well as impact bending fracture of the CFRTTP.

The impact fracture generally occurs near the surface. When the interfacial fracture occurs at the high P_f value (see Fig. 12), the fiber peeling and fiber pull-out are mostly observed at the fuzzy surface zone from surface to 300 μm -depth. Since it is larger than that of the penetration depth of irradiation, the surface zone treated by HLEBI probably enhances the resistance to interfacial fracture as well as impact bending fracture of CFRTTP, resulting in improvement of the a_{uc} value at low P_f value.

On the other hand, HLEBI doesn't improve the a_{uc} value at high P_f value within experimental errors, because the interfacial adhesive force of CFRTTP before irradiation is large enough. Therefore, HLEBI improves the a_{uc} value at low P_f value of CFRTTP sample.

5. Conclusion

In summary, effects of homogeneous low voltage electron beam irradiation (HLEBI) on impact value of carbon fiber reinforced thermoplastic polyetheretherketone (CFRTP) have been found, although the irradiated depth estimated is $177 \pm 32 \mu\text{m}$ at both sides surface of composite sheet with 2 mm thickness.

(1) The experimental impact value (a_{uc}) at low fracture probability (P_f) of 0.13 for CFRTP irradiated at 0.43 MGy (kJg^{-1}) is 78 kJm^{-2} , which is 56% higher than that (50 kJm^{-2}) for CFRTP before irradiation. Thus, the HLEBI enhances the fracture toughness related to impact values at low P_f value.

(2) Although the a_s value is zero for CFRTP before irradiation, HLEBI enhances the a_s value. HLEBI from 0.13 to 0.86 MGy, which exhibits the high a_s value of more than 30 kJm^{-2} , enhances the a_s value. Furthermore, the highest a_s value is more than 55 kJm^{-2} for CFRTP irradiated from 0.43 to 0.65 MGy.

(3) Since HLEBI enhances the Weibull coefficient (n), it also enhances the reproductively of CFRTP samples, as well as increasing the a_s value. The maximum n value is found at 0.43 MGy of HLEBI dose.

(4) The interfacial friction force, as well as the strengthening of both carbon fiber and polyetheretherketone, probably contributes the HLEBI effects to enhance the a_s value of CFRTP, as well as reproductively enhancement with decreasing the experimental errors.

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