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Large pulsed electron beam (LPEB)-processed woven carbon fiber/ZnO nanorod/polyester resin composites

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ABSTRACT

The surface modification of materials by large pulsed electron beam (LPEB) processing is an emerging eco-friendly technique that can be applied to relatively large surface areas. In this study, a polyester-based woven carbon fiber (WCF)/ZnO nanorod hybrid composite was developed using a vacuum-assisted resin transfer molding process. LPEB processing was used to modify the surface of the carbon fiber (CF) composite prior to the growth of the ZnO nanorods. The effects of this electron beam treatment on WCFs were investigated by scanning electron microscopy as a function of ZnO nanorod growth. LPEB treatment resulted in a remarkable increase in the growth of ZnO nanorods. This increase, which resulted in an increase in the electrical resistance of the samples, was further investigated by X-ray diffraction analyses. LPEB-treated samples exhibited higher impact resistance due to strong interactions among the ZnO, CF, and polyester resin.

1. Introduction

Recently, fiber-reinforced composites have been applied in a range of fields due to their relatively high specific strength, stiffness, and toughness [1,2]. While such composites offer certain advantages, they are inherently complex. Composites made of strong fibers and a well-suited matrix may not necessarily result in a strong material. The fiber–matrix interface is equally important in determining the overall performance of the composite [3]. To increase interfacial strength, an alternative interphase approach is to grow nanowires, nanotubes, or microscale whiskers on the surface of the fibers. These features then protrude into the matrix, increasing the surface area for bonding and enhancing the load transfer between the fiber and the matrix [4]. Carbon nanotubes (CNTs) [5], graphene oxides [6], different types of metal-oxide nanorods [7,8], and nanowires are extensively grown on the surface of carbon fibers (CFs) to increase the surface area and interfacial strength.

Among the different processes available to achieve this end, chemical functionalization is often used to modify the surface of CFs so that they react chemically with the surrounding matrix [9]. Such modifications can be made via grafting or exposure to plasma, although chemical or electrochemical oxidation is more common. In the current study, CNTs were grown directly on the surface of CFs via chemical vapor deposition to increase the load transfer capacity of the composite [10]. Because this process does not rely on chemical reactions or the affinity of the resin to the treated fibers, the performance of the final composite is generally independent of the resin system. An alternative approach is based on the growth of radially aligned ZnO nanowire arrays on the surface of CFs [11]. This process exhibited several advantages over CNTs or silicon carbide whiskers, including low temperature (<90 °C) and aqueous growth conditions, which preserved the intrinsic fiber strength [12]. These hybrid fibers exhibited three orders of magnitude increase in surface area and resulted in a 110% increase in interfacial shear strength compared to bare fibers [13].

Although growing ZnO nanorods on carbon fibers is relatively common, growth rates and the levels of improvement are often below expectations because both the growth and interfacial adhesion of ZnO nanorods on CFs are strongly dependent on the surface area of the fibers. To achieve rapid growth and strong adhesion between the ZnO nanorods and the CFs, the surface area of the fibers needs to be relatively high. There are extensive numbers of research carried out on carbon fiber to improve the surface area and interactions with the polymer matrix. Methods like oxygen plasma treatment [14], gamma-ray radiation [15], gas phase oxidation [16], thermal treatment [17] etc. are widely used to improve the interfacial adhesion of the carbon fiber to the polymer matrix. But some of these most common techniques used to increase the surface area of the fiber also destroy the surface bonding characteristics of the fiber, resulting in an overall decrease in composite performance.

Therefore, nondestructive techniques such as large pulsed electron beam (LPEB) treatment that do not affect the interface

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bonding of the CFs are advisable. From the time of basic investigation of the effect of electron beam on polymers by Charlesby, the application of electron beam has spread over almost all fields [18]. Sterilization of medical goods by electron beam treatment is already known for several decades [19]. The cross-linking and the curing of polymers have widely been done by the application of irradiation [20,21]. Burkert et al. synthesized poly(N-vinyl pyrrolidone) based biocompatible hydrogels by electron beam radiation of dry polymer [22]. Moreover, the mechanical properties of the dental composites can also significantly improve by the treatment [23]. A considerable change in physico-chemical surface properties of polymer films was investigated by the irradiation of electron beam [24]. While continuous electron beams are currently employed in a variety of fields, the advantages of microsecond LPEBs have only recently emerged [25]. LPEB techniques are characterized by a high energy density and a large beam diameter of around 60 mm at the target surface [26]. The energy pulse delivered by the LPEB is concentrated to within a very thin layer at the target surface. This surface modification induces rapid heating and cooling with high temperature gradients, which lead to melting, evaporating, ablation, and the formation of a white layer [27]. The overall process increases the surface area of materials like CF and results in strong interfacial interaction between the fiber and nanorods grown on its surface. Nishi el al. applied electron beam treatment without accompanying heat for the crack reduction of carbon fiber to improve the mechanical properties at low temperature [28]. Kim et al. also introduced electron beam treatment on carbon fibers in a controllable way to improve the roughness as well as surface area to efficient stress transfer from carbon fiber to polymer matrix [29].

In this study, the woven CFs (WCFs) was treated by a LPEB process, which was followed by the growth of ZnO nanorods on the surface of the fibers. The ZnO-functionalized carbon fibers were then processed by vacuum-assisted resin transfer molding to create composites with a polyester resin. The carbon fibers were treated with different voltages of LPEBs prior to the growth of ZnO. The effects of the electron beam treatment on the growth of the ZnO nanorods and on the mechanical properties of the composite were investigated in terms of electrical resistance, surface morphology, X-ray diffraction (XRD), and percentage of weight change.

2. Experimental methods

2.1. Materials

T-300 grade WCFs were collected from Amoco Corporation (Chicago, IL, USA) and used as received. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), and hexamethylene tetramine ($C_6H_{12}N_4$) were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as received. Analytical grades of sodium hydroxide (Samchun Pure Chemical Co., Ltd., Pyeongtaek, Korea) and ethanol (J.T. Baker, Phillipsburg, NJ, USA) were used as received.

2.2. Large pulsed electron beam treatment of WCFs

Initially, a WCF sheet was cut into 75 × 75 mm^2 (length × width) squares, rinsed with ethanol solution (see below), and dried in an oven at 100 °C for 10 min. These WCF samples were moved into an electron beam finishing machine (PF32A; Sodick Co., Ltd., Yokohama, Japan) for subsequent surface treatment. The solenoid voltage was kept fixed at 1.5 kV, while the cathode voltage of the instrument was varied from 10 to 35 kV. As we applied the voltage, the electron density penetrate to a certain depth of the carbon fiber. Up to 30 kV, the penetration depth remains optimum and the bonding pattern inside the WCF remain unaffected. The penetration depth was determined on the basis of the water contact angle measurement (Goniometer, DSA100; KRUSS GmbH, Hamburg, Germany). In this process, as the applied voltage increases, the penetration depth also increases. This trend directly increases the surface area of the carbon fiber and hence, the degree of the contact angle decreased as shown in Fig. 1. Beyond 30 kV, the electron density penetration depth crosses optimum level and the property of the WCF decreased. All surface treatment operations were carried out for four standard cycles. The surface roughness of the WCF samples increases following the large pulsed electron beam treatment.

2.3. Preparation of ZnO seed solution and growth solutions

Zinc acetate dihydrate (0.22 g) was dissolved in 400 mL of ethanol at 65 °C and stirred vigorously for 30 min. Ethanol solution (80 mL) was prepared by dissolving 2 mM NaOH in ethanol at 65 °C for 10 min. This ethanol solution was then introduced into the prepared zinc acetate dihydrate solution. Another 320 mL of ethanol was added to the solution bringing the total volume of the mixture to 800 mL. The final solution was stirred vigorously for 30 min without heating to ensure full and uniform mixing. The pH of the seed solution was maintained at 5–6. The resulting transparent solution, which contained a suspension of ZnO particles, was cooled to room temperature over 1 h. The chemical reactions occurring in the ZnO seed solution are as follows [30,31]:

$$Zn^{2+} + 4OH^- \leftrightarrow [Zn(OH)_4]^{2-} \tag{1}$$

$$[Zn(OH)_4]^{2-} \leftrightarrow ZnO_2^{2-} + 2H_2O \tag{2}$$

$$ZnO_2^{2-} + H_2O \leftrightarrow ZnO + 2OH^- \tag{3}$$

$$ZnO + OH^- \leftrightarrow ZnOOH^- \tag{4}$$

To prepare ZnO growth solutions at the desired concentration, zinc nitrate hexahydrate and hexamethylenetetramine ($C_6H_{12}N_4$, HMTA) were mixed at a molar ratio of 1:1. To prepare 20 mM of the ZnO growth solution, 20 mM of HMTA was dissolved in 630 mL of distilled water by stirring for 10 min. This was followed by the addition of 20 mM zinc nitrate and the overall solution was stirred for 30 min. The pH of the growth solution was maintained at 6–8. This final solution was used to grow ZnO nanorods on the treated WCFs. The growth of ZnO nanorods on the electron beam-treated WCF is presented in Fig. 2. The chemical reactions involved in the growth of ZnO and the synthesis of ZnO from OH^- and Zn^{2+} are as follows [32]:

$$C_6H_{12}N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \tag{5}$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{6}$$

$$2OH^- + Zn^{2+} \leftrightarrow ZnO + H_2O \tag{7}$$

2.4. Preparation of the ZnO/polyester woven carbon-fiber samples

LPEB-treated WCF samples were submerged in the aforementioned seed solution for 10 min and then annealed at 150 °C for 10 min to remove the solvent and other organic substances. This process was repeated four times. The treated samples were immersed in a stainless-steel autoclave and sealed. The autoclave remained at 90 °C for 4 h. After 4 h of this hydrothermal processing, the samples were rinsed with deionized water for 20 min to stop the growth of ZnO nanorods. Finally, the fiber samples with the synthesized ZnO nanorods were dried naturally for 1 day.

Vacuum-assisted resin transfer molding (VARTM) was used to prepare final composite materials from the LPEB-treated fiber specimens with ZnO nanorods. Polyester resin was used in all samples. Fig. 3 shows a schematic of the VARTM process starting from the LPEB treatment and concluding with preparation of the final composite sample. Table 1 shows the experimental parameters used in the VARTM process.

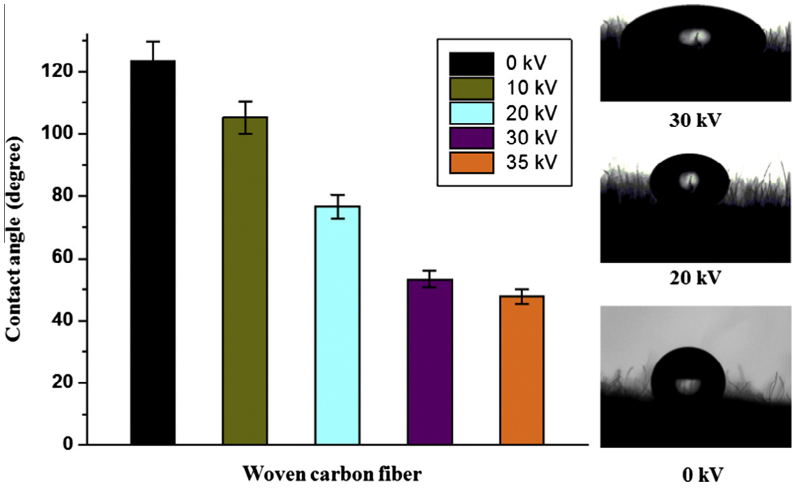

Fig. 1. Contact angle measurement of woven carbon fiber samples treated with different cathode voltages.

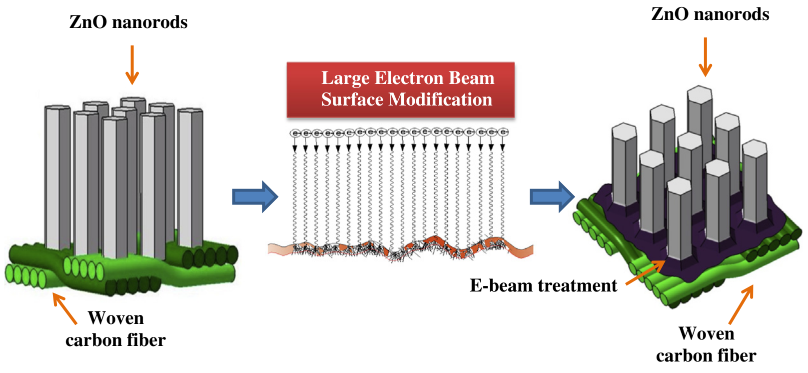

Fig. 2. Growth of ZnO nanorods on large pulsed electron beam (LPEB)-treated woven carbon fiber surfaces.

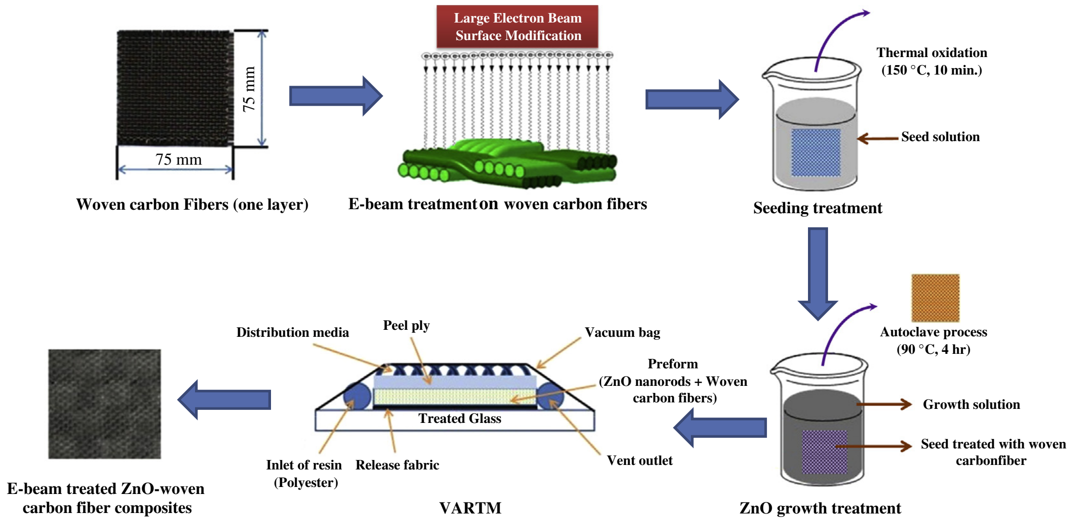

Fig. 3. A schematic diagram shows the vacuum-assisted resin transfer molding (VARTM) processing of large pulsed electron beam (LPEB)-treated woven carbon fiber samples.

3. Results and discussion

3.1. Weight differences

In the preliminary stage of the investigations, the weight change of the WCF samples after ZnO growth was achieved. Table 2 shows the percent weight change of the electron beam-treated samples after the growth of ZnO nanorods. The table shows that the increase in percent weight change of the electron beam-treated samples was greater compared to the untreated samples. The reason was due to the rapid growth of ZnO nanorods after the electron beam treatment. As we moved the applied cathode voltage from

Table 1
Experimental parameters used in vacuum-assisted resin transfer molding (VARTM) processing.

	Samples	Voltage of electron beam (kV)	Solenoid voltage (kV)	No. of cycles
1	Null WCF	–	–	–
2	WCF + seed + ZnO growth solution (20 mM)	–	–	–
3	WCF + electron beam + seed + ZnO growth solution (20 mM)	30	1.5	4
4	WCF + electron beam + seed + ZnO growth solution (20 mM)	25	1.5	4
5	WCF + electron beam + seed + ZnO growth solution (20 mM)	20	1.5	4
6	WCF + electron beam + seed + ZnO growth solution (20 mM)	15	1.5	4
7	WCF + electron beam + seed + ZnO growth solution (20 mM)	10	1.5	4

10 kV to 30 kV, the upsurge in percent weight change also increased. The maximum increase in weight change was observed in samples treated with a 30 kV cathode voltage because at this cathode voltage, the surface area of the WCF was maximized, which induced the higher growth of ZnO nanorods.

3.2. X-ray diffraction analyses

XRD analyses of the samples were performed with a wide-angle X-ray diffractometer (Bruker, Billerica, MA, USA) using crystal-monochromated CuKα radiation in the angular range of 5°–60° (2θ) with a 40 kV operating voltage and a 20 mA current. Fig. 4 shows diffractograms of WCFs with and without electron beam treatment. Diffractogram Fig. 4(a) contains two broad peaks between 15° and 28° for the untreated WCF samples. The presence of new diffraction peaks corresponding to (100), (002), (101), (102), and (110) crystal planes at greater than $2\theta = 30°$ in Fig. 4(b) provides evidence for the growth of ZnO nanorods on the surface of the WCFs [33]. Fig. 4(c) shows a diffractogram of LPEB-treated WCFs with ZnO growth. Note that the intensities of the diffraction peaks of crystal planes are higher than those observed without LPEB treatment. Higher concentrations of ZnO nanorods result in sharper and more intense diffraction peaks. LPEB treatment increased the surface area of the WCFs and facilitated the rapid growth of ZnO nanorods.

3.3. Electrical resistance of the WCF samples

Electrical resistance measurements of the WCF/polyester samples were performed with a 2002 Multimeter (Keithley Instruments, Beachwood, OH, USA). Earlier studies have indicated that the growth of ZnO nanorods on WCFs results in a decrease in electrical conductivity due to the presence of oxygen, which acts as an electron barrier to the WCF and prevents the passage of current [34]. Thus, higher levels of ZnO growth should result in higher electrical resistance in the WCF/ZnO composites. Fig. 5 shows the electrical resistance of CF samples before and after LPEB treatment. The minimum electrical resistance was observed with the bare, untreated WCF samples. In all cases, samples treated with the LPEB had higher resistance values than untreated samples. This is consistent with higher levels of ZnO growth on the treated samples. With increasing the growth of ZnO nanorods on the surface of woven carbon fiber, the surface area of the nanorods also increases. Due to very high surface-to-volume ratio, the nanorods have a strong affinity towards the molecules like O_2, H_2O etc. This phenomena leads to absorb the oxygen/water molecules on the surface of the nanorods that follows the trapping of conducting electron on the nanorods surfaces. This whole process results decrease in effective conduction channel as well as the overall conductance of the nanorods [35]. WCF-composite samples treated with an electron voltage of 10 kV showed a 7.2% increase in electrical resistance relative to bare WCFs. Resistance increased by up to 14.3% and 21.1% as the applied cathode voltage was tuned from 20 kV to 30 kV, probably because of rapid increases in surface area with upsurges in the applied cathode voltage, leading to further increases in ZnO nanorod growth.

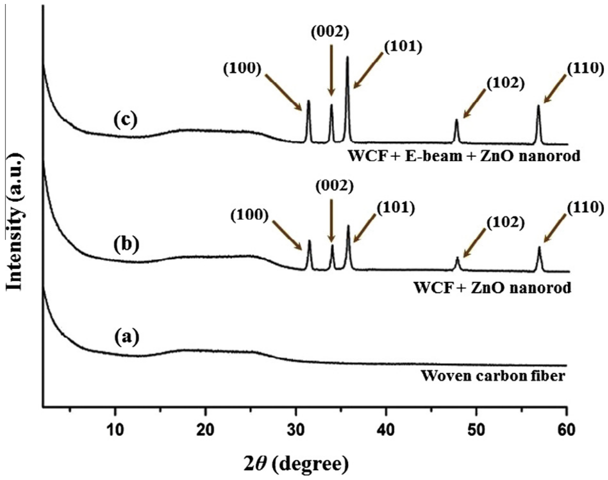

Fig. 4. X-ray diffractograms are shown for (a) woven carbon fibers (WCFs), (b) ZnO grown on WCFs without electron beam treatment, and (c) ZnO grown on WCFs after electron beam treatment (30 kV).

3.4. Scanning electron microscopy

The surface morphology of WCFs with ZnO nanorods was evaluated with and without LPEB treatment using a scanning electron microscopic (SEM; Nanonova 230; FEI, Hillsboro, OR, USA) with a 15 kV operating voltage. Fig. 6(a) shows SEM micrographs of a WCF surface that was not subjected to LPEB treatment. The micrographs show a relatively plain surface in Fig. 6(a) that appeared rougher after the electron beam treatment in Fig. 6(b). The growth of ZnO nanorods on WCFs that had not been LPEB-treated is shown in Fig. 6(c). In this micrograph, the growth of ZnO nanorods was

Table 2
Percent weight change of woven carbon fibers (WCFs) after electron beam treatment.

Sample no.	Sample configuration	Before (g)	After (g)	Wt. change (g)	% Wt. change
1	Null WCF + seed + ZnO growth solution (20 mM)	1.5911	1.5942	0.0031	0.195
2	WCF + electron beam (10 kV) + seed + ZnO growth solution (20 mM)	1.5481	1.5535	0.0054	0.348
3	WCF + electron beam (20 kV) + seed + ZnO growth solution (20 mM)	1.6139	1.6217	0.0078	0.483
4	WCF + electron beam (30 kV) + seed + ZnO growth solution (20 mM)	1.5892	1.5985	0.0093	0.585

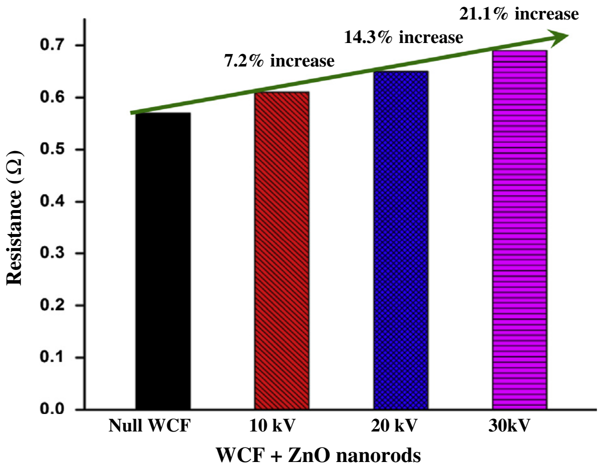

Fig. 5. The electrical resistance of WCF/polyester composites is given for samples with and without LPEB treatment.

relatively low due to the lack of sufficient fiber surface area. Micrographs of ZnO grown on WCF samples treated with LPEBs at 10, 20, and 30 kV cathode voltages are presented in Fig. 6(d)–(f). These images show that as the applied electron voltage was raised, the growth of ZnO nanorods also increased. It is this increase in the surface area of the WCF after LPEB treatment that results in strong interactions between the ZnO nanorods and the fiber surface. The maximum growth of ZnO nanorods, and therefore the highest surface area fibers, was observed at a LPEB voltage of 30 kV.

3.5. Impact tests

The impact energy absorption of ZnO/polyester, LPEB-treated WCF composites was tested with an impact testing apparatus (5982; Instron, Norwood, MA, USA). To fix the specimens prior to testing, the diameter of the circular clamp was 40 mm. The photoelectric sensor-collected data from the initial impact contact point until penetration occurred, or the maximum weight capacity of the testing apparatus was reached. The impact energy absorption of ZnO-grown WCFs is presented in Fig. 6 and is given by

$$E_{total} = E_{rebound} + E_{absorbed} \tag{8}$$

For brittle composites, the rebound energy is negligible. Thus, in such cases, the total energy was almost completely absorbed by the resin and fibers. In low-velocity impacts, the bending deformation energy and the delamination energy are included in the absorbed energy. However, due to the brittle nature of the composites, energy was predominantly absorbed by fiber breakage. The remaining energy, such as global deformation, delamination, and shear-out energy, was absorbed by the impact. The data in Fig. 7 shows that the impact energy absorption of the WCFs that had not been LPEB-treated was minimal. Energy absorption increased to 54.4% with WCFs that had been LPEB-treated at a 10 kV applied voltage. The impact strength of the final composites increased by up to 92.1%, 111.7%, and 125.5% when the applied cathode voltage during LPEB treatment was increased from 15 to 30 kV, with a maximum increase of 153.3%. Such differences in impact energy absorption are presumably due to interactions between the ZnO nanorods and the polymer matrix. Moreover, with increasing the cathod voltage, the growth of ZnO nanorods also increases. This increment leads to enlarge the effective surface area of the nanorods. As a consequence, a significant improvement in interaction within the nanorods surfaces and CF occurs. These interactions, in combination with the polyester resin matrix, allowed the composite to absorb more delamination energy through the WCFs. In addition, the surface of CFs naturally contains hydroxyl, carbonyl, and carboxyl groups. Such functional groups have very strong affinities for ZnO nanorods. For example, a carboxylic acid on a CF surface would react with Zn^{2+} of a ZnO nanorod, forming a strong ionic bond [3]. Also, the presence of two lone pairs of electrons in a carbonyl group would result in a strong affinity for ZnO nanorods [36]. These same functional groups can form strong bonds by reacting with ester groups in the polyester resin.

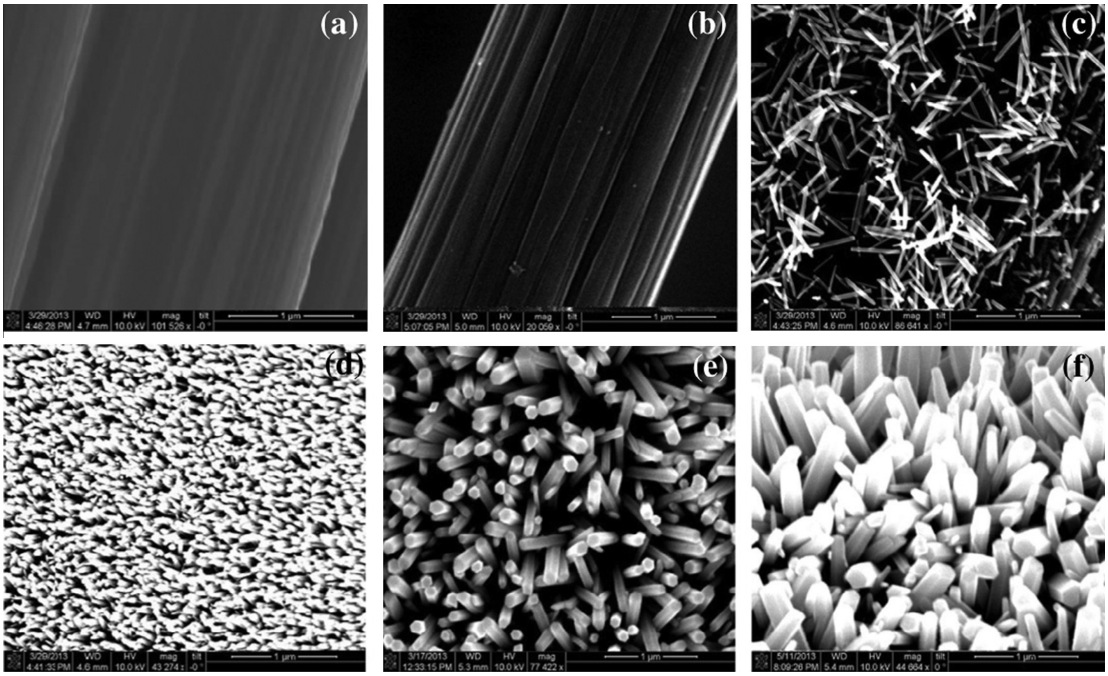

Fig. 6. SEM micrographs show (a) woven carbon fibers (WCFs) before electron beam treatment, (b) WCFs after electron beam treatment, and (c) ZnO nanorods grown on WCFs without electron beam treatment. Also shown are ZnO nanorods grown on WCFs that had been LPEB-treated at (d) 10 kV, (e) 20 kV, and (f) 30 kV.

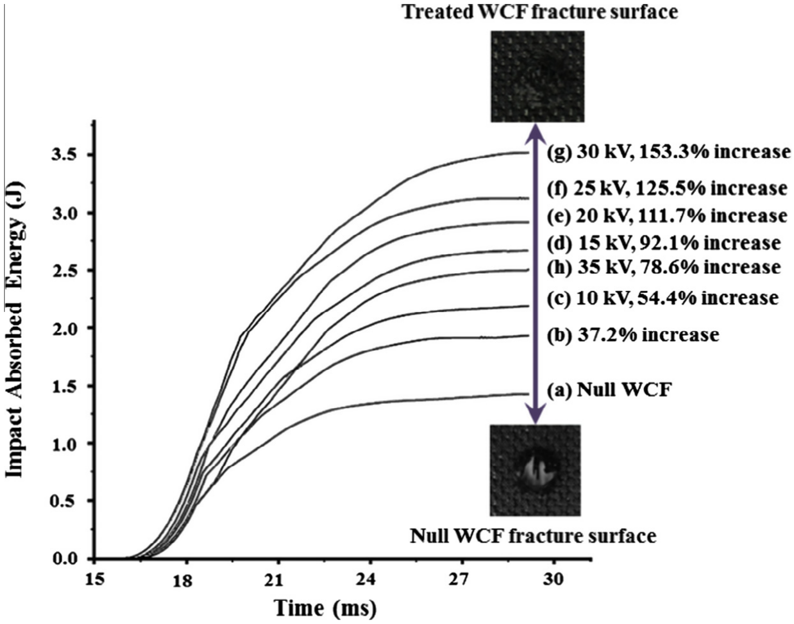

Fig. 7. Total impact energy absorbed by the (a) untreated, bare woven carbon fiber (WCF), (b) WCF + ZnO, (c) WCF + electron beam (10 kV) + ZnO, (d) WCF + electron beam (15 kV) + ZnO, (e) WCF + electron beam (20 kV) + ZnO, (f) WCF + electron beam (25 kV) + ZnO, (g) WCF + electron beam (30 kV) + ZnO and (h) WCF + electron beam (35 kV) + ZnO.

Together, all of these interactions between the functional groups of the CF, ZnO nanorods, and the polyester resin increases the impact strength of the final composite. As the cathode voltage increases up to 35 kV, the impact resistance property seems to be decreased as shown in Fig. 7(h). The reason is probably that the higher voltage applied on the WCF induces the damage on the surface properties of the carbon fiber. Thus, it cannot reinforce the composite property and hence, results decreased final impact resistance values.

4. Conclusions

WCF/ZnO nanorod/polyester resin hybrid composites were developed using LPEB treatment and followed by a VARTM process. Before growing the ZnO nanorods, the surface of the CF was treated with LPEB varying cathode voltages from 10 kV to 30 kV. The optimum level of the cathode voltage was fixed at 30 kV as beyond that level the performance of the CF decreased. SEM images of these fiber surfaces revealed increase in roughness and growth levels of ZnO nanorods after the electron beam treatment. The growth of ZnO nanorods was the greatest following electron beam treatment with an electron voltage of 30 kV. The intensities of crystallinity peaks observed in X-ray diffractograms of the ZnO nanorods were higher for samples that had been LPEB-treated. The samples treated with 30 kV cathode voltage of LPEB treatment showed maximum improvement in percent weight change and electrical resistance compared to other samples. The electrical resistance of the composite samples was increased by up to 21.1% with increases in the applied LPEB voltage from 10 kV to 30 kV. Impact energy absorption increased by up to 153.3% in LPEB-treated samples due to the maximum interaction between CF, ZnO nanorods and polyester matrix.

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