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Grafting of poly(ethylene-*block*-ethylene oxide) onto a vapor grown carbon fiber surface by γ-ray radiation grafting

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Abstract

To modify the surface of vapor grown carbon fiber (VGCF), poly(ethylene-*block*-ethylene oxide) (PE-*b*-PEO, $M_n = 1400$, PEO content = 50 wt%) was successfully grafted onto the surface by using γ-ray irradiation of the PE-*b*-PEO-adsorbed VGCF in solvent-free system. It is found that the percentage of polymer grafting reached 15.0% when the PE-*b*-PEO-adsorbed VGCF was irradiated by γ-ray over 40 kGy dose at 110 °C, but at the lower irradiation temperature of 75 °C, the grafting reaction scarcely proceeded. This indicates that polymer radicals formed by γ-ray irradiation were successfully trapped by VGCF surface above melting point of PE-*b*-PEO. On the other hand, when the dispersion of VGCF in THF solution of PE-*b*-PEO was irradiated, the percentage of PE-*b*-PEO grafting was less than 4.0%. It was confirmed by a field-emission scanning electron microscope (FE-SEM) that the surface of the VGCF was uniformly covered by grafted PE-*b*-PEO. In addition, the surface free energy of ungrafted and PE-*b*-PEO-grafted VGCF was determined.

Keywords: Vapor grown carbon fiber; γ-Ray radiation grafting; Poly(ethylene-*block*-ethylene oxide)

1. Introduction

Vapor grown carbon fiber (VGCF) is a new class of carbon nano-fiber differentiated from carbon nano-tube in its method of production and its lower cost. It is also different from the conventional pitch-based and polyacrylonitrile (PAN)-based carbon fiber in its nano-sized diameter [1]. VGCF is general in the form of annular carbon layers arranged like a tree ring structure. The carbon rods have a high aspect ratio and a nano-sized diameter ranging from 50 to 200 nm, which is between those of conventional carbon fibers (5–10 μm) and of carbon nanotubes (1–50 nm) [2]. Due to their unique physical properties, such as excellent thermal and electrical conductivity, good mechanical behaviour and lower cost of production, VGCF has attracted considerable attention in the last ten years [3,4].

VGCF is usually used as reinforcement, adsorbent and conductive filler. Recently, they are also used in batteries for electrode and separator [5,6]. In most cases, they are used in the form of composite where the polymer is needed as matrices. However, due to the very low surface free energy, nano-size and low bulk density, it is difficult to disperse VGCF in polymer matrix uniformly.

It is considered that the surface treatments of carbon fiber, such as oxidative treatments (including nitric acid [7], plasma [8], corona [9], air [10] and carbon dioxide [11] oxidation), electrochemical treatments [12], coating and grafting [13,14], can modify the surface of VGCF. However, except for oxidation treatment, the surface modifications of VGCF have been few reported. In addition, the surface oxidation causes changes in structures and chemical properties of VGCF. For example, it has been reported that the order of the graphitic structures and the concentration of aliphatic structures in the bulk are reduced, and the pores in VGCF slightly increased [15,16].

We expect that the modification of the VGCF surface by grafting of polymer onto its surface is preferable. In the composite prepared from polymer-grafted VGCF and polymer, the VGCF is covalently bond to polymer matrix. This is often desirable since it provides the best possible

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adhesion and allows for optimal transfer of stress from the matrix to the fiber. We have reported the radical grafting of polymers initiated by azo group previously introduced onto the surface [17] and ligand-exchange reaction of ferrocene containing polymer with aromatic rings of carbon fiber [13,18]. Grafting by direct γ-ray irradiation of polymer-adsorbed carbon black with few functional groups has also been reported [19].

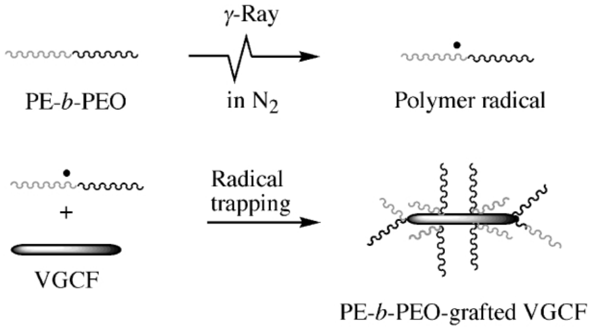
Characterization of VGCF surface is also an important issue for VGCF studies. Structure properties can be recognized by using scanning electron microscopy (SEM) [20], transmission electron microscope (TEM) [21], scanning tunneling microscopy (STM) [16] and X-ray diffractometer (XRD) [22]. Thermodynamic properties, such as surface free energy, however, are difficult to measure due to the low bulk density and small physical size of VGCF. Methods such as contact angle [8,23], capillary-flow [13], capillary-rise [24], thin layer wicking [25] and inverse gas chromatography [10] have been advanced. However, the results of these methods are usually not in agreement with each other.

In this paper, we investigated the grafting of poly(ethylene-*block*-ethylene oxide) (PE-*b*-PEO) onto VGCF surface by using γ-ray irradiation (Scheme 1). The grafting reaction was carried out both in solution and in solvent-free system. To characterize the PE-*b*-PEO-grafted VGCF, field-emission scanning electronic microscope (FE-SEM) was used to observe the VGCF surface change before and after grafting. A comparative study on the surface energy measurements for untreated and PE-*b*-PEO-grafted VGCF was performed by using contact angle detection.

2. Experimental

2.1. Materials and reagents

Vapor grown carbon fiber (VGCF) was obtained from Showa Denko Co. Ltd, Japan. Its average diameter and length are about 100 nm and 5–10 μm, respectively. It was washed with pure water, and dried in vacuum at 120 °C for 24 h before use. Poly(ethylene-*block*-ethylene oxide) (PE-*b*-PEO) ($M_n = 1400$, PEO content = 50 wt%) was obtained from Aldrich Chemical Co. and dried in vacuum at 80 °C for 24 h before use. Analytical grade tetrahydrofuran (THF), ethylene glycol, and heptane purchased from Wako Pure Chemical Industries, Ltd, Japan, were used without further purification.



Scheme 1.

2.2. Radiation grafting of PE-b-PEO onto VGCF surface in solution

γ-Ray irradiation was performed in Co-60 source facility of JAERI (Japan Atomic Energy Research Institute). VGCF-dispersed THF solution of PE-*b*-PEO was irradiated by γ-ray. After the irradiation, the solution was violently stirred at 65 °C for 48 h in nitrogen.

2.3. Radiation grafting of PE-b-PEO onto VGCF surface in solvent-free system

In order to increase the grafting of PE-*b*-PEO onto VGCF surface, radiation grafting of PE-*b*-PEO onto VGCF surface was performed in solvent-free system. First, the PE-*b*-PEO was adsorbed onto the VGCF surface by adding 1.0 g of VGCF to 50 ml of 4.0 wt% PE-*b*-PEO solution of THF. The mixture was stirred at 65 °C for 2 h and the VGCF was separated from the mixture by filtration. The resulting VGCF was dried in a vacuum at 80 °C for 24 h. The amount of adsorbed PE-*b*-PEO on the surface, determined by TGA, is 74% (weight percentage of adsorbed PE-*b*-PEO to VGCF). Afterwards 0.1 g of the PE-*b*-PEO-adsorbed VGCF was transferred into a 5-ml glass bottle and irradiated with γ-ray at the designed temperature.

2.4. Grafting measurement

To remove the ungrafted PE-*b*-PEO, the product was extracted with a Soxhlet apparatus for 48 h with THF. It was previously confirmed that ungrafted PE-*b*-PEO was completely removed by Soxhlet extraction with THF.

The percentage of PE-*b*-PEO grafting was calculated by the following equation:

$$\text{Grafting } (\%) = A/B \times 100$$

where A is the PE-*b*-PEO grafted (g), and B is the VGCF used (g). The amount of PE-*b*-PEO grafted onto the VGCF surface was determined by weight loss when the PE-*b*-PEO-grafted VGCF was heated from room temperature to 500 °C under nitrogen at 10 °C/min with a thermal analyzer (Thermo plus TG 8120, Rigaku Co., Ltd, Japan).

2.5. FE-SEM observation

The morphology of the original VGCF and PE-*b*-PEO-grafted VGCF was observed by a field-emission scanning electron microscope (FE-SEM) at an acceleration voltage of 15 kV with a JSM-6700F (JEOL, Japan) instrument.

2.6. *Contact angle measurement and calculation of surface free energy*

The contact angle of a liquid on the VGCF pellet was detected using a Contact Angle Meter (model CA-X, Kyowa Interface Science Co., Ltd, Japan). The VGCF pellet was prepared under a press of 200 kg/cm^2. The diameter was 10 mm and the thickness was 4 mm. The contact angles of water, ethylene glycol and heptane drops on the original and PE-*b*-PEO-grafted VGCF (grafting, 15.0%) were measured at 20 °C. For each kind of liquid, at least eight measurements were performed and the average value was used. The surface energy was calculated from the contact angle and the surface tensions of liquids.

3. Results and discussion

3.1. *Radiation grafting of PE-b-PEO onto VGCF surface in solution*

We tried the grafting of PE-*b*-PEO onto VGCF surface by γ-ray irradiation of the VGCF-dispersed THF solution of PE-*b*-PEO. That is, 0.1 g of VGCF was dispersed into 5 ml of 2.0 wt% PE-*b*-PEO solution of THF in a 10 ml bottle; then, the mixture was γ-ray irradiated at room temperature. After γ-ray irradiation, the mixture was stirred at 65 °C in nitrogen for 48 h. The results are shown in Fig. 1.

As shown in Fig. 1, the grafting increased with increase in the irradiation dose. The open circles shows the results obtained from the γ-ray irradiation grafting without post-reaction, and the filled circle shows the results obtained from γ-ray irradiation grafting after 48 h post-reaction at 65 °C. It was found that the percentage of grafting slightly increased by the post-reaction at 65 °C: the grafting was less than 4.0%. It may be due to the fact that solvent quenches the generated radicals. The percentage of grafting was considerably lower than that of polymer grafting onto carbon fiber by radical graft polymerization initiated by azo groups previously introduced onto the surface [18].

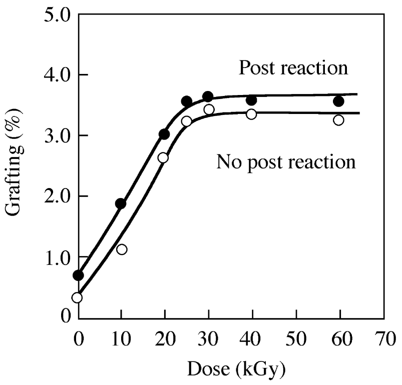


Fig. 1. Relationship between percentage of PE-*b*-PEO grafting and irradiation dose of the radiation grafting of PE-*b*-PEO onto VGCF in THF at room temperature. The open circles shows the results obtained from the γ-ray irradiation grafting without post-reaction, and the filled circle shows the results obtained from γ-ray irradiation grafting after 48 h post-reaction in THF at 65 °C.

3.2. *Radiation grafting of PE-b-PEO onto VGCF surface in solvent-free system*

The radiation grafting of PE-*b*-PEO onto VGCF surface in the solvent-free system was examined. That is, the PE-*b*-PEO was preadsorbed onto VGCF surface from PE-*b*-PEO solution of THF; then, the PE-*b*-PEO-adsorbed VGCF was irradiated at the designed dose and temperature.

Fig. 2 shows the relationship between the percentage of grafting and irradiation dose at different irradiation temperatures of 25, 50, 75, 100 and 110 °C. The irradiation dose rate was fixed to 10 kGy/h. The points at the 0 (dose axial) indicate that the samples are only heated at the corresponding temperature for 6 h.

As shown in Fig. 2, it was found that the grafting was remarkably affected by the irradiation temperature. At the lower irradiation temperature of 25, 50 and 75 °C, the grafting was less than 5.0%. On the contrary, at 100 °C, the grafting at 60 kGy dose reached 7.3%, and at 110 °C, near the melting point (109 °C) of PE-*b*-PEO, the grafting suddenly increased to 15.0%.

On the other hand, at every irradiation temperature, the grafting increased with the increase of the irradiation dose. For example, at irradiation temperature of 110 °C, the grafting increased quickly from 0.9 to 12.4% at the initial irradiation dose of 15 kGy, and then reached the steady state of 15.0% at 40 kGy. On the contrary, without irradiation, the grafting of PE-*b*-PEO on the VGCF was less than 1.0%.

At the lower irradiation temperature, such as 25 °C, even if the radiation dose increased up to 100 kGy, the percentage of PE-*b*-PEO grafting was less than 2.3%. This may be due to the fact that PE-*b*-PEO radicals hardly reacted with the VGCF surface because of the crystalline structure of PE-*b*-PEO.

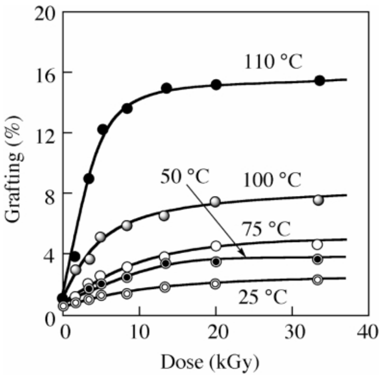


Fig. 2. Relationship between percentage of PE-*b*-PEO grafting and irradiation dose of the radiation grafting of PE-*b*-PEO onto VGCF in the solvent-free system at various temperatures. The amount of adsorbed PE-*b*-PEO on VGCF before irradiation was 74% (weight percent of PE-*b*-PEO on VGCF).

The PE-*b*-PEO grafting onto VGCF was also affected by irradiation dose rate and irradiation atmosphere. As shown in Fig. 3, PE-*b*-PEO-adsorbed VGCF was irradiated at the different irradiation dose rate of 5, 10, 15 and 20 kGy/h at 110 °C in nitrogen and air. The total irradiation dose of every sample was 60 kGy. Either in nitrogen or in air, the grafting of PE-*b*-PEO on VGCF surface slightly decreased with increase in the irradiation dose rate. The grafting of PE-*b*-PEO on VGCF was decreased from 16.1 to 12.3, and 15.4 to 11.9%, when the irradiation dose rate increased from 5 to 20 kGy/h in nitrogen and air, respectively. The slight decrease of the grafting in air may be due to the reaction between the generated polymer radical and oxygen in air.

The grafting of PE-*b*-PEO onto VGCF surface was considered to proceed through the trapping of PE-*b*-PEO radical by the polycondensed aromatic rings on the VGCF [19]. Compared with the rate of PE-*b*-PEO radical generation in the above irradiation dose rate, the rate of radical trapping by VGCF was relatively slow. Therefore, at higher irradiation dose rate, some PE-*b*-PEO radical was quenched before the grafting reaction, resulting in decrease of PE-*b*-PEO grafting.

Crosslinked PE-*b*-PEO formed by irradiation is unable to remove by Soxhlet extraction with THF. However, for the γ-ray-irradiated PE-*b*-PEO in the absence of VGCF, we found that crosslinking of PE-*b*-PEO was less than 7.3% even if it was irradiated under 60 kGy. In addition, the FE-SEM observation indicated that all of polymer covered the VGCF surface. Therefore, the grafting of PE-*b*-PEO onto the VGCF surface through the trapping of PE-*b*-PEO radical was considered as the main reaction under the above condition.

In conclusion, the grafting of PE-*b*-PEO onto the VGCF surface was successfully proceeded by irradiation of PE-*b*-PEO-adsorbed VGCF in the solid state, and the percentage of PE-*b*-PEO grafting onto the surface was much larger than that of radiation grafting in solution.

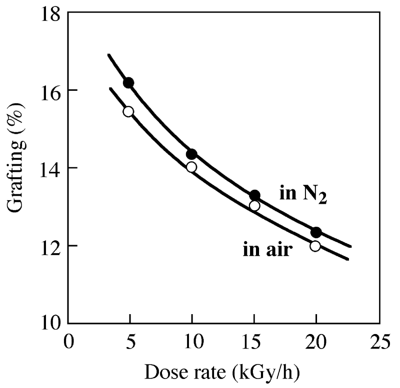


Fig. 3. Relationship between percentage of PE-*b*-PEO grafting and irradiation dose in nitrogen and in air. Irradiation temperature, 110 °C.

3.3. FE-SEM observation of the PE-b-PEO-grafted VGCF

FE-SEM has also employed to monitor the changes in surface structure induced by the grafting of PE-*b*-PEO on VGCF. FE-SEM imagines of original VGCF are shown in Fig. 4(a) and (a′), and those of PE-*b*-PEO-grafted VGCF, grafting = 15.0% in Fig. 4(b) and (b′). As shown in Fig. 4(a) and (a′), the diameter of the original VGCF was about 100 nm, and the surface was very clean and smooth. There was a branch on the VGCF, which was different from the general carbon fiber and carbon nano-tubes. However, the end of the VGCF was not smooth; the annular carbon layers could be seen.

On the other hand, the surface PE-*b*-PEO-grafted VGCF shown in Fig. 4 (b) and (b′) was rough in comparison with original one. This may be due to the fact that a layer of grafted PE-*b*-PEO covered on the VGCF uniformly. In addition, it is interesting to note that the end of the VGCF has more grafted PE-*b*-PEO. Therefore, it could be concluded that the PE-*b*-PEO were grafted onto the VGCF surface, and the grafting of polymer to end of VGCF readily proceeded. There was no distinctly difference in the diameter before and after PE-*b*-PEO grafted could be observed. It was because of that the grafted layer on the VGCF surface was too thin. The calculated thickness of PE-*b*-PEO grafted layer from the weight of grafted PE-*b*-PEO is only about 10 nm, in the scale of monolayer of PE-*b*-PEO on the VGCF surface.

3.4. Contact angle and surface free energy of PE-b-PEO-grafted VGCF

The contact angles of water, ethylene glycol and heptane on the original VGCF and PE-*b*-PEO-grafted VGCF (grafting, 15.0%) were measured at 20 °C. The results are shown in Table 1.

The contact angles of water on the original VGCF and PE-*b*-PEO-grafted VGCF pellet were 114.5 ± 3.7° and 93.4 ± 2.3°, respectively. Therefore, both the surfaces of original VGCF and PE-*b*-PEO-grafted VGCF show hydrophobic nature. It is noted that the water drop contact angle of the VGCF pellet, 114.5°, is relative higher than that of high crystalline graphite (95°). We determined carbon black powders (higher conducting carbon black with no surface function groups, and the diameter is 41 nm) at the same condition, the water drop contact angle is less than 95°. Therefore, the higher contact angel may be due to the pellet

Table 1
Contact angle of liquids on the original and PE-*b*-PEO-grafted VGCF

VGCF	Contact angle (°)		
	Water	Ethylene glycol	Heptane
Original	114.5 ± 3.7	89.8 ± 4.3	0
Polymer-grafted	93.4 ± 2.3	71.6 ± 4.5	0

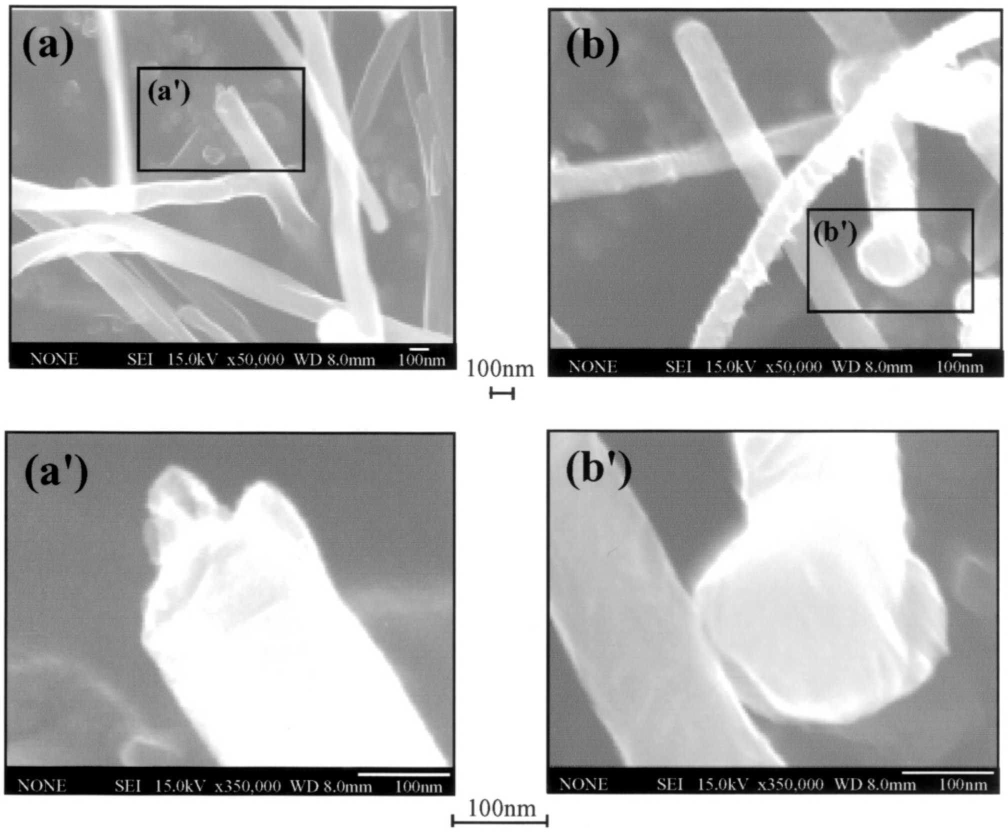


Fig. 4. FE-SEM aspects of (a, a′) untreated VGCF and (b, b′) PE-*b*-PEO-grafted VGCF.

made from the high aspect ratio of the nano-diameter VGCF.

The results are consistent with the fact that VGCF float on the water surface and hardly disperse in water even with violently stirring. The hydrophobic nature of the original VGCF surface was due to the basal graphite planes arranged in considerable concentric circles [15]. The decrease of contact angle of PE-*b*-PEO-grafted VGCF was due to the PEO segments of the grafted PE-*b*-PEO. The main grafting reaction may be based on that between VGCF surface and PEO segments of PE-*b*-PEO. Thus, the VGCF keeps its hydrophobic nature due to the PE segments at the surface.

As shown in Table 1, the contact angles of ethylene glycol on the original VGCF and PE-*b*-PEO-grafted VGCF were 89.8 ± 4.3° and 71.6 ± 4.5°, respectively. The contact angles were not stable, and the deviation was relative large. It may be due to the solvent absorption by grafted PE-*b*-PEO on VGCF. On the other hand, the contact angle of heptane could not be determined. The drop of heptane was soaked into the pellet (sample) quickly.

For the estimation of the surface free energy of the VGCF, we used the Owens-Wendt geometric mean method [26] for water and ethylene glycol. From the contact angles of water and ethylene glycol, the surface free energy could be estimated by means of the Young's equation (1).

$$\gamma_l(1+\cos\theta) = 2\left(\sqrt{\gamma_s^d\gamma_l^d} + \sqrt{\gamma_s^p\gamma_l^p}\right) \tag{1}$$

where γ is the surface free energy (or surface tension), which has two parts, namely, the dispersion (nonpolar) and polar components ($\gamma = \gamma^d + \gamma^p$) [27]. The superscripts of d and p mean the dispersion and polar components, respectively. The subscripts of l and s mean the liquid and solid (VGCF), respectively. The surface tensions of water, ethylene glycol and heptane were obtained from literature [28]. Thus, the surface free energies of original and PE-*b*-PEO-grafted VGCF were calculated from Eq. (1), and the results are shown in Table 2.

The surface free energy of original VGCF was 19.21 mJ/m^2, with a dispersion component of 19.20 mJ/m^2 and a polar component near to zero. Therefore, it is clear that the original VGCF has a low surface free energy with high hydrophobicity. The γ^d of VGCF, determined by inverse gas chromatography, reported by Pogue et al. [10], was 53.5 mJ/m^2. It was very higher than our results. On the other hand, the result reported by Bubert et al. [8], where the γ, γ^d and γ^p of VGCF were 23, 21 and 2 mJ/m^2, respectively, is in agreement with ours. The surface free energies reported by Bubert et al. were obtained by measuring the contact angle of the sample in water, ethylene glycol and *n*-hexane using a micro-balance. However, except the above mentioned free surface energies, they did not show the data of contact angles of those solvents in Ref. [8].

The extremely low surface free energy of VGCF,

Table 2
Surface free energies of PE-*b*-PEO-grafted VGCF

	Materials	Surface free energy (mJ/m^2) γ^d	γ^p	$\gamma = \gamma^d + \gamma^p$
Liquids[a]	Water	21.8	51.0	72.8
	Ethylene glycol	29.3	19.0	48.3
	Heptane	20.1	0	20.1
VGCF[b]	Original	19.20	0.01	19.21
	Polymer-grafted	18.00	4.08	22.08

[a] Values obtained from Ref. [28].

[b] Values calculated from the contact angles in Table 1 and Eq. (1).

19.2 mJ/m^2, which corresponds to that of PTFE surface, was calculated from the higher contact angles using Eq. (1). In another word, Eq. (1) may be not suitable for calculation of surface free energy due to the especial surface made from nano-size carbon fiber. However, we can use it to recognize the surface change of the VGCF before and after polymer grafted.

The surface free energy of PE-*b*-PEO-grafted VGCF was 22.08 mJ/m^2, with a dispersion component of 18.00 mJ/m^2 and a polar component of 4.08 mJ/m^2. Therefore, the surface of PE-*b*-PEO-grafted VGCF shows also a hydrophobic nature. We can note a clear difference between the original VGCF and PE-*b*-PEO-grafted VGCF. That is, the total surface free energy and the polar component were slightly higher than those of original VGCF. Especially, the polar component of the free surface energy of PE-*b*-PEO-grafted VGCF, 4.08 mJ/m^2, was very higher than that of original VGCF, indicating that the PE-*b*-PEO was efficiently grafted onto the VGCF surface. The increased polar component of the PE-*b*-PEO-grafted VGCF is due to the contribution of polar PEO segments of grafted PE-*b*-PEO. However, it is noted that the water drops contact angle of the PE-*b*-PEO-grafted VGCF is relatively higher than that of the PE-*b*-PEO films, which is a hydrophilic material. Therefore, we considered that the grafting of PE-*b*-PEO on the VGCF surface mainly proceeded between the PEO segments and the aromatic rings of VGCF. Thus, the PEO concentration on the PE-*b*-PEO-grafted VGCF surface was expected to be much smaller than PE concentration. The surface of the PE-*b*-PEO-grafted VGCF was considered to be in enrichment of PE.

4. Conclusions

PE-*b*-PEO was successfully grafted onto the VGCF surface by γ-ray irradiation of PE-*b*-PEO-adsorbed VGCF. The maximum PE-*b*-PEO grafting onto VGCF was obtained by the irradiation of the PE-*b*-PEO-adsorbed VGCF with total dose 40 kGy at irradiation dose rate of 10 kGy/h and at 110 °C in nitrogen, reached 15.0%.

Characterization of the PE-*b*-PEO-grafted VGCF could be performed by surface observation using FE-SEM and contact angle measurements. The PE-*b*-PEO-grafted VGCF was covered by polymer uniformly, with a surface free energy of about 22 mJ/m^2.

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