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Grafting of branched polymers onto the surface of vapor grown carbon fiber and their electric properties

Gang Wei[a], Hiroshi Saitoh[b], Kazuhiro Fujiki[c], Takeshi Yamauchi[d,e], Norio Tsubokawa[a,b,e] (✉)

[a] Venture Business Laboratory, Niigata University, 8050 Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

[b] Department of Material Science and Technology, Faculty of Engineering, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

[c] Division of Life and Health Sciences, Joetsu University of Education, 1, Yamayashiki, Joetsu, Niigata 943-8521, Japan

[d] Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

[e] Center for Transdisciplinary Research, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

E-mail: ntsuboka@eng.niigata-u.ac.jp

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Summary

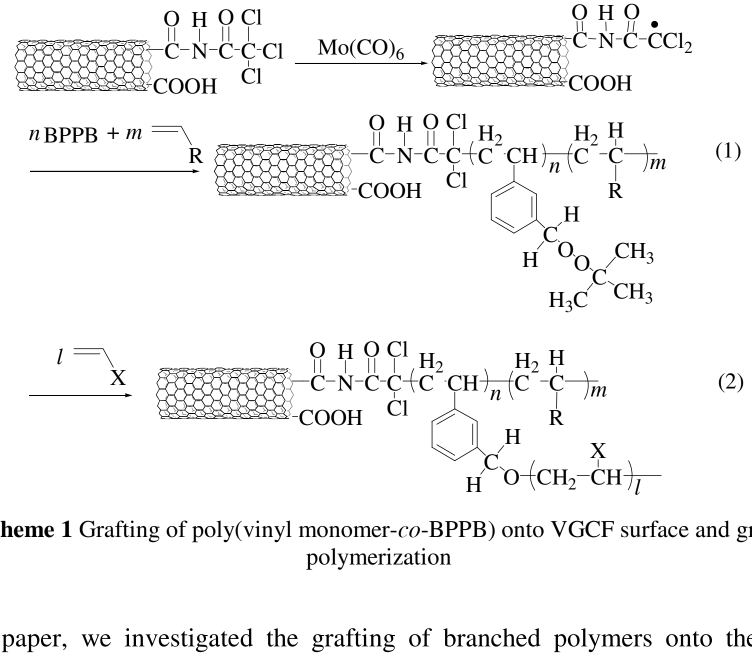
The grafting of branched polymers onto vapor grown carbon fiber (VGCF) surface and their electric properties of the composite prepared from the branched polymer-grafted VGCF were investigated. In the first step, the grafting of copolymers having pendant peroxy groups onto VGCF was achieved by the copolymerization of 1-(*t*-butylperoxy-*i*-propyl)-3-*i*-propenylbenzene (BPPB) with vinyl monomers initiated by the system consisting of $Mo(CO)_6$ and trichloroacetyl groups previously introduced onto the surface. In the second step, the postpolymerization of vinyl monomers was initiated by pendant peroxy groups of grafted poly(vinyl monomer-*co*-BPPB) on the surface to give branched vinyl polymer-grafted VGCF. The dispersibility of VGCF in THF was remarkably improved by grafting of branched polymers onto the surface. The electric resistance of composites prepared from the branched polymer-grafted VGCF suddenly increased when the composites were transferred into solvent vapors and suddenly decreased when they were transferred to dry air.

Introduction

Vapor grown carbon fiber (VGCF) is a new class of carbon nanofiber differentiated from carbon nanotube in its production method [1]. It is also different from the conventional pitch-based and polyacrylonitrile-based carbon fiber in its nano-sized diameter [1]. VGCF is known to be 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 [2]. VGCF has attracted considerable attention in the last ten years due to their unique physical properties, such as excellent thermal and electrical conductivity, good mechanical behavior, and lower cost of production [3,4]. VGCF is usually used as a reinforcing material, conductive filler, and an electrode and separator for batteries [5,6]. In most cases, they are used in the form of composite where the polymer is needed as matrices. However, it is difficult to disperse VGCF in polymer matrices uniformly.

We have reported the radical, anionic, and cationic grafting of polymers onto carbon materials, such as carbon black and carbon nanotube surface, initiated by radical and ionic initiating groups previously introduced onto the surface [7,8]. In addition, we have reported the grafting of hyperbranched polymers by postgraft polymerization initiated by pendant initiating groups of grafted polymer chains on the carbon black and silica nanoparticle surface [9-11]. The hyperbranched polymer-grafted carbon black and silica gave a stable dispersion in organic solvent and polymer matrices.

Therefore, we expect that the grafting of polymer onto VGCF surface is preferable for the modification of the surface. In the previous paper, we have reported the radical and anionic grafting of polymers onto VGCF surface initiated by the system consisting of $Mo(CO)_6$ and trichloroacetyl groups on VGCF [12] and by COOK groups on the surface [13], respectively. More recently, we have succeeded in the grafting by ligand-exchange reaction of ferrocene containing polymers with aromatic rings of VGCF [14] and by direct g-ray irradiation of polymer-adsorbed carbon black and VGCF [15]. These polymer-grafted VGCFs are uniformly dispersed in organic solvents and polymer matrices.



Scheme 1 Grafting of poly(vinyl monomer-*co*-BPPB) onto VGCF surface and graft polymerization

In this paper, we investigated the grafting of branched polymers onto the VGCF surface by two-step polymerization processes. That is, in the first step, the grafting of copolymers having pendant peroxy groups was grafted onto VGCF by the copolymerization of 1-(*t*-butylperoxy-*i*-propyl)-3-*i*-propenylbenzene (BPPB) with vinyl monomers initiated by the system consisting of $Mo(CO)_6$ and trichloroacetyl groups previously introduced onto the surface (Scheme 1 (1)). In the second step, the postpolymerization of vinyl monomers initiated by the pendant peroxy groups of grafted poly(vinyl monomer-*co*-BPPB) on the surface was examined (Scheme 1 (2)). In addition, the electric properties of conductive composite prepared from branched-grafted VGCF will be discussed.

Experimental

Materials and reagents

Vapor grown carbon fiber (VGCF) was supplied from Showa Denko Co. Ltd. Japan. The VGCF is high-density type and has about 8 graphite winding layers with 150 nm diameters and 10-15 μm length. The BET specific surface area and bulk density of VGCF are 13 m^2/g and 0.095 g/cm^3, respectively. VGCF was washed with pure water and dried in vacuum at 120°C for 24 h before use.

1-(*t*-Butylperoxy-*i*-propyl)-3-*i*-propenylbenzene (BPPB) was obtained from Kayaku Akzo Co. Ltd., Japan: its trade name is “Initiator D120”. It was used without further purification. Trichloroacetyl isocyanate and $Mo(CO)_6$, which were purchased from Wako Pure Chemical Ind. Ltd., Japan, were used without further purification. Methyl methacrylate (MMA), styrene, glycidyl methacrylate (GMA), acrylamide (AAm), and phenyl vinyl sulfone (PVS) were purified by ordinary methods before use. Polystyrene (Mw=2.5x10^5) and polyMMA (Mw=1.2x10^5) were purchased from Aldrich Chemical Co. and used without further purification.

Introduction of trichloroacetyl groups onto VGCF surface

In order to introduce carboxyl groups onto VGCF surface, VGCF was treated with mixture of sulfuric acid and nitric acid [12]. Then, trichloroacetyl groups were introduced onto the surface by the reaction of trichloroacetyl isocyanate with surface carboxyl groups. The detailed procedures were described in the previous paper [12,16]. The VGCF having trichloroacetyl groups was abbreviated as VGCF-$COCCl_3$.

Surface grafting of poly(vinyl monomer-co-BPPB) onto VGCF initiated by the system consisting of VGCF-$COCCl_3$ and $Mo(CO)_6$

Into a polymerization tube, 0.10 g of VGCF-$COCCl_3$, 0.04 g of $Mo(CO)_6$, 0.10 mol of BPPB, 0.10 mol of vinyl monomer and 5.0 mL of toluene were charged. The tube was cooled with a liquid nitrogen bath, thawed three times, and sealed under high vacuum. The polymerization was conducted at 60°C under stirring with a magnetic stirrer. After the polymerization, the contents of the polymerization tube were poured into a large excess of methanol to precipitate poly(vinyl monomer-*co*-BPPB)-grafted VGCF and ungrafted polymer. The precipitate was filtered and dried *in vacuo* at 50°C. The conversion of monomer was determined by the following equation:

$$\text{Conversion } (\%) = (A-B)/ C \times 100,$$

where A is weight of precipitate, B is weight of VGCF-$COCCl_3$ charged, and C is weight of monomer charged.

Postgrafting of vinyl monomers initiated by poly(vinyl monomer-co-BPPB)-grafted VGCF

Into a polymerization tube, 0.10 g of poly(vinyl monomer-*co*-BPPB)-grafted VGCF, 0.02 mol of vinyl monomer, and 1.0 mL of *m*-xylene were charged. The tube was cooled with a liquid nitrogen bath, thawed three times, and sealed under high vacuum. The reaction mixture was stirred with a magnetic stirrer at 120°C. After the polymerization, the contents of the polymerization tube were poured into a large excess of methanol. The precipitate was filtered and dried *in vacuo* at 50°C. The monomer conversion was calculated by the above equation.

Percentage of grafting and postgrafting

To separate poly(vinyl monomer-*co*-BPPB)-grafted VGCF and vinyl polymer-postgrafted VGCF from the product, the product was dispersed in THF and the dispersion was centrifuged at $1.5\mathrm{x}10^4$ rpm. The supernatant solution containing ungrafted polymer was removed and VGCF precipitated was dispersed again in THF and centrifuged. The procedures were repeated until no more polymers could be detected in the supernatant solution. The percentage of grafting postgrafting were calculated by the following equations:

$$\text{Grafting } (\%) = (D / B) \text{ x } 100$$
$$\text{Postgrafting } (\%) = (E / F) \text{ x } 100$$

where D is poly(vinyl monomer-*co*-BPPB) grafted onto VGCF, B is VGCF charged, E is weight of the postgrafted vinyl polymer, F is weight of poly(vinyl monomer-*co*-BPPB)-grafted VGCF charged. The weight of poly(vinyl monomer-*co*-BPPB) grafted and polymer postgrafted onto VGCF were determined from the weight loss of the polymer-grafted VGCF when they were heated at 800°C by using of a thermogravimetric analyzer.

Dispersibility of branched polymer-grafted VGCF

The dispersibility of branched polymer-grafted VGCF was compared with that of untreated VGCF. 0.03 g of branched polymer-grafted VGCF was dispersed in 50 mL of THF under irradiation of ultrasonic wave. The dispersion was allowed to stand at room temperature and the precipitation of VGCF was observed in comparison with that of untreated one.

Preparation of electrode and determination of electric resistance in solvent vapor

The conductive composite paste was prepared from branched vinyl polymer-grafted VGCF and vinyl polymer (polystyrene or polyMMA) using THF as a solvent. The content of branched polymer-grafted VGCF in the composite is 25 wt%. The branched polymer-grafted VGCF composite paste was coated onto a comb-like electrode, which was prepared by the screen-printing of conductive Ag/Pd paste onto a ceramic plate. The thickness of the composite on the electrode was about 100 mm. The DC electric resistance of the electrode was recorded by an ohmmeter at 25°C every 5 min in dry air and then in saturated solvent vapor at 25°C. The details of the preparation of the sensor material and comb-like electrode, and the measurement of electric resistance were described in our previous papers [17-19].

Results and discussion

Grafting of poly(MMA-co-BPPB) onto the surface of VGCF initiated by the system consisting of VGCF-COCCl$_3$ and Mo(CO)$_6$

The grafting of poly(MMA-*co*-BPPB) onto VGCF surface by the copolymerization of MMA with BPPB initiated by the system consisting of VGCF-COCCl$_3$ and Mo(CO)$_6$ was investigated under several conditions. The results are shown in Table 1. The untreated VGCF (Run 1), Mo(CO)$_6$ (Run 2), the system consisting of untreated VGCF and Mo(CO)$_6$ (Run 3), and VGCF-COCCl$_3$ (Run 4) have no ability to initiate the copolymerization.

On the contrary, the copolymerization of MMA with BPPB was successfully initiated in the coexistence of VGCF-COCCl$_3$ and Mo(CO)$_6$, and poly(MMA-*co*-BPPB) was successfully grafted onto the surface.

Figure 1 shows the time-percentage of grafting and time-conversion curves in the graft copolymerization initiated by the system consisting of VGC-COCCl$_3$ and Mo(CO)$_6$ at 60°C. It was found that the percentage of grafting increases with progress of the copolymerization and the percentage of poly(MMA-*co*-BPPB) grafting reached maximum value, 12.2% after 24 h, in spite of 60% conversion. This may be due to the fact that the surface initiating groups on VGCF was readily blocked by grafted polymer chains.

Table 1. Graft copolymerization of MMA with BPPB initiated by the system consisting of VGCF-R-COCCl$_3$ and Mo(CO)$_6$

Run	VGCF	Mo(CO)$_6$	Conversion (%)	Grafting (%)
1	Untreated	-	0	-
2	None	0.04	0	-
3	Untreated	0.04	0	-
4	VGCF-R-COCCl$_3$	-	0	-
5	VGCF-R-COCCl$_3$	0.04	65.0	12.2

VGCF, 0.10 g; MMA=BPPB=0.10 mol; 60°C; 24.

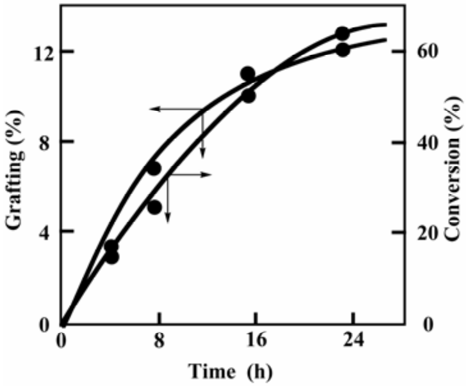


Figure 1. Graft copolymerization of MMA with BPPB initiated by the system consisting of trichloroacetyl groups and Mo(CO)$_6$. VGCF-R-COCCl$_3$, 0.10 g; Mo(CO)$_6$; 0.04 g; MMA=BPPB=0.10 mol; toluene, 5.0 mL; 60°C

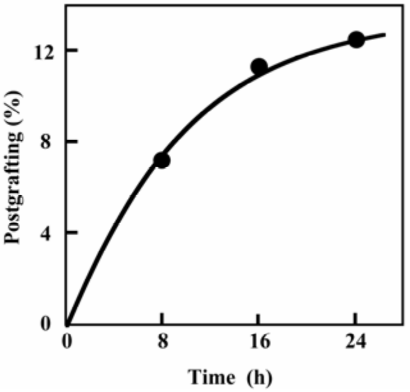


Figure 2. Postpolymerization of styrene initiated by poly(MMA-co-BPPB)-grafted VGCF. poly(MMA-co-BPPB)-grafted VGCF, 0.10 g; styrene, 0.02 mol; *m*-xylene, 1.0 mL; 120°C

Postgrafting of polystyrene onto VGCF initiated by poly(MMA-co-BPPB)-grafted VGCF

The postpolymerization of styrene initiated by poly(MMA-*co*-BPPB)-grafted VGCF was examined. The results are shown in Figure 2. As shown in Figure 2, it became apparent that the polymerization of styrene was successfully initiated by poly(MMA-*co*-BPPB)-grafted VGCF and the conversion increased with progress of the polymerization. The postgrafting of polystyrene also increased with progress of the polymerization and reached 12.5% after 24 h at 120°C.

The results indicate that poly(MMA-*co*-BPPB)-grafted VGCF has an ability to initiate the postpolymerization of styrene. In addition, it is expected that branched polymer, i.e., [poly(MMA-*co*-BPPB)-*graft*-polystyrene] was successfully grafted onto VGCF surface.

Confirmation of grafting of polymers onto VGCF surface by thermal decomposition GC-MS

Figure 3 shows gas chromatogram (GC) of thermally decomposed gas of (A) poly(MMA-*co*-BPPB), (B) poly(MMA-*co*-BPPB)-grafted VGCF, and (C) [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted, polystyrene-postgrafted, VGCF. GC of decomposed gas of poly(MMA-*co*-BPPB)-grafted VGCF was in agreement with that of ungrafted (MMA-*co*-BPPB). In addition, in GC of decomposed gas of [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF, new decomposed gases at retention time 2.0 min and 7.7 min were observed.

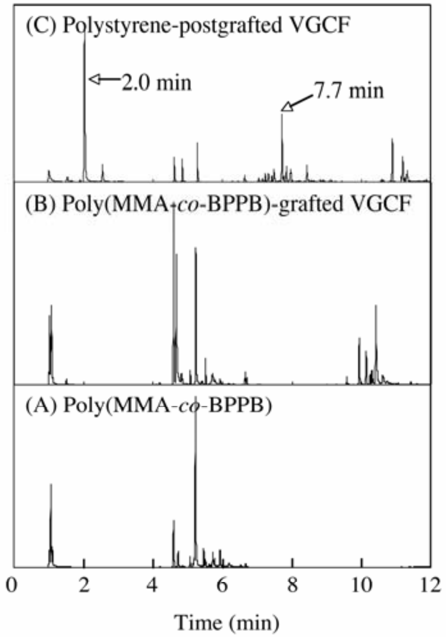


Figure 3. Thermal decomposition GC of (A) poly(MMA-*co*-BPPB), (B) poly(MMA-*co*-BPPB)-grafted VGCF, and (C) polystyrene-postgrafted VGCF.

Mass spectra of decomposed gases of [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF at retention time 2.0 min and 7.7 min were in agreement with those of polystyrene.

These results clearly show that postpolymerization of styrene was successfully initiated by poly(MMA-*co*-BPPB)-grafted VGCF to give [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF.

Postgraft polymerization of vinyl monomers initiated by several poly(vinyl monomer-co-BPPB)-grafted VGCFs

The grafting of copolymers of several vinyl monomers with BPPB onto VGCF was examined by the copolymerization of BPPB with acrylamide (AAm), glycidyl methacrylate (GMA), and phenyl vinyl sulfone (PVS). The results are shown in Figure 4. It became apparent that the copolymerization of vinyl monomers with BPPB were initiated by the system consisting of VGCF-$COCCl_3$ and $Mo(CO)_6$ to give the corresponding poly(vinyl monomer-*co*-BPPB)-grafted VGCF.

The postpolymerization of vinyl monomers initiated by the above poly(vinyl monomer-*co*-BPPB)-grafted VGCF was carried out. The results are also shown in Figure 4. It was found that the postpolymerizations of vinyl monomers are successfully initiated by poly(vinyl monomer-*co*-BPPB)-grafted VGCF to give the corresponding vinyl polymer-postgrafted VGCF.

No relation between the amount of first grafted poly(vinyl monomer-*co*-BPPB) and postgrafting was observed. This may be due to the difference of monomer sequence in grafted poly(vinyl monomer-*co*-BPPB) on VGCF.

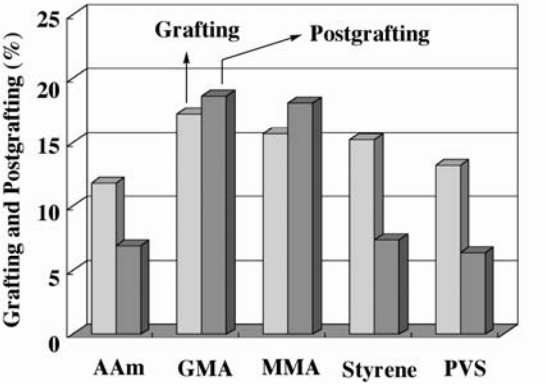


Figure 4. Postgrafting of vinyl polymers onto VGCF initiated by poly(vinyl monomer-*co*-BPPB)-grafted VGCF. Grafting of copolymer: VGCF-$COCCl_3$, 0.10 g; $Mo(CO)_6$, 0.04 g; vinyl monomer=BPPB=0.10 mol; toluene, 5.0 mL; 60°C; 6 h. Postgrafting: poly(vinyl monomer-*co*-BPPB)-grafted VGCF, 0.10 g; vinyl monomer, 0.02 mol; *m*-xylene, 1.0 mL; 120°C; 6 h.

Dispersibility of branched polystyrene-postgrafted VGCF in organic solvent

The dispersibility of branched polystyrene-grafted, [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted, VGCF in THF was compared with that of untreated one and poly(MMA-*co*-BPPB)-grafted VGCF. The results are shown in Figure 5. As shown in

Figure 5, untreated VGCF precipitated within 1 day. On the contrary, poly(MMA-*co*-BPPB)-grafted VGCF and [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF gave a stable dispersion in THF and no precipitation of VGCF was observed even after 3 weeks.

The result suggests that grafted branched polymer chains on VGCF destroy the aggregation of VGCF and interfere with the aggregation of VGCF in solvent.

No remarkable effect of grafted branched chains on the dispersibility of the branched polymer-grafted VGCF was observed.

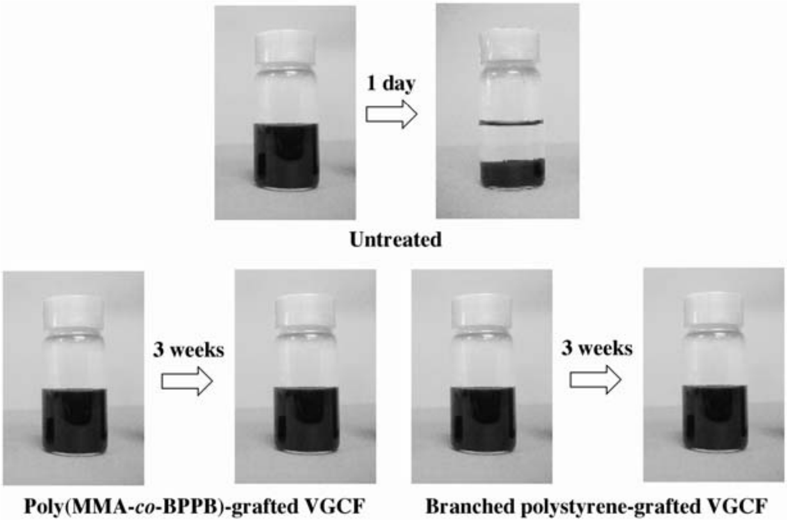


Figure 5. Dispersibility of untreated VGCF, poly(MMA-*co*-BPPB)-grafted VGCF, and [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF in THF at room temperature.

Electric properties of the composite prepared from branched polymer-grafted VGCF

It has been reported that the electric resistance of the composite prepared from crystalline polymer and polymer-grafted carbon black suddenly increases in solvent vapors, which has affinity with the grafted polymer [17-18]. The composite prepared from vinyl polymer and carbon black also respond to solvent vapors [20-26].

Therefore, the response of the electric resistance of the composite prepared from [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF and polystyrene to THF vapor was investigated. The results are shown in Figure 6. In addition, Figure 7 shows the response of the electric resistance of the composite prepared from [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF and polyMMA to chloroform vapor.

As shown in Figures 6 and 7, when these composites were transferred into THF and chloroform vapor, the electric resistance suddenly increased and exceed the determination range (10^9 Ω). And then, the electric resistance suddenly decreased when the electrodes were transferred into dry air. But the electric resistance did not return to the initial value when the electrode was transferred back to the dry air. However, after the second cycle, the response to solvent vapor was stable and reproducible even after 30 cycles of exposure to solvent vapor and dry air.

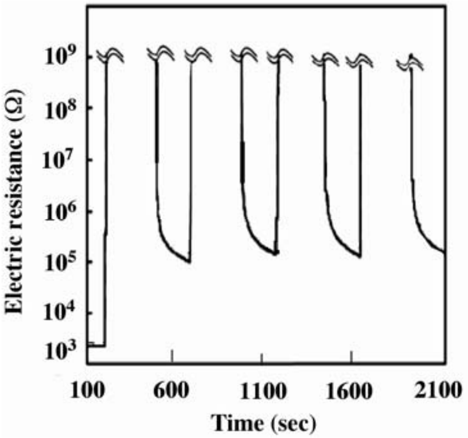


Figure 6. Responsibility of electric resistance of the composite from [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF and polystyrene (branched polymer-grafted VGCF content, 25 wt%) to THF vapor at 25°C.

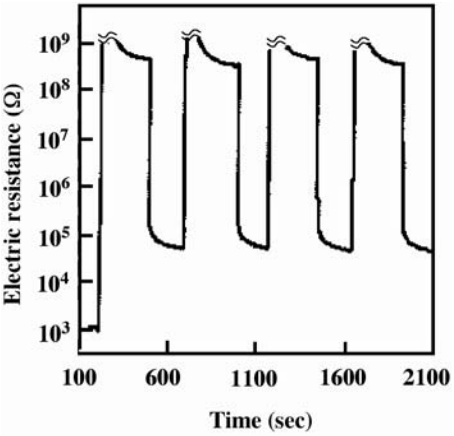


Figure 7. Responsibility of electric resistance of the composite from [poly(MMA-*co*-BPPB)-*graft*-polystyrene]-grafted VGCF and polyMMA (branched polymer-grafted VGCF content, 25 wt%) to chloroform vapor at 25°C.

In the previous paper [12-14], we have reported that the electric resistance of the composite from linear polymer-grafted VGCF suddenly increased in solvent vapor and returned to initial resistance when it was transferred into dry air.

The reason why the electric resistance did not return to the initial value when the electrode transferred back to the dry air is considered to be due to the incomplete desorption of solvent vapor from the composites. The result indicated that branched polymer chains on the VGCF surface have an ability to retain a small amount solvent vapor.

Conclusions

1. The copolymerization of vinyl monomer with BPPB was successfully initiated by the system consisting of VGCF-$COCCl_3$ with $Mo(CO)_6$ to give poly(vinyl monomer-*co*-BPPB)-grafted VGCF.
2. The postpolymerization of vinyl monomers was successfully initiated by pendant peroxy groups of poly(vinyl monomer-*co*-BPPB)-grafted VGCF to give the corresponding branched polymer-grafted VGCF.
3. Branched vinyl polymer-grafted VGCF gave a stable dispersion in THF and no precipitation of VGCF was observed even after 3 weeks.
4. The electric resistance of the composites prepared from branched polymer-grafted VGCF suddenly increased in solvent vapor and suddenly decreased when it was transferred into dry air.
5. The response of the composite to solvent vapor was stable and reproducible even after 30 cycles of exposure to solvent vapor and dry air.

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