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# Oriented Crystallization of Polycarbonate by Vapor Grown Carbon Fiber and its Application

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ABSTRACT: It is known that polycarbonate (PC) is categorized as amorphous polymer and pure PC crystallizes extremely slowly. However, we have recently found that the crystallization of PC was substantially accelerated around 200 °C in the presence of vapor grown carbon fiber (VGCF), having ultra thick multi-walled carbon nanotube (MWCNT) structure. To examine the accelerated crystallization by VGCF, the effect of pre-graphitized VGCF, carbon black, and mesophase pitch based carbon fiber (CF) on the crystallization was evaluated. In addition, polarized optical microscope observation was performed by using PC including magnetically oriented VGCF. It was suggested that the surface of ordered graphite structure from VGCF or CF induced the oriented crystallization of PC along the axial direction of VGCF or CF. To utilize the accelerated oriented crystallization of PC by CF, PC sheet having oriented crystallized surface PC layer was made by annealing the stacked structure of PC sheet and oriented CF sheet at 200 °C. The PC sheet, whose surface was crystallized along CF axial direction, was successfully produced, showing retardation property by polarized optical microscope. [DOI 10.1295/polymj.37.887]

KEY WORDS Vapor Grown Carbon Fiber / Polycarbonate / Crystallization / Carbon Nanotube / Carbon Fiber / Magnetic Field /

Poly(bisphenol-A-carbonate) (PC) becomes now one of important industrial engineering plastics due to its toughness, weatherability, and transparency. PC is usually in amorphous state and regarded as an amorphous polymer. However, PC crystallizes in the presence of low molecular weight organic components.[1,2] Pure PC also crystallizes by the addition of organic salts.[3–5] Recently, it was reported that the effect of molecular weight on the bulk crystallization of pure PC without any additives.[6] When PC ($M_w$ (weight-average molecular weight) = 28400) was annealed at 185 °C, the heat of fusion gradually increased after the induction period of 50 h.[6]

Carbon nanotubes (CNTs) have received considerable attention in terms of mechanical, electric, magnetic, and thermal properties.[7–13] For enhancing these properties in polymer matrixes, a series of investigations in PC/CNT composites have been performed, but were with no evidence of crystallization due to high investigated temperature (260 °C).[7] CNT has large anisotropic diamagnetic property because of oriented stacked graphite layers.[8,9] In recent years, magnetically aligned CNT film has been produced.[10] Anisotropic properties of thermosetting polyester composites including magnetically aligned CNT have been investigated.[11]

Conventionally referred vapor grown carbon fiber (VGCF, general name) has been considered as a thick multi-walled CNT (MWCNT) with defect-laden graphite layers.[12,13] VGCF® (trade name of Showa Denko K.K. Japan, averaged diameter = 150 nm) has been a commercially available VGCF. VGCF® has relatively linear fiber structure, while MWCNTs have mostly curved structures.[14,15] Poetschke *et al.* reported rheological studies of PC/MWCNT composites at 260 °C with no indication of crystallization (probably due to higher temperature).[7] During investigation of PC/VGCF®, however, we have accidentally found that the crystallization of PC was accelerated by annealing around 200 °C in the presence of VGCF® based on experimental results of DSC (differential scanning calorimetry), WAXD (wide angle X-ray diffraction), and dynamic melt rheological measurements.[16]

We have characterized the annealed composites (PC/VGCF® = 95/5 wt. ratio) for 2 h at 160, 180, 200, 220, and 240 °C by means of DSC and WAXD.[16] It was found from DSC that an endothermic peak (Heat of fusion = 19.6 J/g, Peaks = 234.6 (strong), 213.1 (weak) °C) distinctly appeared for the composite annealed at 200 °C for 2 h, and an indication of endothermic peak was observed when annealed between 180 and 220 °C.[16] Similar endothermic peaks (Heat of fusion = 26 J/g, Peaks = 227 (strong), 210 (weak) °C) were reported for pure PC bulk ($M_w$ = 28400, $M_w/M_n$ = 2.07) without additives after 680 h

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annealing at 185 °C.[6] WAXD suggested a distinguished peak appeared at 17.3 deg (the mixture of (020) (17.0 deg) and (202) (17.6 deg) diffraction of PC) when annealing around 200 °C only for 2 h.[16] DSC and WAXD results allowed us to say that PC crystallization was enhanced in the presence of VGCF®. Dynamic melt rheological property as a function of time suggested the increase of storage and loss moduli around 200 °C.

It was reported that MWCNT also crystallizes a certain type of thermoplastic polyimide and polypropyrene.[17,18] However, little is known about the cause and the structure of induced crystallization by VGCF or MWCNT. Here, the effect of pre-graphitized VGCF, carbon black, and mesophase pitch based carbon fiber (CF) on the crystallization was examined. *In-situ* polarized optical microscope observation with a hot-stage as a function of time was performed by using PC including magnetically oriented VGCF. By applying the induced crystallization of PC, a patterning of induced crystallization of PC having different optical property at different location was tried.

## EXPERIMENTAL

### *Materials*

VGCF® (graphitized up to 2800 °C) was supplied by Showa Denko K.K. Japan, and had the average fiber diameter of 150 nm with a sharp peak at 26.2 deg in WAXD trace. Endo *et al.* described the structural detail of VGCF® that VGCF® had amorphous carbon with thickness of around 5 nm which covered the ordered graphite layers of VGCF.[13] We have looked at transmission electron micrograph (TEM) of recent VGCF® kindly shown by Endo's group, and the surface of VGCF® was mostly pure graphite layers and was partially covered by amorphous carbon with the thickness of around 1 nm. Pre-graphitized VGCF® (Showa Denko K.K. Japan), Ketjen Black (EC600JD, Ketjen Black International, Japan), and mesophase pitch based carbon fiber (XN90, Nippon Graphite Fiber Co. Ltd., Japan, Diameter = 10 μm) were also used. The former two samples are amorphous carbon, showing no sharp peak in WAXD. XN90 gave a sharp peak at 26.4 deg in WAXD trace. The surface of CF as received was already coated with a binding agent. CF was used after washing with organic solvents. PC was supplied by Teijin Kasei Co. Ltd., Japan, and has $M_n$ and $M_w$ (number- and weight-average molecular weight) of 20000 and 32000 g/mol from GPC (gel permeation chromatography), respectively. All materials without CF were used as received.

### *Preparation and Annealing of Composites*

PC pellets and carbon material, either VGCF®, un-graphitized VGCF®, or EC600JD, were mixed into the hopper of a twin screw extruder (KZW15-45MG-FKS, Technovel Co. Ltd., Japan, D = 15 mm, L/D = 45), and composites were produced through melt compounding at 250 °C. The annealing of the composite was carried out under hot-press machine (Toyoseiki Seisakusho Co. Ltd., Japan) without pressure. Magnetic force was generated with an apparatus (TM-PSBCW6080-235, Tamagawa Seisakusyo Co. Ltd., Japan), which provided the magnetic field of 2.4 T to the molten composite on the heating unite controlled by a certain temperature profile (heating from room temperature to 270 °C (magnet off) and keeping for 20 min at 270 °C (magnet on, 2.4 T) and cooling down to room temperature (magnet off)).

### *Characterization*

The observation at fractured cross-sections of molded composite parts was carried out by SEM (scanning electron microscopy, S-3500N, Hitachi Japan). Dynamic mechanical analysis (DMA) of PC/VGCF® annealed at different time was performed as a function of temperature (heating rate of 2 °C/min) with bending mode using a solid analyzer (RSAII, TA Instrument, USA) under nitrogen. DSC (MDSC 2920, TA Instrument USA) was measured under the heating rate of 10 K/min. WAXD (Cu K$\alpha$ radiation, 30 kV, 20 mA) was traced by a step-scanning method (1 deg/min, 0.02 deg interval) with RAD-IIB of Rigaku Denki Co. Ltd., Japan. Polarized optical microscope (DX50, Olympus Co. Ltd., Japan) with hot-stage (THM600, Japan Hightech Co. Ltd., Japan) was used for *in-situ* structural observation.

## RESULTS AND DISCUSSION

### *Dispersion and Dynamic Mechanical Analysis*

VGCF® as received had aggregated lump form having lump diameter in the range from 20 to 50 μm.[14] It is important to examine whether VGCF® was completely dispersed in PC by melt mixing. SEM observation was carried out at various fractured surfaces of the composite. Figure 1 shows SEM at a cross-section of molded PC/VGCF® (95/5 wt. ratio) composite sample prepared by hot press method. The observation at various fractured surfaces allowed us to mention that VGCF® was dispersed almost completely without initial aggregated lumps. The averaged length of VGCF® in the composite after melt mixing and molding was evaluated to be 3 μm having distribution from 1 to 16 μm, and its structure was relatively linear (partially curved or bend) without branching structure.[15]

We have confirmed from DSC curves that pure PC gave only the glass transition at 145 °C with no endothermic peak even after annealing between 160 and

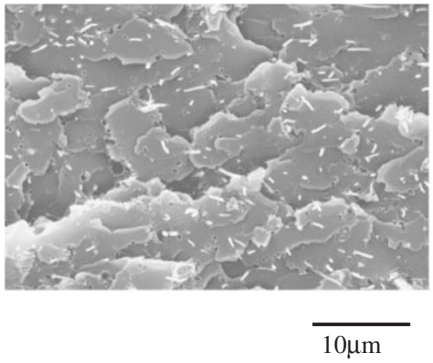


**Figure 1.** SEM picture at fractured cross-section in molded sample of PC/VGCF® (95/5 wt. ratio) composite prepared by hot press method.

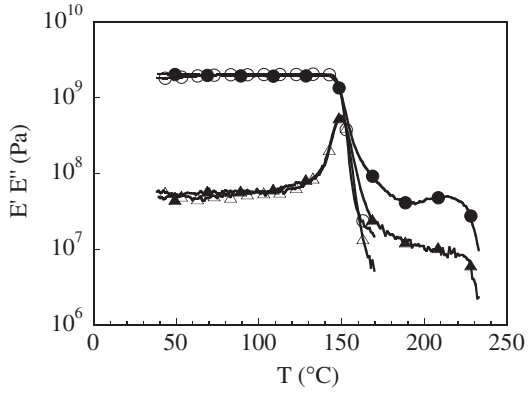


**Figure 2.** Dynamic mechanical analysis (DMA) result of PC/VGCF® (95/5 wt. ratio) composite annealed at 200 °C for 0 min (storage modulus, E′(○) loss modulus, E″(△)) and for 2 h (E′(●) E″(▲)).

240 °C up to 16 h. Figure 2 shows DMA of the composite as a function of temperature with and without annealing for 2 h at 200 °C. The annealing prevented melting-down of samples and gave the appearance of plateau above the glass transition temperature. The DMA result was in good agreement with data from DSC, WAXD, and melt rheology (described in introduction section).[16]

*Effect of Carbon Materials on Induced Crystallization*

To examine the origin of the accelerated PC crystallization, the influence of carbon structure on the crystallization was examined using VGCF®, pre-graphitized VGCF®, and carbon black (Ketjen Black EC600JD). Figure 3 gives the comparison of the first heating DSC curves among three composites (95/5 wt. ratio), PC/VGCF®, PC/pre-graphitized VGCF®, and PC/Ketjen Black, which were all annealed at 200 °C for 2 h. Figure 4 shows the comparison of WAXD among the annealed three composite (at 200 °C for 2 h). The sharp peak appeared at 17.3 deg from PC by the annealing in the presence of VGCF®

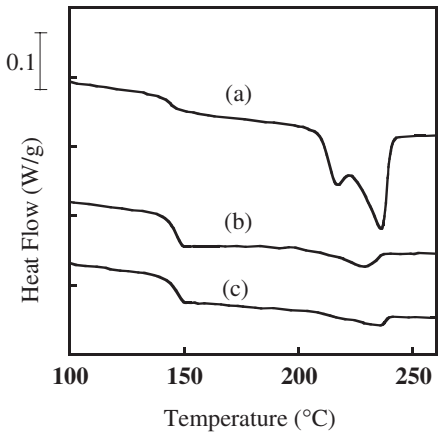


**Figure 3.** The first heating DSC (differential scanning calorimetry, Lower direction is endothermic.) curves at the heating rate of 10 °C/min for PC/VGCF® (95/5 wt. ratio) (a), PC/pre-graphitized VGCF® (95/5 wt. ratio) (b), PC/Ketjen Black (95/5 wt. ratio) (c), which are all annealed at 200 °C for 2 h.

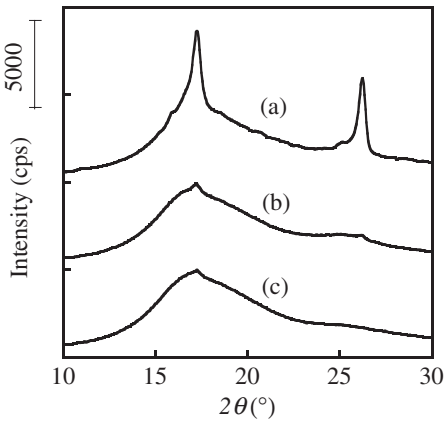


**Figure 4.** WAXD traces for PC/VGCF® (95/5 wt. ratio) (a), PC/pre-graphitized VGCF® (95/5 wt. ratio) (b), PC/Ketjen Black (95/5 wt. ratio) (c), which are all annealed at 200 °C for 2 h.

(the diffraction of (002) at 26.2 deg). The peak at 17.3 deg would be the mixture of the diffraction of (020) (17.0 deg) and (202) (17.6 deg) from PC, since it is known that pure PC has (020) (17.0 deg) and (202) (17.6 deg).[4] Pre-graphitized VGCF® and Ketjen Black (Both have no graphite layered peak around 26 deg in Figure 4.) hardly induced PC crystallization with annealing at 200 °C for 2 h. It would be safe to interpret that the ordered graphite surface from VGCF® promoted PC crystallization, which could be caused by an interaction between graphite and PC.

*In-situ Polarized Optical Microscope Observation around VGCF®*

In order to perform *in-situ* polarized optical microscope observation around VGCF® in PC matrix, the concentration of VGCF® should be minimized as little as possible to avoid overlapping. Figure 5 shows the

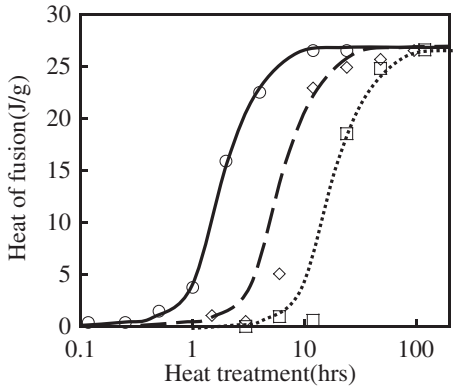


**Figure 5.** Heat of fusion as a function of heat treatment time at 200 °C for various composites including 2 wt % of VGCF® (solid curve), 0.1 wt % (dashed curve), and 0 wt % (dotted curve). The 0 wt % data was also after melt-mixing.

heat of fusion for the composite having different concentrations (2, 0.1, 0 wt % of VGCF®) treated at 200 °C as a function of annealing time. It is practically happened in several polymers that pure polymer with melt-mixing history by using extruder has slightly shorter crystallization induction time compared with that without melt-mixing. This tendency would be most probably caused by invisible tiny dusts which exist in polymer processing room. It should be important to distinguish the real effect of VGCF® from the processing effect. Therefore, we have used melt-mixed PC without VGCF® for 0 wt % data here. The saturated value of the heat of fusion (26 J/g) was in good agreement with what was reported before.[6] It was confirmed in Figure 5 that the concentration could be reduced to 0.1 wt % with keeping the crystallization effect from VGCF® and diminishing that from the matrix.

To examine macroscopic PC crystallization structure nucleated by VGCF®, the *in-situ* optical microscope observation of PC/VGCF® (99.9/0.1 wt. ratio) on hot stage (200 °C) was carried out. We have attempted to observe retardation property around VGCF® using PC/VGCF® composite with randomly dispersed VGCF®. However, it was difficult to judge the retardation property around VGCF® due to the random orientation of VGCF®. Therefore, we have tried to align VGCF® toward one direction with an electro magnet.

A small amount of PC/VGCF® (99.9/0.1 wt. ratio) was hot-pressed between cover glasses (25 μm thickness using a polyimide spacer) and it was placed on the heating unit in the magnet, controlled by an optimal profile (heating to 270 °C (magnet off) and keeping for 20 min at 270 °C (magnet on, 2.4 T) and cooling down (magnet off)). The detail of the optimization of the processing profile to align VGCF® in viscous

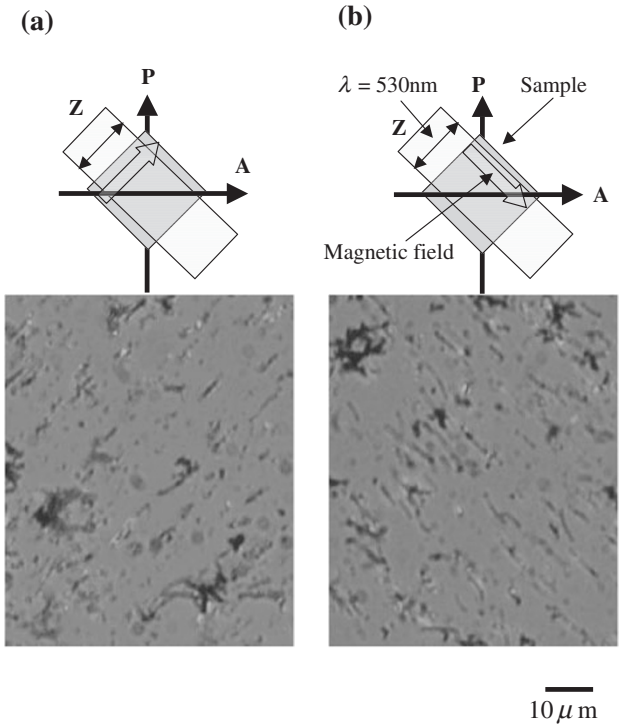


**Figure 6.** Polarized optical micrograph (with coloring plate (530 nm)) of PC including 0.1 wt % of magnetically aligned VGCF®, which was annealed for 2 h at 200 °C. The matrix color was purple for both (a) and (b). The color of the surrounding region around VGCF® was blue (a) and yellow (b), respectively. Please see the real colored figure in graphical abstract section.

molten PC will be reported elsewhere. The polarized optical microscope observation suggested that only VGCF® was oriented (PC was not oriented) toward magnetic direction in the amorphous PC matrix.

The composite (including oriented VGCF®) sandwiched between cover glasses was placed on the hot-stage (at 200 °C) to perform *in-situ* polarized optical microscope observation. Figure 6 shows the *in-situ* optical micrograph of PC/VGCF® (99.9/0.1 wt. ratio) including oriented VGCF® at 200 °C after 2 h. With coloring plate (530 nm), the whole sample was observed as purple color, not depending on the setting direction (see illustrated pictures in Figure 6) of the sample. When the sample was placed in the way described in Figure 6a, the PC region surrounded around VGCF® showed blue from purple by annealing. The area of blue region around VGCF® (Figure 6a) became larger with longer time. When the sample was rotated to the direction described in Figure 6b, the blue region changed to yellow. It means that PC crystals around VGCF® are oriented along the axial direction of VGCF®.

It has been reported that MWCNT accelerated the crystallization in a certain type of polypropyrene and polyimide.[17,18] When MWCNT were entangled one another as lump, the entangled points might

become nucleation points. There was no description about the dispersion of MWCNT. The crystallization structure around a single MWCNT was not known well. Here, VGCF®, having relatively linear structure, was dispersed independently and oriented toward one direction in PC. We have examined WAXD for VGCF®/PC (2/98 wt. ratio) composite (with magnetically oriented VGCF®) annealed at 200 °C (without magnet), showing the oriented diffraction of (020) (17.0 deg) and (202) (17.6 deg) (from PC) toward the axial direction of VGCF® as well as the oriented diffraction of (002) (26.2 deg) (from VGCF®).[16] From this analysis the crystal structure of PC in the presence of VGCF® seemed similar to that of pure PC. This also means that the orientation of crystallized PC (*c*-axis) was mostly similar to that of VGCF®. Taking DSC (Figures 3, 5), WAXD (Figure 4 and ref 16), polarized optical microscope (Figure 6) into consideration, it would be safe to conclude that PC around a single VGCF® (completely dispersed in PC) was crystallized from the surface of VGCF® and PC (*c*-axis) was orientationally crystallized along VGCF® axial direction.

*Application by Using Oriented CF*

Mesophase pitch based carbon fiber (CF) is known to have highly oriented stacked graphite structure. CF used here had a sharp peak at 26.4 deg in WAXD trace. If the ordered graphite surface induces the accelerated crystallization of PC, CF surface could also cause the acceleration. A single CF (cut from long yarn, after washing organic solvent to remove a binding agent) was placed in PC matrix. The PC including a single CF sandwiched between cover glasses was put on the hot-stage to carry out the *in-situ* polarized optical microscope observation as mentioned earlier. The matrix PC was completely amorphous random structure by the observation. The retardation property was observed clearly only at the contacted area of PC on CF as a function of time, which was similar to what was observed in Figure 6 (blue and yellow by rotating the sample). Figure 7 shows the *in-situ* polarized optical micrograph of PC including a single fiber after 2 h at 200 °C, suggesting that PC was crystallized from the surface of CF and PC was orientationally crystallized along CF axial direction.

The composite sheet (1 mm thickness, oriented CF continuous yarn (XN90, the same CF used earlier) in epoxy resin, CF/Epoxy = 70/30 wt. ratio) was utilized to make PC having a patterned retardation property. After heat treatment to solidify the composite sheet, the surface of CF/Epoxy composite was removed off by using a sand paper, so that the substantial amount of CF appeared at the surface. The procedure is illustrated in Figure 8. A patterned orientation

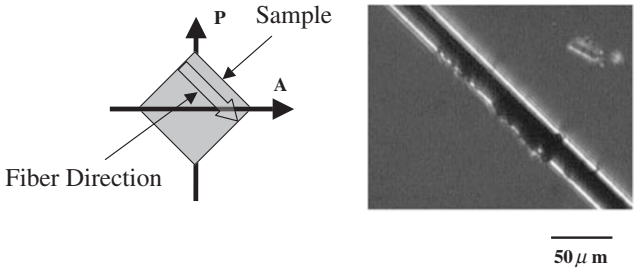


**Figure 7.** Polarized optical micrograph (without coloring plate (530 nm)) of PC including a single CF, which was annealed for 2 h at 200 °C. The color of the surrounding region around CF became bright by annealing at 200 °C as a function of time.

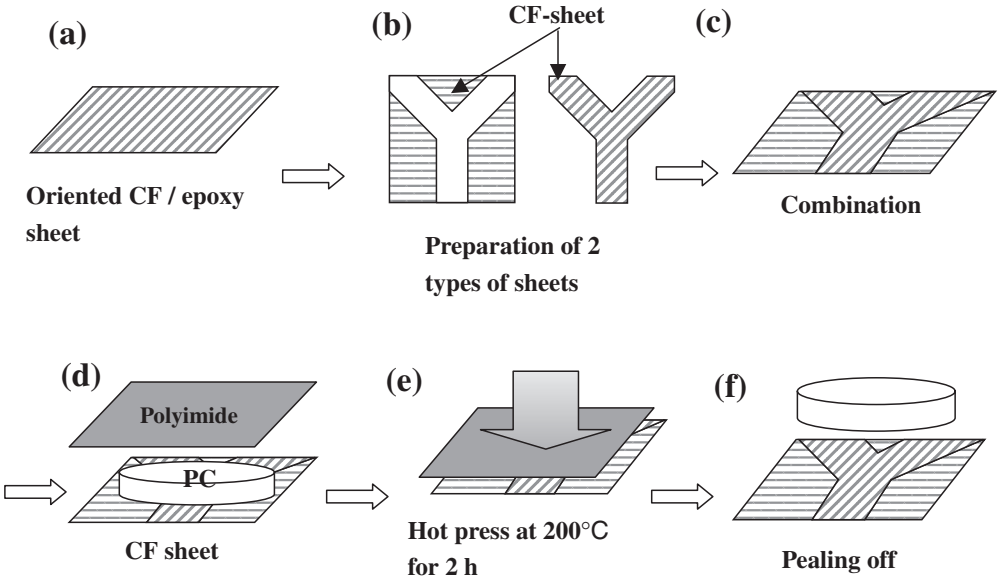


**Figure 8.** A schematic flow chart to make a PC sheet, whose surface molecules were orientationally crystallized, having a patterned structure (the character of "Y"), by using a aligned CF sheet.

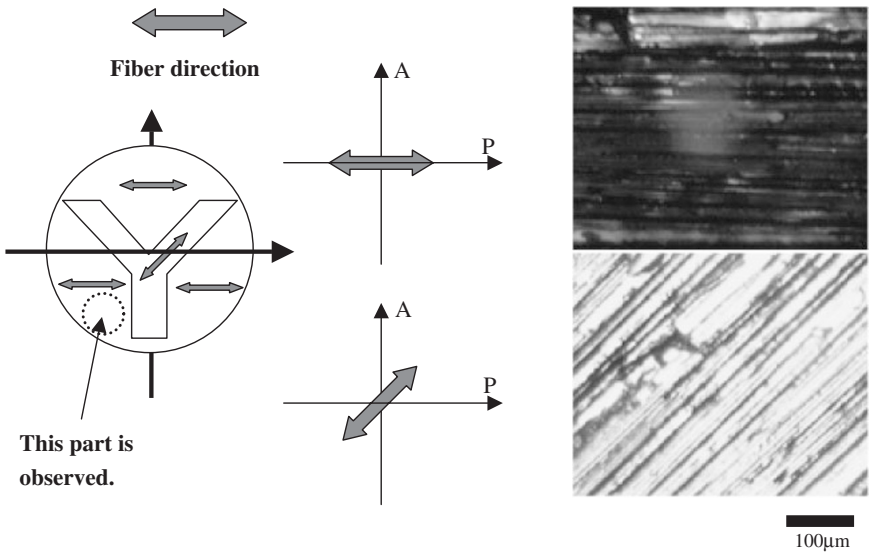


**Figure 9.** Polarized optical micrographs (without coloring plate (530 nm)) of a part of PC sheet, which was produced by the procedure in Figure 8.

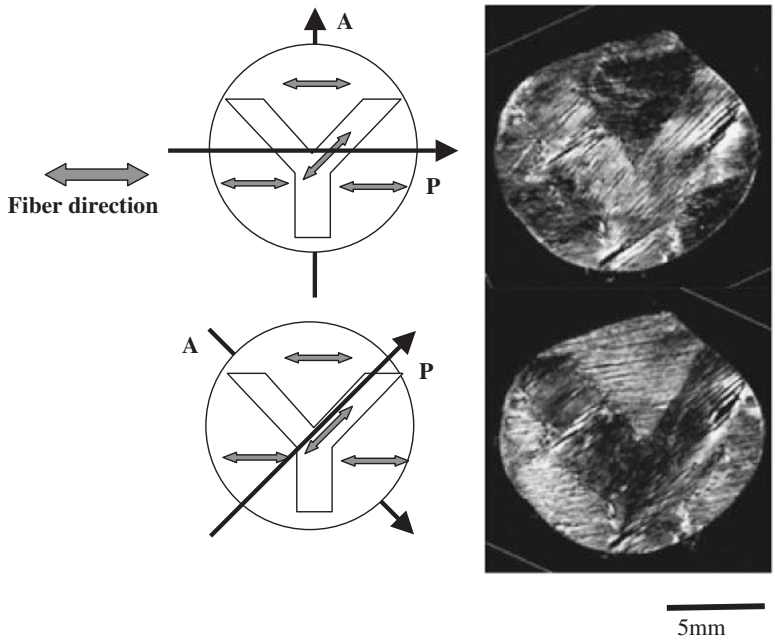


**Figure 10.** Polarized optical micrographs (without coloring plate (530 nm)) of the whole PC sheet having patterned "Y" character, which was produced by the procedure in Figure 8.

of CF (having "Y" pattern) was made from the CF/Epoxy sheet, where the inside and the outside of Y character have different CF orientation. By stacking PC and the patterned CF/Epoxy sheet under hot press (at 200 °C for 2 h), the surface of PC was orientationally crystallized based on the patterned CF axial direction. The CF/Epoxy sheet was removed off from PC. Polarized microscope observation was carried out the PC part without no CF/Epoxy sheet. In other words, the transferring the patterned CF to the PC surface as the orientationally crystallized thin surface layer was tried.

Figure 9 shows two polarized optical micrographs at one part of PC having orientationally crystallized surface layer (without coloring plate). The micrographs exhibited clear retardation property. Figure 10 also gives polarized optical micrographs of the whole part of PC sheet. It was demonstrated that the patterned CF was successfully transferred to the PC surface as the orientationally crystallized thin surface layer. The utilization of graphite surface in polymer engineering might have potential application to open a new polymer processing field.

## CONCLUSIONS

The ordered graphite surface, such as surface of MWCNT, VGCF, and mesophase pitch based CF, accelerated the crystallization of PC around 200 °C from DSC, WAXD, and DMA. Amorphous carbon did not induce the acceleration.

It was demonstrated by *in-situ* polarized optical microscope observation and WAXD that PC around a single VGCF (complete dispersion) was crystallized from the surface of VGCF and PC crystal (*c*-axis) was oriented along VGCF direction.

By applying the above findings, a patterning of retardation property by using orientationally crystallized PC surface was tried. The patterned CF was successfully transferred to the PC surface as the orientationally crystallized thin surface layer.

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