



Interphase structure of carbon fiber reinforced polyamide 6 revealed by microbeam X-ray diffraction with synchrotron radiation



Daigo Kobayashi ^{a, b}, Ya-Ting Hsieh ^b, Atsushi Takahara ^{b, c, *}

^a TORAY, 1515 Oaza Tsutsui, Masaki-cho, Iyo-gun, Ehime 791-3193, Japan

^b Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

^c EROTO Takahara Soft Interfaces Project, Japan Science and Technology Agency, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

ARTICLE INFO

Article history:

Received 23 November 2015

Received in revised form

23 February 2016

Accepted 24 February 2016

Available online 26 February 2016

Keywords:

Polyamide 6

Carbon fiber

Transcrystalline phase

ABSTRACT

Carbon fiber reinforced polyamide 6 (PA6) films were fabricated in this study. A 2 microns polyamide 6 (PA6) transcrystalline layer with positive type birefringence was observed at the interphase region of PA6 and high modulus carbon fiber (HMCF) by using polarized optical microscopy, while no crystal layer was observed at that of PA6 and standard modulus carbon fiber (SMCF). HMCF exhibited higher nucleation efficacy in PA6 matrix than SMCF during cooling process, investigated by differential scanning calorimetry. The crystal form and orientation at the interphase region was further confirmed by microbeam wide angle X-ray diffraction (μ WAXD). The μ WAXD results show that α phase is the major crystalline fraction in PA6/HMCF and PA6/SMCF composites and the α crystalline percentage is slightly increase at the transcrystalline layer of PA6/HMCF composite. The μ WAXD results also suggest that the a axis of α crystals in the transcrystalline layer are predominantly perpendicular to the fiber direction.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon fiber reinforced plastics (CFRP) are used in our daily life. As light, tough materials, thermosetting CFRP are adopted in aerospace industry. The application of CFRP has been spreading into general industry such as automotive and civil engineering. It is believed that, to fabricate high performance CFRP, not only physical properties of carbon fibers (CF) and matrix but also the interfacial properties are important. Therefore, in the past decades, many efforts have been made on investigating the interfacial behavior of CF embedded in plastic matrices [1–12]. Those studies indicate transcrystalline crystals, which growth around the CF with a growth front parallel to the CF boundary line, can be observed in several thermoplastics such as polypropylene [1,2], poly(phenylene sulfide) [3–6], and polyamide [7–11]. The formation of transcrystalline is usually found to improve the interfacial shear strength and some elastic/mechanical properties [9,13]. Recently, Yan et al. reported that the thermal conductivity and heat distortion temperature of polyamide 6 (PA6) near CF area are increased due to a transcrystalline layer formation [11]. However, until now, only few

reports focus on its precise crystal structure because the transcrystalline layer is very thin.

In this study, the interphase crystal structure of PA6 between the CF and PA6 matrix was investigated. PA6, also known as polycaprolactam and nylon 6, has two common crystalline forms (α and γ forms). It has been reported that the α form crystal (monoclinic lattice with $a = 0.956$ nm, $b = 1.724$ nm, $c = 0.801$ nm, and $\beta = 67.5^\circ$) is more thermodynamically stable and has higher Young's modulus than the γ form crystal (hexagonal/pseudo-hexagonal lattice with $a = 0.933$ nm, $b = 1.688$ nm, $c = 0.478$ nm, and $\beta = 121^\circ$) [14–16]. The scattering vectors (q) of the α and γ phases are approximately at 14.15 nm⁻¹ ($200, \alpha_1$), 16.94 nm⁻¹ ($002 + 202, \alpha_2$), 7.95 nm⁻¹ ($020, \gamma$), 15.55 nm⁻¹ ($001, \gamma$), and 16.25 nm⁻¹ ($200 + 20\bar{1}, \gamma$, minor) [14–16]. These two crystalline forms usually coexist in composites with various percentages depending on the molecular weight of matrix, position of the composite (such as the outer or central region of the specimen), additive amount of fillers, and processing conditions [14].

Standard modulus carbon fiber (SMCF) and high modulus carbon fiber (HMCF) were used in order to confirm the influence of CF surface on the PA6 crystal structure near the interfacial region. Those two CF were obtained from polyacrylonitrile-based fiber by carbonization process. The surface structure, density, and mechanical properties of CF can be controlled by carbonization

* Corresponding author. Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan.

E-mail address: takahara@cstf.kyushu-u.ac.jp (A. Takahara).

temperature. The higher the carbonization temperature is applied, the stronger tensile strength/modulus and the better development of graphene layers are obtained [17–22]. Hence, HMCF surface was speculated to have more regular graphite lattice structure than SMCF because HMCF was carbonized at much higher temperature than SMCF. Based on the previous report by Toray Industries, Inc. in 1986, X-ray diffraction (002) reflection and surface graphite Raman spectrum of HMCF was sharper than that of SMCF, indicating a higher graphitization degree of HMCF [22]. The objective of this study is to reveal the PA6 crystal orientation and its proportion of α and γ forms near the interphase region. Synchrotron radiation X-ray diffraction was carried out to reveal the transcrystalline structure in micro order and have a deeper understanding of interfacial properties on CFRP area.

2. Experiment

2.1. Materials

Standard modulus carbon fiber (SMCF) and high modulus carbon fiber (HMCF) whose surface were not oxidized were obtained from Toray Industries, Inc. Surface carbon structure of these carbon fibers were observed by Laser Raman microscope, NSR-5000 (JASCO Co. Ltd), and excited by the 532 nm wavelength light. Fig. 1 shows the Raman spectra of SMCF and HMCF. Both fibers showed G band (1600 cm^{-1}) and the D band (1350 cm^{-1}) peaks. It can be seen that carbon fiber has the mixed structure with sp_3 state carbon and sp_2 state carbon [23,24]. The spectrum of HMCF was sharper than that of SMCF, and G band peak intensity of HMCF was relatively stronger than D band peak intensity. This result suggests that higher oriented graphite grows on the surface of HMCF than SMCF. The surface roughness of SMCF and HMCF were measured by atomic force microscopy (AFM) SPA400 with an SPI4000 controller (Hitachi High-Tech Science Co.) in dynamic force mode which read a frequency change of vibrated probe depending on the distance with the sample. The spring constant of the probe SI-DF-20 (Hitachi High-Tech Science Co.) was 20 N/m. The surface roughness was calculated in square average square root coarseness (Rq) from $500\text{ nm} \times 500\text{ nm}$ square images. The surface roughnesses of SMCF and HMCF were 3.0 nm and 4.3 nm, so the roughnesses of these fibers were almost the same level. Polyamide 6 (PA6), CM1010, was obtained from Toray Industries, Inc. The glass transition

temperature and melting temperature of PA6 are around 50 and $220\text{ }^\circ\text{C}$, respectively. 2,2,2-Trifluoroethanol (TFE) was purchased from Tokyo Chemical Industry Co., Ltd.

2.2. Sample preparation

For the differential scanning calorimeter (DSC) measurement, PA6 pellet (500 mg) and chopped CF (5 mg) were blended in TFE (6 mL) at room temperature. The composite film was prepared by casting the solution onto a 3-cm-diameter dish and drying overnight. After that, the film was cut into $2 \times 2\text{ mm}^2$, and then preheated for 1 min and pressed for 2 min at $250\text{ }^\circ\text{C}$ into a needed shape ($3\text{ cm} \times 3\text{ cm} \times 250\text{ }\mu\text{m}$). After compression, the sample was cooled down to room temperature with cooling rate $10\text{ }^\circ\text{C}/\text{min}$. The neat PA6 film was prepared through the same method.

For polarized optical microscopy (POM) and microbeam X-ray diffraction (μWAXD) measurements, samples of PA6 matrix with a single CF were prepared. A long single CF (SMCF or HMCF with length around 5 cm) was placed between two layers of PA6 films. Samples for POM investigation were hot pressed between two glass slides with a $20\text{ }\mu\text{m}$ spacer on a hot stage at $250\text{ }^\circ\text{C}$. Samples for μWAXD measurement were hot pressed between two teflon plates with a $250\text{ }\mu\text{m}$ spacer by a thermocompressor at $250\text{ }^\circ\text{C}$.

2.3. Differential scanning calorimetry

The non-isothermal crystallization of all samples was investigated with a differential scanning calorimeter, SII DSC 6220 (Seiko Instruments Inc., Japan). Samples about 5 mg were heated at a rate of $10\text{ }^\circ\text{C}/\text{min}$ from $25\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$ under nitrogen atmosphere and the temperature was held at $260\text{ }^\circ\text{C}$ for 10 min to remove the thermal history. The melted samples were then cooled to $25\text{ }^\circ\text{C}$ at a constant rate of $10\text{ }^\circ\text{C}/\text{min}$. The crystallization temperature (T_c) is taken from the exothermic peak at cooling scan.

2.4. Polarized optical microscopy

The transcrystallization phenomenon was investigated via a Nikon polarized optical microscope (Eclipse LV100POL) with two crossed polarizers and a 530 nm retardation plate. Samples were heated at $250\text{ }^\circ\text{C}$ for 5 min to destroy crystals and then moved to $200\text{ }^\circ\text{C}$ for 10 min on a thermal controlled stage to grow crystal layer.

2.5. Crystal form and orientation studies

The crystal structure and preferred orientation of PA6 in composite films were investigated by microbeam X-ray diffraction measurement at BL40XU beam line in SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan). The X-ray beam was monochromatized to a wavelength (λ) of 0.082656 nm and collimated to a $5\text{ }\mu\text{m}$ diameter beam. The distance between the sample and the detector was set at approximately 124.8 mm . The 2D diffraction pattern was detected by X-ray image intensifier and CCD camera (1024×1024 pixels; pixel size $92.5\text{ }\mu\text{m}$). The exposure time for each scan was 10 s. The μWAXD experiments were performed by focusing the beam on the $250\text{ }\mu\text{m}$ thick PA6 and PA6 composites. For the composite samples, the beam was scanned from the CF center to the PA6 nearby in steps of $5\text{ }\mu\text{m}$ as the sketch shown in Fig. 2. Azimuthal histograms of the 2D X-ray diffraction patterns and 1D results were obtained and calculated by using the image analysis program Fit2d. The scattering vector (q) in specular reflectivity is defined by $q = (4\pi/\lambda) \sin\theta$, where λ and θ are the wavelength and incident angle of the X-ray beam from the horizontal position.

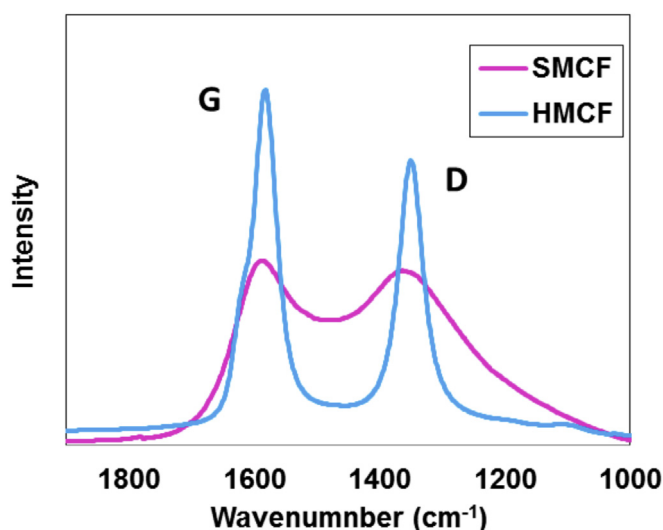


Fig. 1. Surface Raman spectra of carbon fiber SMCF and HMCF.

Download English Version:

<https://daneshyari.com/en/article/5179467>

Download Persian Version:

<https://daneshyari.com/article/5179467>

[Daneshyari.com](https://daneshyari.com)