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고속방사된 Poly(ethylene 2,6-naphthalene dicarboxylate) 섬유의 기계적 성질

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Mechanical Properties of High Speed Spun Poly(ethylene 2,6-naphthalene dicarboxylate) Fiber

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1. Introduction

Poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) is a polyester of increasing commercial interest that can be used in higher temperature applications than PET. The naphthalene rings in its main chain provides greater rigidity to the polymer backbone than the benzene ring in PET, elevating the glass transition temperature and melting point and enhancing the mechanical properties such as tensile modulus and creep resistance.

PEN was reported to have two crystal modifications. Crystallization at relatively low temperature of below 200 °C from the glass or melt in an isotropic state leads to the α crystal form, which is a triclinic unit cell containing one repeating unit. The unit cell parameters determined by Mencik were : a = 0.651 nm, b = 0.575 nm, c = 1.32 nm, α = 81.33 °, β = 144 °, γ = 100 ° and crystalline density 1.407 g/cm^3 [1]. Buchner et al. [2] mentioned the presence of β form crystal, which is a triclinic unit cell containing four chains, and the unit cell parameters are a = 0.926 nm, b = 1.559 nm, c = 1.273 nm, α = 121.6 °, β = 95.57 °, γ = 122.52 ° and crystalline density 1.439 g/cm^3. It was reported that the β modification crystals can be formed if the PEN polymers are melted 280 °C and subsequently crystallized at a temperature higher than 220 °C. The chains are not completely extended, every naphthalene ring is twisted by 180 °. The density of 100 % amorphous PEN is reported to be 1.34 g/cm^3 by Buchner et al. [2] and 1.325 g/cm^3 by Ouchi et al. [3].

There are some publications on the structure and physical properties of high speed spun PEN fibers. Hamana et al. [4] reported that the crystalline structure of high speed spun PEN fibers primarily consists of β modification crystals. Iizuka and Yabuki [5] estimated the ratio of the amount of α and β modification crystals in the high speed spun PEN fibers. Nagai et al. [6, 7] investigated the change of crystal modification during the annealing of high speed spun PEN fibers under stress. Matui et al. [8] and Cakmak and Kim [9] examined the detailed structure of high speed spun and annealed PEN fibers. K. miyata et al. [10] also conducted the ultra high speed melt spinning of PEN up to the take-up speed of 9 km/min and reported that the formation of β modification crystals in the spin line occurs at a relatively low crystallization temperature in comparison with that in an isotropic state.

Up to date, the detailed of the mechanical properties in high speed spun PEN fiber have not been reported in the literature. In our study, we will extensively investigate the mechanical properties of the high speed spun PEN fibers, such as modulus, tenacity, and shrinkage.

2. Experimental

2.1. Material

Poly(ethylene 2,6-naphthalene dicarboxylate) pellet was provided by Teijin Co. Ltd and the intrinsic properties of that are shown in *Table* 1. Prior to the drawing, the polymer was dried and crystallized through two stages. In first stage, the polymer was held at 130 °C for 8 hours under vacuum. In the following stage, the temperature was raised to 210 °C and kept for 2 hours for the crystallization of polymer. The crystallized polymer was preserved at 160 °C under vacuum.

Table 1. The intrinsic properties of polymer

Intrinsic viscosity (I.V.)	0.62 dL/g
Melt viscosity	17,000 poise (290 °C)
Number-average molecular weight	17,500
Glass transition temperature	113 °C
Melting temperature	272 °C

2.2. Melt Spinning

The PEN polymer was extruded from a single-hole spinneret of 1 mm diameter at 320 °C. The through-put rate was controlled to 5 g/min. The filament was wound with a high speed take-up device placed at a distance of 330 cm below the spinneret. The attained highest take-up speed was 8 km/min. The

intrinsic viscosity measured for the resultant fibers was 0.48 dL/g.

2.3. Characterizations

Density was measured at 23 °C using a density gradient column which contained carbon tetrachloride (specific gravity : 1.59) and *n*-heptane (0.68). In order to identify the crystal forms, Wide angle X-ray Diffraction profiles on as-spun samples were obtained using a Rigaku X-ray diffractometer of D/max-III-A type with Ni filtered Cu-Kα radiation and X-ray generator was operated at 30 kV and 15 mA. Tensile properties of 20 mm monofilament were measured by a Fafegraph-M tensile machine of Textechno at the test speed of 20 mm/min. Thermal behavior of the PEN fibers was investigated using a DSC 2901 of TA instrument, and thermal analysis of 3 mg fiber sample was carried out from 30 °C to 300 °C at the heating rate of 10 °C/min. Heat shrinkage was measured by TMA of Seiko TMA at the heating rate of 10 °C/min and the initial load of 5 gf. The dynamic viscoelasticity behavior was investigated using a Toyo Baldwin Rheovibron of DDV-II-C type in temperature range of 30~250 °C, at heating rate of 2 °C/min and frequency of 110 Hz.

3. Results and Discussion

Figure 1 and 2 show the densities and the equatorial WAXD profile of high speed as-spun PEN fiber on the take-up speed. The density increased gently with the take-up speed of up to 5 km/min, but at 6 km/min and above the density increased remarkably. In WAXD profile, above 6 km/min, the reflections from (020) and (200) planes of β crystals were clearly observed at 2θ = 18.6 and 26.6 °, respectively. These peaks became stronger and narrower with an increase in the take-up speed, indicating the development of large and ordered crystallites. Moreover, the coexistence of α crystals was also confirmed from the small shoul

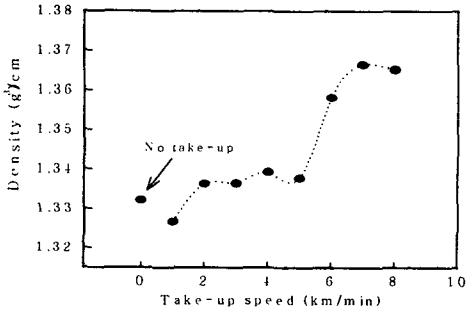

Figure 1. Relationship between density and take-up speed for PEN fibers.

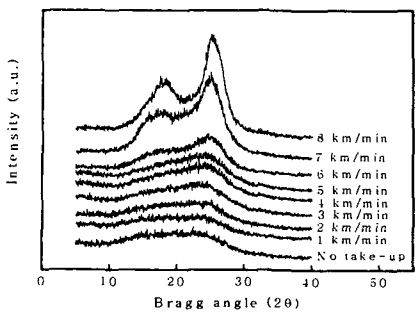

Figure 2. Equatorial X-ray diffraction curves for PEN fibers at take-up speed.

ders at $2\theta = 15.6$ and 23.3 °. These peaks correspond to (010) and (100) reflections of α crystals. At the take-up speed of 8 km/min, however, the intensity of the reflections from α crystal decreased more or less. On the other hand, the initial modulus, specific stress, extension, and work of rupture of as-spun PEN fibers are shown in *Table* 2. It can be known that the mechanical property is improved by high-speed spinning. The initial modulus and the tenacity increased but the strain decreased with increasing the take-up speed.

Table 2. Mechanical properties of PEN fibers spun from high speed spinning

Take-up speed (km/min)	Count (den)	Tenacity (g/den)	Elongation (%)	Work of Rupture (g×cm)
1	42.16	1.57	366.04	283.46
2	21.40	2.34	186.51	106.38
3	14.79	3.71	101.53	68.36
4	10.56	4.75	49.56	33.52
5	8.28	6.75	31.64	25.60
6	6.92	8.40	19.32	15.79
7	5.98	8.44	11.43	7.20
8	5.45	9.19	10.81	6.65

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