KMUTNB Int J Appl Sci Technol, Vol. 8, No. 3, pp. 213–219, (2015)

Structure, Thermal and Mechanical Properties of Non-extracting Ultra-high Molecular Weight Polyethylene Fibers

Apikom Boonyakitkosol, Suttinun Phongtamrug
Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

Sirisart Ouajai*
Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand
Polymer Research Center, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

* Corresponding author. E-mail: sirisart.o@sci.kmutnb.ac.th
Received: 26 June 2015; Accepted: 17 July 2015; Published online: 11 August 2015

Abstract

Gel-spun UHMWPE fibers were produced without an extracting process. Decalin solvent in gel fibers was evaporated rapidly in the first hour and reached equilibrium state after about 24 hours. WAXD patterns shows that the full concentric circular rings were observed for the as-spun fiber and transform into oriented fibers with azimuthal spots on the equator after hot-drawing process. Consistent with the results of DSC thermograms, with DR values greater than 5.0 found the newly developed endothermic peak of the drawn UHMWPE fibers at 150–155°C are attributed to the transition of the constrained orthorhombic into hexagonal crystals. In this study, UHMWPE fiber with modulus as high as 26 GPa and strength about 1.4 GPa can be achieved.

Keywords: UHMWPE fiber, Gel-spinning, Fiber drawing

1 Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a linear polyethylene with molecular weight over 10^6 g mol^{-1} and is known as a high performance polymer with excellent physical properties, such as high toughness, self-lubrication and abrasion resistance, especially in the form of drawn fibers for many potential industrial applications [1]. The tensile strength and the modulus of UHMWPE fibers increase with the drawing, resulting from chain alignment. To allow polymer chain orientation during drawing, UHMWPE polymer chains must have a low entanglement density. However, UHMWPE is difficult or even impossible to process in melt form because of its extremely viscosity, related to the number of entanglements per molecule. An effective way to remove chain entanglements can be achieved by processing the UHMWPE material from a semi-dilute solution in gel-spinning process [2]–[4], in which the polymer chains have partially been disentangled and chains entanglements have been removed.

The gel-spinning method consists of the following three main stages: (first) continuous extrusion of a dilute solution of UHMWPE, (second) spinning of the solution (followed by physical gelation of UHMWPE due to its fast crystallization caused by either cooling of the solution or solvent removal by extraction or evaporation), The fibers at this stage are in the form of gel fibers containing both polymer and significant amount of solvent, and (third) drawing of fibers at

Please cite this article as: A. Boonyakitkosol, S. Phongtamrug, and S. Ouajai, "Structure, Thermal and Mechanical Properties of Non-extracting Ultra-high Molecular Weight Polyethylene Fibers," *KMUTNB Int J Appl Sci Technol*, Vol. 8, No. 3, pp. 213–219, July–Sept. 2015, http://dx.doi.org/10.14416/j.ijast.2015.07.003

elevated temperatures. In the second stage, evaporative solvents such as n-hexane, diethyl ether, n-pentane and toluene are required [3], leading to high processing cost. Hence, the elimination of the solvent extraction process not only reduces production costs, but also reduces the stage of the process. Although many research articles have investigated extracting, drawing process and changes in structures and properties of UHMWPE fibers [2]–[6], however, none of them has discovered and presented a complete description on the non-extracting and drawing process [7]. In this study, the as-spun fibers with different winding speeds were prepared by gel-spinning process without an extracting process. The crystal phase transition, orientation, morphology and mechanical properties of the as-spun and drawn UHMWPE fibers were studied.

2 Experimental

2.1 *Materials*

The ultra-high molecular weight polyethylene (U310 grade) powder with a viscosity-average molecular weight ($\bar{M}v$) 3.2 × 10^6 g mol^{-1} (ISO 1628-3) was purchased from IRPC Public Company Limited (Thailand). Decahydronaphthalene, (Decalin, $C_{10}H_{18}$) mixture of cis-trans reagent grade with boiling point of 189–191°C and the antioxidant (2,6-ditertiary-butyl-p-cresol or DBPC) were produced by Sigma Aldrich Co. LLC.

2.2 *Preparation of UHMWPE fibers*

The UHMWPE powder was dissolved in decalin at a concentration of 8 wt% mixed with 0.5 wt% of DBPC. A mixture was heated in an oil bath up to 150°C and purged with N_2 to prevent oxidative degradation of polymer. Gentle stirring was continuous throughout. The UHMWPE started to dissolve and the solution became a very viscous clear gel. After a homogenization period of 2 hours at 150°C, the solution was rapidly cooled down to room temperature, resulting in gel formation, A piece of gel was cut and fed to the spinning apparatus in gel-spinning process.

In gel-spinning process, UHMWPE gel after cut into small pieces was pumped at 180°C through a single nozzle with a diameter of 0.7 mm and a length of 5 mm. The as-spun fiber (AS) was collected at the speed ranging from 20 to 160 m min^{-1} and quenched into water to form UHMWPE gel fiber, which some decalin still remained in fiber. The drawing conditions of as-spun fibers and draw ratio of hot-drawn fibers (HD) have been determined in Table 1. The drawn fibers derived from as-spun fibers after hot-drawing process are called HD for each of condition. For example HD20 and HD160 stand for the hot-drawn fibers derived from AS20 and AS160, respectively.

In the hot-drawing process, the as-spun fiber was put into a home-made device consisting of 80 cm long heating chamber covered by IR heating tube, one side of the fiber was fed to the chamber and the other side was drawn by gear motor throughout the process. As-spun fiber was carried out at 120°C to various draw ratios. The drawing ratio (DR) is calculated as follows:

$$DR = \frac{GM_2}{GM_1} \quad (1)$$

where, GM_1 is the speed of feeder and GM_2 is the speed of roll up on the other side.

Table 1: Conditions of drawing of gel-spun fibers and hot-drawn fibers

As-spun fibers (AS)		**Hot-drawn fibers (HD)**		
Samples	***Winding speed (m min⁻¹)***	***Gear motor speed (m min⁻¹)***		***DR***
		GM_1	**GM_2**	
AS20	20	0.16	0.16	1.0
AS40	40	0.16	0.48	3.0
AS80	80	0.16	0.80	5.0
AS120	120	0.16	1.11	7.0
AS160	160	0.16	1.43	9.0

3 Characterizations of Fibers

3.1 *Percentage of solvent evaporation*

After gel-spinning, the as-spun fibers were placed under unconstrained state, decalin solvent was evaporated. The percentage of decalin evaporation ($\%D_s$) of as-spun fibers has been calculated with the following equation, where W_0 is the initial weight of as-spun fibers, and W_t is the weight of gel fibers at certain time after gel-spinning.

$$D_s\,(\%) = \frac{W_0 - W_t}{W_0} \times 100 \quad (2)$$

3.2 *Wide-angle X-ray diffraction (WAXD)*

The X-ray fiber diagrams of all samples were carried out by a Rigaku X-ray Diffractometer R-AXIS RAPID II (Japan) - cylindrical camera with a graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation operated at 50 kV and 100 mA. A cylindrical imaging plate was used as a detector.

3.3 *Thermal analysis*

The as-spun fiber and hot-drawn fiber were subjected to the TA instruments differential scanning calorimeter (DSC) model 2910. All scans were performed at a heating rate of 10°C min^{-1} over a temperature ranging from 50 to 250°C under N_2 flow. Samples weighing about 1.0–1.5 mg were placed in aluminum sample pans. The percentage of crystallinity (X_c) of fibers has been calculated with the following equation, where ΔH_m is the enthalpy of fiber sample and ΔH_m^o is the enthalpy of fully crystallized polyethylene, which is 293 J g^{-1} [8].

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \qquad (3)$$

3.4 *Morphologies of fibers*

The surface morphology of the as-spun fiber and hot-drawn UHMWPE fiber were coated with gold, then their morphological structure was observed using S-4800 FE-SEM made by Hitachi.

3.5 *Mechanical test of fibers*

Single UHMWPE fiber was glued onto a 25 mm gauge length paper frame and tensile properties were studied by the Universal Testing Machine (Tinius Olsen, H5K-T0327) in an ambient temperature with a crosshead speed of 12 mm min^{-1} and a 50N load cell.

4 Results and Discussion

4.1 *Solvent evaporation analysis of as-spun fibers*

The as-spun fibers are gradually contracted if they are placed under unconstrained state. Solvent is partially evaporated until equilibrium is reached due to the thermal accumulation after spinning process [9]. Therefore, the concentration of UHMWPE in as-spun fiber will be higher than that in the solution. The changes of solvent evaporation percentage of different as-spun fibers with placing time are shown in Figure 1, the solvent evaporated rapidly increases at the first 60 min, and then gradually increases to a certain value at the placing time over 1500 min. This suggests that the evaporation of as-spun fiber is severe in the first hour and then gradually reaches an equilibrium state after about 24 hours and also indicates that the final %D_s decreases as the winding speed increases, because the fiber contains less solvent and more entangled points at the high winding speed, which influence the solvent evaporation of the as-spun fibers.

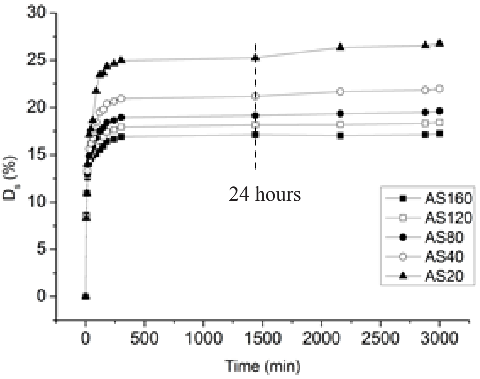

Figure 1: D_s of as-spun fibers versus placing time.

By the evaporation process, solvent is evaporated, leading to reduction of decalin content in the as-spun fibers prior to subjecting to the hot-drawing process.

4.2 *X-ray diffraction analysis*

Wide-angle 2D X-ray patterns of the as-spun and drawn fibers are shown in Figure 2. Full concentric circular rings are observed for the as-spun fibers (see Figures 2 (a) and 2 (c)). More orientation is observed in the as-spun fiber at higher winding speed due to less steric effect of the solvent. After hot-drawing process, the full concentric circular rings gradually transform into discrete azimuthal arcs or spots for the drawn fibers HD20 and HD160 as shown in Figures 2 (b) and 2 (d), respectively. Suggesting more order of crystalline structure after solvent removal by evaporation during hot-drawing at high temperature. In the meantime, the "strain-induced" and newly formed orthorhombic

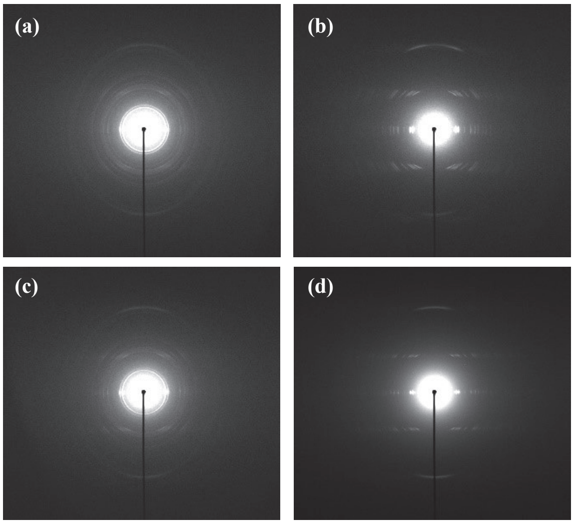

Figure 2: 2D-WAXD patterns of as-spun fibers and hot-drawn fibers at 110°C (a) AS20, (b) HD20, (c) AS160 and (d) HD160.

crystal during the drawing processes of UHMWPE fibers are observed [10]–[12]. That also results in multiple melting endotherms on the DSC thermograms (see Figure 5), bringing into the improvement in the mechanical properties of the fiber which will be discussed extensively in thermal analysis section.

4.3 *Thermal analysis*

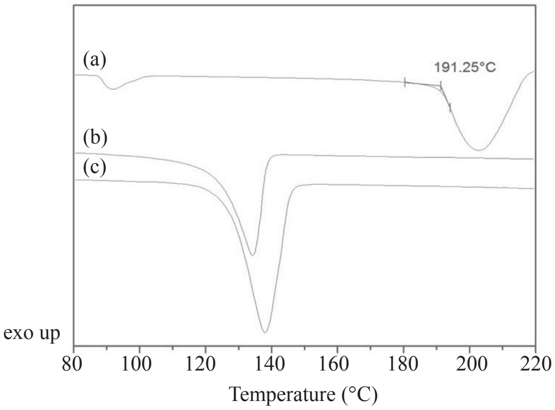

Figure 3: DSC thermograms of (a) UHMWPE gel, (b) UHMWPE U310 powder and (c) drawn fiber.

In the DSC thermograms of the UHMWPE gel in Figure 3 (a), the first peak at 92°C indicates the melting point of the gel polymer. Lower melting point of UHMWPE gel compared to UHMWPE U310 powder (see Figure 3 (b)) may result from the imperfection in the crystal of polymers caused by the gel formation and the presence of decalin solvent. The onset of second endothermic peak starting at 190°C indicates the boiling point of the decalin. The two different peaks indicate the presence of polymer and solvent. Figure 3 (c) shows one peak at 141°C indicating the melting point of the UHMWPE drawn fiber. Shifting of the melting point from 92°C (Figure 3 (a)) to 141°C (Figure 3 (c)) due to transformation of UHMWPE gel to fiber. In addition, the absence of second endothermic peak in the fiber shows the complete removal of the decalin from the fiber.

Table 2 shows the DSC data derived from the melting and cooling curves of different as-spun fibers and drawn fibers, indicating that the melting temperature and percentage of crystallinity of drawn fibers are greater than those of as-spun fibers. Normally, high winding speed and high stress drawing fiber in hot-drawing process tends to form much more crystals and the crystalline structure becomes more regular. This observation contributes to increase in crystallinity and melting temperature.

Table 2: DSC results of different as-spun fibers and drawn fibers at various draw ratios

As-spun fiber					**Drawn fiber of HD20**				
Samples	$T_{m\,(onset)}$ *(°C)*	T_m *(°C)*	X_c *(%)*	ΔH_f *(J g^{-1})*	***DR***	$T_{m\,(onset)}$ *(°C)*	T_m *(°C)*	X_c *(%)*	ΔH_f *(J g^{-1})*
AS20	129.0	136.8	60.2	176.4	1.0	134.3	140.2	69.5	203.7
AS40	129.5	137.7	62.6	183.3	3.0	135.2	140.3	78.1	228.9
AS80	129.7	138.2	71.7	210.1	5.0	135.1	140.1	89.9	263.4
AS120	130.2	138.7	73.0	213.6	7.0	135.2	140.8	94.9	278.1
AS160	130.3	139.1	75.1	220.1	9.0	135.4	141.3	96.0	281.3

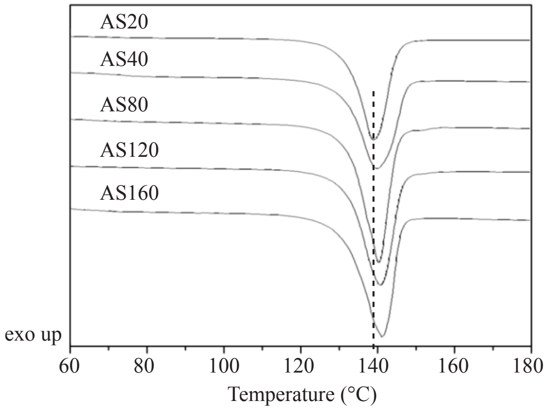

Figure 4: DSC thermograms of as-spun fibers.

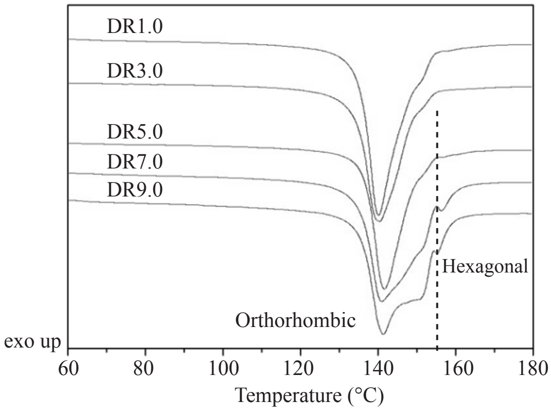

Figure 5: DSC thermograms of drawn fibers with different draw ratios.

Shifting of the endotherm peak attributed to the melting of orthorhombic crystal from 137°C to 139°C is observed with increased the winding speed shown in Figure 4. As a result of the slight orientation of crystalline form with the changing speed. The endotherm peaks of the drawn fibers after hot-drawing process shown in Figure 5, presents the multiple melting endotherms at DR values increasing from 1.0 to 9.0. Interestingly, two an additional peaks at temperatures around 150°C and 155°C are found on the right shoulder of the main melting endotherms of the drawn fibers DR values of 7.0 and 9.0. As the new peak at 155°C is attributed to the melting of hexagonal crystals, which is likely activated by strain-induced orthorhombic into hexagonal phase transition that causes slip of chains.

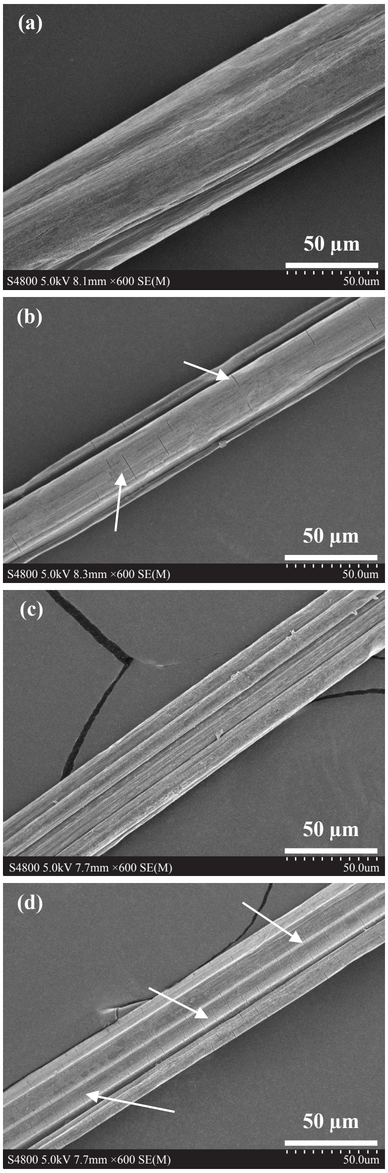

Figure 6: SEM micrographs of the as-spun and hot drawn UHMWPE fibers. (a) AS20, (b) HD20, (c) AS160 and (d) HD160.

Figure 6 shows the morphological surfaces of the as-spun fibers and the drawn fibers with different winding speeds. Defect with transverse bands observed for the drawn fibers (Figures 6 (b) and 6 (d)) may result from smaller stress during drawing. This corresponds to the local crystalline slip due to the effect of drawing tension.

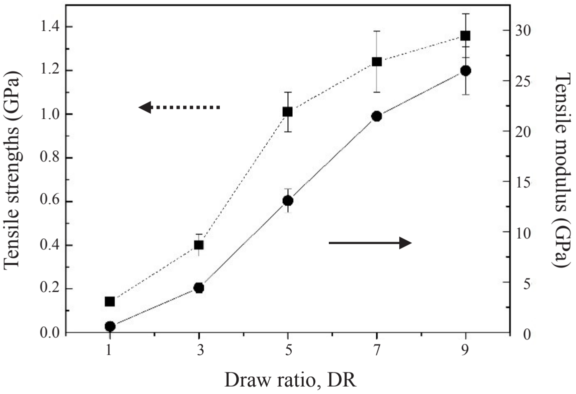

Figure 7: Tensile strengths (■) and Tensile modulus (●) of AS 20-drawn fibers with varying DR values.

4.4 *Mechanical properties*

The mechanical properties of the as-spun fibers and the drawn fibers at different conditions were determined by single-fiber mechanical tests. The elastic modulus, strain at break, and break stress or tensile strength have been calculated.

Table 3: Single-fiber properties of as-spun fibers at different processing conditions

Samples	Modulus (GPa)	Tensile strength at break (MPa)	Strain at break (%)
AS20	0.01 ± 0.001	33.3 ± 0.04	491.9 ± 29.3
AS40	0.5 ± 0.14	37.4 ± 0.03	294.4 ± 47.3
AS80	0.6 ± 0.04	36.1 ± 0.01	209.9 ± 37.3
AS120	1.1 ± 0.01	41.7 ± 0.04	175.1 ± 19.4
AS160	1.2 ± 0.14	77.4 ± 0.06	76.2 ± 19.5

Table 3 shows the mechanical properties of the as-spun fibers, one can see that the modulus and tensile strength of the as-spun are remarkably enhanced with increasing winding speed. In contrast, strain at break decreases with increasing of winding speed. The drawing of as spun fiber was performed with some amount of Decalin in fiber, allowing the slippage of chains with less restriction of chain entanglement. This might result in less amount of voids, therefore the maximum strength as a function of DR, normally found in the drawing of polymer, is not observed. [13].

Figure 7 presents a plot of the tensile modulus and strengths of the drawn UHMWPE fibers versus their DR values. Both modulus and strengths of the as-spun fibers with winding speed of 20 m min^{-1} after hot drawing process were found to improve constantly as DR values increase from 1.0 to 9.0. In this study, UHMWPE fiber with modulus as high as 26 GPa and strength about 1.4 GPa can be achieved.

5 Conclusions

After gel-spinning process for drawing an as-spun fiber, phase separation took place. Decalin solvent was evaporated rapidly in the first hour and reached equilibrium state after about 24 hours. During hot-drawing process, further evaporation of decalin resulted in the orientation of crystals, which is already very high in partially drawn fibers. As shown on the WAXD patterns, the full concentric circular rings were observed for the as-spun fiber and transform into oriented fibers with azimuthal spots on the equator after hot-drawing process. Consistent with the results of DSC thermograms, the abnormally high melting temperatures (150–155°C) found on the newly developed endotherms of the drawn UHMWPE fibers with DR values greater than 5.0 are attributed to the transition of the constrained orthorhombic into hexagonal crystals and the melting of the hexagonal crystals, in which their percentage crystallinity increases significantly from 60.2% to 96.0%. However, drawing with a high draw ratio causes gradual transformation of fibers morphology, defect with transverse bands were observed. The mechanical properties of the as-spun and the drawn UHMWPE fibers, are independent of the winding speed and draw ratio.

Acknowledgments

Special thanks Prof. Kohji Tashiro (Toyota Technological Inst.) for X-ray measurement and discussion.

References

[1] J. W. S. Hearle, *High-performance fibres*, Cambridge: Woodhead Publishing Ltd, 2001, pp. 85–92.

[2] P. Smith, “Ultrahigh-strength polyethylene filaments by solution spinning and hot drawing,” *Polym. Bull. 1*, vol. 1, no. 11, pp. 733–736, 1979.

[3] A. P. de Boer "Polyethylene networks crosslinked in solution: preparation, elastic behavior, and oriented crystallization. I. Crosslinking in solution," *J. Polym. Sci.*, vol. 14, no. 2, pp. 187–210, 1976.

[4] P. Smith, "Ultra-high-strength polyethylene filaments by solution spinning/drawing," *J. Mater. Sci*., vol. 15, pp. 505–514, 1980.

[5] W. Hoogsteen, "The influence of the extraction process and spinning conditions on morphology and ultimate properties of gel-spun polyethylene fibers," *Polymer*, vol. 28, pp. 923–928, 1987.

[6] J. T. Yeh, "Investigation of the drawing mechanism of UHMWPE fibers," *J. Mater. Sci.*, vol. 43, pp. 4892–4900, 2008.

[7] P. Smith, "Ultrahigh-strength polyethylene filaments by solution spinning/drawing, 2. Influence of solvent on the drawability," *Makromol. Chem.*, vol. 180, pp. 2983–2986, 1979.

[8] B.Wunderlich, "Specific heat of synthetic high polymers. VIII Low pressure polyethylene," *J. Polym. Sci.*, vol. 24, pp. 201–212, 1957.

[9] M. Xiao, "Effect of UHMWPE concentration on the extracting, drawing and crystallizing properties of gel fibers," *J. Mater. Sci.*, vol. 46, pp. 5690–5697, 2011.

[10] S. Tsubakihara, "Melting and crystallization of ultra-high molecular weight polyethylene with appearance of hexagonal phase II. Strain-induced crystallization of thermal-contracted sample," *Polym. J.*, vol. 28, pp. 563–567, 1996.

[11] Y. L. Hsieh, "Structural transformation of ultra-high modulus and molecular weight polyethylene fibers by high-temperature wide-angle X-ray diffraction," *J. Polym. Sci. Part B: Pol. Phys*., vol. 35, pp. 623–630, 1997.

[12] P. J. Lemstra, "Basic aspects of solution (gel)-spinning and ultra-drawing of ultra-high molecular weight polyethylene," in S*tructure Formation in Polymeric Fibers*, Salem R., Hanser & Munich, 2000, pp. 185–224.

[13] J. Karger-Kocsis, "Polyolefin fiber- and tape-reinforced polymeric composites" in *Polymer Composites*, vol. 1, Macro and Microcomposites (Eds.: S. Thomas, K. Joseph, S. K. Malhotra, K. Goda and M.S. Sreekala), Weinheim: Wiley-VCH, Chapter 10, 2012, pp. 315–337.