Differentiation of molecular chain entanglement structure through laser Raman spectrum measurement of High strength PET fibers under stress

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Abstract. The aim of this study was to investigate the mechanism for the improvement of mechanical properties of poly(ethylene terephthalate) (PET) fibers based on the concept of controlling the state of molecular entanglement. For this purpose, five different PET fibers were prepared through either the conventional melt spinning and drawing/annealing process or the high-speed melt spinning process. In both cases, the melt spinning process was designed so as to realize different Deborah number conditions. The prepared fibers were subjected to the laser Raman spectroscopy measurement and the characteristics of the scattering peak at around 1616 cm\(^{-1}\), which corresponds to the C-C/C=C stretching mode of the aromatic ring in the main chain, were investigated in detail. It was revealed that the fibers drawn and annealed after the melt spinning process of lower Deborah number showed higher tensile strength as well as lower value of full width at half maximum (FWHM) in the laser Raman spectrum. Narrow FWHM was considered to represent the homogeneous state of entanglement structure, which may lead to the higher strength and toughness of fibers because individual molecular chains tend to bear similar level of tensile stress when the fiber is stretched. In case of high-speed spun fibers prepared with a high Deborah number condition, the FWHM was narrow presumably because much lower tensile stress in comparison with the drawing/annealing process was applied when the fiber structure was developed, however the value increased significantly upon applying tensile load to the fibers during the laser Raman spectrum measurement. From these results, it was concluded that the Laser Raman spectroscopy could differentiate molecular chain entanglement structure of various fiber samples, in that low FWHM, which corresponds to either homogeneous state of molecular entanglement or lower level of mean residual stress, and small increase of FWTH upon applying tensile stress are considered to be the key factors for the improvement of the mechanical properties of PET fibers.

1. Introduction
Poly(ethylene terephthalate) (PET), which is widely used as synthetic fibers, bottles etc., is a polymer with excellent properties such as high mechanical and thermal performances and low cost. Even though the development of PET fibers was achieved long time ago, its tensile strength as well as the ratio of tensile strength of the available fibers to the theoretical value are not high enough in comparison with other commercialized high-strength fibers. This also means that there still is a high
possibility of improving the mechanical properties of currently existing PET fibers. After significant efforts of developing high-strength PET fibers without much success, it is now considered that the control of the state of molecular entanglement is the key element for the significant and essential improvement of mechanical properties [1].

In the cases of high-strength fibers with rigid molecular chains such as poly(p-phenylene terephthalamide) (PPTA), poly(p-phenylene benzobisoxazole) (PBO) etc., entanglement density is considered to be extremely low. In the cases of high-strength fibers with flexible molecular chains such as ultra-high molecular weight polyethylene (UHMWPE), process for decreasing the entanglement density, such as gel spinning, is designed in order to improve the mechanical properties. In the case of PET, however, it has been reported that the improvement of mechanical properties can be achieved through the control of melt spinning conditions to keep Deborah number at a low level [1]. Low Deborah number corresponds to the suppression of the reduction of entanglement density in the melt spinning process. This means that totally opposite strategy in terms of controlling the entanglement density is required for the improvement of the mechanical properties of PET fibers. To explain this behavior, the concept of keeping the homogeneous entangled state of the molecular chains was proposed consulting the results of coarse molecular dynamics simulation. In other words, it has been considered that keeping the narrow distribution of the molecular weight between the adjacent entanglement points is the key concept for obtaining high strength and high toughness fibers, however, direct verification of the relationship between the mechanical properties and entanglement structure of PET fibers has not been completed yet. Therefore, in this study, several types of PET fiber samples prepared under various spinning conditions were subjected to the detailed analysis of the state of molecular entanglement using the laser Raman spectroscopy.

2. Experimental

2.1. Samples

Three types of PET fiber samples produced in our laboratory and two types of PET fiber samples provided from an outside research institution were used in this study (Table1). Melt spinning of PET fibers was conducted in our laboratory using two types of nozzles with different diameters of 5 and 0.5 mm for bringing about opposing high and low Deborah numbers in the spinning process [2]. Orientation and crystallization of the PET molecules to develop fiber structure were achieved either by the high speed melt spinning process or by the conventional low speed spinning and drawing/annealing processes. Regarding the provided fiber samples, one is an ordinary high strength fibers made with the conventional industrial method and the other is the fiber of extremely high strength produced by a newly developed spinning method.

| Sample | Extrusion Temp. (°C) | Through-put Rate (g/min) | Nozzle Diam. (mm) | Take-up Velocity (m/min) | 1st Drawing/Annealing | 2nd Drawing/Annealing | 3rd Drawing/Annealing |
|--------|---------------------|-------------------------|------------------|--------------------------|----------------------|----------------------|----------------------|
| Sample 1 | 300                 | 5                       | 5                | 6000                     | 75 × 5               | 130 × 1.4            | 200                  |
| Sample 2 | 300                 | 5                       | 5                | 400                      | 75 × 5               | 130 × 1.5            | 200                  |
| Sample 3 | 300                 | 5                       | 0.5              | 400                      | 75 × 5               | 130 × 1.5            | 200                  |
| Sample 4 | Provided from an outsource (Prepared through the conventional method) | | | | | | |
| Sample 5 | Provided from an outsource (Prepared through a new method) | | | | | | |
2.2. Tensile strength
Tensile strength and elongation at break of the fiber samples were evaluated through the stress-strain curve measurements using a tensile testing machine (Shimadzu, AG-I) at the strain rate of 50 %/min.

2.3. Laser Raman spectroscopy
Laser Raman spectroscopy measurement was performed on single filaments using a Raman spectrometer (Jasco, NRS-5100) equipped with a 532.26 nm green laser. The power of incident light ranged between 1.5 and 1.8 mW. The focus of the laser was adjusted to the surface of the fiber sample by a confocal microscopy optical system. The Raman spectra between 1350 and 1850 cm\(^{-1}\) was recorded with and without applying the tensile stress of around 180 MPa.

2.3.1. Reproducibility
In order to evaluate the precision and reproducibility of the laser Raman spectroscopy measurement, repetitive measurements were carried out under the same conditions using PET fiber samples. For each measurement, the wavenumber was calibrated measuring the spectral peak of Ne light. After repeated measurements of eight times in the spectrum range between 1350 and 1850 cm\(^{-1}\), the spectral peak at around 1616 cm\(^{-1}\) was subjected to curve fitting by combining the Lorentzian and Gaussian functions. Standard deviations of peak wavenumber and full width at half maximum (FWHM) of scattering peak at around 1616 cm\(^{-1}\) were evaluated from the entire measurements.

2.3.2. Peak analysis
Differentiation of the state of molecular chain entanglement through the laser Raman spectroscopy measurement was attempted analysing the characteristics of Raman scattering intensity at around 1616 cm\(^{-1}\), which corresponds to the C-C/C=C stretching modes of the aromatic ring in the main chain [3]. The shape of the Raman scattering peak near 1616 cm\(^{-1}\) was subjected to curve fitting as stated above and the wavenumber and the FWHM of the peak were obtained. Subsequently, Raman spectroscopy measurement was carried out applying the tensile stress of around 180 MPa to the fiber sample, and the variations of the wavenumber and the FWHM of the peak were evaluated.

3. Results and Discussion

3.1. Tensile strength
Figure 1 shows the stress-strain curves of the PET fibers used in this research. Tensile strength and elongation at break analyzed from the stress-strain curves are summarized in Table 1. The fiber samples produced under various melt spinning conditions showed significantly different mechanical properties. The fiber sample of the highest tensile strength (sample 5), which was produced through a modified melt spinning process, showed a tensile strength of 1.58 GPa and an elongation at break of 11.7%. In the case of fiber sample prepared through the high-speed spinning process with a large diameter nozzle (sample 1), the tensile strength was 0.46 GPa, and the elongation at break was 85.2%.
Table 2. Tensile strength and elongation at break of PET fiber samples prepared through various processing conditions.

| Sample  | Tensile strength (GPa) | Elongation (%) |
|---------|------------------------|----------------|
| Sample 1 | 0.46                    | 85.2           |
| Sample 2 | 1.13                    | 13.4           |
| Sample 3 | 1.21                    | 12.5           |
| Sample 4 | 1.27                    | 11.7           |
| Sample 5 | 1.58                    | 11.7           |

3.2. Laser Raman spectroscopy

3.2.1. Reproducibility As only small differences in the laser Raman spectra were expected when comparing the fiber samples of different mechanical properties as well as comparing those with and without applying the tensile load, firstly, reproducibility of the data acquisition was investigated comparing the results of the wavenumber and the FWHM of scattering peak at around 1616 cm\(^{-1}\) for eight repeated measurements of the same fiber sample. The results are shown in Table 3. Standard deviations of both the peak wave number and that of the FWHM of only about 0.03 were obtained. Through this accuracy test, the reproducibility of the measurement was found to be satisfactorily high enough for the differentiation of the characteristics of fiber samples in this study.

Table 3. The wavenumber and the full width at half maximum of the peak at around 1616 cm\(^{-1}\). Standard deviations of these values are also shown.

| Measurement # | Peak wavenumber (cm\(^{-1}\)) | Full width at half maximum (cm\(^{-1}\)) |
|---------------|-------------------------------|------------------------------------------|
| 1st           | 1615.561                      | 9.488                                    |
| 2nd           | 1615.555                      | 9.468                                    |
| 3rd           | 1615.604                      | 9.500                                    |
| 4th           | 1615.602                      | 9.538                                    |
| 5th           | 1615.607                      | 9.556                                    |
3.2.2. Peak analysis Raman scattering peak located at around 1616 cm\(^{-1}\) has characteristics of changing peak wavenumber and peak width when stress is applied. Figure 2 shows the change of FWHM of the peak around 1616 cm\(^{-1}\) due to the loading of tensile stress for various fibers. Without applying the tensile stress, the FWHM for the melt spun and drawn/annealed fibers prepared using a small diameter nozzle in the spinning process was narrower than that for the fibers prepared using a large diameter nozzle, whereas the high strength fiber prepared with a new method showed the narrowest FWHM in comparison with any other samples. Large nozzle diameter corresponds to a larger Deborah number, whereas the new method for producing high strength PET fibers was designed so as to decrease the Deborah number in the melt spinning process. Accordingly, it was speculated that the spinning process with lower Deborah number leads to the formation of structure with more homogeneous state of molecular entanglement in the as-spun fibers, which eventually causes narrower residual stress distribution in the drawn/annealed fibers. For all the drawn/annealed fibers, increases of the FWHM upon the loading of tensile stress were found to be similar. On the other hand, the FWHM for the high speed melt spun fibers prepared with a large diameter nozzle was narrower than those for the drawn fiber samples. It can be considered that in the high speed spinning process, lower tensile stress was loaded for the formation of fiber structure through the orientation-induced crystallization in the melt spinning process. This may lead to the narrower FWHM because of the lower level of mean residual stress. In contrast, larger increase in the FWHM value was observed for this sample after applying the tensile load. This result suggested that the individual molecular chains between adjacent entanglement points bear the applied stress with significantly inhomogeneous manner in comparison with other drawn/annealed fibers.

|    | 6th  |  7th  |  8th  |
|----|------|------|------|
|    | 1615.523 | 1615.554 | 1615.552 |
| 6th |      |      |      |
| 7th |      |      |      |
| 8th |      |      |      |
| Standard deviation | 0.031 | 0.031 |

**Figure 2.** Variation of FWHM (Full width at half maximum) of Laser Raman spectrum peak at around 1616 cm\(^{-1}\) with application of tensile stress for five different PET fiber samples.

4. Conclusions
As described above, improvement of the mechanical properties of PET fibers showed close correlation with the decrease in the FWHM of the aromatic ring stretch vibration mode peak in the laser Raman spectrum. Suppression of the increase of FWHM upon the loading of tensile stress was also confirmed. These results suggested the applicability of laser Raman spectroscopy for distinguishing the difference in the state of molecular entanglement. In summary, it can be said that narrow FWHM and its small increase upon the application of tensile load are the conditions for achieving the fibers of high mechanical properties.

Acknowledgement
This study is supported by Korean National R&D fund for the international collaboration program of KIAT (Korea Institute for Advancement of Technology)

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