

# Analysis and Discussion of the Modulus–Strain Curves of Poly(ethylene terephthalate) and Polyamide Industrial Yarns

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**ABSTRACT:** The stress–strain and modulus–strain curves from the treatment of tensile test data are more complete and suitable for examining the mechanical properties of fibers than just the stress–strain curve. This article analyzes typical modulus–strain curves of poly(ethylene terephthalate) and polyamide fibers through the physical structure

changes in these fibers during stretching and discusses how to enhance the modulus for industrial use. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 859–862, 2005

**Key words:** microstructure; modulus; polyamides; strain

## INTRODUCTION

Poly(ethylene terephthalate) (PET) and polyamide (PA) yarns are widely used in industry and elsewhere. There are many demands for the mechanical properties of industrial yarns. The parameters obtained from stress–strain curves, such as the breaking intensity, breaking elongation, and initial modulus, are useful but are not able to completely meet all demands. Egbers<sup>1</sup> obtained the modulus–strain curves of polyacrylonitrile through corresponding derivative stress–strain curves in 1963. He mentioned a mathematical model for describing the modulus–strain curves of polyacrylonitrile fibers. In 1983, Lucas<sup>2</sup> calculated the corresponding modulus of all strain data. Then, a mathematical model was developed for fitting the modulus–strain curves of PET industrial yarns. The model giving the best fit of the modulus–strain curve consists of three modified Pearson VII lines. The fitting procedure yields a set of 13 parameters, from which the modulus–strain curve can be fully determined. The 13 parameters, which include 11 calculated parameters plus the breaking strength and breaking elongation, can be stored in a computer, and then the modulus–strain and stress–strain curves can be calculated again. This method provides more precisely fitted modulus–strain curves. However, it needs a tensile test machine with higher sensor resolution. The choice of the parameters is difficult during the fitting used by Pearson VII lines, and so this method is not practical in operation. Chongyou and Yan<sup>3</sup> introduced a cubic spline function to fit a load–strain curve, and the modulus–strain curve was

obtained after derivation. At the same time, they used Pearson VII lines to describe the modulus–strain curve, and the fitting results were good.

The aforementioned research on modulus–strain curves was performed in the basic phase. They did not further relate the modulus changes to the physical structure changes in the fibers. Heuvel and Lucas<sup>4</sup> determined the experimental relations between the physical structure and mechanical properties of a huge number of drawn PET yarns and qualitatively explained the two modulus peaks of modulus–strain curve based on the two-phase model of drawn PET yarns. They explained that the first maximum of the modulus–strain curve represented the disintegration of the entanglement network, and they tentatively interpreted the effect of orientation on the first modulus peak. Higher orientation promoted the formation of denser entanglement networks, and breaking down a denser network required greater force as it contained more physical crosslinks. Therefore, the higher force caused a higher modulus. The second maximum of the modulus–strain curve was due to the narrow tie macromolecule length distributions between the crystalline regions. Van Miltenburg<sup>5</sup> determined the modulus–elongation curves of PET, polyamide 6, rayon, and polyethylene from load–elongation curves by numerical differentiation. All the modulus–elongation curves showed distinct two peaks, except for those of the polyethylene yarns. The modulus–elongation curves were divided into three regions. When the strain was less than 0.1%, the interaction between the molecular chains was strong enough to resist the slip of the chains, so the yarn showed elastic behavior, and the modulus was high. When the strain was between 0.2 and 5%, the modulus declined. This was due to the slippage of the molecule near the amorphous do-

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TABLE I  
Sample Characteristics

Fiber	dtex	Initial modulus (cN tex <sup>-1</sup> )	Breaking elongation (%)	Breaking stress (cN tex <sup>-1</sup> )	Source
PET	277.8	150	12	80	Wuxi Taiji (Wuxi City, China) Chongqing Synthetic Fiber Factory (Chongqing City, China)
PA	1100/48	22	18	60	

mains, crystal regions, and defects. When the strain was greater than 8%, the modulus started to increase because of the increasing macromolecular order. This research on modulus–strain curves illuminated the inner physical structures of the fibers, and we performed valuable work in the fitting of the modulus–strain curves. The tensile testing of PET and PA industrial fibers was carried out, and the data were treated to gain the modulus–strain curves with the mathematical tools of Matlab. The relationships between the modulus changes and the physical structure were systemically analyzed. This study established groundwork for the further research of the relationships between the modulus–strain curves and the processing conditions.

## EXPERIMENTAL

### Samples

The samples are described in Table I.

### Instrument and testing conditions

A Shimadzu DCS-500 (Kyoto, Japan) material tester was used; it was equipped with an automatic data collector. The testing conditions were room temperature ( $20 \pm 2$  deg;C), a humidity level of  $65 \pm 2\%$ , a crosshead speed of 30 mm/min, a crosshead distance of 100 mm, a full sensor range of 500 N, and a 0.2-mm interval between two data points. Thirty samples of each type were tested.<sup>6</sup>

### Modulus–strain curves

We used the method of Lucas to treat the measured data. The pretension value of the load–strain curves was defined as the point at which the tension was smallest above zero. The end point was defined as the point at which the measuring value was distinctly lower than that of the preceding point. The stress ( $\sigma_0$ ) was calculated from the load values, and the linear density of the fiber was corrected by multiplication by  $1 + \varepsilon$  (where  $\varepsilon$  is the strain) to gain the real stress [ $\sigma = \sigma_0 (1 + \varepsilon)$ ]. The stress and strain values were fitted with Matlab to obtain smooth stress–strain curves. The modulus ( $E$ ) values were calculated in the simplest way:  $E = \Delta\sigma/\Delta\varepsilon$ . Finally, we used Matlab to fit the modulus values and plot the modulus–strain curves. Although in

comparison with the former method it was not very precise, it was very simple and could meet our needs.

## RESULTS AND DISCUSSION

Figures 1 and 2 show that there are two peaks in the modulus–strain curves. The first maximum is defined as the initial modulus.<sup>7</sup> The first peak value of PET is higher than the second, but that of PA is the opposite. To analyze the character of the modulus–strain curves from the physical structure, we need to clearly understand the microstructure of the fibers. For PET fibers, there are a number of models describing the structure and performance, such as the aggregation model, two-phase model, and middle-phase model.<sup>8</sup> The aggregation model is suitable for low-density PET at room temperature. The two-phase model perfectly explains the modulus in parallel to the fiber axis.

Traditionally, a two-phase model can adequately describe the microstructure of semicrystalline polymers such as PET. Ordered (crystalline) regions alternate with less ordered (amorphous) domains. A single molecule may run through several crystalline and amorphous regions. Besides, there is the possibility of a molecule folding back on the surface of a crystal to reenter it (Fig. 3).

Depending on the processing conditions, the polymer molecules are more or less oriented along the fiber axis. So-called fibrils are formed. The coherence of amorphous and crystalline domains is found predominantly in the longitudinal direction in the fibrils. Within the crystals, the molecules are well ordered and highly oriented, but they are the opposite in the amorphous domains. When the fiber is loaded, the inhomogeneity of the structure makes the amorphous regions the weak spots in the fiber. Therefore, the molecular arrangement in the amorphous regions is of ultimate significance for the tenacity and modulus of fibers. In this respect, two kinds of amorphous molecules are of great importance. The one kind is the folding of the molecules at the boundaries of crystals. These folded chains cannot contribute to increasing the modulus or strength of the fibers. The other kind is molecules running from one crystal to the other; these are called taut molecules. These molecules with the crystals bear the load. According to the character of the modulus–strain curves, the tensile process can be

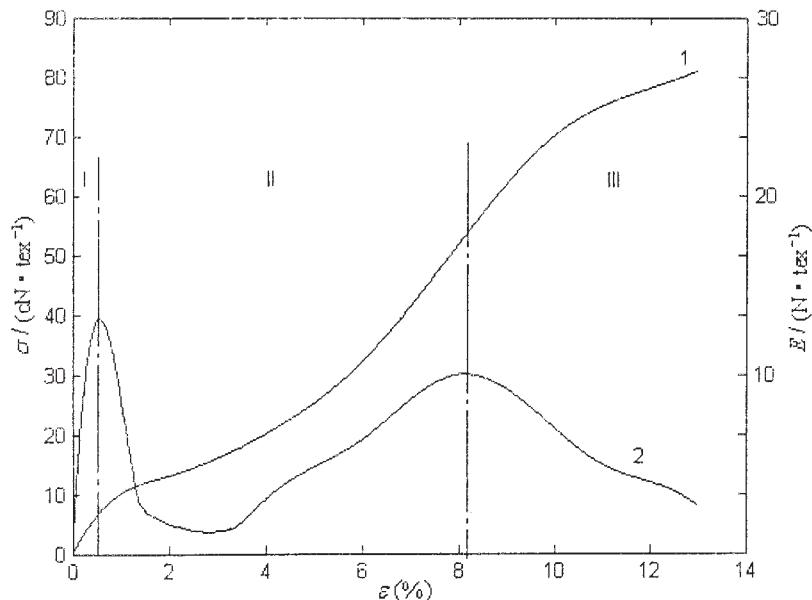


Figure 1 (1) Stress-strain curve and (2) modulus-strain curve (2) of a PET industrial yarn.

divided into three stages. The first stage is from the beginning of the tensile process to the emergence of the first maximum of the modulus. The molecular chains in the amorphous regions are crimped and entangled at first. After the loading, the glycol groups of the PET molecules are elongated and distorted. The entanglement networks and crosslinks between molecules such as hydrogen bonds are broken off. If the load is moved out, the molecules come back instantly, and the strain is about 0.1%. The denser the network is, the greater the force is needed to destroy the network. This greater force causes a higher modulus because the elongation at the first maximum is constant. The second stage is from the first maximum of the

modulus to the second maximum. Loaded continuously, the crimped molecules begin to uncoil. This process is accompanied by conformation transitions. The ester groups at the aromatic rings of PET molecule have a mutual *cis* or *gauche* position. The *trans* conformer is related to the straight parts of the crystalline region, and the *gauche* conformer is related to the bended parts of the amorphous region.<sup>9</sup> When the crimped molecules uncoil, the conformer of the molecules changes from *gauche* to *trans*. This transition is related to a larger strain, so the modulus is low. The third stage is from the second maximum of the modulus to the rupture of the fiber. In this stage, the bond chains of the straight molecules begin to tighten, and

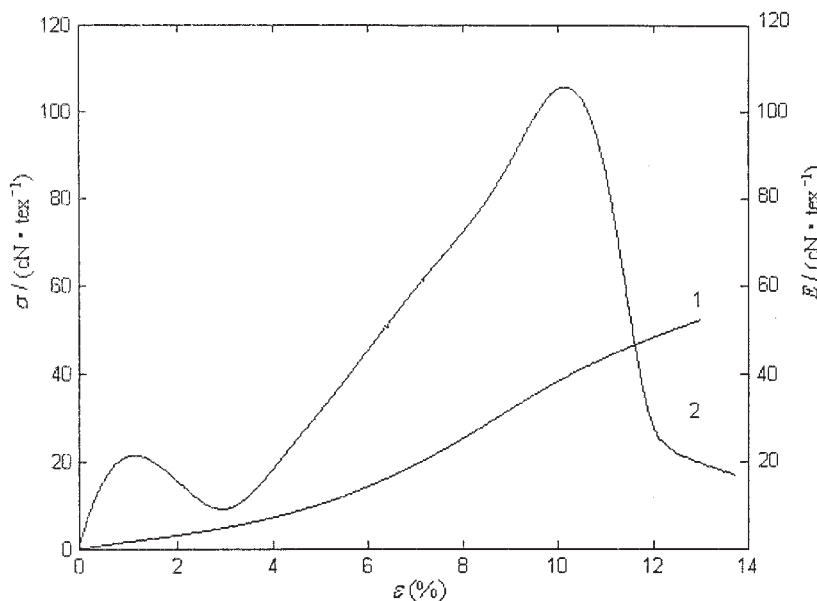


Figure 2 (1) Stress-strain curve and (2) modulus-strain curve of a PA industrial yarn.

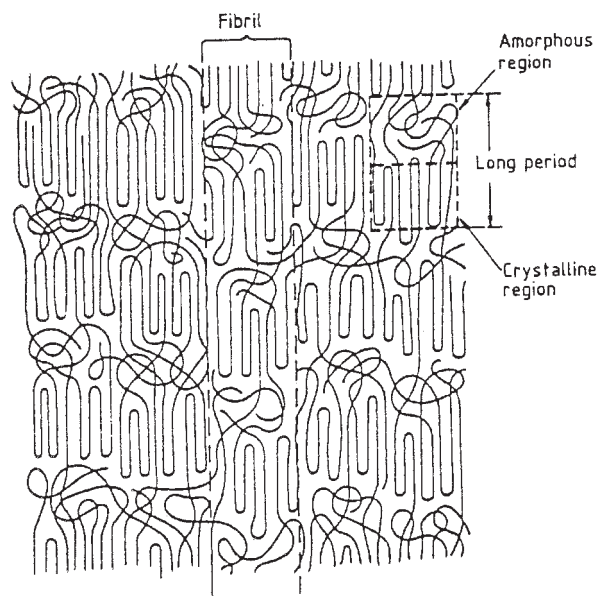


Figure 3 Structural model of a drawn PET yarn.

the strain causes the stretching of covalent bond angles. The crystalline regions start to slip until some molecular rupture is initiated in the amorphous regions. Then, the broken molecules generate local stress concentrations and pores. More and more broken molecules turn the pore into a fracture, and the fiber may rupture finally.

From this discussion, it is not difficult to explain the two peaks of the modulus-strain curves. The two points of maximum resistance to elongation can be used to divide the curve into three regions. The first maximum is the so-called initial modulus in region II (Fig. 2), and it is due to the disintegration of the entanglement network. The lowering of the tensile modulus in the first part of region II can be attributed to the uncoiling of molecular chains in the amorphous phase. Because the strain is large, the lowering of the modulus is very sharp and presents a valley region. Heuvel et al.<sup>9</sup> showed experimentally that the elastic modulus steadily increased in this region. Therefore, it is reasonable to suppose that uncoiling affects the lowering of the nonelastic modulus. In the second part of region II, the molecular uncoiling ultimately leads to the straining of tie molecules, and the covalent bond angles change.

Because the chain modulus of the taut-tie molecules is relatively high, the tensile modulus of the fiber starts to increase. Because of the length distribution of the molecules, the molecules cannot bear the load at the same time, and the modulus increases gradually. A prerequisite for the tie molecules to increase the modulus when becoming taut is that they are constrained by crystals. The scissions of chains cause the modulus to pass through the second maximum. Beyond the second modulus maximum, the broken chain ends recoil, and the amount of gauche increases again. In

region III, with the molecules breaking up and coming out from the crystal, the modulus decreases again.

Comparing Figure 1 with Figure 2, we find that the second modulus maximum of PA is higher than the first one. It is thought that the molecule of the PA fiber curls, having low orientation and strong circumrotations. According to the entanglement network theory, the lower the orientation is, the lower the tenacity is. Therefore, it is easier to break the network. The second modulus maximum of the PA fiber is at the strain of 10%, and that of the PET fiber is at 8%. This also reflects that the PA molecule curls more than that of PET.

## CONCLUSIONS

As discussed previously, the changes in the molecule in the amorphous regions arise from the modulus reduction. The volume fraction of the amorphous region, the length distribution of the tie chains between successive crystals, and the amorphous orientation factor are the main structural parameters used for the discussion of the modulus. Increasing the crystallinity and lowering the contour length distribution will raise the modulus. According to the entanglement network theory, raising the orientation will also raise the modulus.

The modulus valley is a disadvantage for industrial PET and PA fibers, especially for tire cords, in which the fibers are continuously strained at 2–5%.<sup>10</sup> Therefore, raising the modulus of this region is the aim of analyzing the relationships between the physical structures of fibers and the modulus-strain curves. Some high-performance materials, such as PET/Mt and PA/Mt nanocomposites, are on their way. These materials will make the production of new high-performance fibers come true. Giza et al.<sup>11</sup> spun PA/Mt nanocomposites. The modulus of the yarn, which is composed of a 2 wt % Montmorillonite (MMt) dispersion, is greater than that of general PA yarns. In the near future, the equipment and techniques will be further improved and applied to producing and measuring yarns with a variety of structures and properties.

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