

Tie Chains and Modulus of Nylon 6 Fibers

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Synopsis

A large number of nylon 6 fiber samples with varying internal structure were obtained by changing draw ratios, drawing temperature, and quenching immediately after drawing. Modulus of these samples is analyzed by Takayanagi model and fraction of tie chains is obtained. It is observed that the modulus of these samples is directly proportional to the fraction of tie chains.

INTRODUCTION

Synthetic fibers are composed of crystalline and noncrystalline phase. One phase differs from the other in structural regularity, primary dispersion, elasticity, and other properties. Simultaneous presence of both the phases complicates the situation for the interpretation of fiber properties, for example modulus, which requires the exact formulation of the models including coupling between amorphous and crystalline phase.

Takayanagi^{1,2} has assumed the mechanical coupling of the crystalline and amorphous regions for the bulk crystallized polymers with spherulitic structure on the basis of knowledge of crystalline texture obtained by morphological studies and had tried to interpret the difference in mechanical behavior of the samples with different degrees of crystallinity by using suitable model systems. Recently, Takayanagi³ used a model for highly drawn polypropylene considering the tie molecules as one of the components. The tie molecules are formed in the process of unfolding the chains during drawing. They are thought of as a connection in the axial direction of the crystalline blocks they are anchored in. The majority of the tie molecules are located on the outer boundary of microfibrils.³ The first reference to the structure of microfibrils as well as highly extended interfibrillar tie molecules appear in diffusion and deformation studies of Peterlin.⁴

Prevorsek et al.^{5,6} indicate that these extended interfibrillar tie molecules for nylon 6 and other fibers should be considered as a separate phase. According to them, the extended chain interfibrillar domains are the strongest element of fiber structure and have an important effect on fiber modulus, strength, etc. The molecules from the interfibrillar extended chain matrix can form epitaxial intercrystal bridges. Especially in case of nylon 6, which exists in widely different crystal or ordered forms,^{7,8} it may be reasonable to assume that interfibrillar domains exist in some ordered structure. For analysis of modulus of nylon 6 fibers, it may thus be appropriate to consider the interfibrillar domains having modulus equal to that for a oriented crystal with the *c*-axis parallel to the fiber axis.

The present paper deals in analysis of modulus of nylon 6 fibers based on suitable model considering "the role of tie molecules."

CHOICE OF MODELS

It has been shown⁹ that in cases where the properties of the crystalline and amorphous phases are known, the mechanical behavior of the semicrystalline polymers can be reproduced by means of unit cube models. One of these models used by Prevorsek¹⁰ for nylon 6 is based on the assumption that crystallites are embedded in the amorphous matrix. An alternate model assumes that amorphous regions are embedded in crystalline matrix. The models are shown in Figure 1 as A and B, respectively. The two models are not equivalent due to the directional effects in the fibrous system.

In case of model A, the crystallite aspect ratio, i.e., the length to diameter ratio of the crystallites, has a fundamental influence on the load-transfer characteristics and thus the modulus of the fiber.¹⁰ For this model, equal stress-load transfer is approached when the crystallites are platelets oriented perpendicular to the fiber axis. For model B as used by Takayanagi³ the tie chains act as crystalline linkages in series with folded chain crystalline blocks separated by amorphous regions. The description of model B is consistent with Prevorsek's reference of extended chain interfibrillar domains.

The model of Peterlin assumes the taut tie molecules (TTM) bridging the amorphous layers between the crystal blocks and suggests that these TTM would cause the modulus to increase.¹¹ Model B thus appears to be plausible for modulus analysis and is selected for the present analysis. The expression for fraction of tie chains for this model is given in the Appendix.

One of the parameters required for such model analysis is crystallinity. In the case of nylon 6, it may be reasonable to assume that interfibrillar domains have ordered structure and, as a first approximation, are included in X-ray crystallinity.

EXPERIMENTAL

As spun nylon 6 multifilament yarn (140/10/10) were obtained from Shree Synthetics, Ltd. and drawn on a laboratory stretching unit. The draw ratios used for these experiments were 2.5, 3.5, and 4.5. The temperature of the pin in drawing zone was kept at temperatures of 35°C, 70°C, 110°C, 150°C, and 190°C. A quenching system with temperature of about -16°C was used after

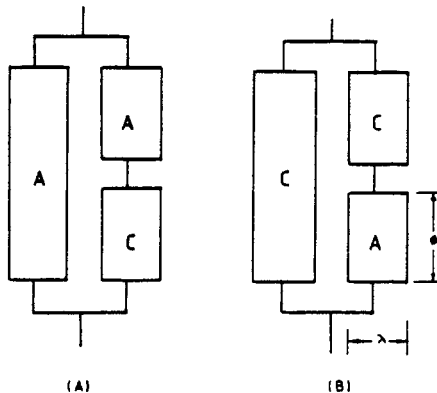


Fig. 1. Mechanical unit cube models: (A) crystallites embedded in amorphous matrix; (B) amorphous regions embedded in crystalline matrix.

the drawing zone to prepare the quenched samples. The samples thus obtained were given dry heat treatment at 120°C for 20 min directly on the bobbins. The heat set samples were used for conducting further experiments.

Density was measured in a Davenport density measuring apparatus. Xylene and carbon tetrachloride were used for setting up the density gradient column.

X-ray diffraction curves were obtained by means of a Norelco wide-angle X-ray diffractometer directly coupled with a Philips dynamaster strip chart recorder. CuK_α radiation were used with Ni-filter. The amorphous pattern for nylon 6 sample was obtained from literature,¹² and it was superimposed onto the experimental scattering curve from the samples. Percent crystallinity was obtained by the following equation:

$$\text{crystallinity } (X_c) = \frac{\int_0^\infty s^2 \cdot I_c(s) ds}{\int_0^\infty s^2 \cdot I(s) ds}$$

where $s = 2 \sin \theta / \lambda$, $\lambda = 1.54 \text{ \AA}$, $I(s)$ = intensity of coherent scattering from specimen at point s , and $I_c(s)$ = intensity of crystalline peak from same point of same specimen, and X_c represents weight fraction crystallinity. It was converted into volume fraction crystallinity by means of density.

The modulus of the yarn was determined with an Instron tensile testing machine (model no. 1112). The rate of extension of 5 cm/min was used, and load-elongation curves were obtained. These were converted to true stress-strain curves. The initial modulus was obtained from a representative curve as the initial slope.

RESULTS AND DISCUSSION

Densities as obtained from density gradient column are given in Table I. Volume fraction X-ray crystallinity was calculated from weight fraction crys-

TABLE I
Density at Different Draw Ratios and Draw Temperature

Draw ratio	Draw temp (°C)	Normal (gm/cc)	Quenched (gm/cc)
4.5	35	1.1271	1.1252
	70	1.1291	1.1260
	110	1.1367	1.1321
	150	1.1261	1.1237
	190	1.1241	1.1222
3.5	35	1.1268	1.1240
	70	1.1310	1.1270
	110	1.1435	1.1291
	150	1.1301	1.1265
	190	1.1288	1.1250
2.5	35	1.1241	1.1227
	70	1.1295	1.1249
	110	1.1335	1.1270
	150	1.1275	1.1241
	190	1.1265	1.1237

tallinity and density. These values are given in Table II. The value of crystalline density for nylon 6 used here is taken as 1.23 gm/cc.¹³ The trend in the variation of density values and X-ray crystallinities with processing parameters are similar as seen from Tables I and II. As Nylon 6 exists in various crystalline and pseudocrystalline forms, the density itself is not a good measure of crystallinity and is not used for analysis of modulus.

The quenched samples have lower X-ray crystallinities as compared to unquenched ones. These data indicate that in normal processes of drawing a slight improvement in the overall crystallinities of sample continues even after the drawing process is over. This is associated with occasional breaking of hydrogen bonds in the unquenched samples and thereby improving the structure of the fibers. The effect of drawing temperature on crystallinity is related intimately to the process of crystallization for nylon 6. The maximum rate of crystallization for nylon 6 in undrawn state is $\sim 140^{\circ}\text{C}$. In the present situation, the stress-induced crystallization also plays a role in addition to the thermal-induced crystallization. As a result of this, the maximum rate of crystallization is expected to shift towards lower temperatures. The maximum crystallinities are observed for samples with drawing temperature of $\sim 110^{\circ}\text{C}$ as seen from Table I and is probably indicative of the shifts mentioned above.

The initial modulus as determined by Instron for the samples are given in Table III. The trend observed in the variation of initial modulus as a function of the draw ratio and drawing temperature are consistent with the reported literature.¹⁴ The effect of quenching immediately after drawing has resulted in a substantial increase in the modulus of the samples. It must be remembered that all the samples were given a treatment at 120°C for 20 min, thereby erasing significant thermal history and relaxing some of the frozen-in stresses in the samples due to quenching processes.

TABLE II
X-Ray Volume Fraction Crystallinities at Different Draw Ratios and Draw Temperatures

Draw ratio	Draw temp ($^{\circ}\text{C}$)	Normal sample (%)	Quenched sample (%)
4.5	35	46	45
	70	51	48
	110	57	51
	150	50	48
	190	49	45
3.5	35	41	38
	70	54	44
	110	62	53
	150	48	44
	190	47	43
2.5	35	47	39
	70	53	48
	110	62	55
	150	51	48
	190	49	44

ANALYSIS OF MODULUS

Modulus analysis on the basis of model B (Fig. 1) has been carried out. It is clear from the equations corresponding to this model (the Appendix) that, in order to apply this method in determining the appropriate model parameters, i.e., values of λ and ϕ , one requires knowledge of E_f , the fiber modulus, E_c , the effective crystalline modulus in the fiber, E_a , the effective amorphous modulus in the fiber, and the product $\lambda\phi$, which represents the volume fraction of amorphous regions. The values for E_c and E_a used here are 24.0 and 0.7 GN/m² as reported earlier.^{15,16} Volume fraction of amorphous regions are obtained from X-ray crystallinities as given in Table II.

Analysis for all the samples have been carried out for vertical and horizontal dimensions of the unit cube models. All these values are reported in Table IV. The values of λ varies in the range of 0.79–0.99. The values of ϕ varies in the range of 0.38–0.70. These values show that the load sharing is mainly of parallel type with strong series–parallel coupling. As described earlier, it would be appropriate to assume that $(1 - \lambda)$ in model B equals the fraction of taut tie molecules (TTM). The fraction of TTM increases with increasing draw ratio as observed from Table IV. The draw ratio 2.5 is far less than natural draw ratio; thus the fraction of TTM chains is much less. With increasing draw ratio, this fraction (TTM) goes on increasing. Details of such transformation from folded crystalline regions to extended chains have been reported earlier.¹¹ The fraction of such TTM is ~5% higher in quenched samples as compared to corresponding unquenched samples. This is related to the freezing of a fraction of TTM chains, which otherwise may reorganize in unquenched samples. There is no significant variation of the fraction of TTM as a function of drawing temperature.

The variation of ϕ is most interesting with drawing temperature. ϕ has a minimum value for drawing temperatures of 110°C. This temperature nearly corresponds to the maximum rate of crystallization under the present drawing conditions. Thus the relative dimensions of amorphous regions along the fiber axis are expected to be smaller, as observed in this analysis. The value of ϕ are

TABLE III
Initial Modulus at Different Draw Ratios and Draw Temperature

Draw ratio	Draw temp (°C)	Normal sample (GN/m ²)	Quenched sample (GN/m ²)
4.5	35	3.62	4.92
	70	3.92	5.63
	110	4.52	5.83
	150	4.32	6.03
	190	3.92	5.33
3.5	35	2.81	3.72
	70	3.22	4.02
	110	3.11	4.13
	150	3.11	4.62
	190	3.02	3.52
2.5	35	1.81	2.21
	70	1.81	2.21
	110	1.91	2.32
	150	2.00	2.41
	190	2.21	2.51

TABLE IV
Dimensions of Unit Cube Models for Different Nylon 6 Samples

Draw ratio	Draw temp (°C)	Normal sample			Quenched sample		
		Vertical dimension	Horizontal dimension	Tie chains	Vertical dimension	Horizontal dimension	Tie chains
		ϕ	λ	$1 - \lambda$	ϕ	λ	$1 - \lambda$
4.5	35	0.61	0.89	0.11	0.66	0.83	0.17
	70	0.56	0.88	0.12	0.65	0.80	0.20
	110	0.50	0.86	0.14	0.62	0.79	0.21
	150	0.58	0.86	0.14	0.64	0.79	0.21
	190	0.60	0.88	0.12	0.68	0.81	0.19
3.5	35	0.64	0.92	0.08	0.07	0.88	0.12
	70	0.50	0.92	0.08	0.64	0.87	0.13
	110	0.41	0.93	0.07	0.54	0.87	0.13
	150	0.56	0.92	0.08	0.67	0.84	0.16
	190	0.58	0.92	0.08	0.64	0.89	0.11
2.5	35	0.55	0.97	0.03	0.64	0.95	0.05
	70	0.48	0.98	0.02	0.54	0.96	0.04
	110	0.38	0.99	0.01	0.47	0.96	0.04
	150	0.51	0.97	0.03	0.55	0.95	0.05
	190	0.53	0.96	0.04	0.60	0.94	0.06

higher in the case of quenched samples, which indicates arrest of the crystallization process. This further emphasises the earlier observation that the process of crystallization continues even after the drawing is completed.

An attempt is made to relate the fraction of TTM with modulus and is shown in Figure 2. It is observed that the relationship is linear. This suggests that, beyond about 5% TTM, the modulus is dependent on the fraction of taut tie chains. This observation is consistent with Prevorsek's suggestion that the modulus is essentially determined by interfibrillar extended chains. These

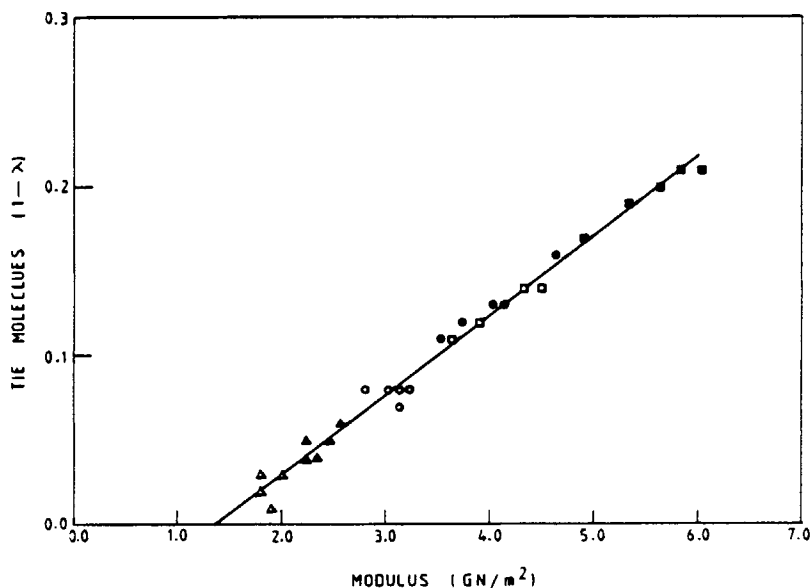


Fig. 2. Fraction of tie molecules as a function of initial modulus for nylon 6 fibers: (Δ) 2.5 normal; (\blacktriangle) 2.5 quenched; (\circ) 3.5 normal; (\bullet) 3.5 quenched; (\square) 4.5 normal; (\blacksquare) 4.5 quenched.

suggestions have been made for poly(ethylene terephthalate) (PET), nylon, and PP fibers. In contrast to the present two-phase model used for nylon 6 fibers for determination of fraction of TTM, a three-phase model was recently used for PET fibers.^{17,18} The intermediate phase for PET fibers was obtained by Lindner's method of X-rays diffraction. A linear relationship between modulus, strength, etc., was observed with the intermediate phase. A similar approach for determination of the intermediate phase is not applicable for nylon 6 fibers as it is not possible to obtain oriented amorphous samples. Further, the interfibrillar regions in nylon 6 fibers probably exist in some kind of pseudocrystalline domains, which justifies present two-phase analysis in terms of Takayanagi's models.

In the limiting case of small fractions of TTM, other factors like crystallinity and entanglements may play a significant role.

There is a large variation in the structure of the fibres in the present investigation, and it may be presumed that the relationship obtained between modulus and TTM is of a general character.

APPENDIX

The fraction of tie molecules is quantitatively evaluated on the basis of the assumption that the modulus of a strained tie molecule is equal to that of crystal along the molecular axis, using the composite model composed of the series and parallel connections of crystalline region (C) and amorphous region (A) shown in Figure 1(B).^{9,19}

The modulus of drawn sample E is calculated on the basis of the above model by the following equation:

$$E = (1 - \lambda)E_c + \lambda((1 - \phi)/E_c + \phi/E_a)^{-1} \quad (1)$$

where E_c = crystal modulus along molecular axis; E_a = modulus of amorphous phase except for tie molecules; ϕ , λ = measures of fraction of series and parallel connection of amorphous phase; and $V_a = \lambda\phi$ = volume fraction of amorphous region. If $\phi = V_a/\lambda$ is substituted in eq. (1), we obtain³

$$1 - \lambda = \frac{V_a \cdot E \cdot (E_c - E_a) - E_a(E_c - E)}{V_a \cdot E_c(E_c - E_a) - E_a(E_c - E)} \quad (2)$$

The fraction of tie molecules $(1 - \lambda)$ can be evaluated from eq. (2).

References

1. M. Takayanagi, *Proc. 4th Int. Cong. Rheol.*, 161 (1965).
2. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 50 (1963).
3. M. Kamezawa, K. Imada, and M. Takayanagi, *J. Appl. Polym. Sci.*, **24**, 1227 (1979).
4. A. Peterlin, *J. Polym. Sci., C* **32**, 297 (1971).
5. D. C. Prevorsek, P. T. Harget, R. K. Sharma, and A. C. Reimschuessel, *J. Macromol. Sci. Phys.*, **B8**, 127 (1973).
6. D. C. Prevorsek, G. A. Tirpak, P. S. Harget, and A. C. Reimschuessel, *J. Macromol. Sci. Phys.*, **B9**, 733 (1974).
7. L. G. Roldan and K. Kaufmann, *J. Polym. Sci.*, **B1**, 603 (1963).
8. J. P. Parker and P. H. Lindenmeyer, *J. Appl. Polym. Sci.*, **21**, 821, (1977).
9. M. Takayanagi, M. Harima, and V. Iwata, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 1 (1963).
10. D. C. Prevorsek, R. H. Butler, Y. D. Kwon, G. E. R. Lamb, and R. K. Sharma, *Text. Res. J.*, **47**, 107 (1977).
11. A. Peterlin, *Polym. Eng. Sci.*, **19**, 118 (1979).
12. A. Jeziorny, *J. Polym. Sci. B*, **10**, 257 (1972).
13. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.

14. H. Hattori, Y. Takagi, and T. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **35**, 1163 (1962); H. Hattori and Y. Takagi, *Bull. Chem. Soc. Jpn.*, **36**, 675 (1963).
15. D. C. Prevorsek, *J. Polym. Sci. C*, **32**, 243 (1971).
16. I. Sakurda, T. Ito, and K. Nakawe, *J. Polym. Sci. C*, **15**, 75 (1966).
17. B. L. Deopura, T. B. Sinha, and D. S. Verma, *Text. Res. J.*, **47**, 267 (1977).
18. B. L. Deopura, V. Kumar, and T. B. Sinha, *Polymer*, **18**, 856 (1977).
19. M. Takayanagi, K. Imada, and T. Kajiyama, *J. Polym. Sci. C*, **15**, 75 (1966).

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