

CONCERNING THE NEGATIVE THERMAL EXPANSION FOR EXTENDED CHAIN POLYETHYLENE

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Thermal expansion coefficients have been measured on ultraoriented polyethylene fibers. Samples were prepared by a solid-state (crystalline) extrusion in an Instron Capillary Rheometer at 136°, 2100 atm. and at a draw ratio of 50. The expansion coefficients between -150 and +50°, perpendicular to the fiber axis, were positive and of the order of $10^{-4} \text{ }^\circ\text{C}^{-1}$. Conversely, parallel to that direction, the observed values were both negative and small, of the order $-10^{-6} \text{ }^\circ\text{C}^{-1}$. Length changes were reversible and reproducible between -150 and $< +50^\circ$. Negative coefficients were attributed to the presence of highly-extended and fully-aligned chains along the fiber. Valuable information about chain conformation, dynamics and lattice perfection can be obtained for the ultraoriented morphologies simply by measuring the linear thermal expansion.

Experimental approaches to achieve theoretical limits for polymer systems have been a cause pursued by many scientists. A particular effort of our laboratory has been to produce thermoplastic morphologies of the highest possible tensile modulus. The goal appears to have practical as well as theoretical merit since the potential so far realized has led to the preparation of polyethylene filaments [1, 2] with tensile moduli as high as glass fibers [3, 4]. The preparation method consists of a solid state (crystalline) deformation process conducted at sensitively-selected conditions. The method represents a special kind of tensile draw at high draw ratios, ~ 50 , calculated as the cross-sectional area ratio of the capillary reservoir to the capillary itself for the solid state extrusion. The reservoir is 0.95 cm and the capillary 0.135 cm in diameter. The remarkable tensile properties [4] of the samples produced in this way are associated with the ultraorientation of the linear (high density) polyethylene chains along the axis of the strand extruded through the capillary. The orientation function for the crystals, as measured by wide-angle X-ray, is near 0.996 ± 0.002 [5]. This corresponds to chain alignment to less than 3.0° of the strand direction. By optical microscopy, the microfilaments within the strands are aligned within the strands with an average deviation of only 0.3° . Total bire-

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fringe measurements have been made on the polyethylene strands which suggest that the residue amorphous content of about 14% is not significantly aligned in the strand direction [5].

Chain extension, in addition to orientation, is a requirement for achieving a high polymer modulus. Nitric acid etch of amorphous chains was thus used with gel permeation chromatography to measure the fraction of chains extended [6]. The results reveal a value, consistent with other qualitative methods, indicating that 15% of the chains are extended at least to 10^3 Å in these ultraoriented polyethylene morphologies [6]. The crystal alignment plus chain extension suggest a component of perhaps 15% of what we have come to call "continuous crystals" [7, 8]. The continuous crystal concept corresponds to an idealized arrangement for polymer chains which are both fully aligned and fully extended with chain ends randomly imbedded in the crystal.

A suggestion by Smith [9] and a paper on polymer single crystal contraction by Baughman and Turi [10] has led us to evaluate our ultraoriented crystals in terms of thermal expansion. The motivation is the dramatic difference in expansion coefficient for amorphous chains and for crystals in the different chain directions. For example, a negative thermal expansion has been reported from X-ray diffraction parameters for the *c*-axis (chain direction) within crystals of polyethylene [11–14]. To be sure, the contraction along the chain axis of the crystal is very small, $-12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ from 20 to 65° and corresponding to about a 2° average twist due to rotation between consecutive planes of C–C bonds [13]. A similar value of $-(1.0-1.2 \times 10^{-5})^\circ\text{C}^{-1}$ has been estimated here from crystal lattice parameter measurements between -150 and $+60^\circ$. Importantly, heretofore the reported macroscopic expansion coefficients of polyethylene have been generally positive [10]. This is due, in good part, to the relatively high and positive thermal expansion for amorphous and unaligned chains, $\sim +2 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ [10]. Expansion is marked even in polyethylene crystals lateral to the chain direction: $a_a = 22 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ and $a_b = 3.8 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ [15].

In this study, a TMS-1 standard thermal expansion attachment was used with a Perkin-Elmer DSC-1B, Norwalk, Connecticut. A 3.0 g loading was used. This is slightly higher than the true zero loading (~ 2.6 g) necessary for the probe to follow contraction. The zero load compensates only for buoyance of the probe. Polyethylene strands of various lengths were studied. The special polyethylene morphologies principally studied here were extruded through a 30° entrance angle brass die at 136° and at 2100 atmospheres. The sample ends were cut smooth by various methods including the use of a microtome. The high density (linear) polyethylene used throughout was Alathon 7050. The number and weight average molecular weights are about 18,400 and 58,500, respectively. Importantly, it has been shown by gel permeation chromatography that there is no bond rupture during the crystal-crystal transformation preparation process [6].

The results of dimensional changes on the macromorphologies of ultraoriented polyethylene strands are shown in Figs 1 and 2. The overall volume change on heating is an expansion due to the extensive dilation perpendicular to the chain

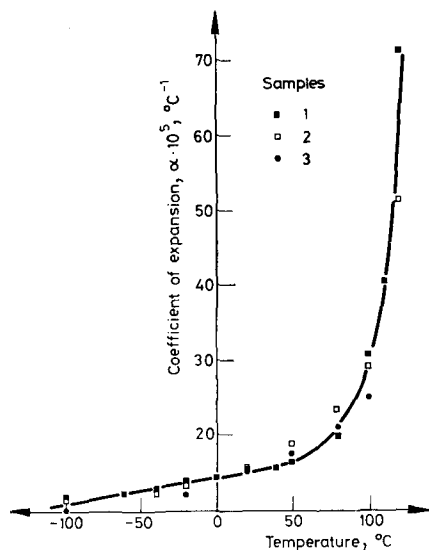


Fig. 1. Coefficient of expansion of ultraoriented high density polyethylene perpendicular to orientation

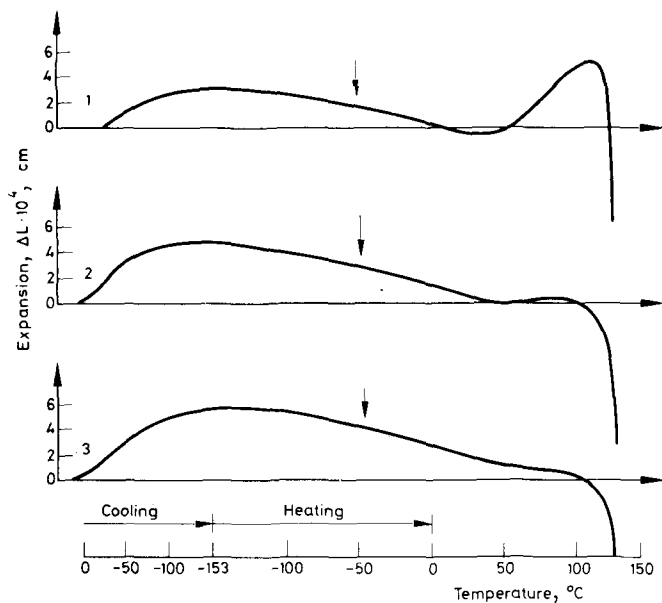


Fig. 2. Dimensional changes with temperature of ultraoriented high density polyethylene parallel to orientation

and strand direction in contrast to the small and negative coefficient along the chain-strand direction.

Figure 1 shows the coefficient of expansion perpendicular to the strand axis measured at a heating rate of 10°/minute up to 133–135°. Consistent results are given on three samples of 0.135 cm in diameter. In the range from –150 to +90°, the diameter changes on the three samples were 3.35, 3.32, and 3.04%. A more rapid expansion was observed at higher temperature between 90 and 133–135° corresponding to an additional 3.25, 3.28 and 3.17%, respectively. Expansion coefficients were determined by drawing a tangent to the thermogram at the desired temperature followed by the determination of the slope and division by sample thickness.

Table 1 and Fig. 2 describe three samples and their dimensional changes on heating and cooling parallel to the chain-strand direction. These three samples are similar but not identical with samples 1, 2 and 3 for expansion experiments parallel to orientation. They were cut from the same strands as those for parallel coefficient measurements and they displayed similar variations in their behavior as the prior three samples. It may be speculated that the one with the lowest expansion perpendicular to orientation resembles, or corresponds to, that which shows a marked positive expansion above +50° in the direction parallel to orientation (sample number 1 in Table 1 and Fig. 2). Similarly, the one with the highest expansion perpendicular to orientation could correspond to that with no expansion above +63° in the parallel arrangement (sample No. 3 in Table 1 and Fig. 2).

Starting at ambient, a remarkable expansion is observed on cooling and a contraction on heating with all changes being entirely reversible below 40°. This ther-

Table 1
Dimensional change of ultraoriented polyethylene in the direction parallel to orientation

Specimen No.	1	2	3
Thickness (cm)	0.305	0.356	0.366
Expansion coefficient at 25°C (°C ⁻¹)	-8.9×10^{-6}	-9.6×10^{-6}	-8.7×10^{-6}
Average expansion coefficient from –153 to 25°C (°C ⁻¹)	-5.8×10^{-6}	-5.9×10^{-6}	-5.3×10^{-6}
Expansion % on cooling from +25 to –153°C	0.10	0.13	0.15
Contraction % on heating in indicated range (°C)	0.12 (–153 to +37)	0.13 (–153 to +53)	0.12 (–153 to +63)
Premelting behavior in the indicated range (°C)	Expansion (37–115)	Slight expansion (53–93)	No change (63–93)
Change in slope	–53	–52	–49

Table 2

Locus of polyethylene chain components in ultraoriented strands

Crystalline component	
(All in extreme orientation as measured by X-ray)	
In extended chains (in "continuous" crystals and/or crystalline "tie" chains)	15 ± 3 %
Strand-oriented chain-folded lamellae	71 ± 3 %
Total by calorimetry	86 ± 2 %
Amorphous component	
(randomly oriented as estimated by birefringence)	
Load supporting	< 0.5 %
In chain folds	> 4 %
In defects; kinks and dislocations	< 10 %
Total by difference	14 ± 2 %

mal reversibility indicates that the observed dimension changes are not due to relaxation processes such as relief of stressed tie chains.

The length change between -150° and ambient is only $\sim -0.1\%$. In each curve, a minor break occurs at $-51 \pm 2^\circ$ which we note but reserve assignment. The break does occur at near the minimum in $\tan \delta$ as measured independently [6], as observed by Wada. Above $+40^\circ$ and prior to complete melting, a distinction is observed between samples which may provide a sensitive characterization of minor variations in thermal history of the strands. Observations in the different cases indicate a marked positive to no further dimensional change up to temperatures for the sizable premelting expansion.

There is a substantial difference in thermograms obtained for the directions perpendicular and parallel to orientation. For the former, a continuous expansion can be observed up to the temperature $\sim 133-135^\circ$ (under used load 3 g). Thermograms have a sharp peak followed by a sudden rapid drop indicating a total structure collapse. However, in the direction parallel to orientation, there is, after contraction, either a marked positive or no further dimensional change and then again ($\sim 90-100^\circ$) a much greater contraction. It is important to note that this effect in the orientation direction is seen far from the melting temperature and that this change is not so sharp as the change in the perpendicular direction near the melting point. From those three measurements given in Fig. 2, it appears that the most perfect sample and/or the best measurements, were the test sample No. 3. Here only a short temperature interval of no dimensional change prior to the accelerating contraction is observed. Note also the increase of temperature up to which samples contract on heating from -150° to $+37, 53, 63$, respectively, for sample Nos 1, 2 and 3. This suggests that there could be even more perfect samples or better performed measurement (especially preparation of perfectly-flat samples) which will display only contraction on heating. The dependence of contraction on

temperature would be similar to that for expansion in the direction perpendicular to orientation, namely increasing rapidly in the upper temperature range. In analogy, if we say that there is a sizable premelting expansion in the direction perpendicular to orientation, there must also most likely be a sizable premelting contraction in the parallel direction. However, it cannot be absolutely confirmed that this accelerating contraction, recorded in our experiments at higher temperature (above 90°), is only and exclusively due to a real contraction in the chain direction. It could be also a consequence of sample preparation or cylindrical geometry, i.e. the result of softening of curved surfaces; the unlikely effect of sample weighing (compression), or due to the increasing mobility and contraction of polymer chains.

Measurements on unit cell parameters have been carried on mostly in the lower temperature regions. For example, Davis et al. did in the region -180 to $+60^\circ$ [12]. A continuous contraction of the unit cell in the chain direction was found up to their highest temperature 60° . It appears that there is no reason why this should not continue at yet higher temperatures. Kobayashi and Keller found that contraction in the chain direction is actually more pronounced in the upper temperature range [13]. They studied unit cell parameters for single crystals (annealed at $120-125^\circ$) and for pressure crystallized polyethylene (4300 atm), $\alpha_c = -2.1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ for the region $20-65^\circ$. For the temperature range $20-125^\circ$, Kobayashi reports a value $\alpha_c = -2.1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. That means, using their values, that α_c between $65-120^\circ$ is $-2.84 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ — more than twice the value for $20-65^\circ$. This suggests that α_c has a similar temperature dependence as α for the perpendicular directions — i.e. rapidly increasing as the temperature approaches the melting point.

From the data in Fig. 2, it may be calculated that, near ambient, strand length changes are predominantly controlled by the chain-extended, continuous crystal component of near 15% [6]. This conclusion adds to prior evidence by nitric acid etching plus gel permeation chromatography which shows there is a major ($\sim 15\%$) crystalline component which extends $> 1000 \text{ \AA}$ [6]. Using the values for expansion coefficients given above, we estimate a negligible amount of unoriented amorphous chains which can be involved in supporting the small tensile loads for measurement along the strand axis. It is perhaps necessary to state that any contribution by the amorphous phase to length changes should come from a series coupling with the extended chain component. Amorphous chains in parallel with continuous crystals do not contribute because of the much lower stiffness of the former. This has been calculated by equating the measured coefficient with the sum of contributions for extended crystals and for an amorphous component; i.e. $-9 \times 10^{-6} = 2 \times 10^{-4} \chi + (1 - \chi)(-12 \times 10^{-6})$ where χ is the fraction of unoriented amorphous chains which controls the length dimension. It is thus important to reiterate that the amorphous content of about 14% (as indicated by thermal analysis and infrared) is essentially randomly oriented as indicated (with large uncertainty) by birefringence [5]. Thus about 86% of the polyethylene chains are crystalline (15% of all chains are estimated to be extended). Thus the folded (non-extended) chains are about 16% amorphous. Added data from low angle X-ray have indicated a

conventional fold period of about 230 Å (5) or of about 180 carbons in the length of a folded crystal. If it is assured that a minimum of 6–8 carbons are involved in a fold, then the folds will account for more than 4% of the amorphous content since all folds are certainly not an adjacent re-entry. To summarize, for the locus of crystalline and amorphous (gauche bond locations) we suggest the over-simplifications given in Table 2.

Kim and DeBatist have also recently reported a negative thermal expansion coefficient for polyethylene [11]. No absolute values are given, however, for their study from 100 K to ambient on a less-defined low-density polyethylene. For a draw ratio of four, we estimate from their data coefficient of expansions of $\sim -5 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ for 60° below ambient to ambient and $-1.5 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ for the full range from liquid nitrogen temperature to ambient. Their plot of length versus temperature is of similar shape as given here in Fig. 2. Significantly, they found, but did not discuss, a break in their expansion curve at -50° which is similar to the break reported here in different samples at -53 , -52 and -49° . An unresolved concern is the magnitude for their negative expansion coefficient which is 0.3 to 5 times higher (depending on temperature range for calculation) than the estimated theoretical limit for extended chain crystals [10].

The simply-obtained and representative linear expansion data given here indicate that valuable information can be obtained on chain conformation and lattice perfection for ultraoriented and chain-extended morphologies. This case of linear polyethylene is dramatic since the thermodynamically most stable morphology involves all extended chains for the planar zig-zag packing in an orthorhombic unit cell. The perfect morphology thus provides no basis for further expansion in the chain direction and a mechanism for contraction as by the theory of rubber elasticity. Thus, chain rotations from trans to gauche will reduce the contour length.

The effects here are predominantly due to extended and oriented crystals. The results also provide some accounting of the location of amorphous chain segments. The negative expansion in the filament direction is remarkable particularly as less than 6% of random amorphous content leads to a positive expansion coefficient for polyethylene [10]. This suggests that a component of continuous crystals is extent in these morphologies and, by another nomenclature, is consistent with the presence of crystalline tie chains.

Based on these concluded preliminary experiments, we would hopefully study subsequently the sensitivity of this expansion coefficient method to the variation in morphological perfection induced by changes in preparation conditions including pressure and temperature.

An interesting feature of these ultraoriented morphologies is related to their unusual expansion characteristics. That is, the ultraoriented polyethylene strands simply do not melt even at temperatures well over their maximum equilibrium atmospheric melting point of near 140° – while they are held at ambient pressure in the capillary used for preparation. This non-melting is because the capillary confines the morphology in the only direction the crystal lattice can expand. Melting is thus prohibited because the chains are unable to change dimension in the

strand length dimension, i.e. at the ends of the capillary, where the sample is exposed to atmospheric pressure.

An added significant ramification of this study involves the use of these special morphologies as strength members in a one-polymer system. The ultraoriented strands melt above the temperature of the conventional morphology of the same polymer by about 5°. Thus the strand can be imbedded in the melt of the same polyethylene to form on cooling a composite of high interfacial strength. Studies of absolute and differential expansion coefficients are thus crucial to properties of the resultant one polymer composite.

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RÉSUMÉ — On a mesuré les coefficients d'expansion thermique de fibres de polyéthylène ultra-orientées. Les échantillons ont été préparés par extrusion à l'état solide (état cristallisé) dans un rhéomètre capillaire Instron, à 136°, 2100 atm., avec un rapport d'étirement de 50. Entre -150 et +50° les coefficients d'expansion perpendiculaires à l'axe des fibres sont positifs et de l'ordre des $10^{-4} \text{ }^{\circ}\text{C}^{-1}$. Les valeurs observées parallèlement à cette direction sont, par contre, négatives et faibles, de l'ordre de $-10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Entre -150 et > 50° les changements de longueur sont réversibles et reproductibles. On a attribué les coefficients négatifs à la présence de chaînes fortement allongées et complètement alignées le long des fibres. On peut obtenir des renseignements précieux sur la conformation des chaînes, la dynamique et la perfection des réseaux dans le cas de morphologies ultra-orientées en mesurant simplement l'expansion thermique linéaire.

ZUSAMMENFASSUNG — Thermische Expansionskoeffizienten wurden an ultraorientierten Polyäthylenfasern gemessen. Die Proben wurden durch Festphasen- (kristalliner) Extrusion in einem Instron Kapillar-Rheometer bei 136°, 2100 Atm. und einem Ziehverhältnis von 50 hergestellt. Die zur Achse der Phase perpendikulären Expansionskoeffizienten zwischen -150 und +50° waren positiv und in der Größenordnung von $10^{-4} \text{ }^\circ\text{C}^{-1}$. Umgekehrt waren die parallel zu dieser Richtung beobachteten Werte sowohl negativ wie auch kleiner, in der Größenordnung von $10^{-6} \text{ }^\circ\text{C}^{-1}$. Die Längenveränderungen zwischen -150 und $> +50^\circ$ waren reversibel und reproduzierbar. Negative Koeffizienten wurden der Anwesenheit stark gedehnter und voll geordneter Ketten längs der Fasern zugeschrieben. Wertvolle Informationen betreffs Kettenkonformation, Dynamik und Gitterstruktur ultraorientierter Morphologien können durch einfaches Messen der linearen thermischen Expansion erhalten werden.

Резюме — Были измерены коэффициенты термического расширения сверхупорядоченных полиэтиленовых волокон. Образцы были получены выдавливанием в твердом состоянии (кристаллическом) в Инстрон Капиллярном Реометре при 136°, 2100 атм и с отношением вытягивания 50. Коэффициенты расширения между -150 и +50° и перпендикулярно оси волокон были положительны и порядка $10^{-4} \text{ }^\circ\text{C}^{-1}$. Однако, в случае параллельно к оси волокон, наблюдаемые значения были отрицательны и малы — порядка $-10^{-6} \text{ }^\circ\text{C}^{-1}$. Изменения длины волокон были обратимы и воспроизводимы между -150 и $> +50^\circ$. Отрицательные коэффициенты были отнесены за счет наличия высоко-растянутых и полностью линейных цепей вдоль волокна. Ценная информация о конформации цепи, динамике и совершенстве решетки может быть просто получена для сверхупорядоченных морфологий измерением линейного термического расширения.