Full Paper: The present paper discloses the changes in the nanostructure as revealed by small-angle X-ray scattering (SAXS) of synchrotron radiation of anisotropic semicrystalline samples of polyester and poly(ether ester) type differing in their chemical composition, while subjected to controlled progressive elongation. From the group of polyesters poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT) were selected. Two PBT-based commercial poly(ether ester)s were also studied differing in the molecular weight of their soft segments (poly(tetramethylene glycol) being 1000 (Arnitel® EM550) and 2000 (Arnitel® EM400), respectively. A blend of PBT and EM550 (40/60 by wt.) was also characterized. All materials underwent the same sample preparation process resulting in highly oriented “bristles” of 1 mm diameter. It was found that $\varepsilon_p$, the elongation at break, strongly depends on the flexibility of the glycol residues of the materials studied – ranging from $\varepsilon_p = 8\%$ for PET that contains ethylene glycol residues, through $\varepsilon_p = 18\%$ for PBT including the more flexible tetramethylene glycol (TMG) up to $\varepsilon_p = 510\%$ for the PEE containing the longest PTMG moieties. During straining the relationship between the external elongation $\varepsilon$ and the changes in the long spacing $L$ was determined. After relaxation from each deformation step the relationship between the tensile set $\varepsilon_s$ and the long period $L$ was also followed and discussed. Such analysis led to a model describing the nanostructure evolution during the deformation–relaxation cycle that finally was verified and refined utilizing the multidimensional chord distribution function (CDF) computed from the anisotropic SAXS patterns.

Deformation Behavior of PET, PBT and PBT-Based Thermoplastic Elastomers as Revealed by SAXS from Synchrotron

Norbert Stribeck$^1$, Stoyko Fakirov$^2$, Anton A. Apostolov$^2$, Zlatan Denchev$^3$, Rainer Gehrke$^4$

$^1$Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, 20146 Hamburg, Germany, Fax: +49 40-4123-6008, eMail: Norbert.Stribeck@desy.de

$^2$Laboratory on Structure and Properties of Polymers, University of Sofia, 1126 Sofia, Bulgaria

$^3$Department of Polymer Engineering, University of Minho, Campus Azurem, 4800–058 Guimarães, Portugal

$^4$HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany

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Introduction

Poly(ether ester) block copolymers exhibit an extraordinary combination of elasticity, toughness, low temperature flexibility, and strength at 150°C. They are now of great commercial importance as engineering type thermoplastic elastomers. This set of properties is related mainly to the existence of cross-links tying the array of macromolecules into an infinite network. In
natural rubber and synthetic elastomers these crosslinks repre-
sent chemical bonds. In thermoplastic elastomers, thermally
labile tie points held together by physical forces replace them.
These junctions may be glassy, crystalline or even hydrogen
bonded molecules or ionic associates.\textsuperscript{[1]}

In order to behave as a thermoplastic elastomer, the
molecules must contain two types of units, blocks or chains
segments forming a soft and a hard phase. The soft chain
segments form an amorphous phase (above the glass transi-
tion temperature $T_g$). They impart elastomeric character to the
copolymer whereas the hard blocks are capable of intermolec-
ular association with other hard blocks; they should form a
solid phase in the service temperature range in order to impart
dimension stability to the array of molecules. At high tem-
perature, dissociation of the physical bonds occurs. The soft and
hard blocks may be arranged in various ways, randomized or
ordered. Their way of ordering affects the physical and me-
chanical properties of the material.\textsuperscript{[1, 2]}

Thermoplastic elastomers are an attractive object for struc-
tural investigations not only because of their peculiar me-
chanical properties, but also because they offer many mod-
eling opportunities due to their crystallizability, multiblock
character and possibility of varying both the block flexibil-
ity and length. There are also a lot of unanswered ques-
tions concerning the deformation mechanism of this class of
polymers as compared to classical rubbers. For this reason
the relationship between macro- and microdeformation was
systematically studied during the last decade\textsuperscript{[3±9]} by means
of small-angle X-ray scattering (SAXS). All studies were
carried out on polyblock poly(ether esters) (PEE) consisting
of so-called “bristles” were prepared by first drawing (\textsuperscript{or}
C in a vac-
uum for 6 h. Measurements were performed with or without
application of stress on high power X-ray sources\textsuperscript{[3±9]} resulting
in high-resolution two-dimensional (2D) SAXS patterns.
Development of methods for the evaluation of such patterns
has been regarded as well.\textsuperscript{[10±14]}

In our early SAXS studies\textsuperscript{[3]} on such samples a directly
proportional increase of the long spacing $L$ with the applied
strain was found for a relative elongation $\varepsilon < 100\%$. At higher
elongation pulling out of tight tie molecules from adjacent mi-
crofibrils occurs and some of the tie microfibrils relax, leading
to appearance of two coexisting long periods. A model was
suggested that described the behavior of the polymer system
under and after application of stress.\textsuperscript{[3]}

In subsequent investigations\textsuperscript{[4, 5]} the model was success-
fully applied to characterize the changes in the SAXS patterns
of a set of 6 different PBT/PEG poly(ether esters) varying in
their hard-to-soft segment ratio. By means of results from
a two-dimensional (2D) detector it was possible to advance
the model, revealing finer details in the copolymer nanostruc-
ture.\textsuperscript{[5]} So at low macrodeformations two-point SAXS pattern
of the oriented PBT/PEG segmented block copolymer were ob-
tained. It was accepted that the morphology of the neat bristle
represents assemblies of parallel crystalline lamellae oriented
perpendicularly to the draw direction. The four-point patterns
observed in the relaxed, unloaded state were explained by a
zigzag arrangement of lamellae, the crystalline layers being
tilted with respect to the drawing direction. The observed mor-
phological transition was found to be reversible and emerged
more and more as the reversing deformation was increased in
the series of straining cycles.\textsuperscript{[3]}

A recent SAXS study\textsuperscript{[6]} with data from a rotating anode
indicated the occurrence of a complex “six-point” SAXS pat-
tern in both stressed and relaxed bristles. Applying comput-
erized graphical analysis of the patterns, we obtained indirect
evidence of a six-point diagram.

Utilizing synchrotron radiation\textsuperscript{[9]} two-, four- and unique
six-point small-angle patterns as well as the corresponding
transitions were clearly recorded. Five deformation intervals,
dependent on the elongation level, were identified for the ther-
mosplastic elastomer in question. The variation of the 2D scat-
tering pattern in the straining cycles resulted in clear evidence
concerning the six-point pattern by demonstrating that it is
arising from two basic morphological ensembles related to the
two- and the four-point fraction of the pattern, respectively.
The former are related to relaxed stacks of domains detached
from the elastic network, and the latter to domains integrated
into it by tie-molecules still operating. This appears to be the
only plausible explanation, because the peak position of the
two-point feature of the SAXS pattern did not respond to the
cycling strain, whereas the four-point feature did so and, more-
ever, the four-point feature vanished more and more as the re-
versing deformation was increased in the series of straining
cycles.\textsuperscript{[12]}

It was concluded that the preoriented polymer bristle can
be considered a bunch of microfibrils that scatter independ-
ently for low deformations. For higher deformations, these
microfibrils correlate in the transverse direction, too, and the
interfibrillar distance was calculated in this case.

There are two goals of this study. Applying the same ap-
proach – namely following the relationship between macro-
and microdeformation by means of SAXS recorded during the
measurement under and without stress we intend (i) to investi-
gate the behavior of commercial PEE comprising as soft seg-
ments poly(tetramethylene glycol) (PTMG), and (ii) to inves-
tigate the behavior of the neat PET and PBT as well as the
blend PBT/PEE and to compare them with the results, obtained
earlier.\textsuperscript{[3±9]} Such a comparison will shed light on the valid-
ity of the models derived from PEE with PEG-based soft seg-
ments\textsuperscript{[3±9]} and will help to better understand the contribution
of PBT hard segment to the entire behavior of PEE.
Experimental Part

Materials

Commercial, engineering grade PET (Yambolen, Bulgaria) and PBT (Aldrich Chemical Company, melt index = 50) were used as homopolymers. Two PEEs (Arnitel®), DSM, The Netherlands), designated as EM400 and EM550, with molecular weight/weight content of the PTMG soft segments 2000/60 and 1000/35, respectively, were used independently and in the blend with PBT. Before preparing the blend the component materials were finely ground and dried at 100°C for 24 h. The blend itself was obtained by mixing of PBT and EM550 in a ratio of 40/60 by wt. The blend components are immiscible. Bristles having approximate diameters of 2 mm were obtained using a Melt Flow Index apparatus (MFI-6542, Donau Electronics, Switzerland) at appropriate temperature, depending on the polymer. The melt was kept in the barrel for approx. 10 min and subsequently extruded through the nozzle (2 mm diameter) into ice-cold water by applying a constant force of 220 N to the plunger.

The as extruded bristles were drawn in a tensile testing machine (Zwick 1464) at room temperature and a strain rate of 20 mm·min⁻¹ to a draw ratio λ = 3.6–4.0, which resulted in a final diameter of about 1 mm, followed by annealing for 6 h with fixed ends in a vacuum oven at 210°C for PET, 180°C for PEE and the blend PBT/PEE.

Methods

Small-angle X-ray scattering measurements under stress were performed using a frame allowing controlled variation of the sample length. Each measurement under stress was followed by one in the absence of stress (in the ‘relaxed state’) before a larger deformation was applied in the subsequent cycle. Thus, the samples were studied in various deformation ranges, depending on their extensibility which was as high as 500% for the PEE EM400. Here an in the following, the elongation was denoted, for example, as ε = λε₀, where the fi rst number represents the tensile set (i.e. the strain at the end of the second domain), and correlations among domains more distant are manifested in consecutive peaks at longer distance. As has been expatiated in several papers,[11,15,16] the CDF is computed from the scattering intensity I(s) by

\[ z(r_1, r_2) = -\mathcal{F}^2 \left( 4\pi^2 (s_1^2 + s_2^2) \{I(s)\}_2 (s_1, s_2) - B(s_1, s_3) \right), \]

with the projection of the scattering intensity on the representative \((s_1, s_3)\)-plane,

\[ \{I(s)\}_2 (s_1, s_3) = \int I(s) \, ds_2, \]

the factor \(-4\pi^2 (s_1^2 + s_2^2)\) being equivalent to the Laplacian in physical space, \(B(s_1, s_3)\) describing a background determined by spatial frequency \(\mathcal{F}\) of \(4\pi^2 (s_1^2 + s_3^2)\) \(\{I(s)\}_2 (s_1, s_3)\), and \(\mathcal{F}^2 \) denoting a 2D Fourier transformation.

Results

Figures 1–7 display the results taken from the homopolymers PET and PBT, of the commercial thermoplastic elastomer of PEE type comprising PTMG as soft segments, of the blend PBT/PEE and two types of the same PEE differing in their hard-to-soft segment ratios. The results are represented as 2D scattering patterns and as graphs showing the long spacings \(L\) as a function of the elongation (\(ε\) or \(ε_r\)). The \(L\) values were calculated by means of the Bragg’s law from the positions of the peak maxima of both two- and four-point scattering patterns. The results shown in Figures 1–7 represent the two basic states of the samples – both under stress as a function of the tensile deformation, \(ε\), and after relaxation as a function of the residual deformation, \(ε_r\).
Figure 1: 2D SAXS patterns (pseudo color) of bristles of PET (PBT), respectively, cold drawn, $\lambda = 3.5$ ($\lambda = 2.3$) and annealed with fixed ends for 6 h at 240 ($180^\circ$C), recorded at room temperature at a forced tensile deformation $\varepsilon$ or tensile set (residual elongation) $\varepsilon_r$ in percent as follows: (a) PET, $\varepsilon = 0$; (b) PET, $\varepsilon = 8$; (c) PET, $\varepsilon_r = 0(5.5)$; (d) PET, $\varepsilon_r = 4.7(8)$; (e) PBT, $\varepsilon = 0$; (f) PBT, $\varepsilon_r = 6.7(16.7)$. The value in parentheses is the forced elongation in percent during the previous measurement under stress. Each square covers the range $-0.15 \text{ nm}^{-1} < s_{12}, s_3 < 0.15 \text{ nm}^{-1}$ with the modulus of the scattering vector defined by $s = (s_{12}^2 + s_3^2)^{0.5} = (2/\lambda) \sin \theta$. Straining direction is vertical.
Figure 2: Long spacing L calculated from two-point patterns, vs. elongation ε or εr for the PET homopolymer: open circles – samples under stress (L(ε)); solid circles – sample in relaxed state (L(εr)). The digits show the sequence of the measurements with the progress of the external elongation ε. The ‘primed’ digits depict measurements without stress at σ = 0 at the respective residual elongation εr.

Unfortunately, due to the shortcomings of the available image plate detector system, it was impossible to obtain reliable information on the effect of deformation on the variation of the total scattering intensity. For this reason corresponding statements are missing in the present study in contrast to previous ones[3-8] performed with conventional X-ray sources.

Let us look at the presented results in the sequence defined by the increasing flexibility of the “soft” chain constituents of the materials studied, i.e., PET, PBT, PBT/PEE, PEE EM550, and PEE EM400. Such a presentation allows one to follow the effect of the chain flexibility on the relationship between macro- and microdeformation, the latter being expressed by the variations of L in the stressed (σ ≠ 0) and relaxed (σ = 0) states.

Figure 3: Long spacing L calculated from two-point patterns, vs elongation ε or εr, for the PBT homopolymer: open circles – samples under stress; solid circles – sample in relaxed state. The meaning of the digits is the same as in Figure 2.

Figure 4: Long spacing L calculated from two-point patterns vs elongation ε or εr for the blend of PBT/PEE 40:60 wt-% (PEE is Arnitel® EM550): open circles – sample under stress; solid circles – sample in relaxed state. The meaning of the digits is the same as in Figure 2.

Figure 1 shows selected SAXS patterns from the deformation-relaxation cycles at different forced (ε) or residual (εr) deformations for bristles of PET and PBT homopolymers cold drawn and annealed with fixed ends. It is important to note that the type of the scattering patterns is the same for the two homopolymers, regardless of the extent and character of deformation (ε or εr), namely all the patterns are of the two-point type. What is changed during these measurements is the shape of the peaks and the distance between the two reflections, which indicates variation of the long spacing with the progress of deformation. These changes are better expressed in the next two figures demonstrating the effect of the level and character of deformation on L. Before discussing these results, let us point out the important difference in the behavior of the two homopolymers. While PET breaks after the measurement at ε = 8% (εb > 8%), PBT displays twice the elongation at break.

Figure 5: Long spacing L calculated from two- and four-point patterns vs elongation ε or εr, for sample PEE (Arnitel® EM550): open circles – sample under stress; filled circles – sample in relaxed state; filled diamond – sample in relaxed state, (L calculated from four-point pattern). The meaning of the digits is the same as in Figure 2.
Figure 6: 2D SAXS patterns (pseudo color) of bristle of PEE (Arnitel® EM400) cold drawn (\(\lambda = 2.3\)) and annealed with fixed ends for 6 h at 180°C, collected in the strained (elongation \(\varepsilon\) in percent) or the relaxed (tensile set \(\varepsilon_r\) in percent) state, respectively: (a) \(\varepsilon = 0\); (b) \(\varepsilon = 0(50)\); (c) \(\varepsilon = 80\); (d) \(\varepsilon_r = 25(80)\); (e) \(\varepsilon = 100\); (f) \(\varepsilon_r = 25(100)\); (g) \(\varepsilon = 140\); (h) \(\varepsilon_r = 25(140)\); (i) \(\varepsilon_r = 51(250)\); (j) \(\varepsilon_r = 106(360)\); (k) \(\varepsilon = 510\); (l) \(\varepsilon_r = 205(510)\). The value in parentheses is the elongation in percent during the previous measurement under stress. Each square covers the range \(s_{12} < s < s_{3}\) with the modulus of the scattering vector defined by \(s = (s_{12}^2 + s_{3}^2)^{0.5} = (2/\lambda) \sin \theta\). Straining direction is vertical.

Figure 6 shows the dependence of \(L\) as a function of the forced (\(\sigma > 0\)) elongation \(\varepsilon\) and residual (\(\sigma = 0\)) elongation \(\varepsilon_r\), for PET. Figure 3 represents the same dependence for PBT homopolymer. Obviously the experimental points for PET (Figure 2) are rather scattered for the two kinds of measurements (\(\sigma > 0\) and \(\sigma = 0\)). For this reason it is impossible to derive any well-defined relationship between deformation and long spacing value. Nevertheless, there are two noteworthy results. First, a completely reversible response of \(L(\varepsilon, \varepsilon_r)\) upon cycling the strain up to \(\varepsilon = 5.5\%\) (Figure 2, points 2, 2’) is observed, whereas there is only partial reversibility at higher deformations. Second, comparing the increase of the long spacing for PET and PBT (Figures 2 and 3), it is observed that for the same elongation interval \(\varepsilon\) the increase of \(L\) for PET is approximately twice that for PBT (Figures 2 and 3).
Quite different is the behavior of PBT displayed in Figure 3. As compared to PET, the dependence of $L$ on the external macrodeformation can be followed in a deformation interval twice longer – up to $\varepsilon_b > 18\%$. Moreover, in the entire interval of $\varepsilon$ a very well expressed linear relationship is observed between the macro- ($\varepsilon$) and microdeformation ($L$). The respective line coincides with that of the affine deformation model, and the deformation is completely reversible up to $\varepsilon = 12\%$.

The similarity of the PET and PBT scattering patterns on the one hand, and the differences between their deformational behavior on the other hand (Figure 2 and 3, respectively), i.e., their macrodeformation limits, the reversibility of deformation and its character (affine or non-affine) lead to a preliminary conclusion regarding the reason for the differences observed. It can be attributed to the different chemical composition – replacement of the ethylene glycol (EG) moieties of PET by the longer and more flexible tetramethylene glycol (TMG) units of PBT.

Let us now examine the deformational behavior of samples containing more flexible segments, those of poly(tetramethylene glycol) (PTMG) found in the thermoplastic elastomer Arnitel® EM400: open circles – sample under stress; filled circles – sample in relaxed state; filled diamonds – sample in relaxed state, $L$ calculated from four-point pattern. The meaning of the digits is the same as in Figure 2.

Figure 7: Long spacing $L$ vs deformation $\varepsilon$ or $\varepsilon_r$ for a PEE sample (Arnitel® EM400): open circles – sample under stress; filled circles – sample in relaxed state; filled diamonds – sample in relaxed state, ($L$ calculated from four-point pattern). The meaning of the digits is the same as in Figure 2.

early, the increase is significantly lower than the prediction of an affine microdeformation.

A common feature of the PBT/PEE blend (Figure 4) and the neat PBT (Figure 3) is the reversibility of the $L$ values measured under and without stress. The corresponding values for the measurements without stress are close to the initial one, although the tensile set $\varepsilon_r$ increases with the progress of the forced elongation $\varepsilon$ and becomes almost half of the latter ($\varepsilon_r \approx \varepsilon/2$), similar to earlier studied PEE samples comprising PEG as soft segments.\cite{1-6}

The next sample of the series is the commercial thermoplastic elastomer Arnitel® EM550 comprising as soft segments 35 wt.-% of PTMG. The dependence of $L$ on $\varepsilon$ and $\varepsilon_r$ for this sample is plotted in Figure 5. The 2D SAXS patterns obtained from this sample are again of the two-point type, as those shown in Figure 1, with the exception of the pattern at $\varepsilon_r = 40\%$ where one observes a trend toward the formation of a four-point diagram, similarly to the next sample (Figure 6) and in accordance with the reports for PEE based on PBT and PEG.\cite{3-9}

What is interesting with this neat PEE is its much higher extensibility. This material breaks at $\varepsilon_b = 120\%$. Furthermore, $L(\varepsilon)$ shows an almost linear increase up to $\varepsilon = 50\%$ and obeys the affine model of deformation. At $\varepsilon = 70\%$ the $L$ value starts to drop significantly, again following a nearly linear dependence. Concerning the $L$ values measured without stress, they are close to the initial one at $\varepsilon = 0$ (Figure 5). Even more, the value obtained at $\varepsilon_r = 70\%$ is slightly below the initial one as found in earlier studies for PEE comprising PEG as soft segments.\cite{3-5}

The last sample also represents a PEE (Arnitel® EM400) including PTMG as soft segments (PBT/PTMG 40:60 by wt.). It should be stressed immediately that its deformation behavior is completely different from that of all previous samples. First, its extensibility is extremely high as compared to the previous materials (Figure 2–5) reaching $\varepsilon_b = 510\%$. Second, the scattering patterns in this large deformational interval vary in type – there are both two-point and four-point diagrams. Selected 2D scattering patterns are displayed in Figure 6.

Analyzing all of these patterns taken in the interval of $\varepsilon$ between 0 and 510% under stress (12 patterns), one can define three deformational ranges characterized by different types of scattering patterns. In the first interval of deformations ($\varepsilon = 0 – 80\%$) the scattering patterns are of the two-point type no matter if they are taken under or in the absence of stress (Figure 6, $\varepsilon = 0$ up to 80%). In the second deformation interval ($\varepsilon = 80 – 140\%$) the scattering patterns are again of the two-point type but a second long spacing is observed when the sample is under stress. (Figure 6, $\varepsilon = 100$ and 140%).

Such a coexistence of two long periods has been found earlier in similar investigations of PEE comprising PEG as soft segments.\cite{3-9}

In the third deformational interval ($\varepsilon = 140 - 510\%$) the two-point scattering patterns are present only in the measure-
ments carried out under stress. Those taken in the relaxed state are distinguished by perfect four-point shape (Figure 6, $\varepsilon_r = 25(140)$ up to $205(510)$).

The results of the quantitative determinations of the long spacings of all the patterns taken under stress ($\sigma \neq 0$) or in the absence of stress ($\sigma = 0$) are presented in Figure 7. The majority of $L$ values are obtained from two-point patterns (Figure 7, ◆◆), and the rest from four-point patterns (Figure 7, diamonds◇). The data in Figure 7 demonstrate also a rather different deformation behavior of this sample in comparison to that of the other ones (Figure 2–5). The very high elongation at break has already been discussed. Further, the $L$ values measured as a function of the forced ($\varepsilon$) or residual deformation ($\varepsilon_r$) formulate at least three well-expressed tendencies. Up to $\varepsilon = 80-100\%$, $L$ increases linearly with $\varepsilon$, the straight line being quite close to that reflecting the affine deformational model. In this interval of $\varepsilon$, the long spacing measured under stress is almost doubling, whereas the corresponding values in the absence of stress ($\sigma = 0$) are very close to the initial one (Figure 7, points 2–5). This means that the macrodeformational changes provoked by the external deformation $\varepsilon$ are completely reversible. This conclusion is supported by the observation that up to a total deformation of $\varepsilon = 50\%$, $\varepsilon_r$ is close to zero (Figure 7).

In the intermediate deformation interval ($\varepsilon = 80–140\%$) a tendency towards simultaneous formation of two long spacings is observed. This was already demonstrated when discussing the 2D SAXS patterns (Figure 6). This result is not surpris-

ing. It has already been observed and interpreted for the case of PEE involving PEG as soft segments.$^{[3\text{-}9]}$

With further progress of the external deformation ($\varepsilon$ up to $510\%$), only one long spacing arising from the two-point patterns ($\sigma \neq 0$) or from four-point patterns ($\sigma = 0$) can be observed. Both of them are much smaller than that registered at lower deformation ($L_1$), being in the vicinity of the initial $L$ value ($L_0$). Nevertheless, they differ in value while those measured under stress ($L_2$) remain constant with values slightly larger than $L_0$. For $\varepsilon_r \leq 100\%$ the measured relaxed long period $L_{rel}$ shows values close to those of $L_2$. For the highest forced ($\varepsilon = 450$ and $510\%$) and residual ($\varepsilon_r = 177$ and $205\%$) deformations the values of $L_{rel}$ are close to the initial value $L_0$ (Figure 7, diamonds).

**Chord Distribution of the Neat EM400 Bristle**

Finally, we present the multidimensional chord distribution functions (CDF) computed from the scattering patterns (Figure 6) as described in the Experimental Part. Figure 8 exhibits the nanostructure of the neat bristle from Arnitel® EM400 before straining. The fiber direction is vertical ($r_3$). $r_{12}$ is the transversal direction in cylindrical co-ordinates. Figure 8a shows the elevated contours from the CDF that exhibit the domain nanostructure. The central pair of peaks (1) describes the basic domain structure. The elongated shape parallel to the equator indicates lamellae with an average diameter of 20 nm.

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**Figure 8:** EM400 neat bristle. Chord distribution function (CDF, logarithmic scale) computed from 2D–SAXS pattern. Fiber direction is vertical. (a) Positive contours describing the domains from the nanostructure. (b) Negative contours describing the lattice properties.
The average layer thickness, as determined from the maximum on the meridian, is \(d = 8.3 \text{ nm}\). Both the soft- and the hard-domain layers contribute to this peak. The second peak (2) describes sandwiches made from two hard domains with a soft layer in between. We propose to address them by the term “bi-domains”. The average bi-domain thickness is 26.6 nm, and tri-domains (3) with an average thickness of 44.3 nm are observed as well. There are fewer bi-domains than mono-domains, and even less tri-domains although in the contour plots they appear emphasized due to a logarithmic scaling of peak heights that was chosen for the reason of clarity. We observe that the diameter of those lamellae which are members of a stack and form bi- and tri-domains is higher (30 nm) than that of the average mono-layers. The number of stacks containing more than 3 lamellae is negligible. A dashed vertical line indicates a very weak lateral correlation among adjacent stacks that is as well present in the contours describing the lattice properties (Figure 8b). The most common lattice property is the long period peak (4). From the position of the maximum we determine \(L = 18.0 \text{ nm}\), which is in good agreement to the value directly extracted from the SAXS pattern (Figure 7). A second (5) and even a third long period peak are observed at 35.2 nm and 53.4 nm in fiber direction and describe correlations among phase boundaries that are placed at double and triple the “lattice constant”, \(L\). In general there is no long-ranging lattice in the studied material, and consequently the negative peaks in the CDF that are related to the lattice property are weaker by one order of magnitude than the positive peaks that describe the ensemble of nanosize domains.

In a résumé, the neat bristle comprises lamellae of hard- and soft domains that are oriented perpendicular to the fiber direction. The average layer thickness is 8 nm. The diameter of the lamellae is varying considerably. Extended layers with a diameter of 30 nm have formed stacks comprising not more than 3 members. Imperfect layers with diameters of less than 20 nm are more frequent than the extended ones. Their correlation with neighboring domains is low.

**Nanostructure Evolution During Strain Cycling**

Figure 9 presents the nanostructure evolution during the straining cycle as revealed in the CDF for low and medium elongation (50% \(\leq \varepsilon \leq 140\%\)).
The left column shows the chord distributions of the domains in the strained state. For all elongations the strong central domain peak exhibits a diamond shape that can be explained by the superposition of lamellae and other, rather compact mono-domains with a low aspect ratio. A separation by hand is impossible. Nevertheless, the bi-domain peak outside the central diamond is a set of four straight and elongated lines. To a first approximation it can be described by a (sub-)stack of two inclined lamellae. The increase of the tilt angle with increasing elongation from $51^\circ$ to $69^\circ$ is indicated in the plots. At 140% strain the linear peak begins to disintegrate into two parts indicating the formation of small domains by disruption of the lamellae. Beginning with an elongation of 100% two well-separated peaks of cylindrical soft- and hard-domains that are located in microfibrils are observed. The peak closer to the center is still constant and thus assigned to the hard domain cylinders with a height of 8.9 nm. The average height of the soft domains from the microfibrils is 21.3 nm at 100% and 25.1 nm at 140%. In the further course of the straining this soft domain height will not increase beyond 28 nm. Instead, the corresponding component will decrease and vanish indicating the maximum extensibility of the soft phase between two hard domains.

The second column shows the bristle in the relaxed state after the previous elongation. We observe a system of lamellar stacks with some orientation distribution about the meridian. Released from 140%, for the first time this orientation distribution of the bi-domains appears to be bimodal, with maxima of the preferential layer orientation at the meridian ($0^\circ$) and at $\approx 47^\circ$. There are no tri-domains with layer shape any more.

The third column shows the lattice peaks in the strained state. The long periods of the microfibrillar component (1) and of the tilted layers (2) are the most prominent features. Several higher orders are present. At $\varepsilon = 140\%$ we observe both a long period of microfibrils under tension (3) and a long period of relaxed microfibrils (4).

The fourth column shows the arrangement of long periods in the relaxed state. Up to the second order the long periods are clear and continuous, indicating an orientation distribution of lamellar stacks that contain not more than three layers.

Figure 10 presents nanostructure evolution during the straining cycle as revealed in the CDF for high elongation ($250\% \leq \varepsilon \leq 510\%$). For the strained state the first column reveals the transition from a macrolattice with hexagonal arrangement of small and compact domains into a pure microfibrillar system with perfect orientation.

Figure 10: EM400 bristle in straining cycle. High elongations. Chord distribution function (CDF, logarithmic scale) computed from 2D-SAXS pattern. Fiber direction is vertical. Elongation $250\% \leq \varepsilon \leq 510\%$ as indicated in the left column. The contour plots of this column show the domain contours of the nanostructure in the strained states. The meaning of the other columns is given in the labels underneath.
The second column, again, shows the relaxed state. It is interesting to notice that, when releasing the stress, the disrupted domains again merge to form stacks of tilted lamellae. The inclination angle now is rather high and almost constant at 60°. The diameter of these lamellae, again, is 30 nm. None of these stacks comprises more than 3 domains. The last two columns show the peaks related to the long periods in the strained and in the relaxed state. In the strained state (3rd column) the emerging microfibrillar component is clearly detected by the row of peaks on the meridian. Their strength is growing as the elongation increasing whereas a long period from some remnant lamellae oriented perpendicular to the fiber axis is vanishing.

**Discussion**

**Effect of Chain Flexibility on the Deformational Behavior of PET, PBT, PEE and PBT/PEE Blend**

The materials subjected to this investigation have a common characteristic feature with respect to their chemical composition. All of them can be viewed as being built from a rigid part and a flexible part. For the two homopolymers PET and PBT the rigid part is the terephthalic acid residue, and for PEE it comprises the PBT hard segments. As to the flexible parts, these are ethylene glycol EG (for PET), tetramethylene glycol TMG (for PBT) and poly(tetramethylene glycol) PTMG (for the PEE). Obviously, the chain flexibility increases from EG to PTMG. This fact is reflected by the values of their glass transition temperatures, \( T_g \), which are 70, 40 and \(-50 \)°C\(^{[21]}\) (the last value is for a PEE comprising PEG as soft segments). Thus it is not surprising that the three polymers exhibit different limits of external deformations, including the blend PBT/PEE (Figure 2–6).

The different chain flexibility, or more precisely the flexibility of the “soft” part of the molecules, is responsible for the quite different fractions of the residual deformation, \( \varepsilon_r \), from the total one, as well as the limit of \( \varepsilon \) below which the change of \( L \) is more or less completely reversible (Figure 2–5, 7). The flexibility of the “soft” parts strongly affects the character of microdeformation, making it to obey or disobey the affine model of deformation. The affine model of deformation can only be applied for the homo PBT and PEE Arnitel\(^{®} \) EM400 (Figure 7).

**Relationship Between Macro- and Microdeformation**

The relationship between macro- and microdeformation is reflected in the relationship \( L(\varepsilon) \). For PET (Figure 2) there is no well-defined relationship. For the other materials one observes a linear relation (Figure 3–5 and 7) that obeys the affine deformation model with the exception of the blend (Figure 4). At low elongations this increase is completely reversible, i.e. the \( L \) values measured in the corresponding deformational interval after removing the stress, are very close to the initial value \( L_0 \) (to be seen best in Figure 7).

In this context it is noteworthy to mention an early observation of Zhurkov et al.\(^{[22]} \) on PA6 films. It has been demonstrated that the SAXS intensity increases continuously with drawing (\( \varepsilon = 12, 14 \) and \( 31\% \)) during the measurement. Performing similar experiments, Fischer and Fakirov\(^{[23]} \) showed that the scattering intensity is very sensitive to strain or stress for PET, too. For instance, measurements carried out on PET sheets of 1 mm thickness drawn five times and annealed at 260°C for 6 h have shown that the SAXS intensity increases sharply and reversibly when the sample is under strain (5–7%) at the time of measurement. If the strain is larger, the scattering intensity increases further but is no longer fully reversible.\(^{[23]} \) Such reversibility (up to \( \varepsilon = 13\% \)) was recently observed for PET in a PET/PE blend (50:50 by wt.)\(^{[24]} \) by both the changes in \( L^{PET} \) and by the variation of the scattering intensity.\(^{[24]} \)

The observed SAXS behavior of PET, either in the blend with PE\(^{[24]} \) or as homopolymer,\(^{[23]} \) as well as the changes of \( L \) for PET and particularly for PBT in the present case, i.e., the increase of the scattering intensity and/or the long spacing with extensional deformation, can be properly explained by the model proposed by Zhurkov et al.\(^{[22]} \) assuming a density decrease of the soft (non-crystalline) phase due to its elongation. Such an explanation is supported by the fact of reversible change of both the intensity and \( L \) values for the respective deformational range. Their behavior suggests that the observed external elongation is related to conformational changes only in the amorphous domains, the crystallites remaining unaffected for these levels of deformation. This mechanism is proven in the case of PEE.\(^{[3–6, 14]} \)

It should be stressed here that such an interpretation of the SAXS behavior (for both intensity and \( L \)) cannot be applied for example to PE in the above-mentioned PET/PE 50:50 by wt. blend. The possible reason for this is that the PE crystallites melt at much lower temperatures (around 120 compared to 255°C for PET). In other words, their mechanical resistance during deformation is lower and during straining defects are introduced in crystallites leading to a decrease of the density difference between the hard and the soft phase that explains the observed continuous decrease of SAXS intensity of PE.\(^{[24]} \)

Reversibility of the long spacing \( L \) in a certain range of lower macrodeformation is expressed in the best way by PBT (Figure 3) and by PEE Arnitel\(^{®} \) EM550 (Figure 7) in this study. As discussed above it is related to conformational changes of the chains in the amorphous intercrystalline regions as repeatedly reported for similar\(^{[25]} \) and other polymer systems.\(^{[26]} \) This conclusion is supported by the observed changes of the shape of the 2D SAXS patterns themselves as shown in Figure 1 and 6 (up to \( \varepsilon = 80\% \)). Application of stress in limited deformational ranges (\( \varepsilon \) up to 18% for homopolymers and up to 80% for PEE) causes the two-point reflections to get closer to one another and to move apart when stress is removed (Figure 1 and 6). These results suggest that at low deformation
levels no substantial persistent morphological changes occur – some of the morphological elements (ensembles of crystalline domains) remain the same as entire entities and keep their internal structure.

Let us now focus on the deformation behavior of the last sample, the PEE Arnitel® EM400, distinguished by the most typical properties for poly(ether ester) (Figure 6 and 7). In addition to the behavior up to \( \varepsilon = 80\% \) already discussed above, in the next range \( \varepsilon = 80-140\% \), in contrast to the rest of the samples, a second periodicity \( L_2 \) appears that coexists with the primary long spacing \( L_1 \) (Figure 6, \( \varepsilon = 100 \) and 140\%, Figure 7). Such a second long spacing \( L_2 \) is reported for PEE comprising PEG as soft segments,\(^{[3,4]}\) the effect having been explained by loosing of interfibrillar contacts in this interval of deformation. The result is relaxation of some microfibrils and the observation of a corresponding shorter long period \( L_2 \). With the further increase of the external deformation \( \varepsilon \) from 140 to 500\%, the first periodicity \( L_1 \) disappears while \( L_2 \) remains constant. A more detailed description of the nanostructure evolution as a function of elongation is given in the description of the corresponding CDF features that reflects all the basic features given here, but adds quantitative data concerning the domain shapes and orientations. It appears noteworthy to mention that both a microfibrillar component and a lamellar component are existing in the material from the beginning, and that a proceeding partition of the inclined bi-lamellae into fragments is already indicated during the initial process of elongation.

All the discussed changes in \( L \) (Figure 7) concern only measurements under stress. From \( \varepsilon = 140\% \), the scattering patterns taken in the absence of stress are of four-point type and the question is, if the material is built from tilted lamellae or from a macrolattice of microfibrils. The CDFs (Figure 9, 10) exhibit the presence of bi-domains from tilted lamellae that support the model of zigzag lamellae.\(^{[5]}\) With increasing reversing-deformation \( \varepsilon \) the tilt-angle is growing to 60° at \( \varepsilon = 510\% \). The trend towards formation of zigzag assemblies of parallel lamellae is strongly enhanced when the sample is not loaded. It increases significantly as the reversing deformation in the straining cycle \( \varepsilon = 200-510\% \) is increased (Figure 6, after \( \varepsilon = 200-510\%, \sigma = 0 \)). Simultaneously, the shape of the scattering patterns taken under stress at \( \varepsilon = 200–500\% \) is closer to the lobe-type than to the four-point type. Such a difference between the scattering patterns suggests substantial morphological changes. These changes are clearly identified in the CDF (Figure 10). It shows in the strained state a disruption of tilted lamellae into smaller pieces. At \( \varepsilon = 250\% \) the fragments have formed a macrolattice with hexagonal order. When the elongation is increased beyond that, the lattice is transformed into an ensemble of microfibrils with little correlation in lateral direction. From the CDF it is clearly deduced that the samples subjected to the highest deformations and thereafter unloaded consist of parallel crystalline lamellae tilted with respect to the fiber axis (FA). A zigzag shaped arrangement of these layers in lateral direction is, on the other hand, not discernible from the CDF. A simplified sketch of the basic states of nanostructure as extracted from the SAXS data is presented in Figure 11.

![Figure 11: Arnitel® EM400 bristle nanostructure as a function of elongation \( \varepsilon \) in the elongated (top) and the relaxed (bottom) state, respectively. A microfibrillar structure always present (like the one outlined in the top right cartoon) is never sketched. A less simplified and more probable view of the tilted lamellae is indicated at \( \varepsilon = 50\% \)](image-url)
If really filled lamellae or only assemblies of blocks are observed cannot be deduced from the presented scattering data. In the latter case a rotation of a lamella could be performed by a more probable process of progressive displacement of adjacent blocks in straining direction.

It is important here to emphasize that for the nanostructure at low and medium elongation: (i) the proximate morphology and the described morphological transition between inclined lamellar assemblies and flat ones is completely reversible; (ii) the trend to the formation of zigzag morphologies (or, the increase of the inclination to the fiber axis in the case of the unloaded samples) strongly grows with the progress of the macrodeformation $\varepsilon$. It can be assumed that such reversible morphological transition contributes to the formation of the elastic properties of thermoplastic elastomers as was suggested previously.[5]

One can assume that the considerable number of molecules connecting parallel lamellae causes a better-coordinated response to the changes of stress and/or of strain. The interfibrillar tie molecules holding together the crystalline domains of neighboring microfibrils are responsible for the more or less smooth distribution of the external stress in the sample. Taking into account the larger amount of amorphous material in the interfibrillar regions than that within the fibrils,[31] the creation of new tie molecules appears more probable to happen in the phase surrounding the microfibrils, than in the amorphous regions from inside the microfibrils.

Conclusions

By performing SAXS measurements during the progressive elongation of some polyesters and poly(ether esters) samples containing glycols with varying length, it was found that the extensibility strongly depends on the flexibility of the glycol residues. It increases from 10% (PET) to 510% (for a commercial PEE Arnitel® EM400).

Studying the relationship between the macro- (or, the external deformation denoted by $\varepsilon$) and the microdeformation expressed by the change of the long spacing $L$, in accordance with previous observations it was established that three typical deformational ranges exist. Within the lowest deformation range (up to 10% for PBT and 80% for PEE), the deformation obeys the affine model and is due to conformational changes occurring only in the amorphous intercrystalline areas. In the next deformation range (80–140%), observable for the PEE samples only, a second periodicity appears as a result of relaxation of a part of the microfibrils owing to a loss of microfibrillar contacts at this level of deformation. Finally, within the third deformational range of PEE (between 140 and 510%), four-point scattering patterns appear when the measurements are performed after removing the stress. Two-point diagrams characterize all measurements under stress. Using the multidimensional chord distribution function (CDF) analysis it was verified that the two-point diagram results from sets of parallel lamellar stacks, being perpendicular to the stretching direction, the four-point diagram is related to stacks of layers, tilted with respect to the longitudinal direction (fiber axis). The transition from one to the other type of lamellar arrangement is reversible. It is believed that this reversibility on morphological level contributes to the deformation reversibility of the thermoplastic materials.

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