Deformation behaviour of poly(ether ester) thermoplastic elastomers as revealed by small-angle X-ray scattering

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The scattering behaviour of thermoplastic elastomers based on poly(ether ester) (PEE) under stress is studied. Bristles of PEE consisting of poly(butylene terephthalate) as hard segments and polyethylene glycols ($M_w = 1000$) as soft segments in a ratio of 50/50 wt% are drawn five times and then annealed with fixed ends. Small angle X-ray scattering (SAXS) measurements are carried out with single bristles subject to stress and with deformations up to 200%. The increase of long spacing L is directly proportional to strain ε (up to $\varepsilon = 100\%$) supporting an affine deformation mechanism. At $\varepsilon = 75$ and 100% two long spacings L_1 and L_2 are observed, L_2 being close to the initial L_1^0 and remaining constant with further increase in ε up to $\varepsilon = 200\%$. The L values measured after removal of the stress (up to $\varepsilon = 30\%$) revert almost to those obtained without stress; further increase in the deformation of the samples leads to a decrease in L values. The effect of stress on the scattering intensity is similar. A model is proposed to explain the scattering behaviour under stress. The affine increase of L with ε is related to the reversible deformation of the amorphous regions. Further increase in ε leads to the elimination of the interfibrillar contacts since tie molecules are pulled out. As a result relaxation of some microfibrils occurs and a second long spacing with a value close to that of the initial one is observed. A microscopic picture of the deformation mechanism and the influence of tie molecules on L are discussed.

(Keywords: thermoplastic elastomers; deformation behaviour; X-ray scattering; long spacing; relaxation)

INTRODUCTION

The poly(ether ester) (PEE) 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 crosslinks tying the array of macromolecules into an infinite network. In natural rubber and synthetic elastomers these crosslinks represent chemical bonds. In thermoplastic elastomers they are replaced by thermally labile tie points held together by physical forces. These junctions may be glassy, crystalline or even hydrogen-bonded molecules or ionic associations[1].

In order to behave as a thermoplastic elastomer the molecule must contain two types of units: amorphous type (above glass transition temperature, T_g) referred to as soft segments or blocks and hard segments or blocks. The soft segments impart elastomeric character to the copolymer while the hard blocks are capable of intermolecular association with other hard blocks; they should form a solid phase within a desired temperature range in order to impart dimension stability to the array of molecules. At high temperature, dissociation of the physical bonds occurs. In order to ensure the formation of a three-dimensional network, each molecule should contain, on average, at least two hard blocks. The soft and hard blocks may be arranged in various ways, randomized or ordered. Their way of ordering affects the physical and mechanical properties of the material[1].

The basic difference in the nature of network formation in classical rubbers and thermoplastic elastomers influences not only their processing conditions but also such a fundamental and characteristic property as their high elasticity and the extent of its reversibility. In the present study an attempt is made to follow the relationship between the macro and micro deformation (the latter reflecting the behaviour of the morphological elements) by means of small angle X-ray scattering (SAXS) with samples under stress and in this way to evaluate and understand the extent of reversibility with the process of the deformation. For this purpose SAXS measurements were carried out on PEE thermoplastic elastomers based on poly(butylene terephthalate) (PBT) and polyethylene glycols (PEG) with or without the application of stress to the samples.

EXPERIMENTAL

The sample material represents a polyblock PEE consisting of PBT as hard segments and PEG as soft segments in a ratio of 49/51 wt%. The synthesis is carried out on a semi-commercial scale as described in reference 2. It should be noted that the starting PEG has $\bar{M}_n = 889$ (according to gel permeation chromatography analysis) and is characterized by a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.30$) as shown in *Figure 1*.

The copolymer has a viscosity $[\eta] = 1.35$ dl g^{-1} and an end carboxy group content (COOH) of 43.10 gequiv g^{-2}. Calculations based on normal kinetics of

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polyester formation and ^{1}H nuclear magnetic resonance (n.m.r.) as well as ^{13}C n.m.r. measurements lead to a degree of polymerization n of hard segments between 4.9 and 4.1, respectively, which corresponds to an average molecular weight of 1050. Assuming a total molecular weight of the copolymer of about 20 000 (for products of technical interest it is about 2×10^4–4×10^4), these data suggest an average total number of blocks of about 20 in each macromolecule. For an extended chain conformation, the soft segments should have a length of about 80 Å while the length of the hard segments should be about 55 Å.

By means of melt extrusion, bristles of diameter of about 1 mm were prepared. These isotropic (according to wide angle X-ray scattering data) bristles were drawn at room temperature on a Zwick 1464 machine with a crosshead speed of 5 mm min^{-1} until the entire sample underwent neck-formation which corresponds to a draw ratio $l/l_0 = 5$, where l and l_0 are the length of the sample in the material after drawing and undrawn material, respectively. The drawn material exhibits a reversible deformation at room temperature of about 50%.

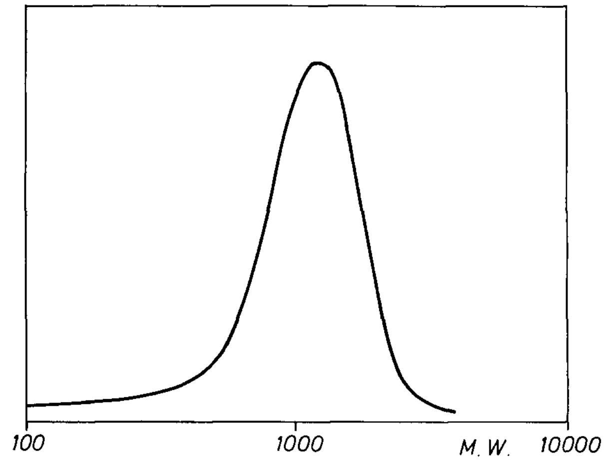

Figure 1 Molecular weight distribution curve obtained from g.p.c. analysis of PEG with $\bar{M}_n = 1000$ (PEG 1000). Solvent: water (flow rate 1.0 ml min^{-1}); standard: polyethylene oxide; column type: TSKGPW (G600, G5000, G3000PW)

The drawn bristles (diameter of about 0.5 mm) were annealed with fixed ends in vacuum at $T_a = 170°\mathrm{C}$ for 6 h. All measurements were carried out with the samples treated in this way.

An X-ray source with rotating anode and a pin-hole collimation was used for the SAXS measurements. The scattering patterns were registered by a two-dimensional position-sensitive detector. The detector is filled with xenon and has a resolution of 0.2 mm in each direction. The two-dimensional scattering patterns consist of 512×512 data points, and the sample-to-detector distance is 80 cm. Calibration was made with Lupolen and with $C_{36}H_{74}$ paraffin. The scattering measurements under stress were performed using a frame allowing a controlled change of the sample length. The scattering data were corrected with respect to the volume changes due to the extension only for the calculation of the intensity maxima. Meridian cuts through the two-dimensional scattering pattern are calculated taking an average over four equatorial pixels. Each pixel corresponds to a detector element of 0.2×0.2 mm^2. Each measurement under stress σ was immediately followed by another one without applying stress ($\sigma = 0$) before applying the next, larger deformation. To describe the larger deformation we use the notation $\varepsilon = ((l/l_1) - 1))100$ where l_1 is the length of the original bristle drawn five times and annealed as described before, and l is the length during the X-ray experiment under stress.

In order to estimate the extent of irreversible deformation during the SAXS measurement without application of stress, stress–strain curves were obtained on an Instron machine using the same drawn and annealed samples and the same mechanical loading–unloading cycle (each 30 min) as during the scattering experiments.

RESULTS

The scattering curves of the drawn and annealed copolymer (PBT/PEG = 49/51 wt%) taken at various deformations as well as without applying stress are presented in *Figure 2*. q represents the magnitude of the scattering vector, and $q = 4\pi/\lambda \sin \Theta$, where λ is the wavelength and 2Θ the scattering angle. It is seen that

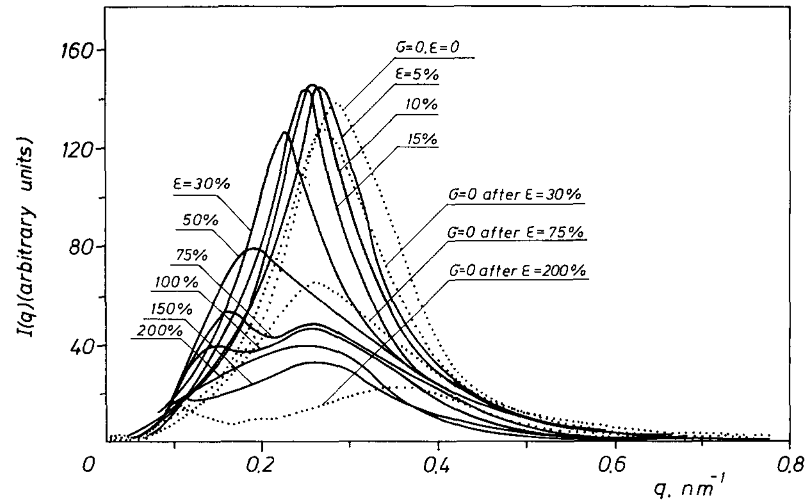

Figure 2 Small angle X-ray scattering curves of drawn and annealed PEE bristles (PBT/PEG = 49/51 wt%) taken under (———) and in the absence of (·····) stress. The numbers denote the relative deformation ε at which each measurement is carried out and the stress σ

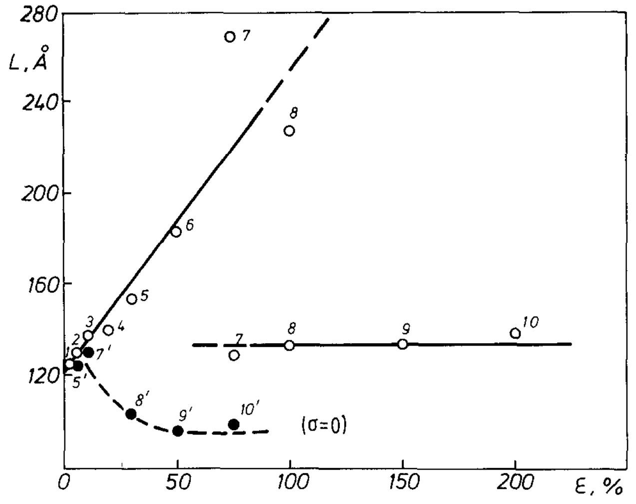

Figure 3 Dependence of the long spacing L on the relative deformation ε at which the measurement is carried out. The numbers denote the sequence of the measurements (the prime sign means measurement in the absence of stress immediately after the respective measurement performed under stress). The data are taken from the curves presented in *Figure 2*

the strain strongly affects the angular position of the curve maxima while the heights are less influenced (up to $\varepsilon = 30\%$).

An unexpected splitting of the peak into two maxima is observed after reaching a macro deformation ε of 75 or 100%. Such a scattering behaviour indicates that a second spacing, much smaller than the first, appears in the system studied.

The effect of the relative deformation ε on the long spacing L is better expressed in *Figure 3*. This plot is derived from the scattering curves of *Figure 2*. Here the lower broken line denotes the influence of ε on L for the samples measured without application of stress ($\sigma = 0$) after previous measurements under stress.

A large increase in L with increase in the relative deformation ε can be observed up to $\varepsilon = 75$–100%. At these values of ε a second long spacing L_2 arises, its value being close to the initial one ($L_1^0 = 125$ Å). With further increase in the relative deformation up to 200%, L_2 remains constant while L_1 disappears.

The effect of the macro deformation ε on L is completely different when the SAXS measurements are performed without application of stress to the sample. Considering these results one should take into account that the unloaded samples always exhibit a plastic deformation, its value increasing with increase in ε. For this reason the experimental points in *Figure 3* (lower broken line) refer to the residual plastic deformation resulting from the respective foregoing measurements under stress.

First of all it should be noted that all measurements performed in the absence of stress (*Figure 3*, lower broken line) are characterized by only one L the value of which is lower (by about 15%) than the value of the starting sample L_1^0. This observation is rather peculiar since the decrease of L is observed with samples distinguished by a plastic deformation of about 50–75%. Moreover, the larger the plastic deformation (as a result of a previous elastic deformation), the stronger the decrease from the L_1^0 value. This drop in L with the progress of the plastic deformation could be related to the drastic changes in the copolymer structure during the elastic deformation. A possible explanation of these changes will be proposed below.

Considering again the relationship between L and the relative deformation ε at which the measurement is carried out (*Figure 3*), the conclusion could be drawn that the increase in L is not only linear but directly proportional to the increase in ε, i.e. an affine deformation mechanism can be assumed. The affine deformation is seen more clearly in *Figure 4* where the relative change in long spacing, L/L_1^0 is plotted *versus* the extension ratio, l/l_1, at which the measurements are performed. The direct proportionality between L and ε is observed up to $= 75\%$, thereafter L drops to values close to L_1^0 and remains almost constant with further increase in ε. It should be noted that the affine relationship between L and ε disappears in the range of ε values where the second long spacing L_2 appears (in the vicinity of $\varepsilon = 75\%$).

The SAXS intensity measured on samples under or without applied stress depends also on the relative deformation ε. The results are plotted in *Figure 5*. One

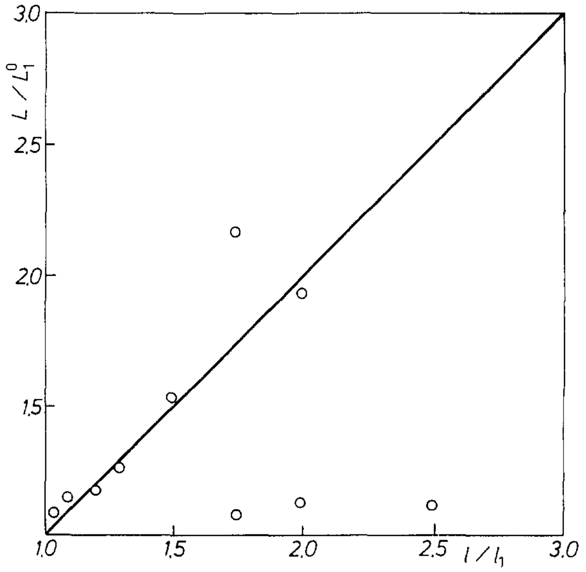

Figure 4 Plot of the change in the long spacing L/L_1^0 as a function of elongation of the sample l/l_1 at which the measurements are carried out with drawn and annealed PEE bristles (PBT/PEG = 49/51 wt%). ———, Affine deformation model

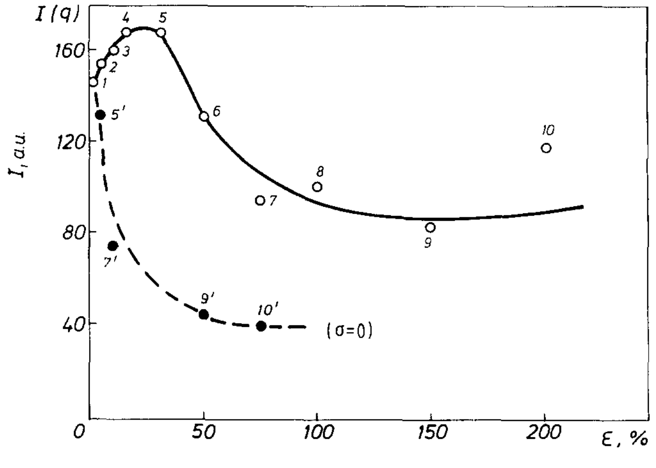

Figure 5 Dependence of the SAXS peak intensity I on the relative deformation ε for drawn and annealed PEE bristles (PBT/PEG = 49/51 wt%) taken under (———) and in the absence (– – –) of stress. The numbers have the same meaning as in *Figure 3*

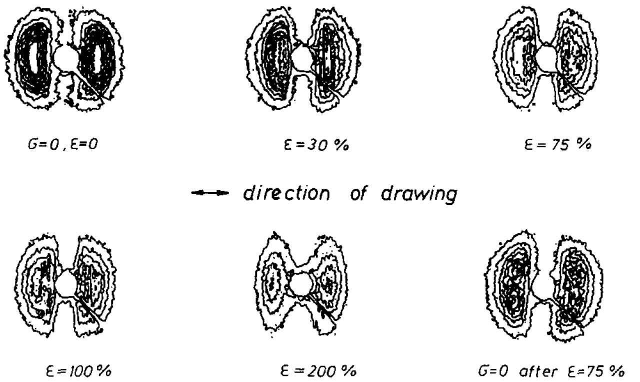

Figure 6 Contour plots of the two-dimensional SAXS data of drawn and annealed PEE bristles (PBT/PEG = 49/51 wt%) taken under or in the absence of stress, as indicated. The direction of stretching is horizontal

can see that with an increase of macro deformation up to $\varepsilon = 30\%$ the scattering intensity increases by only 10%. Thereafter it drops by about 30% (at $\varepsilon = 150\%$) with a second slight increase at $\varepsilon = 200\%$. In contrast to this behaviour, the scattering intensity continuously decreases with the increase in plastic deformation in the case when no stress is applied to the sample (*Figure 5*, broken line). The decrease is more than two times that from samples previously subjected to $\varepsilon = 150$ to 200%. This drastic change in scattering intensity with the process of plastic deformation supports the suggestion of there being profound morphological changes at higher deformations ($\varepsilon = 100$–200%). The changes in the scattering intensity with the relative deformation ε are mainly a result of density changes in both crystalline and amorphous regions. Because of the relatively high chain flexibility, particularly of the soft segments, it seems hard to expect formation of voids during the stretching which could strongly affect the scattering behaviour at very small angles especially in the equatorial direction.

Figure 6 shows four SAXS patterns selected from the measurements described above. It is seen that the shape and in particular the peak position in these patterns change significantly with increase in macro deformation, this observation leading to conclusions on the morphological peculiarities of the respective samples. We do not however, observe significant void scattering at small angles, and voids are not formed at large deformations. The intensity is usually plotted in the direction of applied stress (meridian, see *Figure 2*) while there is negligible scattering in the equatorial direction. The width of the peak perpendicular to stretching direction stays approximately constant up to $\varepsilon \sim 100\%$. Since there is no strong indication for the appearance of a four-point scattering pattern, our procedure for the evaluation of the equatorial scattering is justified.

DISCUSSION

These results reflect the effect of stress on the SAXS behaviour of drawn and annealed thermoplastic elastomers and show three peculiarities: (i) affine increase of L with increase in the relative deformation at which the measurement is carried out (up to $\varepsilon = 75$–100%, *Figure 4*); (ii) appearance of a second long spacing L_2, at $\varepsilon = 75$–100% (*Figure 2*) with a value close to that of the initial sample and remaining almost constant up to $\varepsilon = 200\%$ (*Figure 3*); (iii) in the absence of stress the L values obtained from measurements of samples previously subjected to stress are smaller than the L value of the starting material (*Figure 3*). It should be noted that corresponding changes in the scattering intensity are observed within almost the same deformation ranges (*Figure 5*). All these observations can be explained only by taking into account: the structure formed during the first drawing ($l/l_0 = 5$) and the subsequent annealing ($T_a = 170$°C); the structural changes due to the deformation (up to $\varepsilon = 200\%$) during the measurements performed under stress; and the structural peculiarities of this particular class of polymers, that is, thermoplastic elastomers.

Concerning the crystalline structure of these copolymers, it is proved[3,4] and generally accepted[1,5], at least for the case of poly(ether esters) based on PBT and PEG, that the crystalline regions are built up of hard segments (PBT) and behave in the same way as crystallites of the homopolymer PBT. The amorphous portion of the copolymer contains mainly soft segments (PEG) but includes also a considerable amount of residues of non-crystallized PBT segments.

Schematic presentations of the structure and chain conformation of an isotropic elastomer as well as the same material after drawing and annealing are shown in *Figure 7*. At first glance these two models are similar to those describing the structure of conventional thermoplastics. The basic characteristic features are actually the same—amorphous and crystalline regions organized in alternating layers in the oriented state (*Figure 7b*), giving rise to the long spacing L. At the same time such highly oriented semicrystalline polymers consist of microfibrils being connected by a large number of tie molecules as shown in *Figure 7b*. In this way the amorphous phase can be considered as intrafibrillar (the main portion) and interfibrillar, the latter amounting to 10–15% for poly(ethylene terephthalate)[7] (PET) and PBT[8].

Taking into account the polyblock $(AB)_n$ character of the poly(ether esters) studied and particularly the fact that only one type of the blocks is crystallizable (*Figure 7*), it seems reasonable to assume that the amount of the tie molecules is much larger than in the case of homopolymers (e.g. PET or PBT where much longer parts of the molecules remain in the same crystallite). This difference in the structures of the polyblock copolymers and the semicrystalline homopolymers could result in a specific deformation behaviour of the thermoplastic elastomers.

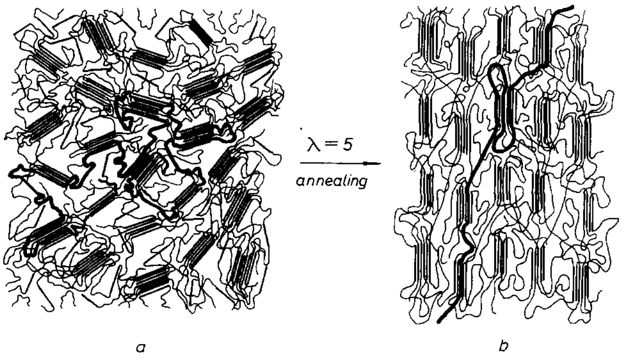

Figure 7 Schematic model of the structure and chain conformation of a thermoplastic elastomer (proposed by Fischer[6] for polyurethane block copolymers) in (a) the isotropic and (b) the oriented ($\lambda = 5$) state

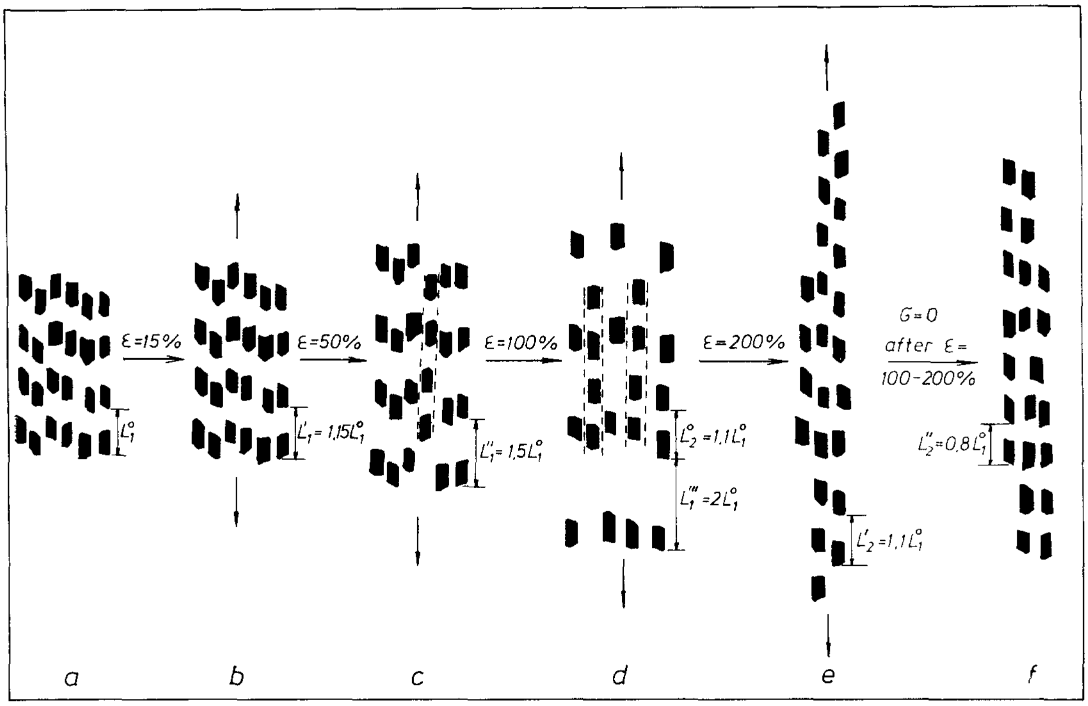

Figure 8 Schematic model of the structural changes of drawn semicrystalline thermoplastic elastomers at different stages of deformation: (a) no stress applied; (b)–(e) under stress; (f) in the absence of stress after being subjected to deformation (only the crystalline regions from *Figure 7* are depicted). – – –, Relaxed microfibrils after elimination of the interfibrillar tie-molecular contacts. For details see text

From the basic model of the structure of oriented thermoplastic elastomers (*Figure 7b*) a further model can be developed describing the structural changes occurring during deformation so as to explain the scattering behaviour of these copolymers under stress. The models reflecting the structural changes at different stages of deformation are schematically shown in *Figure 8*.

The model in *Figure 8a* shows the structure of the starting material (the same as *Figure 7b*) characterized by a long spacing L_1^0. The deformation of the sample within the range $\varepsilon = 10$–20% leads to stretching of the chains in the amorphous regions. The respective expansion of these regions results in a decrease of their density, hence in the increase of the scattering intensity and L by the same percentage. These changes in the SAXS intensity and L values are actually observed (*Figures 5* and *4*, respectively). As far as the inter- and intrafibrillar contacts remain unaffected by these deformations, it is to be expected that the changes described should be reversible, as actually observed in the present case. A similar behaviour is already reported for drawn and annealed PET where the scattering intensity increases with increase in ε up to 10% but it is completely reversible only for an increase up to $\varepsilon = 5\%$[9].

Further deformation of the sample up to $\varepsilon = 50\%$ (*Figure 8c*) again results in an affine increase of the long spacing ($L_1'' = 1.5L_1^0$, *Figures 4* and *8c*) accompanied by a slight decrease of the intensity compared with the initial intensity (*Figure 5*). Again, the affine increase in L can be explained in terms of an extension of the chains in the amorphous regions. At this relatively high deformation ($\varepsilon = 50\%$) a few microfibrils lose their contacts with the adjacent microfibrils and relax. Such a relaxation causes a rise in the amorphous density ρ_a and subsequently a decrease in the scattering intensity (*Figure 5*).

It is reasonable to expect that the number of relaxed microfibrils will grow abruptly with further deformation since increasing numbers of tie molecules will pull out from the neighbouring microfibrils, thus enhancing the relaxation of chain segments in the amorphous regions. At a given stage of deformation ($\varepsilon = 75$–100% in the present case) the amount of relaxed microfibrils is sufficient to give rise to a second long spacing L_2^0. This situation is presented in *Figure 8d*. As far as the first long spacing L_1''' originates from the expansion of amorphous regions, it should be affine with the macro deformation ε ($L_1''' = 2L_1^0$, *Figure 8d*) which is actually observed (*Figure 4*). The second long spacing L_2^0 should be close to the initial L_1^0 or slightly higher in the case of samples under stress ($L_2^0 = 1.1L_1^0$, *Figure 3*). Taking into account the basic idea of this model (*Figure 8*)—relaxation and slipping of microfibrils at high deformations—one can expect the appearance of many long spacings as far as these processes lead to the formation of discrete periodicities in the draw direction.

The increased amount of relaxed microfibrils leads to higher ρ_a values and possibly to a lower crystalline density, ρ_c, due to the introduction of defects in the crystallites by pulling out tie molecules. Both changes in the ρ values lead to a decrease of the scattering intensity (*Figure 5*).

With the further increase in the deformation ($\varepsilon = 150$–200%) the amount of relaxed microfibrils becomes predominant, i.e. the number of stretched microfibrils is not enough to maintain the first long spacing L_1'''. Again the long spacing takes only one value, close to the initial one ($L_2' = 1.1L_1^0$, *Figures 3* and *8e*). For the reasons mentioned in the previous case (*Figure 8d*) a decrease in the scattering intensity should be expected, and it is actually observed (*Figure 5*).

Special attention should be paid to the scattering results obtained in the absence of stress with samples previously measured under stress. These samples always have some residual plastic deformation depending on the

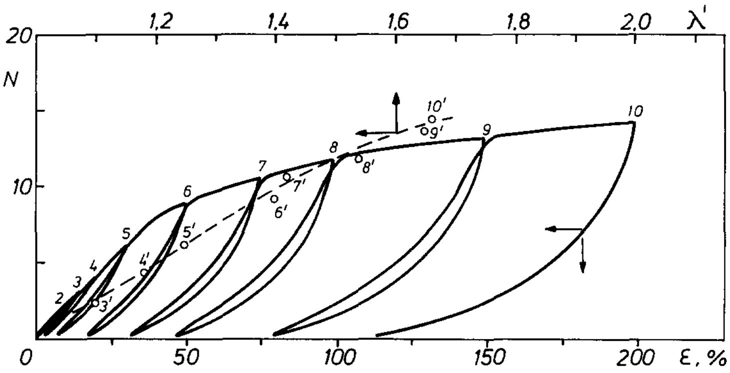

Figure 9 Stress–strain hysteresis curves for drawn and annealed PEE bristles (PBT/PEG = 49/51 wt%). Curves are taken using the same 'loading–unloading' cycle (each one of 30 min) as in the scattering measurements (———, lower axis); (–––, upper axis) the degree of extension λ' as a result of plastic residual deformation caused by the previously applied deformation ε at which the measurements are carried out. The numbers have the same meaning as in *Figure 3*

value of the previously applied deformation. In order to evaluate this plastic deformation, stress–strain hysteresis curves are taken from samples used in the SAXS measurements. The mechanical tests are carried out using the same 'loading–unloading' cycle during the scattering measurements. The results are shown in *Figure 9*. It is seen that the residual plastic deformation strongly increases with the progress of the relative deformation ε. The plastic deformation values obtained from these measurements (*Figure 9*) are quite close to those derived during X-ray studies (*Figures 3* and *5*). The value λ' is calculated as the ratio of the length of the drawn sample with respect to the length of the sample prior to the drawing process allowing for a relaxation time of 30 min.

Considering the scattering behaviour of the samples studied, one has to take into account the presence of residual plastic deformation. As seen in *Figure 3* (broken line), the L measured without application of stress is close to the initial L_1^0 value when the previous deformation amounts to $\varepsilon = 50$–75%, i.e. the stretching and relaxation of the chains in the amorphous regions are reversible. The samples subjected to the highest deformations ($\varepsilon = 150$–200%) and measured thereafter in the absence of stress exhibit a L value smaller by 20% than the initial one (*Figure 3*, dashed line). This peculiar result can be interpreted only in terms of the structural changes described above and presented in *Figure 8*.

The microfibrils free of interfibrillar contacts have more freedom to relax than those in the starting material (*Figure 7b*). The higher extent of relaxation results in shrinkage of the microfibrils and subsequently decreases ($L_2'' = 0.8L_1^0$, *Figure 8f*). The denser packing of the chains in the amorphous regions results in a higher ρ_a value (due to the more defective crystalline structure) leading to a drastic drop in the scattering intensity (more than three-fold; *Figure 5*, broken line).

Our results suggest the assumption that the progressive increase of the residual plastic deformation is a result of the structural changes taking place at very high relative deformations—continuous loss of interfibrillar contacts by pulling out of the molecules and subsequent relaxation and shrinkage of the microfibrils. The lack of interfibrillar linkages required for the transfer of the mechanical forces hampers the regeneration of the initial dimensions. For the same reason, the samples with destroyed interfibrillar bonds are unable to exhibit a high elastic deformation since during extension, instead of stretching, slipping of the microfibrils occurs. In order to restore the elastic properties of the material one has first to regenerate the interfibrillar links. Such experiments are in progress.

Returning to the relationship between the deformation of the sample l/l_1 and the changes of the long spacing L/L_1^0 (*Figure 4*), one has to consider other ways to determine the deformation mechanism more precisely.

Miller[10] and Cooper[11] have studied the deformation response of the polyether soft segments in a polyether–polyester copolymer with composition as follows: dimethyl terephthalate/butanediol/PTMO-2000 = 5/4/1 (molar ratio, which corresponds to a PBT/PTMO wt% ratio of 31/69). The soft segments are deuterated. Two-dimensional small angle neutron scattering data, acquired for various elongations of the sample ($\varepsilon = 0$–200%), have been reduced from the contour plots to a simple $I(q)$ *versus* q form and fitted to a Debye random coil model. In this way the radius of gyration of the soft segment in the directions parallel and perpendicular to the stretching direction has been obtained. The data have been compared further with three models for various deformation mechanisms with respect to changes in the segment radius of gyration with the elongation. The three models are those of affine deformation, junction affine deformation and phantom network, respectively[12].

The data of Miller[10] on the change in the soft segment radius of gyration in the direction parallel to stretching direction do not agree with any of the deformation models. Miller and Cooper[11] explain this discrepancy by the fact that in a block copolymer the crosslink junction point is finite in size. The hard phase serves as the crosslink junction and can deform whereas in the rubber elasticity theory crosslink points are assumed to be point-like and non-deformable.

Beltzung *et al.*[13] studied the deformation in a series of poly(dimethylsiloxane) networks using neutron scattering and found that the phantom network deformation model describes the data best. The materials studied were closer to the ideal elastomer than the block copolymer used by Miller and Cooper[11]. The latter[11] reported that the deformation mechanism can be modelled by a phantom network model, too, at least up to $\varepsilon = 150\%$ in the case of deformation of poly(ether esters) however, only in the direction perpendicular to stretch direction.

A survey of the literature reveals that the phantom network model and the junction affine model describe the deformation behaviour of crosslinked networks fairly well, while the affine deformation model is more appropriate for non-crosslinked materials[11].

It is important to note that direct comparison of the results of Miller[10,11] and those of Beltzung[13] with our results is not possible because they refer to different levels of the molecular and supermolecular hierarchy—the radius of gyration in the first case and the long period in our case.

Discussing the affine deformation mechanism of the system studied it is worth noting another striking observation. The maximum observable value of L under stress of about 270 Å corresponds to the length of two soft and two hard segments (both extended). At least two questions arise with respect to this finding: why do we not observe experimentally higher values of L with further increase of the external stretching; and how to explain the perfect agreement between the maximum experimental value of L and the total length of four alternating blocks?

Both questions could be answered assuming that the length of the section between two crystallites of the tie molecules (regardless if they are intra- or interfibrillar) comprises on average at least two soft and one hard segment (instead of only one soft segment as assumed in *Figure 7b*).

A section of extended copolymer chain as well as the structure of PEE before and after stretching (distinguished by maximum achievable L value) is schematically presented in *Figure 10*.

Our assumption presumes that only less than half of the hard segments can crystallize, i.e. the crystallinity (referred to the PBT amount in the copolymer) could not exceed 50%. This is really the case as demonstrated by our previous[14] measurements of crystallinity using differential scanning calorimetry. It is also generally accepted that the amorphous phase of such systems consists of soft segments as well as non-crystallized hard segments which, in this particular case, dephase with increase in temperature as recently demonstrated[15].

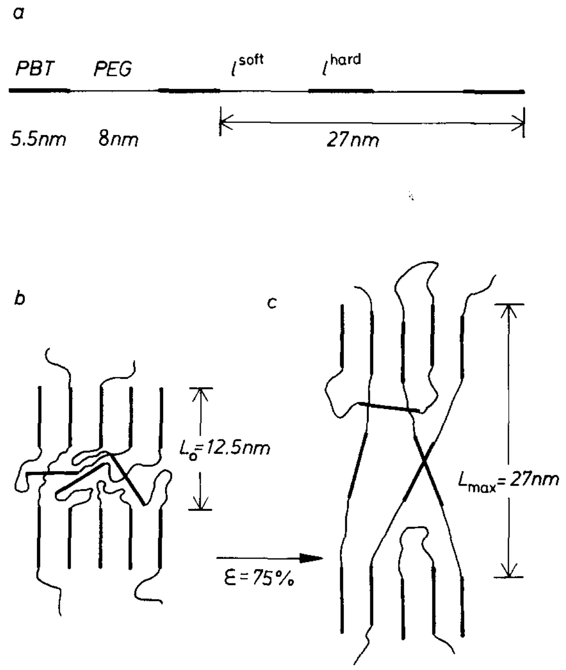

Figure 10 Schematic presentation of the change in molecular structure at high drawing ratio: (a) a section of extended copolymer chain; (b) sample prior to drawing; (c) hard segments are pulled out of crystalline domains and other sequences between the domains become effective as tie molecules resulting in a doubling of the long spacing

The amount of hard segments distributed in the amorphous phase should increase with strain applied due to the pulling out of tie molecules from crystallites as discussed above. Such a process should be effective from the start of stretching for tie molecules whose length between two crystallites comprises only one soft segment. This process is expected to lead to significant decrease in the scattering intensity since a larger number of hard segments is incorporated into the amorphous phase and additional defects are introduced into the crystallites.

From the two experimental observations—a strong decrease in the scattering intensity at strain values of about $\varepsilon = 75\%$ (*Figure 5*) and the value of $L_{max} = 2l_{soft} + 2l_{hard}$ at the same ε value of 75% (*Figure 10*)—the conclusion can be drawn that the length of the chain sections between two crystallites is either equal to one soft segment or to two soft plus one hard segment, the latter being present more frequently.

So far as this conclusion is reasonable, one can understand why the experimentally measured L values do not exceed $L_{max} = 2l_{soft} + 2l_{hard}$. The observation of L values higher than L_{max} assumes there are some chain sections between two crystallites longer than $2l_{soft} + l_{hard}$ or that tie molecules are pulled out from crystallites which already have a segment length in the amorphous region of $2l_{soft} + l_{hard}$. If the pulling out of tie molecules with further increase in deformation (between 100% and 200%) occurs it will contribute to the further destruction of interfibrillar contacts and thus also enhances the relaxation of single microfibrils as discussed before. Hence the external macro deformation is no longer related to the stretching of chain segments in the amorphous regions and does not affect the L values. The latter become much smaller and show a tendency towards the initial L_1^0 value because of the dominating relaxation of the microfibrils and their slipping. Similar deformation behaviour of the styrene–butadiene–styrene triblock copolymer obtained by SAXS is observed by Pakula *et al.*[16].

CONCLUSIONS

By SAXS measurements of drawn (five times) and annealed (170°C) PEE thermoplastic elastomers (PBT/PEG = 49/51 wt%), the effect of sample deformation during the measurements of scattering behaviour is followed. Experiments on samples under stress and with subsequent removal of the stress reveal that:

1. the increase of L is directly proportional to the deformation of the sample within the range 0–100%, obeying the affine deformation mechanism;
2. the changes of L measured under stress and with subsequent removal of the latter are almost completely reversible up to $\varepsilon = 50$–75%;
3. at this deformation level ($\varepsilon = 75$–100%) a second, smaller long spacing appears which remains constant (close to the initial L value) up to $\varepsilon = 200\%$. At the highest deformations the first long spacing disappears;
4. the L values measured after removal of stress are 15% lower than the initial values;
5. from the observation that the maximum L value measured equals the total length of two extended soft and hard segments ($L_{max} = 2l_{soft} + 2l_{hard}$) the conclusion is drawn that a large number (approaching

approximately half of the total amount) of hard segments are located in the amorphous regions. Thus the length of chain sections between two crystallites should be equal to l_{soft} or $2l_{\text{soft}} + l_{\text{hard}}$.

A model is proposed for the description of these changes of the long period L during deformation as well as those in the maximum SAXS intensity. The effect of sample elongation on the behaviour of the microfibrils is considered. The reversible changes of L up to $\varepsilon = 75\%$ are assumed to be related to the deformation of the inter- and intrafibrilar amorphous regions with preservation of the interfibrillar linkages. The further increase in sample deformation up to $\varepsilon = 100\%$ causes partial elimination of these linkages by pulling out the tie molecules. The subsequent relaxation of microfibrils results in the appearance of a second, smaller long spacing. The latter becomes predominant with the increase in deformation up to $\varepsilon = 200\%$. Microfibrils free of interfibrillar contacts have more freedom to relax as compared to those in the starting sample. For this reason the L values measured after removal of stress (after an elongation of $\varepsilon = 150$–200%) are smaller than the initial ones. This model also seems to be applicable to other polyblock thermoplastic elastomers.

From SAXS experiments it is thus possible to reveal detailed information on morphological changes during deformation of thermoplastic elastomers. Detailed microscopic models can be deduced which describe the reversible and irreversible changes in the material. The specific nature of the physical crosslinking points formed by crystallized hard segments in connection with formation of tie sequences in the amorphous phase determine the peculiar mechanical behaviour. Microfibrils are formed during large deformations leading to a mostly non-affine behaviour at large elongations. A detailed study of the process where the mechanical strength of the polymer is regained and the original morphology restored is being carried out.

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