Deformation behaviour of poly(ether ester) thermoplastic elastomers with destroyed and regenerated structure 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 segment and poly(ethylene glycol) ($\bar{M}_n = 1000$) as soft segment in the ratio 50/50 wt% are drawn to five times their initial length and then annealed with fixed ends in order to create a standard initial structure. Samples with largely destroyed structure (by additional drawing) as well as with regenerated structure (by crystallization, solid-state reactions or chemical crosslinking) were prepared. Small-angle X-ray scattering (SAXS) measurements are carried out with single bristles subject to stress and with deformations up to 200%. An affine increase of the long period L with extension ε up to $\varepsilon = 75\%$ is observed in the samples with undestroyed structure. A second L_2 appears at larger ε. Without application of stress two discrete values, L_1^{rel} and L_2^{rel}, are obtained. Qualitatively, the sample with destroyed structure behaves similarly. The deformation behaviour of samples with regenerated structure depends on the method of regeneration: (i) crystallization mostly recovers the previous deformation pattern; (ii) solid-state reactions (additional condensation and exchange reactions) result in an increase of L_1, L_2, L_1^{rel} and L_2^{rel} due to the very high number of interfibrillar contacts; and (iii) chemical crosslinking leads to the appearance of only L_1 and L_1^{rel}. A model is proposed suggesting the existence of two types of lamellae differing in their perfection and origin. The first and more perfect lamellae refer to the starting crystalline lamellae, while the second type of less perfect lamellae are assumed to arise during the additional stretching. The latter comprises hard segments originally dispersed in the amorphous interlamellar layers or pulled out from the neighbouring crystallites. The existence of the two types of lamellae is proved by differential scanning calorimetric measurements.

By variation of the number of intra- and in particular interfibrillar contacts, the predominant role of the tie molecules in the evolution of mechanical properties of these polymer materials is demonstrated. Further, two important concepts are proposed in addition to earlier studies: (i) microfibrillar chemical healing–elimination of the interfibrillar phase boundaries as a result of solid-state reactions and (ii) deformation (by slippage) of ensembles of microfibrils in the chemically crosslinked samples, almost preserving in this way the initial L value and facilitating very high deformations ($\varepsilon = 200\%$).

(Keywords: thermoplastic elastomers; poly(ether ester); deformation behaviour; X-ray scattering; long spacing; relaxation; interfibrillar chemical healing; microfibrillar ensembles)

INTRODUCTION

Thermoplastic elastomers are still attractive subjects for structural investigations not only because of their peculiar mechanical properties but also since they offer many modelling opportunities due to their crystallization ability, multiblock character and possibility of varying both the block flexibility and length. There are also a lot of unanswered questions concerning the deformation mechanism of this class of polymers as compared to classical rubbers.

In a previous study of drawn ($\lambda = 5$) and annealed poly(ether ester) (PEE) thermoplastic elastomers based on poly(butylene terephthalate) (PBT) as hard segment and poly(ethylene glycol) (PEG) as soft segment (PBT/PEG = 49/51 wt%), understanding of the deformation mechanism was attempted by means of small-angle X-ray scattering (SAXS) measurements carried out under stress and in the absence of stress within a broad deformation range ($\varepsilon = 0$–200%)[1]. It was found that up to $\varepsilon = 75\%$‡ an affine increase of L is observed and then a second long spacing L_2 appears, coexisting with L_1 up to $\varepsilon = 100\%$. With the further rise of ε up to 200%, L_1 disappears and L_2 keeps a constant value. In the measurements without application of stress ($\sigma = 0$), i.e. after deformation and subsequent relaxation, one long spacing L_1^{rel} is observed, its value being close to that of the initial one before deformation L_1^0 (up to $\varepsilon = 75\%$) and

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‡ In order to distinguish and emphasize the deformation during SAXS measurements, these being the main subject of the present study, this deformation is denoted by ε, in contrast to the drawing before measurements, for which we keep the more common symbol $\lambda (= l/l_0)$

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decreasing subsequently with increase of ε up to 200%, reaching a constant value.

According to the model previously proposed[1], the affine increase of L with ε is related to the reversible deformation in the amorphous regions. The further increase in ε leads to the elimination of interfibrillar contacts since tie molecules are pulled out of lamellae. As a result, relaxation of some microfibrils occurs, causing the appearance of a second long spacing with a value close to that of the initial one.

In a subsequent study[2] samples differing in both chemical composition and glycol length (PEG 600, PEG 1000, PEG 2000) were used and the general conclusions were confirmed except for the affine deformation mechanism: it was proved to be valid only for the sample PBT/PEG 1000 with composition of 50/50 wt%. Further, an attempt was made to evaluate the amorphous phase distribution. In contrast to homopolymers, the interfibrillar amorphous phase was found[2] to be 40–80% of the total while the crystalline core of the microfibrils is about 0.3–0.8 of their entire cross-section. For the majority of the samples it is shown that the measured L^{max} values equal the sum of the lamellae thickness l_c, plus two soft- and one hard-segment lengths, $L^{max} = l_c + 2l^s + l^h$. Finally, the data obtained[2] suggest that the coexistence of two long spacings during drawing could be related to both microfibril relaxation or formation of a second type of lamellae from the hard segments (being originally dispersed in the amorphous phase), but no preference for one of these contributions could be given[2].

It is important to note that during the measurements described above the originally created structure (drawing $\lambda_1 = 5$ and subsequent annealing close to the melting temperature for 6 h) is completely destroyed. The amount of plastic deformation progressively increases, reaching 50% of the entire deformation and the interfibrillar contacts are eliminated. This demonstrates the important role of the tie molecules, and more particularly of the interfibrillar tie molecules.

In order to study in more detail the role played by the interfibrillar tie molecules, in the entire deformation pattern an attempt was made to regenerate the initial structure, i.e. to recover the interfibrillar contacts destroyed during the additional drawing of up to $\lambda_2 = 2.5$. The present work is a study of the scattering behaviour of PEE samples under external stress or without application of stress using the SAXS technique. Samples with destroyed structure were prepared by additional drawing (λ_2) and those with regenerated structure were prepared by means of three approaches—crystallization, solid-state condensation and exchange reactions as well as chemical crosslinking. They were carefully investigated by SAXS measurements under different deformation conditions.

EXPERIMENTAL

Details on the preparation and characterization of the sample material, its treatment as well as the conditions of the SAXS measurements can be found in ref 1. Here it should be noted only that the starting PEG has $\bar{M}_n = 889$ (according to gel permeation analysis) and is characterized by a quite narrow molecular-weight distribution ($\bar{M}_w/\bar{M}_n = 1.30$); for this reason the samples could be considered as model systems, distinguished by almost constant soft-segment length l^s. After drawing of the bristles (diameter of about 1 mm) to $\lambda_1 = 5$ (5×), they were annealed for 6 h in vacuum at $T_a = 180°C$. Each measurement by SAXS under stress σ was immediately followed by another one in the absence of stress ($\sigma = 0$) before applying the next, larger deformation.

Samples with destroyed and regenerated structure were prepared as follows: Taking into account the observation[1,2] that the 5× drawn and annealed sample (starting material) after stepwise additional drawing up to $\lambda_2 = 3$–4 shows drastic structural changes, this approach was used in the preparation of samples with destroyed structure, i.e. with almost completely eliminated interfibrillar tie molecules. Thus the starting material (with $\lambda_1 = 5$) was drawn additionally at room temperature to $\lambda_2 = 3$–4 and kept with fixed ends for 48 h.

In order to achieve regeneration of the interfibrillar contacts, the samples with destroyed structure were treated in three different ways:

(a) *Crystallization.* Regeneration was attempted by annealing for 1 h at 170°C in vacuum with fixed ends of the samples.

(b) *Solid-state reactions.* Conditions of regeneration were created by annealing for 60 h in vacuum at 170°C[3].

(c) *Chemical crosslinking.* The sample with destroyed structure was kept for 25 h in an acetonitrile solution of benzophenone (0.02 mol l^{-1}) and thereafter evacuated in a quartz tube (for 5 h at 10^{-5} mmHg) in order to remove the solvent. Finally the sample was irradiated in vacuum for 30 min with a mercury lamp (Heraeus Q 600) in order to initiate crosslinking[4]. Benzophenone, playing the role of a photocatalyst, penetrates into the amorphous regions only and it is to be expected that chemical crosslinking does not occur in the crystalline regions, as already demonstrated with a similar approach applied to polyamides[5].

Description of the samples is given in *Table 1*.

The SAXS experiments are performed with a pinhole camera on an 18 kW rotating-anode generator at a wavelength of 0.154 nm. An area gas detector with 512 × 512 pixels is used and the sample–detector distance is typically 70 cm. For data analysis, cuts, for example, parallel to the stretching direction through the two-dimensional image of the detector, are taken, which are mostly discussed in this paper. Further details are described in ref. 1, where also contour plots of the two-dimensional SAXS data can be found.

The calorimetric measurements were performed using a Mettler TA-3000 differential scanning calorimeter (d.s.c.) at a scanning rate of 20°C min^{-1} in an inert atmosphere. From the heat of fusion the degree of crystallinity (referred to the PBT fraction), w_c^{PBT}, was calculated for all the samples before measurements using the conventional approach. The data obtained are shown in *Table 1*.

RESULTS

The scattering curves used for the evaluation of the long spacing L and the maximum intensity I taken at various deformations as well as without application of stress are presented in *Figure 1*. It is seen that the stress strongly affects the angular positions of the peak maxima while their heights are less influenced (up to $\varepsilon = 30\%$). Such curves were taken for all samples described in *Table 1* and the effect of the external stress mainly on the L values obtained from the peak positions was followed.

Table 1 Degree of plastic deformation λ at different treatment stages, annealing temperature T_a and duration t_a as well as crystallinity w_c of PBT/PEG 49/51 wt%

Sample No.	Description	Standard treatment		Additional drawing (destruction of the structure),	Total drawing,	Additional treatment (regeneration of structure)			Degree of crystallinity (referred to PBT) (before measurements),	Final draw ratio (after measurements),
		λ_1	T_a (°C)	λ_2	$\lambda=\lambda_1\lambda_2$	T_a (°C)	t_a (h)	Chemical crosslinking	w_c^{PBT} (%)	λ_f
1	Starting material	5	180	–	5	–	–	–	43	10
2	With destroyed structure	5	180	2.5	12.5	–	–	–	33	19
3	Structure regenerated by crystallization	5	170	2	10	170	1	–	42	20
4	Structure regenerated by solid-state reactions	5	170	2	10	170	60	–	50	17
5	Regenerated by chemical crosslinking	5	150	1.5	7.5	–	–	yes	22	14

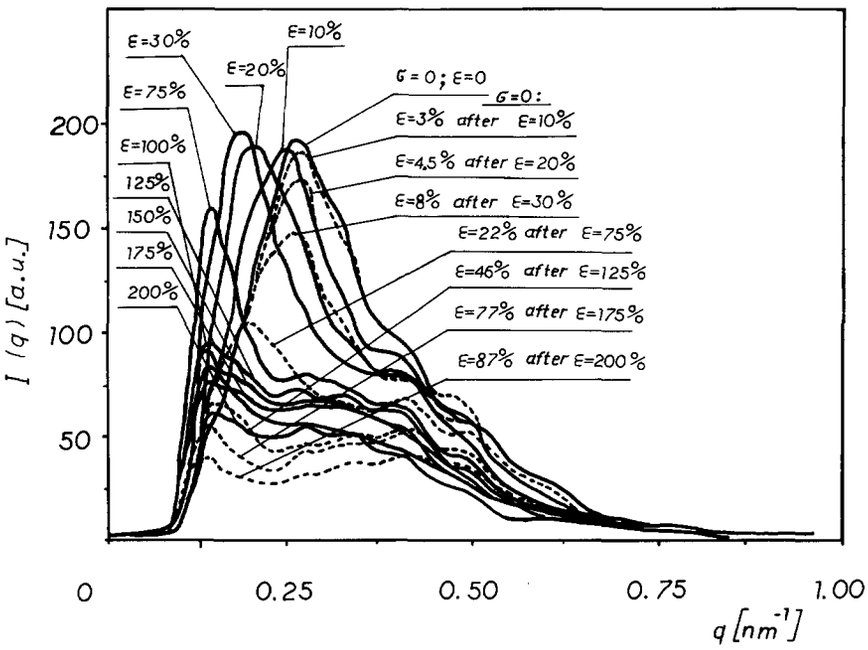

Figure 1 Small-angle X-ray scattering curves of PEE bristles (PBT/PEG = 49/51 wt%) drawn ($\lambda_1 = 5$), annealed and again drawn ($\lambda_2 = 2.5$) (structure destruction) followed by annealing at 170°C for 1 h (structure regeneration) taken under (——) and in the absence of (– – –) stress. The numbers denote the relative deformation ε at which each measurement is carried out and the stress σ; q represents the magnitude of the scattering vector, $q = (2\pi/\lambda)\sin\theta$, where λ is the wavelength (0.154 nm) and 2θ is the scattering angle

The influence of the relative deformation ε during the measurements on the long spacing L in the case of the undestroyed (initial) structure (sample 1, *Table 1*) is better expressed in *Figure 2*. Here and further on, the lower broken lines denote the effect of ε on L in samples measured in the absence of stress ($\sigma = 0$) after previous measurements under stress. In these cases the long spacing value after relaxation L^{rel} was close to the starting L_1^0 for ε up to 75–100% while at higher deformations (100–200%) they dropped below L_1^0. Actually just this observation is the reason for repeating the measurements already performed with samples of the same[1] or different[2] composition. The question arises whether the character of this change is continuous or discontinuous. The measurements performed in the present study using smaller deformation steps reveal that at least with this particular sample (PBT/PEG = 49/51 wt%) two discrete values of the long spacing, L_1^{rel} and L_2^{rel}, are observed. This finding is supported also by the coexistence of both L_1^{rel} and L_2^{rel} in the plastic deformation range $\varepsilon = 25$–50% (*Figure 2*, points 6′ and 7′) corresponding to a previous deformation ε of about 100–125%. Above this deformation level the first L_1^{rel} disappears and L_2^{rel} keeps a constant value that is 20% lower than the starting L_1^0. Otherwise

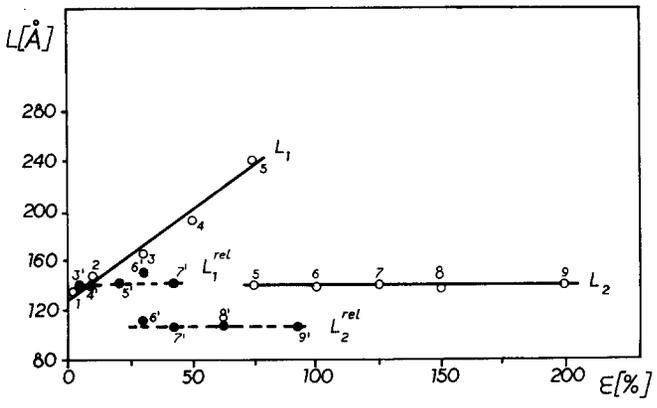

Figure 2 Dependence of the long spacing L on the relative deformation ε at which the measurement is carried out with PEE bristles (PBT/PEG = 49/51 wt%) with undestroyed structure. The numbers denote the sequence of the measurements (the prime sign denotes measurement in the absence of stress immediately after the respective measurement performed under stress). The data are taken from curves such as those presented in *Figure 1*

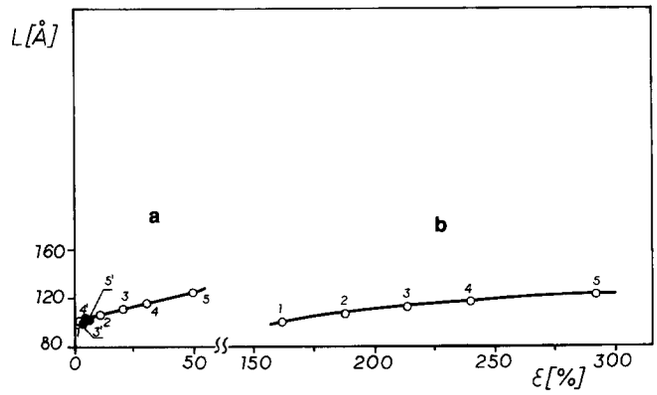

Figure 3 Dependence of the long spacing L on the relative deformation ε at which the measurement is carried out with PEE bristles (PBT/PEG = 49/51 wt%) with destroyed structure. The meanings of the numbers and symbols are the same as in *Figure 2*, and the difference of curves a and b is explained in the text

the scattering behaviour of this sample is the same as already reported[1,2]: an affine increase of L up to $\varepsilon = 100\%$ is observed, then a second long spacing L_2 arises, its value being close to the starting L_1^0 and remaining constant up to $\varepsilon = 200\%$.

Figure 3 shows the dependence of L on ε for the sample with destroyed structure (sample 2, *Table 1*). As mentioned above, the destruction causes elimination of the interfibrillar contacts by pulling out of tie molecules during the additional drawing (up to $\lambda_2 = 2.5$) and prolonged keeping under stress.

At first glance the behaviour of this sample is quite different to that of the sample with undestroyed structure (*Figure 2*, refs. 1, 2) since only one spacing is observed, its value increasing slightly and reversibly up to $\varepsilon = 50\%$ (*Figure 3a*). The initial value of this long spacing corresponds to L_2^{rel} of the sample with undestroyed structure (*Figure 2*) and its maximum value achieved is the same as L_2^{rel} of L_2 of the sample with undestroyed structure (*Figure 2*). This limit in the change of L in the sample with destroyed structure can be understood by replotting *Figure 3a*, taking into account that the measurements were carried out into the range $\varepsilon = 0$–50% after additional drawing ($\lambda_2 = 2.5$) of the predrawn ($\lambda_1 = 5$) and annealed material (sample 2, *Table 1*). Thus the starting length of the sample before the scattering measurements corresponds to a deformation level of $\varepsilon = 150\%$ in comparison to sample 1, *Table 1* and *Figure 2*. The curve replotted in this way shown in *Figure 3b* explains the variation of the long spacing of the sample with destroyed structure in the range between L_2^{rel} and L_2 of the sample with initial structure (*Figure 2*, points 6′–9′ and 6–9): both sample structures are approximately the same at very high deformations ($\varepsilon = 200$–300%).

Figures 4, *5* and *6* show the effect of the relative deformation ε during the measurements on the long spacing L in samples with regenerated structure (samples 3, 4 and 5, *Table 1*).

Figure 4 refers to the case of structural regeneration by relatively short heat treatment with fixed ends of the sample, leading to predominant crystallization and relaxation processes. The scattering behaviour is basically the same as in the case of the sample that has undergone the standard treatment ($\lambda_1 = 5$, $T_a = 180°C$), i.e. the case of undestroyed structure (*Figure 2*). Again two long spacings L_1 and L_2 (measured under stress) and two other discrete values L_1^{rel} and L_2^{rel} (measured without external stress) are observed. Further, the rise of L_1 is again directly proportional to the increase of ε up to 75%, when L_2 appears with a constant value close to L_1^0 up to $\varepsilon = 200\%$. The only striking observation is the very high initial value of $L_1^0 = 175$ Å, in contrast to all samples that are not subjected to additional thermal treatment[1,2].

The results of the same measurements carried out on the sample with structure regenerated through solid-state reactions (sample 4, *Table 1*) are plotted in *Figure 5*. During the thermal treatment (at 170°C for 60 h with free ends), in addition to physical processes (crystallization and relaxation), chemical changes occur (condensation and transreactions) leading to an improvement of the interfibrillar contacts to a greater extent than the physical factors. For this reason different scattering results are observed. The basic characteristic features of the L vs. ε relationship for all samples already studied (*Figures 2–4*, refs. 1, 2) can be found also in *Figure 5*: (i) affine increase of L_1 with ε (up to $\varepsilon = 50\%$) and appearance of a second L_2 at higher deformation; (ii) existence of two long spacings in the measurements without stress, L_1^{rel} and L_2^{rel}, respectively; and (iii) very high initial long period ($L_1^0 = 200$ Å) similarly to the case of regenerated structure by crystallization (*Figure 4*). However, drastic differences

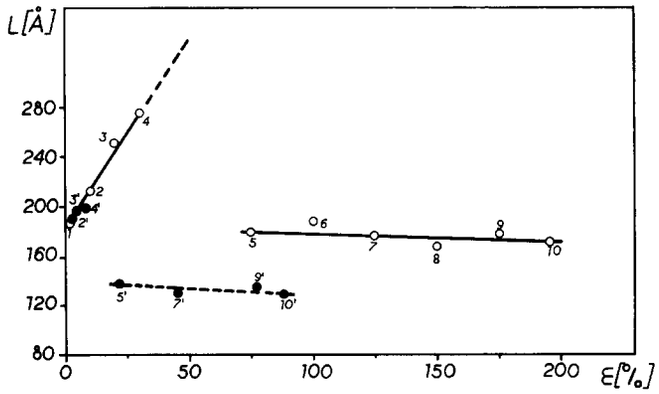

Figure 4 Same as *Figure 3* but the structure of the PEE bristles is regenerated by crystallization

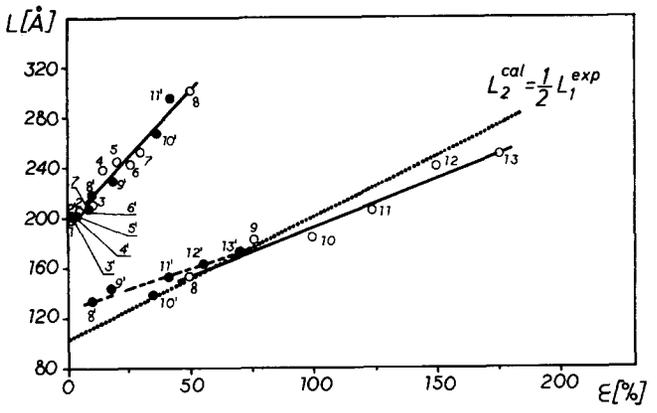

Figure 5 Same as *Figure 3* but the structure of the PEE bristles is regenerated by solid-state reactions. The dotted line corresponds to a calculation as explained in the text

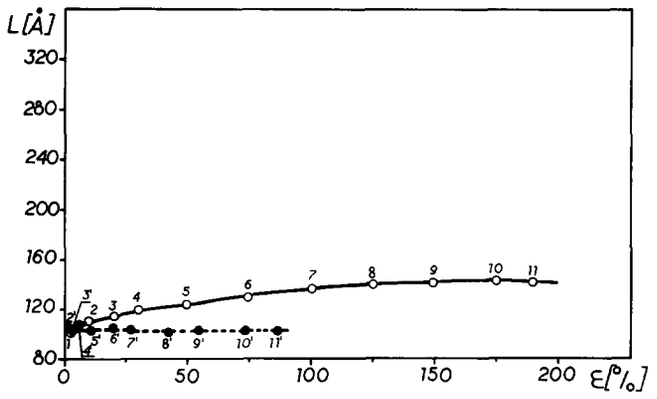

Figure 6 Same as *Figure 3* but the structure of the PEE bristles is regenerated by chemical crosslinking

can also be found: (i) the second long spacing measured under stress is not constant within the deformation range $\varepsilon = 50$–200% and increases linearly from 130 to 240 Å; (ii) the relaxed values L_1^{rel} and L_2^{rel} are no longer constant (as in all previous cases[1,2], *Figure 4*) and increase linearly with ε, parallel to the lines of L_1 and L_2, respectively, in such a way that the changes in L_1^{rel} cover the entire variation range of L_1; and (iii) in contrast to all samples studied (refs. 1, 2, *Figure 4*), the first value of L_2 is much lower than the starting L_1^0 (150 Å against 200 Å).

The last sample with regenerated structure is the crosslinked one (sample 5, *Table 1*). Chemical crosslinking is performed in such a way that chemical bonds are formed mostly in the amorphous regions. This means that a very large number of inter- and intrafibrillar contacts can be expected, strongly affecting the deformation behaviour of the sample.

The dependence of L on ε for this sample is shown in *Figure 6*. As expected, a completely different scattering behaviour during deformation is observed. First of all, measurements both under stress and in the absence of stress reveal the existence of only one long spacing, L_1 and L_1^{rel}, respectively. The starting value L_1^0 is the same as for the sample with destroyed structure (*Figure 3*) and increases continuously (by about 40%) with deformation up to $\varepsilon = 200\%$. Within the same deformation range L_1^{rel} remains constant and equals L_1^0. The slight increase of L_1 and the absence of a second long spacing (both under and without application of external stress) suggests that the chemical network is dense enough to prevent stretching of the chains in the amorphous regions. At the same time it is rather unexpected that the sample still preserves the same deformation ability (up to 200%) as the other samples studied (*Figures 2–5*).

In *Figure 7*, the results on the SAXS maximum intensity measured under or in the absence of external stress in samples with undestroyed, destroyed and regenerated structure are compared. It should be noted that the intensities observed with different samples are not on the same scale; so far corrections with respect to the volume changes caused by deformations have been undertaken only during the deformation of single samples. Regardless of the intensity levels, the qualitative changes resulting from the deformation are quite similar in all samples and are in good agreement with the intensity behaviour already reported for the same[1] and different PBT/PEG ratios[2]. Again in most samples a slight intensity increase with deformation up to $\varepsilon = 30\%$ is observed, followed by an abrupt drop at higher deformations, this drop being stronger up to $\varepsilon = 200\%$ in the case of measurements in the absence of stress.

DISCUSSION

The role of tie molecules in the deformation and relaxation processes

The idea of the importance of tie molecules in determining the deformation properties of poly(ether ester) copolymers is not a new one (see e.g. refs. 6–9). In addition to these studies we followed the behaviour of highly oriented samples, trying to focus on the role played by the interfibrillar tie molecules in the entire deformation pattern.

The SAXS measurements without application of stress on the starting material (drawn 5× and annealed, sample 1, *Table 1*) shown in *Figure 2* as broken lines clearly demonstrate the existence of two discrete long spacings with values that are practically independent of

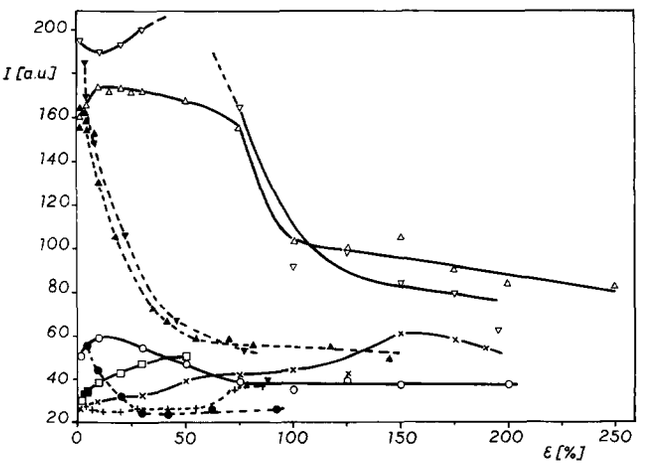

Figure 7 Dependence of the SAXS peak intensity I on the relative deformation for drawn and annealed PEE bristles (PBT/PEG = 49/51 wt%) taken under (——) and in the absence of (– – –) stress. The numbers have the same meaning as in *Figure 2* and the symbols refer to samples with: (○, ●) undestroyed structure, (□, ■) destroyed structure; (▽, ▼) regenerated structure by crystallization; (△, ▲) regenerated structure by solid-state reactions; (×, +) regenerated structure by chemical crosslinking

the deformation (plastic and total as well). The value of L_1^{rel} is close to that of L_1^0 while L_2^{rel} is lower than L_1^0. These observations lead to the conclusion that the two long spacings in the relaxed state reflect the existence of two long periods in the system under stress: L_1^{rel} originates from L_1, and L_2^{rel} from L_2. The fact that $L_1^{rel} > L_2^{rel} \sim L_1^0$ is due to the more favourable relaxation conditions of the macrofibrils after having been stretched during the SAXS measurements to $\varepsilon = 100$–200% when the majority of the interfibrillar contacts are eliminated as a result of pulling out of the interfibrillar tie molecules, as already proposed[1]. Except for this specification of the scattering behaviour in the absence of stress, the sample with untreated initial structure behaves as described earlier[1,2] and fits the general model ideas derived.

The scattering results obtained with the sample with destroyed structure (sample 2, *Table 1*) are completely different. The additional drawing up to $\lambda_2 = 2.5$ (*Table 1*) leads to the elimination of the interfibrillar contacts, slippage of microfibrils and predominating relaxation. This is the reason for the observation of only one long period (*Figure 3a*) with value close to L_1^0 and slightly increasing with the deformation (above 300%). As a matter of fact, the observed long spacing (*Figure 3*) corresponds to L_2 of the previous sample (*Figure 2*), which is obvious from the replotted scattering data taking into account the history of the sample (curve b in *Figure 3*).

The scattering results obtained with samples with regenerated structures (samples 3–5, *Table 1*) are much more interesting and best demonstrate the important role played by the tie molecules, and particularly the interfibrillar ones, in the mechanical behaviour of the material.

Once again, it should be stressed that regeneration aims primarily at the recovery of interfibrillar contacts to the initial level and in some cases even to a higher one by introducing new tie molecules. In the discussion of the scattering results another peculiarity of these samples should also be taken into account: it is related to their morphological structure before the SAXS measurements. In contrast to those studied previously (refs. 1, 2, *Figure 2*), the samples with regenerated structure are drawn before measurements up to $\lambda = 10$ (*Table 1*) rather than only $5\times$ (sample 1, *Table 1*) and for this reason drastic morphological changes take place, as shown below.

Structural regeneration by crystallization results in the recovery of the deformation behaviour, as can be concluded from *Figure 4*. It is rather similar to *Figure 2*, reflecting the behaviour of the sample with undestroyed structure. This similarity suggests that the inter- and intrafibrillar contacts affecting the mechanical properties of the material can be restored by means of a short-time treatment at high temperatures. The only essential peculiarity of this sample is the very high initial value of the long spacing L_1^0 (higher by 40% as compared to L_1^0 of the starting sample). Since the same rise of L_1^0 is observed in the case of structural regeneration through solid-state reactions, this observation will be discussed later.

The scattering behaviour of the sample subjected to structural regeneration through solid-state reactions differs substantially from those of all other samples studied (refs. 1, 2, *Figures 2–4*). Again two long spacings L_1 and L_2 are observed under stress and two other ones, L_1^{rel} and L_2^{rel}, are revealed in the absence of stress (*Figure 5*). However, all four spacings L_1, L_2, L_1^{rel} and L_2^{rel} increase linearly with the deformation (total and plastic one). Such behaviour can be explained by a very high amount of intra- and interfibrillar tie molecules. Physical processes (crystallization and relaxation) and particularly chemical interactions (additional condensation and exchange reactions, transesterification) taking place during the prolonged (60 h) high-temperature (170°C) treatment in vacuum contribute not only to recovering the contacts lost during the structural destruction but also to the creation of numerous new ones. The role played in this respect by the solid-state reactions is particularly important; transesterification reactions between two adjacent ester groups or additional condensation between closely situated chain ends result in the generation of new tie molecules between microfibrils and lamellae. These reactions are mechanically more important when the interacting chains belong originally to two different microfibrils.

The creation of new intra- and interfibrillar contacts (tie molecules) as a result of solid-state reactions is presented schematically in *Figures 8a* and *8b*. Actually, *Figure 8a* shows the case of destroyed structure.

Existence of two types of crystalline lamellae

The sequences with a high draw ratio ($\lambda = \lambda_1\lambda_2 = 12.5$, sample 2, *Table 1*) are essential for the creation of this model. During the additional drawing up to $\lambda_2 = 2.5$ a large amount of tie molecules are pulled out and slippage at the interfibrillar phase boundary occurs (broken line in *Figure 8a*). Pulling out of chain fragments from the neighbouring crystallites introduces new portions of hard segments in the interlamellar amorphous regions. In this way the structure created resembles the starting one (after drawing $\lambda_1 = 5$ and annealing) where the chain section between two subsequent lamellae comprises one hard and two soft segments, as proved for PEE with various compositions[2]. After stretching of such a sample during the measurements up to $\varepsilon = 75$–100% the maximum value of the long period L_1^{max} is achieved and the morphological structure is changed—the hard segments originally dispersed in the amorphous regions are aligned more or less in the draw direction and form a second type of lamellae between the original ones. This process leads to the formation of a second long spacing L_2 with maximum value $L_2^{max} = \frac{1}{2}L_1^{max}$ as demonstrated for PEE with various PBT/PEG ratios[2]. The relaxation of microfibrils after losing their interfibrillar contacts at higher deformation levels ($\varepsilon = 100$–200%) also contributes to the formation of L_2.

It can be concluded that the destroyed structure (after additional drawing up to $\lambda_2 = 2.5$) is characterized by the existence of two types of lamellae. The first one refers to the starting crystalline lamellae. The second type arises during the additional drawing and consists of hard segments, originally dispersed in the amorphous regions of the initial structure. The two lamellar types differ in their perfection and hence in their density. The drastic structural changes occurring during the additional drawing lead to the introduction of hard segments into the interlamellar space as a result of pulling out of tie molecules.

In conclusion, it should be pointed out that the destroyed and regenerated structures have the same characteristic features as the initial ones—alternating

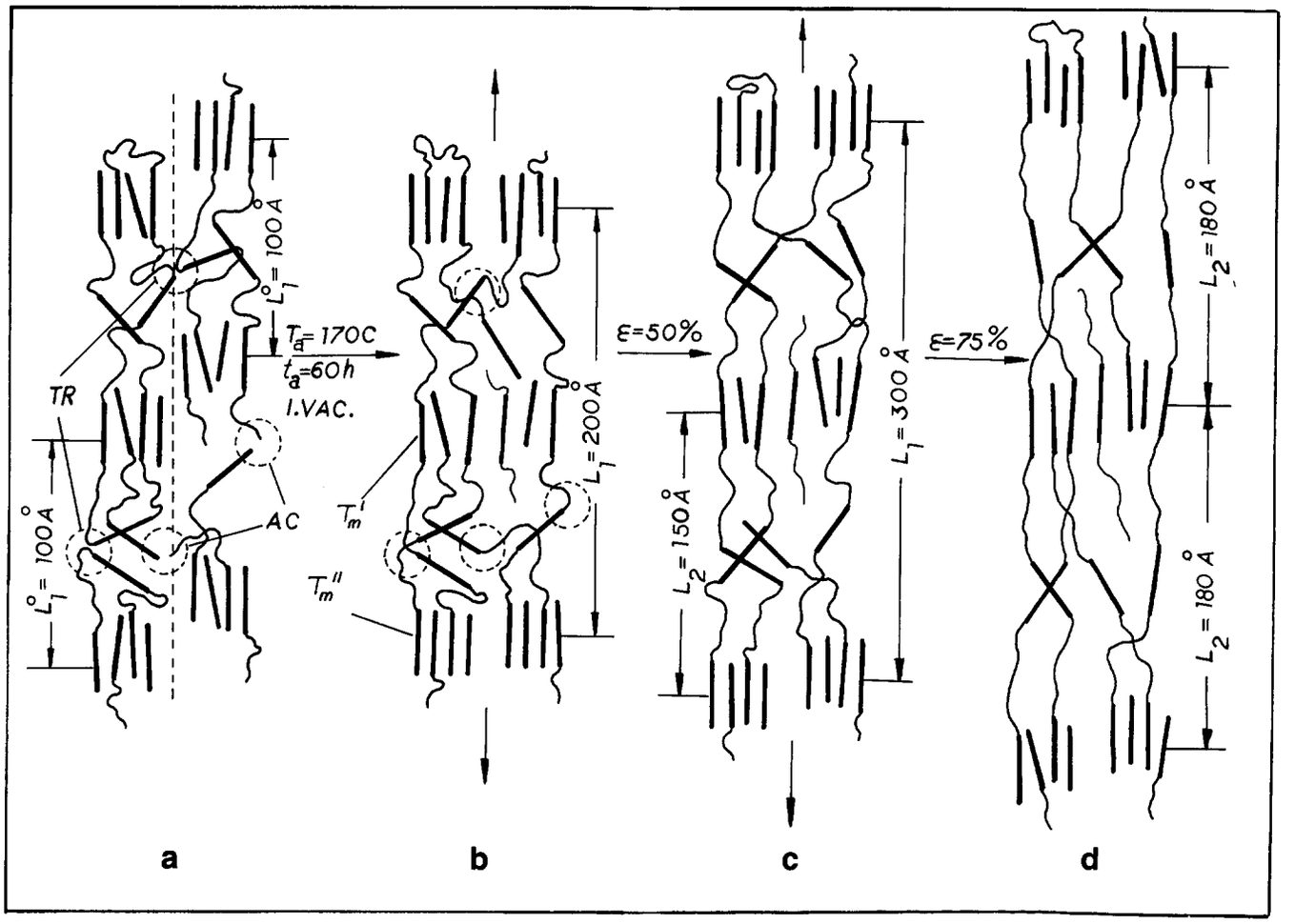

Figure 8 Schematic representation of the structural changes in drawn semicrystalline thermoplastic elastomers after thermal treatment and deformation: (a) After drawing to $\lambda_1 = 5$ and annealing for 6 h at 170°C followed by an additional drawing up to $\lambda_2 = 2.5$ and keeping the stress for 48 h. Hard segments are pulled out of the crystalline domains, and other sequences between the domains become effective as tie molecules (destroyed structure). (b) After additional thermal treatment in vacuum at 180°C for 60 h of the sample from (a) when solid-state reactions take place (regenerated structure). (c) After relative deformation $\varepsilon = 50\%$ of the sample from (b). (d) After relative deformation $\varepsilon = 75\%$ of the sample from (b). The broken line is the interfibrillar interface boundary; TR show locations where transreactions can take place; AC show locations for additional condensation. Other symbols are explained in the text

lamellar sequences and amorphous regions, the latter comprising two soft and one hard segment. The only difference consists of the existence of two alternating types of lamellae for the reasons described above.

The assumption of the appearance of a second type of lamellae is supported by calorimetric studies of all samples under investigation (*Table 1*). The d.s.c. thermograms are displayed in *Figure 9*.

One can see that the thermogram of the sample with undestroyed initial structure (curve a in *Figure 9*) shows two well shaped melting endotherms situated rather close to each other, thus suggesting the occurrence of recrystallization phenomena during heating in the calorimeter. The sample with destroyed structure (curve b) exhibits only one very flat and broad endotherm covering the same temperature range as the previous two distinct peaks (curve a). From the shape of the peak in curve b a very imperfect or, to be more specific, a rather defective structure can be assumed for this sample. After structural regeneration by crystallization, the melting peak is much better developed and situated at a higher temperature (curve c). In addition, another very flat and broad (between 70 and 130°C) endotherm can be detected.

This trend *versus* the appearance of two melting peaks is still much better pronounced after long annealing (60 h instead of 1 h, sample 4, *Table 1;* curve d in *Figure 9*). Two very sharp and clearly separated peaks ($T_m' = 156$°C and $T_m'' = 199$°C) are characteristic of the sample that has undergone structural regeneration through solid-state reactions. Prolonged annealing thus results in the perfection of two types of crystallites leading also to the highest degree of crystallinity w_c (*Table 1*). In addition, it should be noted that T_m' is below the annealing temperature $T_a = 170$°C, i.e. during the treatment these crystallites have been in the molten state and have formed during the subsequent cooling. This is in contrast to the other type of lamellae, which have become more perfect during the same treatment; their melting point has increased considerably ($T_m'' = 199$°C), as compared to the original sample (curve a).

On the basis of d.s.c. data it can be concluded that two types of crystallites really do exist in the samples with regenerated structure, strongly differing in their perfection as demonstrated by their different melting temperatures and degrees of crystallinity w_c (*Table 1*) after prolonged annealing at high T_a. It seems quite reasonable

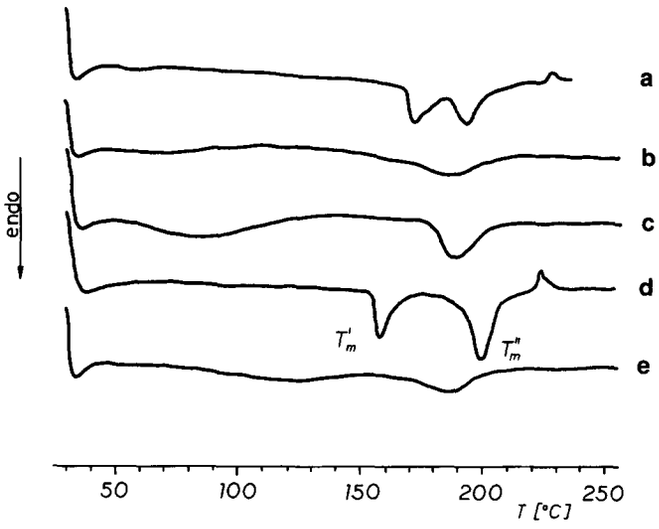

Figure 9 D.s.c. thermograms of PEE bristles (PBT/PEG = 49/51 wt%) with different histories: (a) samples with initial structure (drawn $\lambda_1 = 5$ and annealed, sample 1, *Table 1*); (b) sample with destroyed structure by additional drawing up to $\lambda_2 = 2.5$ (sample 2, *Table 1*); (c) sample with regenerated structure by crystallization (sample 3, *Table 1*); (d) sample with regenerated structure by solid-state reactions (sample 4, *Table 1*); (e) sample with regenerated structure through chemical crosslinking (sample 5, *Table 1*). The melting peaks of the two types of lamellae T'_m and T''_m are indicated

to correlate these two different types of crystallites with the two lamellar types discussed above—the original lamellae and those arising by secondary stress-induced crystallization during the additional drawing. So far the model presented in *Figure 8a* suggests the existence of two types of crystalline lamellae differing in their origin and perfection. It seems to be supported by several observations.

Does crystal thickening exist in block copolymers?

By following the effect of the annealing temperature on the long spacing in polyblock thermoplastic elastomers, a drastic increase of L has been repeatedly reported[10–12]. Similar results are obtained in the present study, as can be concluded by comparison of the starting L_1^0 values of the thermally untreated samples (*Figure 2*) and those of the treated ones (*Figures 4* and *5*). This doubling in L is usually explained[11] by the well known 'crystal thickening' phenomenon in crystalline homopolymers. The basic question arises—how far is this concept applicable to block copolymers with very limited length of the crystalline blocks? We will try to answer this question by the ideas illustrated through the models in *Figures 8a* and *8b*.

The model in *Figure 8a* describing the destroyed structure is characterized by one long spacing with value corresponding to L_2 in the overall deformation pattern, as demonstrated by analysis of the behaviour of the sample with destroyed structure (*Figure 3*).

The next model (*Figure 8b*) reflects the structure regenerated by means of thermal treatment (including the effect of both crystallization and chemical reactions). Let us consider first the influence of the physical processes.

It is well known that thermal treatment close to the melting temperature increases substantially the crystalline perfection. One should take into account that during drawing (structural destruction) a lot of defects are introduced in the crystallites and during subsequent annealing they move out of the crystallites reaching the interlamellar amorphous regions. The density ρ_a of the latter is thus increased. As long as the prolonged thermal treatment is carried out with free ends, relaxation processes occur, leading again to an increase of the amorphous density. It is quite possible that ρ_a approaches in this way the density of the less perfect second type of lamellae ρ_{c2}. As a result a structure is formed, consisting of perfect crystalline lamellae (the original ones) with higher density ρ_{c1}, followed by large areas comprising both the amorphous regions (with ρ_a) and the second type of lamellae (with ρ_{c2} close to ρ_a). Such an increase of the volume of the interlamellar layers (with density $\frac{1}{2}(\rho_a + \rho_{c2})$) leads to a drastic rise in the long spacing (up to two times), as is actually observed (compare L_1^0 in *Figure 2* and *Figures 4* and *5*, refs. 10–12).

It follows that the drastic increase in L after annealing is related to the formation of larger (as compared to the situation before annealing) interlamellar regions incorporating small and very defective crystallites (such as lamellae of the second type in the present case). The density of these areas, $\frac{1}{2}(\rho_a + \rho_{c2})$, is higher than that of the original amorphous phase ρ_a but is still below the increased density of the lamellae of the first type ρ_{c1}, i.e. $\rho_a < \frac{1}{2}(\rho_a + \rho_{c2}) < \rho_{c1}$.

This conclusion is supported by other observations. It was recently demonstrated[2] for a series of PEE with various PBT/PEG ratios that the typical length (for the 50/50 composition) of the extended hard segment l^h is about 50 Å. Direct WAXS measurements of the lamellar thickness l_c of the same sample (after annealing close to T_m) showed that the l_c values are of the same order of magnitude (50–60 Å). This means that the length of the crystallizing hard segments l^h represents a serious limitation on the maximal lamellar thickness. In numerous cases (with $l^h < 50$ Å) it is not possible to achieve the lamellar thickness required by the crystallization conditions. For the same reason essentially no chain folding occurs (except for the compositions with high PBT content, e.g. PBT/PEG = 75/25). Thus it is hard to believe that crystal thickening exists in copolymers with limited block length. The observed increase in L is therefore believed to be due to the formation of larger interlamellar regions during annealing with density lower than the crystalline one, as sketched schematically in *Figure 8b*.

Interfibrillar chemical healing

We come back to the deformation behaviour of the sample with structure regeneration through solid-state reactions (*Figure 5*). Having in common with all the samples described so far the four types of long spacing, L_1, L_2, L_1^{rel} and L_2^{rel}, it behaves however completely differently with elongation—all four long spacings increase linearly with increase of the relative deformation within the entire range (up to $\varepsilon = 200\%$). What could be the reason for such a change of deformation behaviour? It seems reasonable to assume that it is related to the interfibrillar contacts created during prolonged thermal treatment. In the sample with destroyed structure (additional drawing up to $\lambda_2 = 2.5$ for 48 h, sample 2, *Table 1*) and eliminated interfibrillar contacts relaxation and slippage of microfibrils on the microfibrillar interface is enhanced (*Figure 8a*). The most characteristic feature of this structure is the introduction of interfibrillar phase boundaries schematically presented in *Figure 8a* by the

broken line. The regeneration of the structure aims primarily at the elimination of these phase boundaries through formation of interfibrillar contacts as shown in *Figure 8b*. Only through the establishment of these contacts by additional crystallization and particularly by solid-state reactions is it possible to explain the deformation behaviour of this sample (*Figure 5*).

The initial high value of the long spacing L_1^0 increases linearly ($L_1^{max}=300$ Å) up to $\varepsilon=50\%$ when a second long spacing $L_2=150$ Å appears. It increased up to $L_2^{max}=250$ Å at $\varepsilon=200\%$. The rise in L_1 is due to conformational changes (stretching) in the interlamellar regions causing some dilution effect. For this reason the scattering intensity increases (*Figure 7*). At $\varepsilon=50\%$ this dilution effect in the truly amorphous regions is large enough to create a density difference $\rho_{c2}-\rho_a$ sufficient to be registered by SAXS. In this way the second long spacing L_2 appears (*Figure 8c*). At this deformation level ($\varepsilon=50\%$) L_1 and L_2 coexist; with the further rise of ε (75–100%) the density difference $\rho_{c2}-\rho_a$ increases approaching $\rho_{c1}-\rho_a$ and then L_1 disappears (*Figure 8d*). The decrease of ρ_{c1} as a result of the introduction of crystal defects by the pulling out of tie molecules also contributes to bringing both densities closer. In contrast to the other samples (*Figures 2–4*), L_2 increases linearly with the rise of ε up to 200%, thus suggesting that neither relaxation nor slippage of microfibrils occurs, i.e. that quite strong interfibrillar contacts exist. It can be concluded that the linear changes in both L_1 and L_2 originate from conformational changes in the inter- and intralamellar regions without involving elimination of interfibrillar contacts as in the previous cases. This conclusion is supported also by the observation that even the long spacings in the relaxed state, L_1^{rel} and L_2^{rel}, increase linearly with the rise of the deformation quite unlike the previous samples where they remain more or less constant (*Figures 2–4*). Furthermore, the increase of all four types of long spacings, L_1, L_2, L_1^{rel} and L_2^{rel}, is not only linear but also directly proportional to the relative deformation, suggesting an affine deformation mechanism. This is demonstrated for L_2 by the dotted line in *Figure 5*, which is calculated as $L_2^{cal}=\frac{1}{2}L_1^{exp}$.

The last indication in favour of the statement that deformations up to $\varepsilon=200\%$ do not affect the number of the interfibrillar contacts created as a result of solid-state reactions can be found in the maximum achievable values of L_2 and L_1^{rel} (*Figure 5*). The value of $L_2^{max}=250$ Å corresponds to two soft l^s and two hard l^h segments, i.e. $L_2^{max}=2l^h+2l^s$ assuming an extended-chain conformation. Supposing an affine deformation mechanism, the value of $L_2^{max}=250$ Å should be achieved at $\varepsilon=150\%$. Actually it is observed at $\varepsilon=175\%$. The difference of 25% in ε provides an idea about the contribution of the slippage effect of the microfibrils to the deformation observed as a result of the destruction of interfibrillar contacts. Consequently, these contacts are rather strong and remain almost unaffected by deformations of up to $\varepsilon=200\%$.

The observation that $L_{1max}^{rel}\sim L_1^{max}\sim 300$ Å in the same deformation range (total deformation for L_1 and plastic one for L_1^{rel}) leads to the same conclusion. It is important to note here that the affine increase in L_1^{rel} does not necessarily suppose slippage of microfibrils, i.e. the observed plastic deformation in the range of 0 to 50% is a result of irreversible conformational changes in the interlamellar amorphous regions.

The deformation behaviour of the sample with structure regenerated by solid-state reactions (*Figure 5*) as well as the changes taking place during regeneration and subsequent stretching, represented schematically in *Figure 8*, clearly demonstrate that solid-state reactions (additional condensation and transreactions) result in the formation of numerous strong interfibrillar contacts. An important consequence of these changes is the elimination of the interfibrillar phase boundaries existing before. This treatment is shown in *Figure 8a* (broken line). As long as the phase boundary between two microfibrils disappears, one deals with a healing process[3]. At the same time, physical processes (crystallization and relaxation) alone do not lead to the same deformation behaviour (compare *Figures 4* and *6*). The chemical reactions described are the very factors determining these peculiar properties observed with samples 4 and 5. Thus one deals in those cases actually with chemical healing or, more precisely, with interfibrillar chemical healing.

The deformation concept of the microfibrillar ensembles

The deformation behaviour of the sample with structure regenerated by chemical crosslinking (*Figure 6*) differs from those of the other samples (*Figures 2–5*). Only one long spacing under stress and another one in the absence of stress are observed, the second long spacing keeping a constant value close to the initial L_1^0. The first long spacing increases slightly and non-linearly (by about 40%) within the entire deformation range (0–200%). This is rather striking since the long spacings remain almost unaffected even when the highest deformation $\varepsilon=200\%$ is achieved.

Such an 'inconsistency' in the deformation behaviour can be understood by assuming the formation of a rather dense network during crosslinking in both inter- and intrafibrillar amorphous regions. This network restricts the stretching of the chains in the amorphous intrafibrillar layer, which determines the L values. For the same reason the interfibrillar contacts are strong enough in order to prevent pulling out of tie molecules and slippage of separate microfibrils.

In order to explain the usually observed external deformation, one should assume that contacts between ensembles of microfibrils are eliminated during stretching. In this way slippage of these ensembles becomes possible and results in the macrodeformation observed. At the same time the microfibrils within the ensembles remain almost unaffected (while the long spacing increases only at its maximum by 40%, the macrodeformation increases up to $\varepsilon=200\%$).

CONCLUSIONS

By SAXS measurements of thermoplastic elastomers (PBT/PEG = 49/51 wt%) with undestroyed structure (created by drawing 5 × and subsequent annealing), with destroyed structure (by additional drawing up to $\lambda_2=2.5$) and with regenerated structure (by crystallization, solid-state reactions and chemical crosslinking), the effect of sample deformation during the measurements on the scattering behaviour is followed. Experiments on bristles under stress and with subsequent removal of the stress reveal the following points.

(1) The sample with undestroyed structure behaves as described earlier[1,2]—an affine increase of the long

spacing L is observed with the rise of ε up to 75%, when a second long spacing L_2 appears with value close to L_1^0 which remains constant up to $\varepsilon = 200\%$. In addition to the previous studies[1,2], it is found that L measured without stress has two discrete and almost constant values L_1^{rel} (close to L_1^0) and L_2^{rel} (below L_1^0). The basic model discussed earlier[1,2] is confirmed in the present study—the affine increase of L_1 with ε is related to the reversible deformation of the amorphous regions and the appearance of L_2 is due both to relaxation of microfibrils free of interfibrillar contacts[1] as well as to the formation of a second type of lamellae of hard segments originally dispersed in the amorphous regions[2].

(2) The sample with destroyed structure does not follow this general pattern, displaying only one long spacing L_1 and another L_1^{rel} in the deformation range $\varepsilon = 0$–50%, which actually correspond to L_2 and L_1^{rel} in the general pattern as long as the structural destruction is a result of extreme additional drawing (up to $\lambda_2 = 2.5$).

(3) The deformation behaviour of the samples with regenerated structure depends on the method of regeneration:

(i) Regeneration by crystallization recovers the typical deformation behaviour seen before. The only exception is the observation of a very high initial L_1^0 value due to the formation of a larger interlamellar layer with more or less uniform density which differs from that of the crystalline lamellae. This suggests that the increase in L is not related to crystal thickening—a phenomenon typically observed with homopolymers.

(ii) Regeneration by solid-state reactions (additional condensation and exchange reactions) results in a completely different deformation behaviour. Again four long spacings, L_1, L_2, L_1^{rel} and L_2^{rel}, are observed, showing however an affine increase with ε in the corresponding deformation ranges in contrast to all other samples. This behaviour is explained by the large number of intrafibrillar and particularly of interfibrillar contacts created due to the solid-state reactions. The phenomenon of interfibrillar chemical healing is defined. It corresponds to elimination of the interfibrillar phase boundary previously created during extreme stretching conditions (structural destruction). Again a very high initial L_1^0 is observed for the same reasons as in the case of structural regeneration through crystallization.

(iii) Regeneration through chemical crosslinking leads to deviations of the deformation behaviour from the general pattern—only one long spacing L_1 (measured under stress) and another one L_1^{rel} (measured without stress) are observed: they increase slightly with ε (up to 200%). This behaviour is explained by the very high density of the chemical network created during crosslinking. In order to explain the rather small changes of L with ε the concept of slippage of ensembles of microfibrils is introduced.

(4) A model is proposed for the description of the changes in the long period during deformation which also explains the observed change in the maximum SAXS intensity. The basic characteristic feature of this model is the existence of two types of lamellae differing in their perfection and origin. The first and more perfect type of lamellae correspond to the starting crystalline lamellae (after drawing $\lambda_1 = 5$ and annealing), while the second type of less perfect lamellae are assumed to arise during the additional drawing (up to $\lambda_2 = 2.5$). It comprises hard segments originally dispersed in the amorphous interlamellar layers or pulled out from the neighbouring crystallites. The existence of the two types of lamellae is proved by d.s.c. measurements—their melting temperatures differ by 40°C and their respective degrees of crystallinity are estimated to 17% and 30%. Depending on the treatment (thermal or mechanical) the less perfect lamellae can show a mean density quite similar to that of the amorphous regions, which results either in the appearance of an apparent very large L or of a second long spacing L_2. At deformations above $\varepsilon = 75\%$ the latter merges with L_1 and the two types of lamellae become equivalent with respect to their scattering behaviour.

(5) The SAXS studies of PEE samples with model character allowing the variation of the number of intra- and in particular interfibrillar contacts demonstrate quite clearly the predominant role of tie molecules in the formation of mechanical strength in these polymer materials. The thermoplastic elastomers being semicrystalline polyblock systems seem to be very attractive models for carrying out such studies on the structure–properties relationship of polymeric materials.

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