Letter

Investigations on supermolecular structure of gel-spun/hot-drawn high-modulus polyethylene fibres

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Dear Sir

In a recent paper Hofmann and Schulz[1] described investigations on the supermolecular structure of different ultradrawn (draw ratio ≫20) polyethylene fibres. Although the investigated fibres are all produced using essentially the same process, the investigated samples are classified into two groups: 'shish-kebab' fibres (Tekmilon/Mitsui and sample 2, prepared by the authors) and 'smooth' fibres (Spectra 900/Allied Sign and sample 1, also prepared by the authors). The authors claim there are two important differences between the two classes. First, the shish-kebab fibres can be identified on transmission electron microscopy (TEM) photographs, which show a clear lamellar overgrowth. The smooth fibres only show 'negligible lamellar overgrowth'. The second, less gradual and thus more quantifiable difference is the long period, which is extremely small (5 nm) in the case of the shish-kebab fibres. For sample 1 the long period was much larger and for Spectra 900 no long period was visible at all. That the value of 5 nm is indeed very small is clear if one compares it with the smallest values reported for the long period by Martinez-Salazar *et al.*[2], who found no values lower than 6 nm even when the melt was quenched extremely rapidly.

In this letter a different, more likely explanation is given for the small value found for the long period. It is shown that the long period observed is more likely an artefact originating from the added stearate. The possibility that the shish kebabs observed in the TEM micrographs originate from stearate too is also discussed. Inspection of Figures 3 and 4 in Hofmann and Schulz's paper shows at least three orders of the meridional long period. This suggests a very regular packing of the amorphous and the crystalline regions and extremely small deviations in the long period from the average value. If one is prepared to accept that these conditions are fulfilled there remains one important feature of the meridional reflections to be explained. A close inspection of Figure 4 in their paper reveals that the odd orders of the meridional long spacing are relatively stronger than the even ones. In my opinion this effect cannot be explained assuming a normal lamellar stacking of crystalline and amorphous regions of pure polyethylene. The effect is demonstrated here in *Figure 1*, which is a flat-film photograph made by two separate exposures. First the whole film was exposed for 2 h, then after covering the inner portion with the first order reflections with a lead plate, the film was exposed again for 8 h. Now five orders are clearly visible without an overexposure of the first order reflection and the above-stated characteristics are confirmed more clearly.

A more plausible explanation than the one given by Hofmann and Schulz can be found in the additives used during spinning. Hofmann and Schulz state that they used aluminium stearate as an additive and Mitsui most probably also uses a considerable amount of stearate, which can be derived from elemental analysis. Elemental analysis shows that Tekmilon fibres contain 0.004% (w/w) Al and 0.076% (w/w) Ca. If one assumes that the latter, which is the dominant inorganic element is completely present as calcium stearate, this means that Tekmilon contains 1.3% calcium stearate. Such an amount will give a noticeably reflected intensity, especially if the molecules are directed along the fibre axis. In this case the stearate reflections are concentrated in single points in reciprocal space, where the wide angle X-ray scattering (WAXS) reflections given in Figure 4 in the article by Hofmann and Schulz lie on a circle in reciprocal space. This explains why the intensity of the small angle X-ray scattering (SAXS) reflections in Figure 4 is so high relative to the intensity of the WAXS reflections even though there is only 1.3% calcium stearate present. Moreover all phenomena can be explained ascribing the small angle reflections to calcium stearate. The long period indicated by Hofmann and Schulz is 5 nm, which is identical to the value reported in the literature for calcium stearate[3], but the strongest coincidence between literature data[3] and the small angle scattering reported here is the alternating character of the scattered intensities with the order of the reflection which also exists in calcium stearate. This is illustrated in *Figure 2*, where a linear scan through *Figure 1* is reported combined with a diffractogram of pure calcium stearate. In the diffractogram the first order reflection is absent because the scattering angle was too small for the equipment used. The alteration of the intensities is clear in both scattering patterns and the *d*-spacings of the different orders of the long spacing correspond remarkably well. This makes the explanation presented here for the meridional reflections much more likely than that given by Hofmann and Schulz.

For the preparation of samples 1 and 2, Hofmann and Schulz used aluminium stearate as a spinning aid. In the literature less is known about aluminium stearate than calcium stearate but all stearates reported in the JCPDS-International Centre for Diffraction Data powder diffraction files[3] have a long period of ~5 nm. This means that aluminium stearate most probably also has such a long period and that the long period found for sample 2 is related to the aluminium stearate. Because the amount of aluminium stearate added is not

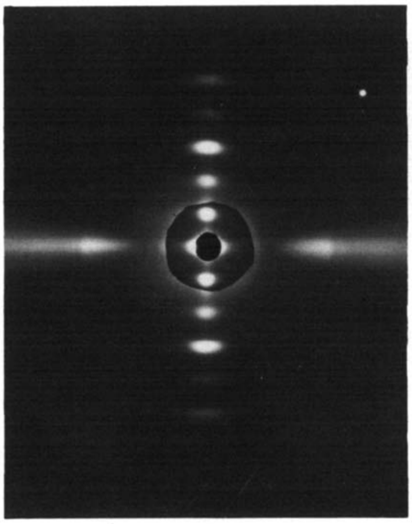

Figure 1 X-ray diffraction pattern of Tekmilon fibre. Sample to film distance = 195 mm. The film is exposed for 2 h and after covering the innermost portion with a lead plate the film is exposed for another 8 h

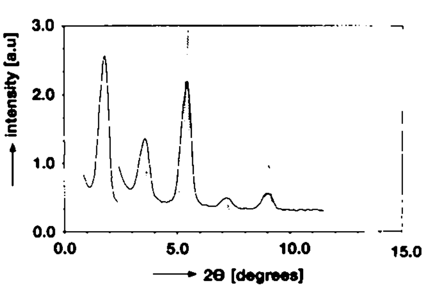

Figure 2 Scattered intensity *versus* scattering angle: ———, horizontal scan through the pattern of *Figure 1*; ·····, diffractometer pattern of pure calcium stearate. The X-ray wavelength = 0.15418 nm

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specified and because no X-ray photographs are included in their paper it is not possible to discuss the differences between samples 1 and 2 on the basis of information given in the paper. Some possibilities have however been suggested by Hofmann for the considerations presented here[4]. The scattering power of aluminium is of course smaller than the scattering power of calcium. Furthermore the orientation of the stearate might be less in the laboratory spun sample 2, because drying and drawing was done simultaneously and immediately after spinning in their process. Finally, Hofmann was not sure about the amount of stearate used. Although he had no reason to assume that it would differ for the two samples, he could not confirm this.

According to Hofmann and Schulz the shish-kebab and smooth fibres can also be distinguished by TEM. No scale bars are given in their micrographs but it seems logical to assume that the kebab structures which are indeed clearly visible in Figure 2 are of a thickness which corresponds to the long period observed with SAXS. If this were not the case the relevance of the micrographs in relation to the rest of the paper would be unclear.

If we compare the TEM work presented here with other electron microscopy work carried out on gel-spun polyethylene fibres, some important differences have to be noted. Let us first refer to the work of Pennings and co-workers, who introduced the shish-kebab structure. In a paper by van Hutten *et al.*[5] some scanning electron microscopy (SEM) photographs are shown of shish-kebab fibres that are prepared by stirring induced crystallization. It should be noted that these structures are best observed on the as-spun fibres and vanish if the fibres are drawn to high draw ratios according to van Hutten *et al.*[6]. Hofmann and Schulz however perform their experiments on samples with very high draw ratios, which makes it surprising that they observe 'shish kebabs'.

Van Hutten *et al.* observed the shish-kebab structures using SEM, without the need of a complicated sample preparation. However other TEM studies have been carried out. Schaper *et al.*[7] investigated shish-kebab fibres produced according to the surface growth method. They studied both the as-grown fibre and the subsequently solid state drawn fibre and also concluded that the lamellar overgrowth, clearly present in the as-grown fibres, entirely vanishes upon zone drawing.

Schaper prepared his samples by chlorosulphonation followed by heavy metal staining and ultramicrotomy parallel to the fibre axis, thus obtaining a sample which is representative for the whole fibre. Hofmann and Schulz however use a surface replication technique, which means that their observations are only representative for the fibre surface. In my opinion it might well be the case that the differing observations of Hofmann and Schulz have to be attributed to the fact that their preparation technique yields a sample which is not representative for the whole fibre, unlike the preparation method used by Schaper *et al.*[7].

It has already been mentioned that Tekmilon (*Figure 1*) contains a lot of stearate. The stearate is added as a spinning aid and will migrate, together with low molecular weight polyethylene fractions, to the surface of the fibre during the spinning process. It is quite likely that the stearate will crystallize there in the form of bi-layers with the polar carboxylate groups oriented towards each other, surrounding the calcium atom. The apolar stearyl groups will tend to align with the polyethylene molecules, thus resulting in a shish-kebab structure with a lamellar thickness of 5 nm.

Thus all the differences observed by Hofmann and Schultz between Spectra 900 and Tekmilon can be explained by the presence of a relatively large amount of stearate in the latter product. This means that the difference between the two types of fibres is in the additives and therefore of no importance to the fibre characteristics. A division into two classes is thus also artificial. Because all the fibres discussed in the paper by Hofmann and Schulz are produced according to the same process this is not surprising.

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