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Kink bands and shear deformation in polybenzobisoxazole fibres

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Kink bands with a thickness ranging from 45 nm to 1.8 μm were observed in polybenzobisoxazole (PBO) fibres examined in the transmission electron microscope. These bands are localized, and oriented at $69° \pm 3°$ with respect to the fibre axial direction. The average shear strain is about 0.7 along the band. Bands of intermediate thicknesses (e.g. 0.1–0.3 μm) are wavy and relatively less uniform than the thin (45 nm) and thick (1.8 μm) bands. Sometimes cracks or voids with a preferential orientation develop in the band, particularly in 0.1 μm or thicker bands. When two bands intersect with each other, a mutual shearing effect seems to occur at the band intersection, where the fibrils or voids in an existing band are reoriented in a new direction, which seems to be determined by the resultant shear displacement of the two bands. Enhanced voiding occurs at the intersection. Under large deformation, buckling occurs at regions populated with bands and band intersections. These observations suggest a shear yielding mechanism for incipient kink bands, and the possibility of a large-scale shear motion under large compression. However, this large-scale shear motion may be lessened if buckling occurs.

(Keywords: polybenzobisoxazole fibres; kink bands; shear deformation)

INTRODUCTION

Kink bands and their formation have been studied extensively for organic fibres. These studies include morphological characterizations by microscopic or analytical methods[1–7], correlations between kinking and compressive failure in fibres[8,9] and composites[10], modelling of kink band formation and kinking with respect to macroscopic properties[11] and others[12,13]. These studies have shown that kink bands are detrimental to fibre compressive strength.

It is generally believed that kink band formation is closely related to the fibrillar morphology of a fibre[14]. However, it is unclear how a band develops and eventually leads to a complicated compressive failure. Earlier studies showed that the bands usually develop in groups localized around a sharp bend[15]. Kinking can be complicated by buckling and fibrillation, especially at the later stages of deformation[16]. The fibre then fails in a catastrophic manner. In a recent study[17], kink bands were found to develop under very slight compression. They appear to form by an initiation and propagation process as observed directly under the scanning electron microscope (SEM). This observation suggests that kinking is induced by shear, characterized by shear strain or displacement along the band, rather than by buckling, in which little or no coherent motion occurs along the band. If propagation is a necessary step for a band to develop, the process can be understood by examining the interactions of bands. In an attempt to gain further understanding of kink band formation, kinked polybenzobisoxazole (PBO) fibres were sectioned using ultramicrotomy and examined in the transmission electron microscope (TEM).

EXPERIMENTAL

Materials and specimen preparation

Cis-PBO used in this study had an inherent viscosity of 26 dl g^{-1} determined at 25°C in 0.2% methanesulfonic acid solutions. PBO fibres were spun from PBO/PPA (polyphosphoric acid) dopes from a laboratory fibre spinning apparatus. The spun fibres were coagulated in water, washed and dried. Fibres were subsequently heat treated under tension. The finished fibre had an average diameter of approximately 15 μm.

Compressive deformation of fibre

Kink bands were produced in fibre by a bending method. Razor-cut, 5 inch (~127 mm) long sections of fibre held between two pairs of tweezers were flexed around a thumb tack (drawing pin) at various locations along the fibre and to various degrees of flex as indicated by the bending angle. The diameter of the pin was approximately 0.05 inch (~1.27 mm) and the fibre bend angle was varied from about 20° to 90°. This technique resulted in kink bands varying in length and population density along the length of fibre.

Optical microscopy

Sections of the deformed fibres were razor cut and taped onto a glass slide for microscopic observation. The samples were examined using a Nikon Optiphot transmitted-light microscope. Selected portions of the fibre were used for electron microscopy.

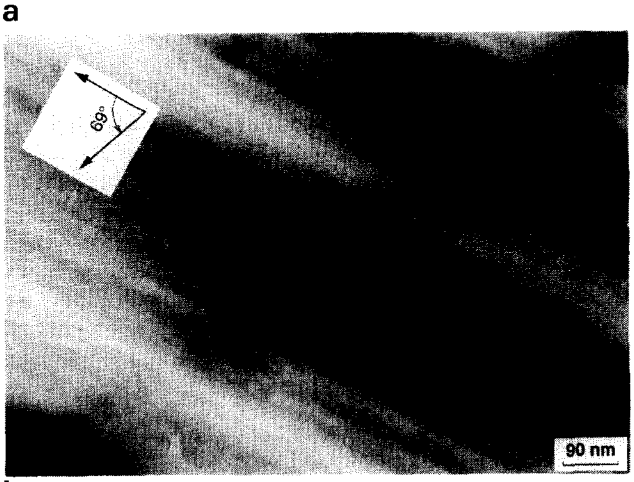
Microtomy and transmission electron microscopy

Fibre sections were taped to sheet polycarbonate and coated with spray acrylic to affix the fibre to the plastic substrate. Small sections of the fibre (< 5 mm) attached to the polycarbonate were cut from the bulk and trimmed for ultramicrotomy. Ultramicrotomy was performed using a Reichert Ultracut E microtome to produce longitudinal sections ranging in thickness from 40 to 80 nm. New areas of the diamond knife were used to ensure a sharp cutting edge, minimizing sectioning artefacts. Sections were collected on 400 mesh thin bar copper TEM grids. This procedure enabled sectioning down the fibre axis by aiding in fibre alignment. Thin sectioned samples were examined using either a JEOL 100 CX or 1200 EX ATEM operating at an accelerating voltage of 100 or 120 kV. TEM bright-field images were recorded on Kodak Electron Image Film 4489.

RESULTS AND DISCUSSION

Thin kink band

Fibres deformed by compression usually develop two sets of mutually intersecting kink bands as shown in *Figure 1a* for a strand of fibre observed under an optical microscope. The angle between the band and the fibre axial direction is about $69° \pm 3°$ as measured from the light micrographs. To understand the ultrastructure of the bands, microtomed thin sections were observed by TEM. *Figure 1b* shows the morphology of a single kink band as viewed in the TEM. The band has a uniform thickness of about 45 nm and clear boundaries separating the kinked and unkinked regions. A common feature observed on microtomed sections at this high magnification is the prevalence of striations along the fibre axis, which are oriented at an angle of about $69° \pm 3°$ with the band. The thickness of the striations ranges from 10 to 60 nm as measured from the micrograph. Judging from the thickness and orientation, the striations are probably related to the fibrillar morphology of the polymeric fibres[14,18,19]. The striations were displaced by the kink band at a constant angle. It was reported[20] that the band angle could vary with the direction of observation. The band extends across the striations with no signs of voiding or fibrillation. These observations are similar to that in fibre composites where fibrils were displaced by a large deformation band developed in the composite under compression[10].


a


b

Figure 1 (a) Optical micrograph showing two sets of intersecting kink bands on PBO fibre. (b) A kink band 45 nm in thickness as observed in a microtomed section of PBO fibre in the TEM

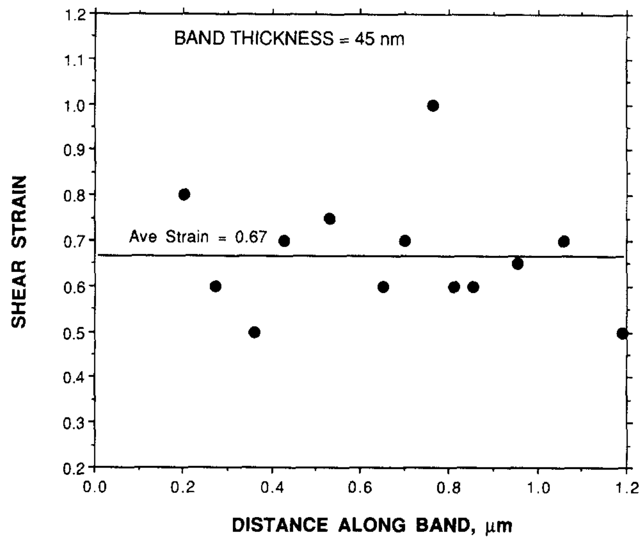


Figure 2 The distribution of shear strain along the kink band as measured by the displacement of striations on the micrograph

The shear strain as measured by the displacement of the striations is plotted along the band in *Figure 2*. This shear strain, defined as the shear displacement divided by the band thickness, ranges from 0.5 to 1 with an average of 0.67. These observations indicate that kinking, at least in the incipient stage, is probably a shear yielding process. The behaviour of the thin kink bands is similar to that of shear bands in glassy polymers in which the band thickness and shear strain are maintained constant[21].

On the fibre surface, steps or bulges are often developed as a result of kinking. It has been unclear as to whether the bulge is a result of buckling or kinking. Both kinking and buckling are used to describe the kink band process[22]. *Figure 3* shows a kink band near the fibre surface. The thickness of the band, averaging 0.3 μm, is less uniform than in the band of *Figure 1*. A few dark bands, oriented at a different angle, are probably bands with a different kink plane. Details of their morphology could not be resolved from this photomicrograph. The step shown on the surface consists of densely packed fibrils oriented along the fibre direction. The shear strain

Figure 3 A step on the fibre surface with a kink band extending from it. The band is wavy in its path and non-uniform in thickness

as measured from the step is about 0.6, consistent with that obtained from the kink band. No fibrillation could be observed inside the step. It is likely that the step is caused by shear along the band in the early stages of deformation. A few voids are observed along the band, notably near the intersections of the dark bands. The voids are apparently related to the band interactions and will be discussed later.

Thick kink band

An area populated with kink bands is shown in *Figure 4*. Two major bands are seen, with voids preferentially oriented in the band. They both are uniform and are thicker than those described above. Band A has a thickness of about 1.8 μm and an average shear strain of about 0.7. Band B is about 1.2 μm thick with a similar strain along the band. These bands appear to have extended across the fibre diameter along a straight path. Notice that the bands were dislocated owing to a split in the specimen. A number of smaller bands, shown in the same figure, are wavy and do not seem to extend across the fibre.

Bands of intermediate thicknesses

Bands of intermediate thickness are usually wavy and have larger thickness variations than the thin and thick bands along their length. *Figure 5a* shows another fibre with a step at the surface. The band has a characteristic angle with the fibre axis but is apparently interrupted a few times along its path. It appears to be affected by the intersecting bands during its propagation, as indicated by the thickness variations at the intersections. *Figure 5b* is a detailed view of the band. The step appears to be a single kink with a shear strain of about 0.6. Unlike thin and thick bands, this band shows poor local uniformity despite the clear shear displacements across the thickness. It also seems to have gradually decreased its thickness as it extended towards the bulk of the fibre, as shown in *Figure 5a*. Eventually the band terminated inside the fibre before reaching the other side of the fibre. The details of band termination could not be observed because of splitting of the specimen. The termination of bands may result from the minute bending force applied.

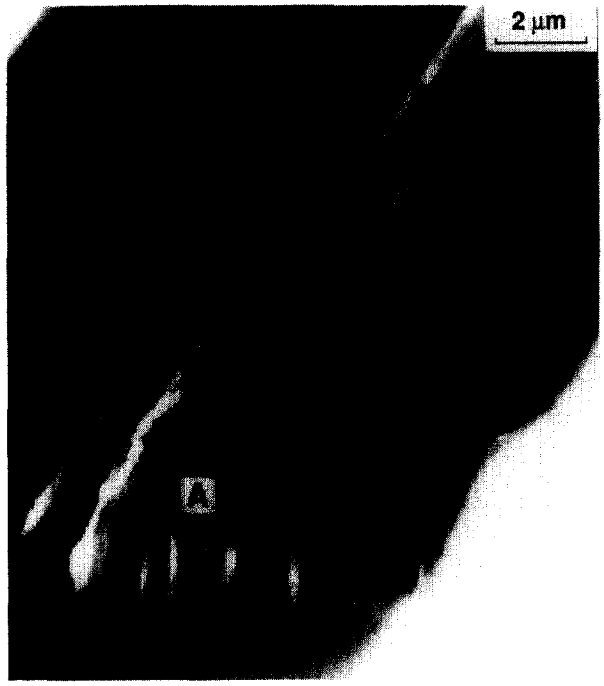


Figure 4 Morphology of kink bands 1.2–1.8 μm thick showing uniform band thickness and voids in the bands. (The longitudinal cracks are probably due to splitting during specimen preparation)

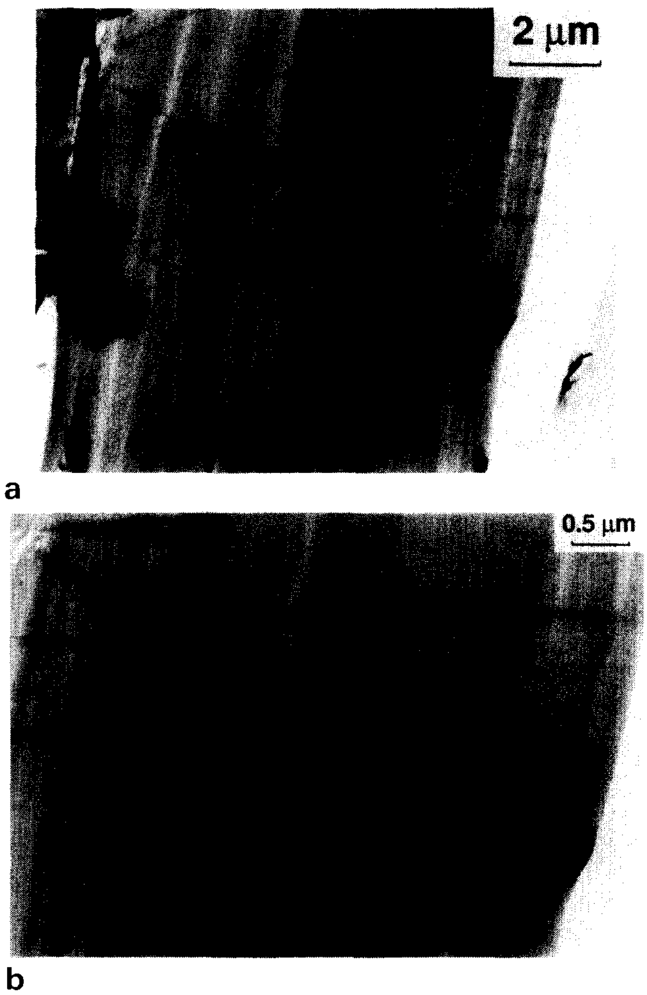


Figure 5 (a) A band with intermediate thickness (0.1–0.3 μm) showing a step on the surface and variations in band thickness along its path. (b) An enlarged view of the step and the band showing the irregularity of the band thickness and boundaries along the length

Void formation inside the kink band

Voids or fibrillation can sometimes develop in or near kink bands under large compressive deformation[16,17]. Since PBO fibre is porous with submicrometre voids[14], it is possible that further voiding could develop, resulting in macroscopic voids. The voids shown in *Figure 4* are apparently located among fibrils and terminate at the boundaries between the band and the non-banded regions. The shear strain determined from the void orientation was found to be consistent with that from the striation measurements. Some of the thinner bands in the same sample also contained voids, suggesting a weakness of lateral connection in the fibre.

Figure 6 is another example showing the interior of a banded region. Despite the separations of the specimen along the fibre direction, the specimen contains a thicker kink band extending across the fibre, and a number of short and smaller bands located above this band as indicated by the arrows. The thick kink band, band A, has voids along its length. These voids are oriented at about the same angle as the band direction, suggesting that the voiding is caused by the bands. The short and smaller kink bands seem also to contain voids, indicating that voiding occurred throughout the fibre. It is noted that these short and smaller bands are populated in the centre of the fibre with little or no evidence of being connected to the surface of the fibre. This observation suggests the possibility that the band either developed from the interior of a fibre without extending to the fibre surface[5], or extended from the surface but terminated in the bulk. Either case suggests the possibility of an ending of a band and supports the initiation and propagation of kink bands. The voids in the kink band, as in shear bands[21], could be attributed to local differential shear strains along the band. Delamination or fibrillation could take place within oriented fibrils.

The intersections of kink bands

Figure 6 also shows an intersection between two kink bands. Band A, as indicated by the arrow, is intersected by another kink band, band B, coming from the other side of the fibre. The plane containing band B is possibly not near-perpendicular to the plane of microtoming, so that a thick and dark image representing tilting of the band towards the axial direction is shown. Near the intersection, band B seems to be reoriented to near-perpendicular to the plane of microtoming, as indicated by the diminishing of the dark image and the presence of a few oriented cracks in the band. Despite the disturbance from some longitudinal cracks in the section, some band interactions could be observed at their intersection. These two kink bands, A and B, seem to be mutually sheared by each other, so that the directions of both bands after the intersection are changed slightly. The fibrils or voids at the intersection are also reoriented to a new direction, which appears to be determined by the resultant shear displacement of the individual intersecting bands. This behaviour seems to be similar to that of the shear bands in polystyrene[23], in which various types of band intersections with mutual shearing effect were observed.

This possibility can be schematically represented in *Figure 7*, in which band A is an existing band and band B is an intersecting band. Both have a constant shear strain of 0.7. At the intersection the already sheared region in band A is now sheared again by band B. As a result, the direction of fibrils in the intersection is reoriented according to the shear displacement of band B. The intersected area, as defined by ABCD, is subjected to further shearing by band B to result in a new and larger area ABC′D′. If a crack already exists in band A, this crack could also be reoriented and enlarged following the second shear process. After the intersection, band B resumes its original propagation from the

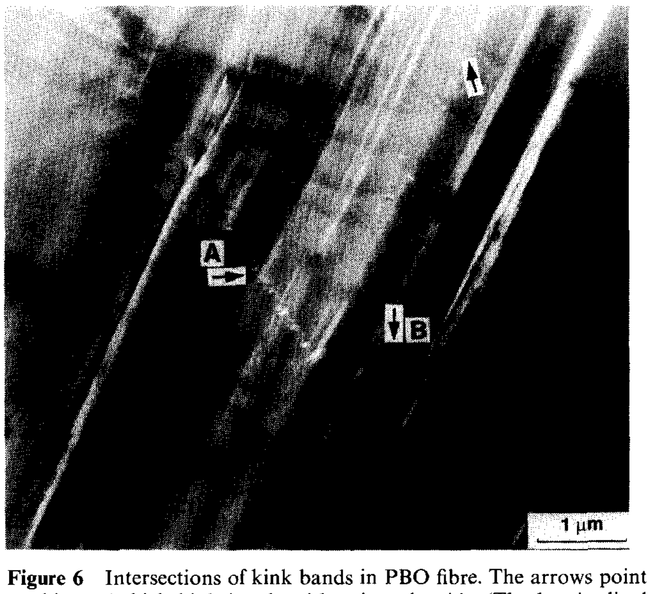


Figure 6 Intersections of kink bands in PBO fibre. The arrows point to thin and thick kink bands with oriented voids. (The longitudinal cracks are probably due to splitting during specimen preparation)

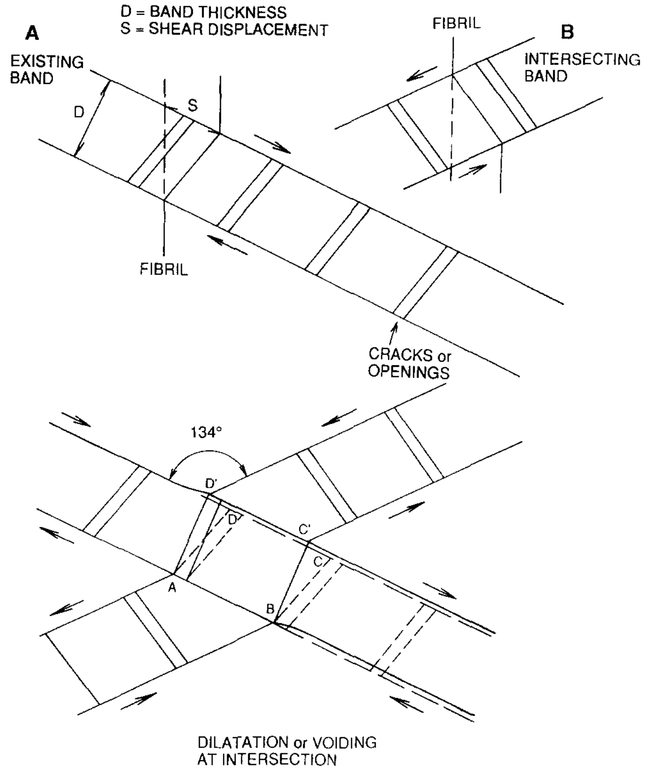


Figure 7 A schematic drawing showing the mutual shearing effect at the intersection of two kink bands. The kinked region, ABCD, can be sheared again by an intersecting band to transform into a new region ABC′D′. Enlarged voiding may result owing to an increase in area at the intersection

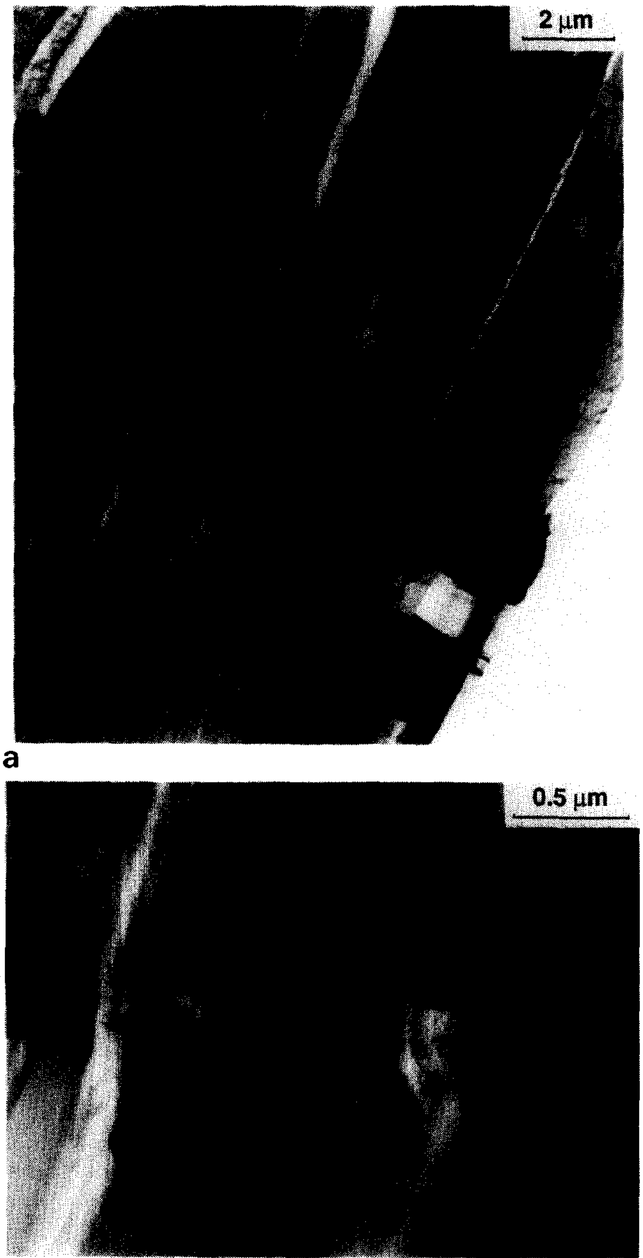


Figure 8 (a) A buckled region with a deformation zone oriented perpendicular to the fibre axial direction. Two major kink bands are adjacent to the buckled region. (b) Enlarged view of a band as indicated by one of the arrows in (a) showing the changed thickness and voids inside the band. (The cracks are probably due to splitting during specimen preparation)

reoriented fibrils in the intersection. Band A, the existing band, is also displaced somewhat, consistent with the new fibrillar orientations in ABC′D′. It is noted that this intersection gives a reduced shear strain, ~0.4, at the intersection as defined by ABC′D′. This behaviour is different from that of the first type of intersection of shear bands in polystyrene[23], despite the same relative direction of the shear strain in the two bands. It is likely that the mutual shearing effect could depend on the degree of orientation and the shear strain of the individual band.

When a fibre is deformed under a large strain, the fibre usually fails in a complicated mode commonly known to include buckling and fibrillation. Earlier studies[17] showed that kink bands could lead to buckling under large deformation. *Figure 8a* shows a thin section through a heavily bent specimen in which severe kinking and buckling have occurred. Because the specimen was straightened before being microtomed, the view of the buckled region may not represent the failed morphology. Two major kink bands intersect with each other inside the fibre as indicated by arrows. Band A is relatively uniform in thickness with many voids. An enlarged view of a portion of band B is shown in *Figure 8b*. The band shows an irregular boundary and seems to be increasing its thickness towards the undeformed region from an existing band as indicated by an array of cracks. This suggests the possibility of a separate large-scale shear motion along an existing band under large deformation. Probably because of the uneven strain under bending, the large-scale shear motion was not complete before buckling occurred. The thick bands as shown in *Figure 4* are also likely results of a large-scale shear motion under a large strain.

The buckled region is manifested by a dark and thick band at the intersections and extends perpendicularly to the fibre surface as shown in *Figure 8a*. Despite relatively poor sample integrity, the bulk is populated with kink bands as indicated by the directional voids with respect to the fibre axis. It is noted that numerous bands and intersections developed in the fibre without extending to the fibre surface or having connections with the buckled region, suggesting an independence of kinking and buckling. This observation indicates that kink bands are developed in earlier stages of deformation independent of buckling, and the possibility that the intersections of kink bands could facilitate buckling under a large strain.

Kinking as a shear process

Observations from this study and earlier work[17] suggest the following phenomenological mechanism of kinking: Kink bands can initiate heterogeneously from local defects, either on the surface or within the fibre, as shown schematically in *Figure 9a*. A band or a packet of bands can develop to their full extent by propagation along a well defined plane as shown in *Figure 9b*. The band is formed by shear yielding as characterized by constant band thickness, shear strain and band angle. Under a large compressive strain, a large-scale shear motion could take place along the band to integrate the band packet into a thicker band with an apparent step on the surface. This process may not be completed across the fibre diameter before buckling takes place. As a result, a band at this stage is sometimes wavy and less uniform in thickness. An idealized picture showing this stage of deformation is shown in *Figure 9c* for completed large-scale shear, and in *Figure 9d* for buckling. Both may result from axial compression or bending.

SUMMARY AND CONCLUSIONS

Kink bands, as thin as 45 nm thick, were observed in PBO fibre by TEM. The shear strain measured from the displacement of striations is 0.7, and is consistent with that measured from a step on the fibre surface. These bands are oriented at $69° \pm 3°$ with respect to the fibre axis.

Bands 1.2 to 1.8 μm thick extending across the fibre are uniform in thickness, having about the same shear strain and band angle as the thin bands. Bands of

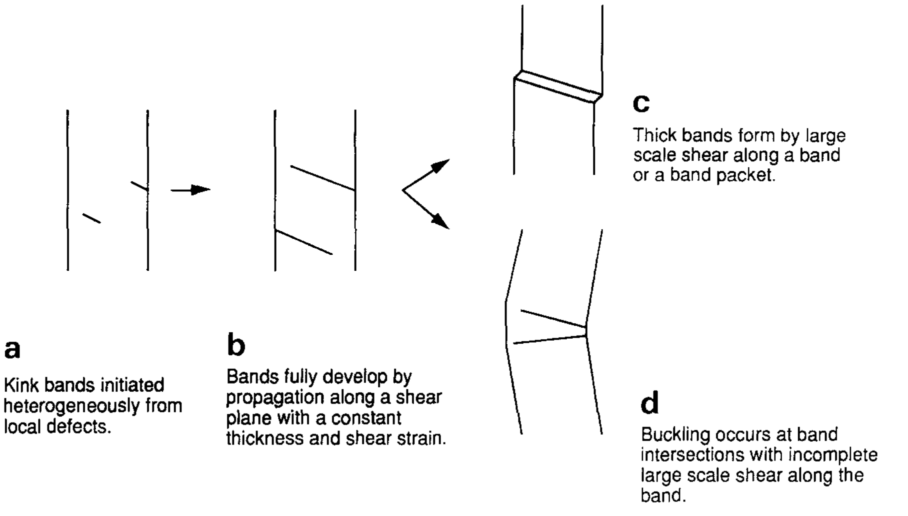


Figure 9 A schematic view on the process of kinking and deformation of PBO fibre under various extents of compression

intermediate thicknesses, 0.1–0.3 μm, are usually wavy and less uniform in thickness. They can terminate inside the fibre or extend to the surface and cause steps.

Voids or cracks sometimes develop in the kink band, particularly for 0.1 μm or thicker bands. They have a preferential orientation consistent with the shear direction along the band. These voids or cracks terminate at the boundaries between the band and the unkinked areas.

When two bands intersect with each other, a mutual shearing effect seems to take place at the intersection. The sheared region in an existing kink band can be sheared again by an intersecting band. The fibrils at the intersection are reoriented to a new direction, which seems to be determined by the shear displacement of the two intersecting bands. The cracks or voids at the intersection could be enlarged by such interactions.

A buckled region appears as a dark band perpendicular to the fibre surface. Buckling seems to occur at regions of populated kink bands and band intersections.

These observations suggest a shear yielding process for incipient kink bands, and the possibility of a large-scale shear motion at later stages of deformation. The latter motion may be incomplete if buckling occurs.

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