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Delineating water trees in cross-linked polyethylene: a new technique

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A new technique has been developed to image water trees in polymeric insulated cables. The method is based upon permanganic etching and enables water trees to be examined either optically or by electron microscopy. Use of transmission electron microscopy allows the water tree and matrix microstructures to be imaged simultaneously. Relationships between polymer morphology and water-tree growth may therefore be studied. The technique and its application to the study of water-tree microstructure in cross-linked polyethylene using optical, scanning electron and transmission electron microscopy, is described.

1. Introduction

1.1. Water treeing

The phenomenon of water treeing may compromise the required service life of medium voltage (MV) cross-linked polyethylene (XLPE) cables. Electric stress in the presence of water, ionic contaminants and oxidation products gives rise to tree-like channels in the insulation from defects in the bulk (bow-tie trees) or at the interfaces with the semi-conducting screens (vented trees). This water-tree growth causes a decrease in the electric strength of the cable, thereby increasing the probability of failure. Although no XLPE cables manufactured by BICC Cables Ltd, Energy Cables Division, have failed after up to 15 years in service as a result of water treeing, there is a need to provide cables with water-tree retardant (WTR) properties to increase confidence in long service life. Improvement of materials, modern manufacturing methods and the use of extruded semi-conducting screens have all contributed to better service reliability of XLPE cables, but cables can, however, be damaged during installation or service with treeing as a consequential result.

1.2. Previous studies

Although water treeing in polymeric insulation materials has been the subject of many investigations over the last 25–30 years, studies to clarify the cause of the phenomenon and to establish methods of its prevention are on-going [1–4]. One aspect under consideration attempts to relate water-treeing behaviour to the morphology of the insulation. Such work started in the early 1980s using the then new technique of permanganic etching, introduced by Olley *et al.* in 1979 [5]. When applied to XLPE, a very common commercial cable insulation material, these studies often resulted in the observation of large spherical structures which were assumed to be spherulites. In addition, voids and channels were also observed, running between these entities [6, 7]. However, large spherulites are not usually present in extruded XLPE and it is now clear that the reported observations stemmed from misuse of the permanganic etching technique, together with subsequent misinterpretation of the observations.

In the original paper [5], it was reported that artefacts could be produced if the wrong etching conditions were employed, but little heed was apparently paid to this warning by some workers. Although artefact formation was not a major problem, as far as the early morphological studies of Olley *et al.* were concerned [8–10], the chemistry of the permanganic etching process was of interest and subsequent detailed studies revealed the mechanism by which artefacts were formed. It was found that, during etching, inorganic crystals are precipitated from the etchant on to the sample surface. These crystals, which are subsequently destroyed during the sample washing procedure, inhibit etching, so leaving the shapes of artefacts behind on the sample [11]. Despite these observations, and the reported result that addition of phosphoric acid to the etchant prevents crystal precipitation and, as a consequence, artefact formation, such modified permanganic etchants were not adopted for the study of cable insulation material.

However, the study of microstructure and its relationship to water trees was not abandoned altogether.

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In 1985, Cappacio *et al.* [12], reported an investigation in which the technique of chlorosulphonation, as introduced by Kanig [13], was employed to study water-tree growth and morphology in different grades of peroxide-cured XLPE. In this approach, thin microtomed sections are stained with a heavy metal and then examined in the TEM. On the basis of their results, which included observations of voids and channels in the water-treed areas, the following mechanism of water-tree growth was proposed. Initially, it was suggested, localized damage occurs within the amorphous material between the lamellae. These weakened regions then develop into voids, which subsequently grow in a direction parallel to the surrounding lamellae, to give the filamentary structures that are observed.

More recently, Phillips [14] used a slight variant of the initially published permanganic etching technique to examine the matrix morphology of peroxide-cured XLPE cables, both aged and unaged. However, the technique was not used to study water trees in field-aged cables.

1.3. Present study

In this work, a modified form of the permanganic etching technique has been used for the first time to study the morphology of XLPE cables in which water-tree growth has been deliberately induced. In addition to the examination of matrix morphologies, a novel technique for successfully delineating water-tree structures has been developed to permit the detailed microstructure of these objects to be examined by both SEM and TEM. Thus, water trees can now be studied with greater resolution and their growth related to the morphology of the surrounding matrix.

1.4. Permanganic etching

The heavy-metal staining of thin samples, prior to sectioning and examination in the TEM, is an approach well suited to the detailed study of lamellae in melt-crystallized polymers. Indeed, techniques of this general type have been employed extensively for the study of polymer morphology over the last 25 years [15–17]. However, in many respects, the application of such an approach to the examination of larger scale structures, such as spherulites and water trees, is not without its problems. For example, imaging limitations related to the local lamellar orientation often results in little or no contrast being generated in certain areas of the image. Where lamellae are viewed edge-on strong contrast is observed. In other regions, where the lamellae do not happen to have their basal planes orientated parallel to the incident electron beam, little image contrast results [18]. For this and other reasons, principally the very thin nature of the specimens employed, conclusions reached by workers using a staining/sectioning approach to study for example, electrical breakdown or large-scale spherulitic architectures, must be examined very critically. Indeed it is only during the 1980s that real progress has been made in understanding the architectures and growth mechanisms of spherulites. This has come about largely through the application of suitably modified permanganic etching techniques to a range of polymers.

Permanganic etching has now enabled a wide range of melt crystallised morphologies to be examined in unprecedented detail without the lamellar projection limitations inherent in chlorosulphonation and other similar techniques [19]. Related studies have also revealed the subtlety of the permanganic reagent, clearly demonstrating how different lamellar populations present in a sample respond to etching and how mechanical damage or irradiation will modify the observed behaviour [20, 21]. By extension, it is natural to look for different responses arising from water-tree damage using a similar approach.

2. Experimental procedure

The samples used in this work were taken from 11 kV XLPE cable cores, triple extruded with semi-conducting conductor and core screens. The cores, manufactured by BICC Cables Ltd, had been aged in water baths held at 70 °C for 3000 h under an electrical stress of 6 kV mm^{-1} at the conductor. Prior to ageing, a 200 mm length of the core screen had been removed and 10 holes each 0.5 mm long reamed into the insulation, with the aim of deliberately inducing water-tree growth at the tips of the holes, as illustrated in Fig. 1. After ageing, sections containing the reamed holes were removed from the cable for optical and morphological studies.

Initially, the cable sections containing the reamed holes were cut open using a microtome, such that the exposed plane intersected the reamed hole as indicated in Fig. 2. This surface was then etched using the techniques described in the following sections. This serves to remove the damaged layer caused by the cutting and introduce surface relief which reflects the different lamellar populations present within the material, their spatial distribution relative to one another and the microstructure of the water tree.

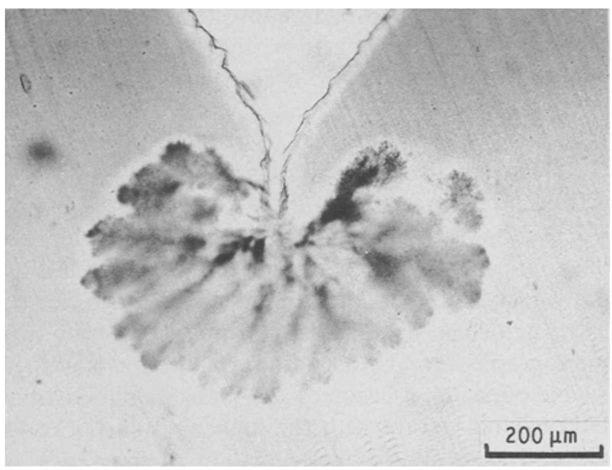

Figure 1 Transmission optical micrograph showing a methylene blue-stained water tree deliberately induced at a reamed hole in the insulation.

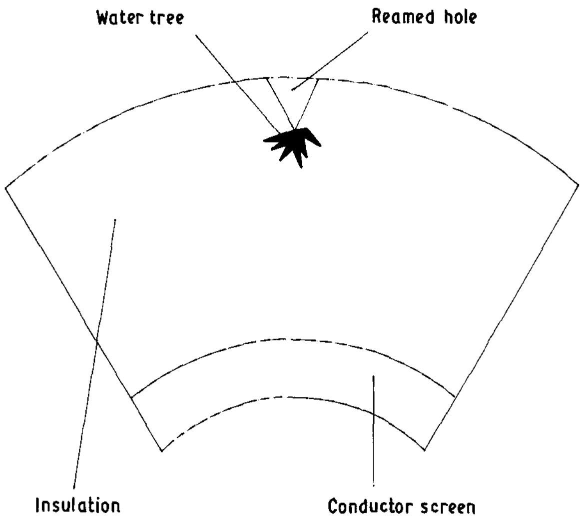

Figure 2 Schematic diagram showing the relationship between the reamed hole, the exposed surface and the water tree.

The etched surfaces were initially examined optically, using a microscope in Nomarski differential interference contrast mode, to ascertain whether or not a water tree had been revealed by the above procedure. Having established that an etched water tree was present, the surfaces were then replicated using a two-stage process. First, an accurate replica of the surface was formed in cellulose acetate. This intermediate replica was then shadowed with a tungsten/tantalum alloy and coated with carbon. Finally, the cellulose acetate was dissolved in acetone to leave the shadowed carbon replica lying on a TEM grid ready for examination.

However, this replicating technique, whilst being experimentally straightforward, is not without its disadvantages. The main drawback concerns the interpretation of the final image and is a consequence of the reversal of the relief that results from the intermediate replication step. For example, if pits are present in the etched surface, they will appear in the intermediate replica as raised domes. Thus, after shadowing, examination in the TEM will appear to reveal the presence of domes with bright tails, the tails being a consequence of shadowing the replica at an acute angle.

In addition to the TEM studies, the samples were also examined by SEM. For this, the etched surfaces were simply sputter coated with gold after the above replication procedure had been completed.

3. Results and discussion

3.1. Permanganic etching

Fig. 3 shows two micrographs of an etched water tree. The optical image of the etched tree is shown in Fig. 3a, whilst in Fig. 3b the same etched surface can be seen, as imaged in the TEM. Comparison of the two micrographs reveals that although the tree is clearly visible optically, it becomes very indistinct amidst the background texture with the higher resolution technique. Indeed at the magnification of Fig. 3b it is difficult to discern any clear evidence of extended structures at all, the only evidence of the existence of the water tree being the rows of voids indicated. In

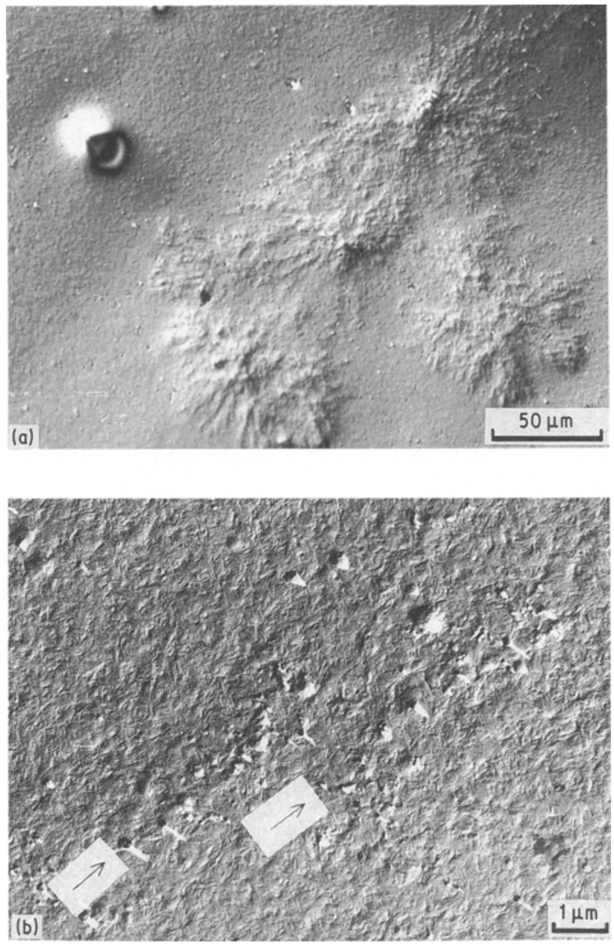

Figure 3 (a) Optical micrograph (Nomarski differential interference contrast) showing a water tree following convential permanganic etching. (b) TEM image of a water tree, again after convential etching and two-stage replication.

discussing such a result, it is necessary to consider the possible structure of a water tree and the technique used to reveal it. As a consequence of these factors, a number of possible explanations exist for the apparently discontinuous nature of the tree shown in Fig. 3b.

Clearly, one interpretation of Fig. 3b is that water trees are simply composed of strings of water-filled voids, and such a structure has indeed been proposed [22]. However, the size of the voids that can be seen in Fig. 3b and the relatively large separation between them is not consistent with the detrimental properties of water trees, unless the intervening material were in some sense highly degraded. However, the material situated between the voids appears identical to that observed in regions well removed from the damaged area, both in terms of its structure and susceptibility to etching (i.e. relief). Because it is well known that permanganic etching is highly sensitive to factors such as material deformation [20] and degradation [21], it would seem that this assertion is unlikely to be correct.

An alternative explanation for Fig. 3b is that the etched surface seen constitutes an approximately equipotential plane within the cable. As water trees grow they inevitably perturb the electric field in their vicinity. Thus, despite cutting the sample as indicated in Fig. 2, it is still possible that the local electric field may contain an appreciable component that is perpendicular to the etched surface. Under these circumstances, the direction of tree growth would similarly be inclined with respect to the etched plane, such that tree channels would appear as circular or elliptical voids (i.e. elongated structures viewed in cross-section).

The final interpretation of Fig. 3b relies not on the possible structure or geometry of the water tree but rather on the technique of permanganic etching used to image it. Consider a plane containing an elongated depression, that is semi-circular in cross-section (i.e. an idealized sample in which an internal surface containing a channel has been exposed by cutting, fracturing or milling). On exposure to a suitable etchant, material will be removed from the surface in a controlled manner. However, certain locations in the sample will be more prone to attack than others, notably in the vicinity of the channel both because of material degradation and also as a consequence of simple geometrical considerations. This process by which channels may be etched-out is shown schematically in Fig. 4. In addition, it is well known from optical studies that although water trees are readily visible when filled with water, prolonged desiccation renders them invisible. Indeed, such structures may be repeatedly dehydrated and rehydrated at will. Thus, an additional potential obstacle to the successful imaging of water trees using etching and TEM lies in the possibility of material relaxation occurring during sample preparation. In chlorosulphonation, sample relaxation is not a problem because this technique not only introduces heavy elements into the polyethylene matrix but also results in the formation of many intermolecular cross-links [23] which serve to restrict subsequent sample relaxation. In view of the above remarks, it would appear that some form of fixation of the tree structure must constitute an essential element in any technique which aims to image voided structures of this type. However, even if relaxation of the water tree could be prevented, etching conditions would still have to be optimized carefully in order to image both tree and matrix microstructure simultaneously.

3.2. Fixation of water trees

In an attempt to overcome the problems outlined above, a novel technique was developed involving the diffusion of a low molar mass compound into the voided water-tree structure, and its subsequent polymerization *in situ*. The aims of this were two-fold. Firstly, the resin would provide mechanical support during sample preparation, and secondly, it would serve to protect the water-treed region from preferential attack during the etching process. In addition, by appropriate choice of monomer and etching conditions, it could be arranged such that the resin would be removed by the etchant at only a slightly faster rate than the surrounding XLPE matrix. Thus, excessive relief would not be generated in the final etched surface. After a period of trials, a proprietary ultraviolet curing acrylic resin, which appeared to fulfil all these requirements was adopted for use.

Specimens containing the reamed holes were soaked in the resin for 3 days and then cured under an ultraviolet lamp. Finally, the sectioning and etching procedures were carried out as described above.

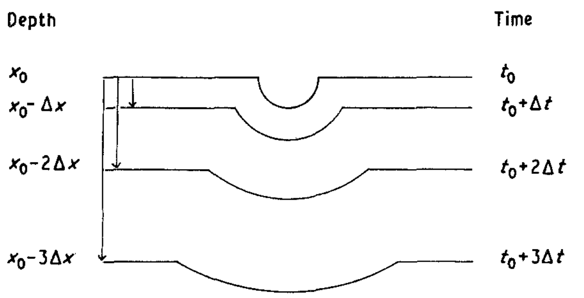

Figure 4 Schematic diagram showing the development of surface relief in the vicinity of a water-tree channel. All surfaces are assumed to be removed at the same rate ($-\mathrm{d}x/\mathrm{d}t$).

3.3. The microstructure of a water tree

Figs 5–9 constitute a series of micrographs showing a single water tree, as revealed by various imaging techniques. The tree that can be seen in these figures was grown in the same material as that previously shown in Fig. 3.

Fig. 5 is an optical micrograph of an etched surface, in which the over-all extent of the tree is clearly visible. In addition, at the right of the field of view, some

Figure 5 Optical micrograph (Nomarski DIC) showing a water tree following fixation and etching. The areas shown in Fig. 7 are indicated. The superimposed squares, seen, for example in the bottom right, are evidence of radiation damage incurred during study in the SEM.

radiation damage is evident, this being a consequence of prior examination of the sample in the SEM. Comparison with Fig. 3a reveals the increased image clarity that has resulted from the use of the modified sample preparation procedure. This conclusion is confirmed by examination of the sample in the SEM. Scanning electron micrographs of the tree are shown in Figs 6 and 7. These reveal the presence of elongated

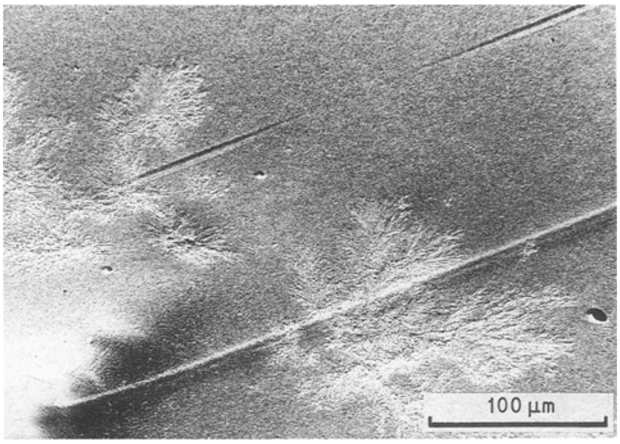

Figure 6 Low-magnification scanning electron micrograph of an etched water tree. The area shown is comparable to that seen in Fig. 5, but with distortion of perspective due to sample tilting.

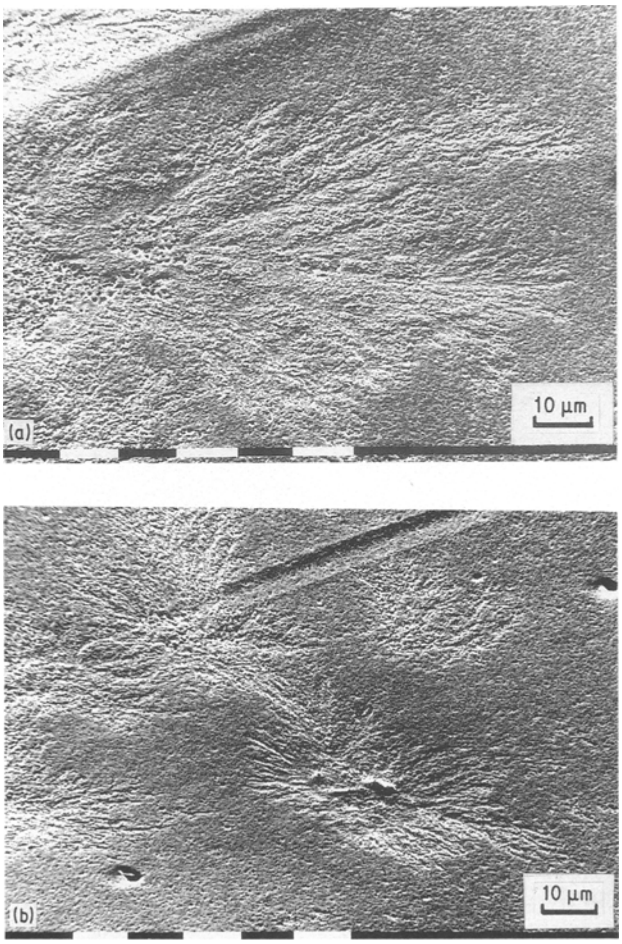

Figure 7 Scanning electron micrographs showing portions of the water tree. Radial channels are evident near the periphery, whilst near the centre of (a), the microstructure can be seen to be highly voided. Less extensive voiding can also be seen within the treed regions of (b).

channels which extend outwards from the centre of the structure in a star-burst fashion. In addition to these features, which are most clearly evident at the centre of Fig. 7a, a densely voided region can also be seen to the left of this micrograph. Two explanations can be proposed for this apparent variation in tree microstructure. Firstly, in the voided region, the tree channels may be inclined at some angle to the etched surface, such that they appear as holes when viewed in cross-section. Alternatively, it is clear from all the micrographs shown that as a water tree develops, the constituent channels branch. Therefore it is not unreasonable that the remaining matrix material should be more highly disrupted near the centre of a tree than at the growth tips. Thus, the highly voided region seen in Fig. 7 may be a simple manifestation of increased matrix damage at the centre of a water tree relative to that which occurs near the tips. At this time it is not possible to speculate further upon the mechanism by which matrix degradation occurs during water-tree growth. However, it would seem reasonable that both the above postulates play a part in accounting for the observed internal variation in tree microstructure.

TEM examination of this same sample again clearly reveals the water-treed area, as shown in Fig. 8. However, this technique enables the lamellar microstructure of the matrix and the relatively coarse structural features of the tree itself to be imaged simultaneously. Fig. 9 shows a detail of the tree system together with the lamellar structure of the matrix. In this micrograph it is the edge of a water tree that can be seen and, as a result, the structure seen varies from intact matrix at the bottom right (region A) to dense tree at the top left (region C).

In region A, the fine lamellar texture of the matrix material can be seen with little or no organization of lamellae into larger scale entities such as spherulites or axialites. Whilst this general morphology is typical of XLPE, it is interesting to note that the lamellae in region A do not appear to be arranged at random, but appear to be preferentially aligned with their long axes oriented vertically. This preferential alignment persists over distances that are very much greater than the dimensions of the lamellae themselves. The tendency

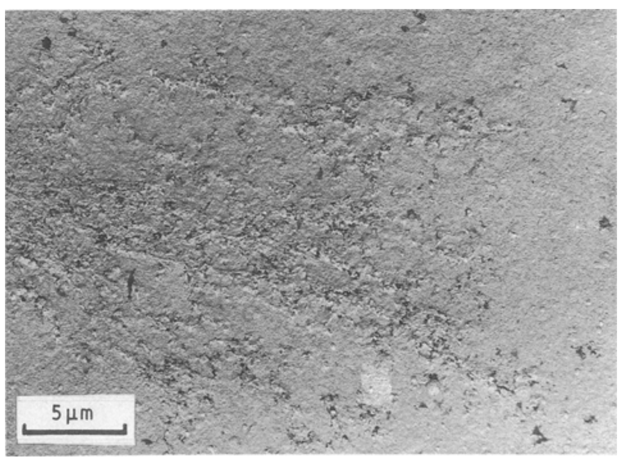

Figure 8 Low-magnification TEM image showing the periphery of a water tree.

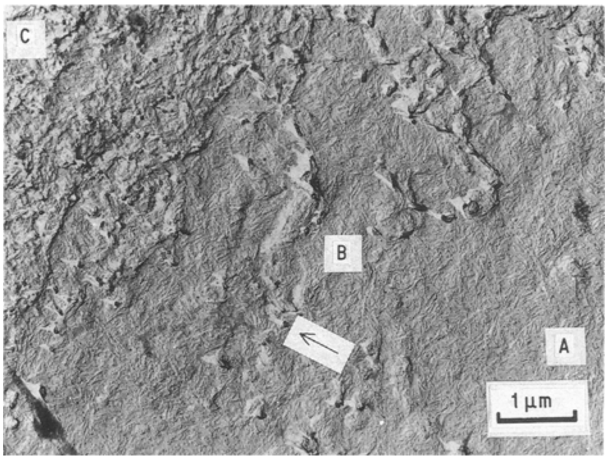

Figure 9 Transmission electron micrograph showing the edge of a water tree. In region A the microstructure of the matrix can be seen. In region B a number of water-tree channels is evident, whilst in region C, the tree channel density is such that extensive image interpretation is impossible.

for one lamellar orientation to apparently dominate can, in very particular circumstances, be attributed to the uni-directional nature of the shadowing process. For example, in cross-hatched polypropylene, image contrast may be reduced in certain areas of the sample where the shadowing direction coincides with the growth direction of one of the near-orthogonal sets of lamellae. Under these circumstances, the visibility of one set of lamellae tends to be enhanced at the expense of the other population [24]. A similar problem may arise in PE that has been aligned by mechanical deformation. Once again, the relationship between shadow direction and lamellar orientation must be carefully adjusted for optimum, unbiased imaging of the morphology [25]. However, both the above systems are highly ordered, being made up of lamellae that are orientationally correlated over large distances. This should not be the case in an XLPE-insulated cable unless the molecular alignment that inevitably occurs during extrusion is unable to relax prior to crystallization. In this way anisotropy of the melt may give rise to an anisotropic lamellar texture.

Conversely, in region C of Fig. 9, there is little evidence of any matrix microstructure whatsoever. The presence of a highly congested array of water-tree channels results in relief that is sufficient completely to obscure finer scale details such as the lamellar texture of the matrix.

At the centre of Fig. 9 (region B) an intermediate situation is evident. The sample shown was prepared for TEM examination using the same two-stage replication procedure described previously, and the shadowing direction was as indicated by the arrow. Once again, some discussion of the observed contrast is helpful in interpreting the image shown. In Fig. 9 there is evidence of extended finger-like structures running from the top of the micrograph towards the bottom through the central region. These features are typically $\sim 0.2\ \mu m$ wide and are characterized by high shadow contrast on their right-hand sides and little contrast to their left. As such, these extended structures constitute channels in the original etched surface (i.e. they were raised in the intermediate acetate replica). A number of circular voids can also be seen in region B. These are believed to correspond to channels viewed in cross-section, both because of the contrast argument outlined above and also due to the lack of any clear, continuous, internal lamellar detail. In addition to the shadow contrast described above, additional mass contrast is often seen to be associated with the tree channels. During replication, material not bound strongly to the etched surface may be stripped off along with the acetate replica. Thus the opaque material seen in Fig. 9 is presumably degraded polyethylene that has been removed from within a tree channel.

So, region B can be understood in terms of an open array of tree channels meandering through the surrounding lamellar matrix. Both the lateral dimensions of these channels and their general appearance is consistent with the SEM images described previously. However, comparison of equivalent scanning and transmission electron micrographs clearly demonstrates the superiority of the former technique as far as the low resolution imaging of the tree structure itself is concerned: the more direct approach resulting in far less "confused" images. Nevertheless, ultimately, it is TEM which offers the greater potential, because the increased resolving power enables tree channels and matrix microstructure to be imaged simultaneously such that the relationship of one to the other may be investigated. Indeed it is interesting to note from Fig. 9 that in region B the tree channels run vertically and also emerge from the etched plane, i.e. along axes parallel to the preferred lamellar basal planes. On the basis of this and previous observations, it would therefore appear that matrix morphology cannot simply be assumed to be isotropic even at the micrometre level and has an important bearing on the subsequent development of tree structures. Further discussion of the relationships between water-tree architectures and matrix morphologies will, however, be deferred to subsequent publications in which results obtained from different matrix materials will be considered.

4. Conclusion

The novel technique described in this paper allows important information about the interaction of water trees with the surrounding matrix morphology to be obtained using both SEM and TEM. It is shown that the water trees in the XLPE system considered are composed of channels which develop between the crystalline lamellae. Profuse branching of these channels yields the dense dendritic structures seen optically. Near the centre of a tree the general appearance is of an open, highly voided microstructure.

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