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Some applications of differential interference contrast microscopy in the study of polymers

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A brief description of the principles of Nomarski double beam interference contrast microscopy is given and the use of this technique in the study of polymeric materials is illustrated with results obtained in these laboratories using both transmitted and reflected light. The results are compared with those obtained using other established microscope techniques.

1. Introduction

The use of various microscope techniques has long been regarded as an important means of examining many aspects of the science and engineering of polymeric meterials.

Electron microscopy, both scanning (SEM) and transmission (TEM), has found many applications relating to polymers. The most notable among these include the use of TEM in the work of Keller [1, 2] in establishing the nature of chain folding in polymer single crystals, the identification of the of the structure of crazes in glassy polymers by Beahan, Bevis and Hull [3], its use in the investigation of the dispersed phases in rubber-modified polymers [4] and the many studies of fracture surfaces using SEM.

Although the resolving power of the optical microscope is less than that of its electron counterparts, it too has been found to be of considerable use in the generation of experimental evidence leading to a greater understanding of the nature of polymers.

The polarizing microscope has been used extensively, both qualitatively and quantitatively, in the morphological studies of amorphous and crystalline polymers [5]. Similarly phase contrast microscopy has been successfully employed in the examination of rubber-modified polymers.

Bright field, transmitted light microscopy using ultra-violet (UV) light as the illuminant has also found a use in the investigation of polymers which, by nature or design, contain regions which will absorb UV radiation. This technique has been successfully applied to study the distribution of low molecular weight additives in polyolefines [6, 7].

The above list of examples is by no means extensive, but it is obvious from examination of the existing literature that the relatively new, and extremely powerful, technique of Differential Interference Contrast Microscopy (DIC) has not been utilized to its maximum advantage in the study of polymers. Dispersed phases have been idientified in ethylene–propylene copolymers using transmitted DIC [8, 9] and Olley and Bassett [10] have described its use in the examination of the surfaces of polyolefine specimens treated with a permanganic etchant.

The object of the present paper is to describe the use and advantages of DIC in the polymer field and to use as illustrations some of the results obtained in these laboratories. It is not our intention at the present time to analyse the results objectively, but simply to demonstrate the undoubted potential of the technique in the study of polymeric systems and to compare the results with those obtained using the other techniques.

2. The principles of differential interference contrast microscopy

Again it is not our intention to provide a detailed description of the technique since, like many workers involved in the microscopy of polymers, we may be regarded as microscope users rather

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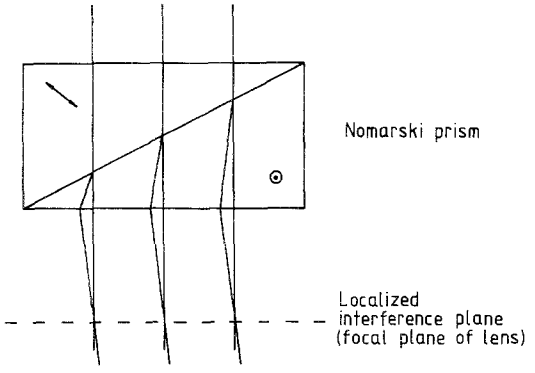

Figure 1 Nomarski prism with the interference plane indicated. Direction of the optical axis, ↔ parallel to the plane of the diagram, ⊙ perpendicular to the plane of the diagram.

than fully fledged microscopists. A more complete description is given by Lang [11].

Basically, the technique involves the differenial splitting of a bundle of plane polarized light to produce a separation of adjacent beams of a few microns, i.e. of the same order as the resolving power of the microscope. The separated beams pass through the specimen and are influenced by it. Differential beam splitting in the present case is achieved via a Nomarski prism (a modified Wollaston prism) which consists of two cemented components made of uniaxial birefringent material such as quartz or calcite. The optical axis of one of these components is parallel to one surface of the prism while the optical axis of the second component lines in a plane perpendicular to the first, but at an angle to the other surface (see Fig. 1). The advantage of the Nomarski prism over the Wollaston is that its interference plane lies outside the prism. (The interference plane of the Wollaston prism lies within its bulk and this leads to the disadvantage that, for higher powered objectives, it cannot easily be located in the image-side focal plane of the lens; so that the Wollaston prism is limited to lower magnifications.)

Referring to Fig. 2, a bundle of plane polarized light with its vibration plane inclined by 45° to the plane of the diagram, on striking the Nomarski prism perpendicular to its surface, is split into two plane polarized waves in the lower component. The vibration planes of these waves are inclined at an angle of 90° to each other and each at an angle of 45° to the incident wave, so that one wave vibrates parallel to the optical axis of the lower component and the other at right angles

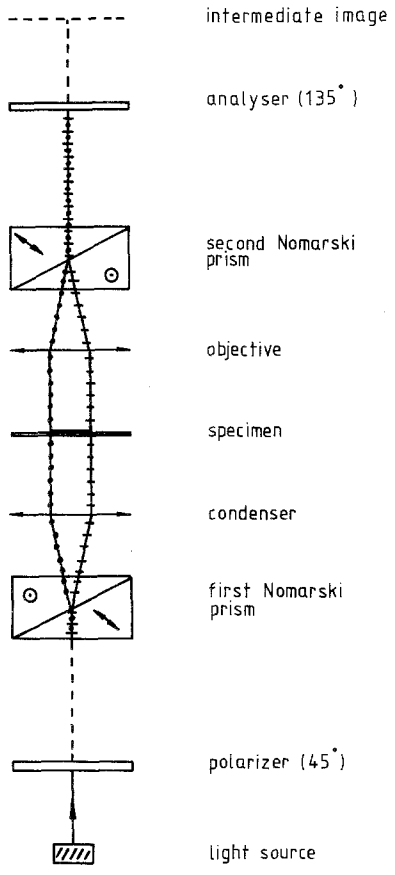

Figure 2 Schematic representation of the double beam interference contrast microscope with two Nomarski prisms. The symbols for the optical axes directions are as in Fig. 1.

to it. At the cemented surface they are deflected by a small angle in different directions. Consequently, they encounter different indices of refraction and, since the propagation speed of a wave in the crystal is inversely proportional to the refractive index, they travel at different speeds within the prism. If the interference plane of the prism is located in the lamp-side focal plane of a condenser the emergent beams will travel along parallel paths, with a slight displacement between them, through the specimen and objective and converge in its image-side focal plane. The two beams are recombined by a second prism, having the same dimensions and optical properties of the first, lying in this plane. After leaving the second prism the beams pass through an analyser inclined at right angles to the polarizer and so produce an intermediate image which may be observed in the eye-piece in the usual way. A differential interference contrast image appears due to the path

differences of adjacent beams resulting from microscopic variations in either the refractive index or the thickness of the specimen when viewed in transmission, or as a result of the minute uneveness or contour of the specimen when observed in reflected light. Obviously in the absence of a specimen or in the presence of a perfectly isotropic specimen, all beams experience identical perturbations and are recombined in the second prism exactly in reverse of the splitting in the first. The result of this is that no interference occurs and a uniform background colour is observed.

In Nomarski DIC the background colour, which is a characteristic of the equipment and is in no way related to the specimen, may be varied by suitable positioning of the prisms. It can be changed from the black and white through grey to a series of colours which arise as a result of destructive interference of certain components of white light, effectively eliminating some wavelengths. This results in a wide range of optical staining possibilities. In our work this has proved to be an added advantage since samples generating only moderate amounts of contrast when viewed in the grey may be interpreted by utilizing the different colours generated in the image by further interference due to the specimen.

Whereas two prisms are necessary in transmitted light, only one is required for reflected light, the same prism being used to split the beam on its first pass and to recombine the two differential beams on the second pass after reflection from the specimen surface (see Fig. 3).

2.1. Characteristics of the image

When viewed in transmitted DIC, transparent specimens containing microscopic regions of even slightly differing refractive index, or regions of varying thickness, produce an image in which the different regions stand out in apparent relief. The amount of contrast depends on the relative path differences of adjacent beams passing through the specimen. One major advantage of the technique is that very small differences in refractive index of the phase structure, which are almost undetectable by other methods, may be immediately obvious.

In reflected light the path difference is caused in the majority of cases by the geometric path lengths travelled by adjacent beams reflected from the specimen surface. Flat regions of the surface

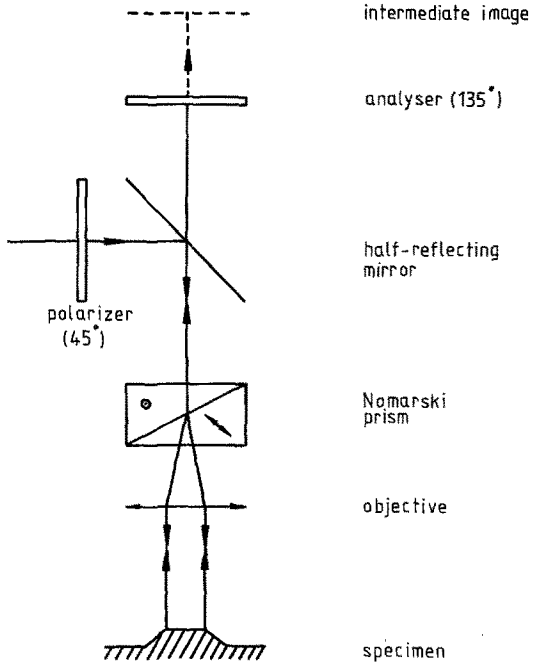

Figure 3 Schematic representation of the double beam interference microscope in the reflected mode. The direction of the optical axes are as in Fig. 1.

produce no interference effect, but contours from one flat region to another will result in an interference image which again appears in relief and, assuming suitable alignment of the prism, contains interference colours. Contrast may also be generated due to differential wave retardation during reflection from areas of different phase on the surface, and because of this some caution should be exercised in the interpretation of the image since its three-dimensional appearance may not be a true representation of the topology of the specimen surface.

3. Experimental details

A Nikon Optiphot Universal microscope was used for all optical micrographs, fitted with either a differential interference attachment "NT" for transmitted Nomarski or "NR" for reflected Nomarski. It is worthy of note that the monochrome film used was Kodak Technical Pan (Estar-AH Base) 2415 which provides contrast enhancement, especially when used in conjunction with a green filter. It combines fine grain with an excellent resolving power and it has been found particularly suitable for this type of photomicroscopy. A polarizing attachment was used for those specimens viewed between crossed polars

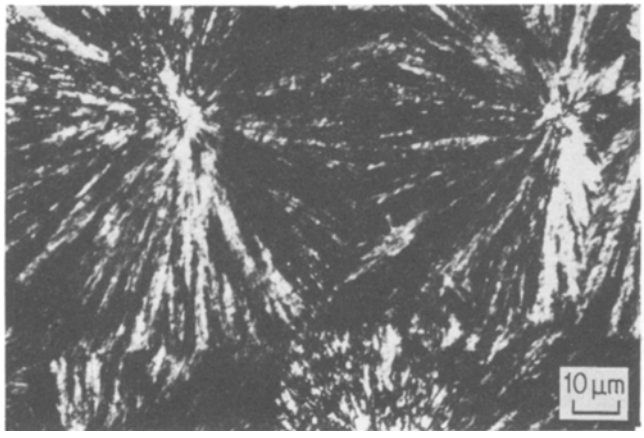

Figure 4 Ethylene–propylene copolymer viewed between crossed polars.

and electron micrographs were obtained using a JEOL JSM-T200 scanning electron microscope with gold coated specimens.

The specimens used varied from thin sections cut by means of a glass-knife microtome to fracture surfaces of different polymers broken at different strain rates as identified in the following section.

4. Examples of results

The following examples are representative of results obtained during various studies on polymeric systems performed recently in these laboratories.

Figs. 4 to 6 show the use of optical microscopy in the study of the morphology of ethylene–propylene copolymers. The materials used in this study were manufactured by a process in which different monomers were introduced into the polymerization reactor at different intervals, and it was thought for a long time that they were true "block" copolymers, i.e. that the ethylene-rich segments of the polymer chain were chemically attached to the proproylene pre-block. All three micrographs were taken in transmitted light using a thin section of specimen (~ 5 μm thick) cut from an annealed block of material using a glass-knife microtome. The specimen in Fig. 4, viewed between crossed polars, shows the characteristic spherulite structure of polypropylene with some evidence of additional fine structure within the spherulite. Fig. 5 is the same material viewed in phase contrast and again the spherulite structure is evident with a dispersed phase present within it. Finally, Fig. 6 is the same field of view as that in Fig. 4 but here the dispersed phase is much more clearly defined; identifiable as distinct regions of about 1 μm in size standing out in apparent relief. The second phase in this material results from the formation of an ethylene–propylene rubber [9] as a consequence of the variation in monomer concentration during the polymerization process. This rubber phase has a different refractive index from that of the polypropylene matrix. The

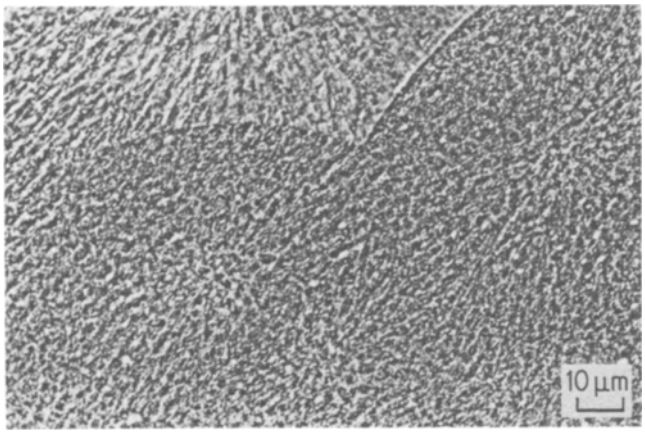

Figure 5 Ethylene–propylene copolymer in phase contrast.

Figure 6 The same field of view as Fig. 4 viewed in transmitted DIC.

implication of these results is that the material is not a true block copolymer, but contains large amounts of free rubber, since the size of the inclusions is too large to be accounted for solely by the presence of ethylene-rich blocks in the polymer chain.

Fig. 7 is an SEM micrograph of the fracture surface of an epoxy resin, fracture having initiated from a flaw on the surface of the specimen. Whilst the gross structure of the fracture surface in this example is very clear, examination of Fig. 8 (the same specimen viewed in reflected DIC) reveals considerable fine detail in the slow growth region which is barely visible in the corresponding SEM micrograph. Particularly obvious in Fig. 8 is the banded structure, the origin of which is not understood.

Figs. 9 and 10 show similar slow growth regions of a crack in polymethylmethacrylate (PMMA) nucleating from a surface flaw. Again, examination of the two micrographs shows a significant increase in the fine detail in this region when observed using reflected DIC. The two regions shown in Figs. 9 and 10 are not from the same specimen and the reason for this highlights an additional advantage of the DIC technique. In the process of obtaining a suitable image in the SEM, the specimen surface suffered considerable damage from the electron beam, rendering it unsuitable for further study. This of course is not a problem encountered in light microscopy.

Fig. 11 is an example of an internal flaw in PMMA from which failure has initiated. Fine lines are seen to radiate from a particulate inclusion situated at the centre of the slow growth region. Again the nature of this fine structure is not certain but it is thought to result from some kind of debris laid down by the advancing craze during slow crack growth.

Figs. 12 and 13 demonstrate the ability of the

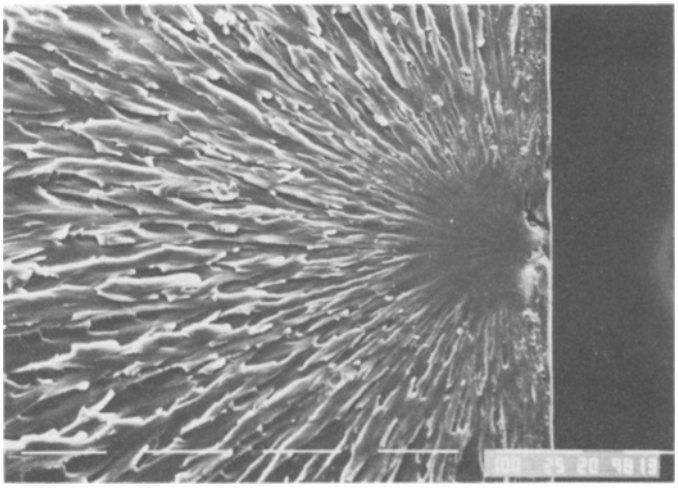

Figure 7 SEM micrograph of an edge failure in epoxy resin.

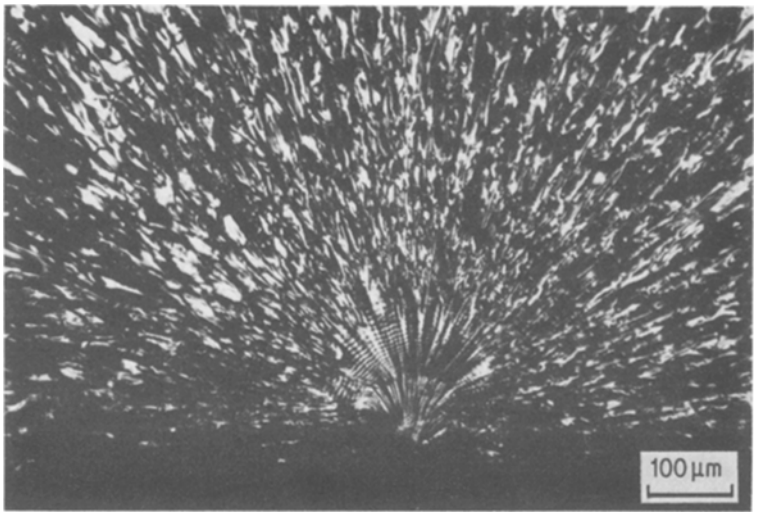

Figure 8 The same view as Fig. 7 in reflected DIC.

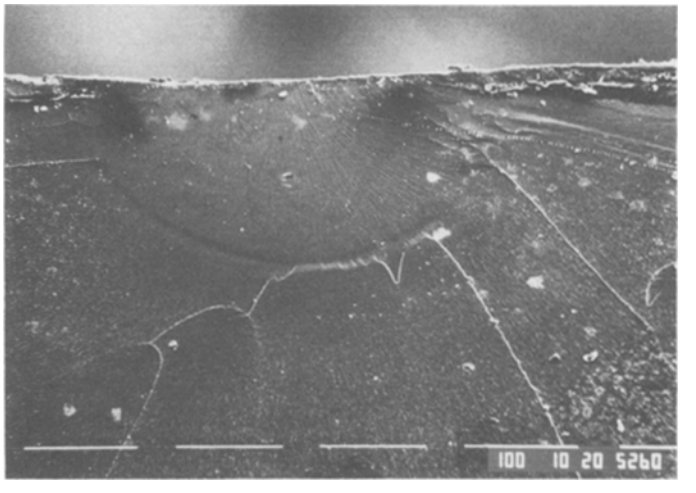

Figure 9 SEM micrograph of an edge failure in PMMA.

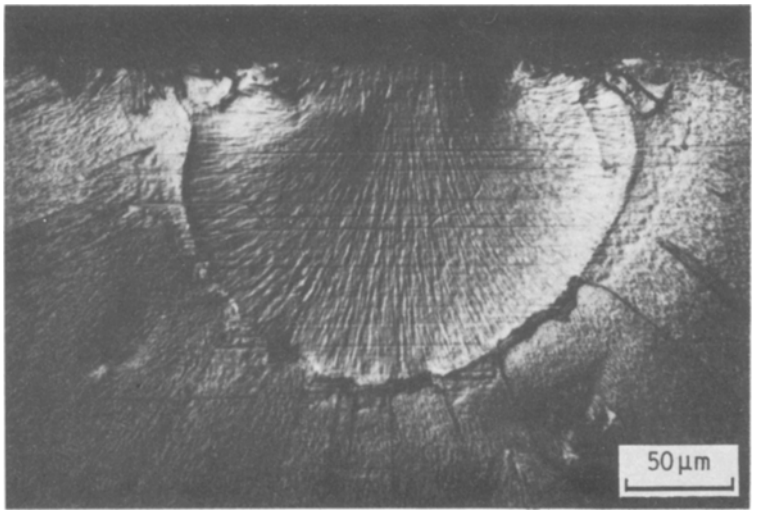

Figure 10 An edge failure in PMMA viewed in reflected DIC.

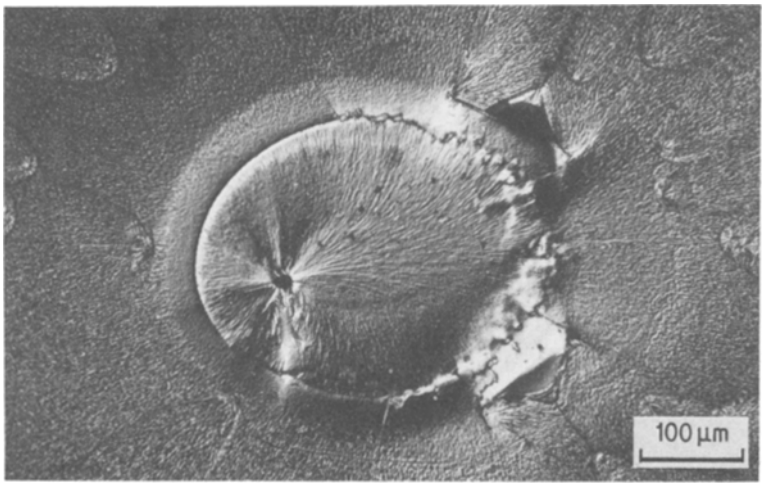

Figure 11 Optical micrograph of an internal flaw in PMMA viewed in reflected DIC.

DIC technique to yield more detail of the fine structure. These two micrographs are of the so-called mist region on the fracture surface of PMMA showing the characteristic parabolic markings. Close examination of Fig. 13 reveals that at the focus of many of the parabolas is a point which appears either to protrude from, or into, the surface. However, as was stressed in the introduction, positive interpretation of this region should be made with caution since the visual effect may originate from more than one cause. Reference to Fig. 12 suggestes that this phenomenon is less evident in SEM, but on occasions slight protrusions as in Fig. 13 have been observed using SEM [12].

Finally, Fig. 14 shows a freshly microtomed surface of an annealed polypropylene homopolymer specimen viewed in reflected DIC. The spherulite boundaries, and the radiating fibrils which make up the spherulite, are clearly visible. It may be that this result is an example of the differential retardation of reflected light beams after striking regions of different phase on the surface. The spherulite boundaries and regions between the crystalline fibrils, being amorphous, have a slightly different refractive index than that of the crystal phase and give rise to a difference in the retardation during reflection of adjacent light beams. It is certainly true that the three-dimensional appearance of the surface structure of this specimen is very much less obvious when viewed using SEM or bright field reflected light microscopy.

5. Conclusion

Examination of the photomicrographs presented here clearly demonstrates the advantages of the use of the DIC technique in some applications

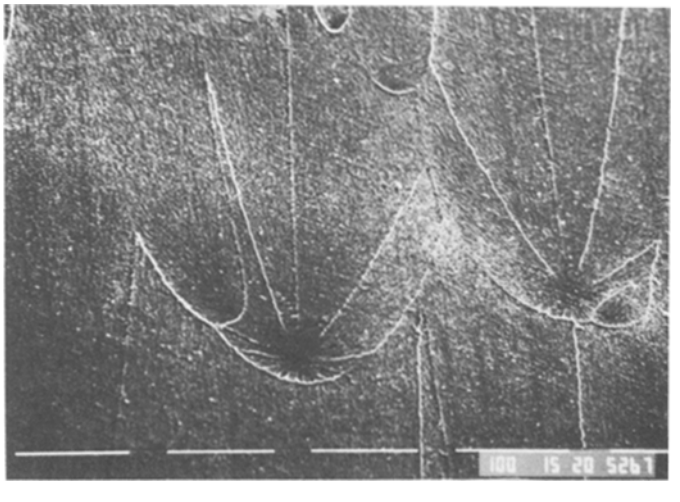

Figure 12 SEM micrograph of the parabolic markings on the fracture surface of PMMA.

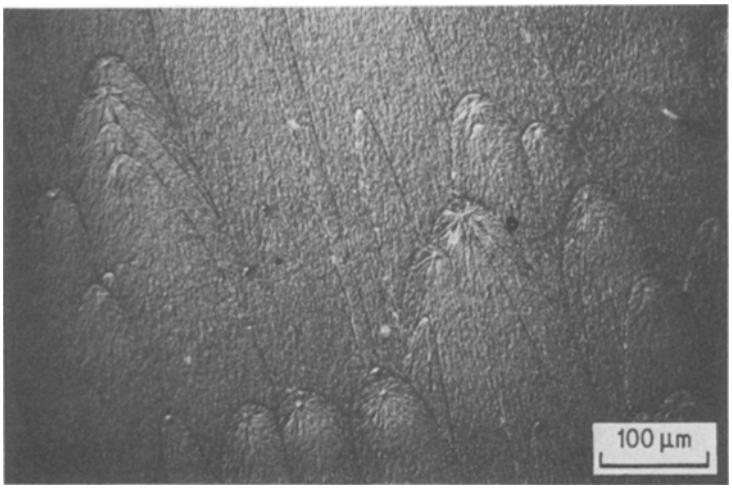

Figure 13 Parabolic markings on the fracture surface of PMMA viewed in reflected DIC.

over other microscope techniques. In particular, the ability of the technique to distinguish between regions of small differences in refractive index within the specimen when viewed by transmitted light and the ability to resolve minute topological differences in specimens viewed in reflection are very useful. In many cases these differences are not immediately obvious when other techniques are employed. DIC has been found to be immensely useful in the study of polymer systems and we feel sure that the examples presented are only a few of those to which the technique may be applied. It is certainly a major tool in these laboratories which is finding an increasing role in our investigations.

Acknowledgements

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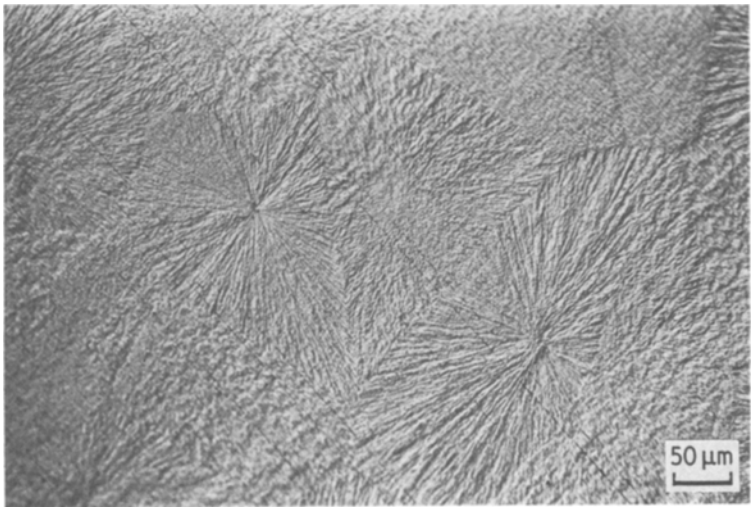

Figure 14 Optical micrograph of a freshly microtomed surface of polypropylene in reflected DIC.

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