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Resin matrices and their contribution to composite properties

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[Plates 1 and 2]

As a result of the increasing use of glass and carbon fibre reinforced plastics in aircraft structures, great emphasis is now placed on the choice of a suitable resin matrix for these demanding applications.

In practice this choice is frequently a compromise between conflicting manufacturing, design and materials requirements, and is further complicated by the great range in chemical variety of available resin matrices. Uncertainty of quality in the manufactured composite and a failure to observe and report on fracture modes occurring during sample testing are among other factors that interfere with the establishment of a body of reliable experimental data.

This paper considers the relation between matrix and composite properties from a number of viewpoints. Examples of materials' requirements for specific component applications are given and, finally, a matrix suitable for aerospace use and factors influencing its formulation is discussed.

Introduction

The most pressing need in composite materials research today is the establishment of a body of reliable information on material properties and behaviour, which can be accepted as trustworthy by the design engineer, and the development of confident and mature shop-floor processes from our present subjective manufacturing techniques. This discussion therefore does not deal in detail with the chemistry of resin matrices, or catalogue their mechanical properties. Instead, the attempt is made to give a perspective view of the frequently conflicting requirements placed on the matrix by a potential application, and to identify ways in which the matrix properties directly, and indirectly, control composite properties.

Preliminary considerations

Any user's list of rudimentary matrix requirements will contain elements which will usually fall into two categories, namely (1) performance requirements; (2) component manufacturing requirements. The elements contained in these lists naturally alter according to application and circumstances but the following example could suit a typical engine application.

I. *Performance requirements*

(*a*) High-temperature capability – high glass transition temperature (T_g).
(*b*) Moisture resistance, and resistance to other environmental (use) fluids.
(*c*) Adequate mechanical properties coupled with (*a*) and (*b*) above, i.e. good properties at

elevated temperature in the presence of moisture, plus a possible application-specific property such as impact resistance.

(*d*) Smoke, fire and toxicity considerations. This is an increasingly important topic for aircraft applications, and a complicated one. Halogenated compounds, for example, added for fire retardancy, may constitute a toxic hazard and may also lower T_g and high temperature performance.

II. *Component manufacturing requirements*

(*a*) Shelf life. For epoxide resins this usually means that a latent curing agent is required, i.e. one that is not activated until heat is applied. Shelf life expectations might be three months at room temperature or twelve months at −18 °C.

(*b*) Tack, i.e. sufficient stickiness for the laminates to self adhere, but too much tack is as unacceptable as too little.

(*c*) Low volatile content. Volatiles may be generated by the chemical reaction involved in curing, or from solvents perhaps added to improve tack.

(*d*) Adequate but not excessive flow under pressure.

(*e*) Easy and economic pressure–temperature cycle (for thermosetting resins, this means post-curing outside the tooling).

(*f*) Freedom from health hazards. Again, this is an increasingly important consideration in the face of the introduction of the Health and Safety at Work Acts.

When taken together, these items constitute a formidable list of requirements, and there is no doubt that the unique combination of properties shown by epoxide resins – controllable viscosity low cure-shrinkage, easy cure coupled with high T_g, generally high mechanical properties and chemical resistance – has given them pre-eminence in the aerospace field, and this paper will concentrate upon these materials. Work is in progress on high T_g thermoplastics – polycarbonate, polyethersulphones, polyphenylene sulphide and the like – but there are considerable worries over long term creep resistance and solvent sensitivity, in addition to processing problems for aligned fibre composites. The particular use of thermoplastics as *blends* with epoxide resins appears to be an invaluable application of general importance and will be discussed later.

Of the remaining readily available commercial materials, phenolic resins and polyimide resins remain as candidates for high temperature use. The former are at a disadvantage owing to their high cure shrinkages, evolution of volatiles during cure and inadequate adhesion, but their low prices and good performance in fire, smoke and toxicity tests may force an eventual reappraisal of their future. Polyimide resins also have excellent fire, smoke and toxicity characteristics and, while relatively expensive and difficult to process, they appear to have found a definite applications niche in, for example, recent versions of the RB162 engine where polyimide components replace epoxy novolac ones. It is to be expected that polyimides will be used in increasing quantities to solve specific high temperature problems.

DIFFICULTIES INHERENT IN PRACTICAL WORK

Two major difficulties impede any attempt to do serious practical work on the relation between matrix and composite properties. The first is that matrix materials, even those produced on a commercial scale and nominally identical, frequently differ in some respect from batch to batch. Since the cure characteristics of epoxide resins may be affected by the presence of even quite small accounts of impurities, the result is a quite considerable variability in mechanical properties and behaviour (Phillips *et al.* 1978). The second major difficulty is the problem of maintaining a high standard of quality in composite manufacture. High quality mouldings are absolutely essential if matrix characteristics are to be correlated with composite properties. Unfortunately, small changes in resin chemistry often produce profound changes in the cure characteristics of a given material and it is then difficult to produce good samples without drastically altering the thermal–pressure cycle.

PROBLEMS IN COMPOSITE MANUFACTURE – VOIDS

The usual result of unsuitable control procedures during composite manufacture is, of course, the subsequent presence of voids in the structure. These arise either because premature gellation takes place before pressure can be properly applied to the matrix to collapse trapped bubbles, or because the premature application of pressure to the moulding effectively expresses all the excess resin before its viscosity has increased sufficiently to withstand the pressure increase.

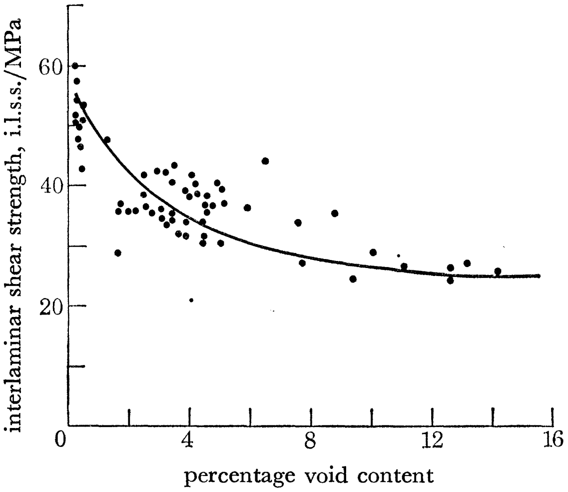


FIGURE 1. Unidirectional interlaminar shear strength plotted against void content for type III/epoxy novolac composite. All failures were interlaminar.

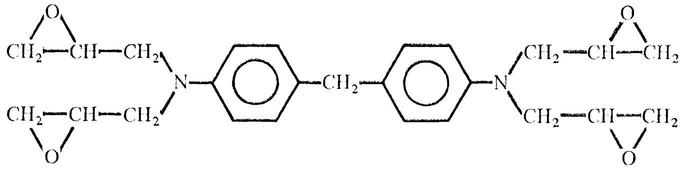
Knowledge of the viscosity characteristics of the resin/hardener combination in use is therefore an essential prerequisite to satisfactory control of the moulding cycle since virtually the only way of manipulating resin viscosity during moulding is by the application of heat. Thus voidage is directly related to matrix characteristics through common links in the manufacturing process. Voids in laminates affect interlaminar shear strength (i.l.s.s.) as measured in the three-point bend short-beam shear test and other similar measurements to an extent that other factors may be overridden, and the presence of voids may therefore interfere with the correct interpretation of the experiment (see figure 1).

WATER ABSORPTION

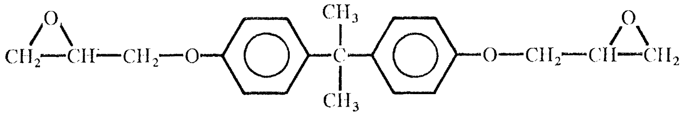
Voids also have a role to play in the resistance of the composite to moisture. Water may permeate into a composite through the resin itself, or through porosity and along exposed fibre surfaces, leading to plasticization and a marked degradation of T_g and resin stiffness, and with these a degradation also of composite i.l.s.s., compression strength and general high temperature performance. The search for hydrothermally stable resin matrix systems for aerospace use is a major present preoccupation for the industry and one in which the results are at present sometimes contradictory.

Experiments show (Judd & Judge 1976) that when the interfacial bond is satisfactory (and this can be arranged for carbon fibre composites) the shear strength is limited by the resistance to water of the resin system itself. There is also some evidence to suggest (M. Hall 1978, private communication) that for carbon fibre composites the matrix degradation experienced following the ingress of water can be partially recovered on drying out and that the hydrothermal stability of the composite is greatly improved by the correct choice of resin and hardener. Generally speaking those combinations that give highly cross-linked structures have been found to be most satisfactory, such as the cyclo-aliphatic resins and polyfunctional epoxides based on the aromatic amines. The diglycidyl ether of bisphenol A, or DGEBA epoxide, which has been a standard matrix for many applications is illustrated; the polyfunctional epoxide based on diaminodiphenyl methane, which is now the basis of virtually all aerospace matrices for carbon fibre both here and abroad, is also shown.

tetragycidyl 4,4′ diaminodiphenyl methane

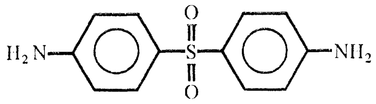


digycidyl ether bisphenol 'A' (DGEBA) $n = 0$

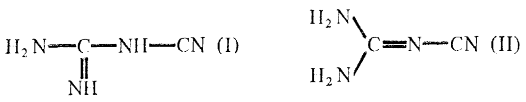


Cyclo-aliphatic resins are not represented because the best known and most intensively researched example, ERLA4617, was unfortunately withdrawn from the market some years ago. The tetraglycidyl diaminodiphenyl methane resin cured with the hardeners illustrated,

diaminodiphenyl sulphone



dicyandiamide



diaminodiphenyl sulphone (DDS), dicyandiamide (DICY) and similar hardeners, produces highly cross-linked, high T_g systems more reactive to the fibre surface than DGEBA resins, more resistant to water attack, and generally tougher than DGEBA and epoxy novolac resins.

Because the DDS cure is sluggish even at moderately high temperatures, a boron trifluoride amine complex is frequently used as a catalyst in association with DDS to produce a more manageable cure cycle, despite the fact that ionic curing agents often have poor humidity resistance. This is a good example of a possible compromise on mechanical properties in an attempt to achieve manufacturing convenience.

Compression failure

The effects of the declining shear stiffness of the matrix, which are evident with a particular resin system with both increasing temperature and water penetration, are also present in comparisons between the properties of systems of different initial stiffnesses. Generally speaking, matrices of lower modulus frequently produce lower values in many of the standard mechanical property tests. This is usually due to the failure of the matrix to sustain the compressive loads being generated in it. For unidirectionally reinforced composites, as opposed to woven cloth composites, DGEBA epoxide resin moduli are normally adequate at room temperature to allow very high bending strains to be sustained without buckling, and when failure takes place a stable tensile failure, utilizing the strength of the fibre, ensues. Unfortunately this is not the case with unidirectionally reinforced thermoplastics, which suffer catastrophic compression-induced microbuckling failures at quite low strains, a feature common to polycarbonate, polysulphone, polyethersulphone, etc. Neither is it the case for glass cloths impregnated with many epoxide and thermoplastic resins which show compression failures in bending due to the 'popping-out' of tows at crossover points on the compressive side of the sample. Thus it is that the designer unfamiliar with these materials may be misled by data in the literature for which the failure modes, although so different, are not recorded. The aetiology of compression testing has been comprehensively treated by Ewins & Ham (1974) and a further discussion will be found in Ewins & Potter (this symposium).

Matrix strength

So far, a case has been made for a hydrothermally stable matrix with a high T_g, and circumstantial evidence presented for a relatively high modulus also. What is the requirement for the strength of the matrix? This is an area of controversy at present, in which one school of thought feels that a large increase in matrix breaking strain is necessary, and another thinks that it is not. It will not be possible to review all the evidence here, but the strength of the matrix is important in its contribution to crack propagation, delamination and the general micro-mechanics of failure. Work at Nottingham University (Owen 1974) and our own work at Rolls-Royce has shown that cracks generated in cross-plied laminates by the short-beam shear test form orthogonally to the resolved tensile stresses in the cross-plied layers (see figure 2(*a*), plate 1).

Provided that the bond between fibre and resin is adequate, therefore, it follows that this test with cross-plied laminates is a measure of the matrix tensile strength. Unfortunately, because of their sensitivity to flaws, the simple measurement of the strength of cast resin specimens, either in tension or flexure, is not a satisfactory guide to the likely performance of any specific system in a composite.

What is required is a toughness criterion in which resistance to micro-crack propagation is represented and high strength can be developed in the presence of flaws. While unsuitable as a matrix for the reasons previously mentioned, polysulphone possesses some elements of this requirement, and in the i.l.s.s. test shows some deformation and flow with good resistance to crack propagation at the laminate interfaces (see figure 2(*b*), plate 1). Brittle resin systems form a smaller number of cracks and exhibit rapid interfacial crack propagation. Recently it has been reported (P. Curtis 1978, private communication) that transverse cracks in cross-plied laminates pass through fibres in the same cross-plied layer. In other words, the crack is not deflected by the fibre interface. The material was a type II carbon fibre with polyfunctional epoxide hardened with DDS and BF_3 MEA.

We have thus encountered once again, but at higher performance levels and with more modern materials, the problems of incipient brittleness observed in the early carbon fibre composite days, with high surface treatment levels and rather brittle matrix systems. However, for other resin formulations, although based on the same highly functional epoxide, the crack propagation behaviour may be quite different, as will be shown later. The remainder of this paper is devoted to a discussion of the formulation of a matrix in current aerospace use, tracing its original conception and outlining some of its advantages and some of its problems.

Formulation of a practical matrix

During the period some ten years ago, when Rolls-Royce Ltd was developing its carbon fibre fan blade work, the matrix problems encountered in the moulding of such a complex shape were severe. It is clear from the preceding discussion that, during the moulding cycle, the resin viscosity must allow mobility, yet be sufficiently high to prevent adventitious leakage of resin from the mould and ensure transmission of the pressure to all parts of the component. Control of this phase is often critical; too high a viscosity leads to oversize mouldings, probably accompanied by fibre ‘wash’, while too low a viscosity results in excessive voidage.

With these constraints in mind it appeared that a mixed epoxy/polysulphone *adhesive* could be adapted to the formulation of a matrix for composites. The system resulting from joint discussions between Rolls-Royce and Ciba Ltd, known as BSL314, was used extensively in the project. It was DGEBA resin with polysulphone as an additive and utilized a latent catalytic hardener. More recently Ciba–Geigy have marketed a much improved but generically similar system, BSL914, which is finding widespread applications in aerospace projects. This is basically a blend between polyfunctional epoxide resins and a thermoplastic polyethersulphone, both with high T_g, yielding a matrix of reasonably high stiffness. The thermoplastic additive controls flow during gellation, and crystalline dicyandiamide dispersed throughout the resin is used as a latent curing agent with rapid cure characteristics to keep occupation time of the tooling to a minimum. This system has excellent shelf life and tack. Thus we see how the manufacturing criteria and some initial performance criteria have been met in practice by the blending together of individually desirable characteristics.

Figure 3 compares the viscosity, temperature and gellation curves of a typical DICY-hardened controlled-flow system with a typical DDS-hardened DGEBA. It is clear that the DGEBA resin is characterized by a viscosity that falls to very low values at temperatures too modest to effect a rapid cure. The control of the pressure–temperature cycle in such a system poses considerable practical problems.

The effect of the presence of the thermoplastic component in the second system is to maintain a relatively flat trend of viscosity decrease with increasing temperature and at higher over all

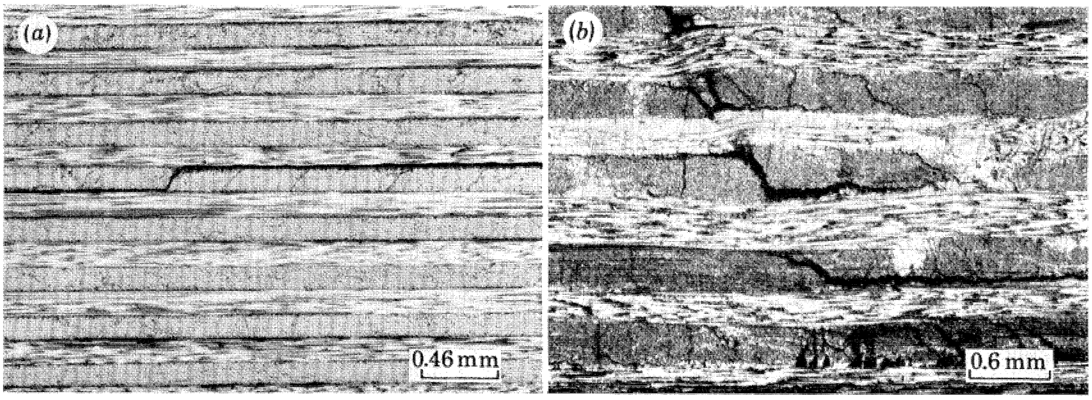


FIGURE 2. Cracks present in cross-plied short beam shear specimens after test. (*a*) Epoxide matrix. Note cracks forming orthogonally to the resolved tensile stress within the cross-plied layer, crack spacing, and propagation of the delamination along opposite interfaces. (*b*) Polysulphone matrix. Note extensive deformation, major crack opening but without extensive interface propagation.

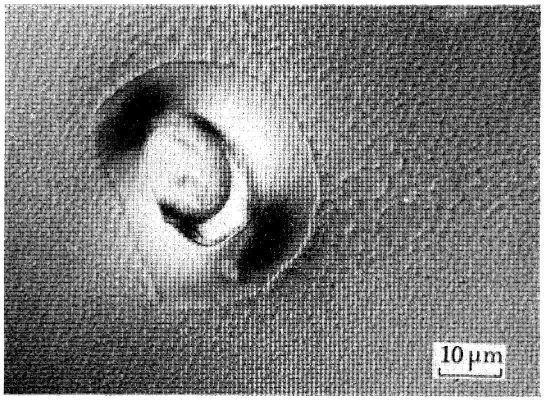


FIGURE 4. BSL914 film after gellation at 165 °C. For full explanation see text.

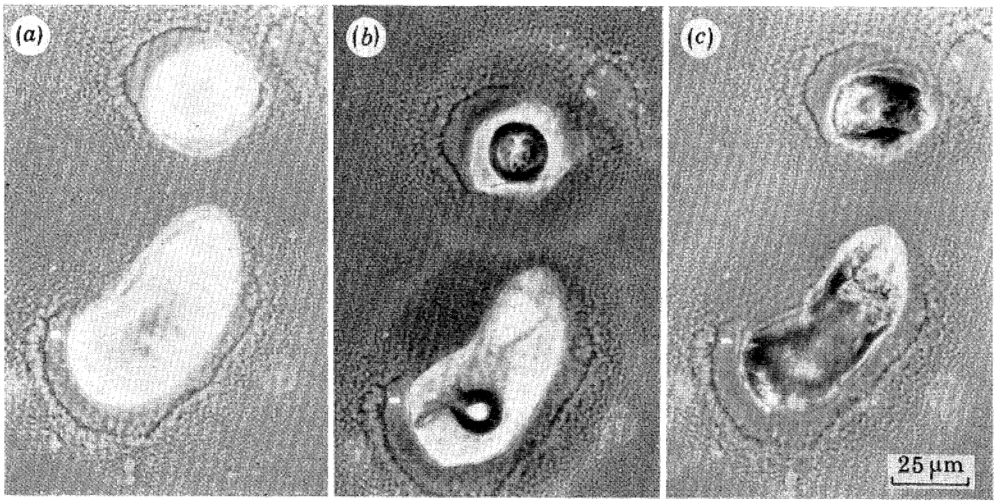


FIGURE 5. Conversion of remnant DICY particles in BSL914 film subjected to further heating in the hot stage microscope: (*a*) after gellation at 165 °C, (*b*) after heating to 210 °C, (*c*) after heating to 220 °C.

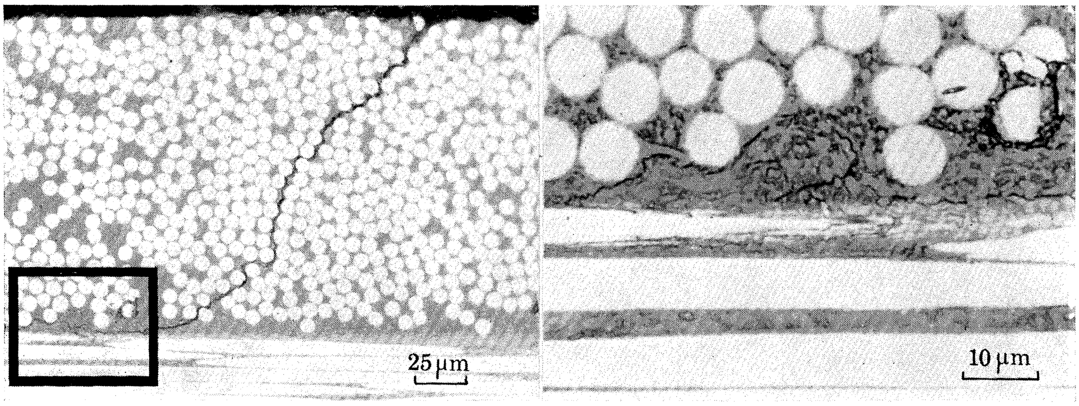


FIGURE 6. Path of translaminar cracks (produced in the i.l.s.s. test) in cross-plied composite (Courtaulds XAS fibre/BSL914). Note that the crack path is confined to the thermoplastic phase. The right-hand figure is an enlargement of the portion of the left-hand figure enclosed in the box.

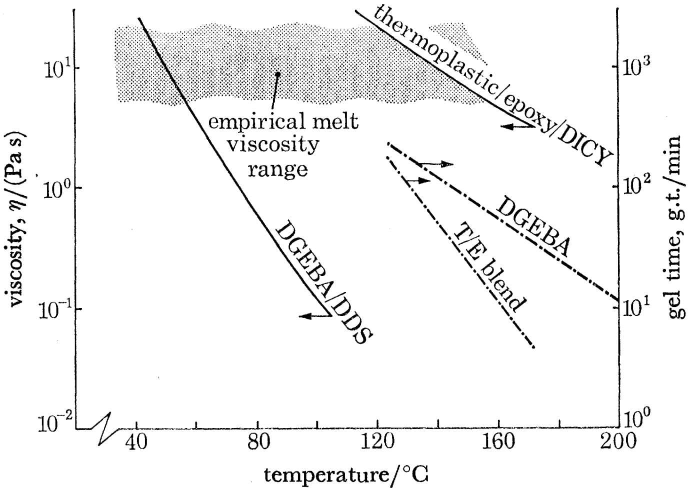


Figure 3. Comparison of viscosity and gel time data as a function of temperature for different epoxide systems. See text for full explanation. ——, Viscosity; — - — - —, gel time.

levels. This characteristic allows the matrix to sustain applied pressure without excessive flow. At the same time the latent hardener is effective in producing a rapid cure above its solution temperature (*ca.* 135 °C) in the epoxide.

Convenient as these processing characteristics are, however, this kind of formulation is not without its own problems. The polysulphone content precipitates during gellation and a phase-separated matrix, which has an influence on the mechanical properties of the composite, results. In the initial formulations the DICY crystals ranged in size from 1 or 2 μm up to about 150 μm. The result of this was that the hardener was frequently filtered, by the fibre pack, from the excess resin expressed during moulding. The component itself retained the excess hardener, and the resin flash, sometimes used for gel-time information, could not be completely cured. The second and fundamentally more interesting result is illustrated in figure 4 (plate 1) which shows a film sample of the matrix after gellation at 165 °C. The general fine scale phase separation is clear, and subsidiary experiments have shown that for this particular system the polysulphone is the connected phase. Also apparent is the isolation of a remnant of a large hardener crystal by the gel, and its effective removal from the reaction field. The chemical concentration gradient near the surfaces of the crystal has affected the cell size of the separating phases to a marked extent, and a temporary pause boundary of the dissolving crystal is discernible. Further dissolution usually occurs before final passivation takes place, leaving a reduced dicyandiamide crystal within a cocoon of apparently single phase resin.

In addition to its action in influencing the local appearance of the phase separated structure, the unreacted DICY can further interfere with composite properties and quality during postcure. DICY reacts to form melamine at a temperature between 205 and 210 °C. The normal reaction is violently exothermic and accompanied by the release of ammonia. Studies of these remnant hardener crystals with the hot stage microscope have shown that they too undergo a transformation in this temperature range (figure 5 (plate 2)).

In practice it is relatively easy for the postcure of a component at a nominal temperature of 190 or 200 °C to drift into the dangerous temperature region by virtue of a poorly controlled oven or fixture, or perhaps as a result of a small exotherm in a thick specimen. Blistered and delaminated components can then occur, when after the initial moulding cycle the component appeared satisfactory.

To avoid the effect of hardener filtration and eliminate the presence of residual unreacted DICY particles, the manufacturers produced a uniformly dispersed hardener consisting of very small particle size (3–6 μm). The phase separation of this system, while of the same type, is now extremely uniform and of fine scale.

If metallographic-style polished sections of carbon composites are produced and lightly etched with methylene chloride or 1,1,2-trichloroethane, these structures can be seen more clearly in the composite form. In cases where resin flow has taken place it is often possible to see flow structures in the matrix, and, by the application of the polishing and etching technique to specimens intended for the short beam shear test, it is also easy to follow the path of cracks developed during the test (as in figure 6, plate 2), and to demonstrate their association with the polysulphone phase for this fibre–matrix combination. The tortuous crack path clearly skirts all the epoxide areas and does not enter the fibres. Any improvement in interlaminar shear strength for this combination, therefore, must involve a study of the polysulphone–epoxide phase relations rather than the initial intuitive response of further fibre-surface treatment.

The epoxy–thermoplastic resin blend systems have many advantages to offer in the composite manufacturing phase. On the other hand care must be exercised in their formulation and use, and in the interpretation of results. Of course the homogeneous matrices have their own problems as mentioned earlier. The phase separated systems have some similarities with the high impact strength two-phase polyblend polymers like polystyrene–poly(methyl methacrylate), on which much valuable work has been done, and it is to be hoped that the current industrial interest in these phase separated matrices will stimulate a similar academic interest in this field too.

The study of industrially useful matrices for composite materials is a neglected area and one which will yield fruitful information of great value to the engineering sector. However, to be successful, such work must be intimately related to an end product via a realistic manufacturing process. Skills must be exercised over a broad front so that the results of a careful and detailed study of model matrix behaviour are not nullified in the final analysis by the production of unsatisfactory or faulty components.

I should like to thank my colleagues M. Hall and W. N. Turner of the Plastics and Composite Materials Laboratory for permission to refer to their work on water absorption and matrix viscosity.

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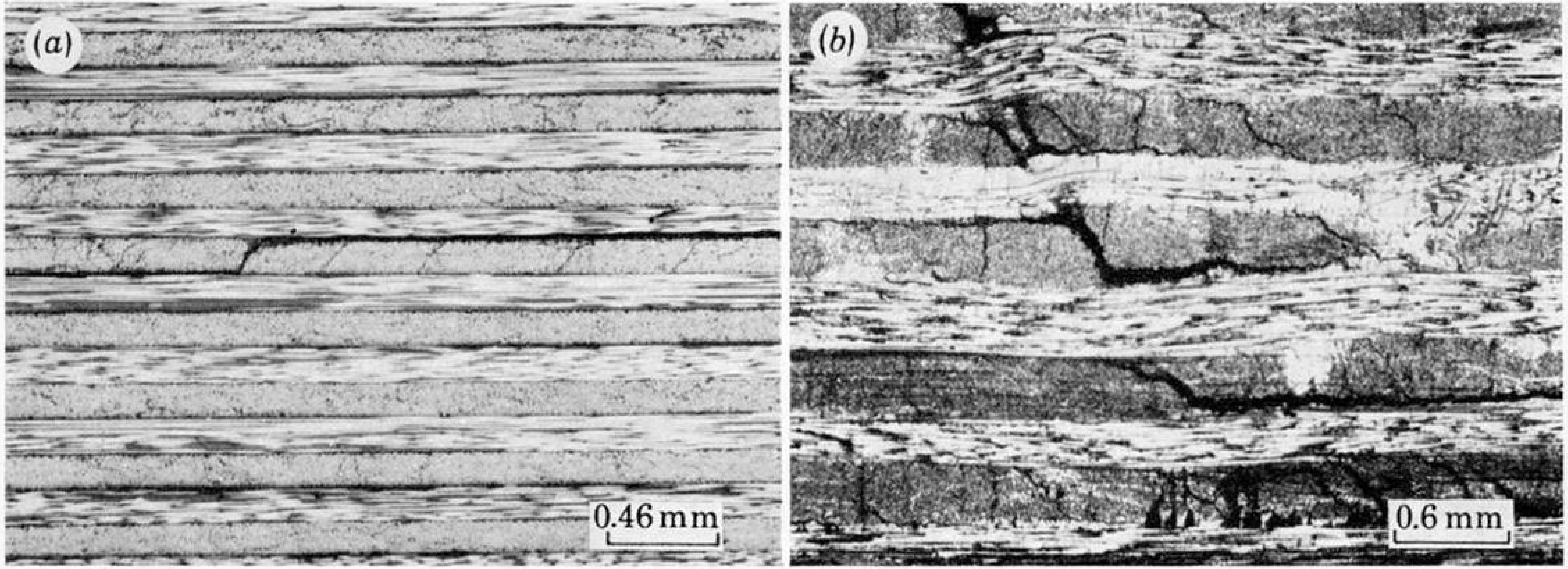

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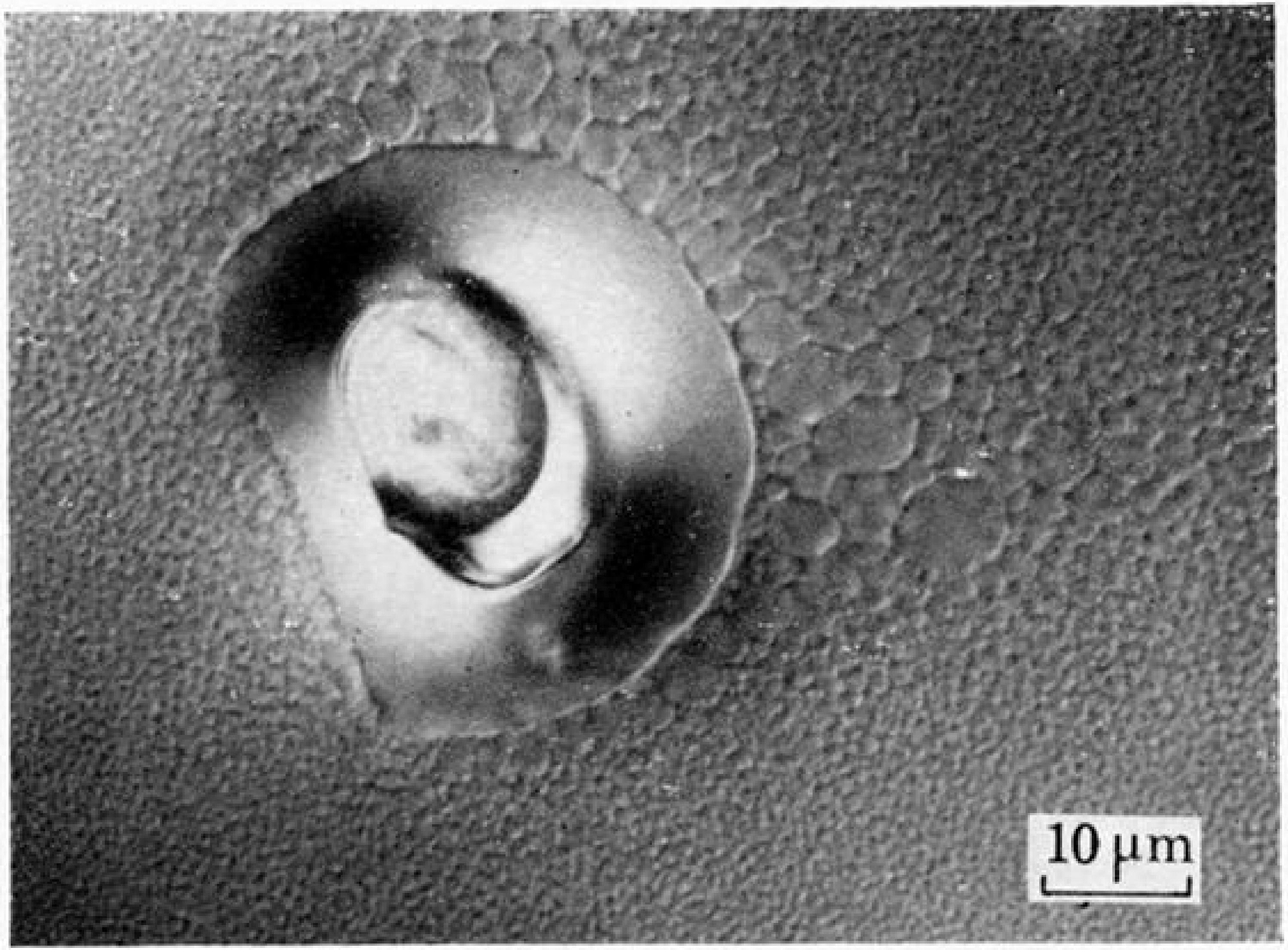
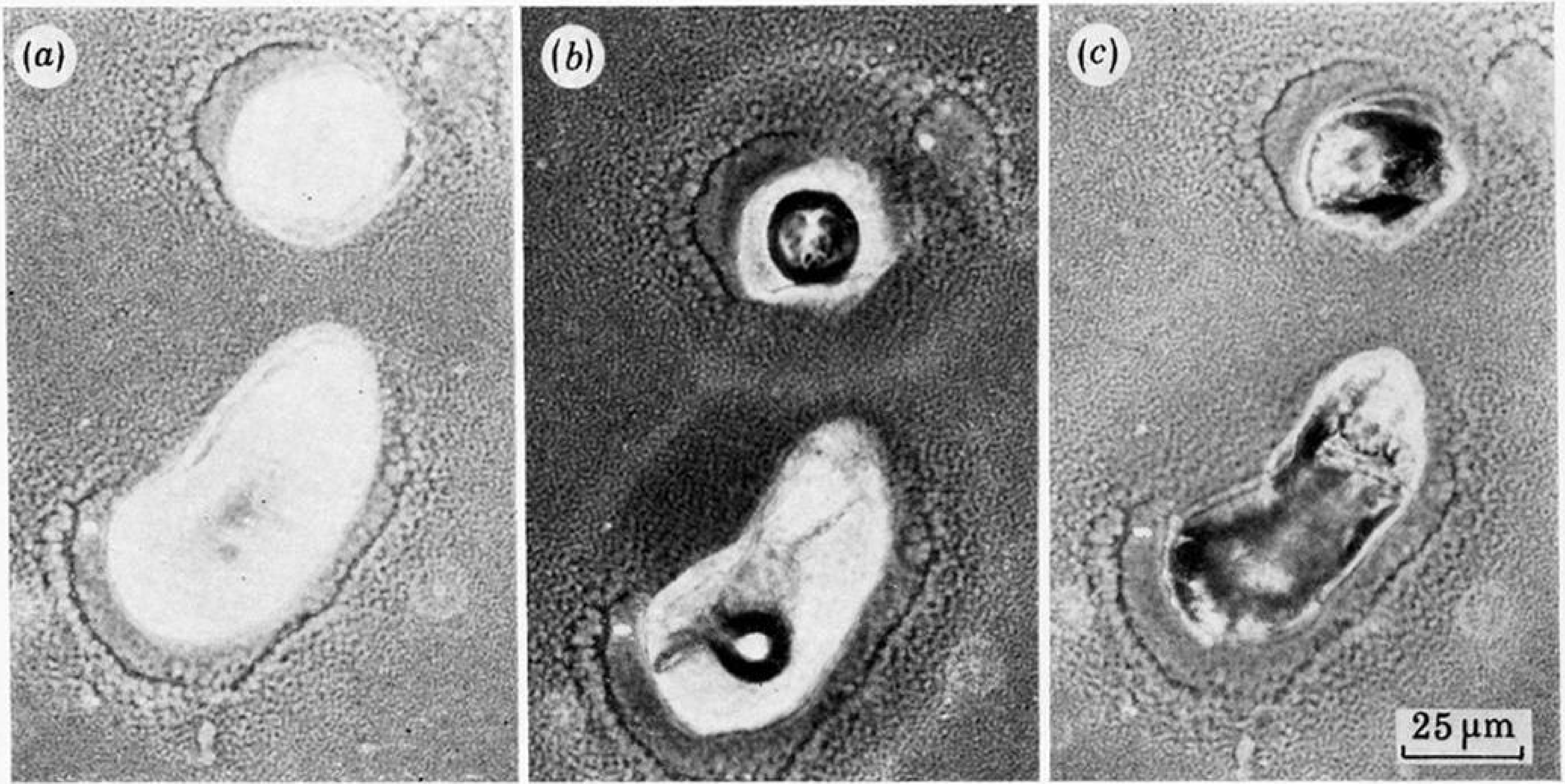


GURE 4. BSL914 film after gellation at 165 °C. For full explanation see text.



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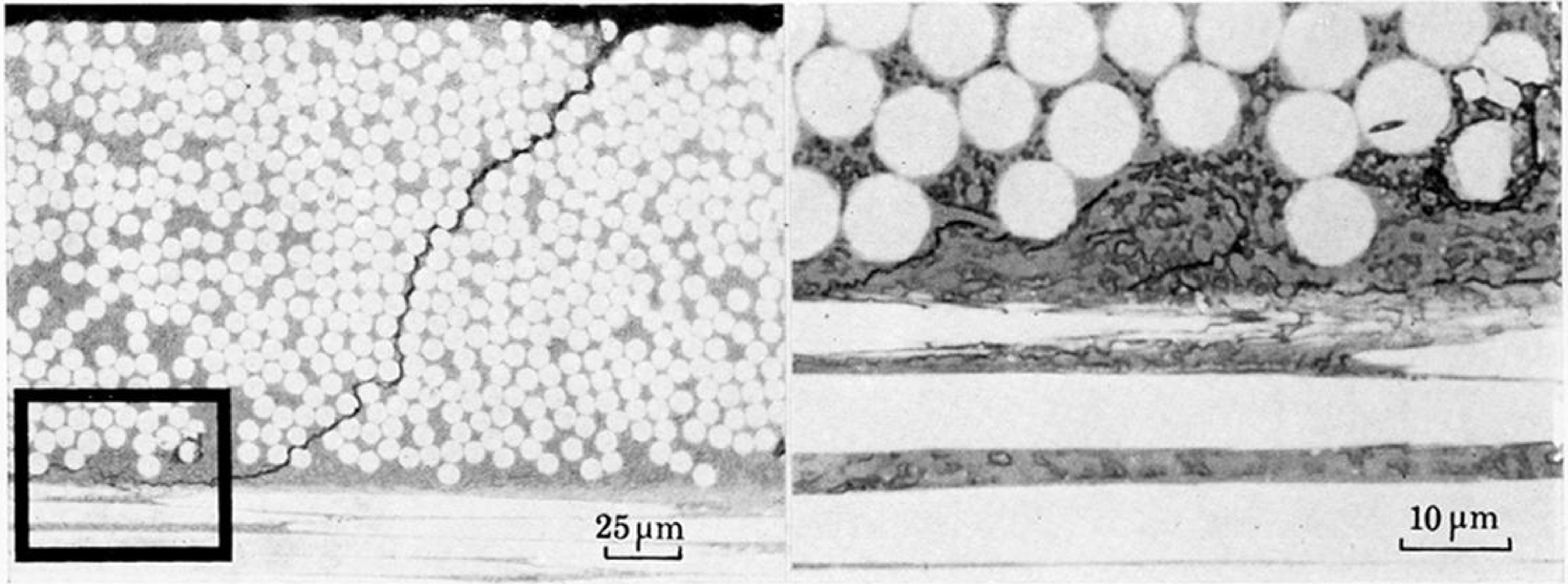

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