THE USE OF MICROFOCUS SYNCHROTRON X-RAY RADIATION AS A NOVEL TECHNIQUE TO STUDY THE INTERFACE IN COMPOSITES

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ABSTRACT

Micro-Focus SAXS is used to study predamaged single fibre composites as well as those composites under load. By a special specimen geometry the stress is concentrated at preselected areas of the specimen. The method allows to pinpoint and to identify local deformation and to follow up individual failure events with spatial resolution of few microns.

The processes of interfacial failure between fibres and resin as well as local failure processes in the resin at stress tips were identified. During interfacial failure the failing process occurs in a region of about 20 nm thickness. In the resin near a fibre break elliptical or lenticular shaped voids of the same order of magnitude were observed.

1. INTRODUCTION

Over the years it has been well established that the strength and toughness of fibre-reinforced materials are determined to a great extent by the interface between the reinforcing fibres and the matrix. Extensive research has been carried out in order to understand the nature of the interfacial bond and to characterise its properties. One of the key aspects concerning the interface is the mode of failure under the application of stress on the composite. A great number of techniques (Raman microscopy, acoustic emission, post mortem electron microscopy, etc.) has been employed until today in order to investigate and understand the mode of failure at the interface and the interfacial bond. In the present study we present a novel and potentially very powerful technique based on small angle x-ray scattering (SAXS) to study the interfacial mechanisms of failure.

2. EXPERIMENTAL

SAXS has been a well-established method to study structural features in the range of nm. The scattering of x-rays is caused by the difference in the electron density of domains inside the material. In the case of the interface of composites, when failure has occurred there is an increased number of micro cracks, voids, and debonded areas in which the density of the material (in this case the matrix) is much lower than it is in the healthy regions where no damage has occurred. It is due to this density difference, that the x-rays are scattered and much valuable information can be obtained through this phenomenon. However, although the method is powerful it is not entirely free of problems. In particular, in order to obtain the best possible results one has to expose the sample for a certain period of time, which is proportional to the brilliance of the x-ray source (brilliance is the number of photons per sample area per second). Furthermore, the study of the interface in composites necessitates the use of very fine beam-spots, which in turn increases the need for high brilliance x-ray sources. The problem may be overcome through the use of synchrotron radiation, which possesses 10^8 times higher brilliance than a standard laboratory x-ray source. The ID13 beamline at ESRF,

Grenoble is one of the very few beamlines in the world to offer very small x-ray beam-spots (< 5 μm), thus allowing spatially resolved studies (1 - 3). This unique feature coupled with the very high brilliance can be exploited in order to study the interface of composites. The very short time of data acquisition (typically in the order of 15 s) allows to employ the technique in a static mode, i.e. post mortem, as well as in a dynamic one, i.e. under the application of stress.

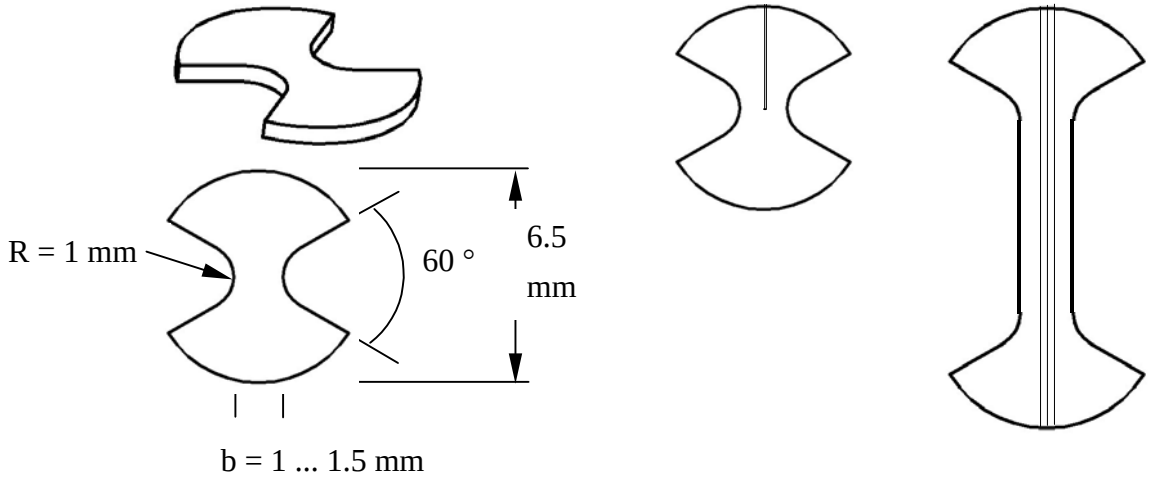
Specimen

Two epoxy systems (resin Rütapox® L1000, hardener Rütadur VE 5194/H and hardener Rütadur VE 5195/H, mixed in the ratio 70 : 18 : 12, precured at 50 °C, and cured at 67 °C and resin/hardener VE 4539, mixed in the ratio 100 : 17, cured at 60 °C [always referred from now on as resin 1, 2, resp.], both from Bakelite), along with Ø 17 μm commercial glass fibres, sized for epoxy resins, (RO99 900 P 196, Vetrotex) were used.

Two types of single, or multi fibre specimens were used, see figure 1. In the first case one or more fibres were embedded in parallel in a dog-bone shaped specimen, with about 1.5 mm width, 1 mm thickness and a parallel length 10 mm. The specimens were pre-stretched to fragment the fibres, and afterwards were investigated. Generally, an online investigation is also possible, but due to the statistical nature of the fragmentation phenomenon it is rather difficult to pinpoint the position, where the fibre will break.

To overcome this disadvantage we have employed a novel geometry of specimens, termed as ‘micro dumbbell’. These specimens have about the same cross section in the middle like the fragmentation specimen. However, due to the steadily changing cross section along the specimen a definite stress concentration appears in the middle of the specimen. In these specimens a continuous fibre can be embedded to get fragmentation. On the other hand, a fibre with the edge in the middle of the specimen can also be embedded. This induces geometrically a stress concentration at the fibre edge during loading, thus localising interfacial failure. A stable interface crack propagation is then possible. The stress development can be checked qualitatively by polarised light in a microscope, following the evolution of photoelastic patterns.

The fibres were brought to position in special moulds of silicon rubber (at the half thickness of the final specimen), the moulds were then filled with the premixed and degassed resin, covered with a release foil and cured in a furnace to produce the final specimen form, or a plate, from which the specimen is the produced by a CNC-milling machine.



micro dumbbell specimen, overall dimensions

micro dumbbell specimen with single edged fibre

fragmentation specimen, side-by-side arrangement of fibres

Figure 1: Geometry of the investigated specimen

Technique

experimental set-up:

A portable computer controlled micro deformation rig was used (self made on the basis of a machine from fa. Kamrath&Weiss). In order to hold the specimen during loading at the same position of the beam spot, both grips move simultaneously to opposite sides. To fix the specimen for static as well as dynamic tests adapted grips were used, which combine form fit with frictional connection, see fig. 2. A conical hole in the middle of the grips keeps the central position of the specimen free for SAXS by the micro focus beam.

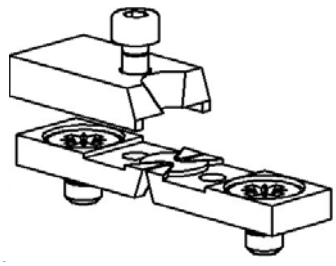


Figure 2: Adapted grips for micro dumbbell specimen

In order to get an online strain mapping of the specimen a grating technique was used [ARAMIS, fa. GOM]. For the different loading steps were recorded not only load and displacement but also images of the slightly structured specimen by a SONY IEEE 1394 monochrome camera (1024 * 768 pixels) with a precision objective lens (Rodenstock macro objective MR 1/4). Observation directly in the beam direction was made possible by introducing a mirror with a hole for the beam. This arrangement enables positioning the camera vertically to the beam. The setup is outlined in fig. 3.

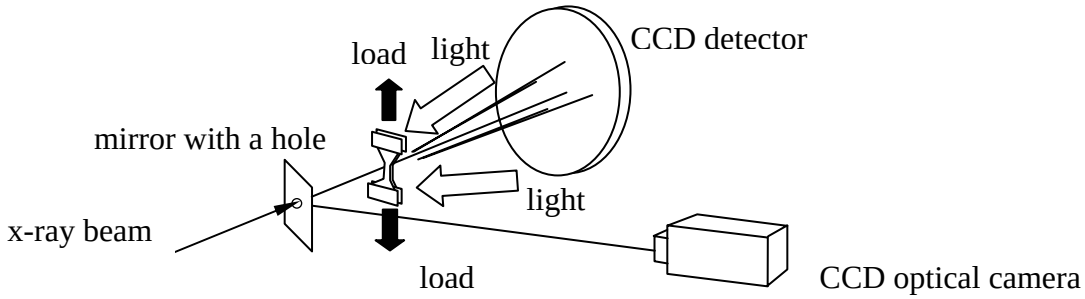


Figure 3: Experimental arrangement for insitu μSAXS, tensile testing and video recording

The specimens were illuminated from the back side through the use of a photodiode array. In this way also the position of the beam with respect to the fibre could be controlled.

3. RESULTS & DISCUSSION

In order to remove parasitic scattering from the air it is usual to subtract the background from the 2D patterns of the specimens. However, since epoxy scatters weakly at the SAXS range, one may chose to subtract the scattering from undamaged epoxy areas next to the damage areas. In this manner, the net contribution to the scattered intensity may be determined. Hence, we chose to apply this correction in our case.

To get an overview, sections of the 2D-patterns of 200 * 200 pixels around the beam position were created. One example is shown in fig. 4.

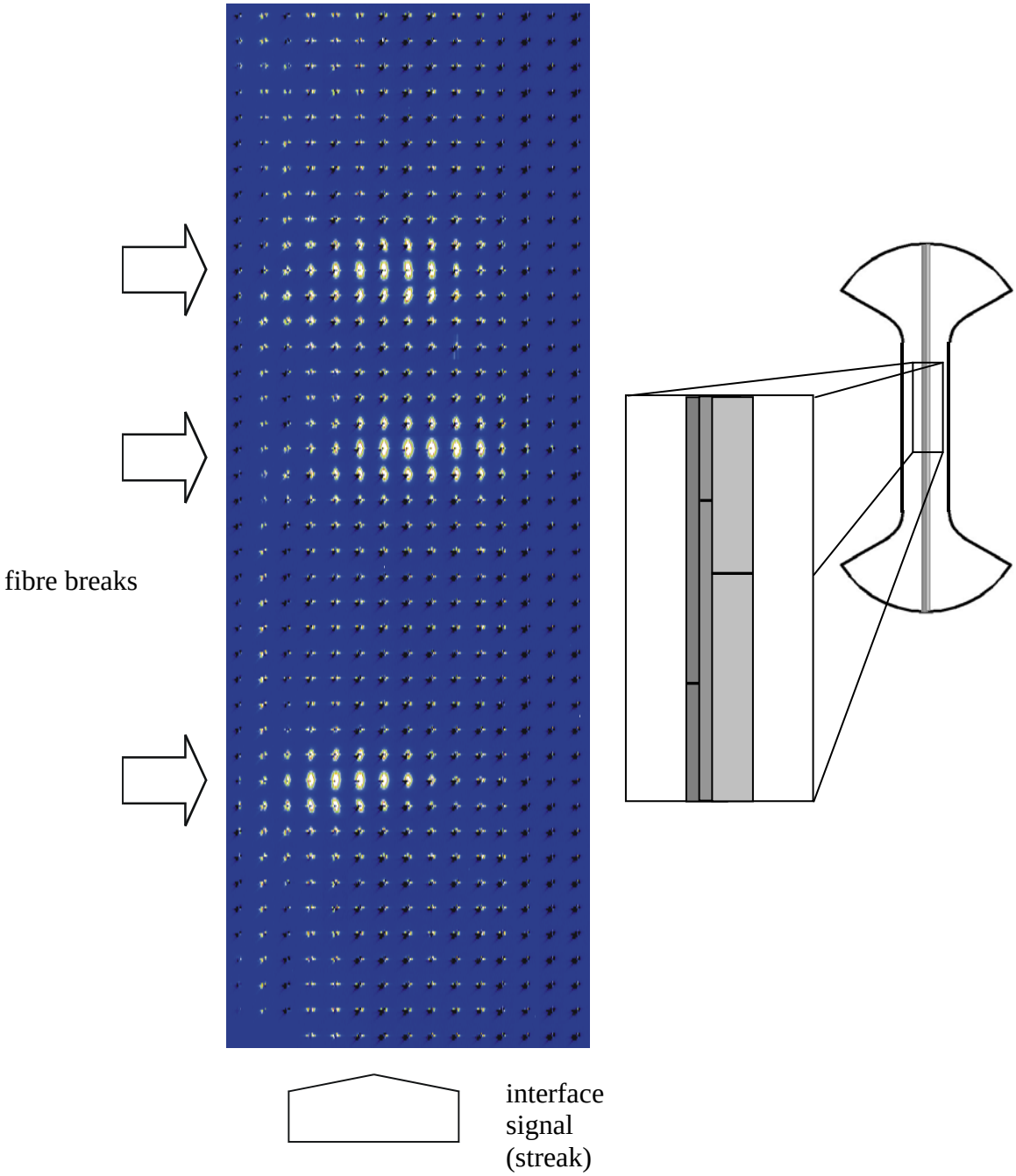


Figure 4: A scan of SAXS patterns (each 200 times 200 pixels from the total detector signal for an epoxy/glass fibre fragmentation specimen. Three fibres lay back-to-back in horizontal direction. After a fragmentation test the composite was scanned around the optically visible fibre fragments for an area of 400 μm in parallel to the fibre axis by 100 μm normal to the fibre axis. The step size was 10 μm by 6.25 μm, and each pattern comes from an area of 5 μm diameter. Three fibre cracks are detected.

There are different characteristic patterns observed: At the failed interface, at the fibre crack zone and in the strongly deformation region of the resin. In figures 5 - 7 the different types of patterns may be seen for comparison.

One may clearly see the areas with a high density of voids, manifested by the higher intensity of the scattered x-rays, and denoted by a sharp white colour. Currently, we are in the process

of quantifying this series of patterns to extract the geometrical dimensions, and the shape of these voids.

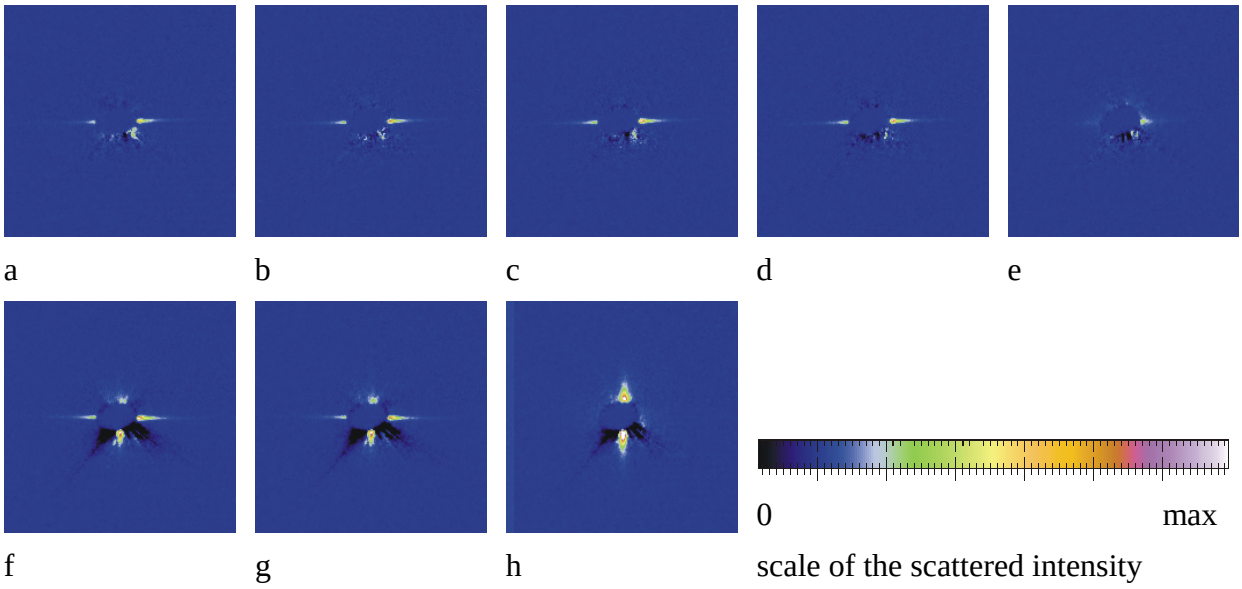
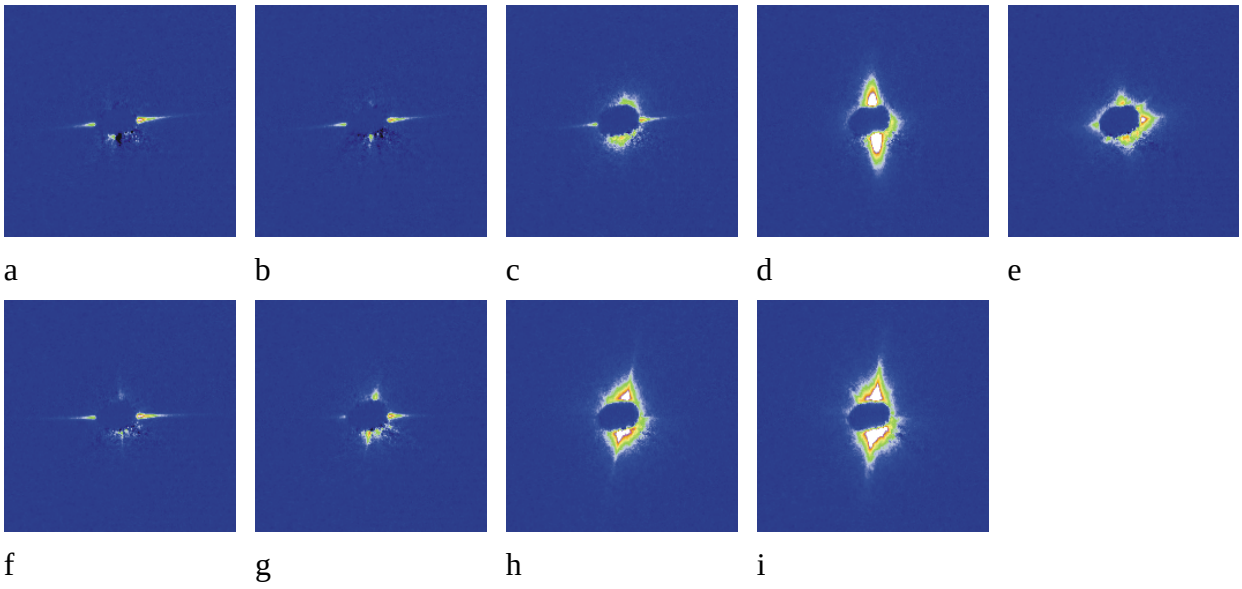
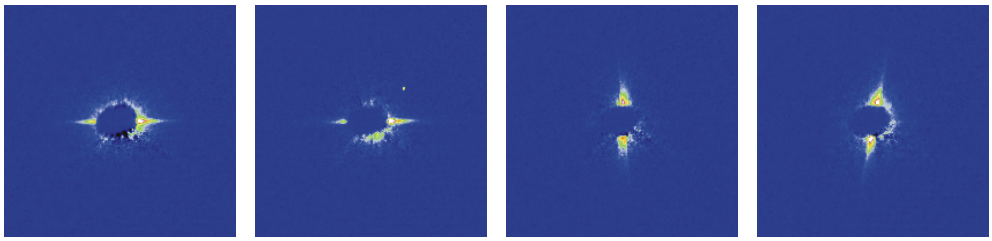


Figure 5: SAXS-patterns of resin 2, micro dumbbell specimen:

Patterns of the unloaded interface, (a) narrow and (b) 200 microns away from the fibre tip, and at different load steps, with local strain of (c) 0.9%, (d) 1.3 %, and (e) 1.8 %

Patterns during loading with local strain of (f) 1.6 % and (g) 1.7 %, and (h) immediately before the specimens failure at 2.5 % local strain, measured about 10 µm away from the fibre





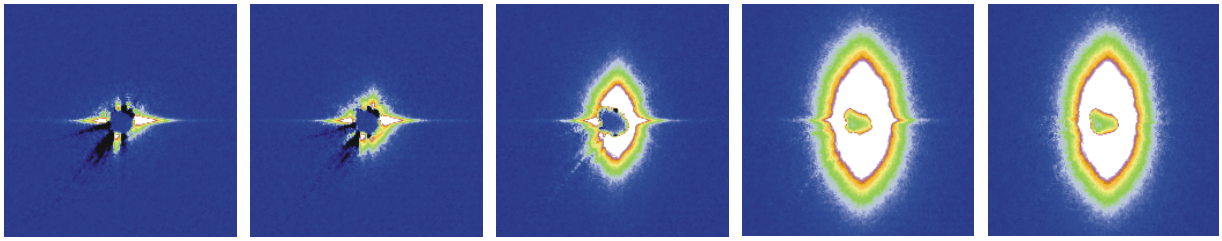
j k l m

Figure 6: SAXS-pattern of resin 1, micro dumbbell specimen:

Static investigation at a strain of (a) 0.7 %, and (b) + (c) 1.4 % as well as (d) immediately prior failure and (e) after failure

Pattern during loading near the interface at local strain of (f) 0.85 %, (g) 1.1 % and (h), (i) after local yielding and started failure from the side of the specimen, in those cases the beam was slightly shifted away from the fibre (about 10 µm)

Static scanning of the predamaged specimen: (j), (k): interface, (l), (m): fibre end – only interface faliure in the vicinity of the fibre end (200 µm)



a b c d e

Figure 7: SAXS- pattern from the fragmentation specimen with resin 1 in fibre direction from the fibre to the fibre crack. Due to the 3 fibres on top of each other a superimposed interface signal (streak) is obtained. After subtraction remains a poor lenticular pattern at the outer right side. (a) pure interface signal, (b), (c) superposition of the streak with the resin signal at the fibre crack, (d) resin signal at the fibre crack, superimposed with the streak, (e) pure resin signal at the fibre crack.

Interface failure

From the failed interface very narrow streaks strong perpendicular to the fibre direction are detected. After integration the 2-d pattern in azimuthally direction over the streak a strong decay of intensity is found, see figure 8.

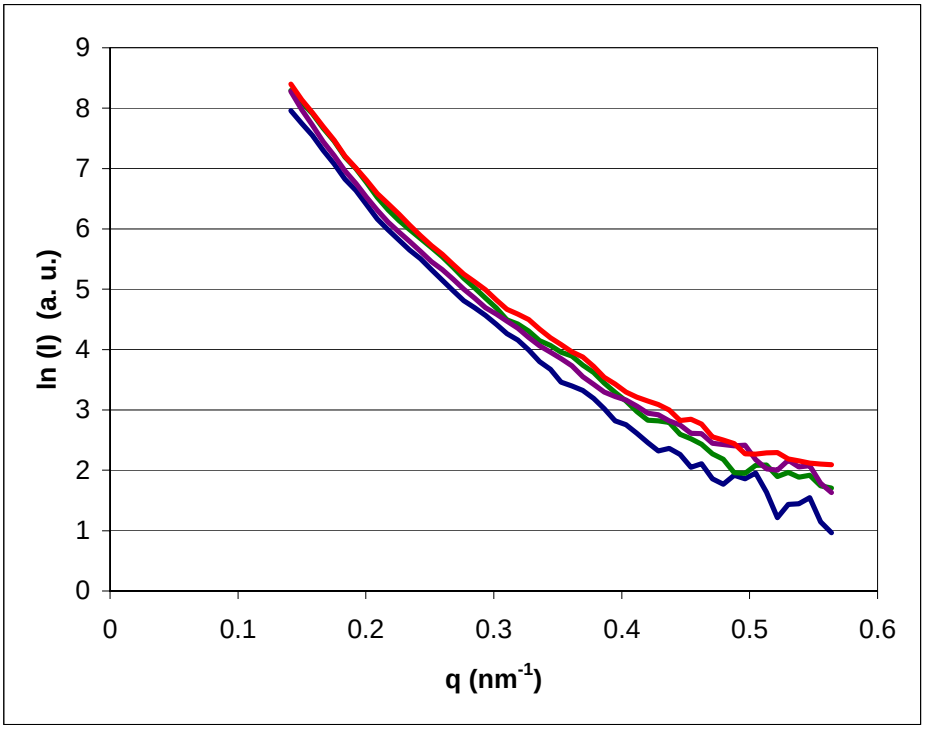


Figure 8: SAXS-1D patterns from failed fibre-resin interface at four different positions along the interface

To analyse the data we chose initially the geometry of a slit, tangentially placed with respect to the fibre with a width of b and with the other two dimensions infinitely large. This results in the following form factor (4). It gives a scattered intensity according to

$$I(q,b) \propto \frac{\left(\sin\left(\frac{qb}{2}\right)\right)^2}{\left(\frac{qb}{2}\right)^2}, \text{ where } q = \frac{4\pi}{\lambda}\sin 2\Theta \text{ is the magnitude of the scattering vector.}$$

The intensity is oscillating with a wavelength of $q_{min} = 2\pi b$. A distribution of slit widths, e.g. modelled by a Gaussian distribution, the effect of a rough interface or the effect of the curvature of the interface diminishes or eliminates these oscillations quickly.

It is surprising, that the interfacial 1D patterns are very similar at different positions of the specimen and also under different loads, as well as for the two different resins and geometries of the specimens. The characteristical length b lies in all cases in the order of 20 nm. It should be noted that we also modelled the 1D SAXS patterns assuming the voids take the shape of an infinitely long rod, and the estimated diameters of the rods were also of the same order of about 20 nm (5). Hence, it may be concluded that the inhomogeneities/voids present in the damaged interfacial zone have a characteristic dimension of about 20 nm.

This means, that no crack opening is observed. The interfaces damaged by failure having different electron densities (as required for x-ray scattering) are all of the same dimension. On the other hand the general lack of oscillations in I(q) (despite some very small ripples in a few cases) show that defect structures are not very regular.

It is notable, that in the case of unloaded composites interface scattering is also observed in the vicinity of the fibre ends, but not at some distance away. The signal is also not distinctly different from that of the definitely broken interface for instance of the fragmentation specimen. This may mean, that there is a x-ray relevant interfacial disturbance not only due to interfacial failure but also due to interfacial stress. It could also be a sign of preexisting damage due to thermal mismatch between the fibre and the matrix, or due to poor interfacial contact at this area.

Fibre crack

In the fragmentation specimens there was a strong signal found at broken individual fibres, which may be seen in fig. 4, as well as in detail in fig. 7. In particular, if the interface signal of the parallel fibres is subtracted a well-balanced lenticular pattern remains with the long axis in fibre direction. Although the fibre ends are shifted visibly in the optical microscope, which means a shift of the order of few hundreds of nm, the bright patterns suggest that these structures are different from those at the interface and fibre failure. The unique signal with steady decay points to a broad distribution of anisotropical voids of imperfections (of elliptical shape) in the immediate vicinity of the fibre crack within the resin.

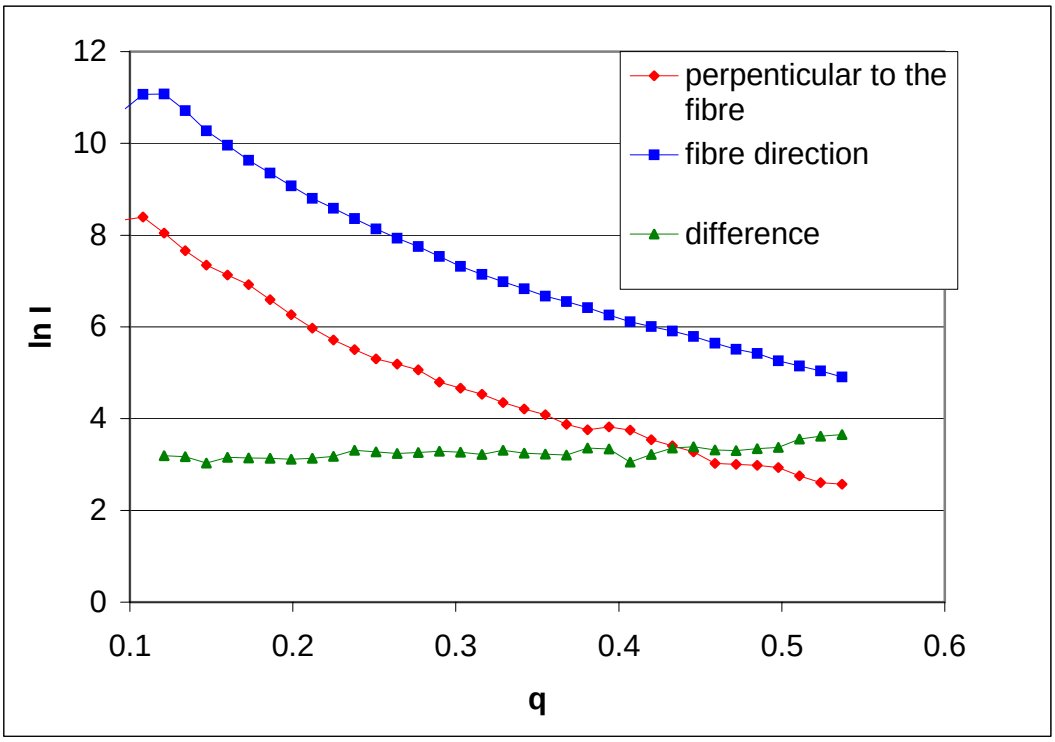


Figure 9: Scattering curve of the locally damaged resin in the fibre direction and vertically to fibre direction of the fragmentation specimen between the fibre fragments.

From the scattering curves there is a slightly smaller decay of the signal in the fibre direction than perpendicularly to the fibre.

Area of strong local deformation of the resin

It was surprising, that the relatively brittle epoxy specimen resin 1 of 1 mm thickness show in some cases yielding-like behaviour, if the thickness is reduced to about 0.5 mm. In the same way in some cases the micro dumbbell specimen showed yielding-like deformation in the middle prior to failure. During this strong deformation no remarkable SAXS signal was observed in comparison with the base material. In contrast to the overstretching at the fibre crack position here due to lateral contraction the matrix did not rip off.

4. CONLUSION

Micro-Focus SAXS is a very useful tool to investigate online the damage and the failure behaviour of single fibre composites. It allows to pinpoint and to identify local deformation and to follow up individual failure events with spatial resolution of few microns. Due to a suitable preselected geometry of the specimen the stress can be localised in the area under investigation.

Mainly two processes could be identified. One is the interfacial failure between fibres and resin. This can take place at very early loading stages without remarkable influence on the overall mechanical behaviour. The second is the local failure processes in the resin causing elliptical voids with dimensions in the range of about 20 nm or small cracks with lenticular shape.

More research is currently ongoing to further elucidate the phenomena associated with interfacial failure in composites.

ACKNOWLEDGEMENTS

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