

# UNDERSTANDING THE LINKS BETWEEN MOLECULAR AND PARTICLE ORIENTATION IN CARBON NANOFIBRE REINFORCED POLYPROPYLENE.

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## SUMMARY

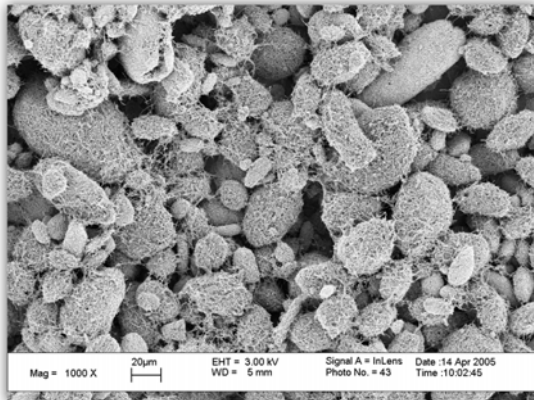
In this study we have investigated how the deformation behaviour of a polystyrene/carbon nanotube (CNF) nanocomposite depends on both molecular and fibre orientation. A commercially available carbon nanofibre was blended with a polydispersed polystyrene and then drawn at a temperature of 115°C to a range of stretch ratios and then frozen. These stretched samples were then redrawn at a temperature of 105°, and at a constant true strain rate. Wide Angle X-ray scattering was used to examine nanofibre orientation and molecular orientation was assessed by examining the true stress/true strain curves.

*Keywords: Nanocomposites, solid state deformation, carbon nanofibres*

## INTRODUCTION

The deformation of a particle filled polymer depends on a number of factors, including the properties of the two phases, particle shape and particle volume fraction. Of particular interest is the effect of the orientation of the two components on the mechanical properties of the composite, either for the orientation of the polymer chains or the particles (if they have an anisotropic shape such as a cylinder). Research over a number of years at Leeds has investigated the effect of orientation on mechanical properties of both polymers and polymer composites. This has established how preferred molecular orientation can produce enhanced, anisotropic, properties in polymers [1-2] and has seen the development of a number of commercial processes for achieving orientation in the solid state, for example the die drawing process [3]. Similar ideas have been developed for fibre filled polymers, for processing in either the melt or solid phase. In injection moulding, where the polymer is molten, orientation is predominantly in the fibre phase [4], whereas if die drawing, or its counterpoint hydrostatic extrusion, is used to produce deformation in the solid phase, then preferred orientation can be generated in both phases [5]. In this study we have investigated how the deformation of a carbon nanofibre filled polystyrene affects the orientation of the two components and how this then affects mechanical properties, and ways to alter the balance. Of particular interest was to assess the effect of changing the balance of orientation of the two phases by changing the testing speed.

## MATERIALS



The polymer matrix used in this study was a commercial polystyrene ( $M_w = 274,000\text{g/mol}$  and polydispersity = 2.74) filled with 10% by weight of commercially available carbon nanofibres (CNF). The CNF were obtained from Applied Sciences Incorporated, grade Pyrograf III PR19PS. These CNF have been widely studied, including by these authors [1], as they are one of the most cost effective carbon nanofibres available.

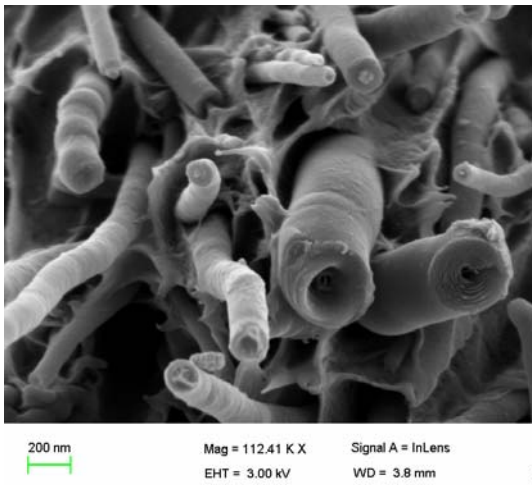


Figure 1 on the left shows details of the carbon nanofibres. The bottom figure shows how the vapour deposition process gives a range of structures: tubular with a range of hole diameters, solid and the so called bamboo structure (top left). It is also seen that the diameter of the fibres is quite varied. In a recent study, Foster [1] determined the average diameter from SEM measurements as  $92 \pm 10\text{ nm}$ .

Figure 1: Details of the Carbon nanofibres

they are in large, highly entangled, bundles, which are many microns across. As with all nanocomposites studies, blending, and dispersion of the CNF, is a crucial aspect. We have followed the recent work of Foster [6], in first blending the fibres using a twin screw extruder (Thermoprism Eurolab), and then sending the resultant pellets once more around the extruder. The extruder temperature was set to  $200^\circ\text{C}$  along the barrel. This has been found to give excellent dispersion of the entangled fibres (see Figure 8 below) while limiting fibre attrition.

## SAMPLE PREPARATION/MECHANICAL TESTING

For the sample preparation and testing, we have followed the protocol established in a recent study of the same unfilled polystyrene [7]. First, a tape of both the unfilled and filled polystyrene was extruded using a small melt spinner, as shown in Figure 2. The barrel of the spinner was held at a



Figure 2: Sample preparation

temperature of 200°C. To ensure no molecular orientation was present in these samples after extrusion, they were annealed for 1 hour at 140°C under a contact pressure in a hot press. Next, the tape samples were drawn in a temperature controlled oven at 115°C to a range of draw ratios up to 4, to induce orientation into both the polystyrene and the CNF. Once the appropriate draw ratio was achieved, the oven was opened and the sample was cooled rapidly using a freezer spray. To assess the effect of orientation, the drawn samples were then retested at 105°C. The tests were carried out on a screw driven tensile tester with an exponentially increasing speed controlled by a specially written Labview code to give a constant true strain rate (0.03 s<sup>-1</sup>). Sample strain during the retest was measured using a Messphysik video extensometer.

The level of nanofibre orientation in the various samples was measured using Wide Angle X-ray Scattering (WAXS). The advantage of using an amorphous polymer as the matrix phase (as opposed to a crystalline polymer such as polypropylene) is that only shows an amorphous halo at a low value of 2θ, while the carbon nanofibres show a sharp clear peak at a 2θ value of 26.6°. Finally, scanning electron microscopy was used to examine the microstructure of the tested composites from the various draw ratios.

## RESULTS

### The effect of draw ratio

Figure 3 shows the true stress/true strain results for a range of samples which had been stretched and frozen at 115°C (at a nominal strain rate of 0.01 s<sup>-1</sup>) and then retested at 105°C.

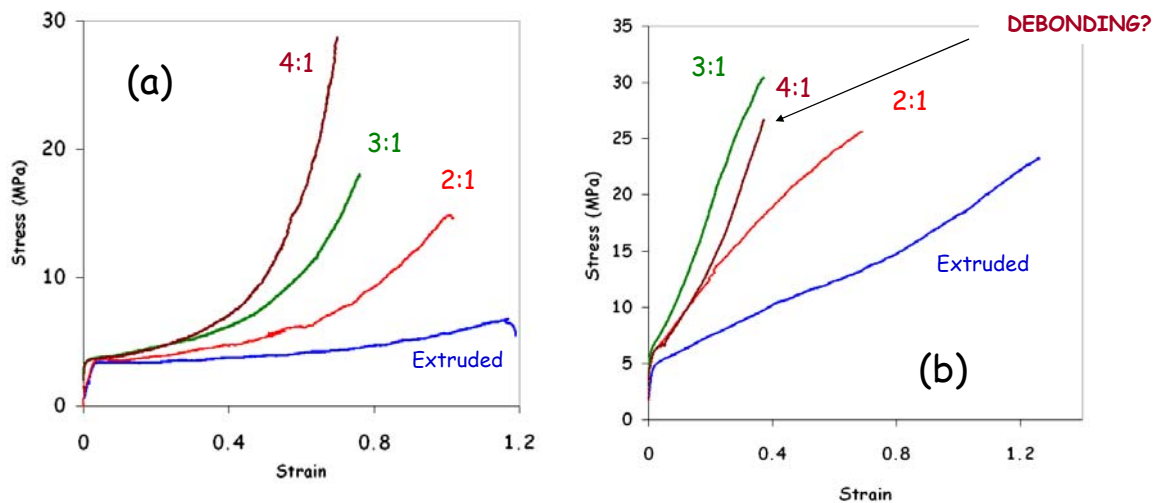


Figure 3: True stress-true strain curves for samples drawn at 115°C, frozen and retested at 105°C: (a) pure polystyrene (b) CNF/polystyrene nanocomposites.

The left hand picture shows the results for the pure polystyrene. It is seen that the curves show a typical shape associated with oriented polymers, with an increasing degree of strain hardening with increasing draw ratio. The pure polystyrene samples also all show an increasing rate of strain hardening with testing strain. The right hand picture shows the analogous results for the CNF filled material. It is clear that the presence of the

fibres has a significant effect on both the strain hardening rate (which is increased) and the shape of the strain hardening region, which is much more linear than seen for the pure polymer samples. The failure stress is increased for all the filled samples while the failure strain of the composite samples is lower: these results are typical for the effect of a stiff reinforcing particle on the deformation behaviour of the softer polymer matrix. The DR=4 sample showed a slightly lower stress than the DR=3 sample.

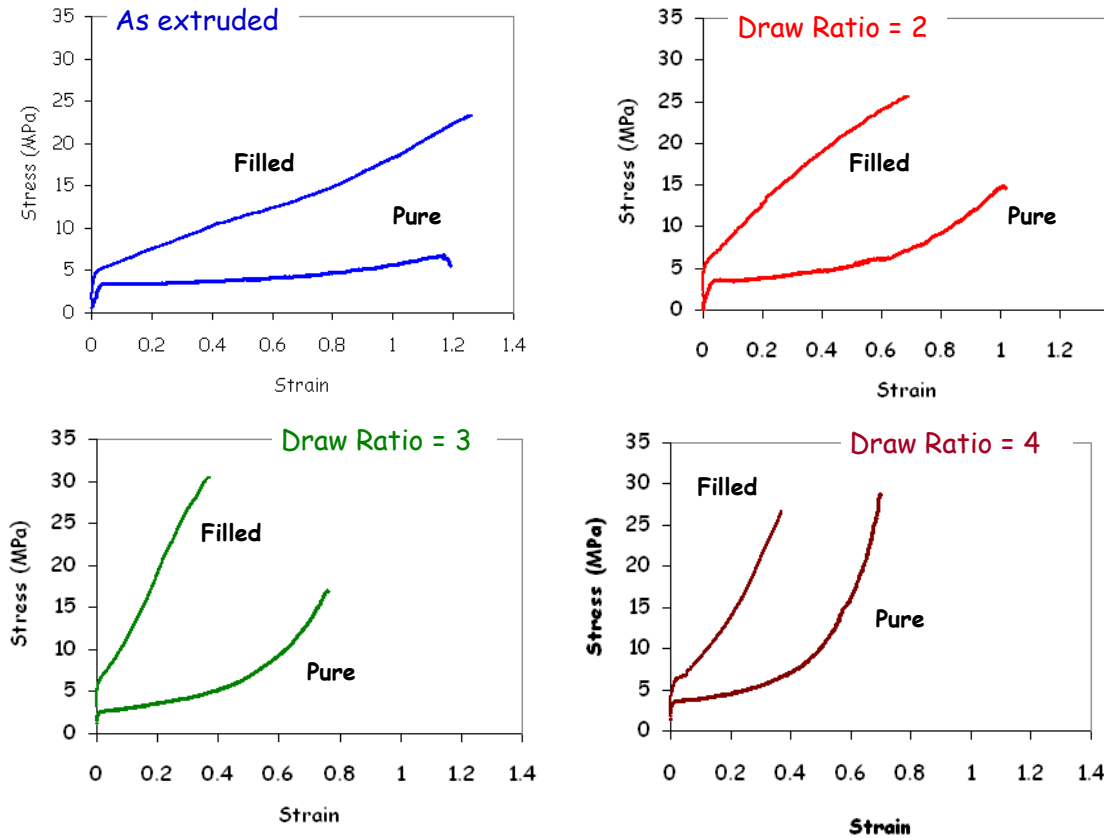


Figure 4: True stress-true strain curves for samples drawn at 115°C, frozen and retested at 105°C:

Figure 4 shows a direct comparison of the deformation of the samples at the various draw ratios. Interestingly, the filled materials tend to fail at a true strain equivalent to that where the pure material begins to strain harden significantly (at a similar true stress of ~6.5MPa). We can speculate that this is caused by increased particle/polymer debonding as the stress begins to rise. The reason for the lower performance of the filled sample at DR=4 could be due to debonding occurring between the hard particles and the softer polystyrene matrix. Debonding is often found in solid state samples deformed to high strains, due to the mismatch in stiffness between the two phases. For example, Cooke [8] found a decrease in sample density with stretch ratio for die drawn glass fibre polypropylene samples.

### The effect of testing speed

For polystyrene, the development of molecular orientation depends on strain rate and temperature, particularly whether the strain rate is faster than the inverse of the average

relaxation times [7] at the appropriate temperature. Recent research [9] has seen significant progress in linking molecular topology to polymer dynamics, in particular, the identification of a number of important relaxation times. These are, the entanglement time,  $\tau_e$  which is the time for a polymer segment between entanglement points to relax, the Rouse time,  $\tau_R$  and the reptation time,  $\tau_d$ , the time for an entangled chain to lose the memory of its previous state by diffusion along its tube. In any deformation process, therefore, the development of molecular orientation at each length scale will depend on the relationship between the strain rate and each relaxation time.

For this polystyrene, which had an average molecular weight of 274,000, the three relaxation times at 115°C were as follows [9].

Entanglement time (s)	Rouse Time (s)	Reptation Time (s)
$\tau_e$	$\tau_R$	$\tau_d$
74	$2.03 \times 10^4$	$4.03 \times 10^5$

Table 1: Relaxation times for polystyrene,  $M_w = 274000$

The first tests, described in the previous section, used a strain rate of  $0.03 \text{ s}^{-1}$  resulted in orientation at all length scales. To assess the effect of testing speed, a sample was drawn to 2:1 using a crosshead speed 100 times lower, that is a starting strain rate of  $0.0003 \text{ s}^{-1}$ . As the inverse of this slower strain rate is significantly greater than the entanglement time, relaxation between entanglements can occur during the drawing process, although orientation on the order of the chain length will still be generated. The interest is to see how this affects the subsequent deformation behaviour, and to assess if the orientation of the fibres is rate dependent. In previous studies (e.g. [10]) we have shown that fibres rotate as predicted by the pseudo-affine scheme, that is the overall change in shape of the sample, and so should be rate independent.

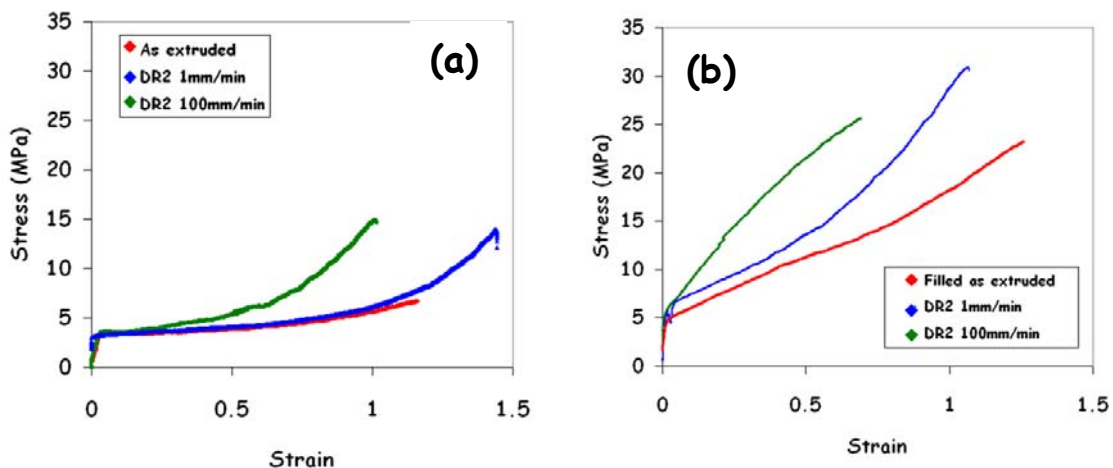


Figure 5: The effect of drawing speed on the subsequent deformation behaviour of pure PS (a) and CNF/PS samples (b) drawn to 2:1: **as extruded: stretched at 100mm/min: stretched at 1mm/min**

Figure 5 shows the effect of the two testing speeds on the subsequent deformation behaviour for (a) the pure PS and (b) the CNF/PS. The pure PS sample drawn at the slower speed shows a delay in the onset of strain hardening compared to the fast drawn samples. However the slowly drawn sample then shows strain hardening, at a similar increasing slope to that seen in the sample drawn at 100mm/min. It is proposed that the delay in the onset of strain hardening in the slowly drawn sample is due to the relaxation of orientation at small lengths scales, as the drawing speed is slower than the inverse of the entanglement time. However, the larger scale orientation is not affected by the testing speed, hence the similar ultimate strain hardening rate.

For the filled samples the trend is similar, but with all the samples showing an increased strain hardening due to the presence of the fibres. For the as extruded sample, the response is almost linear. As the extruded pure PS sample showed a true stress almost independent of strain, we can attribute this increased slope in the filled sample to the presence of the fibres. The sample stretched at 100mm/min show increased strain hardening, but with a decreasing slope above a stress of 15MPa. It is likely that this is due to debonding between the hard fibres and softer PS matrix. Finally the slower drawn sample shows a similar shape to that of the pure PS sample, albeit with an increased level of strain hardening. In the initial part of the curve, it follows the as extruded sample, and then diverges as the PS matrix begins to strain harden.

In order to assess the degree of CNF orientation, SEM pictures were taken from the extruded and drawn samples and Wide angle X-ray Scattering experiments were also undertaken. In the first instance a range of WAXS photographs were taken from the various samples. A sample of the pure CNF showed an isotropic ring at a  $2\theta$  value of  $26.6^\circ$ . The extruded and drawn samples showed both an amorphous ring due to the polystyrene plus the CNF signature. Figure 6 shows a typical WAXS photograph, here for a filled sample drawn to 2:1 at a speed of 100mm/min. It is seen that for this sample, the CNF signature does not stretch evenly around the whole of the ring, indicating preferential fibre orientation along the draw direction (which is vertical in this picture). A complication to the orientation measurements is that SEM pictures of the CNF shows occasional pieces of graphite spheres and other carbon residues, which will give the same contribution to the reflection independent of the process, and will therefore form an isotropic background.

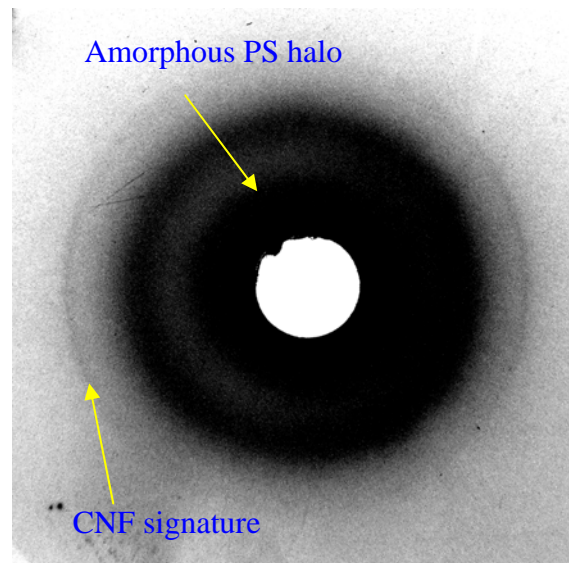


Figure 6: WAXS photograph for CNF/PS drawn to 2:1 at 100mm/min

Figure 7 shows how the width of the circumferential arc changes with draw ratio.

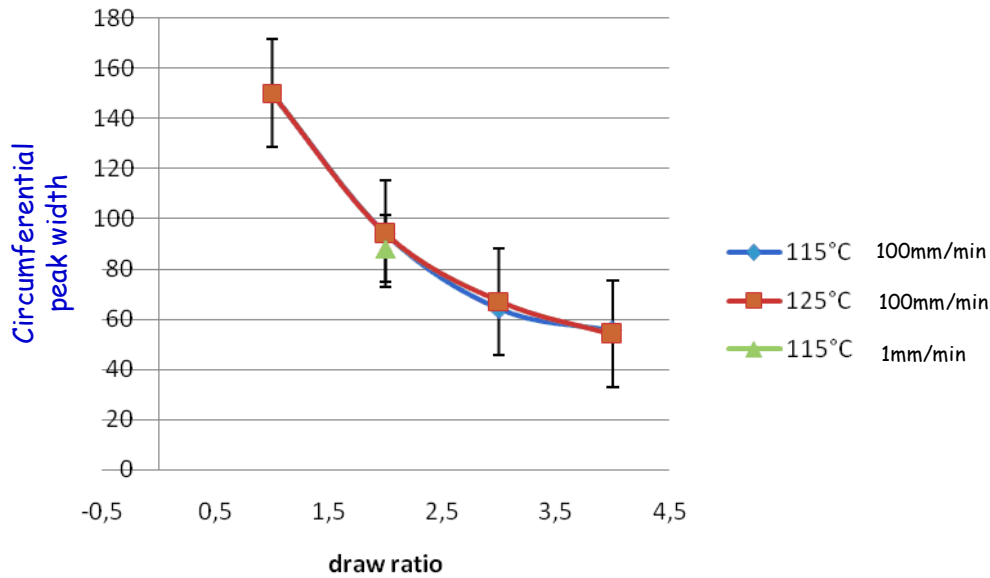


Figure 7: Circumferential arc width ( $2\theta = 26.6^\circ$ ) for different draw ratios.

The results show that the width of the circumferential peak decreases with increasing draw ratio as nanofibres are aligned by stretching. The two samples drawn to 2:1 at different speeds had almost the same peak width. Nanofibre orientation therefore depends on the total strain only (pseudo-affine) whereas molecular orientation (at different length scales) depends on strain rate and testing temperature.

### SEM Studies

In the final part of this study, the microstructure of the samples was examined under an SEM. The surfaces to be examined were produced by freeze fracture after immersing the sample in liquid nitrogen for 5 minutes. Figure 8 shows a fracture surface from an extruded sample

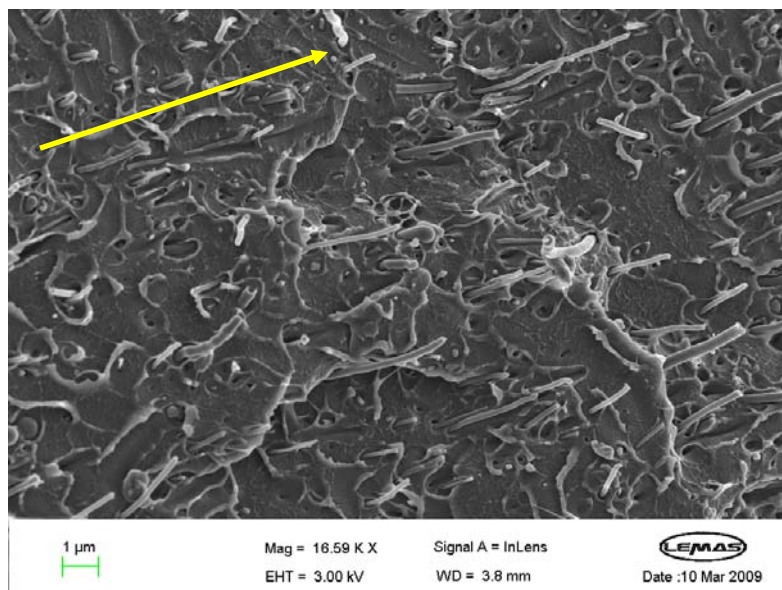


Figure 8: As extruded sample fracture surface: (yellow arrow draw direction).

It is clear from this picture that the extrusion process used to make the samples produced a significant amount of nanofibre orientation, even before drawing takes place (the polymer was annealed to remove any molecular orientation). This is somewhat contradictory to the WAXS results, although the Xray results do create an average orientation across the sample thickness and also includes all the spherical particles and other less refined carbon structures. It is clear the nanofibres are also not straight, which will also affect the WAXS results, and will appear to show the fibres as misoriented.

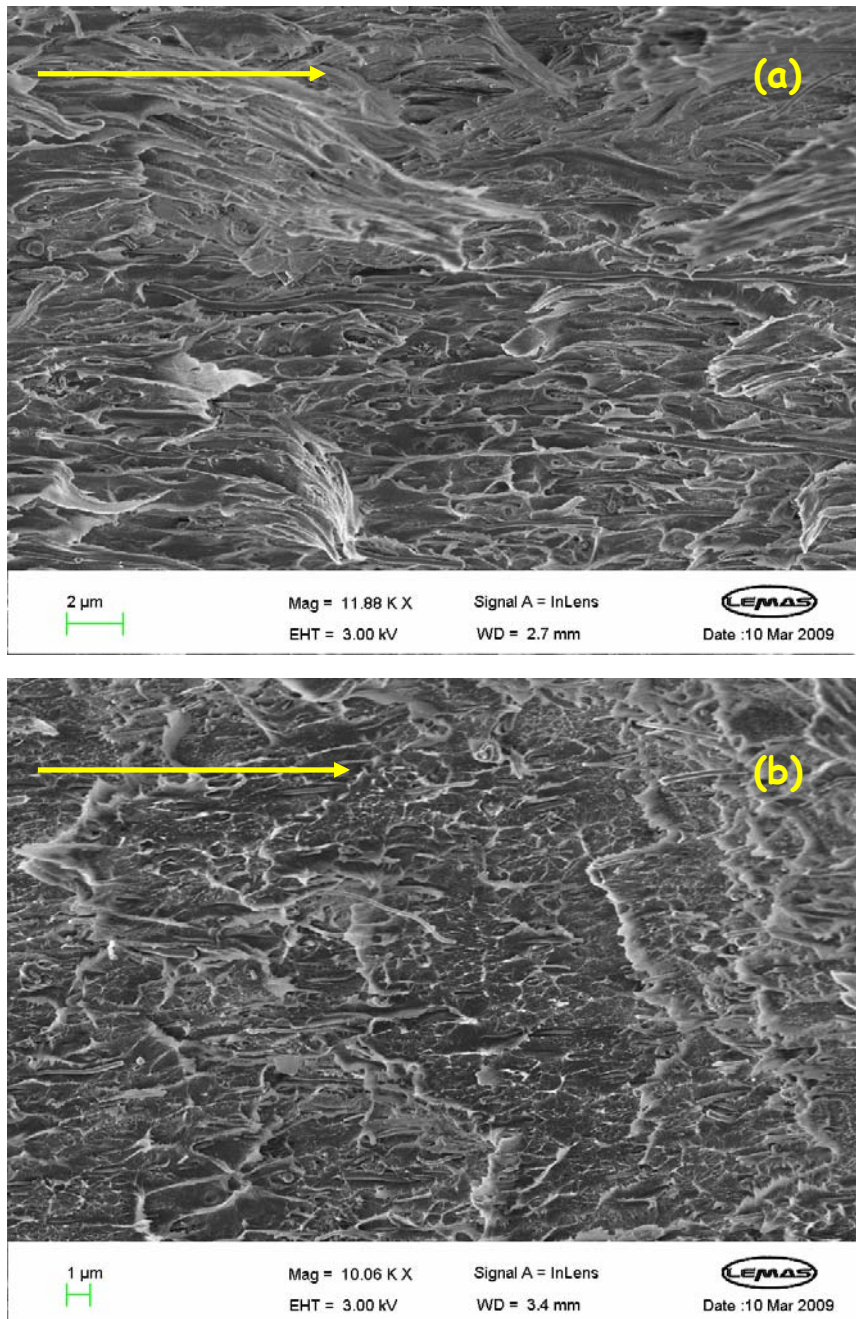


Figure 9: Fracture surfaces of 2:1 drawn samples: a) drawn at 100mm/min b) drawn at 1mm/min



Figure 9 shows the samples drawn to 2:1 at the two different speeds. The surfaces clearly reflect the different level of orientation in the polystyrene matrix phase.

The faster drawn sample shows a much more anisotropic fracture surface aligned to the draw direction and linked to the underlying molecular orientation. The fibres in the 2:1 samples drawn at the faster speed are less visible as the fracture surface is dominated by the matrix. This is even more the case with the higher drawn samples. Figure 10 shows a fracture surface from the 4:1 sample, drawn at 100mm/min, and the fibres are more or less invisible due to the highly anisotropic nature of the fracture of the polystyrene. As seen previously, they still contribute significantly to the deformation behaviour (Figure 4.

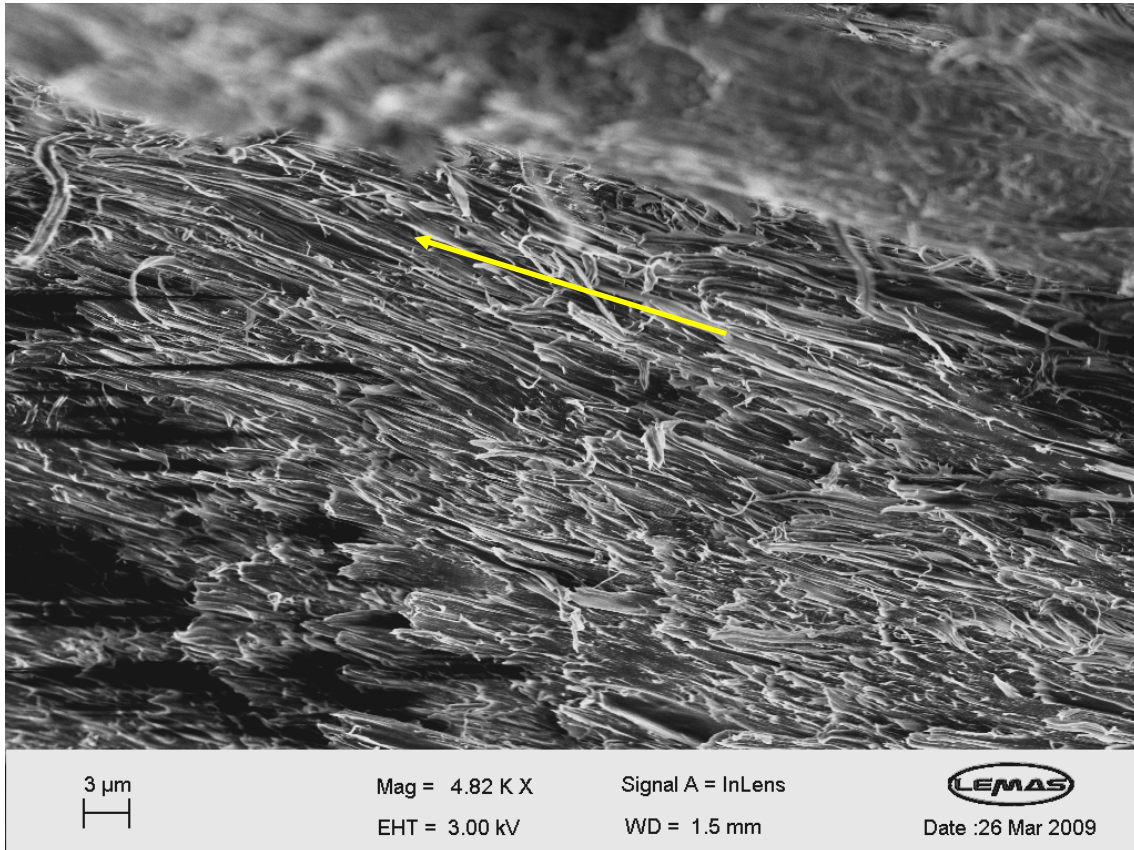


Figure 10: Fracture surface from 4:1 sample, drawn at 100mm/min

## CONCLUSIONS

In this study we have investigated how the deformation behaviour of a polystyrene/carbon nanotube (CNF) nanocomposite depends on the properties and orientation of the nanofibres and the polymer molecules. The deformation behaviour of the pure polystyrene samples showed increased strain hardening which depended on draw ratio. The strain hardening gradient increased with true strain as expected for the deformation of a molecular network. Incorporation of the nanofibres gave a more linear deformation behaviour. The strain hardening rate was seen to decrease at large strain, and large draw ratios, which is expected to be due to matrix/particle debonding. WAXS

measurements showed that nanofibre orientation was increased by drawing, although the fibre orientation was also affected by the original extrusion process. Drawing at a slower speed allowed short range molecular orientation to relax during the drawing process. This was found to significantly affect the subsequent deformation behaviour. WAXS measurements showed that the nanofibre orientation was unaffected by the testing speed.

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