ELSEVIER

The incorporation of carbon nanofibres to enhance the properties of self reinforced, single polymer composites

Peter Hine*, Vivien Broome, Ian Ward*

Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, Leeds, LS2 9JT, UK

Abstract

This paper describes the incorporation of carbon nanofibres (CNF) into polypropylene (PP) single polymer composites, materials where both the reinforcing phase and the matrix phase are PP. The CNF/PP composites were produced from an assembly of highly oriented tapes. The process of making the composites involves heating the tapes to a critical temperature such that a small fraction of the surface of each tape is melted; on cooling this recrystallises to form the matrix of the composite. The production of the composites required optimisation of three stages; incorporation of CNF into PP tapes, orientation of CNF/PP tapes by tensile drawing and hot compaction of the tapes. Results are presented to describe the research and findings in each of these key stages.

Preliminary studies showed that the introduction of small amounts of carbon nanofibres (CNF) significantly improved the properties of isotropic PP. For example, 5% volume addition of CNF gave a 60% increase in the room temperature Young's modulus and a reduction of 35% in the thermal expansion coefficient. Moreover, the percentage enhancement of properties was greater at high temperatures where the stiffness of the PP is much reduced. These results can be very well understood in terms of conventional composite modelling.

In unidirectional CNF/PP hot compacted composites the major improvements in mechanical behaviour are in the direction transverse to the orientation direction, where the CNF can make a proportionately greater contribution to the properties, and as shown by dynamic mechanical behaviour, this is most marked at high temperatures. Composite modelling based on uniform strain with appropriate allowance for the CNF aspect ratio predicts the behaviour extremely well. A very interesting result is that the peel strength of composites produced by hot compaction of woven CNF/PP shows a four-fold increase over woven PP composites and this is increased by another factor of two by the addition of a maleic anhydride compatibiliser. A further interesting result, of some practical significance, is that although the incorporation of CNF into PP causes voiding and some loss of molecular orientation during drawing, the hot compaction process closes and seals the voids, so that the original PP density is recovered.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Carbon nanofibres; Polymer composites; Hot compaction

1. Introduction

Recent research within the IRC in Polymer Science and Technology at Leeds University has established the methodology for converting highly oriented fibres and tapes into single polymer composites by a novel process termed hot compaction [1–5]. The major difference, in comparison with the methods used for producing conventional fibre composites, is that the process utilises only one starting component, a highly oriented polymer fibre or tape,

and relies on choosing suitable conditions of temperature and pressure such that a small proportion of the surface of the oriented phase is melted, which on cooling, recrystallises to form the matrix phase. The strategy is to melt sufficient material to form a matrix phase, while retaining a significant fraction of the original oriented phase. It has been shown that the precise optimum percentage of the melted phase depends on the style of reinforcement, i.e. unidirectional or woven fibres, but 25% appears to be close to optimal. Materials produced using the hot compaction process have the key advantage of molecular continuity between the oriented and the melted and recrystallised matrix phase, resulting in an excellent bond between the two components and negating any problems of compatibility. Furthermore, as the melted phase is produced on the skin of each oriented polymeric element, the matrix phase surrounds each

---

* Corresponding authors. Tel.: +44 113 2333827.
E-mail addresses: p.j.hine@leeds.ac.uk (P. Hine), i.m.ward@leeds.ac.uk (I. Ward).

component so there are no wetting issues as might be present in, for example, film stacking techniques.

Hot compacted polypropylene sheets are now being manufactured in a continuous process by Propex Fabrics Gmbh (formerly BP Amoco Fabrics) in Gronau Germany under the trade name Curv®. The first commercial products exploit the combination of lightweight, good mechanical properties and outstanding impact strength that these materials display: examples include soccer shin guards, automotive protective undertrays and luggage. Although the properties for these applications are satisfactory, other applications have been identified, which require improved properties, particularly at elevated temperatures. In the automotive sector, these include exterior body panels and engine covers. Particle reinforcement of the oriented polymer component is an obvious next step to obtain improved properties, but the size of the oriented elements (usually a few microns in cross section) requires a small sized particle: nanofibres are an ideal candidate for this role. Such an approach has the potential to deliver the target of improved hot compacted sheet performance at a relatively modest weight fraction of the nano-filler, which is desirable both for economic reasons and to retain ductility of the oriented tapes, and hence impact performance and formability, which are key attributes of hot compacted sheets.

The use of nanometre sized particles to reinforce a polymer, most often Nylon or PP, has been extensively reported in the literature. The most widely reported inorganic filler is clay, usually montmorillonite. While the addition of this material has shown significant improvements in the properties of Nylon (for a review of this work see Ref. [6]), due the production of a well-exfoliated clay microstructure, the improvements in properties in non-polar polymers such as polypropylene and polyethylene have been less dramatic, although extensively reported (e.g. Refs. [7–10]). Another potential nano-filler, which has been widely used, is carbon fibre, as there is a range of forms available, some in commercial quantities. In particular, vapour grown carbon fibres have been reported as giving significant increases in the properties of polypropylene (these fibres are often referred to in the literature as carbon nanofibres [CNF]) and are available in 100 g quantities and at a competitive price. One particular CNF, which has been extensively researched, is the vapour grown carbon fibre made by Pyrograf Products Incorporated. A recent paper published by Kumar et al. [11] showed that CNF reinforced polypropylene could be made using conventional melt spinning equipment. These fibres showed a 50 and 100% improvement in modulus and compressive strength, respectively, over unreinforced PP. Although these results are very interesting, the authors showed that the nanofibres were not particularly well aligned, suggesting further improvements could be achieved if higher degrees of alignment of the nano-particles could be achieved. Similar experiments had been conducted previously by one of the authors of this paper [12] and showed comparable improvements for 5% w/w (CNF) reinforced PP fibres.

The production of a hot compacted CNF reinforced polypropylene sheet requires a number of stages, each of

which must be optimised: these include blending the CNF with polypropylene, solid phase drawing to produce CNF reinforced oriented PP tapes and finally the hot compaction process itself. In this paper we will describe the research and findings in each of these key areas, the aim being to bring together the two emerging technologies of hot compaction and nanotechnology to produce a CNF reinforced single polymer polypropylene composite with enhanced properties.

2. Experimental

2.1. Blending CNF with polypropylene

Vapour grown carbon fibres were obtained from Pyrograf Products Incorporated. The grade chosen was one that has already been used by other researchers, Pyrograf III PR19 PS (pyrolytically stripped). The CNF is produced by decomposing hydrocarbons over a metal catalyst to nucleate and grow the carbon fibres. The result of this process is a mass of entangled fibres, as shown in Fig. 1 by the scanning electron microscope (SEM) picture of the as received powder. At a higher magnification (Fig. 2(a)) it is seen that the fibres can nucleate in a number of forms: straight sided fibres are predominant, but the so called 'bamboo' structures are also in evidence: at an even higher magnification (Fig. 2(b)), it can be seen that the fibres are tubular in structure. A major challenge was, therefore, to be able to separate the entangled assembly shown in Fig. 1, without drastically reducing the fibre length, and hence reinforcing efficiency. The polypropylene used in all this work was a homopolymer with a weight average molecular weight, M_w, of 360,000 and a density of 910 kg/m^3.

Reports in the literature suggest a number of possible blending strategies including high shear mixing [13,14] ball milling the fibre assembly before blending [13] and solvent dispersion [14,15]. Initial trials with solvent dispersion were found to leave parts of the original fibre assembly unentangled, so high shear processing was chosen as the preferred route. Blending trials were carried out using a Prism Eurolab 16 twin screw extruder, which has a single mixing zone located
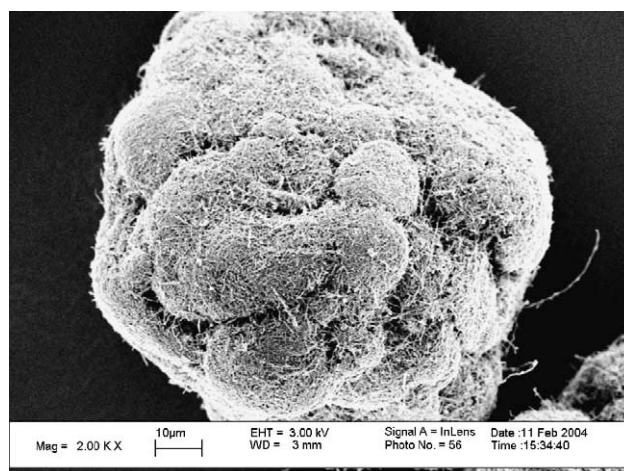

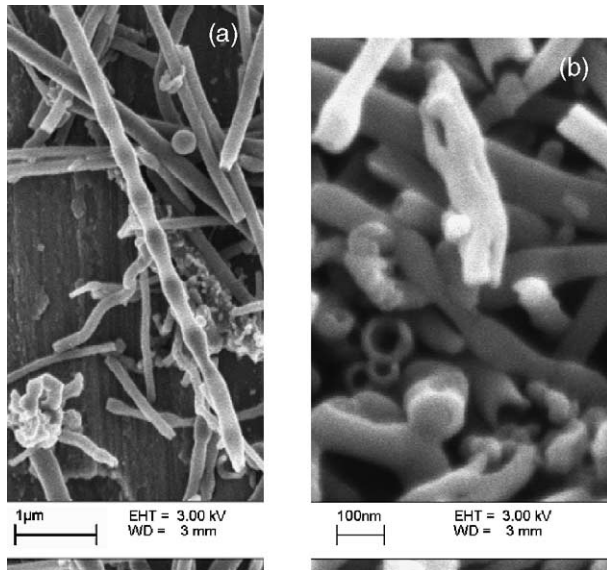Fig. 1. SEM picture of as received CNF powder (PR19-PS).

Fig. 2. Details of CNF powder showing (a) bamboo and fibre structures: (b) tubular structure.

170 mm along the 250 mm screws: batches were made with 2, 4, 6, 10 and 20 wt% of the CNF. The melt zone of the extruder was set to 230 °C and the extruder die at 190 °C. The initial trials (2, 4, 6 and 10%) showed that only 2% by weight of powder could be successfully mixed in a single extrusion, requiring the higher weight percentage additions to pass through the extruder a number of times. After adding in the required amount of CNF, the mixture was then sent through the extruder another two times until visually well mixed (subsequently confirmed by SEM pictures), that is two more passes of the mixing section. The number of passes through the mixing zone for each composite was therefore, 3, 4, 5, and 7 times for the 2, 4, 6, and 10 wt% PP/CNF nanocomposites (Table 1). The 20% blend was made in collaboration with the manufacturers of the extruder, using 650 mm long screws with three mixing zones along their length. For this extruder the CNF could be added in a single pass and was added in front of the final mixing zone. As with the shorter extruder, the mixture was then passed through the extruder for a second time to give improved mixing: this mixture therefore, experienced four mixing zones (Table 1).

For one of the mixtures, 6% by weight of CNF, the fibre assembly was examined after blending by burning the PP matrix off in a furnace for 2 h at 450 °C [14]. SEM analysis of the fibre residue (Fig. 3) showed the fibre assembly to be very well dispersed. Measurement of ∼100 fibres in the SEM showed an average fibre length of 2.53 ± 1.5 μm, which using a

Table 1
Details of the mixing schedules used for each PP/CNF nanocomposite

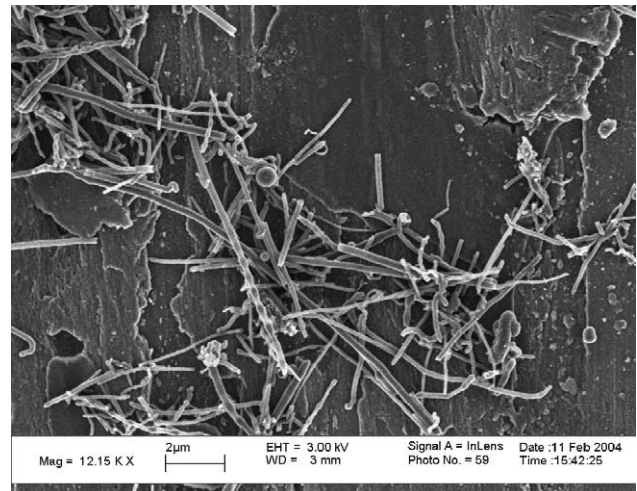| Percent weight addition	Number of mixing stages
2	3
4	4
6	5
10	7
20	4

Fig. 3. CNF assembly after blending and PP burn off (6% w/w sample).

measured average fibre diameter of 152 nm, gave an average fibre aspect ratio of 17. It is clear that high shear blending is successful in breaking up the initial fibre assembly and giving good dispersion, but leads to significant fibre attrition: if the manufacturer's specified length of 50–100 μm in the original assemblies is correct then this is a very significant reduction. This is a key issue noted by other workers in this field. In their excellent review article on carbon nanotubes polymer composites, Andrews and Weisenberger [16] note that the energy input to disperse CNF tends to break them up into short segments [17]. An SEM picture was also taken of a freeze fractured pellet, and this is shown in Fig. 4. Although this picture only shows one area, it was representative and reflects that the CNF are well dispersed and also have been flow aligned during the extrusion process.

As the CNF/PP material represents the matrix of the resulting hot compacted composite, it is important to investigate the effect of the CNF on the PP properties, before proceeding to the tensile drawing process. Stress–strain
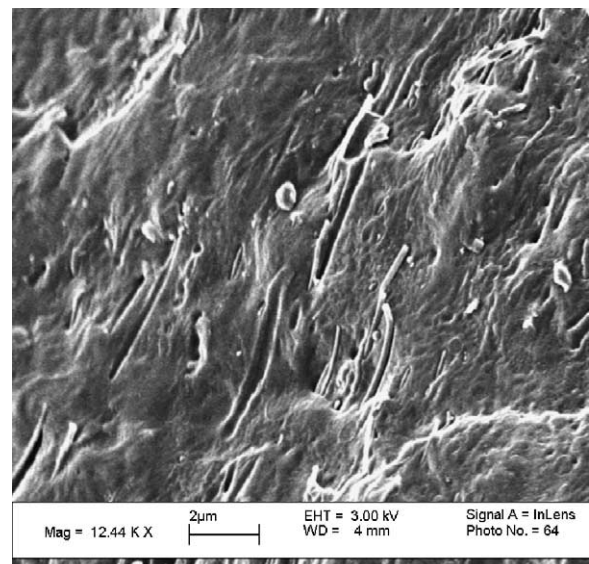

Fig. 4. Freeze fracture surface of blended CNF/PP pellet.

measurements (following ASTM D638) were made on dumb-bell shaped specimens (4 mm wide and a parallel gauge length of 20 mm) cut from compression moulded sheets of the CNF/PP. Tests were carried out at 20 °C and 50%RH, at a nominal strain rate of 10^{-3} s^{-1}. Sample strain was measured using a Messphysik video extensometer.

Any effect of the nanoparticles on the morphology and melting behaviour of the polypropylene was assessed using differential scanning calorimetry (DSC). Tests were carried out using a Perkin–Elmer DSC-7 using a scanning rate of 10 °C/min.

To assess the effect of the CNF on high temperature performance, dynamic mechanical temperature (DMTA) scans (tension mode, frequency 1 Hz, dynamic strain 0.02%) were carried out on samples of PP and 10% w/w CNF/PP.

Compatibility between the nano-particles and the polypropylene is another crucial aspect of this research area. Two different methods were assessed for improving the CNF/PP adhesion: first, we carried out oxygen plasma treatment of the carbon nanofibres, but this was found to have no beneficial effect. Another common technique for improving fibre/matrix compatibility is to introduce a species which will provide a chemical bond between the two phases: the most commonly used species for modifying polypropylene is maleic anhydride [18,19]. Blends were produced using 2% of a maleic anhydride modified polypropylene (Exxelor PO 1015) in the 10% w/w CNF/PP composite.

2.2. Solid state drawing of nanocomposites

Ultimately, continuously drawn oriented PP tapes are required for the hot compaction experiments. To establish the best conditions for drawing, small-scale batch experiments were first carried out using an Instron tensile testing machine and a temperature controlled oven. Dumbbell shaped samples (using the same size as described in Section 2.1) were cut from the compression moulded sheets and drawn at temperatures between 120 and 170 °C at a crosshead speed of 100 mm/min. Tensile tests were then carried out on these drawn samples to establish the optimum draw temperature, which was found to be 140 °C.

Continuous drawing was then carried out using an in-house draw frame and a hot air oven: it was found that the optimum oven temperature had to be increased by 30 °C due to the increased draw speed in the continuous tests, which was of the order of 5 m/min. Continuous drawing required continuous isotropic spun tape, and this was made using a single screw extruder. The four zones along the extruder barrel were set to 175, 200, 215 and 225 °C, and the extruder die (20 mm× 0.25 mm) was set at 235 °C. After the die the tape was extruded onto a hot roller set at 100 °C. Density measurements confirmed no voiding in samples (unfilled and filled) made in this way.

2.3. Preparation of hot compacted samples from drawn tapes

Hot compacted samples were produced from both unidirectionally arranged tapes and from woven tapes, using similar procedures to those described in previously published work [3].

The unidirectional samples ($\sim$55 mm square and 0.5 mm thick) were made by winding the tapes around a metal picture frame, which was then placed under pressure in a hot press and taken to the compaction temperature for a set dwell time (5 min) before fast cooling. A compaction pressure of 700 psi (4.9 MPa) was used throughout.

As will be seen from the subsequent results, unidirectionally arranged tapes produce a hot compacted sheet with very anisotropic properties, which is very informative for interpreting the hot compaction behaviour. A sheet with more balanced properties can be achieved using cloth woven from oriented tapes: this is the arrangement used for the commercial hot compacted PP sheet. Consequently, continuous oriented tapes made from a small number of chosen systems were woven on a hand loom to produce enough woven cloth to make a compacted sample ($\sim$55 mm square and 0.5 mm thick). The compaction experiments on the woven cloth used the optimum temperature ascertained from the unidirectional studies, together with the same compaction pressure and dwell time.

For both the compacted unidirectional samples, and the compacted woven samples, the same range of mechanical tests, as described above in Section 2.1 for the isotropic sheets (stress–strain, DSC and DMTA), was then carried out.

3. Results

3.1. Isotropic CNF filled PP (the matrix phase of the subsequent composite)

Fig. 5 shows typical stress strain curves for a 10 wt% CNF/PP sample, in comparison with a PP sample. It is seen that, as expected, there is a significant increase in modulus and yield stress with incorporation of the carbon nanofibres, accompanied by a fall in the strain at maximum stress. Importantly, the 10% w/w sample is still ductile, which is critical as it is this material which will form the matrix of the resulting hot compacted sheet and previous studies have shown that matrix ductility is crucially important for getting the optimum properties in the final composite. Mechanical tests were carried out on all the CNF/PP composites, and Fig. 6
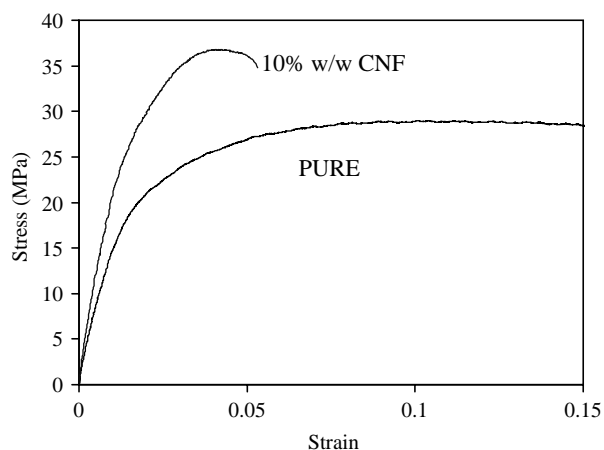
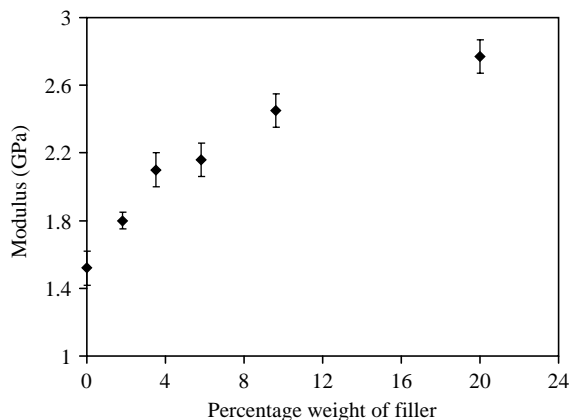Fig. 5. Typical stress–strain curves for pure PP and PP + 10% w/w CNF.

Fig. 6. Young's modulus of samples versus weight percentage of filler.

Table 2
Fibre and matrix properties required for modelling

Carbon nanofibres	E_{11}	240	Manufacturer
	E_{22}	14	Literature/estimated
	ν_{21}	0.26	Literature/estimated
	ν_{23}	0.38	Literature/estimated
	G_{12}	17.5	Literature/estimated
	α_1	−0.4	Literature/estimated
	α_2	26	Literature/estimated
Polypropylene	E	1.52	Measured
	ν	0.3	Measured
	α	109	Measured
Fibre aspect ratio		17	Measured from 6% w/w sample

E and G in GPa, $\alpha \times 10^{-6}\,K^{-1}$.

shows the relationship between the measured Young's modulus and the filler weight percentage. It can be seen that the modulus does not increase linearly with filler percentage, but shows a decreasing benefit at higher filler additions.

The low strain, elastic, behaviour of the CNF/PP composites can be understood using standard composite modelling, as shown recently for nanoparticulate filled polymers by other workers (for exampleRef. [20,21]). Following our previous collaborative research with ETH Zurich [22,23], the chosen modelling strategy is one of two stages: first, predict the properties of a fully aligned short fibre composite unit using the treatment of Qui and Weng [24] and then to regard the actual composite as a partially aligned aggregate of these units [25, 26] assuming uniform strain. Determining values for the elastic constants of the CNF is a key issue about which there has been considerable discussion in the literature for the different forms of carbon nanotubes that are available (CNF, and multi and single walled nanotubes). It is opportune that the longitudinal modulus of the fibre used in this work (Pyrograf III CNF) has been measured directly by Tibbets [27]. The value quoted, and as also reported in Ref. [13,14], is 240 GPa. Assuming this value for the longitudinal Young's modulus (E_{11}) of the CNF, the other elastic constants were estimated following the ideas of Smith [28], who has shown that there is a relationship between the axial Young's modulus and the other four fibre elastic constants for solid carbon fibres. The elastic constants of the polypropylene were determined by direct measurement on dumbbell samples (for dimensions see Section 2.1 above) cut from a compression moulded sheet. A summary of the fibre and matrix properties used in the model calculations are given in Table 2.

As described above, the fibre aspect ratio was only determined for the 6 wt% blend, so this value was used in the theoretical calculations. From the SEM results, the orientation of the nanofibres (and hence the units of structure) was taken to be random-in-the-plane of the compression moulded sheet (i.e. 2D random).

Fig. 7 shows a comparison between the measured Young's moduli of the isotropic PP/CNF composites and those predicted by the model. It is to be noted that for the sample at which the fibre aspect ratio was actually measured, 6 wt%, the agreement

between the measurement and the model is excellent. However, for samples with a lower percentage of fibres, the measured values fall above the prediction while for weight percentages greater than this the predictions are lower, substantially so for the 20 wt% sample. It can be surmised that for the lower percentage samples, which spent less time in the extruder, the fibre attrition could be less and hence the modulus would be higher. For the higher weight percentage the lower values could be due either to higher fibre attrition, or perhaps more likely to aggregation of fibres into bundles (i.e. poor dispersion).

The thermal expansion behaviour of the isotropic CNF/PP composites was also measured using an in-house developed dilatometer. Measurements were made of the changes in length between +15 and +25 °C, to provide an average value for a room temperature of +20 °C. In Fig. 8, the measurements are compared with model predictions following a similar approach to that described above for the mechanical behaviour. For the model predictions, the carbon fibre values were taken from a previous study for a solid carbon fibre with a similar axial modulus [29]: the values are shown in Table 2. It is interesting to note that the thermal expansion behaviour mirrors exactly that for the Young's modulus, with the predictions for the 6 wt% composite being in excellent agreement with the measurements and similar discrepancies for the other
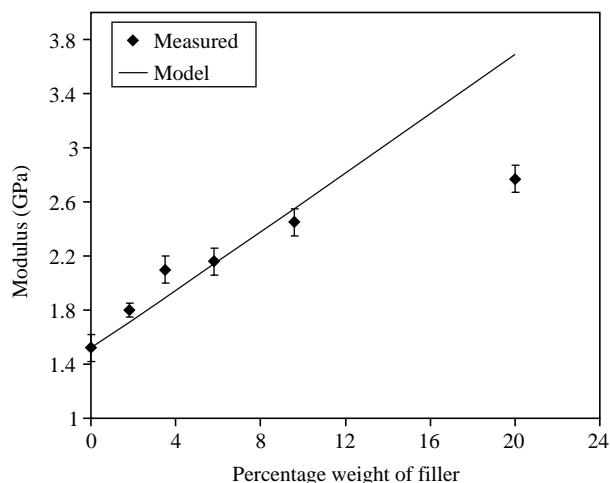

Fig. 7. A comparison between measurements and model predictions for Young's modulus.
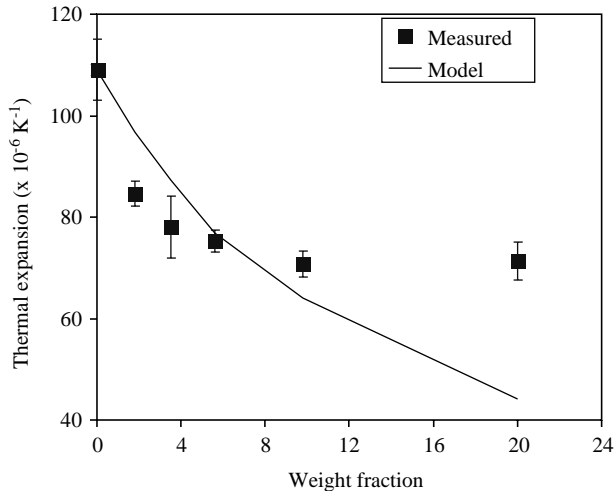
Fig. 8. A comparison between measurements and model predictions for thermal expansion.

Fig. 10. Onset of crystallisation temperature versus filler weight percentage.

materials. For thermal expansion, the measured values for the lower weight percentages are lower than predicted and the higher weight percentages are higher supporting the proposals above regarding the structure of these samples.

The effects of the nanofibres on the morphology and melting behaviour of the composites were examined using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Fig. 9 shows details of the typical polypropylene morphology seen around a CNF in a freeze fractured sample. This SEM picture shows clear evidence for a transcrystalline layer (preferential row crystallisation) around the fibre, suggesting that the fibres are acting as nucleation sites for crystallisation. Crystallisation exotherms measured by DSC for a range of PP and filled PP sample showed that the CNF's act to initiate crystallisation at over 10° higher compared to the PP. It was also found that the higher the amount of CNF, the higher the onset of the crystallisation temperature, as shown by the results in Fig. 10.

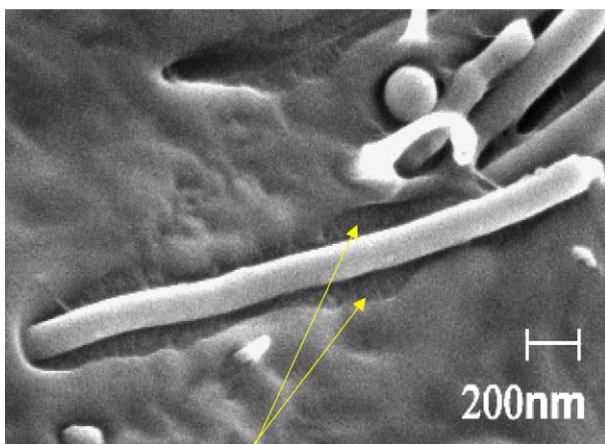The last set of experiments to be carried out on the isotropic sheets were DMTA temperature scans (tension mode at a frequency of 1 Hz). Fig. 11 shows the measured dynamic modulus versus temperature for PP and the 10% w/w CNF/PP composite. These results show that in addition to an improvement in the room temperature modulus, already shown above in Fig. 5, the stiffness of the filled PP sample is greater than that of the PP up to a temperature of 130 °C. As expected, at the higher temperatures the percentage reinforcement effect was much greater than at room temperature.

The same modelling procedure as described above can be used to model the DMTA results over the measured temperature range. Because the average fibre aspect ratio for the 10% w/w composite has not been measured experimentally, for the theoretical calculations the fibre aspect ratio was varied until good agreement with the experimental data at 25 °C was achieved. This aspect ratio (13) was then used to predict the composite modulus at all other temperatures. The fact that this value is lower than that measured experimentally for the 6% w/w CNF/PP composite (17) reinforces the earlier discussion of the results in Figs. 7 and 8. It can be seen from Fig. 11 that the predicted temperature dependence of the CNF/PP composite modulus (black squares), based on the measured properties of the PP matrix, agrees very well with that measured experimentally.
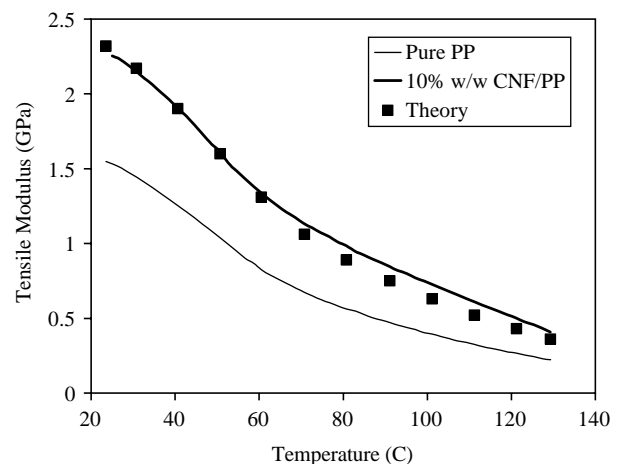

Fig. 9. Details of PP transcrystalline layer around CNF.

Fig. 11. DMTA temperature scans for pure PP and 10% w/w CNF/PP.

3.2. Production and properties of oriented CNF/PP tapes (the reinforcement phase of the subsequent composite)

The next stage in the process was to establish conditions for solid state drawing of the CNF/PP material. Batch tests were first carried out in a temperature controlled Instron oven between temperatures of 120 and 170 °C: subsequent measurements of these samples suggested that the optimum temperature was ∼140 °C. The optimum temperature is considered as that at which the maximum modulus of the drawn sample is achieved for a particular strain rate. At a lower temperature than this there is insufficient thermal energy for molecular re-organisation, while at a higher temperature relaxation of the oriented molecules can occur during the deformation process. Density measurements (using a density column made from a mixture of diethylene glycol and isopropanol) on the drawn tapes showed that the CNF filled PP samples voided on solid state drawing and that the level of voiding increased with both the percentage of filler and stretch ratio. An SEM picture of a freeze fractured sample of a filled and drawn tape (Fig. 12), indicated that the reason was that most of the CNF's were associated with a local void. It is clear that during the solid phase drawing process, the interface between the hard particle and the softer surrounding matrix is a potential weak point in the actual structure. This SEM picture also shows that the drawing process has caused preferential alignment of the carbon nanofibres (the longitudinal axis of the drawn tape is indicated by the arrow on this picture). Attempts were made to measure the development of the orientation of the carbon nanofibres with drawing using wide angle X-ray scattering techniques, but unfortunately the carbon reflection was superimposed on a much stronger one due to polypropylene. Future work will hope to address this important issue.

The batch tests were useful for characterising the drawing behaviour of the filled tapes, but the manufacture of a hot compacted sample requires quantities of continuous material, hence continuously drawn tape. The next set of experiments was therefore, carried out using a continuous drawing frame, drawing spun polypropylene tape through a hot air oven.
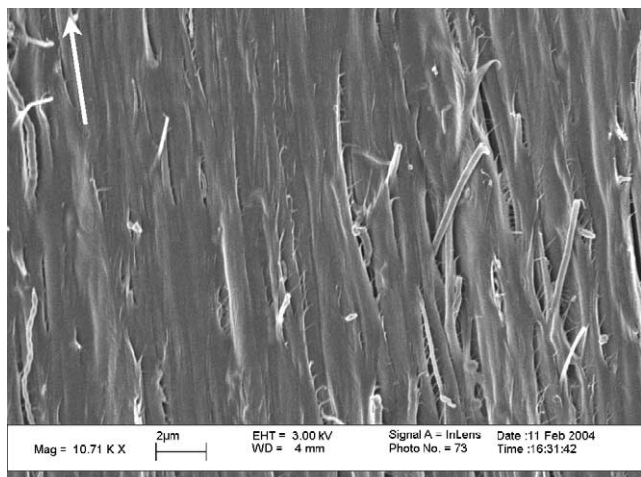

Fig. 12. SEM picture of freeze fractured drawn tape.

Stress–strain measurements on these continuously drawn samples showed that, in contrast to the slowly drawn batch tapes, the fast drawn CNF filled PP had lower properties at a similar draw ratio (10:1). To obtain similar properties to the PP tape, the draw ratio had to be increased to around 11:1 for the filled PP. We can speculate that the debonding and voiding that occurs at the particle/polymer boundary, has the effect of reducing the stress transferred to the matrix phase, and hence reduces the level of matrix orientation, and that this depends on the rate of stretching. We have seen this effect before in the melt processing of other particulate filled materials [30], in that at a similar draw ratio, the matrix orientation in the filled material is lower than that in the unfilled polymer.

Solid state drawing tests were also carried out on the composite, which contained the maleic anhydride modified PP. It was found that the drawn modified tapes had very similar properties to the unmodified ones, in terms of a similar Young's modulus and void content.

3.3. Production and properties of hot compacted samples of CNF/PP

3.3.1. Unidirectionally arranged tapes

For the hot compaction experiments, the decision was taken to focus on only three systems: PP drawn 10:1: 10% w/w CNF/PP drawn 11:1: 10% w/w CNF/(PP+2% maleic anhydride compatibiliser) drawn 11:1. Unidirectionally arranged tapes were compacted as described in Section 2.3. First, samples were made from the PP tapes at compaction temperatures between 185 and 195 °C and DSC experiments were used to assess the optimum compaction temperature. A compacted sample generally shows two peaks when a DSC scan is performed: an upper peak, associated with the original oriented component, and a lower peak associated with the fraction of melted and recrystallised material produced. As the compaction temperature is increased in the optimum range, the lower temperature peak increases in size as the upper peak decreases is size: a proportion of 25% of the lower (matrix phase) peak is considered optimum. In the experiments here, the optimum compaction temperature, for unidirectionally arranged PP tapes, was found to be 189 °C, although a reasonably wide temperature window was found (187–191 °C) where the properties of the compacted sheet did not change markedly. A similar temperature was used for the other two drawn materials.

Density measurements on hot compacted samples showed a recovery of density to that of the original materials before the solid phase drawing where voiding was found to occur. This suggests that the hot compaction process is able to heal, or seal, any voids generated around the tapes during the drawing procedure.

Stress–strain tests were carried out on the unidirectionally arranged samples for the three materials (PP, 10%CNF/PP, and 10%CNF+PP+2%compatibiliser) both parallel (longitudinal) and perpendicular to the original tapes (transverse). The longitudinal stress–strain results were very similar for the three materials, with a failure stress of 240 MPa and an initial

modulus of 7 GPa. The percentage increase in the Young's modulus with the addition of the CNF was found to be much lower than that seen in the isotropic PP samples (Fig. 5). This is to be expected because the preferred molecular orientation produced during solid-phase drawing dominates the properties in this direction. However, the transverse results, particularly the sample with the compatibiliser, showed a 60% increase in stress.

Even more significant were the DMTA temperature scan results, shown in Figs. 13 and 14. The longitudinal results (Fig. 13) confirmed that at room temperature the small strain Young's modulus for filled and unfilled materials was again very similar (as already described above) but the separation between the samples increased with increasing temperature: that is the modulus of the carbon nanofibre filled sample did not fall as quickly as for the unfilled PP sample. For the transverse samples the advantage of incorporation of CNF is much greater, because the oriented tapes contribute much less to the overall stiffness than in the longitudinal direction. The results (Fig. 14) show a very much lower fall in modulus with temperature for the CNF/PP composite compared with the unfilled PP.

3.3.2. Woven tapes

For commercial applications, the arrangement of the oriented elements is usually a woven cloth, because this produces balanced properties in the final hot compacted composite. Consequently, continuous oriented tapes made from the three chosen materials were woven on a hand loom to produce enough woven cloth to make a compacted sample: a range of mechanical tests was then carried out on these samples. In-plane tensile stress strain measurements from the three materials were very similar, because these are determined primarily by the mechanical behaviour of the oriented tapes. This is, of course, the philosophy of the hot compaction process, in producing an all polymer sheet with improved properties due to the presence of molecular orientation. On the other hand, it is expected that the CNF would enhance those properties, which depend mainly on the melted
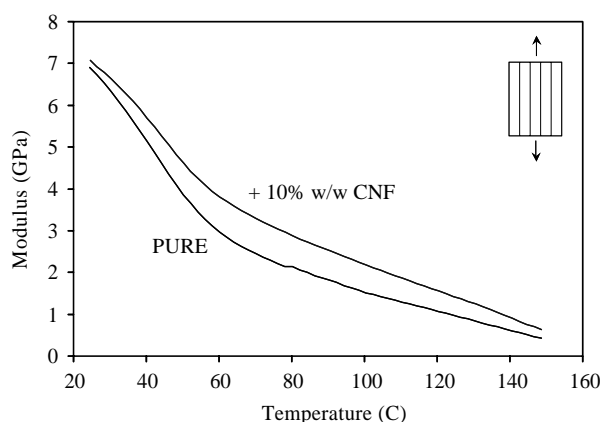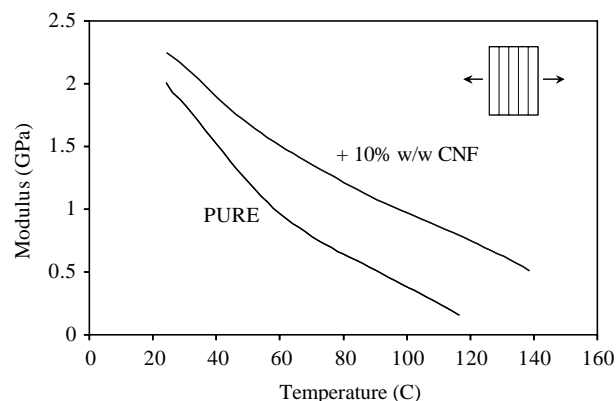

Fig. 14. DMTA temperature scans of unidirectionally compacted samples—tested parallel to tapes.

and recrystallised 'matrix' material, where there is no preferred molecular orientation.

A key experiment, and one that could not be carried out on the unidirectional samples, was the measurement of the interlayer peel strength. It is perceived that the weak point of a hot compacted woven sheet is the interlayer region, because what binds the layers together is only a thin layer (usually a few microns) of the melted and recrystallised matrix material. To measure the strength of this layer, we have previously used a T peel test. During compaction, a thin layer of aluminium foil is placed at one end of the sheet between the central two layers of cloth. After compaction, this aluminium layer acts a starter crack located in the interlayer, and allows a peel fracture to be generated.

Table 3 shows the measured peel load (for a 10 mm wide sample) for the three types of compacted sheet (all compacted at 187 °C). The results show two key aspects: first that the CNF/PP material had a significantly higher peel load compared to the unfilled PP sample, and secondly that the compatibilised blend had an even higher value (nearly an order of magnitude greater than the unfilled PP sample). This result is consistent with a number of other recently reported papers (e.g. Ref. [31]), which describe the beneficial effects of CNF in producing enhanced composite toughness. SEM pictures of peel fracture surfaces for the polypropylene sample showed widespread, large scale, ductility on the CNF/PP fracture surfaces. This large increase in interlayer strength with CNF addition could have a number of benefits, including enhanced thermoformability, which is a key step on the road to commercial exploitation of these materials.

Fig. 13. DMTA temperature scans of unidirectionally compacted samples—tested parallel to tapes.

Table 3
Peel fracture loads for compacted woven samples

	PP (draw ratio=10:1)	10% w/w CNF/PP (draw ratio 11:1)	10% w/w CNF/PP (2%maah) (draw ratio=11:1)
Peel load (N/10 mm)	1.38±0.59	5.9±1.6	10.9±2.6

4. Conclusions

It has been shown that the introduction of a small amount of carbon nanofibres (CNF) can lead to improved performance of polypropylene single polymer composites produced by hot compaction of oriented CNF/PP tapes. The changes in Young's modulus, thermal expansion and dynamic mechanical behaviour are well predicted by simple micromechanical composite modelling. As expected, the improvements produced by the CNF fibres are greatest when the oriented PP tapes contribute least to the composite properties e.g. transverse to the draw direction in unidirectional CNF/PP composites and at higher temperatures when the stiffness of the PP falls and the CNF make a greater contribution to the overall composite properties.

An important result is that the peel strength of a CNF/PP woven fabric composite is very significantly increased and where both CNF and maleic anhydride compatibiliser are introduced almost an order of magnitude increase was observed. This result is likely to be very significant with regard to postforming the hot compacted sheets.

It is also of interest that the drawn CNF/PP tapes showed substantial voiding around the fibres, but the hot compaction process closed and sealed the voids so that the composite density increased to its initial value.

References

[1] Hine PJ, Ward IM, Olley RH, Bassett DC. J Mater Sci 1993;28:316.
[2] Hine PJ, Ward IM, Jordan ND, Olley RH, Bassett DC. J Macromol Sci Phys 2001;B40:959.
[3] Hine PJ, Ward IM, Jordan ND, Olley RH, Bassett DC. Polymer 2003;44: 1117.
[4] Hine PJ, Ward IM. J Appl Polym Sci 2004;91:2223.
[5] Ward IM, Hine PJ. Polymer 2004;45:1413.
[6] Schmidt G, Malwitz MM. Curr Opin Colloid Interface Sci 2003;8: 103.
[7] Galgali G, Agarwal S, Lele A. Polymer 2004;45:6059.
[8] Bafna A, Beaucage G, Mirabella F, Mehta S. Polymer 2003;44:1103.
[9] Zhang Q, Wang Y, Fu Q. J Polym Sci, Part B: Polym Phys 2003;41:1.
[10] Okamoto M, Nam PH, Maiti P, Kotaka T, Hasegawa N, Usuki A. Nano Lett 2001;1:295.
[11] Kumar S, Doshi H, Srinivasarao M, Park JO, Schiraldi DA. Polymer 2002;43:1701.
[12] Gordeyev SA, Ferreira JA, Bernardo CA, Ward IM. Mater Lett 2001;51:32.
[13] Tibbetts GG, McHugh JJ. J Mater Res 1999;14:2871.
[14] Kuriger RJ, Alam MK, Anderson DP, Jacobsen RL. Compos Part A-Appl Sci Manuf 2002;33:53.
[15] Kearns JC, Shambaugh RL. J Appl Polym Sci 2002;86:2079.
[16] Andrews R, Weisenberger MC. Curr Opin Solid State Mater Sci 2004;8:31.
[17] Bai JB, Allaoui A. Compos Part A-Appl Sci Manuf 2003;34:689.
[18] Chung MJ, Jang LW, Shim JH, Yoon JS. J Appl Polym Sci 2005;95: 307.
[19] Pavlikova S, Thomann R, Reichert P, Mulhaupt R, Marcincin A, Borsig E. J Appl Polym Sci 2003;89:604.
[20] Wu YP, Jia QX, Yu DS, Zhang LQ. Polym Test 2004;23:903.
[21] Fornes TD, Paul DR. Polymer 2003;44:4993.
[22] Lusti HR, Hine PJ, Gusev AA. Compos Sci Technol 2002;62:1927.
[23] Gusev A, Heggli M, Lusti HR, Hine PJ. Adv Eng Mater 2002;4:931.
[24] Qiu YP, Weng GJ. Int J Eng Sci 1990;28:1121.
[25] Brody H, Ward IM. Polym Eng Sci 1971;11:139.
[26] Camacho CW, Tucker III CL. Polym Compos 1990;11:229.
[27] Tibbetts GG, Beetz CP. J Phys D: Appl Phys 1987;20:292.
[28] Smith RE. J Appl Phys 1972;43:2555.
[29] Price CD, Hine PJ, Whiteside B, Cunha A.C., Ward IM. Compos Sci Technol. Accepted for publication.
[30] Cooke AH. Ph.D. Thesis, Orientation Studies in Short Glass Fibre Composites, Leeds: Physics Department, University of Leeds; 1997.
[31] Ruan SL, Gao P, Yang XG, Yu TX. Polymer 2003;44:5643.