

The effect of diameter on the mechanical properties of amorphous carbon fibres from linear low density polyethylene

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Summary

The mechanical properties of amorphous carbon fibres, derived from linear low density polyethylene strongly depend on the fibre diameter, which may be attributed to the presence of a skin/core structure in these fibres. High strength carbon fibres could thus be prepared by using thin precursor filaments, that are obtained by a melt-spinning process, in which the spinline is stretched at an elevated surrounding temperature. Careful carbonization of these precursors gives carbon fibres with a strength of 2.16 GPa, a modulus of 130 GPa and a high strain at break of 3%.

Introduction

Carbon or graphite fibres offer a combination of high-temperature resistance, chemical inertia and excellent mechanical properties, which makes them suitable for high-performance applications, such as reinforcement of composites, that are used in aircraft structures and rocket engines [1]. Carbon fibres are prepared by heat-treatment of suitable precursor materials, like mesophase pitches [2] and poly-acrylonitril (PAN) [3]. In search of low-cost starting materials, commodity polymers, such as polystyrene [4] and polyethylene [5] have been introduced as carbon fibre precursors.

The present paper is concerned with the production of amorphous carbon fibres from linear low density polyethylene (LLDPE). Precursor fibres are obtained by melt-spinning and subsequent cross-linking with chlorosulfonic acid, in order to provide the required high-temperature dimensional stability, after which the precursor fibre is carbonized at 900°C. Carbon fibres, having a tensile strength of 1.15 GPa, a Young's modulus of 60 GPa and a high elongation at break (3%) have been prepared by Postema et al. by this route [6].

There is a pronounced effect of the diameter of carbon fibres on their mechanical properties, which is usually ascribed to the presence of surface flaws [7] or sheath/core heterogeneities [8]. In the present paper, it will be shown, that a considerable improvement of the tensile properties is achieved, by using precursor fibres with a small diameter. Thin precursor filaments are obtained by melt-spinning, during which an elevated surrounding temperature is applied to the spinning thread, and occasionally additional hot-drawing and annealing of the melt-spun fibres. Isotropic carbon fibres of 13 μm in diameter, having tensile strengths and Young's moduli of 2.16 GPa and 148 GPa respectively, could be produced in this way.

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Experimental

The polyethylene sample used in this study was LLDPE (LL0209AA from BP, comonomer octene), having a melt flow index of 0.9 gr/10min. Melt-spinning was performed using a piston cylinder apparatus in combination with a take-up device, placed 8 to 46 cm below the spinneret. A capillary die (length 16 mm, diameter 0.25 mm, entrance angle 43°), equipped with a set of metal filters (60 mesh, 120 mesh, $25\mu\text{m}$ and 325 mesh respectively) was used for all spinning experiments. Extrusion rates ranging from 0.13 to 1.9 m/min were applied at spinning temperatures between 170°C and 250°C . In some cases, the spinline was heated using a 30 cm long tubular oven, placed directly under the die-exit. Draw-down ratios were determined from fibre diameter and from the extrusion-/take-up speed ratio.

The melt-spun fibres were treated in an unconstrained way with chlorosulfonic acid (Merck, 98%) at room temperature, for different periods of time. After the treatment, the fibres were washed for 30 min with p.a. chloroform and p.a. acetone respectively and subsequently dried at 50°C in vacuo for at least 3 hours.

Carbonization of the stabilized filaments was carried out in a vertical quartz tube, equipped with an electric heating mantle, under a moderate nitrogen flow. The nitrogen flow was dried over CaCl_2 and freed from oxygen over Cu at 450°C before entering the carbonization tube. Fibre stress during carbonization could be varied by applying different weights to the fibre. The fibres were heated from room temperature to a final heat-treatment temperature of 900°C at different heating rates. After the heat-treatment, the fibres were cooled down to room temperature in about two hours. The temperature in the carbonization tube was measured with a PtRh-Pt "Thermokomp" thermocouple.

Tensile properties of all fibres were determined using an Instron 4301 tensile tester, operating at a crosshead speed of 12 mm/min. Sample gauge lengths of 25 mm for precursor fibres, and 10 mm for carbon fibres were employed. Fibre diameters were measured optically, using a Leitz wetzlar MRO-18 microscope. The mass of the fibres was determined on a 6-decimal or a 7-decimal Mettler balance. Scanning electron micrographs were taken with an ISI DS-130 microscope, operating at 40 kV, using gold covered samples.

Results and discussion

Meltspinning

In order to obtain thin precursor fibres, a prerequisite for preparing high strength carbon fibres, the draw-down ratios (λ) achieved in the drawing process need to be maximized. To this end, a number of processing conditions, such as the temperature of the melt, the extrusion rate, as well as the temperature of the spinline, have been varied. In this way, LLDPE filaments of various diameters are obtained and converted to carbon fibres.

The temperature of the melt appeared to be an important factor, which has a pronounced effect on the maximum attainable draw-down ratio in the melt-spinning process. In the temperature range from 170°C to 205°C , the maximum draw-down ratio increases with increasing spinning temperature, to a maximum of $\lambda=37$ at 205°C . The fibre obtained under these conditions has a diameter of $40\mu\text{m}$ and will be referred to as fibre A. When spinning temperatures exceeding 220°C were used, the maximum attainable draw-down ratio dramatically decreased to $\lambda=2$. Probably, the viscosity of the polymer melt becomes too low at these temperatures, resulting in fracture of the

spinning thread when stress is applied. Fracture of the spinline always occurred at the die exit.

The drawability of the spinline may be further increased by increasing the surrounding temperature of the spinning thread [9]. For this purpose, a 30 cm long, tubular oven was placed around the spinline, directly below the die-exit. When the spinning thread was heated to 100°C, the maximum draw-down ratio, at a spinning temperature of 205°C, was increased from $\lambda=37$ to $\lambda=100$, giving a fibre of 25 μm in diameter (referred to as fibre B). The elevated spinline temperature increases the mobility of the polymer chains and delays the crystallization of the stretched network, leading to considerably higher draw-down ratios. A spinline temperature of 100°C appeared to be optimal. At a spinline temperature of 130°C, the extrudate cannot be collected at any considerable take-up speed, analogous to the situation, observed when spinning temperatures in excess of 220°C are used.

In the melt-spinning process, the temperature of melt, as well as the surrounding temperature of the spinning thread, show the most pronounced effect on the drawability of the spinline. The drawability of the spinline seems to be controlled by 'temperature windows', the same way as it is observed in other fibre drawing techniques [10]. Other spinning conditions affect the maximum attainable draw-down ratio to a lesser extent. For example, higher extrusion rates, in combination with higher take-up speeds, tend to stabilize the spinning thread and suppress spinline fracture. Fibre B ($\lambda=100$) was produced at the maximum extrusion speed, which itself is limited by the onset of meltfracture events. Furthermore, a larger spinline length (spinneret-winder distance) appeared to result in slightly higher draw-down ratios.

In order to obtain LLDPE filaments with diameters below 25 μm , fibre B was hot-drawn in an independent step, by stretching the melt-spun filament in an electric furnace, using a feed- and take-up-bobbin. The maximum attainable hot-draw ratio appeared to be $\lambda_{hd}=2$ at a drawing temperature of 110°C. In this way, it was possible to obtain a fibre of 17 μm in diameter. This fibre will be referred to as fibre C.

Chlorosulfonation

The chemical reaction of chlorosulfonic acid with polyethylene involves the formation of $-\text{SO}_3-$ cross-links between the polymer chains, as was evidenced by IR-spectroscopy [6]. Since the amorphous domains in the fibre structure are most accessible to the reagent [11], the reaction will take place selectively in the amorphous regions and at crystal surfaces at the early stages of exposure to chlorosulfonic acid [12]. Therefore, the cross-link density, required for infusibility, is reached after relatively short reaction times for LLDPE, which inherently has a low crystallinity (25–35%).

LLDPE fibres, obtained by melt-spinning, were subjected to treatment with chlorosulfonic acid at room temperature for different periods of time. The reaction of chlorosulfonic acid with the polymer induces a number of physical changes, such as a gradual change in colour from white to black, a decrease of the fibre's tensile strength, as well as a small amount of linear shrinkage. Since these physical changes occur at the initial stage of chlorosulfonation, they seem to arise from the reaction of chlorosulfonic acid in the amorphous domains predominantly.

The linear shrinkage, resulting from chlorosulfonation, strongly depends on melt-spinning conditions of the fibres. The amount of shrinkage is smaller for fibres obtained under conditions of high temperatures. This effect is likely to arise from differences in the molecular orientation between fibres,

spun at high and at low temperatures respectively. It was suggested by Bikson et al. [13], that the attachment of bulky $-SO_3$ -groups to the polymer chain promotes the *gauche* conformation of adjacent methylene units. When this reaction involves extended chain molecules, it will decrease their end-to-end distance and shrinkage of the fibre will occur. The amount of shrinkage may therefore be related to the amount of orientation of the molecules in the fibre direction and the fraction of extended chain molecules in the amorphous domains. When high spinning temperatures are employed, the extension and orientation of the polymer chains in the elongational flow field, resulting from the draw-down, is opposed by relaxation phenomena [14], leading to weakly oriented fibres. This explains why fibres, produced at high spinning temperatures and elevated surrounding temperatures shrink to a lesser extent upon chlorosulfonation.

It was noticed by Hodge and Bassett [15], that the blackening of the sample proceeds inward from the surface of the sample. The achievement of a homogeneous cross-link density throughout the sample is thus controlled by the diffusion of the acid molecules into the fibre. For thick filaments, long treatment times (10–18 hours) are necessary, which leads to the formation of cracks on their surface [6]. For thinner filaments, shorter treatment times (4–7 hours) are sufficient, which prevents this crack formation, as was revealed by SEM. The presence of cracks is highly unfavourable, since it prohibits the application of high stresses during carbonization.

Carbonization

Precursor fibres, treated with chlorosulfonic acid for different periods of time, were pyrolyzed by heating the filament from room temperature to 900°C at a controlled rate, and keeping them at this temperature for five minutes. During this treatment, a considerable shrinkage of the fibre was observed, especially in the temperature range from 160°C to 450°C . The linear shrinkage amounted to approximately 30% for all filaments, irrespective of the preparation conditions of the precursor fibres, heating rate and fibre stress during carbonization. The heat-treatment is also accompanied by a

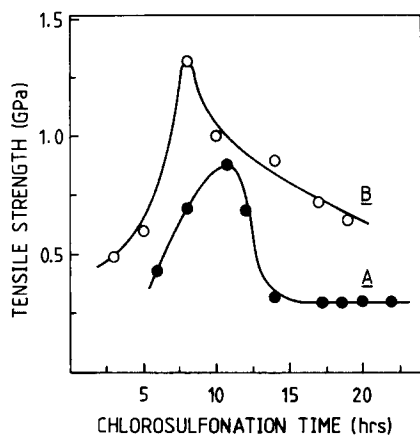


Fig. 1. The effect of chlorosulfonation time on the mechanical properties of carbon fibres, prepared from fibre A (●) and fibre B (○).

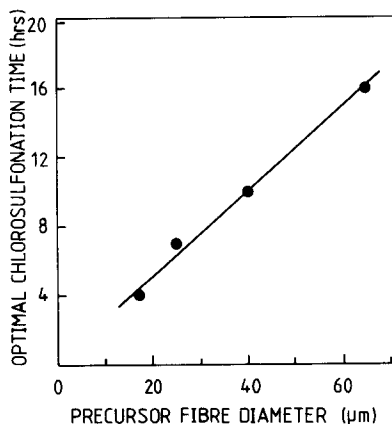


Fig. 2. The optimal chlorosulfonation time as a function of precursor fibre diameter.

substantial reduction of fibre diameter and the mass of the fibre decreases to approximately 20% of its original value, due to the evolution of gas products. The mechanical properties of the fibres changed drastically as a result of the carbonization treatment.

Fig. 1 shows the tensile strength of the carbon fibres, prepared from fibres A and B as a function of the reaction time of these LLDPE filaments with chlorosulfonic acid. As is seen, the tensile strength of the carbon fibre depends very critically on the state of cross-linking in the precursor fibre. For the oxidative stabilization of PAN precursors, a similar effect of under- and over-stabilization on the mechanical properties of the carbon fibre was observed [16]. Furthermore, the optimal chlorosulfonation time is determined by the diameter of the original LLDPE filament, as is shown in fig. 2. This linear relation indicates, that the chlorosulfonation treatment is not a purely diffusion-controlled process, which is explained by the fact that the acid molecules interact chemically with the fibre. The aspect of diffusion implies that differences in cross-link density, between the core and the surface of the stabilized fibre, are to be expected.

At this stage, the carbonization process has not been optimized with respect to heating rate and fibre stress during pyrolysis. Under the conditions applied, a maximum tensile strength of 1.32 GPa was achieved by stabilization and subsequent carbonization of fibre B. In order to optimize the process, the same precursor was carbonized under various stresses at a range of heating rates. The results are shown in fig. 3 and fig. 4. The effect of carbonization stress on the mechanical properties is explained in terms of the surface textures of the carbon fibres, produced under different conditions. Carbonization under a small stress was shown to give rise to rough surface textures, whereas carbon fibres, produced under high stresses appeared to be very smooth [6]. Surface irregularities are generally known to depress the mechanical performance of carbon fibres [7]. When taken into account, that the fibre shrinkage during pyrolysis is independent of carbonization stress, and that the carbonization product is completely

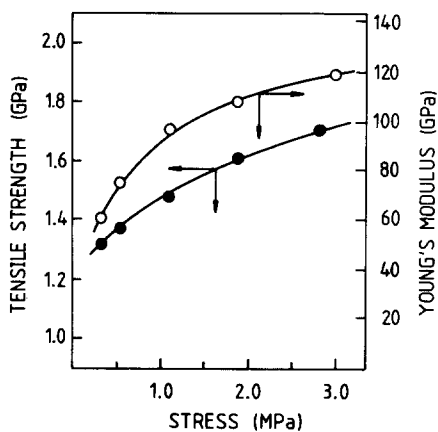


Fig. 3. The effect of fibre stress during pyrolysis of fibre B on the mechanical properties of the resulting carbon fibres.
Heating rate : 26°C/min.

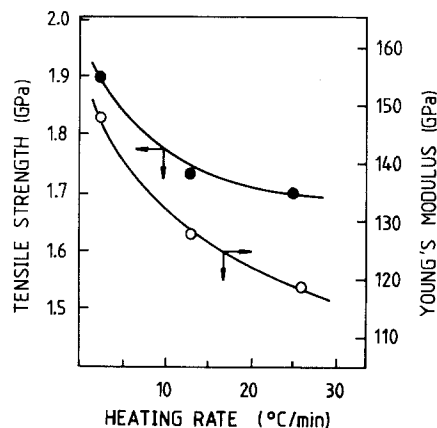


Fig. 4. The effect of heating rate during pyrolysis of fibre B on the mechanical properties of the resulting carbon fibres.
Fibre stress : 2.8 MPa

isotropic, it is evident that the variation of tensile properties with carbonization stress does not arise from orientation effects.

It is seen in fig 4, that the tensile properties steadily increase with decreasing heating rate. This effect can be interpreted in terms of micropores, created upon diffusion of volatiles to the outside of the fibre. During pyrolysis, the weight loss is approximately 80 %, which means that a considerable amount of material is transported to the outside of the fibre. SEM revealed a great population of micropores, ranging in size from 20 nm to 80 nm, on the surface of a carbon fibre, that was produced at a high heating rate. No effect of heating rate on the mechanical properties was found for carbon fibres, derived from phenolic resin, where a low volume of gaseous products is evolved during pyrolysis [17].

The above results demonstrate, that the mechanical properties of amorphous carbon fibres, derived from melt-spun LLDPE filaments, can be improved considerably by carefully selecting the processing conditions in the carbonization stage. An increase in strength from 1.32 GPa to 1.90 GPa, and an increase in Young's modulus from 60 GPa to 148 GPa could be achieved for carbon fibres, obtained by stabilization and carbonization of fibre B, by applying lower heating rates and higher stresses to the fibre during the heat-treatment. WAXS shows, that the 1.90 GPa fibre is completely amorphous and isotropic, which explains the high strain at break of 3% of the fibre. According to elemental analysis, the fibre contains 90% C, 1.5% H and 8.5% of other elements.

Until now, we have considered carbon fibres, prepared by stabilization and pyrolysis of melt-spun fibres only. An additional precursor (fibre C) was obtained by hot-drawing fibre B to a ratio of $\lambda_d=2$ at a temperature of 110°C. Carbonization of this hot-drawn fibre, however, appeared to be very difficult and fracture frequently occurred during pyrolysis. Fibres that were carbonized successfully showed very poor tensile strengths, ranging from 0.2 to 0.3 GPa, after the treatment. Annealing (constrained, for 44 hours in silicone oil at 110°C) of this hot-drawn precursor, however, resulted in an enormous increase in the mechanical properties of the carbon fibres, obtained from it. An average tensile strength of 2.16 GPa, and a Young's modulus of 130 GPa could be achieved for carbon fibres, prepared from fibre C, after its anneal-treatment. Probably, residual stresses in the precursor, introduced by hot-drawing and relieved upon annealing, are responsible for the poor mechanical properties of the carbon fibres, manufactured by direct carbonization of the hot-drawn fibre. Residual stresses may cause chain rupture during chlorosulfonation and heat-treatment, leading to an incoherent carbon structure with a low strength and modulus.

Fig. 5 shows the ultimate tensile properties of the carbon fibres obtained in this study as a function of their diameter. There is a strong increase in both tensile strength and modulus with decreasing diameter, especially below 30 μm . Assuming that thicker filaments contain a greater number of surface flaws may explain the effect of fibre diameter on tensile strength, however, it cannot explain the sharp increase in Young's modulus with decreasing diameter. The effect of fibre diameter on both properties seems to arise from the contribution of a strong and stiff outer texture, that becomes more important as the diameter of the fibre decreases [8]. This type of sheath/core heterogeneity may originate from the stabilization treatment, which is mainly controlled by the diffusion of chlorosulfonic acid into the fibre. Therefore, the outer sheath is expected to be more densely cross-linked in the chlorosulfonation treatment.

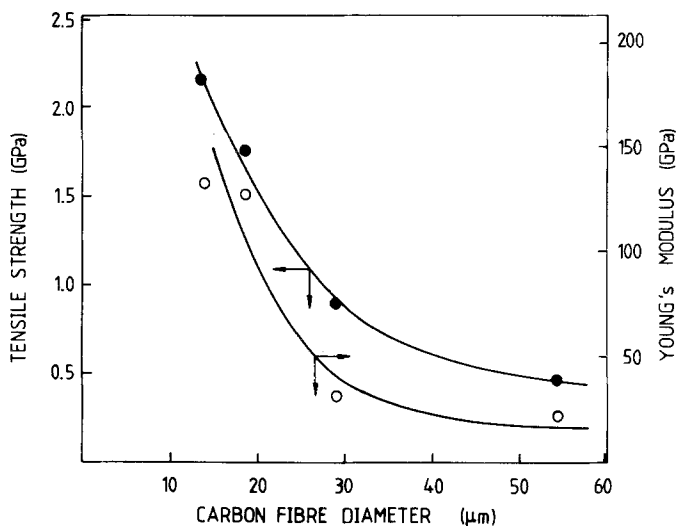


Fig. 5. The effect of carbon fibre diameter on the ultimate mechanical properties.

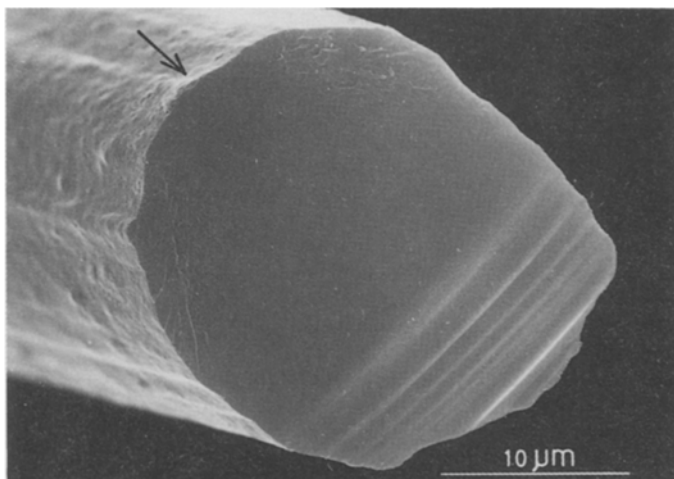


Fig. 6. Scanning electron micrograph of the fracture surface of a 1.90 GPa carbon fibre.

Fig. 6 shows the fracture surface of a 1.90 GPa carbon fibre, prepared from precursor fibre B. It does not reveal skin/core heterogeneity, as it is observed at fracture surfaces of, for instance, pitch-based carbon fibres [2]. It should be kept in mind, however, that the skin/core structure in these fibres is of an entirely different nature (i.e. orientation of crystallites), and may not be revealed at fracture surfaces quite as obviously in our case. Fracture seems to be initiated at the surface of the

fibre (indicated by arrow), creating a 'dimpled' cleavage path, perpendicular to the fibre. The fracture surface is, however, not entirely flat, but it is curved and extended in a 'shear-lip', indicating some ductile behaviour. In tensile testing, a high strain at break of 3% was found, which is explained by the isotropic nature of the fibres. Please note that the curved fracture surface conceals the circular shape of the fibre.

Conclusions

Because of a pronounced effect of the diameter of LLDPE-based carbon fibres on their strength and modulus, these properties could be improved considerably by using thin precursor fibres. Thin LLDPE filaments could be obtained by application of elevated spinline temperatures in the melt-spinning process, which leads to an improvement of the maximum attainable draw-down ratio. Careful carbonization of these filaments gave 17 μm thick carbon fibres with a tensile strength of 1.90 GPa and a modulus of 148 GPa. By additional hot-drawing of melt-spun filaments, even thinner precursor fibres were obtained, that could be converted to 13 μm carbon fibres, with a strength of 2.16 GPa and a modulus of 130 GPa. It was necessary to anneal the hot-drawn fibres in order to remove residual stresses, introduced by hot-drawing. Most likely, the diameter effect arises from the presence of a strong and stiff outer sheath, of which the contribution to the mechanical properties is more dominant in thinner carbon fibres.

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References

1. W. H. Gardner, *Tappi Journal* **71**, 124 (1988)
2. L. S. Singer, *Carbon* **16**, 408 (1978)
3. W. Watt, *Carbon* **10**, 121 (1972)
4. Sumitomo Chemical Company Ltd., British Patent 1,406,378
5. S. Horikiri, J. Iseki and M. Minobe, U.S. Patent 4,070,446
6. A. R. Postema, H. de Groot and A. J. Pennings, *J. Mater. Sci.* **25**, 4216 (1990)
7. J. W. Johnson, *Appl. Pol. Symp.* **9**, 229 (1969)
8. B. F. Jones and R. G. Duncan, *J. Mater. Sci.* **6**, 289 (1971)
9. A. J. Pennings, M. Roukema and A. van der Veen, *Pol. Bull.* **23**, 353 (1990)
10. Y. Termonia, S. R. Allen and P. Smith, *Macromolecules* **21**, 3485 (1988)
11. G. Kanig, *Kolloid Zeitschrift* **251**, 782 (1973)
12. J. Martinez-Salazar, A. Keller, M. E. Cagiao, D. R. Rueda and F. J. Baltá Calleja, *Coll. & Pol. Sci* **261**, 412 (1983)
13. B. Bikson, J. Jagur-Grodzinski and D. Vofski, *J. Pol. Sci., Pol. Phys. Ed.* **19**, 23 (1981)
14. G. Marrucci, *Pol. Eng. Sci* **15**, 229 (1975)
15. A. M. Hodge and D. C. Bassett, *J. Mater. Sci.* **12**, 2065 (1977)
16. O. P. Bahl and L. M. Manocha, *Carbon* **13**, 297 (1975)
17. J. Economy and R. Y. Lin, *J. Mater. Sci.* **6**, 1151 (1971)