JOURNAL OF MATERIALS SCIENCE 25 (1990) 4216–4222

Amorphous carbon fibres from linear low density polyethylene

A. R. POSTEMA, H. DE GROOT, A. J. PENNINGS
Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Carbon fibres with good mechanical properties have been produced from linear low density polyethylene (LLDPE). The melt-spun LLDPE fibres were made infusible by treatment with chlorosulphonic acid. The cross-linked fibres were pyrolysed at temperatures between 600 and 1100° C under tension, in a nitrogen atmosphere, within 5 min. Carbon fibres prepared at 900° C had a tensile strength of 1.15 GPa and a Young's modulus of 60 GPa. The elongation at break was extremely high, up to 3%. The carbon yield of the process was 72 to 75%.

1. Introduction

In the last 30 years there has been extensive research into the production of carbon fibres. Their outstanding mechanical, chemical and physical properties makes them suitable for a wide range of applications. Commercial processes have been developed for the production of carbon fibres from polyacrylonitrile (PAN), rayon and pitches, having strengths of 4.8 to 7.0 GPa and Young's moduli of 200 to 400 GPa. Excellent reviews on this subject have been published [1–5].

In these commercial processes the preparation of a precursor fibre still seems to be complicated. A lot of papers have been published on the preparation of the PAN precursor fibre [e.g. 6–13]. Spinning of mesophase pitches results in very brittle precursor fibres, which are difficult to handle, but affords carbon fibres with high modulus and strength at a low cost [14–16]. Many attempts have been made to produce alternative precursor fibres [1, 2, 17–20].

It seems of great technological interest to know whether carbon fibres can be made starting with polymers, which can be easily synthesized, spun and converted into a suitable precursor fibre, at a low price. In a study of the influence of chlorosulphonation on the mechanical properties of high-strength polyethylene (PE) fibres [21] it was recognized that the treated fibres were highly thermal stable (infusible). Although carbon fibres made from PE have been patented [22] it seems to be valuable to investigate this route of carbon fibre production extensively, because of the simplicity and cheapness of the production of the precursor fibre. Our previous study [21] showed the enormous accessibility of the disordered domains in the PE fibres to chlorosulphonic acid. To obtain high cross-link densities and because of its easy melt-spinnability we took in this, study, linear low density polyethylene (LLDPE) as the starting material.

It will be shown that carbon fibres can be produced with strengths of 1.15 GPa and Young's moduli of 60 GPa. Quite unexpected was the high elongation at break of these fibres of almost 3%. These properties were achieved by treating melt-spun LLDPE fibres with chlorosulphonic acid to a maximum Young's modulus, whereafter these precursors were heat-treated at 900° C, during very short reaction times, applying little stress to the fibre.

2. Experimental details

2.1. Precursor fibre

Using a piston cylinder apparatus, equipped with a conical die (exit diameter 0.25 mm, length 23 mm, entrance angle 43°) LLDPE (BP; $[\eta] = 1.40\,\mathrm{dl\,g^{-1}}$ in decalin, 135° C; $H = 98.5\,\mathrm{J\,g^{-1}}$, $T_m = 127.6°\,\mathrm{C}$) fibres were prepared by melt-spinning at 170° C, with a speed of $4\,\mathrm{m\,min^{-1}}$, and stretching to the ultimately attainable draw-ratio. Two fibres were made: fibre A, having a maximum draw-down of 20; and fibre B, having a maximum draw-down of 65, which could be achieved by using a metal filter (pore size 85 μm) during spinning.

The fibres were treated in an unconstrained way with chlorosulphonic acid (HSO_3Cl, Merck, 98%) at room temperature for different periods of time. After treatment, the fibres were thoroughly washed with chloroform (20° C) and acetone (40° C; dried over anhydrous $CaSO_4$) respectively for 15 min and dried to constant weight (2 h) in vacuo at 50° C.

2.2. Preparation of the carbon fibre

The carbonization of the precursor fibres was carried out in a glass (quartz) tube, equipped with an electric heating mantle, in a nitrogen atmosphere (dried over anhydrous $CaCl_2$ and deoxygenized over copper at 450° C). The heat-treatment temperature, time and fibre-stress (by applying a mass on the filament) during carbonization could be varied. The fibre-stress during carbonization was calculated from the mass on the fibre and the initial fibre cross-section of the precursor. The tube temperature was measured with a "THERMOKOMP" PtRh–Pt thermocouple.

0022–2461/90 $03.00 + .12

2.3. Characterization of the fibres

Tensile properties of the fibres were measured on an Instron (4301) tensile tester, equipped with a 10 N load cell, at a cross-head speed of 12 mm min^{-1}. The gauge length of the specimen was 25 mm for the precursor fibres and 10 mm for the carbon fibres. Cross-sections of the fibres were measured using a Leitz Wetzlar MRO-18 microscope. For each filament the tensile strength at break, the Young's modulus and the elongation at break were determined as the average of five measurements. All the filaments were made in duplicate. The mass of the fibres were determined on a six decimal balance (Mettler M5).

Scanning electron micrographs (SEM) were taken with an ISI-DS 130 microscope operating at 40 kV, using gold-covered samples.

Infrared spectra were taken with a Bruker IFS 88 FT-IR spectrophotometer from, with chlorosulphonic acid treated, LLDPE films. The 10 μm films were made by casting a 5 wt % LLDPE solution in tetrachloroethylene at 110° C, and drying *in vacuo* at 50° C.

3. Results and discussion

The process of the preparation of the carbon fibre actually consists of three stages, i.e. the melt-spinning of the LLDPE, the chlorosulphonation of the LLDPE fibre and the conversion of the precursor into carbon fibres.

3.1. Melt-spinning of LLDPE

Two fibres were prepared from LLDPE by melt-spinning. In the case of fibre A the LLDPE-melt was spun at 170° C and the fibre was wound on a bobbin with the highest possible winding speed. It was also possible to draw the fibre in a, more laborious, independent stage. For instance a LLDPE fibre, spun without draw-down, could be hot-drawn at 100° C to a maximum draw-ratio of 26. Further use of this fibre in the next process stages (chlorosulphonation at room temperature for 16 h) yielded, under optimized conditions (see later) a carbon fibre with moderate mechanical properties, namely a tensile strength of 0.25 GPa and a Young's modulus of 18 GPa.

The maximum draw-ratio of the spinline at ambient temperature (draw-down) appeared to be 20. Applying a filter with a pore-size of 85 μm during spinning the maximum draw-ratio increased to 65 (fibre B). Most likely, in this case, during spinning the entanglement network disintegrated into flow units [23] and partial disentangling occurred. The reduction of the number of entanglements meant that higher draw-ratios in the spinline could be obtained.

3.2. Chlorosulphonation of the LLDPE fibres

The two LLDPE fibres were treated with chlorosulphonic acid at room temperature, for various periods of time. During chlorophonation the mass of the fibre increased by more than 150% (Fig. 1) due to the attachment of heavy groups on the polymer chains. By following the reaction with infrared spectroscopy, it was recognized that $-SO_3-$ bridges were formed [24]. In Fig. 2 four IR spectra, taken after various reaction times, are presented, showing an increase of vibrations with wave numbers: 1390 to 1320 cm^{-1}, 1200 to 1130 cm^{-1}, 1060 to 1020 cm^{-1} and 930 to 870 cm^{-1}. Remarkably, no –OH and SO_2–Cl vibrations were detected, indicating that every chlorosulphonic acid molecule reacts twice, splitting a hydrogen and chlorine atom. It was also possible to use sulphuric acid (H_2SO_4) as the cross-linking agent*. This reaction resulted in IR spectra identical to the chlorosulphonic acid ones. On the other hand sulphuryl chloride (SO_2Cl_2) did not react at all with the LLDPE fibre.

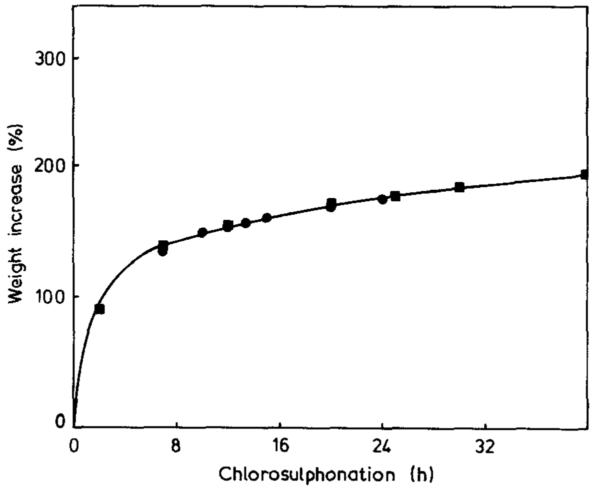

Figure 1 Relative weight increase of the LLDPE fibres as a function of chlorosulphonation time at room temperature (■ fibre A, ● fibre B).

During the reaction the fibres became black and shrank about 60% (Fig. 3). This was also observed during the chlorosulphonation of linear polyethylene (LPE) fibres [21]. The shrinkage of the PE fibres can be ascribed to the distortion of the crystallites caused by repulsion of electronegative groups on the crystal surface [25] as well as by swelling of the crystallites leading to the relaxation of the extended chains to a random configuration [21]. The amount of shrinkage of both LLDPE fibres was the same, suggesting that the fraction of extended chains and the length of the extended chain crystals was similar. DSC measurements of the LLDPE fibres revealed a heat of fusion of 75 J g^{-1} for both fibres and SAXS measurements indicated similar long periods of approximately 20 nm.

In contrast to the LPE fibres, the weight increase due to chlorosulphonation for the LLDPE fibres was extensive (150% for LLDPE as opposed to 40% for LPE). This high saturation level, which can only be reached by using a PE with small crystallites and numerous disordered domains (i.e. a low density PE), appears to be necessary in order to obtain a carbon fibre with appropriate mechanical properties. The high saturation level was one of the reasons for taking the LLDPE in this process. Firstly, we had attempted to make carbon fibres of highly oriented LPE fibres [21]. High orientations of the precursor often seems to

---

*A single, non-optimized, experiment using sulphuric acid (96%) as the cross-linking agent (cross-link time 8 h at 120° C, followed by 4 h at 180° C) revealed, after pyrolysis at 900° C, carbon fibres with a tensile strength of 0.26 GPa and a Young's modulus of 20 GPa.

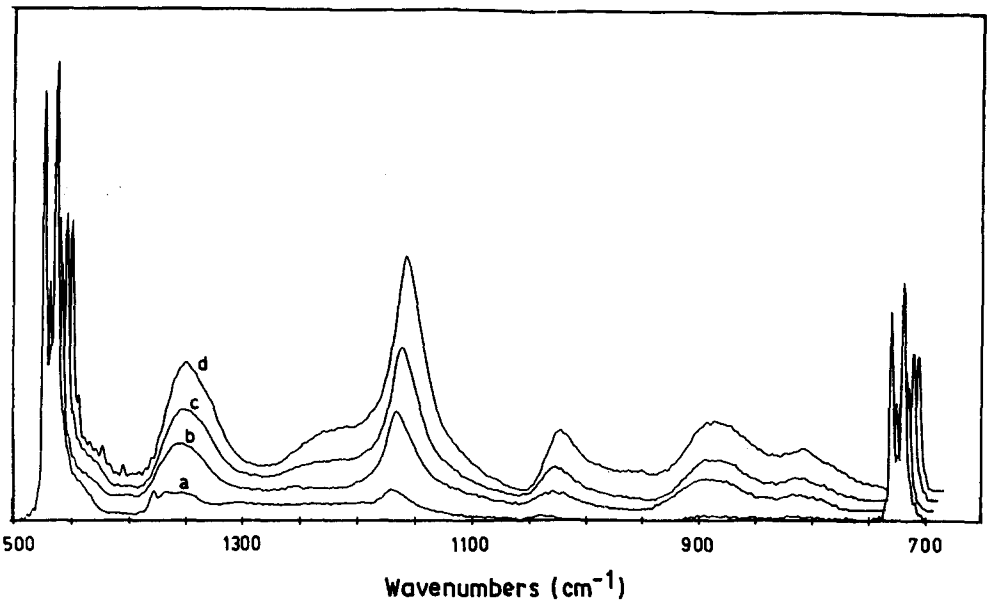

Figure 2 IR spectra of LLDPE films treated with chlorosulphonic acid for different periods of time. a t = 30 min, b t = 1 h, c t = 2 h, d t = 4 h.

be necessary to achieve high-strength–high-modulus carbon fibres [6–13]. Unfortunately, the chlorosulphonized LPE fibres [21] immediately fractured at high temperatures under little tension. Pyrolysis without tension yielded fibres which were too brittle for handling. These results can most probably be ascribed to an insufficient crosslink density.

After the LLDPE fibres were treated with chlorosulphonic acid, the mechanical properties of the developed precursors were measured. In Fig. 4 the tensile strengths of the precursor fibres are presented as a function of chlorosulphonation time. It shows that during the reaction the strength decreases. Fig. 5 presents the Young's moduli of the precursor fibres. Although the strength decreases, the Young's modulus of the precursors initially increases to 2.45 GPa corresponding to 250% of its original value, probably due to the cross-linking of the polymer chains with chlorosulphonic acid. The reduction in tensile strength can be attributed to cracks which arise in the fibre surface caused by chemical degradative stress-cracking [21], which is revealed by electron microscopy. Fig. 6 presents a SEM micrograph of fibre B after treatment with chlorosulphonic acid (12 h), showing small cracks longitudinal and perpendicular to the fibre axis. The blister-like structures at the edges of the cracks, which appear as the fibres are washed after treatment with chlorosulphonic acid are striking*. According to Griffith [26] fracture will be initiated at flaws, cracks or other imperfections. These cracks may reduce the tensile strength dramatically.

Fibre B, which was spun by applying a filter, attained its maximal Young's modulus in a shorter period of time than fibre A. The crystallinity of both fibres appeared to be constant (measured by DSC) and no structural differences could be distinguished from WAXS and SAXS experiments. In the chlorosulphonation stage two competitive reactions will occur simultaneously, i.e. cross-linking of chains [21]

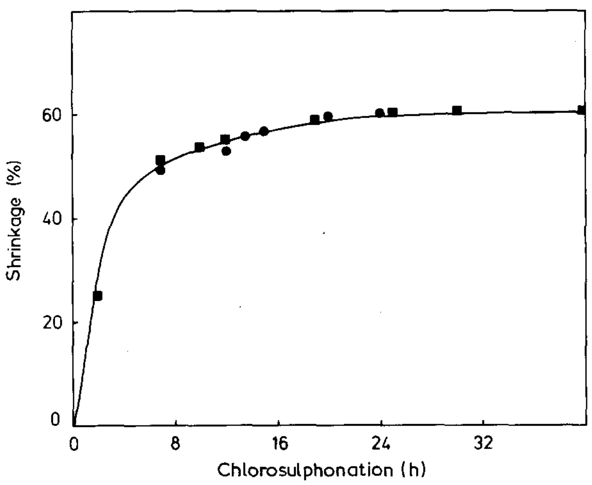

Figure 3 Shrinkage of the LLDPE fibres as a function of chlorosulphonation time at room temperature (■ fibre A, ● fibre B).

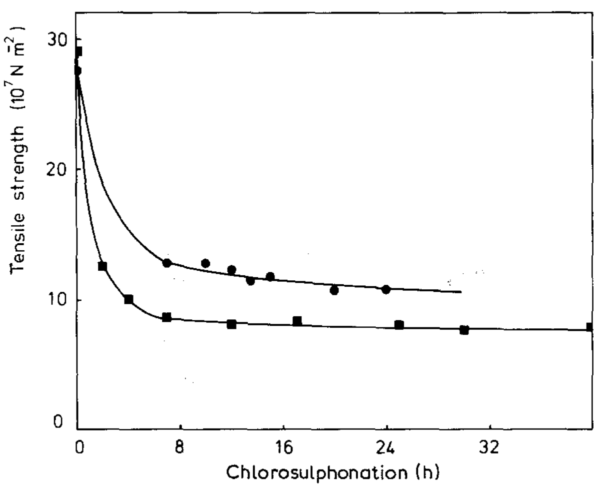

Figure 4 Tensile strength of the precursor fibres as a function of chlorosulphonation time at room temperature (■ fibre A, ● fibre B).

---

*It was not possible to destillize the remnants of chlorosulphonic acid from the treated fibres, in order to elucidate the washing process.

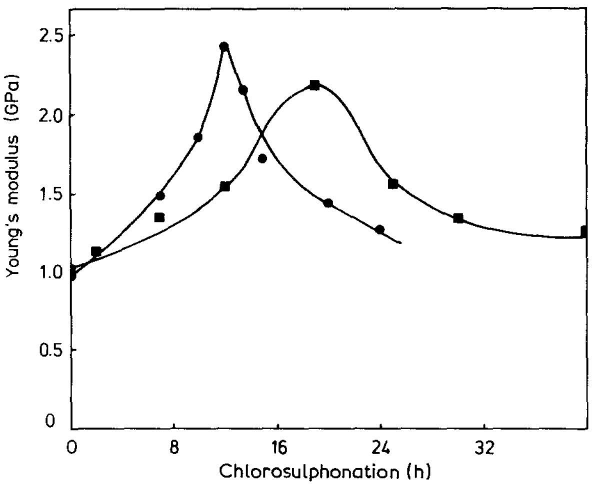

Figure 5 Young's modulus of the precursor fibres as a function of chlorosulphonation time at room temperature (■ fibre A, ● fibre B).

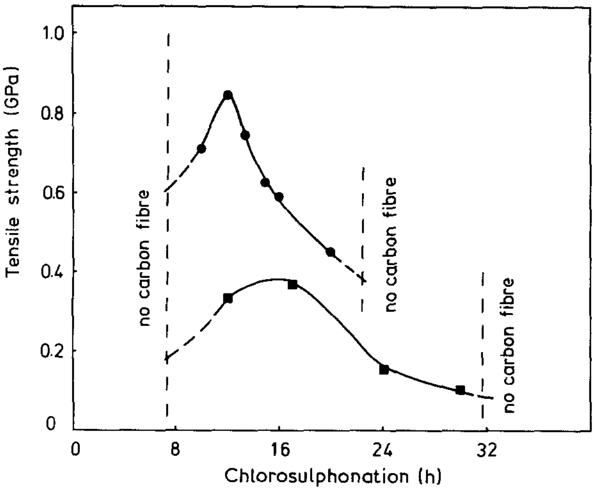

Figure 7 Tensile strength of the carbon fibres after heat-treatment at 900° C, during 5 min. The applied filament stresses were: fibre A (■) 0.065 MPa, fibre B (●) 0.793 MPa.

and scissioning of chains under tension [27]. Due to the shrinkage of the fibres (Fig. 3) during chlorosulphonation entanglements and tie molecules will be under tension. The rate of the scissioning reaction (and thus the effectiveness of the cross-linking reaction) will depend on the number of these stressed chains. For fibre B the number of entanglements is lower than for fibre A, and the cross-linking reaction will be more effective. For this reason the maximal Young's modulus of fibre B is attained in a shorter period of time than for fibre A (Fig. 5), and the tensile strength of fibre B will always be higher than for fibre A after the same reaction time (Fig. 4). At longer reaction times the Young's modulus decreased again. At that moment the distortion of the fibrillar crystals and a partial digestion [29] seemed to dominate the cross-linking resulting in a fibre with a lower Young's modulus.

3.3. Conversion of the precursor into carbon fibres

The precursor fibres were converted into carbon fibres by pyrolysis at 900° C in a nitrogen atmosphere, for 5 min at a constant stress. We also investigated the carbonization stage by applying heating and cooling rates as high as possible (estimated at 600 to 900° C min^{-1}). The draw-backs of this approach are that the gaseous by-products must be transported very rapidly from the inside to the outside of the fibre during pyrolysis and that cooling of the fibre at high rates may lead to residual stresses which decrease the mechanical properties.

Figs 7 and 8 display the tensile strength and Young's modulus, respectively, of the prepared carbon fibres as a function of the chlorosulphonation time of the LLDPE fibre. It illustrates that LLDPE fibres which were treated with chlorosulphonic acid for short periods of time (i.e. $t < 8$ h) could not be converted to a carbon fibre. For these fibres the cross-link density seems to be insufficient, resulting in fracture of the fibres during pyrolysis. The application of longer chlorosulphonation times of the LLDPE fibres resulted in an improvement of the mechanical properties. If the chlorosulphonation time was extended the mechanical properties after pyrolysis diminished again. Attempts to prepare carbon fibres from "40 h-chlorosulphonized" fibre A and "24 h-chlorosulphonized" fibre B failed. Presumably precursors, which were too extensively chlorosulphonized (i.e. a mass

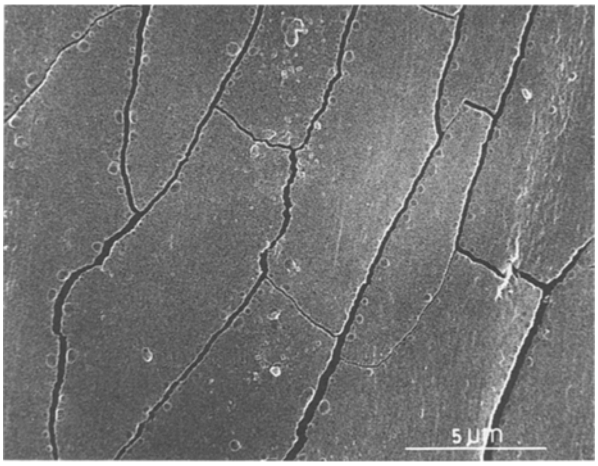

Figure 6 SEM micrograph of the surface of a chlorosulphonated LLDPE fibre showing longitudinal and perpendicular cracks (fibre B).

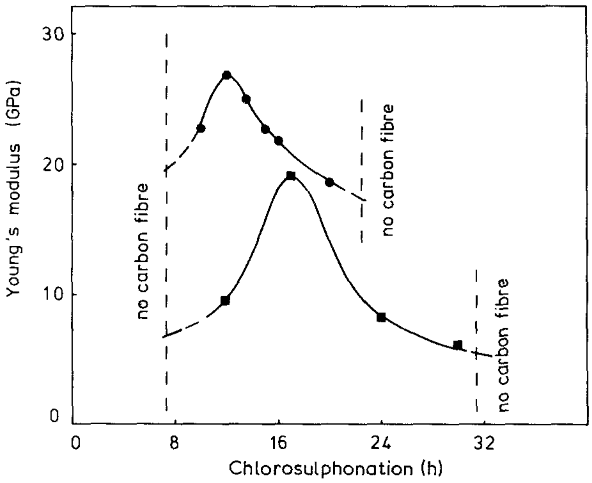

Figure 8 Young's modulus of the carbon fibres after heat-treatment at 900° C, during 5 min. The applied filament stresses were: fibre A (■) 0.065 MPa, fibre B (●) 0.793 MPa.

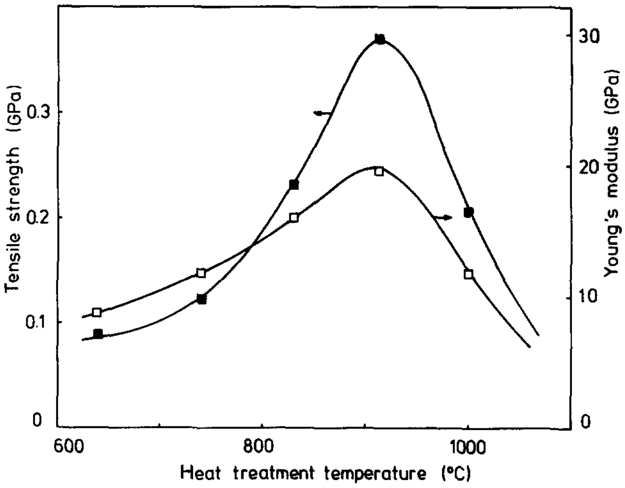

Figure 9 Tensile strength and Young's modulus of carbon fibres obtained from precursor A (chlorosulphonation time 16 h) as a function of heat-treatment temperature (heat-treatment time 5 min; applied stress 0.065 MPa).

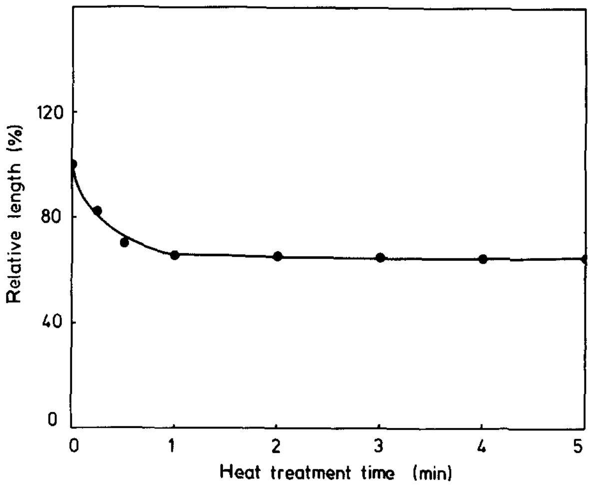

Figure 11 Relative length of the carbon fibres as a function of heat-treatment time (heat-treatment temperature 900° C; filaments A and B).

increase of almost 200%) convert too rapidly, resulting in heterogeneous structures in the carbon fibre. These effects of under- and overstabilization are also known for PAN precursors [9]. The maximal mechanical properties of the carbon fibres were achieved for both fibres after different chlorosulphonation times. For fibre A after 16 h and for fibre B after 12 h. Obviously, carbon fibres with the best mechanical properties can be obtained by using precursor fibres with the highest Young's moduli (Fig. 5).

In order to achieve the ultimate mechanical properties the pyrolysis conditions were optimized. Fig. 9 presents the tensile strength and Young's modulus of fibre A after pyrolysis at various heat-treatment temperatures at a constant stress and heat-treatment time. A heat-treatment temperature of 900° C yielded fibres with optimal mechanical properties at these reaction conditions. At higher temperatures the strength decreased again. A similar decrease in mechanical properties has been reported for PAN-based carbon fibres [28]. The strength of carbon fibres is controlled by both surface and internal flaws [18]. Surface flaws could be removed by suitable surface treatments [29].

For PAN-based carbon fibres the strength decreased above 1400° C [30], which was ascribed to an increased shearing of crystallites causing stress concentrations and ultimately to the formation of failure cracks. At 900° C the influence of the heat-treatment time was investigated. Fig. 10 presents the relative mass of the fibre as a function of heat-treatment time. It illustrates that the pyrolysis stabilizes within 2 min and that the gaseous by-products can be transported rather quickly from the inside to the outside of the fibre. In the initial 30 sec the fibre shrinks (although some stress was applied on the fibre) to 65% of its initial length (Fig. 11). In this period the temperature was too low for pyrolysis (see Fig. 10), indicating that this shrinkage has to be ascribed to a further relaxation of oriented chain parts in the precursor fibre and is not induced by, for instance, dehydrogenation or intermolecular cyclization. Employing the optimal heat-treatment temperature and time, the fibre stress was optimized by changing the applied load during pyrolysis. Fig. 12 shows the dependence of the tensile strength and Young's modulus of fibre A on the applied stress. Maximal mechanical properties (tensile strength 0.55 GPa; Young's modulus 25 GPa) were obtained by

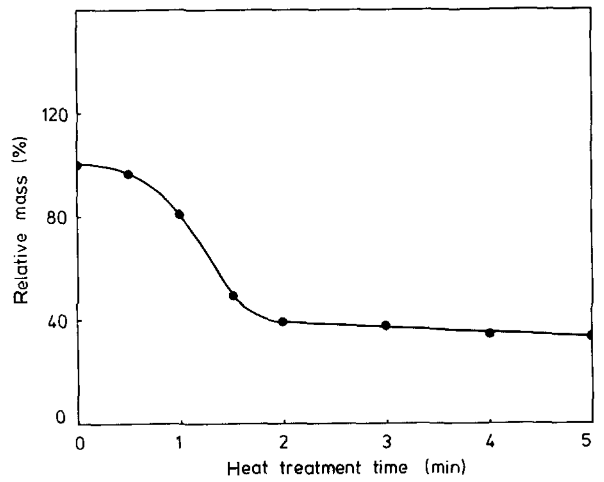

Figure 10 Relative mass of the carbon fibres as a function of heat-treatment time (heat-treatment temperature 900° C; filaments A and B).

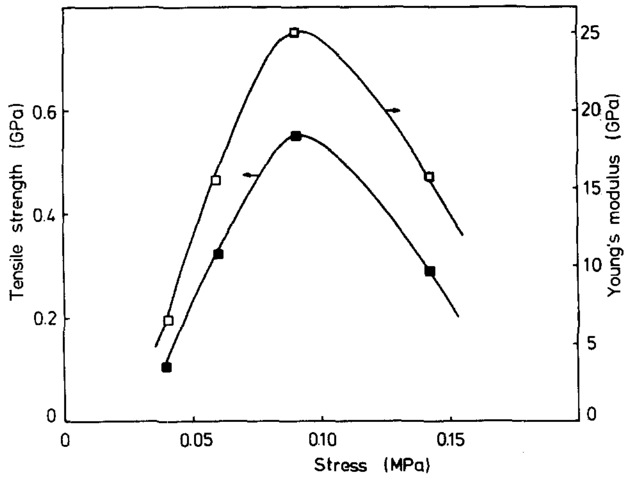

Figure 12 Tensile strength and Young's modulus of carbon fibres obtained from precursor A (chlorosulphonation time 16 h) as a function of the applied stress (heat-treatment temperature 900° C; heat-treatment time 5 min).

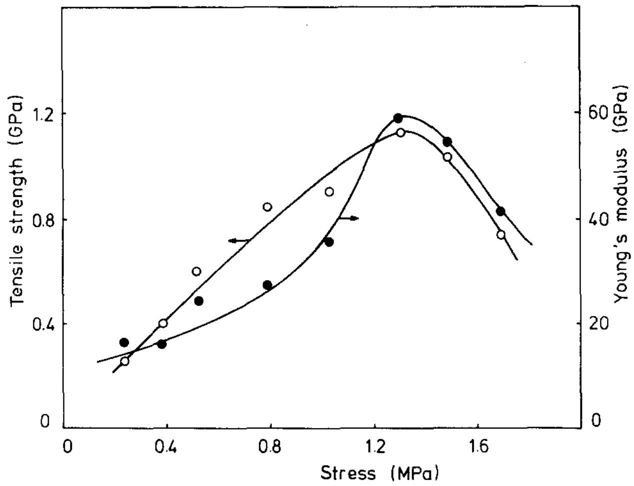

Figure 13 Tensile strength and Young's modulus of carbon fibres obtained from precursor B (chlorosulphonation time 12 h) as a function of the applied stress (heat-treatment temperature 900° C; heat-treatment time 5 min).

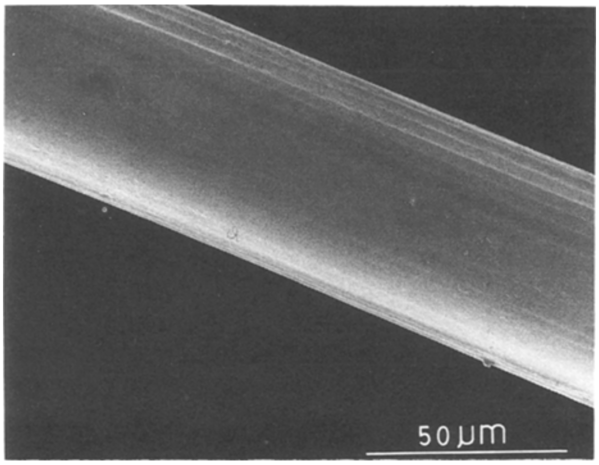

Figure 15 SEM micrograph of the surface texture of a carbon fibre made at 900° C from precursor B (heat-treatment time 5 min, stress 1.3 MPa).

applying a stress of 0.10 MPa. At higher stresses WAXS measurements indicated some crystallization in the carbon fibre, contrary to amorphous structures in the strongest fibres. A low level of crystallization can result in heterogeneous structures, giving rise to inferior properties [30].

The higher strength of fibre B meant that higher stresses could be used during pyrolysis, under identical reaction conditions (temperature, time) (Fig. 13). A tensile strength of 1.15 GPa and Young's modulus of 60 GPa were obtained. These fibres were 40 µm thick. There are many indications in literature that much stronger fibres can be obtained by starting with thinner precursor fibres. For instance, carbon fibres of 8 µm, prepared from phenol–hexamine polymers, were twice as strong as 20 µm thick carbon fibres [19]. Not only the fibre diameter but also the fibre cross-sectional shape [31] seems to affect the mechanical properties of the carbon fibres. The elongations at break for these LLDPE-based carbon fibres were remarkable. In all cases the elongation at break ranged from 2.5 to 3.0%, which is extremely high for carbon fibres.

The carbon yield after the total process is very important in the production of carbon fibres. Calculations from Figs 1 and 10 indicated a carbon yield of 72%, whereas elemental analysis combined with Fig. 10 revealed a value of 75%. The prepared carbon fibres contained 88.1% C, 1.2% H, 1.1% N and 9.6% other elements. The relative high percentage of other elements can most likely be reduced by applying longer heat-treatment times and higher heat-treatment temperatures [1, 2].

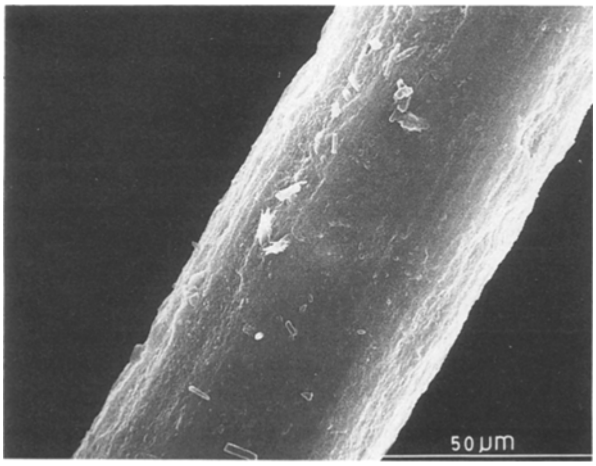

Figure 14 SEM micrograph of the surface texture of a carbon fibre made at 900° C from precursor A (heat-treatment time 5 min, stress 0.10 MPa).

The origin of the differences in ultimate mechanical properties between fibre A and fibre B has to be traced back to the precursor stage. The surface textures of fibre A and fibre B after pyrolysis were quite different. In Fig. 14 a scanning electron micrograph shows the rather crude surface texture of a carbon fibre made from fibre A, by applying the optimal pyrolysis conditions. Fig. 15 presents a smooth surface texture of a carbon fibre made from precursor B by applying the optimal pyrolysis conditions. Remarkably, the surface cracks of the precursor (see Fig. 6) completely vanished in the carbonization stage.

Future experiments will be concentrated on the use of a filter with a smaller pore-size in the melt-spinning process in order to reduce the number of entanglements in the precursor fibre, thinner fibres and higher heat-treatment temperatures during pyrolysis.

4. Conclusions

The possibilities of producing carbon fibres from LLDPE have been investigated. The main conclusions and advantages follow.

(1) LLDPE fibres can be easily prepared by a combination of melt-spinning and draw-down.

(2) The LLDPE fibres can be made infusible by cross-linking with chlorosulphonic acid, at low temperatures.

(3) The infusible LLDPE fibres can be converted under tension to amorphous carbon fibres at 900° C within 2 min.

(4) LLDPE-precursors with the highest Young's moduli could be converted to carbon fibres with the best mechanical properties.

(5) The carbon yield in this process is almost 75%.

(6) The prepared carbon fibres have proper mechanical properties, i.e. tensile strength 1.15 GPa; Young's modulus 60 GPa. The elongations at break were extremely high, up to 3%.

These conclusions are drawn for a process in which very high heating and cooling rates were applied during the carbonization stage.

Acknowledgement

The authors wish to acknowledge Dr G. Capaccio of B.P. company for providing the LLDPE sample. This study was financially supported by AKZO, The Netherlands.

References

1. J. B. DONNET and R. C. BANSAL, "Carbon Fibres" (Marcel Dekker, New York, 1984).
2. W. WATT and B. V. PEROV, "Strong Fibres" (Elsevier, Amsterdam, 1985) ch. XII–XIV.
3. D. J. JOHNSON, *Chem. and Ind.* **692** (1982).
4. M. SANTAPPA, *J. Indian Chem. Soc.* **LIX** (1982) 321.
5. Y. S. KO and G. P. DAUMIT, Proceedings Fiber Production Conference, Greenville 5A-18 (1986).
6. N. GRASSIE and R. McGUCHAN, *Eur. Polym. J.* **7** (1971) 1503.
7. S. B. WARNER, D. R. UHLMANN and L. H. PEEBLES, *J. Mater. Sci.* **14** (1979) 1893.
8. R. B. MATHUR, O. P. BAHL and K. D. KUNDRA, *J. Mater. Sci. Lett.* **5** (1986) 757.
9. M. K. JAIN and A. S. ABHIRAMAN, *J. Mater. Sci.* **22** (1987) 278.
10. M. K. JAIN, M. BALASUBRAMANIAN, P. DESAI and A. S. ABHIRAMAN, *ibid.* **22** (1987) 301.
11. O. P. BAHL and L. M. MANOCHA, *Carbon* **12** (1974) 417.
12. *Idem, ibid.* **13** (1975) 297.
13. E. FITZER and D. J. MÜLLER, *ibid.* **13** (1975) 63.
14. J. B. BARR, S. CHWASTIAK, R. DIDCHENKO, I. C. LEWIS and L. S. SINGER, *Appl. Polym. Symp.* **29** (1976) 161.
15. D. D. EDIE and C. C. FAIN, Proceedings Fiber Production Conference, Greenville 6B-1 (1986).
16. S. OTANI, *Carbon* **3** (1965) 31.
17. J. ECONOMY and R.-Y. LIN, *J. Mater. Sci.* **6** (1971) 1151.
18. H. ASHITAKA, Y. KUSUKI, S. YAMAMOTO, Y. OGATA and A. NAGASAKA, *J. Appl. Polym. Sci.* **29** (1984) 2763.
19. K. KAWAMURA and G. M. JENKINS, *J. Mater. Sci.* **5** (1970) 262.
20. E. FITZER, W. SCHAEFER and S. YAMADA, *Carbon* **7** (1969) 643.
21. A. R. POSTEMA and A. J. PENNINGS, in "High Modulus Polymers" edited by A. E. Zachariades and R. S. Porter (Marcel Dekker, New York, 1988) ch. 13.
22. S. HORIKIRI, J. ISIKI and M. MINOBE, US Patent 4070446 (1978).
23. J. SMOOK and A. J. PENNINGS, *J. Mater. Sci.* **19** (1984) 31.
24. G. SOCRATES, "Infrared Characteristic Group Frequencies" (Wiley, London, 1980).
25. B. BIKSON, J. JAGUR-GRODZINSKY and D. VOFSI, *J. Polym. Sci., Polym. Phys. Edn* **19** (1981) 23.
26. A. A. GRIFFITH, *Phil. Trans. R. Soc. London* **A221** (1921) 163.
27. J. MARTINEZ-SALAZAR, A. KELLER, M. E. CAGIAO, D. R. RUEDA and F. J. BALTÁ CALLEJA, *Coll. Polym. Sci.* **261** (1983) 412.
28. R. MORETON, W. WATT and W. JOHNSON, *Nature* **18** (1967) 690.
29. O. P. BAHL, R. B. MATHUR and T. L. DHAMI, *Polym. Eng. Sci.* **24** (1984) 455.
30. G. A. COOPER and W. WATT, *J. Mater. Sci.* **6** (1971) 60.
31. D. D. EDIE, N. K. FOX, B. C. BARNETT and C. C. FAIN, *Carbon* **24** (1986) 477.

Received 27 May
and accepted 13 September 1988