# Studies on the preparation of strong/stiff polymeric fibres

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## SUMMARY

This thesis presents several studies on the preparation of strong and/or stiff polymeric fibres. The low density and high strength of these fibres make them very suitable for applications in stronger and lighter materials.

The ultimate mechanical properties of a fibre is a manifestation of the way in which the macromolecules respond to applied stress. The fracture of a fibre can occur by breaking either the primary covalent bonds of the polymeric backbone and/or the secondary bonds (V.d. Waals, hydrogen, etc.) through molecular 'pull-out'. To obtain a high-strength polymeric fibre it is necessary to start with a polymer with a high theoretical strength of the polymeric backbone. Unfortunately, in practice this theoretical strength has never been reached. The reason for this, is the presence of defects in the fibre structure, like flaws and cracks, stress-concentrations, weak-links and topological defects. The most severe type of flaw in the fibre structure may arise from trapped entanglements, which are the weak spots where fracture is bound to be initiated. The reduction of the number of trapped entanglements and the improvement of molecular orientation and chain extension has been the working hypothesis in this thesis in order to prepare high-strength polymeric fibres.

One of the routes to improve molecular orientation and chain extension is by spinning dilute solutions of high molecular weight flexible polymers followed by hot-drawing. In this thesis this route is applied to the preparation of high-strength polyethylene and poly(L-lactide) fibres.

In the gel-spinning process of ultra-high molecular weight polyethylene (UHMWPE) (chapter 2), at higher production rates, the highly elastic solutions may give rise to flow instabilities. This immediately leads to fibres with poor mechanical properties. These flow instabilities originate from the adsorption of the long macromolecules to the wall of the die. Stretching in the spinline may suppress this phenomenon to some extent but has the disadvantage that it also reduces fibre strength. This reduction in fibre strength is attributed to the rupturing of the entanglement network which causes flaws in the fibre after hot-drawing. The adsorption could be diminished by decreasing the residence time of the

molecules in the die. Increasing the spinning temperature from 170-200 °C was also an effective way to reduce the tendency of the polymer molecules to be adsorbed. It was possible to prepare PE filaments, with high-strengths, at a speed of 1500 m/min.

During the gel-spinning process of UHMWPE, excessive crazing in the fibre surface was observed (chapter 3). The moment of craze initiation depends on the solvent applied in the spinning process. By applying decalin as the solvent, the crazing takes place in the spinline, whereas by applying paraffin oil the crazing takes place during evaporation of n-hexane after extraction of the solvent. The existence of the crazes in the gel-fibre leads to moderate mechanical properties, after hot-drawing, and should be prevented. From electron microscopic studies it was recognized that the length of the fibrils in the crazes strongly correlates with the contour length between entanglements in the polymer solution, indicating that almost no entanglements are lost during spinning.

The high-strength of the polyethylene fibre is always attained by hot-drawing of the porous gel-fibre. The porosity causes large amounts of stress-concentrations dispersed homogeneously in the fibre. From a study into the drawing behaviour of melt-spun polyethylene fibres (chapter 4) it was found that the drawing can take place at significantly higher deformation rates if the fibres contain a relative great amount of stress-concentrations which promote multiple-yielding. Due to the multiple-yielding the local deformation rate is low and fibre failure is suppressed.

Applications of the high-strength PE fibre in composite materials require an appropriate interfacial bonding between the matrix and the fibre. By treating the PE fibre with chlorosulfonic acid (chapter 5) the fibre could be made suitable for reinforcing gypsum plaster. Due to chemical degradative stress-cracking, starting at surface irregularities, a rough surface developed which improved the interfacial bond-strength at least by 4.8 times. Unfortunately, the existence of little cracks in the fibre surface lowers the fibre strength. On the other hand, the Young's modulus of the PE fibre could be increased by more than fifty percent, by this treatment with chlorosulfonic acid.

The PE fibre, treated with chlorosulfonic acid appeared to be highly thermal stable (infusible). This observation stimulated us to investigate

whether the highly oriented PE fibres could be converted into high-strength carbon fibres (chapter 6). To obtain high cross-link densities in the precursor fibre, it appeared necessary to start with a PE fibre having small crystallites and numerous disordered domains. This was attained by melt-spinning of linear low density poly-ethylene (LLDPE). The melt-spun fibres were made infusible by cross-linking with chlorosulfonic acid, at room temperature. The cross-linked LLDPE fibres were pyrolysed at temperatures between 600-1000 °C under tension in a nitrogen atmosphere, within 5 minutes. 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 72-75%.

In the second part of this thesis the dry-spinning/hot-drawing process of poly(L-lactide) (PLLA) was investigated. PLLA is a biocompatible and biodegradable polymer which can find application as, for instance, a small-sized suture in microsurgery.

The preparation process can be divided into two processes, i.e. a dry-spinning process in which the PLLA fibre is spun from solutions of 4 wt% PLLA in mixtures of chloroform (good solvent) and toluene (poor solvent) (40/60), near the θ-conditions, and a hot-drawing process in which the PLLA chains are oriented and extended, at elevated temperatures.

In order to investigate the effects of various variables of the dry-spinning process on the ultimate mechanical properties, it is necessary to apply an optimised hot-drawing process on the as-spun fibres. The hot-drawing process of the as-spun PLLA fibres (chapter 7) appeared to be very sensitive to the applied temperature and deformation rate. Inhomogeneous drawing, leading to inferior fibre properties, takes place below 180 °C and at higher temperatures by applying high deformation rates. Under these conditions the deformation proceeds in the semi-crystalline state of the PLLA by shear. Homogeneous deformation could be achieved in a temperature gradient by applying low deformation rates, so that the deformation may take place in the liquid state of the polymer, which after displacement of topological defects transforms into fibrous crystals by strain-hardening. In this way PLLA fibres with a tensile strength of 2.3 GPa have been produced.

The ultimate tensile strength of PLLA fibres is mainly confined to the morphology of the as-spun fibres. A study on the influence of the

temperature of the surrounding of the spinline on the morphology and ultimate mechanical properties of PLLA fibres, after hot-drawing, (chapter 8) showed that the morphology is affected by the rate of solidification of the PLLA. By way of phase-separation during spinning, porous filaments were achieved with network structures depending on the ambient temperature of the spinline, leading to ultimate tensile strengths after hot-drawing varying between 1.1 and 2.2 GPa. A tensile strength of 2.2 GPa was achieved by applying an ambient temperature of 25 °C. At this temperature phase-separation and crystallization were suppressed so that homogeneous as-spun filaments were formed.

The morphology of the as-spun PLLA fibres was also affected by the extrusion rate and the winding speed in the spinning process (chapter 9). Both high extrusion rates and high winding speeds may lead to demolition of the entanglement network due to rapid phase-separation and oriented crystallization. Fibres, which contain destructed entanglement networks will have poor tensile strengths after hot-drawing. The demolition of the entanglement network can be prevented by avoiding spinline stretching and applying a pseudohyperbolic die, in which the elongational deformation rates are low. In this way PLLA fibres could be prepared at rates upto 180 m/min, having a tensile strength of 1.5 GPa after hot-drawing.