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Structure-properties relationships in polymeric fibres

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

1994

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Penning, J. P. (1994). *Structure-properties relationships in polymeric fibres*. s.n.

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Summary

The present thesis is concerned with the relation between the preparation, structure and (mechanical) properties of fibrous polymeric materials. The aim of this work is to establish how the mechanical behaviour of polymeric fibres should be interpreted in terms of their structure, and how this specific structure develops during the various stages of the preparation procedure. The studies presented in this thesis are mainly concerned with fibres obtained by solution-spinning of flexible polymers. The main part of this work deals with high-strength fibres from ultra-high molecular weight polyethylene (UHMWPE) prepared according to the gel-spinning/hot-drawing technique. The conversion of polyethylene into carbon fibres has also been examined. The final chapters of this thesis are concerned with biodegradable fibres from poly(lactides), and in particular with the effects of copolymerization on the preparation and properties of these materials.

As outlined in Chapter 1, the production of high-strength fibres from flexible polymers usually involves mechanical stretching of the material, which produces a high degree of orientation of the long-chain molecules in the direction of the fibre. The extensibility of the material is determined by the amount of interaction between the individual chains. The most important type of interaction in this respect is the chain entanglement, which can be thought of as a temporary physical crosslink. High molecular weight polymeric materials can thus be regarded as an entanglement network. The deformation behaviour of this network can be described in terms of the entanglement spacing, i.e. the average length of a chain segment connecting two entanglement points. In Chapter 2, this concept is applied to the hot-drawing process of gel-spun UHMWPE fibres. The entanglement spacing in a polymer that is solidified from solution can be derived from the volume fraction of polymer in this solution using De Gennes' scaling laws. The maximum draw ratio of the entanglement network (i.e. the draw ratio at which the chain segments between entanglements are completely extended, λ_n) can be calculated using conformational statistics. For an UHMWPE fibre obtained from a 5% spinning solution, a value of $\lambda_n=30$ was calculated in this way. The actual maximum draw ratio of the fibre under optimum drawing conditions was found to be $\lambda = 100$, indicating that a substantial slippage of the entanglement point takes place during hot-drawing. Up to draw ratios of $\lambda \approx 30$, a number of physical properties of the drawn fibre (shrinkage, melting point and degree of crystallinity) increase steeply with increasing draw ratio and the initial structure of the undrawn fibre is transformed into a fibrillar morphology. At higher draw ratios, the drawing process results in a gradual improvement of this fibrillar morphology and the physical properties of the fibre reach a limiting value. Apparently, the drawing process consists of two stages and the transition between the two occurs approximately at the maximum network draw ratio of $\lambda_n = 30$: the polymer chains are effectively extended between entanglement points at the first stage of the draw-

ing process, whereas chain slippage becomes predominant at the draw ratio where full chain extension is expected.

It was observed that the force at which the fibre breaks in the tensile test becomes independent of the draw ratio beyond λ_n . This force can be regarded as a measure of the absolute number of load-carrying chains in the fibre cross-section. Since the diameter of the fibre steadily decreases with increasing draw ratio, this means that the improvement of fibre strength (force/unit area) results from a progressively more efficient packing of the same number of load-carrying in the fibre's cross-section. This observation is consistent with the idea that drawing beyond λ_n involves substantial chain slippage, since elongation of the fibre can take place without a decrease in the absolute number of chains that transmit forces in the fibre direction.

The interpretation of the strength of UHMWPE in terms of the fraction of load-carrying chains is investigated in more detail in Chapter 3. The basic element of the fibrillar structure that is formed in the drawing process is the microfibril, that is thought to consist of an almost infinite sequence of crystalline blocks, interrupted by disordered domains, in which imperfections like chain entanglements are collected. In the disordered domains, the stresses are transferred by so-called taut tie molecules (TTM) that connect two consecutive crystalline domains. On the basis of our experimental data, the fraction of TTM in the disordered domains (β) is evaluated using the Takayanagi approach. A linear relation was found between the observed tensile strength of the fibre and the TTM-fraction. Interestingly, if this relation is extrapolated to a TTM fraction of $\beta = 1$, a value of 36 GPa is found for the strength of the perfect fibre. This value is in very good agreement with the theoretical strength of polyethylene as it is determined by other methods.

The results presented so far have shown that the strength of UHMWPE fibres can be adequately described in terms of the fine structure of the microfibril, i.e. on a dimensional level in the nanometer range. However, it has been observed in a wide variety of materials, including UHMWPE fibres, that the strength of a sample depends on its macroscopic dimensions, a phenomenon referred to as the size effect. Chapter 4 reports the results of an experimental study of size effects in high-strength UHMWPE fibres. Both the effects of testing length (longitudinal size) and fibre diameter (transversal size) on tensile strength have been examined. It was found that in fibres with moderate Young's moduli the strength of the fibre decreases with increasing testing length. This phenomenon is observed in almost every fibrous material, and points to the presence of a distribution of defects along the length of the fibre. This is consistent with the moderate moduli of the fibres, reflecting the structural imperfection of the material. As the modulus of the fibre increases, however, the length effects become weaker and disappear completely in high-modulus fibres. The absence of length effect can be considered as a unique material property, and demonstrates that high-modulus UHMWPE fibres are free of (macroscopic) defects. Apparently, the discrepancy between the experimental and theoretical strength

of high-modulus fibres originates from intrinsic, or microscopic, defects, as discussed in Chapter 3. It is therefore quite surprising that a relatively pronounced effect of fibre diameter on tensile strength was observed in these high-modulus fibres. A possible explanation for the diameter effect in fibres with a more or less perfect structure is given in terms of the continuum mechanics approach.

Although the short-term mechanical properties of gel-spun/hot-drawn UHMWPE fibres are excellent, the performance of the material under static loading conditions (creep) is rather poor. In Chapter 5, the general aspects of the creep behaviour of UHMWPE fibres are discussed and the possibilities of improving the creep resistance by means of chemical crosslinking are investigated. The creep behaviour of UHMWPE fibres can be regarded as a thermally activated flow process, and from the dependence of the creep rate on the applied stress it can be derived that the activated events are extremely localized (activation volumes in the order of 30\AA^3). This result suggests that creep of UHMWPE fibres is associated with a deformation mechanism in the crystalline regions of the fibre. However, it was observed that the draw ratio of the fibre, as well as the concentration of the spinning solution strongly affect the creep rate, indicating that the state of entanglement in the solid polymer also has to be considered in relation to the creep behaviour. Crosslinking experiments showed that the introduction of chemical crosslinks is only partially effective in reducing the creep rate of the fibre, and that creep cannot be completely removed upon crosslinking, even when the extent of the network formation is fairly high. This points to some kind of 'intrinsic' flow process that is not affected by the presence of crosslinks. This intrinsic flow process may very well be associated with the crystalline domains in the fibre structure. From this point of view, it will be very difficult to remove the creep of high-strength UHMWPE fibres and, at the same time, preserve the highly crystalline fibre structure and extraordinary short-term mechanical properties.

The conversion of polyethylene into carbon fibres is described in Chapter 6. Polyethylene is a low cost starting material, it has a high carbon content and can easily be converted into ductile filaments by spinning and drawing techniques. Since polyethylene has a low softening temperature, the precursor fibres need to be stabilized by means of cross-linking with chlorosulfonic acid prior to carbonization. In order to achieve a homogeneous cross-linking of the material, the precursor fibre should have a low crystallinity which is achieved by using linear low density polyethylene (LLDPE) as starting material. Previous work on the production of carbon fibres from LLDPE has shown that the diameter of the fibre has a pronounced effect on its mechanical properties. Therefore, it is necessary to obtain thin precursor filaments, which can be achieved by stretching the spinning thread at an elevated surrounding temperature. Careful carbonization of these filaments gave $17\ \mu\text{m}$ 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 $13\ \mu\text{m}$ carbon fibres, with a strength of 2.16

GPa and a modulus of 130 GPa. It appears to be necessary to anneal the hot-drawn fibres in order to remove residual stresses, introduced by hot-drawing. It is likely that the diameter effect, that is observed in fibres with diameters in the range from 13 - 55 μm 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. The presence of a sheath/core structure probably originates from the stabilization treatment which is controlled by the diffusion of chlorosulfonic acid into the LLDPE fibre.

Chapters 7 and 8 are concerned with the preparation and properties of biodegradable fibres from poly(lactides), which may find application as high-strength, resorbable suture materials. From the point of view of biodegradation rate and possible inflammatory tissue reactions, materials with a low degree of crystallinity are preferred in such applications. Fibres with a low level of crystallinity have been prepared using copolymers of L-lactide with D-lactide and ϵ -caprolactone. The preparation of fibres from polylactide networks, obtained by copolymerization of L- and D-lactide with the tetrafunctional spiro-bis-dimethylenecarbonate has also been investigated. In analogy to previous work from our laboratories concerning poly(L-lactide), copolymer fibres were prepared according to a dry-spinning/hot-drawing procedure. During dry-spinning, the low crystallizability of copolymers hinders a rapid solidification of the fibre, allowing re-entangling of the macromolecules to take place, resulting in fibres with low drawability. Spinning from poorer solvent systems resulted in fibres with an enhanced drawability, but the improvement of the maximum draw ratio is not accompanied by a similar increase in strength. The maximum attainable strength for a 80/20 copolymer of L-lactide and ϵ -caprolactone appears to be 1.05 GPa, which is about half of the maximum strength of fibres prepared from the PLLA homopolymer. The crystallinity of the copolymer fibre is about 15%.

A comparison of the drawing behaviour of semi-crystalline and completely amorphous copolymer fibres very clearly shows the importance of crystallization during drawing with respect to the achievement of orientation of the polymer chains. These results are corroborated by drawing experiments on crosslinked polylactide copolymers (Chapter 8). Hot-drawing of fibres from a linear, non-crystallizable 85/15 L-/D-lactide copolymers resulted in poorly oriented fibres, even under the optimum drawing conditions. A fibre network from 85/15 L-/D-lactide that is very lightly crosslinked with spiro-bis-dimethylenecarbonate, on the other hand, could be effectively oriented by means of hot-drawing. The maximum attainable strength for the two types of amorphous polylactide are 185 MPa and 500 MPa for the linear and the crosslinked material respectively. In the light of their mechanical properties, the amorphous, oriented fibre networks hold great promise as biodegradable suture materials.