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Short aramid-fiber reinforced ultra-high molecular weight polyethylene

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Summary

Ultra-High Molecular Weight Polyethylene (UHMWPE) is frequently used in artificial joints because of its high wear resistance. To extend the lifetime of these joints even further, it is necessary to decrease the wear rate. The wear rate may be decreased by blending UHMWPE with short aramid fibers. On account of the extremely high viscosity of UHMWPE mixing was accomplished by swirling the UHMWPE powder and the chopped fibers with compressed dry nitrogen, and a composite with fairly uniformly distributed and randomly oriented fibers was obtained by compression moulding. The failure behaviour of the composite changes from ductile for low fiber content to brittle failure for higher fiber content. The deviation of the experimental Young's modulus from the theoretical value can be explained by, among others, the void content. Preliminary results show that the wear rate of UHMWPE indeed decreases with incorporation of the aramid fibers.

Introduction

On account of the high wear resistance, Ultra-High Molecular Weight Polyethylene (UHMWPE) is highly suitable to be used as a construction material in orthopaedics for the manufacture of hip-joints and knee prostheses (1,2,3). The current clinical practice of using UHMWPE as hip-joint protheses in younger patients, with an expected lifetime more than 20 years, has generated renewed concern about the wear and durability of UHMWPE (4).

To extend the lifetime of artificial joints, it is necessary to decrease the wear rate, which in turn reduces the amount and volume of debris generated. Addition of fibers, like the aramid (Poly(p-phenylene terephtalamide) (PPTA)) fibers, to polymers is known to improve their mechanical properties, but also their tribological properties (5). According to Friedrich fiber reinforcements are most effective in the range of lower speeds, higher contact pressure, and smooth counterpart, conditions met in hip prostheses (6).

Besides its excellent wear properties, PPTA is a good candidate for use as a reinforcement in high-performance-low-weight composite materials, because of their low density, high Young's modulus, and tensile strength properties (7,8). In addition Wan et al. and Wening et al. have shown that *in vitro* the PPTA fibers show no cytotoxic or mutagenic activity (9,10).

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A disadvantage of UHMWPE is its high viscosity. It limits the possibility of filling the polymer by mixing the fibers in the melt (11). Therefore mixing was accomplished by swirling UHMWPE powder and the chopped fibers with compressed dry nitrogen. During this mixing charges were generated on both the UHMWPE powder and PPTA fibers, which seems to have an important influence on the homogeneity of the mixture and therefore on the fiber dispersion in the composite; an important factor affecting the mechanical properties. A composite with a random in-plane orientation could now be made by compression moulding the UHMWPE powder-PPTA fibers mixture.

There are a few more factors which have influence on the properties of the composite: fiber content, fiber aspect ratio, fiber orientation, void content, fiber matrix adhesion, fiber and matrix properties, and processing methods (12).

Voids in materials are an important cause of loss of strength and premature failure. Voids in short-fiber polymer composites may arise from entrapped air introduced during the compounding and processing stages inside fiber agglomerates, which are difficult to break up and to eliminate during compression moulding (13). In general, the void content increases with fiber concentration. Voids are observed even in unfilled polymers, indicating that the fiber's presence is not necessarily the only source of voids (14,15).

The modulus of composites is a bulk property and has been represented by a large number of equations. A well-known one is the 'rule of mixtures' equation (12):

$$E_c = \eta_0 E_f V_f + E_m V_m \qquad (1)$$

with E the modulus, V the volume fraction, the subscript f and m refer to fibers and matrix respectively, and η_0 the orientation factor. η_0 = 3/8 for in-plane random fiber distributions and η_0 = 1/5 for a three-dimensional random distributions.

This paper deals with the preparation of PPTA fiber reinforced UHMWPE composites and the influence of the volume fraction of fibers on the mechanical properties of the composite. This is done because before the wear resistance of the UHMWPE/PPTA composite can be determined, it is necessary to investigate the possibility of making a PPTA fiber reinforced UHMWPE composite with a homogenous fiber distribution.

Experimental

The finish of the PPTA, Twaron^R fibers, with a length of 6 mm from Akzo Nobel was removed by Soxhlet extraction in dichloromethane. The fibers were vacuum-dried prior to all experiments. The UHMWPE (HiFax 1900 from Hercules), with an average molecular weight of 4 - 10^6 kg - $kmol^{-1}$, was used as received. Dicumylperoxide (DCP, DiCup R, Hercules) was purified prior to use by recrystallization from methanol.

Mixing of the PPTA fibers with DCP was realized by dispersing the fibers in an n-hexane solution of the DCP and subsequently evaporating the solvent (16). In order to get a fairly homogenous composite, mixing was accomplished by swirling the necessary amounts of UHMWPE powder and fibers with compressed dry nitrogen (2). The composites were obtained by compression

moulding of the UHMWPE powder/PPTA fibers mixtures at 180 °C for 3 hours at a pressure of about 30 atmospheres. The samples were slowly cooled to room temperature under pressure. The fiber distribution was investigated with a Axiophot light microscope with a meeler FP 800 controller.

Tensile tests were performed on dumb-bell shaped specimens (dumb-bell shape: ASTM D1708-93, thickness 1 mm) at room temperature using an Instron (4301) tensile tester, equipped with a 5 kN load-cell, at a cross-head speed of 20 mm/min. The gauge length was 25 mm. The reported tensile data are the mean values of at least eight tests. Although the ASTM D1708-93 standard does not permit the determination of moduli, we have used the obtained values primary for the sake of comparision. The moduli presented in this paper are therefore only relative values.

The void content was calculated from density measurement. Void volume fraction was calculated from the measured density, ρ, and calculated density, ρ_c :

$$V_v = 1 - \frac{\rho}{\rho_c} \qquad (2)$$

The density of the composites were measured with the ASTM 792-91 method, with paraffin oil as liquid. The void free density of the composite was calculated from the density of the pure polymer and that of the fiber.

$$\frac{1}{\rho_c} = \frac{(1-W)}{\rho_p} + \frac{W}{\rho_f} \qquad (3)$$

with W the fiber weight fraction. The density used for PPTA fibers was $\rho_f = 1.45$. The density for UHMWPE, ρ_p, had to by determined for each composite, because this value is influenced by the weight fraction of crystallinity. The crystallinity was calculated by the heat of fusion from the melting of the crystals measured by a Perkin Elmer DSC 7 instrument. The value of 293.1 J/g is used for enthalpy of crystallizaton of 100 % crystalline polyethylene.

Scanning electron micrographs were used to observe the fracture surfaces of the composites.

Results and discussion

Mixing of the components

A proper dispersion of the fiber is necessary to achieve uniform composite properties. For instance, a cluster of short fibers, instead of uniform dispersed fibers, will only weaken the composite due to the fact that fibers on the inside of the cluster are not contributing to the properties. These clusters may even act as actual failure sites. A disadvantage of UHMWPE is its high viscosity, which limits the mixing of the polymer in the melt. Therefore blending was accomplished by swirling the UHMWPE powder and chopped PPTA fibers with compressed dry nitrogen to achieve a homogenous mixture. On account of the compressed dry nitrogen, opposite surface charges will be generated on the UHMWPE powder and PPTA fibers. This electrostatic attraction could be responsible for the coherence of the two components, leading to a uniform dispersion of the fiber, which is necessary to achieve uniform composite properties. With this method a fiber volume percent up to 30 can be achieved.

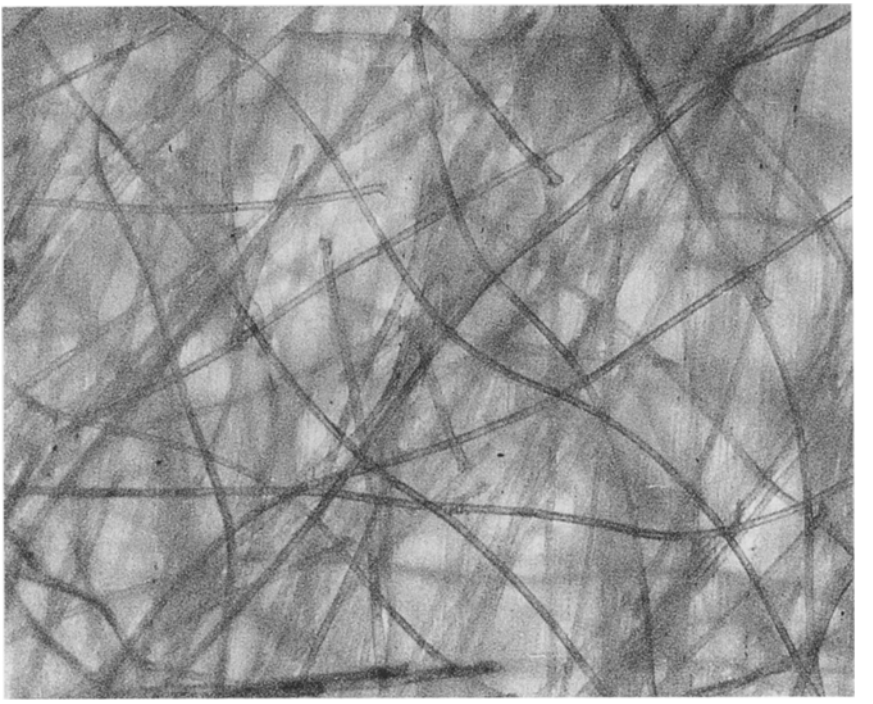

Figure 1. *Light Microscope Micrograph of 10 volume % 6 mm chopped PPTA/UHMWPE composite.*

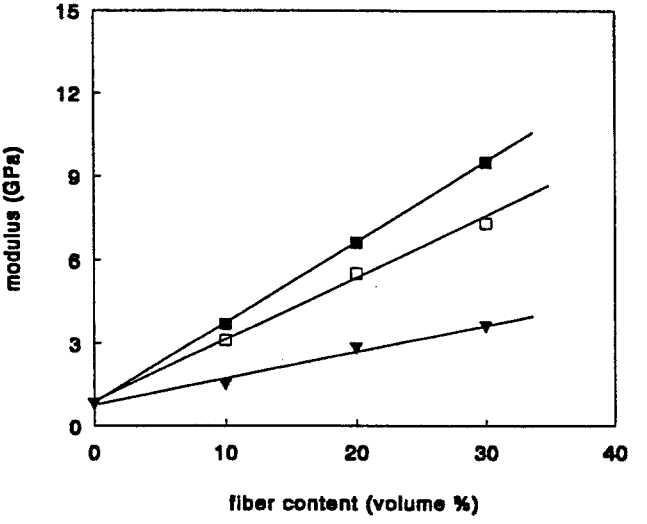

Figure 2. *The experimental (▼), theoretical (■), and modified theoretical (□) modulus vs fiber content.*

Figure 1 shows a light microscope micrograph of the 10 volume % 6 mm chopped PPTA/UHMWPE composites. It shows that the chopped fibers are fairly uniformly distributed and randomly oriented in the composite.

Mechanical properties

Composite tensile strength and modulus are dependent upon, among others, fiber distribution, fiber length, fiber content, and void content. The dependence of the Young's modulus upon the weight percentage of the fiber is given in Figure 2. The elastic modulus increases with increasing fiber content. The modulus increases with the addition of fiber because extension of the matrix is prevented by the high modulus fibers.

Figure 2 also shows the theoretical Young's moduli with increasing fiber content. The theoretical Young's moduli are calculated with the rule of mixtures (eq. 1) with $\eta_0 = 3/8$. The deviation of the experimental moduli may be explained by, among others, the presence of voids. Figure 3 shows the increase in voids concentration with fiber content. It should be mentioned that voids are observed even in unfilled compression moulded UHMWPE, indicating that the fiber's presence is not necessarily the only source of voids. Taking this void content into account, the volume of the composite can be defined as: $V_c=V_f+V_m+V_v$. Because of this volume change, the volume fractions in the rule of mixtures change to lower values, which cause lower theoretical moduli, which are also shown in Figure 2. The remaining deviation is caused by the difference in Poisson contractions of the fibers and the matrix, fiber length and fiber ends, and packing defects (12).

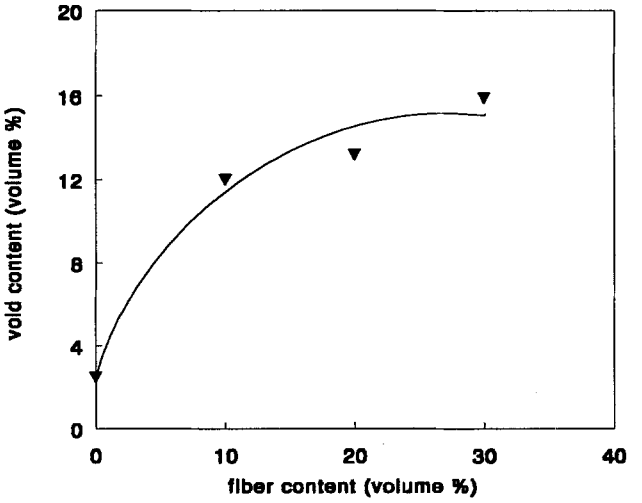

Figure 3. *Void content vs fiber content for 6 mm chopped PPTA/UHMWPE composite.*

The influence of the fiber on the ultimate and yield tensile strength is much more complex. The composites with 20 and 30 volume % 6-mm chopped fibers show brittle failure, while the other composites with the lower fiber content show a ductile failure. Figure 4 shows the stress-strain curves of the 6-mm chopped PPTA fiber/UHMWPE composites with an increasing amount of fiber. The difference in failure behaviour is obvious.

The pure UHMWPE shows a yield point, plastic deformation, and breaks at an elongation of 370 %. With the incorporation of the fibers, the plastic deformation is largely inhibited and the composites break at a lower elongation with a lower ultimate tensile strength. The composites with 20 and 30 volume % 6-mm chopped fibers show no yielding at all, but break in a brittle manner. In general, the ultimate tensile strength increases if there is adhesion between the matrix and the fiber (17). In other words, the lower ultimate strength of the composites may be caused by the low adhesion between the PPTA fibers and the UHMWPE matrix.

The yield stress appears to be very crucial since it gives information about the maximum allowable load without considerable plastic deformation. In the literature there are a lot of examples of filled polymers which show yield stress depression with increasing fiber content (18,19). This behaviour is not observed in our case. From Figure 4 it is clear that the composites show higher yield stress than the pure UHMWPE and increases with fiber content.

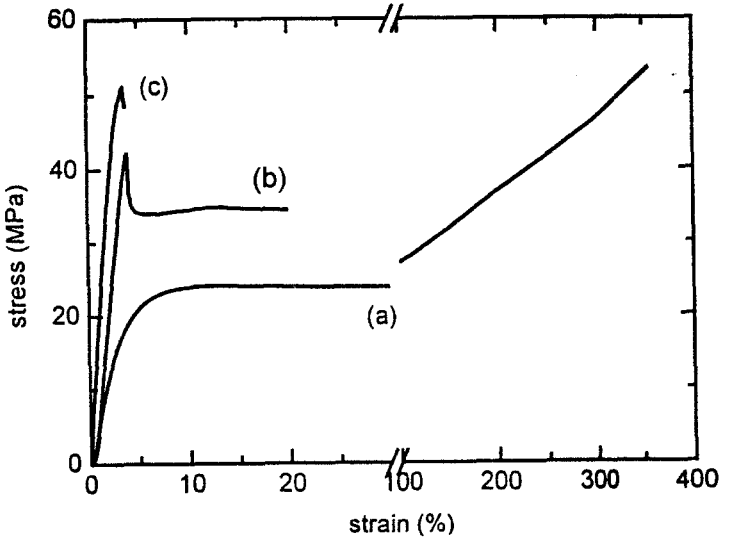

Figure 4. *Stress-strain for a) pure UHMWPE, b) 10 volume % 6 mm chopped PPTA/UHMWPE composite, and c) 30 volume % 6 mm chopped PPTA/UHMWPE composite.*

To improve the fiber-matrix adhesion, the use of dicumylperoxide (DCP) was investigated. It may be possible that the radicals formed during compression moulding abstract hydrogen from both the UHMWPE chains and the PPTA fibers. The obtained radicals may combine to give a chemical bonding between the matrix and the fiber or crosslinking in the matrix. Instead of an enhancement

of the mechanical properties a small depression is observed with the higher (0.3 weight percent) DCP content. The same tendency is observed in the pure UHMWPE (1). At a low DCP concentration the mechanical properties are not influenced much by the crosslinks reaction, but at a higher crosslink density the crystallinity of the UHMWPE drops and the Young's modulus, tensile strength and yield stress decrease. Thus in the composite the DCP causes only crosslinks in the UHMWPE matrix and no chemical bonding between the fibers and matrix.

According to Lauke, the fracture process of a short-fiber reinforced thermoplastic can be described as follows (17): for a small applied stress bonding exists along the fiber-matrix interface. With increasing load the shear stress at the interface increases, and at a critical point debonding starts at the fiber tips and propagates along the fiber sides. As a result of friction and adhesion, sliding at the broken interface may be inhibited until a higher stress is achieved. By initiation of the sliding processes, that part of the external load which is transmitted to the fibers is diminished. The matrix, which is not restrained by the fibers, carries a larger part of the load, and it is capable of larger deformations, and begins to flow. Figure 5 shows the fracture surface of the 10 volume % 6-mm PPTA fiber/UHMWPE composite. This fracture surface clearly shows plastic deformation of the UHMWPE matrix and clean fibers from which the matrix is completely debonded. In the case of the 20 and 30 volume % fibers no plastic deformation of the UHMWPE matrix is observed because of the brittle fracture.

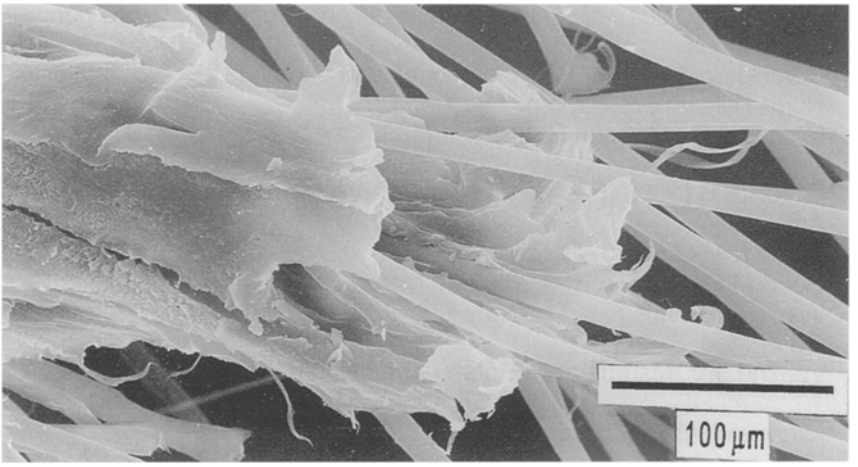

Figure 5. *SEM-micrograph of the fracture surface of 10 volume % 6 mm chopped PPTA fiber/UHMWPE composite.*

Conclusions

This study clearly indicated that it is possible to make a short-PPTA fiber/UHMWPE composite with fairly uniformly distributed and randomly oriented fibers by mixing the UHMWPE powder and chopped PPTA fibers by compressed dry nitrogen. The failure behaviour of the composite changes from ductile to brittle by increasing fiber content. The Young's modulus and yield stress of the

composite increase with incorporation of the fibers. The lower ultimate tensile strength of the composites compared with the pure UHMWPE indicates that there is no good adhesion between the PPTA fibers and UHMWPE matrix. It seems that the use of DCP has no influence on the adhesion. It only introduces crosslinks in the UHMWPE matrix.

The deviation of the experimental modulus from the theoretical value can be explained by, among others, the presence of voids. To eliminate the voids a higher temperature and pressure is necessary during processing. Other factors which causes the deviation are the differences in Poisson contractions, fiber length, fiber ends, and packing defects. This suggests that a higher modulus may be observed if the mixing of the chopped PPTA fibers and UHMWPE can be improved.

Preliminary results shows that with a pin-on-disk method the wear rate of UHMWPE indeed decreases with the incorporation of the short PPTA fibers. Further studies are necessary and will be published in the near future.

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References

1 de Boer J (1984) PhD thesis, University of Groningen, Groningen, The Netherlands
2 Wevers R (1984) MSC thesis, University of Groningen, Groningen, The Netherlands
3 Dumbleton J H (1981) Tribology of natural and artificial joints. Elsevier, North-Holland Amsterdam
4 Cooper J R , Dowson D, Fisher J (1993) Wear 162-164: 378
5 Vishwanath B, Verma A P, Kameswara Rao C V S (1993) Wear 167: 93
6 Friedrich K (1986) Friction and wear of polymer composites. Elsevier Amsterdam
7 Northolt M G (1980) Polymer 21: 1199
8 Dobb M G, Robson R M (1990) J. Mater. Sci. 25: 459
9 Wan H, Williams R L, Doherthy P J, Williams D F (1994) J. Mater. Sci. Mater.Med. 5: 441
10 Wening J V, Marquardt H, Katzer A, Jungbluth K H (1995) Biomater. 16: 337
11 Minkova L (1994) Colloid Polym. Sci. 272: 115
12 Hull D (1981) An introduction to composite materials. Chan R W, Thompson M W, Ward I M, eds. Cambridge University Press, Cambridge
13 Vaxman A, Narkis M, Siegmann A, Kenig S (1989) Polym. Comp. 6: 449
14 Matsuka S (1961) J. Appl. Phys. 32: 2334
15 Barnetson A, Hornsby P R (1995) J Mater. Sci. Let. 14: 80
16 Posthuma de Boer A, Pennings A J (1976) J. Polym. Sci. 14: 187
17 Akin-Öktem G, Tinçer T (1994) J. Appl. Polym. Sci. 54: 1103
18 Akin-Öktem G, Tinçer T (1993) J. Mater. Sci. 28: 6313
19 Chacko V P, Farris R J, Karasz F E, (1983) J. Appl. Polym. Sci. 28: 2701
20 Lauke B, Schultrich B, Barthel R (1985) Comp. Sci. Techn. 23: 21