Dispersion of pristine CNTs in UHMWPE solution to prepare CNT/UHMWPE composite fibre

X. Y. Hao*,1,2, A.-T. Chien2, X. Y. Hua3, J. Lu4 and Y. D. Liu2

Carbon nanotubes (CNTs) dispersion in polymer matrices uniformly remains a challenge. Uniform dispersion of CNTs within ultra high molecular weight polyethylene (UHMWPE) solution is the first step to achieve CNT/UHMWPE fibres with excellent properties. Several approaches have been tried. Composite powder was acquired by coating CNTs on UHMWPE powder, then, dissolved in decalin, through gel spinning, higher stronger composite fibre is fabricated.

Keywords: CNT, UHMWPE, Composite fibre

Introduction
Ultra high molecular weight polyethylene (UHMWPE) fibre has been used in a wide and ever increasing range of applications such as personal and vehicle ballistic protection, cut-resistant gloves, apparel and ropes. However, the highest strength of the commercial UHMWPE fibre only reaches 10% of its theoretical value.

CNTs are excellent candidates for producing composite fibres due to unique combination of properties: high modulus, high tensile strength, large aspect ratio, flexibility and resilience, and chemical stability. CNT/polymer composite fibres have potential applications in structural composites used in civil, automobile and aerospace industry. UHMWPE is non-polar polymer, which is difficult to be combined with pristine CNTs. In order to enable them to combine, chemically or physically modified CNTs have been used to reinforce various fibers, and shows property improvements. But these methods can not give full play to the reinforcing effect of CNTs. Compared with CNTs modified by acid, a graft modification and coupling agent etc, better result can be expected by using un-modified CNTs, since grafted functional groups or usage of third agent are detrimental to CNTs template effect which induce highly aligned molecular chains in its vicinity. Our strategy is to use pristine CNTs to template the orientation of UHMWPE chains to achieve better tensile properties.1-12 The research activities mainly focus on approaches that are practically feasible to disperse CNTs.

Experimental procedure

Materials
The CNTs used in this study were multiwall carbon nanotubes with diameter of 20–30 nm and length of 30–40 μm, which were kindly provided by Professor Fei Wei’s group of Department of Chemical Engineering, Tsinghua University. UHMWPE with diameter of 80 μm, was purchased from Beijing No.2 Assistant Plant.

Solution
CNTs were added to o-dichlorobenzene (DCB). Ultrasonic treatment was applied to obtain a homogeneous distribution of CNTs with concentration of CNTs 80 mg/1 L DCB. In a three-necked flask equipped with an overhead mechanical stirrer and Liebig condenser assembled for reflux and heated to 130–170°C to obtain a 2%UHMWPE-0.5%antioxidant (di-butyl-p-cresol)-decalin solution. (All blend ratios described in the text relate to weight ratios of gross weight.) To prevent degradation of UHMWPE, the solution was carried out under nitrogen. CNTs-DCB solution was subsequently added to the UHMWPE-decalin solution. The excess amount of solvent was evaporated by vacuum distillation at 120°C, while stirring, to obtain the desired solution concentration of 2%UHMWPE.

Gel spinning
As soon as the UHMWPE solution was transferred into an extruder, which was preheated to 135°C, the spinning process started. The extruded UHMWPE passed through an air gap, then, entered an ice water pool for gel spinning. Then the spun fibre was passed through hexane bath to remove decalin at room temperature. The spun fibre was hot drawn by passing through silicon oil with 130 and 140°C respectively.

Coating
UHMWPE particles and CNTs were mixed by triple abrader for 8 h to form CNT/UHMWPE composite
particles. Then were dissolved in decalin, gel spun, and hot drawn as above.

Results and discussion

The best solvent for CNTs is DCB, with solubility of 95mg CNTs per litre DCB. CNTs do not dissolve in decalin, which is best solvent for UHMWPE gel spinning. DCB dissolves mutually with decalin. But aggregation of CNTs appears, when CNT/DCB solution is drop-wisely added into UHMWPE/decalin solution with temperature ranging from 90 to 180°C (Fig. 1). It is hard to disperse CNTs in UHMWPE without acid or a graft modification methods, because, at high temperature (above 80°C), CNTs separates out from DCB, or N,N-Dimethylformamide (DMF) solution, etc. While UHMWPE gels from decalin or DCB below 100°C.

In order to solve phase separation, DCB was used instead of decalin. DCB, antioxidant and UHMWPE powder were mixed together in a reactor at 150°C, with nitrogen (N₂) protection to get UHMWPE/DCB solution with concentration of 2% UHMWPE. CNT-DCB solution was added drop by drop into UHMWPE/DCB solution, along an insertion horn of sonication below the upper level of UHMWPE/DCB solution. The process lasted about 10–30 min until the solution became homogeneous. But the viscosity of the solution was too low to draw fiber. The reason is that the sonication or DCB leads to degradation of UHMWPE.

From our previous study, DCB is not a good solvent for gel spinning. Therefore, we try to avoid using DCB. UHMWPE particle and CNTs were mixed by triple abrader with a treatment time of 6 h to form CNT/UHMWPE composite particles. CNTs disperse uniformly on surface of UHMWPE powder without being cut short. After the composite particle is dissolved in decalin, we can see that CNTs disperse optically uniformly (Fig. 2). We can see CNTs disperse well under microscope (Fig. 3) as well. From reactor, composite fiber can be drawn out directly, with higher strength (Fig. 4).

By gel spinning and hot drawing, composite fibre with diameter of 18-8 μm is gotten (Fig. 5). By regulating epitaxial growth of UHMWPE on pristine CNTs surface, nano-hybrid shish-kebab (NHSK) with CNTs shish and UHMWPE kebab can be grown. This type of nanostructure can significantly improve interfacial interaction between fillers and polymer matrix. So reinforcement potential of nanofillers with high aspect ratio (L/D) can be realised. Under further stretching, kebab of
UHMWPE will be transformed into highly extended chains along with fiber axis. Post-spinning hot drawing process enhances orientation, exfoliation and the mechanical properties of the CNT/UHMWPE composite fibre. We will take further steps to improve the exfoliation of CNTs in UHMWPE and carry out tensile strength test of composite fibre later.

Based on our research, we believe that coating approach can be used for CNT/Kevlar and other composite fibres as well. The research results can be further expanded to achieve industrialisation.

Conclusions

By triple abrader process, composite particles with core (UHMWPE)-shell (CNTs) structure is produced. The coating method is an effective way to achieve uniform dispersion of pristine CNTs in solution of UHMWPE. CNTs initiate UHMWPE crystallisation to form nano-hybrid shish-kebab structure. Pristine CNT/UHMWPE composite fibre is fabricated by gel-spinning and hot draw process.

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References