

MULTIWALL CARBON NANOTUBE REINFORCEMENT OF POLYACRYLONITRILE FIBERS

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Introduction

Aligning multiwall carbon nanotubes (MWNTs) with the direction of load is desirable for maximizing tensile reinforcement in composites. This has been accomplished by spinning composite fibers containing MWNTs[1]. The shear and elongational flow fields inherent to fiber processing cause the MWNTs to align with the fiber axis. Efficient stress transfer from the matrix to the MWNTs is also a crucial component for maximizing reinforcement. In an effort to address both of these issues, this paper reports the use of functionalized MWNTs as aligned reinforcing nano-fibers in a polyacrylonitrile (PAN) fiber matrix with the goal of producing carbon/MWNT composite fiber with enhanced physical properties. A variety of chemical vapor deposition derived MWNTs have been previously evaluated as reinforcement including: as-produced MWNTs (used as harvested from the reactor substrate) and graphitized MWNTs (heat treated to 2800°C under flowing He)[1], but recent emphasis has been placed on improving the interfacial adhesion of the PAN matrix to the embedded MWNTs through chemical modification of the MWNT surface. Investigation is focused on the use of methacrylate functionalized MWNTs which have been copolymerized with acrylonitrile (mispMWNTs) as reinforcement in PAN/MWNT composite fiber.

Experimental

Surface Treatment

The mispMWNTs mentioned above, underwent a series of chemical treatments prior to composite fiber processing. An initial oxidation of the surface of the MWNTs was carried out via Fenton's reaction or a short ball-milling procedure in the presence of KOH. The hydroxyl functionalities bonded to the nanotubes were then reacted with methacryloyl chloride to attach methacrylate groups to the MWNT surface. In a final step, acrylonitrile was polymerized in-situ with these methacrylated MWNTs to copolymerize PAN oligomers to the nanotube surface as depicted in Figure 1. It is expected that the attachment of the PAN chains to the MWNTs will not only significantly improve bonding between the nanotubes and the bulk PAN matrix, but have the additional benefit of enhancing the dispersion of the MWNTs in the carrier solvent, dimethylacetamide (DMAc) in which PAN is soluble.

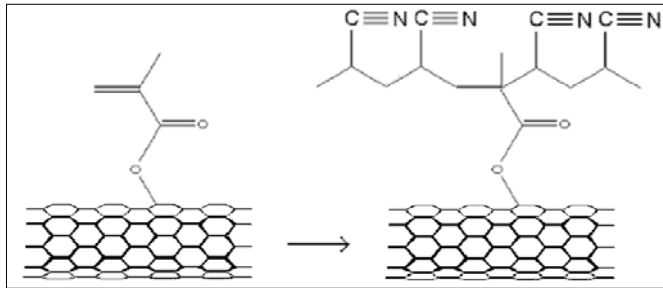


Figure 1. Free radical polymerization of acrylonitrile and simultaneous copolymerization of the methacrylated MWNTs into the PAN.

Processing

The mispMWNTs were dispersed in DMAc using ultrasonic energy. Subsequently sufficient PAN powder was added to yield the required concentration of mispMWNTs in the final fiber. The amount of DMAc present was controlled to produce a 20 wt.% PAN solution after dissolution. This dispersion was then transferred to a 10mL glass syringe and heated to 140°C for 15-25 min to dissolve the PAN. The resulting spinning dope was spun into fiber using a purpose designed, laboratory scale dry-jet wet spinning apparatus shown in Figure 2[1].

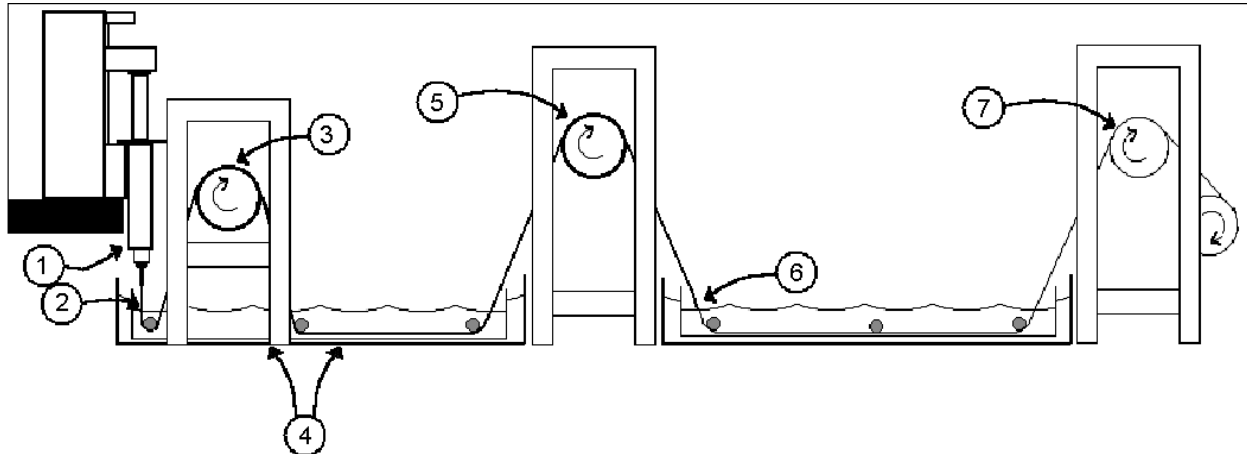


Figure 2. 1. Extrusion 2. Drawdown 3. Initial Take-Up 4. Coagulation 5. Secondary Take-Up 6. Hot Stretch 7. Final Take-Up

The resulting mispMWNT/PAN composite fibers were characterized via light and electron microscopy and by single fiber tensile testing (ASTM D3822-96). Tows of each were also stabilized in air under constant length by slowly heating to 300°C followed by carbonization under flowing N₂ up to 1450°C. These composite carbon fibers were characterized by single fiber tensile testing (ASTM D3379-75).

Results and Discussion

Spinning composite dopes of MWNTs dispersed in a PAN solution was greatly facilitated by attaining a truly homogeneous dispersion of the MWNTs. The

mispMWNTs displayed superior dispersibility and dispersion stability in comparison to untreated MWNTs. Ink-like dispersions were achieved at up to 2.7 wt.% mispMWNTs in DMAc by ultrasonically dispersing the mispMWNTs into the DMAc prior to the addition of PAN powder. These superior dispersions have greatly facilitated composite fiber processing and fiber homogeneity. Fiber spinning of concentrations of > 10 wt.% mispMWNTs in PAN appear possible.

Currently, for the PAN fibers reinforced with mispMWNTs, significant changes in yield and break strength are not occurring indicating the need for higher volume fractions of nanotubes in the fibers. The existence of a critical volume fraction of nanotubes to prevent matrix failure and impart strengthening is being explored[2]. Increases in modulus are occurring in a linear fashion, but do not follow a rule of mixtures or Halpin-Tsai trend for a $E_{\text{MWNT}} = 1\text{TPa}$ and a mispMWNT aspect ratio > 100. In fact the data fit these models for $E_{\text{MWNT}} = 0.085\text{TPa}$, which is approximately an order of magnitude below predicted and measured MWNT moduli values[2]. This indicates imperfections in the interfacial bonding or interfacial slippage at low strain, and underlines the need for further optimization of the PAN-nanotube interface. Nevertheless a 27% improvement in modulus was observed at a 5 wt.% mispMWNT concentration.

Beyond the elastic deformation region, the effect of mispMWNTs on the flow curves of the composite PAN fibers is quite different from that produced by the inclusion of as-produced or graphitized MWNTs. The strain-hardening of PAN fibers under plastic flow follows a quadratic dependence on the strain as the PAN chains extend and align. The addition of as-produced or graphitized MWNTs caused an increase in the break strain and lowered the rate of strain hardening, leading to increases in toughness of these fibers[1]. This is similar to that reported in ultra-high molecular weight polyethylene films reinforced with MWNTs[3]. With increasing mispMWNT loading, the opposite effect was observed. Decreases in break strain at constant break stress indicated higher resistance to plastic flow, probably due to an increased hindrance of the PAN chains to plastic flow. Examination of the fracture surfaces of the fibers containing mispMWNTs indicated that good wetting of the nanotubes was achieved, manifested by the presence of a polymer sheath coating the mispMWNTs, as well as a balling up effect[4] of the PAN matrix on the protruding mispMWNTs as shown in figure 3.



Figure 3. SEM micrograph of a fracture surface of a 5 wt.% mispMWNT/PAN composite fiber showing the 'balling-up' effect on the nanotube surface

Carbon fibers produced from the mispMWNT/PAN polymer fibers by thermal processing all displayed a reduction in break strength and break strain compared to unfilled carbonized PAN fibers. During carbonization radial shrinkage of the carbonizing matrix led to some protrusion of nanotubes through the fiber surface, and a general increase in the surface roughness of the fiber. This caused premature failure of the composite fibers. Efforts are underway to optimize composite fiber carbonization to minimize defects.

Conclusions

Obtaining optimal reinforcement of PAN fibers and subsequent carbon fibers using MWNTs remains a challenge. The use of mispMWNTs has led to markedly improved dispersion of the MWNTs allowing for more homogeneous and facile fiber processing at increasing concentrations of MWNTs. Less than predicted, but continuous increases in elastic moduli of the composite fibers indicate further need for interfacial optimization and understanding. Shortcomings in composite fiber strengthening indicate the need for higher volume fractions of aligned nanotubes in the composite fibers. Processing of higher concentrations of MWNTs into a composite fiber with minimal fiber defects is the current goal of this research, and it has been shown that chemical modification of the MWNTs is a step in the right direction.

References

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