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Compressional Behavior of Carbon Nanotube Reinforced Mesophase Pitch-based Carbon Fibers

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Abstract: The tensile-recoil compressional behavior of the carbon nanotube reinforced mesophase pitch (MP)-based composite carbon fibers (CNT-re-MP CFs) was investigated by using Instron and SEM. The CNT-re-MP CFs exhibited improved, or at least equivalent, compressive strength as compared with commercial MP-based carbon fibers. Particularly, when CNT of 0.1 wt% was reinforced, the ratios of recoil compressive strengths to tensile strength of CNT-re-MPCFs were much higher (the difference is at least 10 % or higher) than those for the commercial counterparts and even than those for PAN-based commercial carbon fibers. FESEM micrographs showed somewhat different fractography from that of a typical shear failure as the CNT content increased.

Keywords: Carbon fibers, Carbon nanotubes, Mixing, Scanning electron microscopy, Fracture

Introduction

High performance fibers, such as high modulus and high strength carbon fibers (HMHS CFs) and aramid fibers, have been widely used as reinforcements for composites. However, their poor compressional strength, which is usually one-tenth to one-fifth of their tensile strength, has been a detrimental factor limiting their wider applications. Much effort has thus been expended to overcoming such a drawback by studying the relationship between compressive failure mechanism(s) and microstructure(s) of HMHS CFs [1]. It has been argued that internal pores plays an important role in compressive failure of HMHS CFs because the pores provide space for microbuckling, which leads to compressive failure [2-4]. It was thus suggested that the removal of pores or the filling of pores with some kind of epitaxially grown crystallites or nano-reinforcements might be effective for the improvement of compressive strength of HMHS CFs [5].

In a recent study [6], it has been reported that carbon nanotubes (CNTs) could be incorporated into mesophase pitch to form CNT reinforced, mesophase pitch-based carbon-fibers (CNT-re-MPCFs). CNTs have been generally recognized as promising reinforcements for polymer or carbon matrices due to their superior mechanical properties [7-11]. Therefore, we were interested in determining if there was any improvement in the compressional performance of these CNT-re-MPCFs in which nano-sized reinforcements are dispersed in micron-sized carbon matrices. It would also be interesting to see how the fracture surfaces resulting from compressive failure are influenced by the CNT reinforcements. Thus, we first report the tensile-recoil compressional behavior of the CNT reinforced mesophase pitch (MP)-based composite carbon fibers (CNT-re-MP CFs). Then, the compressional fractography is examined and discussed in comparison with that for the conventional MP-based carbon fibers.

Experimental

Carbon nanotube reinforced mesophase pitch-based carbon-fibers (CNT-re-MPCFs) were prepared by a method described in detail in an earlier study [6]. A synthetic mesophase pitch (AR-HP grade, Mitsubishi Gas Chemical Company: $T_{softening} \approx 270\,^{\circ}C$) was intensively mixed with multiwalled carbon nanotubes in concentrations ranging from 0 to 0.3 wt% using a Brabender intensive mixer (285 °C under nitrogen gas flow for 10 min). The solidified mixture was transferred to a spinning apparatus consisting of an extruder fitted with a 12-hole spinnerette having capillary diameters of 150 μm. Fiber samples were coded as S0, S1, and S3 corresponding to the CNT content of 0, 0.1, and 0.3 wt%, respectively. The as-spun fibers were oxidatively stabilized at 290 °C for 7 h to render them infusible, and then subsequently carbonized at 2400 °C in helium atmosphere. For tensile-recoil compression test, individual fibers were mounted on card-holders of the 5 cm gauge length and extended in an Instron to the desired tensile stress level. The individual fiber was then cut at the center of the gauge length so that both halves of the fiber recoiled naturally, and then were either broken or remained intact depending on the applied stress level. The critical compressive strength for a given type of fiber was determined

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Table 1. Comparison of mechanical performances between experimentally developed CNT-re-MP CFs and commercially available PAN- and MP-based carbon fibers

	Precursor	Code	Diameter (μm)	Tensile strength (GPa)	Recoil compressive strength (GPa)	Recoil/tensile (%)	Ref.
Experimental	MP-based	S0	14.4 ± 0.04	2.3 ± 0.3	0.5 ± 0.1	22	
		S1	8.1 ± 0.03	2.5 ± 0.3	1.0 ± 0.1	40	
		S3	12.0 ± 0.04	1.3 ± 0.4	0.4 ± 0.1	31	
Commercial	MP-based	P-55	10.3	2.1	0.5	24	2
		P-75	9.7	2.0	0.5	25	
		P-100	9.8	2.2	0.4	18	
	PAN-based	M40J	5.2	4.9	1.0	20	4
		M50J	5.2	4.3	0.7	16	
		T800H	5.0	6.4	1.6	25	
		T1000	5.0	7.1	2.2	31	

for 25 samples as the average stress at 50 % breakage-probability from the plot of the applied stress vs. breakage-probability [2]. After recoil, both halves were carefully collected and examined under a field emission scanning electron microscope (FESEM, JEOL JSM-6330F, Japan), operated at 5.0 kV and about 12.0 μA to study the compressive fractography.

Results and Discussion

Table 1 contrasts the measured compressive strengths of the experimental fiber samples with the reported tensile-recoil compressive strengths of some commercially available PAN- and MP-based carbon fiber samples, together with their tensile strengths and fiber-diameters. It is interesting to note that the compressive strengths of the experimental fibers, CNT-re-MPCFs, are improved, or at least equivalent, as compared with commercial MP-based carbon fibers. Moreover, it is noteworthy that the ratios of recoil compressive strengths to tensile strength of CNT-re-MPCFs are much higher (the difference is at least 10 % or higher) than those for the commercial counterparts and even than those for PAN-based commercial carbon fibers. Amongst the experimental fibers, S1 exhibits the best performance in both tensile and compression modes. This suggests that there is some reinforcing effect of CNTs as well as the thin diameter effect, and that there could be an optimum concentration of CNTs.

Figure 1 shows fracture surfaces after tensile-recoil compression of CNT-re-MPCFs. It was observed that S0 and S3 fibers exhibit fractographic features typical of shear failure, but S1 fibers exhibit somewhat different features. That is, the fracture surface of S1 fiber is formed obliquely with much corrugated surface morphology and shallower angle to the cross-section. In contrast, the fracture surfaces of S0 and S3 form an angle of 45° to the fiber axis, which is typical of shear failure.

The shear failure mechanism has typically been reported for commercial MP-based HMHS carbon fibers, but buckling failure mechanism that results in stepped or rather corrugated fracture surfaces is more common for PAN-based HMHS carbon fibers [2]. It has been argued that this different failure behavior is responsible for the higher compressive strength of PAN-based carbon fibers than that of MP-based carbon fibers. However, in the case of S1 samples, Figure 2 clearly shows that the compressive failure occurs with a long axial splitting of carbon stacks, which leads to the formation of the corrugated and stepped fracture surface.

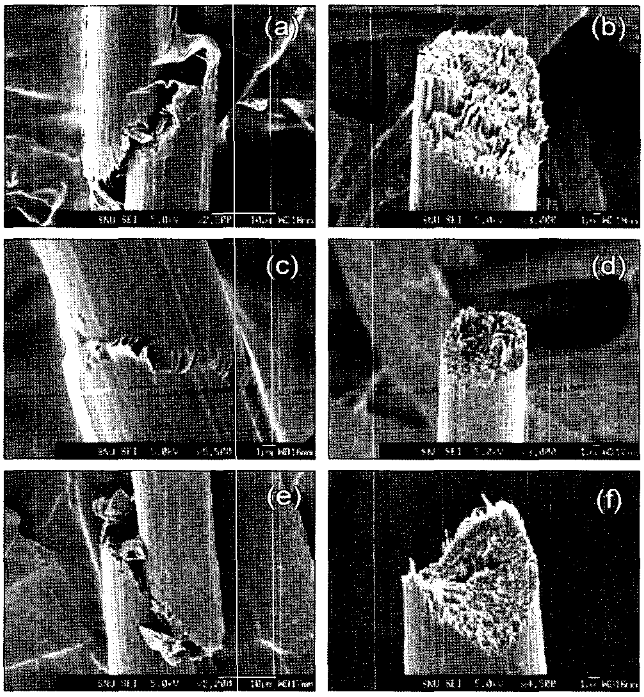

Figure 1. FESEM micrographs to show fracture surfaces of carbon fibers collected after recoil compression test: S0 fibers ((a), (b)), S1 fibers ((c), (d)), and S3 fibers ((e), (f)).

This type of combined deformation of typical shearing

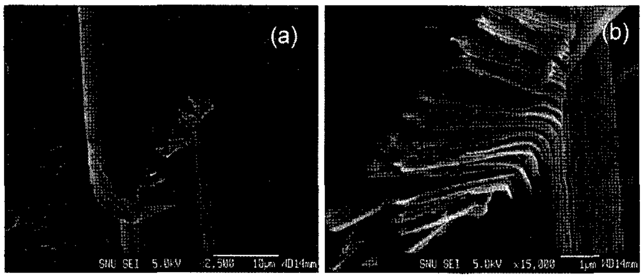

Figure 2. FESEM micrograph to show fracture morphology of S1 fiber.

accompanying long axial splitting may explain why S1 exhibits the highest compressional strength, the highest ratio of recoil compressional strength to tensile strength, and highly corrugated and axially splitted fracture surface with shallower angle to the cross-section. It may be too early to draw some definite conclusion on the role of CNTs in S1 fibers during recoil-compression, but it can be speculated that CNTs are at least deterring an abrupt shearing that leads to an early failure, by inducing long axial splitting to dissipate the deformation energy. However, it is not clear at this stage which one precedes the other between shearing and axial splitting. It is noteworthy at this stage that S3 fibers containing 0.3 wt% CNTs still exhibit improved ratio of recoil compressional strength to tensile strength even though they show a typical shear failure. This observation suggests that the CNT reinforcements definitely play a role in improving compressional strength of MP-based carbon fibers. But, if the amount of CNTs increases over some optimal amount, then their contribution to the improvement of compressional strength becomes less, and such carbon fibers fail by typical shear failure. This may imply that CNTs tend to orient along the crystallites in carbon matrix so that the overall failure mechanism is governed by the highly oriented crystallites, but CNTs act as a kind of energy splitter or dissipater along the fiber axis.

Conclusion

It was found from this work on the tensile-recoil compressional behavior of the carbon nanotube reinforced mesophase pitch-based composite carbon fibers (CNT-re-MP CFs) that the CNT-re-MP CFs exhibited improved, or at least equivalent, compressive strength as compared with commercial MP-based carbon fibers. Amongst the experimental fibers, S1 fiber (CNT content of 0.1 wt%) exhibited the best performance in both tensile and compression modes. The fracture surface of S1 fiber was formed much corrugated surface morphology and shallower angle to the cross-section than the typical shear failure angle. These observations suggest that the CNTs tend to orient along the crystallites in carbon matrix and act as a kind of energy splitter or dissipater along the fiber axis. But, if the amount of CNTs increases over optimal amount, their contribution to improving compressional strength becomes less, and such carbon fibers fail by a typical shear failure.

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