

NANOTUBE REINFORCED POLYMER COMPOSITES

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Introduction

Fibrous materials have long been used as ballistic improvement components. Silk, Kevlar, Nylon, polyester, polypropylene and glass fibers have been used as one main ballistic improving component. The fibers are mixed with 10-20% binder, usually a network-forming polymer [1,2]. Most of the ballistic protective strength is due to the fibers while the polymer is the binding entity that provides structural stability. Bulk thermoplastics, as well as glass fiber and ceramic [3] reinforced thermoplastics are also utilized as ballistic materials. Thermoplastics show in general lower ballistic resistances than the fibrous materials.

To better design materials with superior ballistic properties, it is primordial to know what are the factors that will affect the ballistic resistance of materials. Stiffness, transition temperatures, thermal stability, molecular weight, compatibility, and sensitivity to humidity are few factors that may affect these properties [1,2].

At the macroscopic level processing methodology also affects the ballistic resistance of these materials. It is also crucial to know the effect of the impacting projectile on the reinforcing fillers and the binder. Kevlar shows superior behavior after impact, the fibers subdivide, while most of the other fibers brake due to their brittleness or heat instability.

Correlating the structure versus properties of a polymer can be beneficial in designing a material with high ballistic resistance. The bonding along the macromolecules, such as covalent bonding, their strength, their length, their intermolecular interactions such as polar, non-polar or hydrogen bonding are perceived to be important. This depends on the functional group present along the backbone of the polymers. Stiffness is improved by cyclic and aromatic substituents while long aliphatic chain will improve their flexibility. The thermal properties are also altered by functional groups. It is well known that thermal oxidative stability is increased by aromatic groups and decreased by aliphatic groups. The interactions, between the filler and the polymer matrix, are one of the determining factors; high interactions and miscibility have the potential to lead to impressive improvements. Protection of the armor from the environment is also an

important factor, certain fibers are very sensitive to humidity, and this will affect negatively their ballistic protective properties [1,2]. All of the above properties such as the strength of covalent bonds, the intermolecular interactions between filler and the matrix, and their thermal properties will affect the physics of the impacting projectile [4,5].

The intent of this program was to develop nanotube-polymer composites with superior ballistic protective properties. The unusual properties [6] of carbon nanotubes suggest their light weight, their ease to functionalize [7-10], their rigidity and stability to high temperature and moisture might provide an advantage over currently used fibers as reinforcer for thermoplastics. Nanotubes (multi-wall nanotubes (MWNT's), and double-wall nanotubes (DWNT's), are promising prospects as active constituents for high strength materials and other applications. It is well known that in order to be useful and processed into armors, the nanotubes may require chemical functionalization to achieve homogenous blending and compatibility with the polymeric matrix.

The primary polymer selected was polycarbonate [11], one of the most used transparent ballistic armor materials [2,3]. To better understand the mechanism of interaction, or binding process between the two components, a series of polycarbonates were investigated. The polycarbonates with viscosity number varying from 39 to 67 cc/g, for low molecular weight to high molecular weight polymers, respectively, were investigated. Polydicyclopentadiene [12] and polyurethane, two network forming binders, are also investigated, cross-linking may consolidate fibrous materials that have potential for ballistic applications. Composites were produced by dispersing the as-grown nanotubes and functionalized nanotubes in the above polymer matrices to compare their structural integrity and ballistic protective properties. Well-aligned nanotubes in polymer thin films and composites were also produced.

Experimental

The nanotube polymer composites were prepared by dispersing the nanotubes in a solvent (dichloromethane) or in the monomer (dicyclopentadiene) prior to adding the polymer solution or the initiator, respectively. The

polymer dispersions are poured into a container, covered until the excess solvent is evaporated. The polycarbonate films obtained, are cut into small pieces, dried in a vacuum oven and pressed at 280°C and either 6000 psi or 18, 370 psi. While the paste obtained with the polyurethane is melted, mixed with the melted curing agent, pressed at 70psi in a mold, and heated at 50°C for 20 minutes then at 115°C for 19 hours. The nanotube-dicyclopentadiene dispersion is protected with a blanket of nitrogen, and a ROMP ruthenium catalyst is added to polymerize the mixture to the desired shape. Thin polymeric films with aligned nanotube are obtained by coating the aligned as-grown nanotubes with a diluted polymer solution. The films are dried and cut into 1 in. x 1 in. squares, which are placed in a mold and melt-pressed at 255°C and 5500 psi. Functionalization of the nanotubes is conducted in aqueous media in the presence sodium hypochlorite, followed by acid treatment to yield the polyhydroquinone nanotube adducts. The latter is modified to the polyimine adducts by action of thionyl chloride and a primary amine. The modified nanotube adducts were characterized by FTIR, SEM and TEM. Cylindrical specimen composites were tested mechanically and ballistically.

Results and Discussion

Since the dispersion stability is a prime factor for the production of uniform homogeneous nanotube-polymer composites with high quality properties, most of the dispersion of non-modified nanotubes in dichloromethane, dicyclopentadiene, polycarbonate and polyurethane oligomer solutions in dichloromethane, are stable as long as continuous stirring or sonication is maintained. The amount of nanotubes dispersed in the polymer range from 9% to 50% concentration by weight. Dicyclopentadiene polymerized completely at the boundaries of the mold while at the center only partial polymerization occurred when large amount of nanotubes and the use of retardant are used. Metallic impurities also affected negatively the polymerization of dicyclopentadiene. This inhibition was alleviated when larger mold, magnetic stirring and small amount of solvent were used. However functionalized nanotubes, polyimine (Figure 1) nanotube adducts with long flexible group, are the exception. They formed stable solutions in dichloromethane and homogeneous dispersion in polymers. Oxidation of the nanotube (Figure 1) alone did not improve their solubility in dichloromethane. The functionalized nanotubes (Figure 2b-d) were completely open, when both processes, sonication under high power, and oxidation at ambient temperature are conducted consecutively. Sonication alone at high power in dichloromethane did indeed open the tube completely (Figure 2b). One can not tell exactly if the opening occurred at the end of the nanotubes or in the middle by

TEM. But when the oxidation is conducted alone, opening of the end are very selective and partial opening occurred (Figure 2c). One can adjust the time and the oxidant concentration to control the opening of the tubes.

Uniform dispersion of nanotubes in these composites is only one criterion; however, good miscibility and strong adhesion between the nanotubes and the polymeric matrices are also prime factors for achieving improved mechanical properties. It was found those composite properties, attributed to improved bonding between the matrix and the nanotube improved sharply when low molecular weight polycarbonates were used in figure 3. A 180% improvement in compressive strength was achieved for the composite (at 10% nanotube content) made from the lowest molecular weight polycarbonate relative to the non-filled polymer, while properties deteriorated in some higher molecular weight polycarbonates when nanotubes were added. The strength of the polycarbonate composites was further increased by combining low molecular weight polymer (Figure 4), and by increasing the nanotube content up to 40%, figure 5. Chemical modification of the nanotubes did indeed improve miscibility, uniformity of dispersion, by introducing long alkyl groups, but did not affect the compressive strength of high molecular weight polycarbonates.

The nanotube-polycarbonate composites had superior ballistic resistance than the virgin polycarbonates in these preliminary tests. Alignment of the nanotubes (figure 6) in the polymer provided even greater ballistic resistance properties than the randomly dispersed nanotubes. However the nanotubes did not provide any improvement for the polycyclopentadiene and the polyurethane in these preliminary tests.

Conclusion

Based on the limited tests thus far, the apparent primary factor for compressive strength improvement in nanotube-reinforced polymers is the presence of low molecular weight materials in the polymer matrix. Low molecular weight polycarbonate exhibited a greater improvement in properties when reinforced with nanotubes, while higher molecular weight polymers showed less improvement, or even weakened properties. Combining low with high molecular weight polymer improved the compressive strength and the toughness of the composite. Functionalizing the nanotubes with long aliphatic flexible chains also improved homogeneity and uniformity of the composites, but short functional polar group did not. Additional work remains to identify the mechanism of nanotube-polymer interaction and failure modes of nanotube-polymer composites under compressive stress.

References

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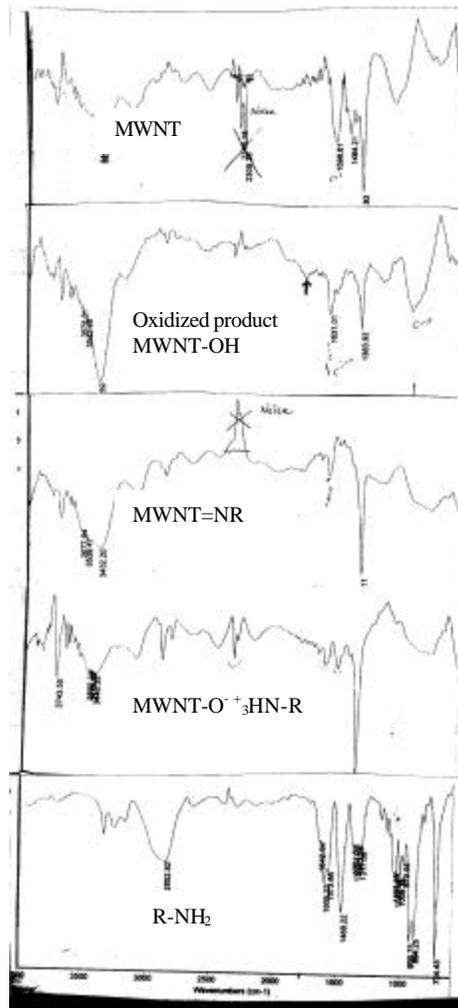


Figure 1. FTIR spectra of starting material and functionalized arc grown MWNT.

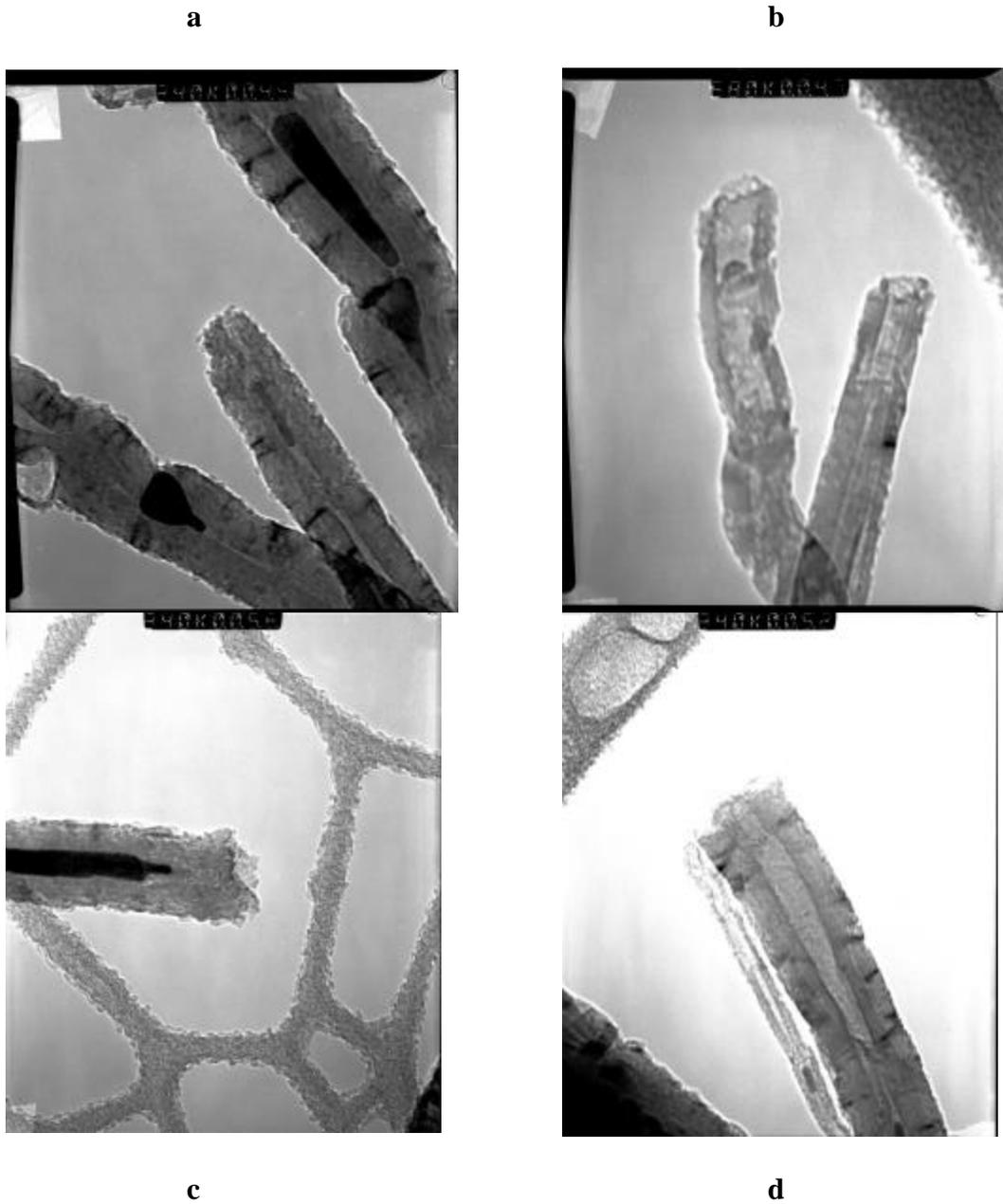


Figure 2. TEM photographs of tips of vapor grown MWNT after chemical and/or physical treatment. a) Acid treated b) Acid treated and high power sonicated c) Acid treated and oxidized d) Acid treated, high power sonicated and oxidized

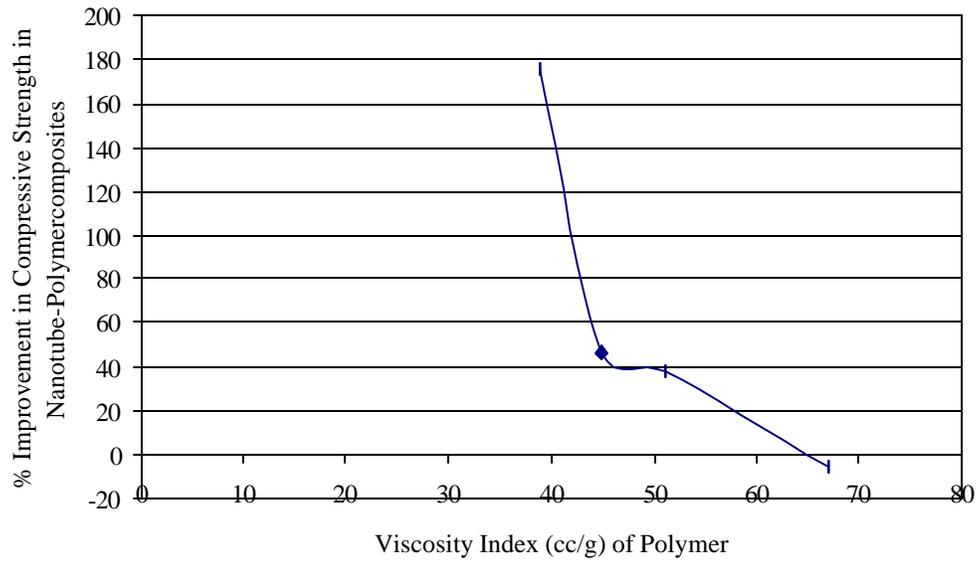


Figure 3. Polycarbonates Viscosity Index Versus Percent Improvement in Compressive strength nanotube-polymer composites

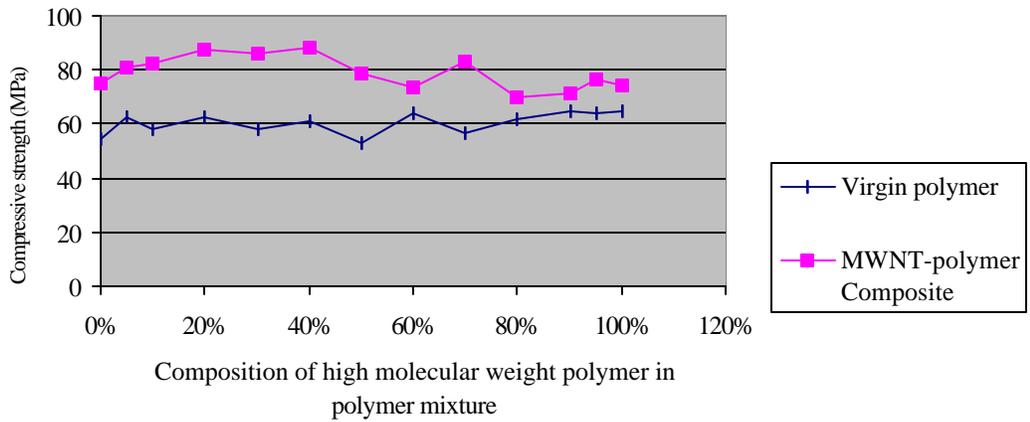


Figure 4. Compressive strength of virgin polycarbonate mixtures and MWNT-polycarbonate mixture composites

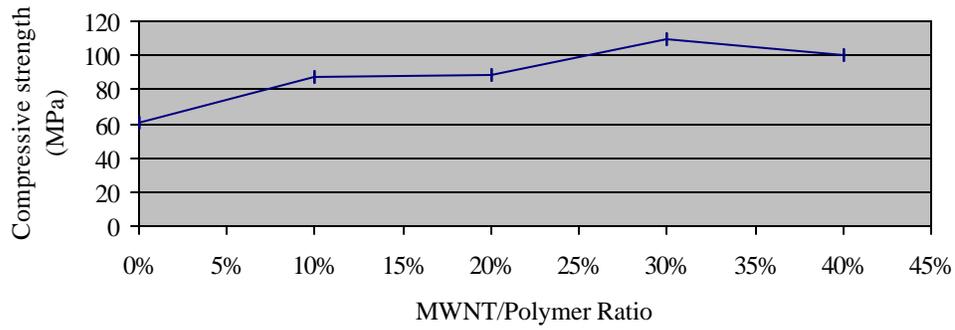


Figure 5. MWNT-polycarbonate composites compressive strength versus MWNT content

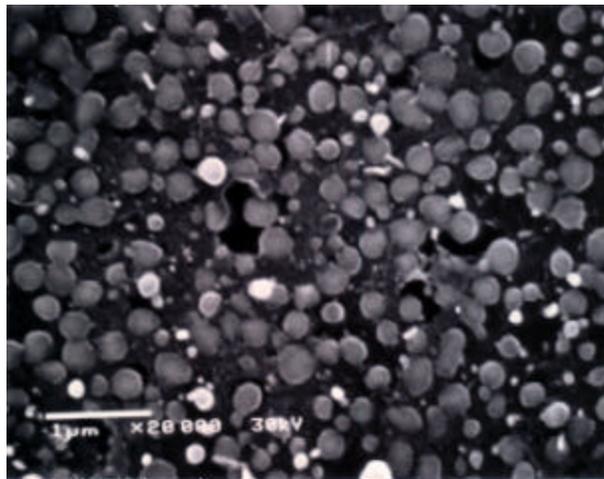


Figure 6. SEM photograph of aligned multiwall-nanotubes-Polycarbonate films, Z-axis view