

# Recoverable Lightweight Nanocomposites

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## ABSTRACT

The demand for lightweight and strong structures continues to rise especially for weight critical applications such as aerospace and automotive. It is also desired that the materials can recover after being deformed. In this work, we fabricated a special lightweight material, nanocarbon foam, and then reinforced the foam by infiltrating the thermoplastic polymer into the foam to form a nanocomposite. The strength of nanocomposite is 13 times higher than the foam while the density is increased less than 6 times. Heating the deformed nanocomposite to the temperature around the glass transition temperature range of polymer results in the full strain recovery of the nanocomposite. It is remarkable that the recovery in both structure and property can be repeated.

**Keywords:** nanocomposite, nanocarbon foam, porous material, recovery

## 1 INTRODUCTION

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers. Carbon nanotubes (CNTs) are a typical nanomaterial for nanocomposites due to their spectacular mechanical, electrical, and thermal properties. For special applications, the materials including nanocomposites are made with porous structures in a controlled porosity. Generally, the rigid nanocomposites have high strength but cannot recover after failure. Some flexible nanocomposites have good elasticity, however, their strength is usually low. Few research focus on both the strength of nanocomposites and their recovery from deformation. In this work, a simple and scalable method has been used to fabricate a CNT based porous material, nanocarbon foam (NF), and poly(methyl methacrylate) (PMMA) was chosen as a second phase into NF to form a composite foam (CF). PMMA has a high strength with a relatively low temperature of glass transition ( $T_g$ ) and the NF is super-elastic and stable. The combination of NF and PMMA allows the CF to have a higher compressive strength and, at the same time, the recovery capability both in structure and strength.

## 2 EXPERIMENT

The materials used to fabricate NFs were multi-walled CNTs, polyacrylonitrile (PAN), polymer microspheres (Sunjin Chemical Co., Ltd), and solvents. The multi-walled CNTs (General Nano, LLC) have an average diameter of 7 nm and length of 1–2 mm. The PAN powder has 150 kg mol<sup>-1</sup> molecular weight. The CFs were prepared from NFs and dissolved PMMA granules. PMMA granules (Plexiglas 8N, Evonik) were chosen as the second phase for producing CFs because of its high strength and low density.

The NFs were made by using a typical template method [1]. The microspheres with the average diameter of 11  $\mu$ m were used to determine micro-scale cells in the NFs. PAN was used to reinforce the CNT network by locking the contacted CNTs and generating connections among CNTs. Because PAN was converted into nano-graphitic structures through carbonization process [2] the cross-linked CNT networks form the cell walls of the micro-scaled cells in the NF.

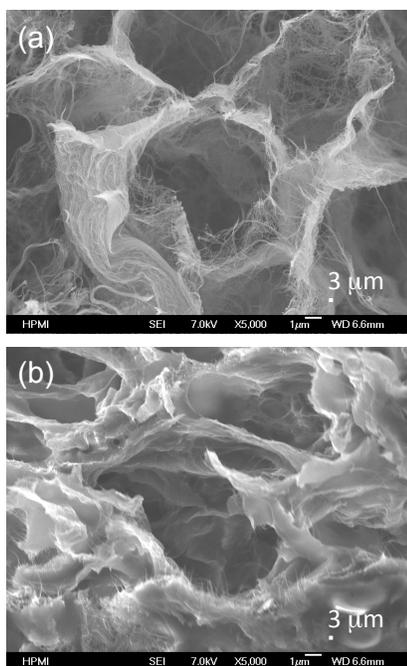
The CF was produced by infiltrating thermoplastic polymer, PMMA, into the NF in a solution process. In order to control the amount of PMMA infiltrated in the NF, varying concentrations of PMMA solution were made by dissolving PMMA granules in acetone. In a typical process, the NF sample was immersed in the PMMA solution which was heated to 60°C for 1 hour. During this time, the sample was compressed several times to move the air trapped inside the structure and ensure the infiltration sufficient. When the sample was taken out from the solution, the PMMA solution sticking on the sample surfaces was removed by a tissue paper. During drying, the sample was placed inside a tube rotating at a speed of 20 rpm. This is to prevent the polymer from settling down due to gravity and to ensure a uniform polymer infiltration throughout the structure. The CF was further dried at 60°C in a vacuum oven to completely remove the solvent. Generally, PMMA infiltration does not cause the size change of the sample, but the increase of sample weight. The density of CFs is directly related with the amount of PMMA infiltration.

The structure of the samples was observed by using scanning electron microscopy (SEM, JEOL-JSM7401F). The mechanical properties were evaluated by using mechanical test machine (Shimadzu AGS-J). The loading

rate for both loading and unloading was set at 0.3 mm per minute for compression tests in the range of 0 - 60% strain. For the CFs with different densities, loading data was collected before and after recovery. Recovery of the CFs was completed through a thermal treatment at 130°C.

### 3 RESULTS AND DISCUSSION

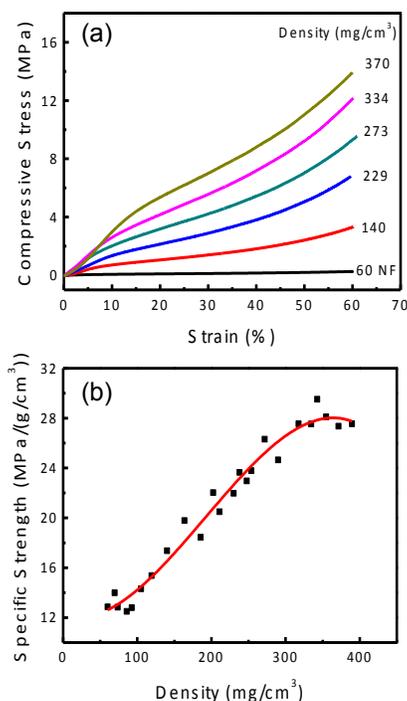
The NF is a porous carbon material based on CNTs and other forms of carbon (Fig. 1a). Because the cell size of the foam is determined by the size of polymer microspheres, using polymer microspheres as template allows for a better control over the size of the cells and the porosity of the foam. The SEM images show that the micro-scaled cells are uniformly distributed in the foam. The cross-linked CNT network acts as the wall of the cells while generating pores in nanometer scale within itself as shown in Fig. 1a. The NF is an open cell foam and is exceptionally elastic [1, 2].



**Figure 1.** SEM images show the structure of the NF (a) and CF (b). The cell wall of the foam is formed by CNT networks with nano-scale pores. The density of the foam is 26 mg/cm<sup>3</sup> and the average size of micro-scale pores is  $\phi$ 11  $\mu$ m. The density of the nanocomposite is 332 mg/cm<sup>3</sup>. It can be seen clearly that the pores of the nanocomposite are preserved while the walls have become visibly denser due to the deposition of polymer (PMMA) onto the CNTs in the cell wall.

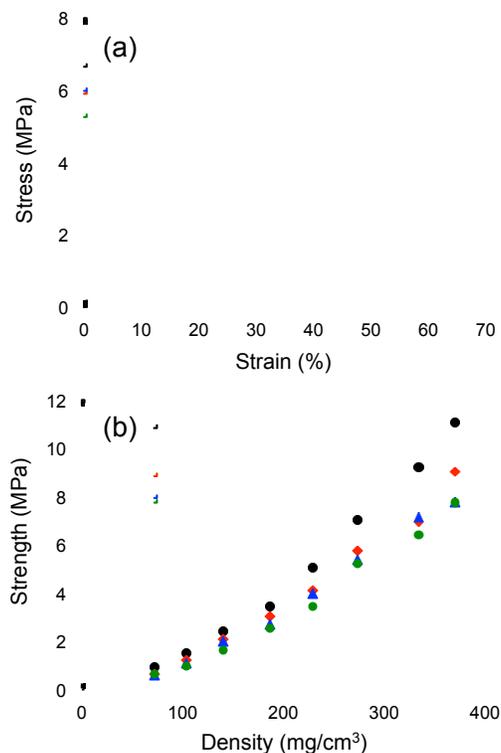
The CFs are made by infiltrating PMMA into NFs as the second phase. Unlike the infiltration process reported in literatures, our process only coats the polymer on to the surface of the CNTs in the cell walls (Fig. 1b). The as-prepared composite remains a porous structure. With the increase of the concentration of the PMMA solution, the density of the CF increases. The polymer coatings reinforce

the wall of the cells in the foam effectively [3]. Figure 2a shows the compressive stress – strain curves of the NF and CFs with different density. As shown in Fig. 2a, three stages of deformation are observed, which are the initial linear behavior, linear plateau region, and the final densification. The initial slope was used to calculate the elastic modulus [4]. The modulus and compressive strength is obviously improved with the addition of PMMA. With the density increasing 6.5 times from 60 mg/cm<sup>3</sup> to 389 mg/cm<sup>3</sup>, the modulus increases 6.5 times from 4.7 MPa to 30.2 MPa, and the strength at 50% strain increases 13.4 times from 0.8 MPa to 10.7 MPa. The density dependence of specific strength of CFs is shown in Fig. 2b. The specific strength increases slowly when the density is less than 100 mg/cm<sup>3</sup> and it increases almost linearly with the density in the range of 100-350 mg/cm<sup>3</sup>. In the infiltration process, the PMMA will locate at the joints of CNTs in the CNT networks first and then expand to coat the whole CNTs. When the amount of PMMA is not large enough, the part between two joints in the CNT network will not be fully coated. These uncoated CNTs are the weakest parts of the bulk and easily bend under compression. Therefore, the strength increases slowly at lower density. When all the CNTs are coated, the compressive strength increases rapidly. With the increase of the PMMA infiltration, the PMMA fully coated on CNTs, filled the pores in the cell walls, increased the thickness of the cell walls, and decreased the porosity of CF. Over infiltrating of PMMA results in the decrease of CF's specific strength because the increase of the strength is slower than that of the density.



**Figure 2.** (a) The compressive stress-strain curves and (b) the specific strength of the NF and the CFs with different densities.

The CFs are not elastic. When compressed, the permanent deformation occurs due to the plastic deformation undergone by the polymer. Because the PMMA is a rigid polymer, compression causes cracks and breaks in PMMA. After compressed, the CF is deformed permanently and the cells flattened in the direction of the applied force. It is found that the deformed CFs can be recovered both in structure and strength by simply using heat. When the deformed CF is heated to 130°C on a heater, its shape recovered back to that before compression and it is elastic. The recovered CF becomes rigid again when its temperature is lower than PMMA's  $T_g$  (105°C). SEM observation demonstrated that the structure of a recovered CF is very close to that before compression. The thicknesses data of the samples before the compression test and after recovery are collected for all samples with different density and initial size. The data shows that the CFs are well recovered.



**Figure 3.** Stress vs. strain curves of the CF with a density of 229 mg/cm<sup>3</sup> (a) and density dependence of the strength at 50% strain (b) before and after 3 recovery operations. Black line indicates the result of the 1st compression test. The red, blue, and green lines indicate the mechanical property of the CF after the 1st, 2nd, and 3rd recovery, respectively.

Heating the deformed nanocomposite to the temperature around the  $T_g$  range of polymer, results in the full strain recovery of the nanocomposite. It is because that the polymer assumes a soft and rubbery behavior beyond  $T_g$  [5], while the intrinsically elastic CNTs, which are still surrounded by polymer, are able to rebound and exhibit their elasticity by overcoming the force applied by the

enclosing polymer upon the reduction in its Young's modulus. This proves that the robust CNT network formed at the beginning was not damaged during the deformation process.

The compressive strength of CFs was tested to evaluate the recovery of CFs. Figure 3a shows the compressive stress-strain curves of the CF with a density of 229 mg/cm<sup>3</sup>. There is a relatively large reduction in strength between the first deformation and the 1st recovery, but small changes among the 1st, 2nd, and 3rd recoveries. It is possible that these differences are due to the processes of fabrication and thermal treatment. For the 1st compression test, the sample was prepared from solution process that made the PMMA infiltrates into the NF. After the 1st test, the recovery of the CF was due to the thermal treatment at 130°C. When the temperature is higher than the  $T_g$  of PMMA, the PMMA is soft and the recovery of the CNT network will rearrange the PMMA in the CNT networks on cell walls. The distribution and the coating of PMMA around CNTs might be more uniform through solution process than thermal treatment. The strength at 50% strain of CFs is shown in Fig. 3b. The results indicate that the recoverability of CFs depends on their density. The CF with lower density has better recovery capability. With the increase in density, the CFs' strength has a higher reduction in the 1st recovery. However, their recoverability repeats well after the 1st recovery. At lower density, a thin PMMA layer is coated on CNTs, the heat treatment process can recover the structure to its original status well. While at higher density, PMMA fills the spaces in cell walls and increases the wall thickness, the failed PMMA structures cannot be fully recovered through thermal treatment and the failure of the PMMA structure might cause damages in the CNT network, which reduces the strength of the CFs. The CFs have relative high strength compared with other foams with the same density [6, 7] and they are recoverable. Such combination will expand the application of the porous nanocomposites.

## 4 CONCLUSION

In this work, the nanocomposites are made by infiltrating thermoplastic polymer (PMMA) into an elastic nanocarbon foam which has uniform pore size. The microstructures of the nanocomposites were observed and mechanical properties were tested. The results indicate that the strength increases more than 13 times while the density just changes around 6 times due to the addition of the polymer. The morphology and compressive strength of the deformed nanocomposites can be recovered through thermal treatment. The relatively high strength and the recovery capability make the nanocomposite a promising material allowed to have a easy maintenance process and extend service life. Because the CNT networks in the CFs are thermally and electrically conductive, the recovering treatment can be simplified by using IR light or electricity, which will be the further research.

## REFERENCE

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- [1] Y. Cui and M. Zhang, "Fabrication of Cross-Linked Carbon Nanotube Foam Using Polymethylmethacrylate Microsphere as Template," *J. Mater. Chem. A* 1, 13984 (2013).
- [2] Y. Cui and M. Zhang, "Cross-links in Carbon Nanotube Assembly Introduced by Using Polyacrylonitrile as Precursor," *ACS Applied Materials & Interfaces* 5 (16), 8173–8178 (2013).
- [3] M. S. Jamal and M. Zhang, "Carbon nanotube based hybrid nanocarbon foam." *Mater. Res. Express* 4, 1 (2017).
- [4] M. C. Saha, E. Kabir, S. Jeelani, "Enhancement in Thermal and Mechanical Properties of Polyurethane Foam Infused with Nanoparticles," 479, 213–222 (2008).
- [5] M. Dixit, S. Gupta, V. Mathur, K. S. Rathore, K. Sharma, N. Saxena, "Study of glass transition temperature of PMMA and CdS-PMMA composite," *Chalcogenide Letters* 6, 131-136 (2009).
- [6] P. Moongkhamklang, V. S. Deshpande, H. N. G. Wadley, "The Compressive and Shear Response of Titanium Matrix Composite Lattice Structures," *Acta Mater.* 58 (8), 2822–2835 (2010).
- [7] M. F. Ashby, *Case Studies: Material and Shape-Materials Selection in Mechanical Design* (Fourth Edition). *Materials Selection in Mechanical Design*, 2011, 277–297.