

# Preparation of carbon nanotube/PMMA nanocomposite in supercritical carbon dioxide

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## Abstract

Nanocomposites of well dispersed single wall carbon nanotube (SWNT) in polymer matrix are expected to have improved electric, thermal, and mechanical properties. The extent of dispersion and the adhesive interactions between the nanotubes and polymer are important criteria for a successful process. A novel method to prepare SWNT/polymer nanocomposite by in-situ polymerization in supercritical carbon dioxide (scCO<sub>2</sub>) is presented in the study.

The surfaces of SWNTs are first functionalized with amino ethyl methacrylate (AEMA) and then copolymerize with methyl methacrylate (MMA) via in-situ polymerization in supercritical CO<sub>2</sub>. The supercritical solvent featuring controllable liquid-like density, reduced viscosity, and enhanced diffusivity facilitates the transport of monomers into the entanglement area or interstitial space in SWNT bundles. In-situ polymerization enhances dispersion of SWNTs; tethered PMMA chains on the nanotube surface increase the chemical affinity with the polymer matrix. FTIR shows clear evidence of surface coupling of the nanotubes and tethered PMMA. Electron microscopy analysis from SEM and TEM reveal a much enhanced dispersion of nanotube bundles in polymer matrix and excellent surface coverage of PMMA on SWNTs even after several washes with organic solvents. Surface functionalization with AEMA is found to be critical to the success of fabricating the nanocomposites. The success of functionalization of SWNT followed by polymerization using this method can be generalized to other polymeric systems.

## Introduction

There have been growing interests in carbon nanotube (CNT) reinforced polymeric materials. Compared to traditional composites with other filler materials, CNT composites have superb mechanical, thermal and electronic properties. One of the major challenges facing the preparation of CNT/polymer nanocomposite is dispersion of CNTs in polymer matrix. The fact that CNTs tend to form tightly or loosely packed bundles severely limits its application in composite materials. Recently, CNTs were functionalized with various chemical agents to enhance interaction between CNT surface and polymer matrix rendering better impregnation. Some studies have shown that polymer chains can be chemically tethered to CNTs. However, due to the slow dynamics and the entropic barrier hindering polymer chains entering confined space, no significant sign of debundling or swelling of entangled CNTs was reported.

In this paper, we report on using supercritical carbon dioxide (scCO<sub>2</sub>) as a media for the synthesis of carbon nanotube/PMMA nanocomposite. Through functionalization of CNT surfaces with small molecules containing double bonds followed by in situ polymerization with MMA monomers in scCO<sub>2</sub>, PMMA chains can grow on CNTs and open up the entangled area. The functionalization also enhances the dispersion of CNTs in the reaction medium. Taking advantage of the extremely high diffusivity and controllable solvation strength of scCO<sub>2</sub>, the reactant (monomer) can reach virtually everywhere in the system, thus the monomer/CNT contact area is maximized. Recently, these unique properties of scCO<sub>2</sub> have attracted interests for the processing of CNT related materials. Thanks to the superb transport property of scCO<sub>2</sub>, modified “bulky balls” were dissolved in scCO<sub>2</sub> and inserted into CNTs. Besides, scCO<sub>2</sub> is a “green” solvent, making this method an environmental friendly one.

### Experimental Section

The SWNTs were first treated in 70% HNO<sub>3</sub> using microwave oven<sup>1</sup>. Then, the acid treated carbon nanotubes (SWNT-COOH) were refluxed with AEMA overnight in DMF. The AEMA modified carbon nanotubes (SWNT-AEMA) were obtained after removing the excess AEMA by slow washing with distilled water and ethanol. The modified SWNT was then mixed with monomers and polymerized in supercritical CO<sub>2</sub>. A detailed description of the experimental setup and temperature/pressure control can be found elsewhere<sup>2</sup>. In a control experiment set, pristine SWNTs were added into the same polymerization mixture for reaction.

### Results and Discussions

Typical PMMA particles synthesized with dispersion polymerization in scCO<sub>2</sub> usually have a size range of hundreds to thousands of nanometers. At the early stage of dispersion polymerization, oligmer/polymer will undergo homogeneous nucleation. Introducing reactive CNTs with high surface area can induce heterogeneous nucleation. It was found that polymerization occurred simultaneously in the dispersed PMMA colloids and on the surface of CNTs, where polymers will develop into a coating layer. The latter mechanism resembles precipitation polymerization in comparison to dispersion polymerization due to the fact that the reaction sites are constrained on the immobile solid substrates instead of the dispersed polymer particles in the medium.

Shown in Figure 1 are the SEM images of original CNT/PMMA composite samples, in which the PMMA particles and polymer film coated on CNTs were clearly observed. To verify that some PMMA molecules are covalently bonded onto CNT surfaces, the original samples were intensively washed with acetone or/and THF to extract the physically attached PMMA molecules. SEM images of the sample after the extensive washing are shown in Figure 2. Although TGA quantification experiment was not carried out due to the small amount of samples prepared, it is clearly found that a significant portion of polymer is still left on the CNT surface after the washes, indicative of the existence of covalent bonds between polymers and CNTs.

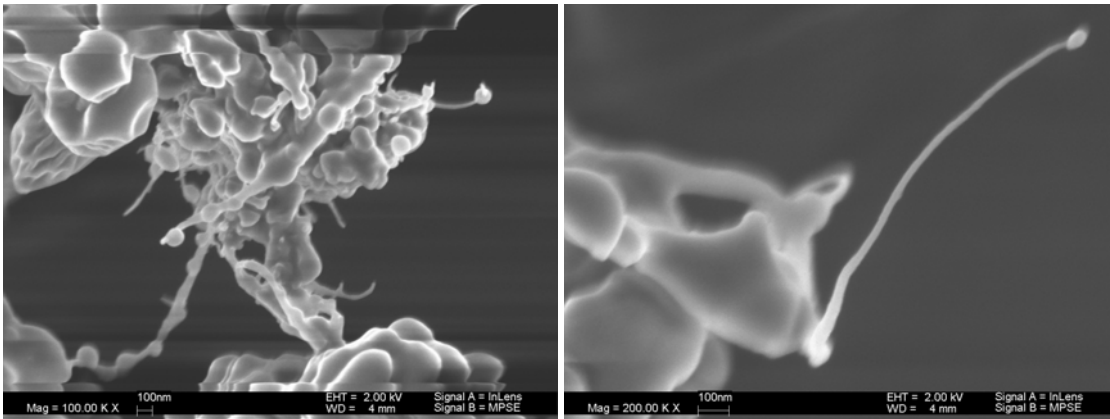


Figure 1. SEM micrographs of CNT/PMMA composites indicate that CNTs are completely coated with polymer; excessive PMMA forms agglomerated particles.

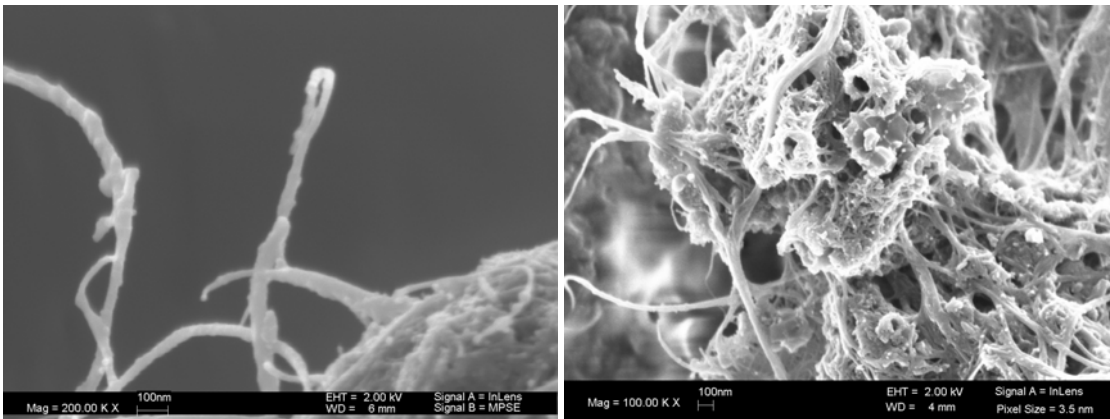


Figure 2. After extensive washing, PMMA coating on CNT surface still remained, indicating chemically bonded PMMA chains.

In addition to the SEM results presented above, FTIR data also shows clear evidence of surface coupling of the nanotubes and tethered PMMA. TEM examination demonstrated uniform PMMA surface coating on the nanotube surface.

## Conclusion

Using in-situ polymerization, CNT/PMMA nanocomposite was successfully prepared in  $scCO_2$  in this study. PMMA was found chemically connected to CNT surfaces through copolymerization with AEMA molecules. Excellent surface coverage of CNTs with PMMA throughout all samples was achieved, owing to the superb diffusivity and controllable solvation strength of  $scCO_2$ , which allows complete wetting of CNT surfaces with reactants.

## Reference

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- 2) B. Yue et al. Powder Technology **2004**, 146, 32-45.