
Supercritical Fluid Assisted Processing of SWNT/Polymer Composites

R. Ozisik and L. S. Schadler

*Rensselaer Polytechnic Institute, Materials Science and Engineering Department,
Troy, NY 12180, USA. E-mail: ozisik@rpi.edu*

ABSTRACT: Supercritical carbon dioxide assisted processing is being used to disperse and distribute single walled carbon nanotubes in polymers. As part of this scientific effort, nucleation of supercritical carbon dioxide was investigated using spherical silica nanofillers of uniform size. The effects of both the filler size and the filler surface chemistry on nucleation of supercritical carbon dioxide were investigated using dynamic light scattering, transmission and scanning electron microscopy, thermogravimetric analysis, and statistical analysis. Results indicate that supercritical carbon dioxide saturation pressure, silica size, and silica surface chemistry all play important role in the nucleation and final pore morphology. Modifying the surfaces of silica with fluoroalkanes proved to be more effective in increasing pore density and decreasing pore size compared to reducing (bare) silica size from 150 nm to 15 nm. Processing and experimental analysis were performed in collaboration with Profs. Juan Baselga and Juan Carlos Cabanelas of Universidad Carlos III de Madrid, Spain.

INTRODUCTION (LIMIT: 1 PAGE)

The current NSF award (CMMI-0500324) supports the processing of single walled carbon nanotube dispersion and distribution in polymers using supercritical carbon dioxide assisted processing. This work is being performed at Rensselaer Polytechnic Institute.

The objective of the IREE grants was to establish research collaboration between Universidad Carlos III de Madrid, Spain and Rensselaer Polytechnic Institute, Troy, New York. The Spanish scientists were specialized on chemical surface modification techniques, which we lacked a tour institution, and silica. The IREE grants enabled three different researchers to visit Spain on two different occasions. Ryan Schneider (graduate student) and Prof. Rahmi Ozisik visited Spain during the summer of 2007. Ryan Schneider spent 3 months in Spain and synthesized silica nanoparticles. During the fall of 2008, Katelyn Parker (graduate student) visited Spain and spent 3 months working Under the guidance of the Spanish scientists. Katelyn prepared silica/PMMA nanocomposites, foamed them with supercritical carbon dioxide and characterized their pore morphology using various experimental techniques. Both Ryan Schneider and Katelyn Parker were chosen based on their academic achievements. In addition, they were given extensive training before going to Spain. Prof. Ozisik was an assistant professor when the IREE grant was awarded. He is currently an associate professor.

Universidad Carlos III de Madrid, Spain, is the foreign institution that is involved in this project. We worked with the Department of Materials Science and Chemical Engineering, and Institute of Chemical and Materials Technology. Two professors were the main contacts:

- Prof. Juan Baselga Llidó: Prof. Baselga is one of three full professors at the Department of Materials Science and Chemical Engineering. Prof. Baselga is the head of the Department of Materials Science and Chemical Engineering, and the director of the Institute of Chemical and Materials Technology.
- Prof. Juan Carlos Cabanelas: Prof. Cabanelas is an associate professor in the Department of

Materials Science and Chemical Engineering.

Profs. Baselga and Cabanelas perform research activities in the fields of inorganic filler surface modification, modification of polymers using inorganic fillers, epoxy synthesis, and fluorescence spectroscopy. These fields form the strengths of the Spanish group. The inorganic fillers that are of interest to Profs. Baselga and Cabanelas range from spherical fillers (such as silica) to layered fillers (such as kaolin). Their research involves chemical modification of inorganic filler surfaces to control the interfacial properties, and therefore, control the properties of polymer composites. Their current focus is to separate individual nanoparticles from agglomerates, so that each nanoparticle can be chemically altered for ultimate control of interfacial and property control. In addition, they are using Atom Transfer Radical Polymerization (ATRP) to grow organic molecules from the surfaces of inorganic particles and create 3-dimensional nanostructures.

The Department of Materials Science and Chemical Engineering houses fully functional organic synthesis laboratories, polymer processing laboratory with single and twin screw extruders, and melt spinning equipment. In addition the following equipment is available to characterize materials: Various mechanical testing equipment such as Instron tensile tester, Charpy and Izod testers; various rheometers; capillary rheometer; Dynamic Thermal Mechanical Analyzer (DMTA); UV-VIS spectrometer; FT-IR spectrometer; fluorescence spectrometers; Fluorescence Thermal Spectrometer (a unique equipment providing thermal characterization along with fluorescence spectrometry); Differential Scanning Calorimeter; Thermogravimetric Analyzer (TGA); wide angle X-ray with temperature control up to 1600 °C; optical microscopes; and scanning electron microscope.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION (LIMIT: 1-1/2 PAGES)

Our current (on-site) work emphasizes processing of single walled carbon nanotube composites. However, in order to get a better understanding of supercritical nucleation thermodynamics and kinetics, we decided to use fillers that provide a simple geometry (spherical versus ropes/tubes), therefore, we chose silica nanoparticles. Our Spanish counterparts were specialized in both chemical surface modification techniques and all forms of silica, therefore, our interests overlapped but we had complementary expertise.

In all cases, the 3 American researchers (Rahmi Ozisik, Ryan Schneider, and Katelyn Parker) used the accommodation provided by the university, hence, we were in a walking distance to the laboratory. We had weekly meetings with both Profs. Juan Baselga and Juan Carlos Cabanelas, and worked with other graduate students in their groups. We received formal training on experimental equipment that we used and we were allowed to use any equipment that we needed.

The program of the research carried out in Spain is as follows. Poly(methyl methacrylate), PMMA, and silica/PMMA nanocomposites containing two different sized silica particles (150 and 15 nm) and two different surface modifications (bare and modified with fluoroalkanes) were foamed using supercritical carbon dioxide (scCO₂) at various saturation pressures. Silica nanoparticle size distribution and dispersion in PMMA matrix was investigated with dynamic light scattering and transmission electron microscopy, respectively. Pore density and pore size distribution analysis were performed by image analysis of scanning electron microscopy pictures of fracture surfaces. Main conclusions of the work carried out in collaboration with Spanish scientists are as follows:

- Fluorination of silica nanoparticles did not change their dispersion in PMMA as shown by transmission electron microscopy analysis. Number of nanoparticles present in the system was a function of silica size only. In addition, entrapped carbon dioxide analysis showed that the difference of CO₂ present in various samples (including neat PMMA) at constant pressure is less than 5%. These two findings indicate that in the nanocomposite samples, the amount of nucleation centers and amount of CO₂ present is similar at constant pressure and constant silica size.
- SEM image analysis (Figures 1-3) showed that a transition from homogeneous to heterogeneous nucleation takes place when silica nanoparticles are added to PMMA. The average pore size in

neat PMMA was 3-15 times greater than that observed in various silica/PMMA nanocomposites, and the pore density in neat PMMA was 2-3 decades lower than those observed in silica/PMMA nanocomposites. However, the final relative densities of all samples were very similar suggesting that addition of silica nanoparticles is not useful if density is the only parameter of concern.

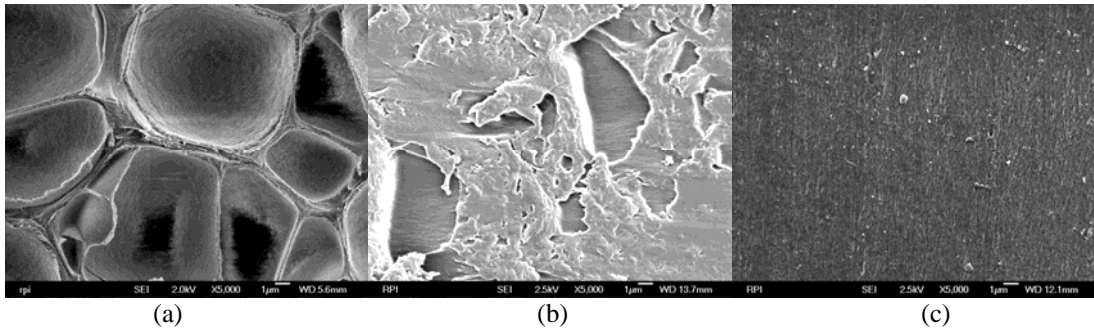


Figure 1. SEM micrographs of neat PMMA after $scCO_2$ processing at different saturation pressures: (a) 17.9 MPa, (b) 10.3 MPa, and (c) 8.3 MPa.

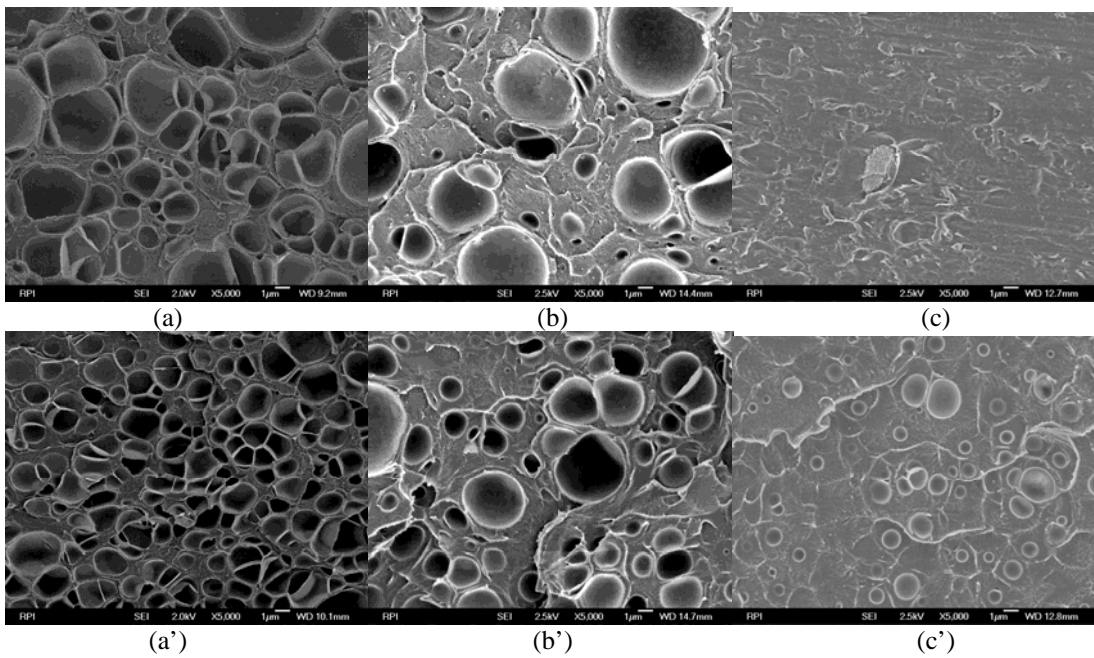
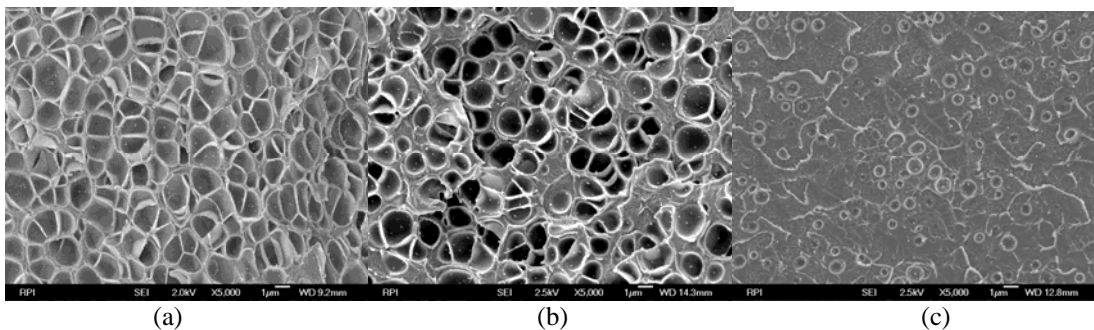


Figure 2. SEM micrographs of bare silica/PMMA nanocomposites foamed at various saturation pressures: (Left column) 17.9 MPa, (Middle column) 10.3 MPa, (Right column) 8.3 MPa. Pictures on the top row correspond to 150 nm silica and those on the bottom row correspond to 15 nm silica.



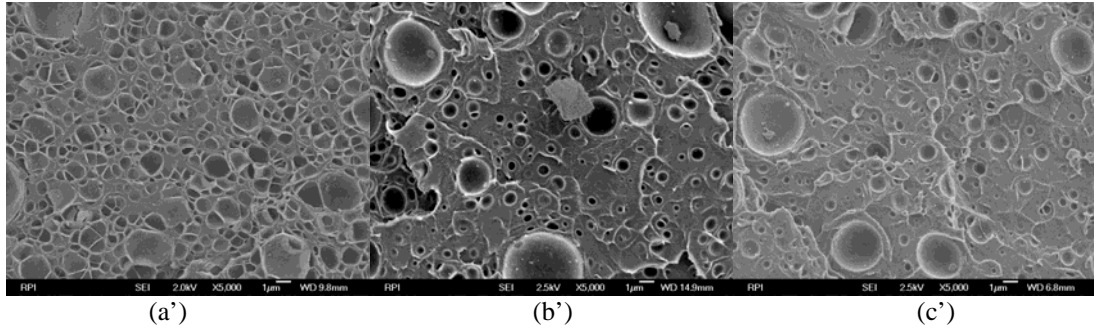


Figure 3. SEM micrographs of fluorinated silica/PMMA nanocomposites foamed at various saturation pressures: (Left column) 17.9 MPa, (Middle column) 10.3 MPa, (Right column) 8.3 MPa. Pictures on the top row correspond to 150 nm silica and those on the bottom row correspond to 15 nm silica.

- Results indicated that agglomeration has a strong effect on nucleation and as a result on the final pore morphology. Heterogeneous nucleation was influenced by both filler size and filler surface chemistry. Changing the size of the filler influences the surface curvature and the number of nucleation centers available. Both of these factors showed a strong effect on pore morphology. Decreasing filler size provided many more nucleation centers but increased relative surface curvature and led to greater critical Gibbs free energy of nucleation. The combined effect increased the pore density.
- It is well known that presence of fillers decrease the activation energy of nucleation by providing an interface (polymer/filler) for the $scCO_2$ to aggregate. This effect leads to the decreased pore size in the final foam because many more nucleation events take place (due to increased number of nucleation centers) compared to neat polymer. Activation energy of the fluorinated silica containing nanocomposites is lower than bare silica containing nanocomposites because of the higher affinity of $scCO_2$ to fluorocarbon groups. Observed pore size ratios confirm this finding.
- A nucleation boundary, beyond which no nucleation takes place, was constructed by performing foaming at various saturation pressures (Figure 4). Both decreasing filler size and favorable CO_2 -filler interaction shift the nucleation boundary to lower saturation pressures.

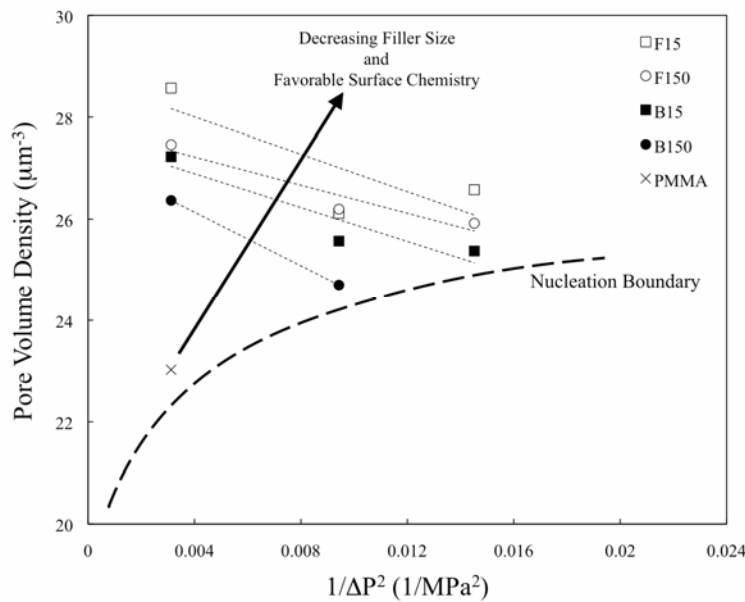


Figure 4. Pore density as a function of saturation pressure. Dashed lines are linear least squares fit to data.

BROADER IMPACTS OF THE INTERNATIONAL COOPERATION (LIMIT: 1-1/2 PAGES)

The international research experience provided the following broader benefits:

- Exposed an assistant professor to international collaboration. Prof. Ozisik was able to establish three other international collaborations through this IREE grant and opportunities it provided.
- Two American students were able to spend 3-months each in a foreign country. They learned Spanish customs, Spanish language, and experienced scientific life at a foreign university.
- A female student was employed through the IREE grant.

In addition to these broader benefits, our main research activity was supported by the international collaboration tremendously. The know-how gained through this collaboration is now currently being applied to SWNT polymer nanocomposites.

During their stay, the American visitors attended scientific conferences (Nanoscale Science and Technology Forum, Madrid, June 2007), musical concerts, social parties and outings, museums, and took weekend trips to various locations in Spain.

As part of our collaboration, Prof. Julio Bravo and a female graduate student (Artemia Loayza Arguelles) visited Rensselaer Polytechnic Institute for a period of 4 weeks and 8 weeks, respectively. We expect to continue our collaboration with the Spanish scientists in the future.

DISCUSSION AND SUMMARY (LIMIT: 1 PAGE)

We would like to recommend that short exploratory visits be allowed under the IREE program to enable the PI(s) to establish a working relationship.

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 0500324. The NSF program officer for the current grant is Shaochen Chen.

BRIEF BIOGRAPHIES OF RESEARCHERS (SAMPLES BELOW)

Rahmi Ozisik received the B.S. degree in Mechanical Engineering from the Bogazici University of Istanbul, Turkey, in 1990. He received his M.S. degree in Polymer Engineering and his Ph.D. degree in Polymer Science from the University of Akron in 1996 and 1999, respectively. Following his Ph.D., he worked as a post-doctoral researcher with Prof. Ulrich W. Suter at the Institute of Polymers, Swiss Federal Institute of Technology, Zurich, Switzerland. He worked as a research associate at the University of Akron in 2001. He joined Rensselaer Polytechnic Institute as an Assistant Professor of Materials Science and Engineering in 2002. He has been promoted to Associate Professorship in 2007. Research interests include polymers, polymer nanocomposites, plastic deformation in polymeric glasses, glass transition and dynamics, and supercritical fluid assisted processing..

Ryan Schneider received his B.S. in Physics from Clark University in 2006. He received his M.S. degree in Materials Science and Engineering from Rensselaer Polytechnic Institute in 2007. He is currently a Materials Engineer at the Z Corporation in Massachusetts.

Katelyn A. Parker received her B.S. in Chemical Engineering from Clarkson University in 2007. She currently is a graduate student at the Materials Science and Engineering Department, Rensselaer Polytechnic Institute.