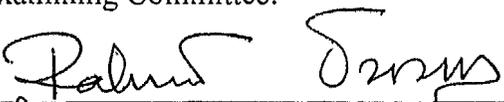


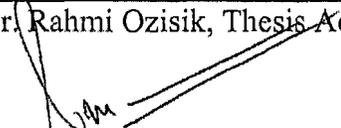
**Supercritical Fluid  
Assisted Processing of Nanoparticle/Polymer Composites**

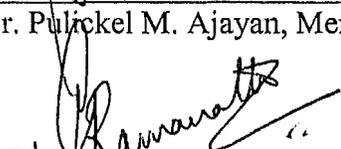
By  
Kumin Yang

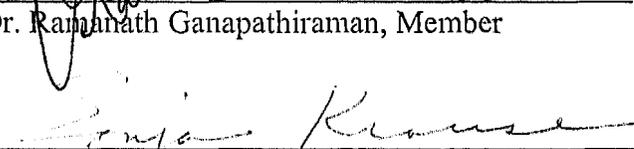
A Thesis Submitted to the Graduate  
Faculty of Rensselaer Polytechnic Institute  
in Partial Fulfillment of the  
Requirements for the degree of  
DOCTOR OF PHILOSOPHY  
Major Subject: Materials Science & Engineering

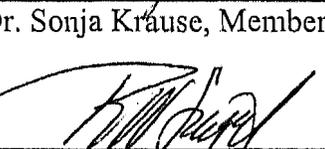
Approved by the  
Examining Committee:

  
\_\_\_\_\_  
Dr. Rahmi Ozisik, Thesis Adviser

  
\_\_\_\_\_  
Dr. Pulickel M. Ajayan, Member

  
\_\_\_\_\_  
Dr. Ramanath Ganapathiraman, Member

  
\_\_\_\_\_  
Dr. Sonja Krause, Member

  
\_\_\_\_\_  
Dr. Richard W. Siegel, Member

Rensselaer Polytechnic Institute  
Troy, New York

May, 2006

## ABSTRACT

An experimental study was carried out to determine the effects of supercritical fluids on the nanoparticle dispersion for various nanoparticle/polymer systems. The nanoparticles were classified according to forces that hold them together. They were as follows: 1) strong electrostatic interactions (montmorillonite); 2) physical entanglements (carbon fibers); 3) weak electrostatic interactions (untreated alumina); and 4) polar interactions (modified alumina). A novel, continuous supercritical fluid assisted processing setup was designed that utilized a flow adjustable die. For the case of strong electrostatic attraction, well dispersed clays were realized when both requirements were fulfilled: 1) selecting an organic modifier that was thermodynamically compatible with the polymer matrix, and 2) applying a sufficient degree of shear stress. Keeping the organic modifier constant, neither longer residence time nor the same level of shear stress improved the state of clay dispersion once a critical morphology was established. In the absence of supercritical fluids, pressure improved the clay delamination by reducing the free volume of the polymers and thereby augmenting the interaction between the chains, and ultimately increasing the viscosity and the wall shear stress. Using supercritical fluids such as carbon dioxide or 1,1,1,2-tetrafluoroethane (R-134a) did not ameliorate the clay dispersion for the 95/5 N6-L/20A because it resulted in an increase in the free volume and a decrease in the melt viscosity. For the carbon fibers/polystyrene system, the rapid expansion of the supercritical carbon dioxide (scCO<sub>2</sub>) did not improve the state of dispersion. This was due to the carbon fiber microstructure whose highly interwoven, physically entangled fibers resisted fiber pullouts or fracture. Spherical alumina, both untreated and modified,

were also investigated in polystyrene using an autoclave at 17.7 MPa and 40 °C. All agglomerates were found inside the cells and the cell size increased with agglomerate size. For the untreated alumina, the sudden expansion of the carbon dioxide did not alter the size of the agglomerates. This was probably caused by the weak interaction of scCO<sub>2</sub> with the untreated alumina and the relatively strong electrostatic interactions and van der Waals force between the nanoparticles that keep the agglomerate intact upon depressurization. In contrast to the three aforementioned cases, only the large agglomerates ( $L \geq 15 \mu\text{m}$ ) of the modified alumina showed signs of any catastrophic fragmentation. It was possible to speculate that the medium and small agglomerates lacked the surface coating which may have lead to their intact structure. The total alumina volume percent affected by the rapid expansion of the scCO<sub>2</sub> was a large value of 32.9%. The fluorinated modifiers used had a high degree of solubility with the scCO<sub>2</sub> at the processing conditions and therefore, the scCO<sub>2</sub> in the modified alumina was able to diffuse easily into the agglomerate compared to the untreated alumina. Large agglomerates can absorb more scCO<sub>2</sub> than smaller ones; and therefore have an adequately larger bursting pressure to overcome both the hydrogen bonding between the modified alumina nanoparticles and the weak electrostatic interactions. The bubble nucleated in the agglomerate was expected to undergo both elongation and shearing during the expansion process, transferring energy in the form of complex stress fields. Higher applied pressure may lead to further dispersion of the modified nanoparticle agglomerates.