Oriented Nanocomposite Extrusion

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ABSTRACT
Nanocomposites, with superior material properties, have promising potential applications in almost every field. The present work aims at obtaining the nanocomposites of aluminum nanoparticles that are uniformly dispersed in a polymer matrix and carbon nanotubes (CNTs) that are consistently cross-linked and with the desired orientation in a polymer matrix using Twin Screw Extrusion (TSE) through microchannels. In order to identify the variety of polymer matrices that can be employed, rheometric measurements of the polymer samples with variable loading of nanoparticles were conducted. An accelerated increase in viscosity with increased loading of CNTs and a novel shear-thickening phenomenon were observed. An extensive Navier-Stokes computational fluid dynamics model for viscous flow through rectangular microchannels was developed using Knudsen analysis to test the feasibility of microchannel extrusion. Furthermore, due to its ability to describe phase separation and ease of parallelization, a three-dimensional lattice Boltzmann model is being developed to predict the behavior of nanoparticles in the flowing polymer matrix. A silicon microchannel die with several thousand microchannels etched in a parallel array was designed and is being fabricated. The channels are sized such that the mean length of a nanoparticle is between one and two channel widths and a laminar flow with no-slip develops boundary layers within each channel. The structure of the nanocomposites has been characterized with scanning electron microscopy and atomic force microscopy. A corresponding variation of concentration with varying gray level intensity was observed and confirmed. Although significant optical effects were observed in the nanocomposites, no apparent effect on the mechanical properties was detected.

INTRODUCTION
Nanocomposites are generating tremendous interest due to the enhancement of the physical properties associated with the dispersion of nanoparticles or nanotubes within the matrix material. The potential applications for polymer nanocomposites encompass a wide variety of fields including aerospace technology, energetic materials, automobile industry, electronic and electric components and food packaging. To fabricate nanocomposites, researchers have tried both batch and continuous processing techniques [1]. The present work discusses the development of twin screw extrusion (TSE), a continuous processing technology, to fabricate two different nanocomposites – aluminum (Al) nanoparticles uniformly dispersed in a polymer matrix and carbon nanotubes (CNTs) consistently cross-linked with the desired orientation in a polymer matrix.

EXPERIMENTAL METHODS
A development scale twin screw extruder at the University of Maryland is being used to fabricate the nanocomposites (Fig. 1). The twin screw extruder is very flexible and supports a wide variety of melt formulations, feed systems and die designs. It consists of modular barrel design with six independently controlled temperature zones. The materials can be fed in any of the
six zones to serve the operating requirements. Loss-in-weight feeders are used to feed solids and volumetric pumps are used feed liquids. The die zone has a provision to include an optical probe, which can be used to obtain the residence time distribution of the processed material. A more detailed description of the apparatus is provided elsewhere [10, 13].

In the present work, 80 nm Al nanoparticles are used as the filler. A polyolefin elastomer called Engage 8140 was chosen as the polymer matrix due to its light weight, good processability and moderate tensile strength. Di-Octyl Adipate (DOA), a plasticizer, is used to make a colloid of the nanoparticles to aid better dispersion when fed to the melt in the extruder. Other conventional solvents such as Isopropyl alcohol and Darvon C are being considered. On the other hand, to fabricate the nanocomposites containing CNTs, a Poly-Ethylene Terminated Imide, PETI-298, was selected as the polymer matrix. Tetraethylene Glycol and 1-Methyl Naphthalene were selected as the dispersants and Sodium Dodecyl Benzene Sulfonate was selected as the surfactant to prevent nanotube aggregation.

**COMPUTATIONAL FLUID DYNAMICS**

To obtain the feasibility of extrusion and better understand the flow fields in microchannels, a computational fluid dynamics (CFD) study was undertaken. A Knudsen analysis of a wide range of microchannel cross-sections, molecular weights, thermal expansion coefficients and processing temperatures was performed to determine the nature of flow conditions at several points through a broad range of parameter values. Based on the analysis, the fluid flow through the microchannels was treated as a simple Newtonian, non-slip flow through an array of rectangular ducts. The closed form solution for velocity and volumetric flow rate are given as:

A number of MATLAB flow simulations were run at varying fluid viscosities, back pressures, channel sizes, and length to width ratios. Fig. 2 shows a plot of the volumetric flow rate vs. the viscosity of the melt. From this plot, the outlook to preferentially up to 2 wt% CNTs through 25µm x 25µm and larger cross-sections is very good. In summary, the closed form Navier-Stokes CFD analysis successfully reduced the study range of the process pressure from 300-1300 psi to 500-700 psi, the width to length ratio from 1:25-1:1000 to 1:250-1:500 and the channel cross-section from 5µm x 5µm -50µm x 50µm to 30µm x 30µm -40µm x 40µm.

Furthermore, there is an ongoing effort to simulate the behavior of CNTs in a polymer using the Lattice Boltzmann (LB) method due to its ability to describe phase separation and ease of parallelization [12]. The LB method was qualitatively validated by comparing the velocity profiles it predicted with those resulting from the closed form Navier-Stokes analysis conducted using MATLAB and the finite element analysis conducted using FEMLAB.
RHEOMETRIC STUDY

Viscosity measurements of various polymer matrices with variable loading of CNTs were conducted simultaneously with the CFD simulations. Each nanocomposite was compressed into a 1.5 mm thick by 25.4 mm diameter disk and the viscosity data was acquired using a Rheometric Scientific RDA III rheometer. Fig. 3 shows the results of the rheometric tests on nanocomposites of CNT in PETI-298. It can be seen that as CNT loading of PETI-298 increases beyond 1 wt% the CNT-loading level vs. viscosity relationship begins to deviate from the linear correlation. In addition, individual experiments in 1-3 wt% loading range validated the presence of nearly ten-fold shear thickening phenomena within the initial 2-5 minutes of each run as shown in Fig. 4.
Currently, a similar rheometric study is being conducted on three other polymers – Nylon, Poly-Carbonate and Poly-Methyl Meth-Acrylate, to investigate the suitability of these polymers in making the nanocomposites as compared PETI-298.

DIE DESIGN

A novel microchannel die (Fig. 5) is being fabricated for the extrusion of nanocomposites. The die shall have several microchannels that are etched (using deep reactive ion etching and optical lithography) in a parallel array with a constant or slightly tapered channel width and fixed height. The channels are sized such that the mean length of a given nanoparticle or nanotube is between one and two channel widths and laminar flow with no slip develops boundary layers within each channel. 500 m Pyrex channel cover plates were incorporated into the design to facilitate real-time observation of channel flow. The four channel boundary layer will tend to orient the nanotubes in the direction of the flow. The combined particle dispersion and high pressure extrusion characteristics of the TSE are ideal to deagglomerate the nanoparticles or nanotubes and overcome the resistance offered by the microchannel die to the viscous flow respectively. To aid the processing, the die is designed to be oriented vertically at the exit of the die-housing. To get an insight to the nanocomposite extrusion and to quantify the operational parameters of the TSE, a few preliminary experiments were conducted with the existing temporary dies (Fig. 6).
CHARACTERIZATION

Fig. 6 The slit, square and round dies used for the preliminary experiments.

Fig. 7 shows the nanocomposites of Al nanoparticles in Engage 8140 resulting from extrusion through the slit die shown in Fig. 6. Engage 8140 with no fill can also be seen in Fig. 7. It was observed that the increase in the concentration of the nanoparticles corresponded to an increase in gray level of the extrudate. The gray level variations were measured \textit{in situ} with an optical probe and have been used to obtain the residence time and residence volume distributions. These distributions can be used to understand and optimize the mixing process [13]. To confirm the variation of the concentration with varying gray level intensity, samples at selected location were subjected to pyrolysis and the weight of the Al nanoparticles was estimated. The maximum concentration corresponding to the highest gray level intensity was estimated to be 1 wt\% and the lowest concentration corresponding to the least gray level intensity was estimated to be 0.1 wt\%.

In order to determine the effects of Al nanoparticles on the mechanical behavior of Engage 8140, Shore A hardness measurements were performed at various locations of the extrudate. The Shore A hardness of pure Engage 8140 was reported by the vendor as 85. The hardness values of the nanocomposites did not vary significantly from this value indicating that a very dilute reinforcement from the nanoparticles. Experiments are underway to investigate the effects of higher concentration of nanoparticles on the mechanical behavior of the polymer matrix.

The structure of the nanocomposites was examined using a scanning electron microscope and an atomic force microscope. Fig. 8 is an image of the surface of the nanocomposite with 1 wt\% Al loading. The microscopy showed that the Al nanoparticles are uniformly dispersed in the polymer matrix without any apparent aggregates. Microscopy being a qualitative analysis, more quantitative characterization techniques are being explored. Efforts are underway to obtain the element mapping using the energy dispersive x-ray spectrometry. This provides a quantitative result to estimate the concentration and the distribution of the Al nanoparticles in the polymer matrix. A microtensile tester is being setup in combination with the atomic force microscopy to estimate the displacement fields upon the application of load on the surface and hence the mechanical properties of the material.
CONCLUSIONS
Nanocomposites of uniformly dispersed Al nanoparticles in Engage 8140 have been successfully fabricated. Residence time and residence volume distributions obtained from the preliminary experiments are being analyzed to achieve better understanding of the mixing process. This forms a strong foundation and paves way to the fabrication of oriented, well dispersed and deagglomerated CNTs in various polymer matrices using the TSE technology. Navier-Stokes based CFD modeling has shown that microchannel extrusion of viscous, two-phase polymer melt is feasible. Rheometry experiments have provided the evidence of a novel shear thickening phenomena. The microscopy of the surface of the extrudate has confirmed the efficient dispersion resulting from the TSE processing. While there were significant optical effects from the dilute addition of nanoparticle, there were no apparent effects on the mechanical properties.

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REFERENCES