Microinjection molding of polymer/multi-walled carbon nanotube nanocomposites

Shengtai Zhou, Andrew Hrymak, and Musa Kamal

The filler distribution within micromoldings may be significantly affected by molding conditions, mold geometry, and the selection of polymer matrices.

Traditionally, injection molding has been geared for the mass production of components in industry sectors where polymeric materials play a large part (e.g., automotive and electronics), as a result of their weight advantage and ease of processing.[1,2] With the recent advent of microinjection molding (μIM) technology, the merits of polymeric materials have been further exploited to meet the increasing demands of microparts (μ-parts) in areas of biomedical and microelectromechanical systems.

The definition of μ-parts is typically based on part weight (i.e., less than a few mg, and in some cases within the order of a few μg), part dimensions (i.e., several micrometers), and part-dimension tolerance (e.g., in the μ-range for microfluidic cells).[4] These critical features distinguish μIM from the conventional injection-molding process. For instance, the very large surface-area-to-volume ratio of μ-moldings necessitates the fast filling of mold cavities to prevent the premature solidification of polymer melts. Higher molding temperatures and injection speeds are therefore generally employed in μIM. As a result of this, however, severe shearing and extensional conditions are usually present in the resultant μ-moldings. Previous studies[5,6] have been primarily focused on replication (i.e., the ability of the molded μ-parts to duplicate the features of mold cavities), and the mechanical properties of unfilled plastics molded by μIM. The effects of the molding conditions and mold geometry on the properties of nanofiller-loaded polymeric composites have not, however, been fully explored.

We recently investigated the influence of these factors on the dispersion of multi-walled carbon nanotubes (CNTs) within μ-parts.[3] For this purpose, we prepared polystyrene (PS)/CNT nanocomposites to be molded by the masterbatch dilution process. We used a mold with a three-step decrease in the thickness configuration along the flow direction.[7] The μ-part was subsequently divided (i.e., mechanically separated using a scalpel) into three different sections based on thickness (namely, the thick, middle, and thin sections). We were not able to obtain an intact thin section using this cutting practice, but successfully obtained suitable thick and middle sections. We subsequently measured
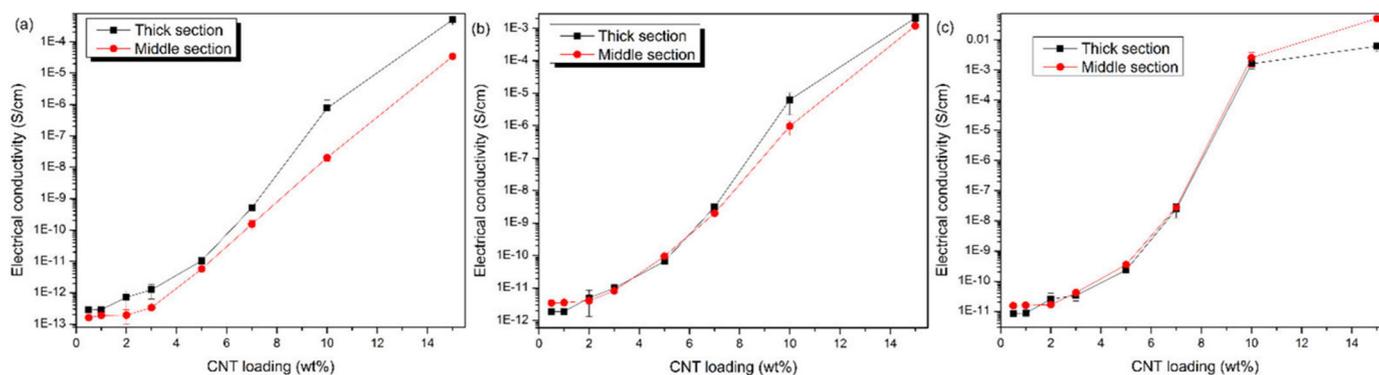
Figure 1. *Direct current conductivity measured across directions of (a) thickness, (b) width, and (c) length for the thick and middle sections of the polystyrene/multi-walled carbon nanotube (PS/CNT) μ-parts as a function of CNT content.*[3]
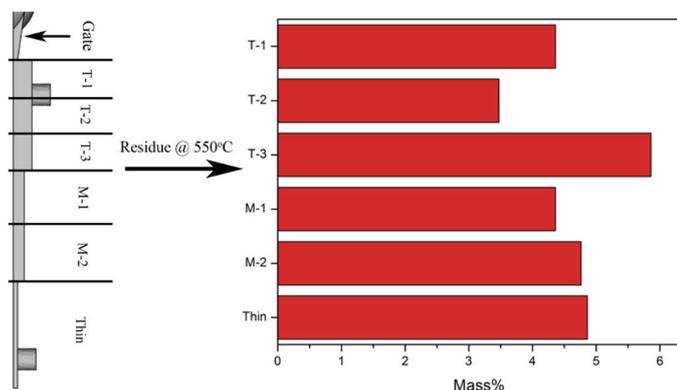
Figure 2. The overall distribution of CNTs along the flow direction of the μ-parts, which were separated into seven parts (i.e., Gate, T-1, T-2, T-3, M-1, M-2, and Thin) using a sharp knife. The boundary of each section is marked by black lines in the left image. These parts were then subjected to thermogravimetric analysis, from which residues were obtained (right).

the direct-current electrical conductivity through these parts in three different directions. The sections have the same width and length (2.4 and 5.0mm, respectively), with thicknesses of 0.85 and 0.50mm for the thick and middle sections, respectively. Our results show that melt temperature does indeed affect the development of conductive networks within the μ-molding. The μ-parts molded at higher melt temperatures show higher values of electrical conductivity, confirming that an increase to the melt temperature facilitates the formation of a conductive network. We attribute this result to the higher mobility of polymer chains at higher molding temperatures. Additionally, the degree by which the CNTs are orientated along the flow direction in the fabricated μ-parts is enhanced by increased shearing and extensional effects (i.e., those that arise due to the reduced mold-cavity thickness, high injection speeds, and elevated melt temperature). These higher shearing conditions lead to a higher degree of CNT alignment.

To investigate the percolation threshold (i.e., the filler loading at which the electrical conductivity is dramatically increased) of our μ-parts, we measured the electrical conductivity of the thick and middle sections as a function of CNT-loading concentration (see Figure 1). Our results indicate that the threshold, which we measured in different directions with respect to the melt-flow direction, shifts to higher CNT-loading concentrations (5–7 weight percent, wt%)—see Figure 1(a–c)—compared to those of polymer/CNT composites molded via other techniques (3wt%). This finding is in agreement with the results reported by Abbasi and coworkers.[8]

To detect the geometrical effect of the mold cavity on CNT dispersion within our μ-moldings, we sectioned samples along the flow direction with respect to the gate region and analyzed the results using

thermogravimetric analysis (see Figure 2). The results reveal that the overall dispersion of CNTs within the molded μ-parts is not uniform. This nonuniformity may occur as a result of the complex flow patterns (i.e., contraction and vortex flows) that are encountered in irregular mold cavities such as these. The very high shearing and extensional effects may represent another contributing factor.

We also studied the influence of the μIM process parameters on the conductivity of CNT-filled polypropylene (PP) nanocomposites.[9] Our morphology observations indicate the presence of CNT aggregates in the resultant PP/CNT μ-parts, and an absence of these aggregates in their PS/CNT counterparts. We ascribe this difference to the effect of the host polymers. In this case, the crystallization effect of PP chains leads to CNT being expelled into the amorphous region of the matrix, thereby affecting the CNT dispersion. We also found that the number of CNT aggregates decreases as the shear rate along the flow direction increases.

In summary, our work shows that molding conditions and host-polymer-matrix selection can have a significant effect on the microstructure of μ-parts containing CNTs. Generally, our results indicate that the ratio of conductivity measured parallel and perpendicular to the flow direction is higher for the middle section than the thicker section, indicating a higher orientation of CNTs in the middle section. Therefore, the disentanglement of large CNT aggregates within μ-parts is beneficial to the formation of a conductive network in the flow direction. We are currently further investigating the effect of host-polymer selection on the dispersion of CNTs within μ-parts.

Author Information

Shengtai Zhou, Andrew Hrymak, and Musa Kamal
Department of Chemical and Biochemical Engineering
The University of Western Ontario
London, Canada

Shengtai Zhou obtained his MSc from Sichuan University in Chengdu, China, and is currently a PhD student at the University of Western Ontario under the supervision of Andrew Hrymak and Musa Kamal. His research focuses on the μIM of carbon-filled polymer composites.

Andrew Hrymak is a professor of chemical and biochemical engineering, and dean of the Faculty of Engineering.

Musa Kamal is an emeritus professor in the Department of Chemical Engineering, and a professor at McGill University, Montreal, Canada.

References

1. M. R. Thompson, G. H. Motlagh, K. J. Oxby, and A. N. Hrymak, *Multiple percolation in a carbon-filled polymer composites via foaming*, **J. Appl. Polym. Sci. 115**, pp. 646–654, 2010. doi:10.1002/app.30177

2. M. Weber and M. R. Kamal, *Microstructure and volume resistivity of composites of isotactic polypropylene reinforced with electrically conductive fibers*, **Polym. Compos. 18**, pp. 726–740, 1997. doi:10.1002/pc.10325

3. S. Zhou, A. N. Hrymak, and M. R. Kamal, *Electrical and morphological properties of microinjection molded polystyrene/multiwalled carbon nanotubes nanocomposites*, **Polym. Eng. Sci.**, 2016. doi:10.1002/pen.24352

4. B. R. Whiteside, M. T. Martyn, P. D. Coates, P. S. Allan, P. R. Hornsby, and G. R. Greenway, *Micromoulding: process characteristics and product properties*, **Plast. Rubber Compos. 32**, pp. 231–239, 2003. doi:10.1179/146580103225002650

5. J. S. Chu, **Characterization of micro injection molding process and its products**, PhD thesis, McGill University, Canada, 2009.

6. N. Zhang, J. Chu, C. J. Byrne, D. J. Browne, and M. D. Gilchrist, *Replication of micro/nano-scale features by micro injection molding with a bulk metallic glass mold insert*, **J. Micromech. Microeng. 22**, p. 065019, 2012. doi:10.1088/0960-1317/22/6/065019

7. M. R. Kamal, A. Derdouri, and R. El-Otmani, *Structure development in micro injection molding of polyoxymethylene*, **Proc. PPS 28**, pp. O–MK–258, 2012.

8. S. Abbasi, P. J. Carreau, and A. Derdouri, *Flow induced orientation of multiwalled carbon nanotubes in polycarbonate nanocomposites: rheology, conductivity, and mechanical properties*, **Polymer 51**, pp. 922–935, 2010. doi:10.1016/j.polymer.2009.12.041

9. S. Zhou, A. Hrymak, and M. Kamal, *Microinjection molding: influence of molding parameters on the electrical conductivity of polypropylene filled with multi-walled carbon nanotubes*, **Proc. SPE ANTEC**, pp. 1167–1171, 2016.