ELECTRICALLY CONDUCTIVE AMORPHOUS THERMOPLASTIC COMPOSITES
CARBON FIBER-CARBON BLACK INTERATIONS AND FIBER ORIENTATION IN ELECTRICALLY CONDUCTIVE AMORPHOUS THERMOPLASTIC COMPOSITES

By
GHODRATOLLAH HASHEMI MOTLAGH, B.Sc., M.Sc.

A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

McMaster University
©Copyright by Ghodratollah Hashemi Motlagh, September 2007
DOCTOR OF PHILOSOPHY (2007) McMaster University
(Chemical Engineering) Hamilton, Ontario, Canada

TITLE: Carbon Fiber-Carbon Black Interaction and Fiber
Orientation in Electrically Conductive Amorphous
Thermoplastic Composites

AUTHOR: Ghodratollah Hashemi Motlagh

SUPERVISORS: Dr. Michael R. Thompson
Dr. Andrew N. Hrymak

NUMBER OF PAGES: xix, 186
Abstract

An electrically conductive thermoplastic composite (ECTPC) consists of electrically conductive filler(s) at a concentration above percolation threshold distributed in an insulating polymer matrix. The high concentration of the filler required to achieve high electrical conductivity for ECTPC is usually accompanied with the deterioration of mechanical properties and a large increase in the viscosity which prevents feasible processing of these materials in common polymer processing equipments such as injection molding machinery. The initial focus of this work was to control these drawbacks by using combinations of conductive fillers namely carbon fiber (CF) and carbon black (CB) to create a hybrid-filler composite. Cyclic olefin copolymer (COC), an amorphous polyolefin, was used as the matrix material. It was found that carbon black and carbon fiber synergistically contribute to the transport of electrons through the matrix. The synergism exists at various filler concentrations including when one of the fillers was present below its percolation threshold, but not at high carbon fiber content. Results showed that where the concentration of CF was several fold higher than carbon black a good trade-off between viscosity and conductivity can be achieved so that the obtained composites can be reasonably processed in common processing equipment e.g. in an injection molding machine.

Carbon fiber is preferred to carbon black as it leads to ECTPC with higher electrical conductivity and lower viscosity. However, the high aspect ratio fibers preferentially align in the flow direction leading to ECTPCs which have electrical conductivity several orders of magnitude greater in the in-plane rather than through-plane. We focused on foaming as a strategy to reorient the fibers toward the through-plane direction in foam injection molding. Through a fractional factorial experimental design, the effect of injection rate, melt temperature and mold temperature on electrical conductivity was screened at two levels for foam and nonfoam COC/CF(10 vol%)-CB(2 vol%) injection molded composites. It was
found that foaming significantly enhanced the through-plane fiber orientation and through-plane conductivity of the hybrid composite at low injection rate and high melt temperature. The concurrence of the melt flow and bubble growth was considered to be the key mechanism for fiber reorientation while the cell size and shape should not disrupt the conductive path spanning the bulk of the material.

The importance of the relative length scale of the fillers on cell size and subsequently, electrical conductivity was investigated by injection molding. Results showed that where the length scale of the filler was comparable to the cell size, as for foamed COC/CF composites, the conductivity considerably decreases with foaming. The drop was greater in the through plane direction and smaller in the in-plane direction for the composites with larger average fiber length. Also smaller cells led to a larger drop in the composite conductivity. It was observed that where the length scale of the filler was much smaller than the cell size as such for COC/CB composites, foaming enhanced the electrical conductivity particularly in the through-plane directions and its effects became more pronounced at lower carbon black concentrations. It was proposed that induced carbon black coagulation by foaming was the main reason for the observed improvement in conductivity. For COC/CF-CB hybrid composites, enhancement in through-plane conductivity, particularly at CB concentration below percolation, via foaming inferred that CB aggregates significantly contributed in improving fiber-fiber contacts.

Reorientation of the fibers by foaming was found to be very dependent on processing conditions. High viscosity and fiber-fiber interactions can hinder fiber rotation. The general understanding of the investigation was that fiber reorientation may occur where the cells are much larger than the fibers. In comparison, a series of nonfoam injection molded composites containing CF, CB and CF-CB were foamed in a batch process to avoid flow effects. The insignificant change in fiber orientation with foaming proved that fibers can not
rotate by the growth of an adjacent cell in the absence of shear. Also, a large drop in electrical conductivity with foaming as compared to the foam injection molded composites suggested that particle relocalization can not occur in batch foaming.
Acknowledgments

I am very glad that I can use at least this page to profoundly thank the people who helped and supported me to pursue my PhD study at McMaster University:

My supervisors Dr. Michael Thompson and Dr. Andrew Hrymak, for their invaluable role in guiding, inspiring and encouraging me during these years. I learned not only a lot of scientific and engineering knowledge from them but also the beauty of ethics, integrity and dedication in the academic environment.

Iran Ministry of Science, Research and Technology to give me the chance to conduct my PhD at McMaster University by awarding me a full scholarship covering my tuition fees as well as living expenses for me and my family.

Ontario Centres of Excellence’s Emerging Material Knowledge for the financial support of this research.

Dr. Robert Pelton and Dr. Gu Xu as members of my supervisory committee for their valuable guidance, remarks, advice and criticism. I also extend my gratefulness to them for allowing me to use some of their lab devices for my experiments.

Dr John Vlachopoulos, as the chair of my comprehensive examining committee, for his time, patience and guidance. I am also very grateful to his friendship, warm conversations and encouragement. He is a non-forgettable character.

Paul Gatt for his exceptional and unique role and technical support by making molds, conductivity measurement apparatus, sample machining and a lot of other valuable technical needs.

Elizabeth Takacs as CAPPA-D lab manager for the trainings on the equipments.
Brendan Job, Brandon Shiplo and Keith Oxby as summer students who significantly helped me in conducting my experiments in the summer of 2006 and 2007.

Gord Slater (Electrician), Warren Reynolds (MMRI lab manager), Doug Culley (lab Technologist), Chris Butcher (optical microscopy specialist), Marcia West (Microtoming specialist), Steve Koprich (SEM specialist), Glynis de Silveira (manager, BIMR analytical services) and Glen Leinweber (lab technician) for their instructions and valuable help in conducting my experiments and analysis.

Kathy Goodram, Lynn Falkiner, Andrea Vickers and Julie Birch, secretaries at our department, for their unseen but vital responsibilities.

My colleagues and friends in the department: Dr Velichko Hristov, Dr Henrich Krump, Abdullah Al Otaibi, David D’agostino, Art Tinson, Karen Rogers, Lou Diflavia, Tayyeb Hamid, Maryam Emami, Xiaonan Qin, Damyan Kanev, Andrew Mikhail, Alex Yeung and Jinling Liu for their friendship, constructive discussions and support.

Asbury Carbons with special thanks to Dr Albert Tamashausky, Lydall (Bill Lonstein), Ticona (Matt Noon), Toho (Steve Hoy), Dempsey Corporation, Inco and AkzoNobel for providing raw materials and supplies.

Dr. Rohollah Bagheri From Isfahan University of Technology, Dr. Seied Reza Ghaffarian, Dr Naser Mohammadi and Dr. Hossein Nazokdast from AmirKabir University of Technology.

And my wife Zahra Samiei for her love, patience and support. I would not be able to succeed without her sacrifice and encouragement. My son for being
there as the beauty of life and the gift and sign from The Unique, The Truth, The Infinitive.

My mother Shokat Lak and my father Hojjatollah Hashemi Motlagh, without them and without their inspiration, support and love I would never exist and be who I am. They sacrificed their lives for me to grow up and accomplish. I dedicate this work to them. My sisters and my brother for the times being together and their love and encouragement.
Table of Contents

Abstract iii

Acknowledgments vi

Table of Contents ix

List of Figures xiii

List of Tables xviii

Chapter 1: Research Objectives 1

1.1. Introduction 1

1.2. Thesis Objectives 4

1.3. Thesis Outline 4

References 5

Chapter 2: Background and Literature Review 7

2.1. Introduction 7

2.2. Applications of Electrically Conductive Polymer Composites 8

2.2.1. Electrodes 9

2.2.2. Resistance Heating 10

2.2.3. Sensors 10

2.2.4. EMI/RFI Shielding 10

2.2.5. Bipolar Plates 11

2.3. Electrically Conductive Polymer Composites 12

2.3.1. Percolation Threshold 14

2.3.2. Carbon Black Composites 15

2.3.3. Carbon Fiber Composites 18

2.3.4. Synergism in Hybrid Composites 20
Chapter 3: COC Composites Containing Carbon Fiber and Carbon Black: Electrical Conductivity, Rheology and Synergism

Abstract

3.1. Introduction

3.2. Experimental

3.2.1. Materials

3.2.2. Procedures

3.2.3. Analysis

3.3. Results and Discussion

3.3.1. Single-filler composites

3.3.2. Hybrid CB/CF filler composites

3.4. Discussion of Conductive Synergism

3.5. Conclusions

References

Chapter 4: Improved Through-Plane Electrical Conductivity in a Carbon Filled Thermoplastic via Foaming

Abstract

4.1. Introduction

4.2. Experimental

4.2.1. Materials

4.2.2. Procedure

4.2.3. Analysis
Chapter 5: Electrical Conductivity of Carbon Black and Carbon Fiber Foam Polymer Composites

Abstract

5.1. INTRODUCTION

5.2. EXPERIMENTAL
5.2.1. Materials
5.2.2. Procedure
5.2.3. Analysis

5.3. RESULTS
5.3.1. Foam Cellular Structure
5.3.2. Fiber Orientation
5.3.3. Electrical Conductivity
5.3.4. Batch Foaming

5.4. DISCUSSION
5.4.1. Fiber Orientation
5.4.2. Electrical Conductivity
5.4.3. Overview

5.5. CONCLUSIONS

REFERENCES
6.1. Conclusions .......................................................... 167
6.2. Contributions to Knowledge .................................. 169
6.3. Recommendations for Future Work ...................... 170

Appendix A: Fiber Length ........................................... 171

Appendix B: Simplified rotation of a fiber by bubble growth 176

Appendix C: Process Related Influences ....................... 178
  C.1. Back Pressure .................................................. 178
  C.2. Hold Pressure .................................................. 181
  C.3. Mold Thickness ............................................... 183

Appendix D: Fraction of carbon black aggregates in vicinity of cells
................................................................. 185
List of Figures

Figure 2.1. Electrical percolation threshold in electrically conductive polymer composites ____________________________ 15

Figure 2.2. Optical micrograph showing fiber orientation distribution through the side view of an injection molded PA66/glass fiber (33 wt%) rectangular specimen [Shokri and Bhatnagar, 2006]. ____________________________ 27

Figure 2.3. Typical curve for shear viscosity versus shear rate of polymer melts 28

Figure 2.4. Schematic velocity profile for Newtonian and shear thinning fluids between parallel plates ------------------ 28

Figure 3.1. Cutting pattern to prepare samples for electrical conductivity measurements ____________________________________ 53

Figure 3.2. In-plane and through-plane conductivity of COC/CB and COC/CF composites _____________________________________ 58

Figure 3.3. Storage modulus (G') and complex viscosity (η*) of COC composites at 0.15 (rad/s) ___________________________________________ 60

Figure 3.4. In-plane electrical conductivity of hybrid composites compared with single-filler composites ____________________________________ 61

Figure 3.5. Optical micrograph from polished surface of COC/CF (20 vol %). View is parallel to the mold plates and arrow shows the radial flow direction. ____________________________________________ 62

Figure 3.6. Average fiber length for COC/CF composites with and without 3 vol% CB ____________________________________________ 63

Figure 3.7. Through-plane/in-plane conductivity ratio (anisotropy) for single-filler and hybrid composites ____________________________________________ 65

Figure 3.8. Dependence of through-plane conductivity on the extent of removed skin ____________________________________________ 67

Figure 3.9. Viscosity-conductivity correlation for hybrid composites _______ 69
Figure 3.10. SEM micrograph from fractured surface of the COC composite containing 5 vol% CF and 0.75 vol% CB

Figure 4.1. Conceptualization of fiber rotation in the presence of bubble growth.

Figure 4.2. Cutting pattern to prepare samples for electrical conductivity measurements: samples for longitudinal and transverse measurements (top) and samples for through-plane measurements (bottom).

Figure 4.3. 3D Diagram showing a fiber with the defined parameters in Cartesian coordinate to determine fibre orientation.

Figure 4.4. Cumulative cell size distribution of foamed samples obtained by optical microscopy from polished LW plane at the T location shown in Figure 4.2.

Figure 4.5. Cell morphology of the foamed composites in the LT plane: a) Run (6) produced at 10 cc/s, melt temperature of 300°C and mold temperature of 80°C and b) Run (7) produced at 100 cc/s, melt temperature of 260°C and mold temperature of 80°C.

Figure 4.6. Cumulative bubble elongation distribution of the factorial design foamed composites in the LT plane.

Figure 4.7. Micrographs showing (a) in-plane and (b) through-plane orientation of carbon fibers at the core for Run (4) taken by reflected light microscopy.

Figure 4.8. Cumulative orientation factor (f_T) distribution of the factorial design composites in the core.

Figure 4.9. Micrographs from reflected light microscopy showing the fiber and foam distribution within injection molded composites in the core (a) non-foamed composite A (b) foamed composite B with 10% reduced density (c) foamed composite C with 20% reduced density.

Figure 5.1. Sampling pattern for electrical conductivity measurements of the injection molded bar produced by mold A.
Figure 5.2. The shear viscosity versus shear rate at 260 °C for the injection molded composites 118

Figure 5.3. SEM image showing cell morphology for composite A5 (COC/cCF10, void content 15 vol%) in the LT plane. L horizontal direction and T vertical direction 122

Figure 5.4. Optical image showing cell size and fiber length distribution for composite A5 (COC/cCF10, void content 15 vol%) at the core in the LW plane. L horizontal direction and W vertical direction 123

Figure 5.5. Cumulative fiber orientation factor (fT) distribution at the core for the solid and foam injection molded COC/mCF(15) (obtained from LT plane) 127

Figure 5.6. Optical micrographs showing fiber orientation in the core of solid and foam injection molded COC/mCF(15) composites (left: A1, solid; middle: A2, void content 21 vol% and right: A3, void content 26 vol%). 127

Figure 5.7. Electrical conductivity of COC/CB(4.2) and COC/CB(3.4) composites. “core” corresponds to the samples with machined LW skin (0.6 mm on each side) 129

Figure 5.8. Electrical conductivity of nonfoam and foam injection molded COC/mCF(15 vol%) and COC/cCF(10 vol%) composites produced by mold A at 5 cc/s. a: before machining LW skin and b: after machining LW skin (0.6 mm). 131

Figure 5.9. Electrical conductivity of nonfoam and foam injection molded COC/mCF(15 vol%) and COC/cCF(10 vol%) composites produced by mold C at 10 cc/s. 133

Figure 5.10. Electrical conductivity of COC/cCF(10)-CB(0.75) and COC/cCF(10)-CB(2.5) composites prior and after LW skin removal (0.6 mm). 135
Figure 5.11. Fractured surface of batch foam composite a1 (COC/cCF10CB2.5, void content 29 vol%) obtained by SEM (flow direction is from left to right and vertical is the thickness direction). 139

Figure 5.12. Micrographs showing fractured surface of batch foam composites obtained by SEM (flow direction is horizontal and vertical is the thickness direction). 140

Figure 5.13. SEM images from fractured surface of batch foam composites showing interaction of bubbles and fibers. 142

Figure 5.14. Schematic showing rotation of a single fiber by a growing cell. 144

Figure 5.15. Schematic showing fiber-fiber interactions that interfere with the rotation of a fiber by a growing cell. 145

Figure 5.16. Optical micrographs showing matrix rich areas among fiber rich areas for composite A4 (COC/cCF10). Left: LW plane and Right: LT plane. 145

Figure 5.17. Diagram showing uniform and homogenous distribution of cells. 147

Figure 5.18. SEM image of the fractured surface of foam injection molded COC/CB3.4: (a) a large cell and the surrounding solid areas. Area b and c as shown on the image are presented at higher magnifications in Figure 5.18 (b) and (c). 152

Figure 5.19. SEM micrographs from fractured surface of COC/CB(3.4 vol%) composite: (a) nonfoam composite. 158

Figure A.1. Fiber length distribution of nonfoam injection molded COC/mCF (15 vol%) composite. 172

Figure C.1. The hypothetical diagram comparing decrease in the number of fiber-fiber contacts by the presence of small and large cells. 180

Figure C.2. Effect of hold pressure on the electrical conductivity of foam injection molded COC/cCF(10)-CB(2.5) composites at 15% reduced density. “core” corresponds to the samples with machined LW skin (0.6 mm). 182
Figure C.3. Electrical conductivity of injection molded COC/CB(3.4) composites produced by mold B (thickness 6.2 mm) and mold A (thickness 3.1 mm). a: before removing LW skin and b: after removing LW skin (0.6 mm).
List of Tables

Table 3.1. Properties of COC polymer* ________________________________ 50
Table 3.2. Properties of carboneous fillers* __________________________ 51
Table 3.3. Carboneous-filled COC formulations ________________________ 57
Table 3.4. Standard percolation model parameters for single-filler composites 58
Table 3.5. Electrical conductivity of hybrid composites with one filler below percolation ________________________________ 70
Table 3.6. Comparison of experimental results and model predictions for single-filler and hybrid composites __________________________ 74
Table 4.1. Fractional factorial design to produce injection moulded samples __ 85
Table 4.2. Properties of the foamed composites prepared according to the fractional factorial design ________________________________ 89
Table 4.3. Orientation factors in three principal directions (L,W and T) for the factorial design injection molded samples ______________________________ 96
Table 4.4. Electrical conductivity results$^a$ for factorial design injection molded composites (10 vol% CF and 2 vol%CB) in the L, W and T directions. __ 99
Table 4.5. Results of the factorial analysis showing the effects of factors on fiber orientation factor and electrical conductivity ________________________________ 101
Table 4.6. Injection molding conditions for injection moulded composites (10 vol% CF and 2 vol%CB) with CBA powder ________________________________ 103
Table 4.7. Electrical conductivity of the composites (10 vol% CF and 2 vol%CB) with CBA powder. Reported conductivity values have been multiplied by 10$^5$. ______________________________________ 104
Table 4.8. Orientation factors for composites with CBA powder _______ 105
Table 5.1. Properties of the conductive fillers' __________________________ 113
Table 5.2. Acronyms used in this study for material compositions _______ 114
Table 5.3. Dimensions of centre-gated molds used to produce injection molded composites 116
Table 5.4. Specification of injection molded composites 1 117
Table 5.5. Cell size of the foam injection molded composites 124
Table 5.6. Fiber orientation factors of the injection molded composites 126
Table 5.7. Properties of the injection molded composites foamed by batch process 137
Table 5.8. Electrical conductivity of compression molded [Motlagh et al 2007] and injection molded COC/CB composites. Numbers in the brackets relate to conductivities of the samples after LW skin removal (i.e. core) 157
Table 5.9. Summary for the effects of foaming on electrical conductivity 161
Table A.1. Fiber length of carbon fiber precursors and selected composites from Table 5.4 (IM= injection molding/molded). 173
Table C.1. Effect of back pressure on the properties of foam injection molded COC/cCF(10). 179
Chapter 1

Research Objectives

1.1. Introduction

Polymers are generally recognized as insulating materials and have been used in numerous applications in place of metals, glass, wood, ceramics, leather etc., whether or not their insulating property has been required. However, the idea of using polymers in applications where electrical conductivity is needed has turned attention toward developing electrically conductive polymer systems [Seymour, 1983; Shirakawa et al, 1977; Blythe and Bloor, 2005; Stewart, 2005]. There have been two major approaches to produce these systems: synthesizing new polymer materials which are intrinsically conductive; and adding conductive materials to an insulating polymer in order to obtain a conductive material system. Examples of intrinsically conductive polymers include polyaniline, doped polypyrrole and polythiophene. But the use of these materials is very limited due to the high cost and lack of being readily melt-processed. The use of filled electrically conductive material systems has grown quickly by introducing electrically conductive polymer composites (ECPC) which have reasonable cost and can be processed by common polymer processing methods such as extrusion and injection molding. The most commonly used conductive additive has been carbon black; however, the list of useful fillers has grown over the last decade to include carbon fiber, graphite, metal coated carbon fiber, metal coated graphite, carbon nanotubes, carbon nano fibers, expandable graphite, metal fibers and metal
powders. These conductive fillers must be added at concentrations above their percolation thresholds, to transform an insulating polymer into an ECPC.

ECPCs can be tailored for use over a broad range of characteristic electrical conductivity categories, including antistatic ($10^{-9} - 10^{14}$ S/cm), electrostatic dissipation ($10^{-5} - 10^{-9}$ S/cm), semi-conductive ($10^{-2} - 10^{-4}$ S/cm) and highly conductive (0.1-100 S/cm) applications. Examples of highly conductive applications include electromagnetic interference shielding (EMI) (0.1-1 S/cm) and bipolar plates for proton exchange membrane fuel cells (10-100 S/cm). As a matter of fact, to generate these highly conductive composites a large amount of the conductive filler must be added to the polymer matrix. Those filler levels usually lead to extremely high viscosity and deterioration of mechanical properties for the obtained composite. High viscosity restricts the processability of the material in extrusion and injection molding. Therefore, lowering the filler loading to reduce viscosity and improve mechanical properties has been the main focus of several research groups towards developing suitable ECPCs for higher electrical conductivity applications such as EMI shielding applications and bipolar plates.

Combinations of conductive fillers have shown some signs of synergistic effects i.e. the electrical conductivity of a composite containing combined filler types (hybrid composite) is higher than those containing the corresponding single fillers at the same volume content [Mighri et al, 2004; Balta Calleja et al, 1988; Clingerman et al, 2002; Zhong et al, 1991; Drubesti et al, 2005]. These hybrid composites attempt to achieve conductive pathways at lower filler concentrations by using different aspect ratios or magnitudes of size. However, this topic has not been distinctly explored over a range of concentrations for the fillers and is complicated by the fact that synergism has not been clearly addressed before now. In particular, previously published studies which considered hybrid composites
have only handled filler concentrations above the individual component’s respective percolation threshold. Moreover, the correlation between rheology and conductivity for hybrid and single filler composites has not been widely reported in the literature. In the present work we investigate this relationship between rheology and electrical conductivity for a carbon fiber-carbon black hybrid composite in a cyclic olefin copolymer thermoplastic matrix over a range of concentrations including below percolation.

While hybrid composites offer the potential for synergism, the practice of making such materials is much more complicated compared to the single filler composite. Processing of very small, low aspect ratio fillers are difficult due to poor dispersion, and high aspect ratio fillers are challenged by their preferential orientation assumed in a flow field. Based on equivalent surface area, fibers compared to powders exhibit lower percolation threshold and thus higher electrical conductivity. Preferential alignment of the fibers within a shear flow field results in reduced flow resistance compared to lower aspect ratio fillers of similar volume content. For injection molded parts, such as bipolar plates or thin casings for EMI shielding, conductivity in the through-plane direction (perpendicular to the MFD) is 1-3 orders of magnitude lower than for in-plane conductivity (parallel or transverse to the MFD). For EMI shielding applications a random fiber orientation would provide higher shielding effectiveness [Lee et al, 2005] while for bipolar plates, conductivity is required exclusively in the through plane direction [Mehta and Cooper 2003]. Therefore, manipulation of the injection molding process to promote random or through plane fiber orientation is of crucial importance to extend applications of hybrid (or even just fiber alone) conductive polymer composites.

This work will focus on one proposed method to partially disrupt the preferred orientation displayed by carbon fibers in a shear flow field, namely
foaming. Foaming involves the nucleation and growth of gas bubbles in a polymer melt, which if present during mold filling are theorized to affect fiber orientation, and consequently the anisotropic electrical conductivity properties of molded composites. The electrical conductivity of foam injection molded carbon black, carbon fiber and hybrid carbon black-carbon fiber composites have been compared to understand the relationship between bubble morphology and filler reorientation and importance of correlation between length scales of bubble and particle size with electrical conductivity.

1.2. Thesis Objectives

The main objectives of this work are classified in two stages:

1) To understand the effects of combinations of carbon fiber (CF) and carbon black (CB) on the electrical conductivity and rheology of their respective composites, and,

2) To examine the effect of foaming on filler (fiber and particle) orientation, as well as the morphology and electrical conductivity of CF, CB and CF+CB hybrid composites.

1.3. Thesis Outline

This thesis contains published work and consists of the following chapters:

- Chapter 2 provides background information and a literature review on the relevant aspects of this research. It introduces conductive polymer systems and their applications and specifically reviews in detail, electrically conductive carbon black and carbon fiber thermoplastic composites. Rheology of filled polymers, flow induced fiber orientation in injection molding and foam injection molding are the subsequent topics in this chapter.
• Chapter 3 investigates combinations of carbon black and carbon fiber as conductive fillers at various concentrations, to achieve composites with enhanced electrical conductivity and reduced viscosity. The work in Chapter 3 has been published in *Journal of Polymer Science Part B Polymer Physics*, 45, 1808-1820, 2007.

• Chapter 4 investigates the effects of foaming on electrical conductivity and fiber orientation of injection molded plaques from olefin copolymer containing 10 vol% carbon fiber and 2 vol% carbon black. It uses a fractional factorial experimental design to identify the important processing factors for improving the through-plane electrical conductivity. This work has been published in *Polymer Engineering and Science*, 48, 4, 687-696.

• Chapter 5 investigates the foam injection molding process with special attention toward the effects of fiber length and cell size on fiber reorientation and electrical conductivity. It also considers the correlation between relative size of the cells and length scale of the particles with resulting electrical conductivity for the foam composites. This work is intended for submission to a relevant refereed journal.

• Chapter 6 states the main conclusions and contributions to knowledge of the thesis and recommendations for future work.

References

- Drubetski, M; Siegmann, A; Narkis, M (2005) *Polym Compos*, 26, 454-464
- Stewart, R (2005) Plast Eng, 61(8), 19-26
- Zhong, S; Kazacos, M; Burford, R P; Skillas-Kazacos, M (1991) J Power Sources, 36, 29-43
Chapter 2

Background and Literature Review

2.1. Introduction

Polymers have been widely used as electrical insulating materials for decades. The inherently non-conducting characteristic along with ease of processing and shaping have led to versatile application of polymers as insulating materials in communication, electrical and electronic products. Typical examples include cell phone parts, connectors and chip capacitor bases attached to the surface of printed circuit boards, coaxial cable coatings for television and radar equipment and power wires and cable coatings [Blythe and Bloor, 2005; Stewart, 2005]. Polymer properties can also modified so they can also be used for a variety of applications where electrical conductivity is required.

Polymers containing double bonds in their backbone, known as conjugated polymers, can exhibit electrical conductivity many orders of magnitude higher than conventional insulating polymers. These inherently conductive polymers came to the attention of researchers when Shirakawa et al [1977] discovered that the electrical conductivity of conjugated polymers, such as polyacetylene, can be further increased by several orders of magnitude via doping with electron acceptors such as iodine. This significant discovery by Shirakawa et al. [1977] was recognised by the award of a Nobel Prize in 2000. This new class of
polymers are sometimes referred to as *Organic Metals* due to their metal-like electrical conductivity. It was expected that this class of polymers could replace metals in batteries and conductive wires. However, the material loses its conductivity over time and is not stable in the presence of oxygen. New generations of inherently conductive polymers, such as polyaniline, doped polypyrrole and polythiophene were subsequently synthesised and were shown to be much more stable [Billingham and Calvet, 1989]. They have been used in electrochromic, electroluminescent and optoelectric devices, such as light-emitting diodes or flat-panel light emitting displays, biomedical and environmental sensors, shielding materials, corrosion protection, antistatic coatings, catalytic and rectifying electrodes and actuators [Jagur-Grodzinski, 2002]. Despite these various applications, inherently conductive polymers remain relatively constrained in their uses since they can not be easily melt processed and products made from them exhibit poor mechanical properties and are often quite expensive due to the costs of the conductive polymers. Alternatively, the older technology of creating electrically conductive polymer composites, which are composed of conductive fillers added to an insulating polymer matrix, are making a resurgence in popularity to fulfil new demand for these materials. These polymer composites can be melt processed by conventional polymer processing equipment, modified as would be the case for other filled polymers, such as extruders or injection molding machines and their physical mechanical properties can be readily manipulated as required by the application [Blyth and Bloor, 2005].

### 2.2. Applications of Electrically Conductive Polymer Composites

Electrically conductive fillers such as metal powders, metal fibers, carbon black, carbon fibers and carbon nanotubes are dispersed into an insulating plastic matrix above a threshold concentration to produce electrically conductive polymer
composites. There is growing interest toward composites based on thermoplastics instead of thermosets as they can be processed in their melt state by methods such as extrusion and injection molding. The advantages often sought by selecting conductive polymers (over more traditional materials such as metals) are their low density, good chemical resistance and barrier properties, as well as being more readily formed into complex shapes without expensive secondary processing steps. The major applications for electrically conductive composites, depending on the magnitude of the electrical conductivity, can be divided into the following categories [Huang, 2002]:

- antistatic applications (10⁻⁹ to 10⁻¹⁴ S/cm),
- electrostatic dissipation applications (10⁻⁵ to 10⁻⁹ S/cm),
- semi-conducting materials (10⁻² to 10⁻⁴ S/cm), and
- conductors (>10⁻¹ S/cm).

The last category is the most challenging for polymer composites but is growing in importance for modern applications. Advanced engineering applications such as electromagnetic and radio frequency interference shielding (EMI/RFI) require materials exhibiting approximately 1 S/cm in electrical conductivity while bipolar plates for fuel cell stacks require considerably higher conductivity of 10-100 S/cm. Consumer-based applications include resistance heating, positive temperature coefficient (PTC) switches for auto-regulating electrical heaters, thermoelectric energy conversion, sensors and polymer solder [Chung, 2004]. Some of these products are explained in more detail here.

2.2.1. Electrodes

Some electrochemically active electrode materials such as manganese dioxide are not electrically conductive. Therefore, a conductive additive such as
carbon black is added to the electrode material along with a thermoplastic binder such as polyvinylidene fluoride or polytetrafluoroethylene [Frysz et al., 1996].

2.2.2. Resistance Heating

The flow of electrical current through a resistor produces heat by resistance heating (otherwise known as Joule heating). Polymer composites containing carbon fiber or carbon black have been found useful in this regards as heating element, and as suitable alternatives to metal alloys, ceramics, graphite and concrete [Hung et al, 1987].

2.2.3. Sensors

Electrical phenomena can be used to detect changes in the structure of a material brought on by strain, damage and temperature. Piezoresistive materials are particularly sensitive in this regards with the application of strain or stress. Polymer-carbon fiber composites are such materials. Changes in strain, stress or the evolution of damage result in altered structural properties such as fiber orientation and fiber-fiber contact which in turn change the conductivity of the composite [Muto et al., 1992; Wang and Chung, 2001]. Change in electrical conductivity due to temperature is referred to as a thermistor effect. Laminates of polymer carbon fiber composites show such an effect and are used as sensors to measure temperature [Wang and Chung, 1999].

2.2.4. EMI/RFI Shielding

Many electronic devices such as computers and cell phones emit electromagnetic waves, also called radio frequency waves, which if not shielded can interfere with the operation of other electronic devices and conversely their own operation can be interfered by other likewise devices. Electromagnetic
shielding (EMI) or radiofrequency shielding (RFI) is the absorption or reflection of electromagnetic waves by a material. EMI shielding is of great importance as the number of electronic devices grows and device size decreases. In addition, governments globally are increasingly regulating manufacturers of electronic devices to meet certain EMI shielding standards before commercialization of a product is allowed. In reflection, which is the primary mechanism in EMI shielding electromagnetic waves interact with mobile charge carriers, electrons or holes, in the shielding material. Although it is not necessary that the shielding material be conductive, increased conductivity enhances the shielding effectiveness [Chung, 2004]. Metals are the most common materials for shielding; however, polymer composites containing conductive fillers are becoming increasingly viewed as more acceptable candidates for EMI shielding applications [Tzeng and Chang, 2001; Huang and Wu, 2000; Saltzberg et al., 1996]. Polymers are light-weight and can be molded into any shape which reduces or eliminates seams. Seams that usually exist in metal sheets can cause leaking of electromagnetic waves through the shield and reduce their overall shielding effectiveness [Chung, 2004].

2.2.5. Bipolar Plates

For a proton exchange membrane fuel cell (PEMFC) the power supplied by an individual cell is around 1 V, which is barely enough for even the smallest applications. To increase the amount of electricity generated, several individual cells are combined together in series. Bipolar plates are used to connect these cells in series. Bipolar plates have several important functions in the fuel cell stack:

i) conduct the relatively small current from the anode of one cell to the cathode of another without major loss;
ii) control the flow of reactant gases and byproduct water vapour within a cell; and
iii) regulate heat transfer within a cell [Larminie and Dicks, 2003].

The bipolar plates must have many strictly specified properties in order to meet these functions. Different material systems have been used to make bipolar plates, mostly graphite, metal, carbon/carbon composites and polymer carbon composites. Each system has its advantages and disadvantages. Graphite is brittle and needs machining. Stainless steel encounters corrosion issues, and carbon/carbon composites must go through an expensive and complicated fabrication step followed by a machining process. Polymer/carbon composites are the most recent approach to manufacture bipolar plates. The matrix can be a thermost set or thermoplastic and can be injection or compression molded. This composite system exhibits good electrochemical stability and the manufacturing method is very simple and inexpensive in comparison with other methods. The major concerns are obtaining the specified electrical conductivity levels (i.e. 100 S/cm) and enough mechanical strength (crush strength>3000 psi) at a low thickness, simultaneously [Mehta and Cooper, 2003; Onischak et al, 1999].

2.3. Electrically Conductive Polymer Composites

Addition of electrically conductive fillers to an insulating polymer matrix is a common route to prepare electrically conductive polymeric materials. The choice of polymer matrix is determined by cost, availability, processability, stability, physical mechanical properties and other specific considerations for a particular application. Although the polymer matrix can be thermoplastic or thermost, the former is preferred due to the availability of melt processing equipments such as extruders and injection molding machines to convert thermoplastics into any shape at relatively low cost and large quantities. The other advantage of thermoplastic is the possibility to recycle which can be a crucial matter depending on environmental regulations and issues of responsible care.
With the exception of inherently conductive thermoplastics such as PANI which exhibit poor melt processability, other commercial thermoplastics fall in the category of insulating materials. A few thermoplastics such as polyphenylene sulphide (PPS) exhibit electrical conductivity levels which are several orders of magnitude higher than many others such as polyolefin family. Therefore, the usage of less insulating matrix would create a composite with higher electrical conductivity but may not necessarily serve the other property requirements, such as the chemical resistance required of a bipolar plate. The choice of filler to enhance conductivity of the polymer depends on its density, size, shape, inherent electrical conductivity, cost and physical chemical properties. Metal fillers have excellent electrical conductivity but suffer from their high density which diminishes the light weight advantage of polymer composites. In addition many metals like copper experience oxidation of the metal surface either by processing or in their service environment, which in turn deteriorates its electrical conductivity. Carbon fillers include:

- carbon black [Huang, 2002],
- carbon fiber [Mironov et al., 2002; Feller et al., 2002; Tsotra and Friedrich, 2003; Clingerman et al., 2001a].
- graphite [Kalyon et al., 2002; Clingerman et al., 2001b]
- carbon nanofibers [Kuriger et al., 2002]
- carbon nanotubes [Potschke et al., 2004; Bai and Allaoui, 2003; McLachlan et al., 2005; Lanticse et al., 2006].

These carbon fillers offer a broad range of conductivity to customize an electrically conductive polymer composite. These carbon species are thermally stable, lightweight and chemically inert, which makes them compatible with the typical applications of polymers. To further improve the electrical conductivity of carbon materials they can be coated with metals. These metal-coated carbon fillers
such as nickel-coated graphite particles and nickel-coated carbon fibers possess high electrical conductivity values close to that of metals but considerably lower density [Weber and Kamal, 1997]. Since this research mainly focused on carbon black and carbon fiber as conductive fillers, they will be discussed in greater detail below.

### 2.3.1. Percolation Threshold

Figure 2.1 shows that as the concentration of electrically conductive filler gradually increases in an electrically insulating polymer matrix, the resultant composite behaves as an insulating material until a certain concentration is reached. Upon reaching that concentration, known as the *percolation threshold*, electrical conductivity of the composite rises by several orders of magnitude with only a small increase in filler content whereafter the composite conductivity falls in the semi-conducting region. Further addition of conductive filler creates a conductive material. With a percolation network of filler established in the polymer, a continuous path of conductive particles forms so that electrons can travel from one surface to another through the material. The magnitude of the conductivity and attributed percolation threshold depends on filler size, geometry, aspect ratio, polymer-filler interaction, morphology of polymer and processing method. Conductivity also varies with the dispersion and distribution of the filler in the polymer matrix determined by the processing history of the material such as mixing and molding methods [Lux, 1993; Huang, 2002; Di et al., 2004; Bigg, 1979; Mironov et al., 2002; Kalyon et al., 2002; Gul et al., 1972].
2.3.2. Carbon Black Composites

Carbon black (CB) is an amorphous form of carbon with a structure similar to disordered graphite. Furnace black, thermal black, lampblack, channel black, and acetylene black are five types of CB manufactured by companies. Different processes generate carbon black products with various physical and chemical properties. For instance, the conductivity of CB products on the market can vary from 1 to 100 S/cm. Carbon black is composed of prime particles fused into primary aggregates. Van der Waals forces cause these aggregates to join into more loosely assembled agglomerates. The aggregate size and shape, and the
number of particles per aggregate determine the structure of CB. A CB characterized by primary aggregates composed of many primary particles, with considerable branching and chaining, is referred to as a high-structure CB. Surface area, structure and surface chemistry are three important characteristics of CB. In polymer composites, a CB with larger surface area and porosity, higher structure and lower number of oxygen groups on its surface gives a lower percolation threshold and higher electrical conductivity [Sichel, 1982; Donnet, 1976; Huang, 2002]. Based on the carbon black type, the percolation threshold may vary from 2 - 11 vol% in a similar polymer matrix [Sichel, 1982; Huang, 2002; Heiser et al., 2004; Yoon et al., 2004]. Janzen [1975] proposed the following equation to estimate the percolation threshold of carbon black in polymer matrices:

$$\varphi_c = \frac{1}{1 + 4\rho V}$$  \hspace{1cm} (2.1)

where $\varphi_c$ is percolation threshold, $\rho$ is the density of carbon black (g/cm$^3$) and $V$ is dibutylphthalate (DBP) value of carbon black in cm$^3$/g.

Polymer morphology, polymer-filler interaction and mixing state are other factors which influence the percolation threshold and the subsequent conductivity of the composite. Semi-crystalline polymers often exhibit a lower percolation threshold due to the rejection of carbon black particles from the crystalline regions, thus concentrating in the amorphous regions. Therefore, lower percolation often corresponds with higher crystallinity. For example, as the crystallinity increased from 10-15% to 80% for a polypropylene composite filled with carbon black, the percolation threshold decreased from 5 vol% to around 2 vol% carbon black [Wu, 1996; Huang, 1996]. On the other hand, a higher percolation threshold is observed for polymers with better polymer-filler interaction. For instance, percolation thresholds of 2-4 wt% CB in PP and 25 wt%
CB in polyamide 6 have been reported [Tchoudakov et al., 1996]. They explained that better interaction between CB aggregates and polyamide 6 leads to more uniformly distributed aggregates that shifts the creation of a continuous network of CB aggregates to higher CB concentrations.

Kim et al. [1999] observed that increased mixing time of CB in a polymer melt can strongly decrease electrical conductivity. With increased mixing time, aggregates are distributed more evenly so that the number of connected aggregate clusters decreases. In general, processing conditions can affect the state of mixing for conductive fillers, namely distribution and dispersion that can change the electrical conductivity of the resulted composite.

In immiscible polymer blends, selective distribution of CB into the continuous phase alone can produce conducting material which requires lower filler content to reach similar conductivity levels compared to a homogeneous system. Furthermore, percolation can even occur at lower filler concentrations if the CB locates mostly at the interface of a co-continuous blend. Localization of CB can result in lower viscosity and better process-ability [Huang, 2002; Narkis et al., 2000; Tchoudakov et al., 1996; Feng et al., 2003].

According to several publications the maximum conductivity for a polymer/CB composite at the highest loading, which varies due to the properties of CB, is around 0.1-0.5 S/cm. This increase in conductivity is accompanied by a huge increase in composite viscosity (at least one order of magnitude at low shear rates and 2-4 folds at high shear rates) [Huang, 2002; Clingerman, 2001b; Mighri et al., 2004].
2.3.3. Carbon Fiber Composites

Graphite, a crystalline allotrope of carbon black, consists of ordered in parallel graphene layers in which carbon atoms are hexagonally bonded together. The structure of an ideal graphite fiber consists of parallel planar layers of graphene, well oriented along the fiber axis. According to the manufacturing process, there is a distinction between carbon fibers and graphite fibers. Fibers which are heat treated at 1000-1500 °C, are called carbon fibers, while those heat treated above 2000 °C, are called graphite fibers. Carbon fibers possess disordered graphite structure and amorphous carbon black regions. As a general rule with increasing heat treatment temperature, the portion of the graphitic structure increases compared to the amorphous carbon black regions leading to higher modulus and electrical conductivity. Carbon fibers have lower modulus and electrical conductivity compared to graphite fibers. Electrical conductivity can vary from 500 S/cm for a regular carbon fiber, to 5000 S/cm for a graphite fiber [Peebles, 1995; Cytec, 2007].

Electrical conductivity of a polymer/carbon fiber composite depends on fiber characteristics such as aspect ratio, diameter and intrinsic conductivity, polymer properties including conductivity, crystallinity and surface energy, and composite properties including fiber content, fiber orientation and fiber-matrix interaction. Longer fibers give a lower percolation threshold [Bigg, 1979]. Tsotra et al. [2003] studied an epoxy/ carbon fiber composite and observed percolation thresholds of 19.8 vol%, 8 vol% and 5.3 vol% for fiber lengths of 82 μm, 145 μm and 325 μm respectively. Clingerman [2001a, 2001b] reported similar trends: 4 vol% and 8 vol% for milled and chopped carbon fiber with aspect ratios of 14 and 9.5, respectively.

composites to observe its effect on electrical conductivity. They found that conductivity could vary up to three orders of magnitude depending on the fiber orientation. For injection molded samples, the through-plane conductivity was two orders of magnitude less than the longitudinal conductivity and transverse conductivity was one order of magnitude lower as compared to the longitudinal direction. A skin-core morphology was observed in which fibers were more aligned in the longitudinal direction on the skin than the core. For compression molded samples the transverse and longitudinal conductivities were the same while through-plane conductivity was lower by two orders of magnitude. Surprisingly, both longitudinal and transverse conductivity were higher for samples prepared by compression molding than injection molding. They associated this observation to the average fiber length that was much higher for the compression molded composites compared to the injection molded parts due to more rigorous fiber breakage in injection molding. At the same concentration the composite with longer fibers gives higher conductivity. They also postulated that the percolation threshold decreased with more random orientation due to more fiber-fiber contacts. Dani and Ogale [1996] reported a percolation threshold of 42 vol% and 34 vol% for aligned skin region and random oriented core region, respectively in injection molded polyamide 6,6/CF composites. They showed that resistivity can be lower by three and six orders of magnitude for transverse and through-plane direction compared to longitudinal direction.

Clingerman et al. [2002] reported the highest electrical conductivities of thermoplastic/carbon fiber composites known of in the literature of 10 S/cm and 160 S/cm for injection molded polyamide 6,6 with carbon fiber at a volume fraction of 29.5 vol%, and polyamide 6,6/nickel coated carbon fiber (17.8 vol% or 30 wt%) respectively. Weber and Kamal [1997] similarly reported ~100 S/cm for their compression molded PP/nickel coated carbon fiber (20 wt%).
2.3.4. Synergism in Hybrid Composites

It has been reported that combinations of different electrically conductive fillers show synergism which can be capitalized upon in order to decrease the amount of conductive filler needed to reach a target electrical conductivity value [Mighri et al., 2004; Balta Calleja et al., 1988; Clingerman et al., 2002; Zhong et al., 1991; Drubestki et al., 2005]. It has been hypothesized that appropriate combinations of conductive fillers create interconnected networks. Most recently, Clingerman et al. [2002] showed that binary and ternary filler combinations such as graphite, carbon black and carbon fiber in polyamide-6,6 and polycarbonate exhibit higher electrical conductivity than single filler systems. Similar findings were reported by Drubetski et al. [2005] who observed that the addition of 4 wt% carbon black to polypropylene/carbon fiber composites improved conductivity. Carbon filled polypropylene and polyphenylene sulfide were investigated by Mighri et al. [2004] for bipolar plate fabrication. The authors noted that the combination afforded lower viscosity for equivalent conductivity based on total filler weight fraction.

2.3.5. Rheology of Filled Polymer Composites

Addition of solid particles, such as glass spheres or fibers, to a fluid increases the viscosity of the fluid. This increase depends on particle properties such as particle shape, particle size, surface area, size distribution, surface roughness, aspect ratio and particle concentration, and polymer-filler interactions. Generally, in terms of particle shape, three categories can be determined: three dimensional (3D) fillers that correspond to spheres such as glass beads; two dimensional (2D) fillers of platelet-like shape, such as mica; and one dimensional (1D) fillers such as glass fibers with high aspect ratio. The increase in viscosity by adding fillers is the highest for 1D fillers followed by 2D and then 3D fillers;
assuming other factors such as characteristic particle size, volume fraction and filler surface area are similar [Shenoy 1999, p246].

Particle size strongly influences the rheology of filled polymers. The smaller the particle size, the larger the surface area and the higher will be the viscosity of the filled polymer due to larger solid-melt interaction [Lobe and White, 1979; Tanaka and White, 1980a]. From a rheology perspective, the response of larger particles to deformation is mainly determined by hydrodynamic forces while for small particles, normally less than 0.5 microns, the response to deformation is primarily due to particle-particle interactions. London dispersive forces and coulombic interactions are the main contributors of particle-particle interaction [Tanaka and White, 1980b]. As a result, composites containing fillers with small particles demonstrate yield stress, which is due to the formation of a temporary network with a finite strength that particles form by strong associations with other adjacent particles. Yield stress increases with increasing filler concentration and surface energy, and decreasing particle size [Shenoy, 1999, p247].

With increased filler concentration the magnitude of particle-particle interactions increase slowly at first and then become excessively larger as the concentration increases. The onset of particle-particle interactions depends on the geometry and surface activity of the particles. Higher aspect ratio fillers [Gurland, 1966; Kitano et al., 1980] require lower concentrations at which particles start to interact and as the surface roughness [Kitano et al. 1980] of the particle changes so too does the rheology of polymer composite. With increasing surface roughness for filler, the resistance to flow increases which leads to increased viscosity.

Particle size distribution is yet another influential factor at high filler loadings. A unimodal distribution gives the highest viscosity based on nominal particle size when all other properties are held the same [Ward and Whitmore, 1950; Eveson, 1959; Lee, 1969; Groto and Kuno, 1982&1984; Mokube, 1981;
G Gillespie, 1983]. With increasing modality the viscosity decreases particularly from shifting from a unimodal to bimodal distribution of particles. Particle size distributions with modality greater than trimodal often show very little difference from trimodal on viscosity [Farris, 1968]. In a bimodal distribution, the particle size ratio and concentration ratio of small particles-to-large particles are important factors in minimizing the viscosity of the composite at a certain concentration [Chong et al., 1971]. The viscosity is not considerably reduced if the particle size ratio is less than 0.1 because the small particles can easily migrate through the interstices of the large spheres [Milewski, 1978]. In fact by increasing the modality, the small particles fill the free spaces among the larger particles which leads to an increase in maximum packing fraction. The advantage of using bimodal particles has been extended to fiber/particle mixtures which can also provide composites with higher packing fraction considering suitable particle size and concentration due to fiber diameter and aspect ratio.

Agglomeration increases the viscosity as agglomerates trap portions of the surrounding polymer melt in their inter-particle spaces, resulting in a system with higher apparent filler content [Nielsen, 1974].

The viscosity of polymer/carbon black composites strongly depends on the properties of carbon black. Viscosity increases with increasing surface area, porosity and structure, and decreasing particle size and apparent density [Verhelst et al., 1977; Sichel, 1982].

For carbon fiber composites Carneiro and Maia [2000] reported a significant increase in the shear viscosity of PP/carbon fiber (30 wt%) at low shear rates, i.e. below 1 s\(^{-1}\), compared to that of the unfilled polymer. But at shear rates above 100 s\(^{-1}\) no significant increase in viscosity was observed. They showed that composites with longer fibers exhibit higher viscosity due to the higher extent of interaction between fibers. However the increase in viscosity, due
to an increase in fiber length, decreases as the shear rate increases. In fact at higher shear rates fiber alignment, and not fiber length, is the dominant factor determining the viscosity.

Dynamic rheometry gives insight to study particle-particle interactions and composite structure. Complex viscosity, storage modulus, loss modulus and tangent delta are the dynamic rheological properties that can be used to assess the rheological, molecular and structural properties. Measurements are usually carried out in strain sweep or frequency sweep. At constant frequency a decrease in complex viscosity or storage modulus with strain is a symptom of network break-up [Shenoy, 1999, p339]. The largest concern for this measurement method is in regards to the detectable linear viscoelastic range available for study. For unfilled polymers the linear viscoelastic region is normally very broad, while for filled polymers it shifts toward low strains until it may even disappear at concentrations close to the maximum packing fraction [Bigg, 1983]. Thus dynamic rheological properties are obtained at low strain levels. Above the linear viscoelastic region, an increase in strain at a constant frequency is accompanied by decrease in shear modulus and complex viscosity [Bigg, 1983].

With increasing filler concentration, complex viscosity or storage modulus increases by orders of magnitudes [Poslinski et al., 1988; Bigg, 1983]. At higher concentrations, a solid like behaviour is observed i.e. storage or loss modulus becomes independent of frequency [Bigg, 1983].

Dow et al. [1990] investigated dispersions of alumina in polyethylene. They showed that agglomeration increases dynamic viscosity and promotes shear thinning behaviour. Bigg [1982, 1983, 1984] and Althouse et al. [1983] investigated the influence of surface treatment on dynamic rheological response. They found that silane or titanate coupling agents increase the viscosity of alumina filled polyethylene over the entire frequency range. They concluded that the surface modifiers led to coupling of the filler particles and the polymer chains.
With increasing degree of agglomeration or increasing polymer-filler interaction, viscosity increases.

2.4. Flow Induced Fiber Orientation

Alignment of short fibers in laminar shear flows has been reported in many experimental and theoretical studies. Preferential fiber alignment is also found in extensional flows. In a classic theoretical study by Jeffery [1922] ellipsoids dispersed in a viscous creeping flow showed that high aspect ratio ellipsoids rotate periodically because no stable equilibrium orientation exists, but they spend a large fraction of the time aligned with the flow so that most of the particles align with the streamlines. Later Batchelor [1970] developed a theory for high aspect ratio cylinders (fibers) suspended in a viscous fluid and obtained similar results. The thinner the fiber, the less the velocity mismatch and the slower the fiber rotates out of its aligned orientation. In contrast, in pure extensional flow, a perfect alignment is available with time [Batchelor, 1971]. These statements are true for dilute suspensions of fiber which is suspensions with fibers that do not interact with each other. Non-dilute suspensions of fibers have greater difficulties in achieving fiber alignment. Steric interactions between fibers prevent fibers from rotating freely into aligned orientations [Folgar and Tucker, 1984; Arp and Mason, 1977; Jackson and Advani, 1986; Anczurowski and Mason, 1967a,b].

Three different concentration regimes are often cited:

i) a \textit{dilute} regime in which the characteristic fiber separation distance is greater than the fiber length,

ii) a \textit{semi-concentrated} regime in which this characteristic separation distance is less than the fiber length but greater than the fiber diameter, and

iii) a \textit{concentrated} regime in which fibers are separated by only a few fiber diameters.
These regimes can be classified by fiber volume fraction ($\Phi_v$) and aspect ratio (AR). For example, for a fiber with AR=50, if $\Phi_v < 0.04\%$ then the suspension referred to as dilute, while if $0.04\% < \Phi_v < 2\%$ then suspension is semi-concentrated, and if $\Phi_v > 2\%$ the suspension considered to be concentrated [Papathanasiou, 1997, p9-15]. The flow of fiber suspensions has extensively studied by early works of Mason [Mason, 1957; Chaffey, 1965; Anczurowski and Mason, 1967a, 1967b & 1968; Arp and Mason, 1977] and more recent works of Tucker and Advani [Tucker and Advani, 1994; Ranganathan and Advani, 1991].

During the injection molding of thermoplastics, three microstructural regions are generally observed [Bright et al., 1978; Bright and Darlington, 1981; Spahr et al., 1990; Bay and Tucker, 1992; Gupta and Wang, 1993; Darlington and Smith, 1987; Akay and Barkley, 1991]. The skin layer is near the mold wall. The shear zone (shell zone) which is the region beneath the skin. And finally, the core region which is the center of the mold. These layers are shown by an optical micrograph taken of an injection molded PA66/glass fiber (33 wt%) rectangular specimen in Figure 2.2. As the melt enters the mold it solidifies on the mold wall while the melt at the core, within the flow front, advances into the mold. The extensional flow that occurs at the free surface of the melt front (known as fountain flow) moves the melt from the core to the cavity walls, which leaves a highly stretched layer of solidified polymer near the mold wall [Mavridis et al., 1988; Bay and Tucker, 1992; Gupta and Wang, 1993]. A random-in-plane orientation is usually observed in the skin layer since the melt solidifies on the wall before the gapwise velocity profile can shear the fibers to align them in the flow direction. The skin layer forms as the polymer solidifies during filling. The thickness of the skin layer depends on cooling rate and filling time [Kamal and Papathanasiou, 1993]. In the shear zone, fibers become highly oriented along the main direction of flow caused by shearing due to the parabolic velocity profile. The core usually maintains a transverse fiber orientation. The expanding flow in
the vicinity of the gate orients the fibers primarily in the transverse direction to
the main flow. The flow in the core, possessing a flat velocity profile across the
thickness of the cavity, transports the created transverse orientation downstream
without significant reorientation. The relative thickness and orientation of shear
zone and core region strongly depends on the velocity profile which in turn
depends on rheological behavior of the melt. For example a low power law index
melt, i.e. highly shear thinning, has a significantly larger flat velocity portion
leading to a thicker core [Bright and Darlington, 1981; Darlington and Smith,
1987]. Addition of fillers can promote a flatter velocity profile in the gap
direction, leading to a thicker core [Ranganathan and Advani, 1993; Tang and
Altan, 1995; Chung and Kwon, 1995].

Numerous experimental works have examined effect of different
parameters on fiber orientation in injection molding. Gate design strongly
influences fiber orientation at the core. Point or centre gated designs create
diverging flow in their vicinity which cause orientation of the fibers in the
direction of elongation [Bay and Tucker, 1992; Gupta and Wang, 1993]. On the
other hand film or sprue gates create moldings which have strongly transverse
oriented fibers [Bay and Tucker, 1992; Sanou, 1985; Darlington and Smith,
1987]. Even for gates which lead to transverse core orientation, at slow injection
speeds aligned core orientation can be observed [Bright et al., 1978; Gupta and
Wang, 1993]. Bright associated this effect to the low shear rate at which viscosity
is in the plateau region (Figure 2.3) and consequently the melt flows like a
Newtonian fluid leading to a parabolic velocity profile (Figure 2.4). Therefore at
low injection rates there is significant shear at the core which can reorient some of
the initially transversely oriented fibers toward the flow direction. In contrary at
high injection rate the shear thinning behavior of the melt leads to a flatter
velocity profile which can not significantly influence the initial orientation formed
in the vicinity of the gate. In addition, at low injection speeds, solidification at the
wall becomes significant and reduces the cross section of the flow as the flow progresses away from the gate. This provides a converging flow situation which can orient the fibers in the flow direction [Bright et al., 1978; Gupta and Wang, 1993].

Figure 2.2. Optical micrograph showing fiber orientation distribution through the side view of an injection molded PA66/glass fiber (33 wt%) rectangular specimen [Shokri and Bhatnagar, 2006].
Figure 2.3. Typical curve for shear viscosity versus shear rate of polymer melts

Figure 2.4. Schematic velocity profile for Newtonian and shear thinning fluids between parallel plates
Long injection times due to slow injection speeds also show significant solidification of the melt on the wall resulting in moldings with thinner core [Akay and Barkley, 1991].

The effect of cavity thickness was investigated by Bouti et al. [1989] for glass flake reinforced polypropylene and by Fisa and Rahmani [1991] for glass filled polypropylene. They found that with increasing the cavity gap size the core thickness/gap size increases. As a rule of thumb, as the wall temperature increases, thickness of the core increases [Vincent and Agassant, 1986; Gupta and Wang, 1993; Akay and Barkley, 1991].

It has been shown that packing pressure can reorient during-filling-aligned fibers in the flow direction into the transverse direction at the instant of filling [Shokri and Bhatnagar, 2007; Malzahn and Schultz, 1986]. The viscosity of the melt at the end of filling time determines the degree of rotation.

Shokri and Bhatnagar [2006] examined the effect of melt and mold temperature on the fiber orientation of glass filled polyamide 66. They found that increasing these temperatures signifies the degree of transverse alignment in the core and shell layers.

Spahr et al [1990] and Bouti et al [1989] studied the influence of concentration on particle orientation in injection molded glass fiber and glass-flake filled polypropylene. They found that increasing concentration was accompanied by an increase in the transversely oriented core.

Also, models have been developed to semi-quantitatively predict fiber orientation distribution in different geometries [VerWeyst and Tucker, 2002; Vincent et al., 2005; Hine et al., 2005; Han et al., 2002; Michaeli et al., 2002; Larsen, 2000; Cintra and Tucker, 1995; Chung and Kwon, 1996; Ranganathan and Advani, 1993; Baraldi et al., 1992]. However, for reliable predications, models need to account for a number of issues, including: interaction of fiber
orientation and flow kinematics during filling of concentrated suspensions, effect of packing, development of consecutive models for concentrated fiber suspensions, effect of melt elasticity, and the effects of longer fibers where their length is comparable to the cavity thickness [Papathanasiou 1997, p160].

Generally, fiber orientation can be controlled not only by processing and geometrical parameters such as gate design, injection speed, packing pressure, but also by special techniques such as SCORIM ‘shear controlled orientation injection molding’ [Allan and Bevis, 1987]. Flow-induced-orientation has poor tailorability and in many cases is not achievable in the desired direction. Therefore external controlling sources such as electric and magnetic fields have been also proposed as alternatives to align fibers Electrostatic [Okagawa et al., 1973; Itoh et al.,1994; Vyakarnam and Drzal, 1997] or magnetic [Hatta and Yamashita, 1988; Yamashita et al., 1989; Zauscher and Humphery, 1997] fields can be used to control fiber orientation in fluids.

2.5. Polymer Foams

A two-phase solid/gas material in which gas bubbles are dispersed in a polymer matrix is called a polymer foam, cellular polymer, or expanded polymer. If the cell walls are not ruptured, the foam is referred to as closed cell structure. Conversely, it is referred to as an open cell structure if only the struts remain intact. Gas bubbles are introduced into the polymer matrix by physical blowing agents (PBA) such as nitrogen, carbon dioxide or low boiling hydrocarbons, or by chemical blowing agents (CBA) such as sodium bicarbonate and azodicarbonamide which decompose at elevated temperatures and release gaseous materials [Throne, 1996].

The reduced density resulting from foaming, lower material usage and hence usually lower cost have been the general advantages of using polymer
foams. Today polymer foams are a unique class of engineered materials, which are used in packaging, thermal and electrical insulation, buoyancy, and structural applications such as decks, road pavements, sandwich panels, and so on. Their uniqueness arises from their diverse functionalities such as impact strength, thermal and dielectric resistance and permeability while still maintaining high strength and stiffness to weight ratio which can be tailored to achieve properties taking over the limits of other classes of engineered materials. All these benefits can not be achieved without attaining proper foam morphology and structural design [Gendron, 2005].

2.5.1. Foam Injection Molding

Foam injection molding is a common method to produce foam parts. Usually a chemical blowing agent (CBA) is dry blended with polymer pellets and fed to the extruder of the injection unit, first to melt the polymer and then decompose CBA to evolve gases that dissolve into the polymer melt. The resulting melt/gas mixture is accumulated at the end of extruder under high pressure. The pressurized gas laden melt is injected into the mold at a volume smaller than the mold volume. The sudden pressure drop creates a super-saturated state for the dissolved gas which initiates nucleation of small bubbles. In the next stage, these bubbles grow rapidly until the gas pressure inside the bubble reaches equilibrium with the pressure in the melt. The size of bubbles primarily depends on the number of nucleated bubbles. Growing bubbles may reach other bubbles and coalescence occurs. In the case of thermoplastic foam injection molding, the mold wall temperature is below the solidification point of the polymer. Therefore bubble growth will freeze when the melt around it reaches the solidification temperature. At the end of the cooling process, the bubble shape and structure stabilizes and the part will take the final shape. In the aforementioned skin layer, the high viscosity of the melt and low gas pressure arising from low temperature prevents the appearance of any gas bubbles in the cross section of the skin layer.
Therefore, the molded part has a sandwich like structure consisting of a foamed core encapsulated by a solid nonfoamed skin. Due to this ‘sandwich structure’, injection molded thermoplastic foam parts are often referred to as *structural foams*. Injection molded structural foams may suffer from poor surface quality at some processing conditions. This problem has been attributed to bubble nucleation and growth at the advancing flow front. These bubbles are elongated and transferred to the mold wall by the action of fountain flow and solidify there [Throne, 1996].

Bubble nucleation can be *homogeneous* or *heterogeneous*. In the latter case, a bubble is nucleated at a foreign substrate found in the melt. The main barrier to nucleate a bubble is the increase of surface energy due to the formation of new surfaces. Heterogeneous nucleation is the favoured mode to start foaming if the substrate is energetically beneficial towards forming a new gas phase. Therefore, the role of supersaturation on nucleation rate is much less than the presence of a low energy substrate. For viscous polymer melts, homogenous nucleation has rarely been observed since all commercial resins contain contaminants or additives such as antioxidants. To further enhance heterogeneous nucleation, nucleating agents are often used to facilitate bubble formation and create finer cells [Advani and Arefmanesh, 1993].

Non-uniform cell size in foam injection molding is a common issue. Gas bubbles first nucleate at locations where the dissolved gas concentration is higher. Since the concentration of gas is not uniform in the melt, some bubbles will nucleate earlier and have more time to grow during flow, while other bubbles may nucleate later and have less time to grow. However, other factors such as the non-isothermal condition of the melt or mold geometry also contribute to a non-uniform cell size [Vilamizar and Han, 1978; Advani and Arefmanesh, 1993].
Bubble growth proceeds by two mechanisms: rapid growth due to the sudden pressure drop when melt enters the cavity and by slow growth due to diffusion of gas from the surrounding melt into the bubble during mold filling. The shape of a bubble is deformed by the stresses in the melt flow; therefore, the shape of bubbles is often non-spherical [Vilamizar and Han, 1978]. The total process time for cell growth and stabilization reduces as the nucleation density increases [Favelukis, 2004].

Among different processing parameters, injection speed is the most important factor influencing cell morphology [Han and Yoo, 1981]. Higher injection speed gives finer and more uniform cell size. It is accompanied by higher injection pressure and shorter filling time. Bubbles have less chance to form in the runner which in turn leads to a higher gas concentration in the melt upon entering the mold. Higher gas concentrations in the melt result in the formation of more bubbles. The nucleated bubbles can now grow until the melt fills the mold - a short time at high injection speed - leading to a smaller cell size. Also, at high injection speeds there is an increase in viscoelastic stress in the melt so that the melt needs a longer time to relax [Han and Yoo, 1981], which retards the formation of bubbles.

Melt temperature is another factor influencing cell morphology. Lower melt temperature increases the melt viscosity, thus slowing melt relaxation and lowering the gas diffusion rate. As a result, fewer bubbles form and slower bubble growth occurs at lower melt temperatures.

Mold temperature can also be used to control cell morphology. Higher mold temperatures create more uniform cells due to a smaller temperature gradient within the mold gap. Lower mold temperature results in higher viscosity, lower gas diffusion rate and slower melt relaxation for the melt near the wall, which retards bubble growth [Vilamizar and Han, 1978; Han and Yoo, 1981].
By increasing CBA content, the gas concentration in the melt increases, which gives rise to the number of nucleated cells as well as growth rate. In addition, the viscosity of the melt decreases with increasing gas concentration. However, if the amount of gas evolved from an excessive amount of CBA goes beyond the gas solubility limit for the melt, gas pockets form in the melt and will appear in the final product as large bubbles. The solubility of a gas in the melt is significant contributing factor to the processability and resulting morphology of the foam. For example, the solubility of $\text{N}_2$ is less than $\text{CO}_2$ in many polymer melts leading to faster bubble formation and more uniform cell size [Vilamizar and Han, 1978].

Last but not least, a significant process parameter to control the foam structure is the size of the shot. An injection shot size smaller than the capacity of the mold cavity leaves more space and longer time for the bubbles to grow, resulting in larger cell size and lower part density [Han and Yoo, 1981].

Han and Yoo [1981] have shown theoretically that the elasticity of polymer melt can also be an important factor in bubble formation and growth. They found that at high injection speed, elasticity assisted bubble growth in its early stage and retarded it in its later stage while the opposite trend occurred at low injection speeds. Their theoretical results were in agreement with their experimental observations. Yue et al. [2007] simulated diffusion-driven expansion of a 2D cell as well as the thinning of a film between a bubble and a free surface. Their results showed a two stage process: a rapid initial expansion for the cell followed by slow drainage of the film between the cells. Increase in melt viscoelasticity leads to acceleration of the initial cell growth and delays the film drainage in the second stage. Elongational viscosity associated with melt strain hardening significantly controls the biaxial elongation of the melt at the cell
surface. Strain hardening helps to stabilize the foam structure by suppressing cell-cell coalescence and cell burst. Their findings were consistent with prior experimental results saying that increase in melt strength leads to smaller, more uniform cell size and greater foam expansion due to less cell-cell coalescence and cell burst.

References

- Althouse, L M; Bigg, D M; Wong, W M (1983) Evaluating the effectiveness of filler surface treatments, Plastics Compounding, 6, 71.
- Arp, P A; Mason S G (1977) Interactions between two rods in shear flow, J Colloid Interface Sci, 59, 378.
G Hashemi Motlagh, PhD Thesis, Chemical Engineering, McMaster University, April 2008

- Billingham, N C; Calvet, P D (1989) *Advances in Polymer Science*, 90, 1-104
- Bright, P F; Crowson, R J; Folkes, M J (1978) A study of the injection speed on fiber orientation in simple moldings of short glass fiber-filled
- Dow, J H; Sacks, M D; Shenoy, A V (1990) Dispersion of alumina particles in polyethylene melts, Ceram Trans (Ceram Powder Sci III), 12, 431-442.
- Feller, J F; Linossier, I; Grohens, Y (2002) Mat Lett, 57, 64-71
- Frysz, C A; Shui, X; Chung, D D L (1996) J Power Sources, 58 (1), 41.
- Han, C D; Vilamizar, C A (1978) Studies on structural foam processing I. The rheology of foam extrusion, *Polym Eng Sci*, 18, 687-698
- Hine, P; Duckett, A; Caton-Rose, P; Coates, P D; Jittman, P; Chapman, C; Smith, G (2005) Fibre orientation: Measurement, modeling and knowledge based design, *Plas Rub Comp*, 34(9), 417-424.
- Lanticse, L J; Tanabe, Y; Matsui, K; Kaburagi, Y; Suda, K; Hoteida, M; Endo, M; Yasuda, E (2006) Shear-induced preferential alignment of carbon nanotubes esulted in anisotropic electrical conductivity of polymer composites, *Carbon*, 44, 3078-3086.
- Muto, N; Yanagida, H; Nakatsuji, T; Sugita, M; Ohtsuka, Y; Aray, Y (1992), *Smart Mater Struct*, 1, 324.
- Okagawa, A; Cox, R G; Mason, S G (1973) Particle behavior in shear and electric fields VI. The microrheology of rigid spheroids, *J Colloid Interf Sci*, 47(2), 536-587.


- Tsotra, P; Friedrich, K (2003), *Composites Part A*, 34, 75-82.


- Vincent, M; Giroud, T; Clarke, A; Eberhardt, C (2005) Description and modeling of fiber orientation in injection molding of fiber reinforced thermoplastics, *Polymer*, 46(17), 6719-6725.
- Wang, S; Chung, D D L (1999) *Comp Interfaces* 6(6), 497
Chapter 3

COC Composites Containing Carbon Fiber and Carbon Black: Electrical Conductivity, Rheology and Synergism

This chapter is the paper published as:

This paper examines the existence of synergism for combinations of carbon black and carbon fiber at various concentrations above and below percolation, in regards to electrical conductivity of the final polymer composite. The work provides the first known detailed study of the collaborative interactions between these two fillers over a broad range of concentrations, leading to the establishment of electron pathways across a molded part. The sought outcome was to identify a formulation strategy which would maximize conductivity yet maintain the material viscosity in a range suitable to injection molding machinery.
Abstract

This paper investigates electrical conductivity and rheological aspects of cyclic olefin copolymer (COC) composites containing both carbon fiber (CF) and carbon black (CB) at various concentrations. The different formulations of carbon filled COC were compression molded in such a manner that the formed circular sheets exhibited preferred in-plane filler orientation. Through-plane and in-plane conductivity were measured by 2-probe and 4-probe methods, respectively while an ARES rheometer in dynamic mode was employed to measure the storage modulus and complex viscosity. It was found that formulations with CF:CB ratios around 3 and where the CB content was close or below its critical percolation concentration resulted in higher electrical conductivity while maintaining the viscosity of the composite at a level acceptable for polymer processing machinery. For those composites containing both fillers, collaborative associations between the CB and CF fillers were found in the established percolating network structure, producing measured conductivities which exceeded the estimated values by the additive rule by up to 6 fold. An empirical expression to handle hybrid filler systems is proposed in this work based on the standard percolation model.

3.1. Introduction

Polymer composites are an attractive alternative to both metals and graphite for bipolar plates used within fuel cell stack construction because of their relatively low cost, good mechanical and chemical properties, and most notably, their ease of fabrication into complex geometries [1]. Several efforts are currently underway to manufacture bipolar plates from polymer composites [4-11]. The greatest challenge for this class of materials is their low inherent electrical conductivity, a feature that can be overcome with high loading of conductive additives, though at the expense of processability. Additives shown to improve
electrical conductivity in polymers include: carbon fiber [12-16], nickel-coated carbon fibers [16-17], stainless-steel fibers [17-18], graphite [19-20], carbon nanofibers [21], carbon nanotubes [22-25], exfoliated graphite [26-28], and carbon black [29]. With increasing filler content, the electrical conductivity increases, as does the viscosity of the polymer; for example, with 25 wt% carbon black in polypropylene, it was shown [8] that the electrical conductivity increased from $10^{-17}$ S/cm (characteristic of the resin) to 0.1 S/cm while the shear viscosity at 100 s⁻¹ increased from 70 Pa-s to more than 1000 Pa-s. In order for mass production of bipolar plates to reach its economic target [2-3], less than $10/kg or less than $10/KW, the polymer composite needs to be able to take advantage of an economically-favorable process like injection molding rather than compression molding. Unfortunately, the high viscosities found for previously developed carboneous-filled polymers precluded use of such machinery. It is for this reason that our research group along with others [5,8,30] has turned their attention towards studying strategies for lowering the percolation threshold of economical carboneous-filled polymer systems, thereby lowering the content of fillers needed to reach the desired conductivity levels for bipolar plates and the viscosity of the polymer as it is processed.

Research investigating the percolation behavior of carbon black filled polymers is quite extensive [29,31]. Effectively, carbon black establishes a percolating network structure within the matrix of a polymer, which extends across the thickness of the fabricated part. Other filler types such as carbon fibers or stainless steel fibers have been more recently studied, and found to create composites with higher conductivity and usually feature a lower percolation threshold (i.e. the concentration of additives necessary to achieve a continuous network structure) compared to carbon black [8,17,20]. The most recent urgency for improving the processability of such highly conductive composites in conventional polymer processing equipment has seen the introduction of double
or triple percolation materials [29,32-36]. Another recent strategy uses a mixture of different aspect ratio fillers such as carbon black and carbon fibers [16,37,42] or carbon black and graphite [30,38]. The latter strategy is examined in this work as we investigate the suitability of a new carboneous-filled polymer for bipolar plate manufacturing.

It has been reported by several papers that combination of electrical conductive fillers shows synergism, which can be capitalized upon in order to decrease the amount of conductive filler needed to reach a specific electrical conductivity value [8,30,37,39,40]. Most recently, Clingerman et al [30] showed that binary and triple combinations of graphite, carbon black and carbon fiber in polyamide-6,6 and polycarbonate gives higher electrical conductivity than single-filler systems. Similar findings were reported by Drubetski et al. [40] who observed that the addition of 4 wt% carbon black to polypropylene/carbon fiber composites improved the conductivity. Carbon filled polypropylene and polyphenylene sulfide were compared by Mighri et al [8] for bipolar plate fabrication. The authors noted that the combination afforded lower viscosity for equivalent conductivity based on total filler volume.

None of these recent studies have investigated combined conductive filler (hybrid) systems over a range of concentrations. There is also some question regarding the definition of synergism currently used in the literature for conductive polymers incorporating multiple types of carboneous fillers. In this paper, the electrical conductivity and rheological properties of a carboneous filled cyclic olefin copolymer (COC) are studied over a broad range of filler concentrations. The work will evaluate possible advantages for using different filler combinations, such as conductivity synergism and improved processability.
3.2. Experimental

3.2.1. Materials

Cyclic olefin copolymer (COC, Topas 6013S-04 supplied by Ticona) was chosen as the matrix polymer (Table 3.1). COC is a new class of amorphous polyolefins with higher mechanical properties and thermal stability compared to commodity polymers such as polypropylene or polyethylene. The material also exhibits excellent chemical and barrier properties, and a low specific gravity. The amorphous character of this polymer was an important consideration for this study to avoid the confounding influence of crystallization on the percolation behavior of the fillers; phase segregation of the carbon black by rejection of the filler from the matrix crystals has been noted to increase conductivity and different levels of the filler influences the structure of the crystals [41-42]. The absence of crystallinity should also minimize the positive temperature coefficient (PTC) effect, which is an important consideration for material selection in bipolar plates.

Table 3.1. Properties of COC polymer*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Index</td>
<td>14 g/10 min (260 °C 2.16kg)</td>
</tr>
<tr>
<td>Apparent Density</td>
<td>1.02 g/ml</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>140 °C</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>63 MPa</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>2900 MPa</td>
</tr>
<tr>
<td>Volume Resistivity</td>
<td>&gt;10^{16} Ω.cm</td>
</tr>
<tr>
<td>Heat distortion temperature at 0.45 MPa</td>
<td>130 °C</td>
</tr>
</tbody>
</table>

* Data given by the supplier
Table 3.2. Properties of carboneous fillers*

<table>
<thead>
<tr>
<th>Properties</th>
<th>Carbon Black (CB)</th>
<th>Carbon Fiber (CF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>10-100</td>
<td>625</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.8</td>
<td>1.78</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>100-120</td>
<td>360</td>
</tr>
<tr>
<td>Aggregate size (nm)</td>
<td>30-100</td>
<td>-</td>
</tr>
<tr>
<td>Pore volume (DBP, ml/100 g)</td>
<td>480-510</td>
<td>-</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>1250</td>
<td>1.1</td>
</tr>
<tr>
<td>Fiber diameter (µm)</td>
<td>-</td>
<td>7.5</td>
</tr>
<tr>
<td>Fiber length (µm)</td>
<td>-</td>
<td>5000</td>
</tr>
</tbody>
</table>

* Data given by suppliers

3.2.2. Procedures

Samples with differing filler content were prepared in a Haake 3000 Rheomix batch mixer at 60 RPM and 300°C for 12 min. Mixing temperature was chosen at the upper limit of the processing range for Topas 6013S-04 in order to decrease the viscosity of the melt and therefore minimize the breakage of the carbon fibers. The formulations of the compounds produced in this study are listed in Table 3.3. The compounds were formed into preformed disks, 65 mm dia. And 12 mm thick, for subsequent compression molding into circular sheets of 150 mm dia. And 2 mm thickness. The preformed disks were compression molded in a hydraulic hot press at 250°C under 35 Mpa ram pressure. This setup was chosen to introduce radial flow during the molding of the sample sheets; radial flow was important for producing preferential in-plane orientation of the fibers in a similar manner to that found in injection molding. Rectangular (45mm ×6 mm) and disk shape (dia. 20 mm) specimens were cut from the compression
molded sheet according to the pattern shown in Figure 3.1 for further characterization.

3.2.3. Analysis

Theoretical density was calculated according to Eqn 3.1 and was compared with the measured density value obtained from the buoyancy method, to check the amount of filler in the COC composites containing CB:

\[ \rho_c = (1 - \phi_{CF} - \phi_{CB})\rho_{COC} + \phi_{CF}\rho_{CF} + \phi_{CB}\rho_{CB} \]  

(3.1)

where, \( \rho_c \) is composite density, \( \phi_{CF} \) and \( \phi_{CB} \) are the volume fraction of CF and CB in the composite, and \( \rho_{COC}, \rho_{CF} \) and \( \rho_{CB} \) are the densities of COC, CF and CB, respectively as reported by the manufacturers.

Electrical conductivity was measured using a 4-probe and 2-probe method for the in-plane and through-plane directions, respectively. Each reported value was based on a
minimum of 7 and 3 samples for in-plane and through plane directions, respectively. The voltage range used for these analyses was kept as close to 0.5-1 VDC as possible, to remain consistent with fuel cell operation and to minimize the occurrence of joule heating. V-I curves obtained for several composites confirmed ohmic behaviour in the voltage range examined. In-plane measurement, in accordance with ASTM C611, used the rectangular specimens (described above) which were placed between two gold coated copper electrodes and a constant DC current was applied by an Agilent 6441C power source. The voltage drop was measured by a second set of probes between two points on the sample, separated by a distance of 30 mm, using an Agilent 3440A multimeter. There is no standard procedure for measuring through-plane conductivity at
present; therefore, the method was adopted from previously reported procedures in the literature [5,8-10]. Our through-plane measurement of electrical conductivity was done using disk-shaped cut samples (dimensions previously given) placed between two gold plated copper electrodes. In order to minimize the contact resistance, conductive carbon paper (Technimat 6100-070 supplied by Lydall) was placed between the two electrode-sample surfaces. Constant DC current was applied while the sample was kept under a constant compressive pressure of 10 Mpa and the potential drop was measured between the two electrodes. The applied compressive force was the minimum value which corresponded to the lowest achievable contact resistance between the electrodes and the sample assembly.

To measure the fiber length distribution (FLD), samples were ashed in an electrical furnace at 550 °C for 10 min to burn out the polymer. The fibers collected in this manner were found to be consistent with the solvent digestion technique, both in weight fraction and fiber length. To obtain good separation of the fibers for analysis, the collected specimen from the furnace was dispersed in xylene and the subsequent mixture was spread over a microscope slide. The prepared sample was then observed under an optical microscope after the solvent had evaporated. Image analysis using Sigma Scan Pro 3.0 (Jandel Scientific) was done for at least 1000 fibers per prepared specimen. To visualize carbon fiber orientation, rectangular samples collected from the compression-molded sheet were mounted in epoxy resin and metallographically polished with an automatic Struers polisher. Digital images taken of the polished surface by microscopy were qualitatively analyzed. To visualize the network structure of carboneous fillers in the composite samples, scanning electron microscopy (SEM) was used to visualize carbon black aggregate size, spacing between aggregates, and the distribution of carbon black in vicinity of carbon fibers. The specimens for SEM were prepared by cryogenic fracture.
Measurement of the complex viscosity ($\eta^*$) and the storage and loss modulus ($G'$ and $G''$) of the different formulations were done on an ARES (TA Instruments) parallel-plate rheometer over a 0.1-100 rad/s frequency sweep range. A constant strain was chosen for the measurements based on the determined linear viscoelastic region for each material from strain sweep testing. In steady mode, shear viscosity was measured versus shear rate for 0.01-10 s$^{-1}$. Both tests were conducted at 260°C in the rheometer.

3.3. Results and Discussion

The measured carbon fiber content and density values of the prepared compounds, as listed in Table 3.3, were found close to the formulation concentrations and density estimated by Eqn 3.1. The highest single-filler loadings that could be prepared by the batch mixer, due to its torque limitations or that would adequately flow in the compression molding apparatus were 9 vol% and 30 vol% for carbon black and carbon fiber, respectively and 23 vol% for the combination.

3.3.1. Single-filler composites

Figure 3.2 shows the electrical conductivity of COC/CF and COC/CB compounds for the in-plane and through-plane directions. Similar to findings noted by other authors [20,40], the increase in electrical conductivity was more rapid with increasing Ketjenblack CB content compared to the chopped CF, especially when the carboneous filler concentration was low (i.e. approximately below 15 vol%). This was due to the high surface area and branched structure of the nanoscale CB aggregates which resulted in the development of a higher number of conductive paths at low filler contents compared to the micron size CF. At higher carboneous loadings, CF appeared to demonstrate greater electrical conductivity than CB (if
its trends can be reasonably extrapolated) which resulted from its high aspect ratio (ca. 40 L/D) and increased inherent electrical conductivity. The figure also shows that the in-plane conductivity was higher than the through-plane for both CF and CB composites despite the former having larger anisotropy than the latter. Orientation of the particles preferably takes place in the in-plane direction during squeezing of the preformed disk into the circular sheet during compression molding. Anisotropy in the electrical conductivity of CF composites due to preferential orientation of the fibers, both in injection molding and compression molding, has been previously reported [17,43]. The carbon black aggregates can also orient in the flow field, but their lower aspect ratio compared to the carbon fiber minimized the extent of anisotropy observed for CB composites. Anisotropic electrical conductivity has been reported previously for carbon black-filled polymer composites [44].

Included in Figure 3.2 are the fitted (in-plane) trendlines for the two filled systems using the standard percolation model which, is given as:

\[ \sigma_C = \sigma_F (\varphi - \varphi_{\text{Crit}})^t \]  

(3.2)

where \( \sigma_C \) is conductivity of composite, \( \sigma_F \) is conductivity of conductive filler, \( \varphi \) is volume fraction of conductive filler (where \( \varphi > \varphi_{\text{Crit}} \)), \( \varphi_{\text{Crit}} \) is the volume fraction of filler at the percolation threshold, and \( t \) is the critical exponent. \( \varphi_{\text{Crit}} \), \( \sigma_F \) and \( t \) are given in Table 3.4 for all trendlines shown in the figure. The estimated values of \( \varphi_{\text{Crit}} \) are in good agreement with those reported by Clingerman [20] for carbon black (i.e. 2.5 vol%) in both polycarbonate and polyamide-6,6 but are slightly lower than the 3.5 vol% given for carbon fibers in polyamide-6,6 by the same author. The difference in \( \varphi_{\text{Crit}} \) for the carbon fiber can be attributed to differences in aspect ratio of the filler and the influence of the resin on final properties; no polymer-filler systems similar to the ones used in this work are presently found in the literature for direct comparisons.
<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Filler Content (vol %)</th>
<th>Total Content (wt %)</th>
<th>Theoretical density (g/cc)</th>
<th>Measured density (g/cc)</th>
<th>Equivalent filler content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF1.5</td>
<td>1.5</td>
<td>2.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF3</td>
<td>3</td>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF5</td>
<td>5</td>
<td>8.37</td>
<td>1.053</td>
<td>1.050</td>
<td>7.81</td>
</tr>
<tr>
<td>CF10</td>
<td>10</td>
<td>16.16</td>
<td>1.091</td>
<td>1.090</td>
<td>16.13</td>
</tr>
<tr>
<td>CF20</td>
<td>20</td>
<td>30.26</td>
<td>1.166</td>
<td>1.164</td>
<td>30.00</td>
</tr>
<tr>
<td>CF30</td>
<td>30</td>
<td>42.65</td>
<td>1.242</td>
<td>1.236</td>
<td>41.92</td>
</tr>
<tr>
<td>CB0.5</td>
<td>0.5</td>
<td>0.88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB1.5</td>
<td>1.5</td>
<td>2.62</td>
<td>1.027</td>
<td>1.022</td>
<td>1.57</td>
</tr>
<tr>
<td>CB3</td>
<td>3</td>
<td>5.2</td>
<td>1.039</td>
<td>1.036</td>
<td>4.65</td>
</tr>
<tr>
<td>CB6</td>
<td>6</td>
<td>10.12</td>
<td>1.062</td>
<td>1.058</td>
<td>9.32</td>
</tr>
<tr>
<td>CB9</td>
<td>9</td>
<td>14.86</td>
<td>1.086</td>
<td>1.085</td>
<td>14.79</td>
</tr>
<tr>
<td>CF2.5CB0.75</td>
<td>2.5</td>
<td>0.75</td>
<td>5.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF2.5CB3</td>
<td>2.5</td>
<td>3.00</td>
<td>9.25</td>
<td>1.057</td>
<td>1.055</td>
</tr>
<tr>
<td>CF5CB0.75</td>
<td>5</td>
<td>0.75</td>
<td>9.59</td>
<td>1.059</td>
<td>1.054</td>
</tr>
<tr>
<td>CF5CB1.5</td>
<td>5</td>
<td>1.5</td>
<td>10.81</td>
<td>1.065</td>
<td>1.061</td>
</tr>
<tr>
<td>CF5CB3</td>
<td>5</td>
<td>3.00</td>
<td>13.18</td>
<td>1.076</td>
<td>1.074</td>
</tr>
<tr>
<td>CF5CB6</td>
<td>5</td>
<td>6.00</td>
<td>17.8</td>
<td>1.100</td>
<td>1.095</td>
</tr>
<tr>
<td>CF10CB1.5</td>
<td>10</td>
<td>1.5</td>
<td>18.44</td>
<td>1.102</td>
<td>1.091</td>
</tr>
<tr>
<td>CF10CB3</td>
<td>10</td>
<td>3.00</td>
<td>20.63</td>
<td>1.114</td>
<td>1.100</td>
</tr>
<tr>
<td>CF10CB6</td>
<td>10</td>
<td>6.00</td>
<td>24.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF20CB1.5</td>
<td>20</td>
<td>1.5</td>
<td>32.23</td>
<td>1.178</td>
<td>1.172</td>
</tr>
<tr>
<td>CF20CB3</td>
<td>20</td>
<td>3.00</td>
<td>34.2</td>
<td>1.190</td>
<td>1.175</td>
</tr>
</tbody>
</table>
Table 3.4. Standard percolation model parameters for single-filler composites

<table>
<thead>
<tr>
<th></th>
<th>In-plane</th>
<th>Through-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon fiber</td>
<td>Carbon black</td>
</tr>
<tr>
<td>$\sigma_F$ (S/cm)</td>
<td>625</td>
<td>11.3</td>
</tr>
<tr>
<td>$\varphi_{\text{Crit}}$ (vol%)</td>
<td>2.73</td>
<td>2.75</td>
</tr>
<tr>
<td>$t$</td>
<td>3.46</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3.2. In-plane and through-plane conductivity of COC/CB and COC/CF composites
The rheological changes to the developing percolating network of carboneous filler as a result of increased filler content in our COC composites were followed by plotting the storage modulus and complex viscosity, as shown in Figure 3.3. The $G'$ and $\eta^*$ values given in the figure corresponded to an oscillatory frequency of 0.15 rad/s where large-scale motion of the polymer chains dominated the rheological response of the material. This region was sensitive to changes in the microstructure attributed to the presence of a percolating network of carboneous filler within the polymer matrix [45]. Based on the rheological response shown in the plots for the two fillers, a region at low carbon content existed (i.e. below 1.5 vol% for CB and ~4-5 vol% for CF) where the rheology of the COC composite was relatively unaffected by their addition. For carboneous filler loading in this region, the electrical conductivity of the prepared composites was below the detectable range of our apparatus (i.e. <$10^{-9}$ S/cm); these filler concentrations are thought to lie below the percolation threshold for our material. With subsequent increase in filler concentration within the matrix, the viscosity and storage modulus of the COC composite increased rapidly as a percolating network of filler developed in the polymer matrix. We note that for an equivalent volumetric loading of filler, i.e. 10 vol%, that the viscosity of the COC/CB material was three orders of magnitude higher than the COC/CF composites. Increased stiffening of the matrix was observed as the content of fillers increased, due to the restricted segmental motion of the polymer chains.

An important selection criterion of formulations suitable for economical bipolar plate manufacture is seeking a trade-off between improved conductivity and maintaining processability attributes like viscosity so that injection molding remains feasible. Comparing Figures 3.2 and 3.3, it was observed that carbon black was considerably more effective than carbon fiber for increasing the electrical conductivity based on both achievable magnitude and a specific volume.
On the other hand, using carbon fibers provided composites with lower viscosity at the same level of electrical conductivity. Though the differences between carbon black and carbon fiber became less at higher conductivity values, for example at 0.02 S/cm the viscosity of the CF-filled composite was less than 10% that of the CB-filled system while at 0.6 S/cm the viscosity of the CF-filled composite was 30% that of the CB-filled system. In general, the trends in electrical conductivity and viscosity (or storage modulus) based on total carbon content appeared to closely follow one another for the carbon black filled composites (COC/CB) and to a much lesser extent for the carbon fiber filled composites (COC/CF). These findings were similar to those reported by Wu and Zheng [45] in their studies of high-density polyethylene (HDPE) composites containing either carbon black or carbon fibers where they found a good correlation of resistivity and dynamic rheological properties for CB composites but no evidence of such a correlation for CF composites. The studies of both
Migler and Douglas [46] for HDPE and Potschke [47] for polycarbonate, also reported a good correlation between conductivity and the shear modulus for multiwalled carbon nanotube fillers.

### 3.3.2. Hybrid CB/CF filler composites

The in-plane electrical conductivity of the hybrid-filler composites containing both carbon black and carbon fiber is reported in Figure 3.4. As seen in the figure, the addition of carbon black to the compounds containing 5 or 10 vol% CF increased their electrical conductivity above the value for a COC/CF composite of similar total carbon content – a possible indication of synergism which is discussed later in the paper.

![Figure 3.4. In-plane electrical conductivity of hybrid composites compared with single-filler composites](image-url)
Figure 3.5. Optical micrograph from polished surface of COC/CF (20 vol %). View is parallel to the mold plates and arrow shows the radial flow direction.

At these levels of carbon fiber present, the added carbon black appears to contribute to the establishment of conductive pathways within the matrix, similar to the findings of other researchers [8,30,37,39]. However, as the total carbon content increased for these composites, further increases in CB concentration appeared to have a diminishing impact on the improvement of electrical conductivity. By 20 vol% CF, the addition of 1.5 or 3 vol% CB had a negligible change on the electrical conductivity of the composite. By this concentration of carbon fibers in the composite, there were sufficient fiber-fiber contacts (as
Figure 3.6. Average fiber length for COC/CF composites with and without 3 vol% CB

demonstrated by the micrograph in Figure 3.5) that the addition of CB no longer provided any new conductive pathways but rather seems to add to the bulk of the existing network. For all of the hybrid-filler composites presented in Figure 3.4 it can be seen for a constant total carbon content that as the carbon fiber concentration was increased, the electrical conductivity decreased. This attribute of the hybrid-filler composite system was partly explained by significant fiber breakage during processing. Figure 3.6 illustrates the change in average fiber length for composites with 5, 10 and 20 vol% CF and either no CB included or 3 vol% CB added. The results show that fiber damage increased with increasing CF
concentration, particularly favoring the breakage of longer fibers. This finding is consistent with processing studies examining fiber breakage [48] where increasing fiber-fiber collisions occur as the fiber concentration was increased in the melt. Interestingly, despite the fact that the viscosity of these composites increased by at least an order of magnitude (to be noted in subsequent discussion) by the inclusion of 3 vol% CB, the fiber length was not significantly affected. This result is contrary to the results of Forgacs and Mason [49] and possibly suggests poor transmission of the viscous stresses across the melt-fiber interface.

The through-plane conductivity of the hybrid-filler composites displayed similar trends to that found the in-plane measurements. Addition of CB to composites with 5 or 10 vol% CF enhanced the through-plane conductivity in respect to COC/CF composites, whereas it did not improve the electrical conductivity at 20 vol% CF. The anisotropy in conductivity within these COC composites was studied by examining the ratio of through-plane/in-plane conductivity for increasing total carbon content as shown in Figure 3.7. The single-filler COC/CB composites showed the least anisotropy (i.e. highest ratio values) in conductivity compared to the COC/CF composites and hybrid-filler composites. Conversely, the hybrid-filler composites showed similar anisotropy to that of the single-filler COC/CF composites despite the inclusion of the CB along with the fibers. For all hybrid-filler composites (and the COC/CF), the conductivity ratio appeared to increase up to 20% total carbon content; higher carbon content had no impact on further enhancing the through-plane conductivity. The similarity of the hybrid composite to the COC/CF composite indicated preferential orientation of the fibers within these composites, caused by the radial flow in the compression molding process, had a dominant effect on the with total filler content but whereas the COC/CB composite may ultimately achieve a ratio of unity, there was no evidence that the composites containing
fibers would ever approach equivalent conductivity in both directions of measurement – at least not while the continuous phase was the polymer.

For selected samples, the skin layer from both sides of a circular disk was gradually removed by polishing with silicon carbide paper. Figure 3.8 shows the progressive increase in through-plane conductivity as the skin layer was removed, reaching a plateau after a thickness of approximately 100 μm had been taken away. For all samples examined, the conductivity of the core was greater than the original molded specimen indicating that the percolating network was not well
developed through the skin layer of these materials for through-plane conductivity. The inclusion of carbon black was shown to reduce the anisotropy in conductivity between the skin and core layers of the molded composite; the difference in through-plane conductivity between skin and core layers was 60% for the hybrid filled composite while for the COC/CF composites, this difference was as large at 110% at the lower filler concentration. The lower conductivity in the skin could be attributed to either lower carbon content in this local region of the molded part, or more likely, due to greater preferential aligned fibers in the direction of flow in the skin due to high shear [50-51]. Analysis of the two COC/CF composites mounted in epoxy and observed by optical microscopy showed that fibers within the 100 μm thickness defined as the skin herein exhibited average fiber orientation angles of 17° and 22° for 5 vol% and 20 vol% CF, respectively; an orientation angle of zero indicates fibers aligned parallel to the flow direction. In the core of the samples, the fibers showed significantly greater out-of-plane orientation with average orientation angle of 21° and 30° for the COC composites with 5 vol% and 20 vol% CF, respectively. Up to 1500 fibers were counted in this analysis. It was noted during this analysis that the number of fibers per unit viewable area was identical between the skin and core regions, indicating no concentration difference. The changes in conductivity based on part thickness for all composites shown in Figure 3.8 were therefore, a result of preferential orientation of the fibers in the skin layer compared to the core. The highly aligned fibers in the skin would exhibit an effective aspect ratio approaching unity in regards to a conductive path in the through-plane direction as the fiber orientation angle approaches zero and therefore, the local percolation threshold for CF was shifted to higher volume fraction as a result. In a future paper we will discuss a method for reducing the displayed preferential orientation of the fibers in order to improve the through-plane-to-in-plane conductivity ratio.
Figure 3.8. Dependence of through-plane conductivity on the extent of removed skin

The influence of both carbon black and carbon fibers on the rheology of the hybrid-filler COC composite is shown in Figure 3.9, with electrical conductivity values displayed for the same materials. As the total filler content was increased to obtain composite materials with higher conductivity, the viscosity simultaneously increased. However, the results showed that the rate of increase of viscosity versus conductivity (as the filler content was increased in the material) varied depending on the CB/CF ratio. Once the highest inclusion of carbon fibers (20 vol% CF) was reached in the hybrid-filler composite, the addition of CB increased the viscosity of the polymer without any significant
enhancement in the electrical conductivity. It appears that no hybrid composite had a lower viscosity than the CF composites when compared at same level of conductivity. There were, however, a number of hybrid composites with higher electrical conductivity but lower viscosity than CB composites. For example, samples CF5CB6 and CF10CB3 were two composites with equivalent conductivity, yet the viscosity of the latter was almost an order of magnitude lower. Generally, composites higher in fiber content and containing moderately low carbon black content (CF10CB1.5 and CF10CB3) offered improved conductivity while maintaining the processability of the material in conventional processing equipment.

One may ask why consider using a hybrid composites when suitable electrical conductivity at the lowest viscosity can be obtained with the COC/CF composites? The logic for using COC/CF is reasonable when anisotropy of the final product is not an issue, which rarely is the case. The case of a bipolar plate for a fuel cell stack is a prime example where the important direction of conductivity is contrary to the direction that CF will preferentially align during molding operations. Hybrid filler composite using a low aspect ratio filler like carbon black as one of its constituents makes more sense for systems where conductive pathways must be developed out-of-plane to the flow direction yet the high viscosity attributed to use of this filler at sufficient concentrations prevents its exclusive use in continuous processes like injection molding. With the arguments for out-of-plane conductive enhancement in mind and the improvement observed in through-plane conductivity up till 20 vol% total carbon content shown in Figure 3.7, the optimal hybrid filler composites from this work are considered to be CF10CB1.5 and CF10CB3. These materials offer maximum through-plane to in-plane conductivity and the lowest viscosity based on equivalent conductivity. A recommended strategy for gaining conductivity-viscosity synergy.
would seem to require adding CB close to its critical concentration into carbon fiber-filled composites.

Figure 3.9. Viscosity-conductivity correlation for hybrid composites

3.4. Discussion of Conductive Synergism

The literature states that combining conductive fillers, when one of the fillers is below its critical concentration, does not improve the electrical conductivity of the final composite [37,40]. In Table 3.5, the conductivities of hybrid composites with one component well below its critical concentration as a
single-filler were compared to the conductivity of relevant single-filler composites. Contrary to the findings of those earlier studies, the addition of CB at 0.75 vol% significantly enhanced the conductivity of a composite containing 5 vol% CF by almost an order of magnitude in the in-plane direction and by five times in the through-plane direction. The improvement in conductivity was even greater when 1.5 vol% CB was added to the composite with 5 vol% CF. Similarly, though to a lesser extent, the addition of 2.5 vol% CF improved the conductivity of 3 vol% CB composite. These findings indicate that CB and CF do not establish co-continuous network structures within the composite, but rather cooperatively contribute to the conductive pathways formed in the material. This is a difficult

Table 3.5. Electrical conductivity of hybrid composites with one filler below percolation

<table>
<thead>
<tr>
<th>Case</th>
<th>CF (vol %)</th>
<th>CB (vol %)</th>
<th>In-plane Conductivity (S/cm)</th>
<th>Improvement (folds)</th>
<th>T-plane Conductivity (S/cm)</th>
<th>Improvement (folds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
<td>0.0013</td>
<td>-</td>
<td>1.5 x 10^{-5}</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.75</td>
<td>0.023</td>
<td>18</td>
<td>1.6 x 10^{-4}</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.5</td>
<td>0.081</td>
<td>62</td>
<td>9.4 x 10^{-4}</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3</td>
<td>0.028</td>
<td>-</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>3</td>
<td>0.093</td>
<td>3.2</td>
<td>0.007</td>
<td>1.4</td>
</tr>
</tbody>
</table>

phenomenon to capture visually, yet SEM analysis of the fractured surface of the composite with 0.75 vol% CB and 5 vol% CF (shown in Figure 3.10) shows that CB aggregates form in the vicinity of CF fibers. In order to discuss synergism for our particular material system, it was necessary to first establish that the fillers had the capacity to interact.
The challenge comes from how one defines conductive synergism within the context of a hybrid filler system. Should a conductive value, which exceeds the volumetric additivity for these two fillers as equivalent single-filler composites be the sole criteria for synergism? This approach assumes two independent networks and calculates the resultant conductivity based on two parallel conductors relevant to each network:

\[
\sigma_C = \varphi_A \sigma_A + \varphi_B \sigma_B
\]  

(3.3)

where, \( \sigma_C \) is the conductivity of the hybrid composite and \( \sigma_A \) and \( \sigma_B \) are the conductivities of single-filler composites at volume fractions \( \varphi_A \) and \( \varphi_B \) respectively. However, as already established earlier in this section, the two fillers in our system do not appear to establish independent networks and as shown in Figures 3.2 and 3.4, the measured conductivity values of both single-filler and hybrid-filler composites do not display a linear dependency on filler concentration which would be the standard axiom of additivity. There is also the issue of differences in the inherent conductivity of the different fillers which should be considered when evaluating synergism. The inclusion of the inherent conductivity of these fillers would seem necessary to establish a basis of evaluation in this regard.

Instead of the expression for linear additivity of hybrid filler composites stated in Eqn (3.3), a modified variant using the standard percolation model (Eqn. 3.2) is first considered so that the non-linear influence of filler content on conductivity can be expressed within the context of additivity. The fitted parameters for each single-filler composite using the standard percolation model (given in Table 3.4) can be used to obtain conductivity values at any filler loading equal to the total filler loading in the hybrid composite. The arithmetic average for electrical conductivity of a hybrid by additivity can be calculated by:
where, $\sigma_{CF}$ and $\sigma_{CB}$ are conductivities of single-filler composites at the same total filler content as the hybrid material, and $\varphi_{CF}$ and $\varphi_{CB}$ are carbon volume fractions of CF and CB in the hybrid as defined by:

$$\varphi_{CF} = \frac{\varphi_{CF}}{\varphi_{CF} + \varphi_{CB}} \text{ and } \varphi_{CB} = 1 - \varphi_{CF} \quad (3.5)$$

The results obtained in this manner are given in Table 3.6 as the “additive model”. As seen in the table, for all combinations of CF and CB, except at 20 vol% CF, the experimental in-plane conductivity results were well above those values obtained from the additive model, implying synergism for the CF/CB hybrid composites. Likewise, but to a lesser extent, the through-plane conductivity results were higher than the predicted results by the additive model for most hybrid composites except at 20 vol% CF.

With the recognition that additivity can not reasonably approximate the resulting conductivity of a hybrid filled composite, a simple expression was sought to improve this estimation without being held up by the complexity of the microstructure of the composite. The standard percolation model is the simplest and most often used of the available empirical models for estimating electrical conductivity. A hybrid percolation model can be written in the form of standard percolation model (Eqn. 3.2):

$$\ln \sigma_C = \varphi_{CB} \ln \sigma_{CB} + \varphi_{CF} \ln \sigma_{CF} \quad (3.4)$$

$$\sigma_{\text{hybrid}} = \sigma_{F(\text{hybrid})} \left[ (\varphi_{CF} + \varphi_{CB}) - \varphi_{\text{Crit(\text{hybrid})}} \right]^{\text{hybrid}} \quad (3.6)$$
where, $\sigma_{\text{hybrid}}$ is the electrical conductivity of hybrid composite, and $\varphi_{\text{Crit(hybrid)}}$, $t_{\text{hybrid}}$ and $\sigma_{F(\text{hybrid})}$ are the percolation threshold, critical exponent and electrical conductivity of the material, respectively, which can be obtained by:

$$
\sigma_{F(\text{hybrid})} = \varphi_{CF} \sigma_{CF} + \varphi_{CB} \sigma_{CB} \\
\varphi_{\text{Crit(hybrid)}} = \varphi_{CF} \varphi_{\text{Crit(CF)}} + \varphi_{CB} \varphi_{\text{Crit(CB)}} \\
t_{\text{hybrid}} = \varphi_{CF} t_{CF} + \varphi_{CB} t_{CB}
$$

This model becomes the standard percolation model when the volume fraction of one filler approaches unity and therefore, satisfies the previous example concerning calculating the conductivity of a composite with 15 vol% CF based on the conductivities of the composites with 5 and 10 vol% CF.

We use Eqn. 3.6 as a simple tool to estimate the electrical conductivity values of all hybrid composites examined in this paper (Table 3.6). As seen, a better match was found using the hybrid percolation model rather than the additivity model when compared against the experimental data, particularly for the in-plane results.
<table>
<thead>
<tr>
<th>Composite</th>
<th>In-plane (S/cm)</th>
<th>Through-plane (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Additive model</td>
<td>Experimental</td>
</tr>
<tr>
<td>CF5</td>
<td>0.0013</td>
<td>0.0013</td>
</tr>
<tr>
<td>CF10</td>
<td>0.072</td>
<td>0.070</td>
</tr>
<tr>
<td>CF20</td>
<td>1.43</td>
<td>1.69</td>
</tr>
<tr>
<td>CF30</td>
<td>6.96</td>
<td>5.78</td>
</tr>
<tr>
<td>CB3</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>CB6</td>
<td>0.367</td>
<td>0.367</td>
</tr>
<tr>
<td>CB9</td>
<td>0.706</td>
<td>0.706</td>
</tr>
<tr>
<td>CF2.5CB3</td>
<td>0.035</td>
<td>0.093</td>
</tr>
<tr>
<td>CF5CB0.75</td>
<td>0.006</td>
<td>0.023</td>
</tr>
<tr>
<td>CF5CB1.5</td>
<td>0.019</td>
<td>0.081</td>
</tr>
<tr>
<td>CF5CB3</td>
<td>0.079</td>
<td>0.290</td>
</tr>
<tr>
<td>CF5CB6</td>
<td>0.355</td>
<td>1.89</td>
</tr>
<tr>
<td>CF10CB1.5</td>
<td>0.177</td>
<td>0.596</td>
</tr>
<tr>
<td>CF10CB3</td>
<td>0.341</td>
<td>1.83</td>
</tr>
<tr>
<td>CF10CB6</td>
<td>0.823</td>
<td>4.92</td>
</tr>
<tr>
<td>CF20CB1.5</td>
<td>1.92</td>
<td>1.98</td>
</tr>
<tr>
<td>CF20CB3</td>
<td>2.46</td>
<td>2.02</td>
</tr>
</tbody>
</table>
3.5. Conclusions

The electrical and rheological properties of a carbon filled cyclic olefin copolymer composites were studied for formulations with varying concentrations of carbon fiber and carbon black fillers. The two fillers separately give similar trends in conductivity based on filler content but significantly differ in regards to their impact on viscosity. A strategy was sought for combining the fillers in order to improve the conductivity of the composite without increasing its viscosity beyond the capacity of processing equipment like an injection molding machine. It was observed that the two fillers synergistically contributed to the development of electron pathways within the matrix except at high CF loadings. At the same
time, reasonable processability of the composites (considering its viscosity in respect to traditional processing equipment) was found when the carbon fiber was much higher than the carbon black in the matrix, CF:CB ratio around 3 based on volume fraction. The CB content in these formulations should be kept close to its critical percolation concentration to prevent large increases in the viscosity of the composite. A proposed hybrid model was found to give better estimates of the electrical conductivity of these hybrid carbon black-carbon fiber composites than the additive model.

References

2. DOE Hydrogen Program, FY 2005 Progress Report, VII.D Bipolar Plates, VII.D.1 Scale-up of Carbon/Carbon Composite Bipolar Plates, 863-869
5. Blunk, R. H. J.; Lisi, D. J.; Yoo, Y; Tucker, C. L. AiChE 2003, 49, 18-29
28. Meng, Y. Polymer Nanocomposites 2006, 510-539
31. Balberg, I. Carbon 2002, 40, 139-143
32. Feng, J.; Chan, C-M, Li, J-X. Polym Eng Sci 2003, 43, 1058-1063
34. Mallette, J. G.; Marquez, A. Polym Eng Sci 2000, 40, 2272-2278
46. Migler, K. B.; Douglas, J. F. Nanofabrication and Processing, 32-33
49. Forgacs, O. L.; Mason, S. G. J Colloid Sci 1959, 14, 457-472
Chapter 4

Improved Through-Plane Electrical Conductivity in a Carbon Filled Thermoplastic via Foaming

This chapter is a paper published as:
G. H. Motlagh, A. N. Hrymak, and M. R. Thompson “Improved Through-Plane Electrical Conductivity in a Carbon-Filled Thermoplastic via Foaming”, Polymer Engineering and Science, 48, 4, 687-696. This paper is the major work of G. H. Motlagh. Part of the analysis has been done by Branden Job and Brandon Shiplo under the supervision of G. H. Motlagh.

This paper establishes foaming as a suitable processing technology for disrupting the preferential fiber orientation that occurs in a shear flow and shows how the morphological changes influence through plane electrical conductivity. The paper builds upon the previous work cited in Chapter 3, making use of those material formulations which demonstrated synergistic effects between the two fillers in regards to electrical conductivity.

Abstract
Flow-induced orientation of the conductive fillers in injection molding creates parts with anisotropic electrical conductivity where through-plane conductivity is several orders of magnitude lower than in-plane conductivity. This paper provides insight into a novel processing method using a chemical blowing agent to manipulate carbon fiber orientation within a polymer matrix.
during injection molding. The study used a fractional factorial experimental design to identify the important processing factors for improving the through-plane electrical conductivity of plates molded from a carbon filled cyclic olefin copolymer (COC) containing 10 vol% carbon fiber (CF) and 2 vol% carbon black (CB). The molded COC plates were analyzed for fiber orientation, morphology, and electrical conductivity. With increasing porosity in the molded foam part, it was found that greater out-of-plane fiber orientation and higher electrical conductivity could be achieved. Maximum conductivity and fiber re-orientation in the through-plane direction occurred at lower injection flow rate and higher melt temperature. These process conditions correspond with foam flow during filling of the mold cavity, indicating the importance of shear stress on the effectiveness of a fiber being rotated out-of-plane during injection molding.

4.1. Introduction

Electrically conductive thermoplastic composites are growing in demand within the energy, electronic, and medical sectors for applications such as thermal switches, EMI shielding, blood sensors, and fuel cell bipolar separator plates. The advantages often sought by selecting these conductive polymers, over more traditional materials such as metals or ceramics, are their low density, good chemical resistance and barrier properties, as well as being more readily formed into complex shapes without expensive secondary processing steps. The conductivity of these materials is dependent upon the volume content, inherent conductivity, surface and interfacial properties, and aspect ratio of the fillers incorporated [1-6]. Polymer composites containing low aspect ratio powder type fillers, such as carbon black, exhibit a relatively uniform volumetric conductivity throughout a molded part; however, they are not easily processed by extrusion or injection molding due to their extremely high viscosities. Low aspect ratio fillers tend to have a higher percolation threshold characteristic, as compared to high
aspect ratio fillers at equivalent surface area. Therefore a large amount of the additive must be added to the polymer in order to achieve significantly higher conductivity, compared to the inherently insulating base material, and as a result the molten material exhibits shear viscosities too high for traditional processing machinery [5-6]. In place of powders, high aspect ratio conductive fillers (such as carbon fibers) have been used as the polymer composites exhibit a lower viscosity due to their relatively low percolation threshold and preferential fiber alignment within a flow field [6]. The preferential orientation of high aspect ratio fillers in the flow direction within molded parts leads to anisotropic electrical properties favoring electron transport predominantly in the in-plane direction [6-8]. This fact is not necessarily a negative depending on the application; however, for uses in which conductivity through one of the opposing planes is more highly desired, materials with near exclusive in-plane conductivity are not deemed suitable. In addition, a unidirectional fiber composite exhibits the highest percolation threshold while a randomly oriented fiber composite has the lowest percolation threshold due to more fiber-fiber contacts [9]. The present work examines a method of disrupting the preferential orientation of high aspect ratio fillers during the processing of electrically conductive composites through foaming. A previous paper by the authors [6] studied the conductivity-rheology relationship in order to formulate hybrid filler composites suited to injection molding processes.

Wilson [10] discussed the possibility of re-orientation of glass fibers due to bubble growth in composite foams, as shown in Figure 1, though Wilson never reported experiments to prove his theory. He speculated that bubble growth in close proximity to a fiber would result in out-of-plane reorientation; though such circumstances are not easily achieved since it is known that the glass fibers in composite do not act as nucleating sites during foaming [11,12]. Yang et al. [13] prepared carbon nanofiber-polystyrene composites by solution casting and found that the foam composite had a similar conductivity and percolation threshold to its
solid composite counterpart. None of the studies mentioned above demonstrated the feasibility of using foaming as a mechanism for controlling fiber orientation. Therefore, this work examines the effect of foaming at different processing conditions on the fiber orientation and consequent electrical conductivity of injection moulded polymer composite plates. Matrix viscosity, fiber length, and the kinetics of bubble growth versus solidification are all expected to influence the mechanics of fiber re-orientation phenomenon. The principle outcome sought in this work is a strategy for maximizing the through-plane to in-plane conductivity ratio within a molded sheet.

Figure 4.1. Conceptualization of fiber rotation in the presence of bubble growth.
4.2. Experimental

4.2.1. Materials

Cyclic olefin copolymer (COC), (Topas 6013S-04 supplied by Ticona, MFR 14 cm³/10min @ 260°C, 2.16 kg) was chosen as the matrix polymer as it represents a suitable candidate for bipolar plate manufacturing. The amorphous character of this polymer was also an important consideration for this study to minimize concerns regarding crystallization affecting the fiber orientation. The carboneous fillers used in this study included 5mm-long, 7.5 µm diameter PAN-derived chopped carbon fibers (CF) (AGM-94 from Asbury Carbons) and a high surface area carbon black (CB) (Ketjenblack EC-600JD from Akzo Nobel with aggregate size of 30-100 nm and surface area of 1250 m²/g). Electrical conductivities of the used COC, CF and CB as reported by the suppliers were $<10^{-16}$ S/cm, 625 S/cm and 10-100 S/cm, respectively. Further properties of the fillers have been reported in a previous paper [6].

A masterbatch exothermic chemical blowing agent (CBA) was used for the trials, IM 2240 supplied by Dempsey Corporation. The CBA masterbatch contained 20 wt% 5-Phenyl tetrazol (PHT) which was the active component involved in the evolution of nitrogen gas for foaming. The carrier resin of the masterbatch was polycarbonate. The CBA was selected for its high decomposition temperature which suits the conditions necessary for processing the COC polymer in an injection molding machine. The onset of decomposition for CBA was determined by TGA analysis to be 225°C with the majority of gas evolved at 240°C.
4.2.2. Procedure

A Leistritz ZSE 27-40 co-rotating twin screw extruder with side feeder was used to produce the composite material used in the study. A temperature profile of 260 °C for barrel zones 2-9 and 250°C for zone 1 and the die was used and a constant screw speed of 100 RPM was selected. COC pellets and carbon black (CB) were fed to the first block of the TSE by a weight-loss feeder, while a CF masterbatch (prepared on a Haake Rheocord batch mixer) was introduced into the melt by a side feeder half way down the length of the machine. The screw design was configured to maximize distributive mixing by use of comb elements and minimize shear through the limited use of 30° and 60° kneading blockings after the melting zone. The compounded material (prior to injection molding and foaming) contained 10 vol% CF and 2 vol% CB.

An Arburg 55 ton injection-molding machine with a 30 mm 20 L/D plasticating unit was used to prepare rectangular plaques with face dimensions of 14.5cm x 3cm and a thickness of 3mm. A 2⁴⁻¹ fractional factorial design was used to evaluate several different processing factors as shown in Table 4.1, which produced both foamed and non-foamed samples. The factors examined were blowing agent content, injection flow rate, melt temperature and mold temperature. All other processing factors were kept constant for the trials except packing pressure, which was set at 500 bar for all non-foamed runs and not used for the foamed runs. To produce the foamed samples, IM2240 pellets were dry blended with the composite pellets and fed into the hopper. The temperatures of the first three zones for the plasticating unit were always set below 220°C to prevent premature decomposition of CBA and gas loss, while the temperatures of the last two zones on the plasticating unit and nozzle were set above 240°C to obtain full decomposition. The injection nozzle was also equipped with a shut-off nozzle to prevent gas loss.
4.2.3. Analysis

As shown in Figure 2, the injection moulded plaques were cut using a high pressure water jet into 3.75 mm × 27 mm rectangular samples for which in-plane electrical conductivity was measured along the long (L) and short (W) axes using a 4-probe method. Disks of 20mm diameter were cut by the same method for determination of through-plane (T) electrical conductivity using a 2-probe method. These measurement techniques are described in a previous paper [6]. A minimum of 7 and 3 samples for the in-plane and through plane measurements, respectively, were used for each reported value. In most cases, the applied voltage was kept around 0.5-1 V in order to minimize joule heating; however, due to the broad range of the conductivities this was not always possible.

Table 4.1. Fractional factorial design to produce injection moulded samples

<table>
<thead>
<tr>
<th>Run</th>
<th>CBA, IM2240 (wt %)</th>
<th>Injection flow rate (cc/s)</th>
<th>Melt temperature (°C)</th>
<th>Mold temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>10</td>
<td>260</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>10</td>
<td>300</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>100</td>
<td>260</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>100</td>
<td>300</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>10</td>
<td>260</td>
<td>120</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>10</td>
<td>300</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>100</td>
<td>260</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>100</td>
<td>300</td>
<td>120</td>
</tr>
</tbody>
</table>
Figure 4.2. Cutting pattern to prepare samples for electrical conductivity measurements: samples for longitudinal and transverse measurements (top) and samples for through-plane measurements (bottom).

The density of the produced samples was determined by the buoyancy method. To measure the fiber length distribution (FLD), samples were ashed in an electrical furnace at 550 °C for 10 min to remove the polymer. Initial examination showed that fibers collected in this manner were consistent with the solvent digestion technique. To obtain well spaced fibers for viewing under the microscope, the collected fibers from the furnace were suspended in xylene, and then spread over microscope slides. Digital images were taken of the slide under an optical microscope after the solvent had evaporated, and these micrographs were analyzed using Sigma Scan Pro 3.0 image analysis software from Jandel Scientific to quantify the lengths of at least 1000 fibers from each sample. To characterize carbon fiber orientation and foam structure, composites were mounted in epoxy resin and metallographically polished with an automatic Struer polisher. Digital images taken of the polished surface by reflective optical microscopy were quantitatively analyzed using Northern Eclipse 6.0 software. By
adjusting the grey scale and contrast for the images, we were able to distinguish fibers or cells in order to measure either fiber orientation or cell size. The distributions were determined from the analysis of approximately 1500 fibers and 1000 foam cells. To quantitatively express the orientation state of the fibers, 3-D orientation factors were calculated according to the following expressions:

\[
\begin{align*}
    f_x &= \frac{1}{n} \sum \cos^2 \alpha \cos^2 \beta \\
    f_y &= \frac{1}{n} \sum \sin^2 \alpha \cos^2 \beta \\
    f_z &= \frac{1}{n} \sum \sin^2 \beta
\end{align*}
\]  

Figure 4.3. 3D Diagram showing a fiber with the defined parameters in Cartesian coordinate to determine fibre orientation.
where, \( \alpha \) and \( \beta \) are the in-plane and out-of-plane orientation angles respectively as defined in Figure 3. The parameter \( \alpha \) was directly determined by the image analyzer while \( \beta \) was calculated from the dimensions of the major (b) and minor (a) axes of the elliptical fiber shape shown in Figure 3 and given in Equation (4):

\[
\beta = \sin^{-1}\left(\frac{b}{a}\right)
\]

Depending on the characterized polished plane, the X and Y subscripts in Equations (1) and (2) were arbitrarily specified for the polished plane axes while \( Z \) in Equation (3) was the axis perpendicular to the polished plane. For example, when analyzing the LW polished plane, \( f_X = f_L, f_Y = f_W \) and \( f_Z = f_T \). The fiber orientation calculations were constrained such that each orientation factor could only vary from 0 to 1 and \( f_L + f_W + f_T = 1 \). For a composite with random oriented fibers \( f_L = f_W = f_T = 1/3 \) and for a composite with unidirectional orientation in the L direction \( f_L = 1 \) and \( f_W = f_T = 0 \). For the core region of the foamed samples, orientation factors \( f_L, f_W \) and \( f_T \) were determined in all three planes (LW, LT and WT) and the arithmetic average was reported as a single value to demonstrate the order of the orientation in L, W and T directions. For the skin region, orientation factors were only obtained from the WT plane and compared with the orientation state in the core WT plane.

### 4.3. Results

The electrical conductivity values reported in this paper were intentionally low in favor of using standard fillers, which are relatively simple to compound into the material. For higher conductivities, the foaming strategy could also be used with metal-coated carbon fibers and carbon nanotubes. The filler concentrations used in this work were selected based on compression molding trials previously reported [6]. In that earlier work, radial flow was used to orient...
the fibers in order to achieve reasonably representative samples as would be produced on an injection-molding machine, albeit at low shear.

4.3.1. Microstructure of the foamed composite

The nominal, maximum and minimum cell sizes observed among the different foamed composites are tabulated in Table 4.2. According to the measured apparent densities included in the table, the resulting void fraction in the foamed composites was relatively consistent for the different samples at 18%. The nominal cell size varied between 20 to 45 \( \mu m \), where the smallest and largest cell

<table>
<thead>
<tr>
<th>Table 4.2. Properties of the foamed composites prepared according to the fractional factorial design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
</tbody>
</table>

Average standard deviation for reported density, fibre length and cell size values were 1%, 5% and 11%, respectively.
size was observed for Runs 6 and 7, respectively. The relatively small cell size found in all these foams was largely attributed to the high viscosity of the composite [6]; though, the carbon black may have also partially contributed as nucleating sites during foaming. The cell size distributions of foamed composites are presented in Figure 4.4 indicating a non-uniform cell structure with a broad range of sizes. As seen in the figure, the samples from Run 6 featured less than 3% of the cells present were larger than 100 μm, the approximate length of the fibers, while Run 7 had 20% of its cells larger than 100 μm.

The flow field within the mold cavity can significantly elongate the shape of a bubble depending on the extent of shear present during foam growth [14].

**Figure 4.4.** Cumulative cell size distribution of foamed samples obtained by optical microscopy from polished LW plane at the T location shown in Figure 4.2.
Similar to cell size, the shape of the foam cells was considered to have a possible influence on the path of electrons passing through the formed composite part. A set of micrographs are presented in Figure 4.5 showing the LT plane of the foamed samples for Runs 6 and 7 which correspondingly demonstrated the highest and lowest conductivities, respectively. It can be seen for the Run 7 sample that the bubbles present were highly elongated with their major axis more closely orientated in the L direction. The orientation of their major axes was measured and it was determined that the bubbles were oriented with an average angle of 20° and 31° out of the LW plane for Runs 7 and 6, respectively. Cumulative distribution of the bubble elongation in the LT plane, defined as the ratio of the major axis to the minor axis of a bubble, is shown in Figure 4.6. As seen it appeared that Run 7 had more elongated bubbles than the other foam runs. Therefore, the samples from Run 7 had the largest cell size in the LW plane and these bubbles were sheared along the flow and less bubble expansion took place towards the T direction resulting lower fibre re-orientation.
Figure 4.5. Cell morphology of the foamed composites in the LT plane: a) Run (6) produced at 10 cc/s, melt temperature of 300° C and mold temperature of 80°C and b) Run (7) produced at 100 cc/s, melt temperature of 260° C and mold temperature of 80°C.
Figure 4.6. Cumulative bubble elongation distribution of the factorial design foamed composites in the LT plane.

4.3.2. Fiber Characterization

The dispersion of fibers within a polymer melt is often a complex task, as sufficient mixing must be achieved to separate the individual fibers from their as-supplied bundles and then homogeneously distributed throughout the polymer matrix. As summarized in Table 4.2, the nominal fiber length was around 100 μm after processing with little variance in the fiber dimension noted between the different samples, regardless of whether they were processed with the blowing
agent. From an original fiber length of 5 mm within the bundles, the resulting separated fibers were found to exhibit substantial breakage due to processing; fracturing which was attributable to the original size and mechanical strength of the fibers, the concentration of the fibers, the viscosity of the matrix, and the level of shear applied [15-16]. These smaller fibers found in the compounded samples would have increased the needed filler concentration to establish a percolating network structure within the molded sample [3], but they were intentionally produced in this manner under the assumption that fibers with similar dimensions to the foam bubbles would result in more noticeable changes in the final orientation of the filler. Future studies will test the validity of the correlation between fiber length and bubble size on the resulting degree of re-orientation.

The orientation of the carbon fibers in the core and skin regions of the moulded specimens was quantified by the orientation factors \( f_L, f_W \) and \( f_T \) in Table 4.3. The core measurements were taken from 0 to 0.5 mm away from the mid-plane (through-plane axis) while the skin measurements were made at distance of 1.5 mm from the mid-plane of the specimen. Differences between the skin and core in terms of fiber morphology are commonly reported in the literature for injection moulded parts [17, 18] with the majority of fibers highly aligned in the longitudinal (L) direction within the skin, and randomly within the LW plane for the core. According to the table, the resulting orientation factors within the skin and core regions of the non-foamed composites were found to be in good agreement with the findings of those previous works. Such preferentially alignment of fibers in the skin resulted from the streamlines of an advancing flow front (i.e. fountain flow) as well as the higher shear stress applied to the fibers close to the mold wall [19, 20]. Orientation of fibers for the W direction in the core was attributed to the expanding flow leaving the gate to fill the width of the mold cavity. The flat velocity profile, resulting from the non-Newtonian rheology of the melt, preserved that transverse fiber orientation as the melt advanced to fill
the whole mold [18]. In addition, the greater orientation of fibers in the W direction could have occurred during the packing stage [21]. Of particular interest to this work were the results of fiber orientation in the T direction (through-plane). As indicated in Table 4.3, generally both in the core and the skin, $f_T$ was much smaller than $f_L$ and $f_W$ for the non-foamed samples, confirming our expectation that the fibers become preferentially oriented in the flow direction for both injection flow rates used in these trials. This can be visually observed in Figure 4.7 where most of the fibers were seen lying in the LW plane. The ratio of $f_T:f_L:f_W$ is consistent with the injection moulded samples reported in the literature [22,23].

Comparing $f_T$ values of the foamed and non-foamed composites in the core from Table 4.3, it can be seen that bubble growth influenced out-of-plane rotation of the fibers for all tested processing conditions. The most notable increase for $f_T$ was by three-fold corresponding to the conditions for Run 6, which resulted in a value that was now comparable to $f_W$ and $f_L$. In the skin, the foam composites still had significantly larger $f_T$ values than the non-foamed composites; though this difference was much smaller than the difference found in the core. To examine these findings in more detail, the cumulative distribution of $f_T$ was presented in Figure 4.8 for all eight runs. According to the graph, the majority of all fibers (~80%) in the non-foamed samples were oriented in-plane and $f_T$ never exceeded 0.5. Conversely, the majority of the foamed samples showed an incremental improvement in the quantity of fibers now oriented out-of-plane. For the foamed sample produced from Run 6 as little as 30% of the fibers remained oriented in-plane with the vast majority oriented out-of-plane with $f_T$ values as great as 0.9. Finally as seen in Table 4.3, contrary to the non-foamed composites, $f_L$ was higher in value than $f_W$ for the foamed composites in the core indicating preferential orientation in the L direction rather than W direction. The lack of a packing stage or bubble growth may have created the observed preferred fiber orientation.
Table 4.3. Orientation factors in three principal directions (L, W and T) for the factorial design injection molded samples

<table>
<thead>
<tr>
<th>Run</th>
<th>Fiber length (μm)</th>
<th>f_T Core</th>
<th>f_W Core</th>
<th>f_L Core</th>
<th>f_T Skin</th>
<th>f_W Skin</th>
<th>f_L Skin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101</td>
<td>0.079</td>
<td>0.41</td>
<td>0.51</td>
<td>0.059</td>
<td>0.33</td>
<td>0.61</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>0.076</td>
<td>0.43</td>
<td>0.49</td>
<td>0.052</td>
<td>0.33</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>102</td>
<td>0.052</td>
<td>0.49</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>102</td>
<td>0.065</td>
<td>0.51</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>94</td>
<td>0.099</td>
<td>0.39</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>98</td>
<td>0.210</td>
<td>0.36</td>
<td>0.43</td>
<td>0.077</td>
<td>0.34</td>
<td>0.58</td>
</tr>
<tr>
<td>7</td>
<td>106</td>
<td>0.109</td>
<td>0.36</td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>105</td>
<td>0.101</td>
<td>0.32</td>
<td>0.58</td>
<td>0.074</td>
<td>0.30</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Average standard deviation for reported f_L, f_W and f_T values were 11%, 13% and 13%, respectively.
Figure 4.7. Micrographs showing (a) in-plane and (b) through-plane orientation of carbon fibers at the core for Run (4) taken by reflected light microscopy.
4.3.3. Electrical Conductivity

The conductivity values for both foamed and non-foamed COC composites are reported in Table 4.4. The magnitude of the deviations stated was reasonable for polymer composites. Due to the low aspect ratio carbon fibers used in this work, the electrical conductivities of the samples were relatively low, in the order of $10^{-5}$ S/cm. First examining the through-plane values, higher measured conductivity was generally found for the foamed composites compared to the non-foamed counterparts when produced at low injection flow rate. The greatest
improvement in through-plane conductivity was found for Run 6, which previously noted corresponds with the highest degree of fiber reorientation found (i.e. $f_r=0.21$ in Table 4.3) and the finest cell morphology (referring to Table 4.2 and Figure 4.4). For the other foam samples, Runs 5 and 8 yielded conductivities similar in magnitude to their non-foamed counterparts. Considering the volume exclusion effect of the gas phase in the foamed samples, lowering the volume fraction of carbon filler in the moulded sample, the through-plane electrical conductivity values determined for these three samples indicate a marked improvement in electron transport through the composite material can be achieved with the right foaming conditions. On the other hand, Run 7 demonstrated the lowest conductivity among the foamed samples, which was

Table 4.4. Electrical conductivity results\(^a\) for factorial design injection molded composites (10 vol% CF and 2 vol%CB) in the L, W and T directions.

<table>
<thead>
<tr>
<th>Run</th>
<th>$\sigma_T$ (S/cm) $\times 10^5$</th>
<th>$\sigma_W$ (S/cm)</th>
<th>$\sigma_L$ (S/cm)</th>
<th>$\sigma_{\text{average(LWT)}}^b$ (S/cm)</th>
<th>$\sigma_L/\sigma_W$</th>
<th>$\sigma_L/\sigma_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
<td>3.0</td>
<td>6.7</td>
<td>1.32</td>
<td>2.2</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>1.27</td>
<td>12.0</td>
<td>43</td>
<td>8.65</td>
<td>3.5</td>
<td>350</td>
</tr>
<tr>
<td>3</td>
<td>1.46</td>
<td>1300</td>
<td>822</td>
<td>116</td>
<td>0.7</td>
<td>273</td>
</tr>
<tr>
<td>4</td>
<td>4.9</td>
<td>1020</td>
<td>2680</td>
<td>238</td>
<td>3.0</td>
<td>343</td>
</tr>
<tr>
<td>5</td>
<td>0.90</td>
<td>913</td>
<td>1300</td>
<td>102</td>
<td>2.1</td>
<td>2108</td>
</tr>
<tr>
<td>6</td>
<td>31.4</td>
<td>2030</td>
<td>2280</td>
<td>525</td>
<td>1.1</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
<td>14.4</td>
<td>43</td>
<td>2.02</td>
<td>3.0</td>
<td>1655</td>
</tr>
<tr>
<td>8</td>
<td>0.66</td>
<td>447</td>
<td>1970</td>
<td>83.4</td>
<td>6.4</td>
<td>6876</td>
</tr>
</tbody>
</table>

Reported conductivity values have been multiplied by $10^5$.

\(^a\) Average standard deviations for the data shown were 33%, 22% and 36% for L, W and T directions, respectively.

\(^b\) All average values are geometric average.
somewhat unexpected since according to Figure 4.8 it possessed a larger fraction of fibers orientated out-of-plane compared to Runs 5 and 8. However, as indicated earlier, the samples from Run 7 were found to have larger bubbles than the other foams and those bubbles observed in the LT plane were more elongated. Since all of the foams in these trials exhibited the same degree of porosity (based on part density), the notion of a volume exclusion effect does not appear to adequately explain the low conductive value for Run 7. It would appear from these results that the foam morphology plays a significant role in achieving high conductivity values, as opposed to our previous belief that maximizing out-of-plane fiber orientation was the only important factor.

The last two columns in Table 4.4 indicate the anisotropy in the conductivity for the composites. In general, the conductivity through the materials was higher in the main direction of the flow (L) followed by the transverse direction of the flow (W) and finally perpendicular to the main flow direction (T). This is in agreement with the fiber orientation results in Table 4.3. Looking at the individual \( \sigma_L/\sigma_W \) and \( \sigma_L/\sigma_T \) average values for the foam and non-foam runs revealed that the L/W anisotropy was relatively low and comparable between the two material systems, and yet the L/T anisotropy was found to be much larger and significantly more so for the foamed samples. On a basis of similar average conductivity as displayed in Table 4.4, Runs 4 and 6 can be compared to show the differences in anisotropy between the non-foam and foam composites – the results indicate that the foam composite has less anisotropy, with lower \( \sigma_L/\sigma_T \) and \( \sigma_L/\sigma_W \) ratios.

4.3.4. Analysis of the DOE Factors

The results of the factorial analysis including the effects of CBA and processing conditions on fiber orientation and electrical conductivity are shown in
Table 4.5. Since a half fraction factorial design was used in this study, both main effects and two-way interactions can be studied. Considering the responses elicited by the factors on the through-plane (T) properties as our main interest, it was seen that among the main effects that CBA had the largest influence on through-plane fiber orientation (fT) while melt temperature was the dominant factor on through-plane conductivity. On the other hand, an increase in CBA decreased the through-plane conductivity, which can be attributed as a volume exclusion effect. Therefore, improvement of the through-plane fiber orientation by foaming was not necessarily accompanied by an improvement in through-plane conductivity. Morphological properties such as cell size and shape were also important to improving the through-plane conductivity by foaming, as previously stated. Melt temperature was another important main factor in fiber orientation. An increase in melt temperature resulted in an increase in fT. Conversely, increasing injection flow rate or mold wall temperature reduced fT.

<table>
<thead>
<tr>
<th>Effect</th>
<th>fT</th>
<th>fW</th>
<th>fL</th>
<th>σT</th>
<th>σW</th>
<th>σL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBA (IM2240), A</td>
<td>0.062</td>
<td>-0.103</td>
<td>0.043</td>
<td>-0.25</td>
<td>0.6</td>
<td>0.65</td>
</tr>
<tr>
<td>Injection flow rate, B</td>
<td>-0.034</td>
<td>0.023</td>
<td>0.013</td>
<td>-0.43</td>
<td>0.52</td>
<td>0.58</td>
</tr>
<tr>
<td>Melt temperature, C</td>
<td>0.028</td>
<td>-0.008</td>
<td>-0.023</td>
<td>1.17</td>
<td>0.59</td>
<td>0.81</td>
</tr>
<tr>
<td>Mold temperature, D</td>
<td>-0.034</td>
<td>-0.003</td>
<td>0.038</td>
<td>0.25</td>
<td>0.46</td>
<td>0.43</td>
</tr>
<tr>
<td>AB+CD</td>
<td>-0.015</td>
<td>-0.058</td>
<td>0.073</td>
<td>-1.39</td>
<td>-1.76</td>
<td>-1.36</td>
</tr>
<tr>
<td>AC+BD</td>
<td>0.023</td>
<td>-0.028</td>
<td>0.008</td>
<td>0.52</td>
<td>0.34</td>
<td>0.15</td>
</tr>
<tr>
<td>AD+BC</td>
<td>-0.026</td>
<td>-0.003</td>
<td>0.028</td>
<td>-0.12</td>
<td>0.11</td>
<td>0.29</td>
</tr>
</tbody>
</table>
For L and W directions, analysis of the main effects showed that an increase in CBA content and processing conditions corresponded to an increase in $\sigma_L$ and $\sigma_W$ and that melt temperature was the dominant factor in changing conductivity along these directions.

Generally seen in the table, the magnitude of influence for two-way interactions were not dramatically lower than main effects, meaning that they played an important role on fiber orientation and conductivity. The interaction between injection speed and CBA content confounded with melt and mold temperature interaction had the largest (negative) effect on the electrical conductivity for all directions, meaning that the high injection flow rate in the presence of CBA (foaming) diminished the electrical conductivity the most, which is in agreement with our observations made in the previous sections.

4.3.5. Examining the blowing agent

It was considered early in this work that the blowing agent residuals could contribute to the conduction of electrons through the material. To evaluate this concern, the same compounds used for injection molding, both with and without IM2240, were prepared in a batch mixer and allowed to fully de-gas before compression molding into test plaques. Geometrical averaged conductivities of $0.14 \pm 0.02$ S/cm and $0.22 \pm 0.04$ S/cm were obtained for the compound without and with IM2240, respectively. Based on these values, it was concluded that the organic residuals of the blowing agent had no significant impact on the observed conductivities in this work.

In the trials discussed so far, the degree of foaming has not been properly examined. Using the findings from the DOE trials to identify a suitable processing condition, the effects of the blowing agent were further investigated. One non-foam (A) and two foam composites with different levels of foaming (B
Table 4.6. Injection molding conditions for injection moulded composites (10 vol% CF and 2 vol%CB) with CBA powder

<table>
<thead>
<tr>
<th>Run</th>
<th>Injection flow rate (cc/s)</th>
<th>Melt temperature (°C)</th>
<th>Mold temperature (°C)</th>
<th>CBA powder wt%</th>
<th>Shot size (%)</th>
<th>Injection pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>100</td>
<td>370</td>
<td>0</td>
<td>100</td>
<td>370</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>300</td>
<td>80</td>
<td>2</td>
<td>86</td>
<td>285</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>78</td>
<td>280</td>
<td>2</td>
<td>78</td>
<td>280</td>
</tr>
</tbody>
</table>

and C) were produced as stated in Table 4.6. For these samples, a PHT powder (containing 99% active ingredient) at 2 wt% had been used instead of the masterbatch to act as the blowing agent. The content of powder CBA used had the equivalent concentration of active ingredient to 10 wt% IM2240 masterbatch. The pure PHT allowed the addition of higher CBA content with much less volumetric effect on the composite compared to the IM2240 concentrate, since no carrier resin and much less inorganic residue were being incorporated; lower volumetric disturbance was important to maximize the volumetric content of the carbon fillers in the matrix. As seen in Table 4.7, through-plane and LWT averaged electrical conductivity of the foam composites (B and C) were higher than the non-foam composite. With a higher degree of foaming (i.e. comparing the densities of B and C composites) it was found that electrical conductivity improved in the T and W directions but became lower in the L direction. Conductivity in the T direction improved by more than one order of magnitude from sample A to sample C similar to improvement observed in the factorial design experiments where Run(6) had through-plane conductivity by more than one order of magnitude higher than the average through-plane conductivity of the non-foamed composites. The value of \( \sigma_L / \sigma_T \) was now significantly decreased (by about two orders of magnitude for foam composite (C)) compared to non-foam.
Table 4.7. Electrical conductivity of the composites (10 vol% CF and 2 vol% CB) with CBA powder. Reported conductivity values have been multiplied by $10^5$.

<table>
<thead>
<tr>
<th>Run</th>
<th>Density (g/cc)</th>
<th>$\sigma_T$ (S/cm) x $10^5$</th>
<th>$\sigma_W$</th>
<th>$\sigma_L$</th>
<th>$\sigma_{average}$</th>
<th>$\sigma_L / \sigma_W$</th>
<th>$\sigma_L / \sigma_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.12</td>
<td>1.60</td>
<td>2370</td>
<td>2230</td>
<td>203</td>
<td>0.94</td>
<td>1393</td>
</tr>
<tr>
<td>B</td>
<td>1.01</td>
<td>26.0</td>
<td>2270</td>
<td>3820</td>
<td>609</td>
<td>1.68</td>
<td>147</td>
</tr>
<tr>
<td>C</td>
<td>0.91</td>
<td>86.1</td>
<td>2660</td>
<td>1270</td>
<td>662</td>
<td>0.48</td>
<td>15</td>
</tr>
</tbody>
</table>

The average standard deviations for the reported conductivity data shown were 24%, 10% and 10% for L, W and T directions, respectively.

Composite (A) without diminishing the average electrical conductivity. The orientation factor of fibers for these foam composites are presented in Table 4.8. As seen, there was an improvement of through-plane conductivity by foaming denoted by the increase of $f_T$. From optical microscopy it was found that composite (C) had a thicker core than composite (B), namely 1.9 mm and 1.4 mm respectively. It would appear that the negative effect of reducing the volume fraction of the conductive material within the moulded part by foaming was minor in comparison to the gain in electron pathways obtained through fiber re-orientation, in regards to the property of through-plane electrical conductivity. Micrographs in Figure 4.9 demonstrate that many more fibers were oriented in the T direction for the foamed composites compared with the non-foam composite. Despite introducing non-conductive bubbles to the composite, the average conductivity of the foamed composites was higher than the non-foamed composite. This could be due to the fact that bubble growth causes the conductive fillers to become more concentrated in the remaining polymer. Finally, it is worth mentioning that the magnitude of conductivity values for sample C are close to those of Run 6 from the factorial experiments (Table 4.1) which had been produced under similar processing conditions. This suggests repeatability of the results.
Table 4.8. Orientation factors for composites with CBA powder

<table>
<thead>
<tr>
<th>Run</th>
<th>Core</th>
<th></th>
<th></th>
<th>Skin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f_T</td>
<td>f_W</td>
<td>f_L</td>
<td></td>
<td>f_T</td>
<td>f_L</td>
</tr>
<tr>
<td>Non-foamed</td>
<td>A</td>
<td>0.06</td>
<td>0.51</td>
<td>0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foamed</td>
<td>B</td>
<td>0.127</td>
<td>0.4</td>
<td>0.47</td>
<td>0.081</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.127</td>
<td>0.34</td>
<td>0.54</td>
<td>0.083</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Figure 4.9. Micrographs from reflected light microscopy showing the fiber and foam distribution within injection molded composites in the core (a) non-foamed composite A (b) foamed composite B with 10% reduced density (c) foamed composite C with 20% reduced density.
4.4. Discussion

Improvement of fiber orientation in the through-plane direction is of great importance to improving through-plane electrical conductivity. As observed in our results here and also as reported by others [7,8], through-plane conductivity of injection moulded composites is 2-3 orders of magnitude lower than in-plane conductivity. This major drawback hinders use of conductive polymer composites in applications where conductivity is required to be greater in the through-plane direction. Based on the optimal conditions from the DOE trials, we surmise that the mechanism for fiber re-orientation required bubble growth in the presence of shear. A low injection flow rate condition likely resulted in foam flow during mold filling (i.e. bubbles were nucleated and grew as the material filled the cavity) [12]. It is thought that the driver for fiber reorientation was the shear forces acting upon a fiber once being pushed out-of-plane by adjacent bubble growth. Future studies are needed to show bubble growth in relation to the flow field. The benefit of higher melt temperature, as indicated by the DOE analysis, was the reduction in the melt viscosity which lowered the resistance on the fiber to rotate in the flow field. The carbon fiber concentration in this study was held in the vicinity of the percolation threshold (i.e. 10 vol% for an average length of ~100 μm); however, had the carbon fiber concentrations been substantially higher then fiber reorientation by bubble growth may not have significantly occurred. Higher fiber content would lead to greater viscosity of the melt and increased fiber-fiber interactions, both foreseeably acting as obstacles to fiber rotation. Using fiber-particulate hybrid systems has the advantage of avoiding the necessity for a fully percolated network of fibers.

The electrical conductivity property of a foamed sample was found to be dependent not only on fiber orientation, but also on porosity, cell size, and cell shape. Smaller, more uniformly shaped bubbles corresponded with higher conductivity. The potential negative influence resulting from the volume
exclusion effect of the gas phase was never observed in this work, rather there appeared to be a benefit to concentrating the carbon filler in the polymer pathways between bubbles which led to higher conductivities. The presence of larger and more elongated bubbles along the L direction may have created a tortuous path for the electron transport in the through-plane direction.

Besides improving through-plane conductivity, foaming offer many advantages and disadvantages which must be considered by the user [11,24]. For filled composites like our material, the plasticizing effect of dissolved gases generated by blowing agents will certainly be viewed as a positive during processing, though the reduction of mechanical properties will need to be considered in material selection [12].

4.5. Conclusions

The main goal of this research was to investigate whether foaming could sufficiently disrupt the preferential flow induced alignment of fibers during mold filling and increase the frequency of their orientation in a more favourable direction to improve through-plane conductivity. It was found that foaming at low injection speed and high melt temperature could enhance the through-plane fiber orientation factor by more than two folds, and consequently through-plane electrical conductivity by more than one order of magnitude. The concurrence of the melt flow and bubble growth is considered to be the key mechanism for fiber reorientation while the cell size and shape play an important role so as to not disrupt the conductive paths spanning the bulk of the composite.
References

Chapter 5

Electrical Conductivity of Carbon Black and Carbon Fiber Foam Polymer Composites

The following chapter has been formatted consistent with the previous two chapters but has not been submitted to a peer-reviewed journal. G. H. Motlagh is the major contributor to this chapter. He has also supervised Keith Oxby who carried out some of the analysis.

Abstract

This chapter describes investigations into the effects of foaming on electrical conductivity for a carbon-filled cyclic olefin copolymer (COC) composite incorporating both carbon fibers (CF) and carbon black (CB). The foaming was conducted in both batch and continuous processes using a high pressure batch vessel and an injection molding machine, respectively. Samples were analyzed for cell size, fiber length, fiber orientation and electrical conductivity. In injection molding, foaming was observed to enhance electrical conductivity in the through-plane direction for materials containing only CB or composites containing both filler types but reduced this property for the CF composites. Increasing cell size and fiber length reduced the detrimental effect of foaming on electrical conductivity of CF composites. The gas exclusion effect was more pronounced for the through plane conductivity than the in-plane conductivity. The batch studies proved that significant fiber reorientation and particle relocation do not take place due to cell growth because of the extremely high viscosity of the matrix and absence of flow hydrodynamic forces. Batch
foaming exhibited significantly reduced electrical conductivity as compared to the foam injection molding indicating that particle localization likely happened during molding.

5.1. INTRODUCTION

Polymers are traditionally insulating materials, but electrically conductive polymers have served as an interesting and relatively new category which can ultimately replace metals in some electrical conductive applications. The addition of conductive fillers such as metal powders, carbon black, carbon fiber, graphite and carbon nanotubes to an insulating matrix can provide suitable pathways for electrons, resulting in conductivity values in the order of $10^{-5}$ to $100$ S/cm [Blythe and Bloor, 2005; Huang, 2002; Weber and Kamal, 1997]. However, the concentration of the conductive filler(s) must exceed the percolation threshold—either individually or in combination—, a level where the dispersed additive(s) are in suitable proximity to one another, to allow electrons to traverse from one side of a molded part to the other. Generally, with the generation of a percolating network of filler in the polymer matrix, there is an accompanying increase in melt viscosity and decrease in the mechanical properties of a manufactured part. In comparison to powders, conductive fibers in a polymer matrix exhibit a lower percolation threshold, lower melt viscosity and higher mechanical strength. Electrical conductivity is dependent upon the orientation of the fibers when fibers are the only conductive additive included in the polymer composite.

Injection molding is the preferred method to mass produce parts, especially with complicated shapes, at lower cost. In high shear flow such as that found in injection molding, fibers tend to align in the flow direction (in-plane). Particularly for thin products, fibers do not significantly orient in the thickness direction (through-plane), perpendicular to the flow, leading to demonstrated
conductivity several orders of magnitude lower than in the in-plane direction [Weber and Kamal, 1997; Dani and Ogale, 1996]. This is a drawback which prevents using injection molding for shaping fiber composites as conductive materials for applications where through-plane conductivity is needed. Foaming has recently been demonstrated as a possible technique to enhance through-plane electrical conductivity of injection molded carbon fiber and carbon black hybrid composites provided suitable processing conditions can be determined [Motlagh et al., 2008]. However, further detailed evaluation is required to understand how bubble growth in the flow field affects the dispersed nature of carbon black and carbon fiber in the matrix and the effects on conductivity in- and out-of-plane. There are few publications reporting on the electrical conductivity of foam polymer composites [Yang et al., 2005] and none make reference to the relationship between particle size and cell size in regards to electrical properties. The present work will examine the influence of foaming on the electrical conductivity of injection molded materials, with particular attention given to the relationship between length scales for fillers and foam cells. Both batch and continuous foam experiments will be reported upon to provide an appropriate level of understanding of the morphological interactions.

5.2. EXPERIMENTAL

5.2.1. Materials

Cyclic olefin copolymer (COC), an amorphous copolymer of ethylene and norbornene, (Topas 6013S-04 supplied by Ticona, MFR 14 g/10min @ 260°C, 2.16 kg) was used as the matrix polymer. The amorphous matrix was intentionally selected to eliminate any effects of crystallization on the developed composite microstructure and resulting properties. PAN-derived chopped carbon fiber (cCF) supplied by Asbury Carbons and milled carbon fiber (mCF) from Toho Tenax America were used along with a high surface area carbon black (CB) from Akzo
Nobel (Ketjenblack EC600JD) as conductive fillers. The properties of these fillers are given in Table 5.1. A masterbatch exothermic chemical blowing agent (CBA), IM 2240 supplied by Dempsey Corporation, was used for the foaming agent in the foam injection molded composites. The CBA masterbatch contained 20 wt% 5-Phenyl tetrazol which was the active component involved in the evolution of nitrogen gas for foaming. The carrier resin of the masterbatch was polycarbonate. The CBA was selected for its high decomposition temperature which suits the conditions necessary for processing the COC polymer in an injection molding machine. The onset of decomposition for CBA was determined by TGA analysis to be 225 °C with the majority of gas evolved at 240°C. The acronyms used for material compositions are given in Table 5.2.

**Table 5.1. Properties of the conductive fillers**

<table>
<thead>
<tr>
<th>Properties</th>
<th>CB²</th>
<th>cCF²</th>
<th>mCF²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>10-100</td>
<td>625</td>
<td>598</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.8</td>
<td>1.78</td>
<td>1.8</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>100-120</td>
<td>360</td>
<td>350</td>
</tr>
<tr>
<td>Aggregate size (nm)</td>
<td>30-100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pore volume (DBP, ml/100 g)</td>
<td>480-510</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>1250</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Fiber diameter (µm)</td>
<td>-</td>
<td>7.5</td>
<td>7</td>
</tr>
<tr>
<td>Fiber length (µm)</td>
<td>-</td>
<td>5000</td>
<td>175</td>
</tr>
</tbody>
</table>

¹ Data given by suppliers

² CB=carbon black, cCF=chopped carbon fiber and mCF=milled carbon fiber
Table 5.2. Acronyms used in this study for material compositions

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>COC</td>
<td>Cyclic olefin copolymer</td>
</tr>
<tr>
<td>mCF</td>
<td>milled carbon fiber</td>
</tr>
<tr>
<td>cCF</td>
<td>chopped carbon fiber</td>
</tr>
<tr>
<td>CB</td>
<td>carbon black</td>
</tr>
<tr>
<td>CF(x) CB(y)</td>
<td>Composite containing (x) vol% carbon fiber and (y) vol% carbon black</td>
</tr>
</tbody>
</table>

5.2.2. Procedure

COC/mCF(15 vol%), COC/mCF(25 vol%) and COC/CB(8 vol%) were prepared in a Leistritz ZSE 27-40 co-rotating twin screw extruder (TSE) at a nominal temperature of 260 °C and 100 RPM. COC pellets were fed to the first block of the TSE by a weight-loss feeder, while mCF or CB was introduced into the melt by a side feeder half way down the length of the machine. The screw design was configured to maximize distributive mixing by the use of comb elements and minimize shear through the limited use of 30° and 60° kneading blockings after the melting zone. COC/cCF(40 vol%) was prepared by force feeding of COC and cCF blend to the main port of a 2-inch Davis Standard single screw extruder with a zero compression screw at low speed. The extrudate was crushed in a grinder and was thoroughly mixed to obtain a homogenous compound. This method was utilized to obtain a precursor masterbatch of cCF and COC with the maximum possible fiber length. Our previous experience had shown that preparing cCF precursor in a batch mixer was accompanied with severe fiber breakage [Motlagh et al., 2007]. On the other hand, the configuration of our side feeder for the TSE did not allow for the addition of the cCF directly. Except for the COC/(mCF 15 vol%) compound studied in this paper which was
directly prepared, all other compounds discussed were made by letting down the precursor concentration(s).

An Arburg 55 ton injection-molding machine with a 30 mm 20 L/D plasticating unit and one of three rectangular center-gated molds (molds A, B and C given in Table 5.3) were used to shape the composites. The molds were different in cavity thickness or width but had approximately the same length. We were interested to see how these changes in mold dimensions would influence the foam morphology and consequent electrical conductivity. The temperature profile of the plasticating unit and nozzle were set at 30°C, 210°C, 210°C, 250°C, 290°C and 300°C respectively from the hopper to the nozzle. The temperatures of the first three zones were below 220°C to prevent premature decomposition of CBA and gas loss, while the temperatures of the last two zones on the plasticating unit and nozzle were set above 240°C to obtain full decomposition.

The injection nozzle was also equipped with a shut-off nozzle to prevent gas loss. Injection speed was set to 5 cc/s for mold A (otherwise specified) and 10 cc/s for mold B and C to approximately have the same amount of shear rate during injection. These processing conditions were already shown to be optimal for obtaining high electrical conductivity [Motlagh et al. 2008]. The feed material was prepared by the dry blending of suitable amounts of COC pellets and the required precursors, and for foamed samples 5 wt% of the chemical blowing agent. The formulations are summarized in Table 5.4. The main factors of study for the experiments were:

- carbon fiber length (mCF or cCF)
- composition (CB, CF and CF-CB)
- degree of foaming (void content)
- process related factors: mold type, back pressure, hold pressure
Table 5.3. Dimensions of centre-gated molds used to produce injection molded composites

<table>
<thead>
<tr>
<th>Mold</th>
<th>Description</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>thin bar</td>
<td>130</td>
<td>12.5</td>
<td>3.1</td>
</tr>
<tr>
<td>B</td>
<td>thick bar</td>
<td>130</td>
<td>12.5</td>
<td>6.2</td>
</tr>
<tr>
<td>C</td>
<td>plaque</td>
<td>145</td>
<td>30</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 5.1. Sampling pattern for electrical conductivity measurements of the injection molded bar produced by mold A
**Table 5.4. Specification of injection molded composites**

<table>
<thead>
<tr>
<th>Code</th>
<th>Filler</th>
<th>Shot Size</th>
<th>Holding Pressure</th>
<th>Void content</th>
<th>Density (g/cc)</th>
<th>STDEV</th>
<th>Injection pressure</th>
<th>Measured Mpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>COC</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.017</td>
<td>0.002</td>
<td></td>
<td>782</td>
</tr>
<tr>
<td>A1</td>
<td>mCF15</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.128</td>
<td>0.004</td>
<td></td>
<td>1125</td>
</tr>
<tr>
<td>A2</td>
<td>mCF15</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.888</td>
<td>0.008</td>
<td></td>
<td>898</td>
</tr>
<tr>
<td>A3</td>
<td>mCF15</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.83</td>
<td>0.008</td>
<td></td>
<td>864</td>
</tr>
<tr>
<td>A4</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.072</td>
<td>0.004</td>
<td></td>
<td>1086</td>
</tr>
<tr>
<td>A4R1</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.096</td>
<td>0.005</td>
<td></td>
<td>1036</td>
</tr>
<tr>
<td>A4R2</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.086</td>
<td>0.003</td>
<td></td>
<td>1042</td>
</tr>
<tr>
<td>A5</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.923</td>
<td>0.012</td>
<td></td>
<td>987</td>
</tr>
<tr>
<td>A5R1</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.917</td>
<td>0.007</td>
<td></td>
<td>990</td>
</tr>
<tr>
<td>A5R2</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.925</td>
<td>0.008</td>
<td></td>
<td>1008</td>
</tr>
<tr>
<td>A6</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.828</td>
<td>0.015</td>
<td></td>
<td>894</td>
</tr>
<tr>
<td>A7</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.839</td>
<td>0.005</td>
<td></td>
<td>922</td>
</tr>
<tr>
<td>A10</td>
<td>CB3.4</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.045</td>
<td>0.005</td>
<td></td>
<td>1172</td>
</tr>
<tr>
<td>A11</td>
<td>CB3.4</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.893</td>
<td>0.003</td>
<td></td>
<td>1086</td>
</tr>
<tr>
<td>A12</td>
<td>CB4.2</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.052</td>
<td>0.001</td>
<td></td>
<td>1390</td>
</tr>
<tr>
<td>A13</td>
<td>CB4.2</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.906</td>
<td>0.006</td>
<td></td>
<td>1147</td>
</tr>
<tr>
<td>A20</td>
<td>cCF10CB0.75</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.084</td>
<td>0.007</td>
<td></td>
<td>1278</td>
</tr>
<tr>
<td>A21</td>
<td>cCF10CB0.75</td>
<td>85</td>
<td>1000</td>
<td>16</td>
<td>0.914</td>
<td>0.006</td>
<td></td>
<td>1146</td>
</tr>
<tr>
<td>A22</td>
<td>cCF10CB2.5</td>
<td>100</td>
<td>1000</td>
<td>17</td>
<td>0.915</td>
<td>0.005</td>
<td></td>
<td>1218</td>
</tr>
<tr>
<td>A23</td>
<td>cCF10CB2.5</td>
<td>85</td>
<td>1000</td>
<td>17</td>
<td>0.915</td>
<td>0.005</td>
<td></td>
<td>1218</td>
</tr>
<tr>
<td>B10</td>
<td>CB3.4</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.967</td>
<td>0.004</td>
<td></td>
<td>760</td>
</tr>
<tr>
<td>B11</td>
<td>CB3.4</td>
<td>85</td>
<td>1000</td>
<td>0</td>
<td>0.847</td>
<td>0.001</td>
<td></td>
<td>865</td>
</tr>
<tr>
<td>C1</td>
<td>mCF15</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.12</td>
<td>0.005</td>
<td></td>
<td>738</td>
</tr>
<tr>
<td>C2</td>
<td>mCF15</td>
<td>85</td>
<td>1000</td>
<td>0</td>
<td>1.00</td>
<td>0.005</td>
<td></td>
<td>685</td>
</tr>
<tr>
<td>C3</td>
<td>mCF15</td>
<td>75</td>
<td>1000</td>
<td>0</td>
<td>0.896</td>
<td>0.012</td>
<td></td>
<td>659</td>
</tr>
<tr>
<td>C4</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>1.086</td>
<td>0.005</td>
<td></td>
<td>727</td>
</tr>
<tr>
<td>C5</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.994</td>
<td>0.007</td>
<td></td>
<td>672</td>
</tr>
<tr>
<td>C6</td>
<td>cCF10</td>
<td>100</td>
<td>1000</td>
<td>0</td>
<td>0.854</td>
<td>0.007</td>
<td></td>
<td>709</td>
</tr>
<tr>
<td>P10</td>
<td>cCF10</td>
<td>85</td>
<td>1000</td>
<td>0.24</td>
<td>0.828</td>
<td>0.015</td>
<td></td>
<td>582</td>
</tr>
<tr>
<td>P20</td>
<td>cCF10</td>
<td>85</td>
<td>1000</td>
<td>0.24</td>
<td>0.857</td>
<td>0.021</td>
<td></td>
<td>617</td>
</tr>
<tr>
<td>P20R</td>
<td>cCF10</td>
<td>85</td>
<td>1000</td>
<td>0.21</td>
<td>0.863</td>
<td>0.005</td>
<td></td>
<td>615</td>
</tr>
<tr>
<td>P50</td>
<td>cCF10</td>
<td>85</td>
<td>1000</td>
<td>0.09</td>
<td>0.987</td>
<td>0.013</td>
<td></td>
<td>598</td>
</tr>
<tr>
<td>P50R</td>
<td>cCF10</td>
<td>85</td>
<td>1000</td>
<td>0.08</td>
<td>1.004</td>
<td>0.007</td>
<td></td>
<td>640</td>
</tr>
<tr>
<td>P100</td>
<td>cCF10</td>
<td>85</td>
<td>1000</td>
<td>0.09</td>
<td>0.988</td>
<td>0.03</td>
<td></td>
<td>634</td>
</tr>
</tbody>
</table>

1 Back pressure 10 MPa for all samples except A7 with 20 MPa. A, B and C in sample codes denote the mold type used according to Table 5.3. Injection speed: 5cc/s for mold A and 10 cc/s for molds B and C.
The concentrations of mCF and cCF was selected so that the obtained composites were above the percolation threshold but still had sufficiently low viscosity to be processed in the injection molding machine. Likewise a minimum of 3.4 vol% CB was chosen for injection molded COC/CB composites to ensure that the final molded composites will be conductive. For hybrid composites 0.75 vol% and 2.5 vol% CB was used to evaluate the role of carbon black below and around percolation where there is a good trade off between viscosity and conductivity [Motlagh et al., 2007]. As a relative comparison, the viscosity as a function of shear rate at 260°C for some of the injection molded nonfoam composites is given in Figure 5.2. Virgin and injection molded COC have been also reported in the graph as the base for comparison.

Figure 5.2. The shear viscosity versus shear rate at 260 °C for the injection molded composites
5.2.3. Analysis

The test specimens from each composite produced in mold A were prepared in accordance with the displayed sample cuts shown in Figure 5.1. The 40mm \( \times \) 10.5mm rectangular samples were used to measure electrical conductivity along the long (L) and the thickness (T) axes. The 12.5mm \( \times \) 3.5mm were cut for determination of electrical conductivity in the width (W) direction. For molds B and C samples were also cut at the same distances from the gate as for mold A.

Measurements in the L and W directions (in-plane: \( \sigma_L \) and \( \sigma_W \)) were carried out by the four probe method while the 2-probe method was used to measure electrical conductivity in the T direction (\( \sigma_T \), through-plane). In the 2-probe method, carbon paper (Technimat 070 supplied by Lydall) was placed between the electrode and the sample, and the sandwich arrangement was compressed at 10MPa applied pressure to minimize the contact resistance. \( \sigma_L \) and \( \sigma_T \) were also measured after removing the 0.6 mm polymer skin layer from each side of the sample in the LW plane. A minimum of 5 samples were used for each reported value.

The density of each produced sample was determined by the buoyancy method. The measurements of the fiber length distribution (FLD), carbon fiber orientation and foam structure were done by optical microscopy using digital image analysis software, in the same manner as reported in previous papers [Motlagh et al., 2007& 2008]. The same samples cut for electrical conductivity analysis were used to characterize these properties. A twin-bore capillary rheometer (Rosand) was used to compare the shear viscosity data at 260 °C for injection molded nonfoam composites. Three runs were performed for each
composite and the average was reported after Bagley [1960] and Rabinowitsch [Dealy and Wissbrun, 1999] corrections were made.

5.3. RESULTS

The variability in measured material attributes was generally small for bulk properties, though quite large for electrical conductivity which tended to be much more sensitive to the heterogeneity of filler dispersion. For material density and foam cell size, the maximum standard deviation was 1.1% and 8%, respectively. Material density was used to confirm the filler concentration in the molded non-foamed parts and determine the porosity of the foamed parts. The maximum standard deviations among fiber orientation factors (fL, fW and fT) was 24%. For electrical conductivity, the maximum standard deviation was 74%.

Mainly due to fiber breakage during processing, a broad fiber length distribution was observed in the composites. The average fiber length obtained for injection molded parts containing cCF was approximately 50% larger than those containing mCF. The intention was to study the effects of fiber length on fiber reorientation by foaming and the consequent electrical conductivity (further details in Appendix A).

5.3.1. Foam Cellular Structure

Figure 5.3 shows the distribution and shape of the cells for the foam injection molded composite A5 (COC/cCF10, void content 15 vol%). A shear zone is observed close to the mold wall where cells are larger and elongated in the flow direction whereas cells are finer and near circular in the core. This was the typical morphology observed for all the foam injection molded composites. Table 5.5 shows the cell size of the foam composites obtained from the core. The
average cell size values measured from three planes (LT, WT and LW) are relatively close which suggest that bubble shape is nearly isotropic. Obviously cell density and average cell size are primarily a function of void content rather than composition and mold type. As the void content increases, cell size increases and cell density decreases remarkably. If the number of cells remains unchanged from lower void content \((P_1)\) to higher void content \((P_h)\), the cell diameter must increase by a factor of void content ratio i.e. \((P_h/P_1)^{1/3}\). However by comparing the cell size of A2 / A3 and A5 / A6 pairs for the WT plane in Table 5.5 it can be observed that the average cell diameter has increased significantly more than the void content ratio. This suggests that by increasing void content the number of cells has decreased due to faster cell growth compared to nucleation rate.

The first three rows (samples AF, ACF and ACB) in Table 5.5 show that the addition of a small amount of CB or mCF to COC slightly decreased the average cell size and increased the cell density. By analyzing these samples using light microscopy we observed that the number of large bubbles (>300 microns) significantly decreased when CB or mCF was added. In other words, the uniformity of the cell diameter improved. The reduction in \(D_w/D_n\) ratio from 1.6 for AF composite to around 1.4 for ACF and ACB composites supports the improvement in cell size uniformity. The cell density for CB composites (A11 and A13) is not much different than that for CF composites (A3 and A6). Moreover hybrid composites does not show a significant change in cell density compared to CF composites (consider A5, A21 and A23).

The average cell size typically ranges from 30 to 70 microns which is smaller than typical average fiber lengths of 120 microns for mCF and 180 microns for cCF composites (Figure 5.4) but much larger than typical CB aggregate size (200 nm).
Figure 5.3. SEM image showing cell morphology for composite A5 (COC/cCF10, void content 15 vol%) in the LT plane. L horizontal direction and T vertical direction
Figure 5.4. Optical image showing cell size and fiber length distribution for composite A5 (COC/cCF10, void content 15 vol%) at the core in the LW plane. L horizontal direction and W vertical direction.
Table 5.5. Cell size of the foam injection molded composites

<table>
<thead>
<tr>
<th>Code</th>
<th>Filler</th>
<th>Foam Code</th>
<th>LT plane</th>
<th>WT plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(D_n)</td>
<td>(D_w)</td>
</tr>
<tr>
<td></td>
<td>vol%</td>
<td>vol%</td>
<td>((\mu m))</td>
<td>(\times 10^6) cell/cm(^3)</td>
</tr>
<tr>
<td>AF</td>
<td>------</td>
<td>11</td>
<td>45</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(33)*</td>
<td>(56)</td>
</tr>
<tr>
<td>ACF</td>
<td>mCF0.27</td>
<td>11</td>
<td>37</td>
<td>51</td>
</tr>
<tr>
<td>ACB</td>
<td>CB0.17</td>
<td>12</td>
<td>40</td>
<td>56</td>
</tr>
<tr>
<td>A2</td>
<td>mCF15</td>
<td>21</td>
<td>48</td>
<td>82</td>
</tr>
<tr>
<td>A3</td>
<td>mCF15</td>
<td>26</td>
<td>64</td>
<td>133</td>
</tr>
<tr>
<td>A5</td>
<td>cCF10</td>
<td>15</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(35)</td>
<td>(43)</td>
</tr>
<tr>
<td>A6</td>
<td>cCF10</td>
<td>24</td>
<td>67</td>
<td>82</td>
</tr>
<tr>
<td>A7</td>
<td>cCF10</td>
<td>23</td>
<td>31</td>
<td>41</td>
</tr>
<tr>
<td>P100</td>
<td>cCF10</td>
<td>20</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(33)</td>
<td>(44)</td>
</tr>
<tr>
<td>A11</td>
<td>CB3.4</td>
<td>21</td>
<td>57</td>
<td>64</td>
</tr>
<tr>
<td>A13</td>
<td>CB4.2</td>
<td>22</td>
<td>63</td>
<td>69</td>
</tr>
<tr>
<td>B11</td>
<td>CB3.4</td>
<td>27</td>
<td>76</td>
<td>117</td>
</tr>
<tr>
<td>A21</td>
<td>cCF10-CB0.75</td>
<td>14</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td>A23</td>
<td>cCF10-CB2.5</td>
<td>16</td>
<td>28</td>
<td>35</td>
</tr>
<tr>
<td>C3</td>
<td>mCF15</td>
<td>21</td>
<td>37</td>
<td>60</td>
</tr>
<tr>
<td>C6</td>
<td>cCF10</td>
<td>20</td>
<td>37</td>
<td>63</td>
</tr>
</tbody>
</table>

*Numbers in the () are measured from LW plane.
5.3.2. Fiber Orientation

Fiber orientation factors measured from the injection molded composites are shown in Table 5.6. For either foam or nonfoam composites, $f_T$ was smaller at the skin than the core while $f_L$ was larger at the skin than the core. This is the typical orientation state observed for injection molded parts. In the core, nonfoam composites had larger $f_w$ than the foam composites, which is in agreement with previous results in chapter 4. Based on previous work, it was expected that $f_T$ at the core increases due to foaming. As seen in Table 5.6, composites C1-C6 produced by mold C (same mold used in the previous work), $f_T$ increased from ~0.1 for the nonfoam composites to ~0.15 for the foam composites. However, the results do not show enhancement in $f_T$ by foaming for most composites produced by Mold A and B. Only sample A3 (COC/mCF15 foamed 25%) and A23 (COC/cCF10-CB2.5 foamed) indicated a significant improvement in $f_T$. To better show this improvement, the cumulative distribution of $f_T$ is shown in Figure 5.5 for composites A1 (solid), A2 (lower void content) and A3 (higher void content). The distribution for A2 is not remarkably different from A1, but for A3 c. 30% of the fibers have $f_T$ larger than 0.3 compared to 10% for A1 and A2. Micrographs in Figure 5.6 show that foaming induces fibers to be more oriented toward the thickness (T) direction. The micrograph for A2 (Figure 5.6, the middle image) shows a specific area where only fibers close to a large bubble have turned into the T direction. Therefore, it can be concluded that fiber reorientation is likely to happen when nucleated cells grow to bubbles quite larger in diameter than fiber length. The micrograph for A3 shows the typical improved through-plane fiber orientation state for this composite. Higher degree of foaming and consequently larger cell size of 64 microns for A3 compared to 48 microns for A2 may have been a major factor in providing improved $f_T$ for A3.
Table 5.6. Fiber orientation factors of the injection molded composites

<table>
<thead>
<tr>
<th>Code</th>
<th>Foam vol%</th>
<th>Comment</th>
<th>Location</th>
<th>LT plane</th>
<th>LW plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( f_T )</td>
<td>( f_L )</td>
</tr>
<tr>
<td>A1 0</td>
<td></td>
<td></td>
<td>core</td>
<td>0.12</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>mCF15</td>
<td></td>
<td>skin</td>
<td>0.07</td>
<td>0.55</td>
</tr>
<tr>
<td>A2 21</td>
<td></td>
<td></td>
<td>core</td>
<td>0.13</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.08</td>
<td>0.53</td>
</tr>
<tr>
<td>A3 26</td>
<td></td>
<td></td>
<td>core</td>
<td>0.22</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.04</td>
<td>0.50</td>
</tr>
<tr>
<td>A4 0</td>
<td></td>
<td>cCF10</td>
<td>core</td>
<td>0.12</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>back P 10 MPa</td>
<td>skin</td>
<td>0.05</td>
<td>0.60</td>
</tr>
<tr>
<td>A5 15</td>
<td></td>
<td></td>
<td>core</td>
<td>0.10</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>back P 10 MPa</td>
<td>skin</td>
<td>0.03</td>
<td>0.60</td>
</tr>
<tr>
<td>A6 24</td>
<td></td>
<td></td>
<td>core</td>
<td>0.08</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.03</td>
<td>0.62</td>
</tr>
<tr>
<td>A7 23</td>
<td></td>
<td>back P 20 MPa</td>
<td>core</td>
<td>0.12</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>back P 20 MPa</td>
<td>skin</td>
<td>0.04</td>
<td>0.67</td>
</tr>
<tr>
<td>P100 9</td>
<td>Hold P 100 MPa</td>
<td>core</td>
<td>0.10</td>
<td>0.61</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.03</td>
<td>0.67</td>
</tr>
<tr>
<td>C1 0</td>
<td></td>
<td>mCF15</td>
<td>core</td>
<td>0.11</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>core</td>
<td>0.15</td>
<td>0.55</td>
</tr>
<tr>
<td>C2 11</td>
<td></td>
<td>CCF10</td>
<td>core</td>
<td>0.16</td>
<td>0.54</td>
</tr>
<tr>
<td>C3 20</td>
<td></td>
<td></td>
<td>core</td>
<td>0.14</td>
<td>0.56</td>
</tr>
<tr>
<td>C4 0</td>
<td></td>
<td>CCF10</td>
<td>core</td>
<td>0.15</td>
<td>0.62</td>
</tr>
<tr>
<td>C5 9</td>
<td></td>
<td></td>
<td>core</td>
<td>0.14</td>
<td>0.58</td>
</tr>
<tr>
<td>C6 21</td>
<td></td>
<td></td>
<td>core</td>
<td>0.13</td>
<td>0.62</td>
</tr>
<tr>
<td>A20 0</td>
<td></td>
<td>cCF10CB0.75</td>
<td>core</td>
<td>0.08</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.03</td>
<td>0.68</td>
</tr>
<tr>
<td>A21 16</td>
<td></td>
<td>cCF10CB0.75</td>
<td>core</td>
<td>0.05</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.03</td>
<td>0.67</td>
</tr>
<tr>
<td>A22 0</td>
<td></td>
<td>cCF10CB2.5</td>
<td>core</td>
<td>0.11</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.02</td>
<td>0.71</td>
</tr>
<tr>
<td>A23 17</td>
<td></td>
<td>cCF10CB2.5</td>
<td>core</td>
<td>0.20</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>skin</td>
<td>0.04</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Figure 5.5. Cumulative fiber orientation factor ($f_T$) distribution at the core for the solid and foam injection molded COC/mCF(15) (obtained from LT plane).

Figure 5.6. Optical micrographs showing fiber orientation in the core of solid and foam injection molded COC/mCF(15) composites (left: A1, solid; middle: A2, void content 21 vol% and right: A3, void content 26 vol%).
5.3.3. Electrical Conductivity

All the composites in this study showed similar or slightly lower conductivity for the W direction (\(\sigma_W\)) than that for the L direction (\(\sigma_L\)). Also the trend for change in \(\sigma_W\) with foaming was in the same manner as for \(\sigma_L\) with foaming. Therefore in order to keep the graphs less complex only \(\sigma_L\) as representative of in-plane conductivity and \(\sigma_T\) (through-plane) will be reported in this study. In addition \(\sigma_{3D}\), the geometrical average of \(\sigma_L\), \(\sigma_W\) and \(\sigma_T\), is included in the results to show the overall change in conductivity of the materials.

5.3.3.1. Carbon Black Composites

Figure 5.7 illustrates the conductivity results for nonfoam and foam COC/CB composites at two CB concentrations of 3.4 vol% and 4.2 vol%. For the non-foam composites, \(\sigma_L\) is larger than \(\sigma_T\) by one order of magnitude at higher CB content but it is three orders of magnitude larger than \(\sigma_T\) at the lower CB content. Through-plane conductivity of nonfoam COC/CB(3.4 vol%) after removing the LW skin (0.6 mm on each side) was only one order of magnitude lower than \(\sigma_L\) (compare with three orders of magnitude before removing the skin). Carbon black migration from the mold wall effectively reduces the concentration at the skin and consequently the electrical conductivity most considerably in the proximity of the percolation threshold [Hong et al., 2004]. By foaming, the conductivity in all directions increased, though most notably in the through-plane direction and for lower CB concentration. The results indicate improvement in \(\sigma_L\) by a factor of 5 and increase in \(\sigma_T\) by two orders of magnitude for COC/CB(3.4) before the skin removal. After the skin removal (shown as the core results) still enhancement in \(\sigma_L\) by a factor of 5 and increase in \(\sigma_T\) by one order of magnitude are observed. The observed enhancement is likely due to the more segregated network of carbon black aggregates induced by foaming. For the nonfoam CB3.4 composite the ratio of \(\sigma_L/\sigma_T\) was 614 and 8 before and after the skin removal,
respectively. But for the foam composite they decreased to 21 and 3, before and after the skin removal, respectively. The foam CB composites exhibit significantly more isotropic electrical conductivity. Second, the magnitude of increase in through-plane conductivity by skin removal was much larger for the non-foam composite than the foam composite. This behavior showed that for the foam CB composite the skin properties (CB concentration, distribution and orientation) were more similar to the core properties compared to those in the nonfoam CB composite.

**Figure 5.7.** Electrical conductivity of COC/CB(4.2) and COC/CB(3.4) composites. “core” corresponds to the samples with machined LW skin (0.6 mm on each side)
5.3.3.2. Carbon Fiber Composites

Figure 5.8 shows the electrical conductivities for nonfoam and foam injection molded COC/mCF(15vol%) and COC/cCF(10vol%) composites prepared in mold A, both in their original state and after their skin layers were removed. For the original non-foamed COC/mCF(15) and COC/cCF(10) composites, $\sigma_L$ was 2-3 orders of magnitude larger than $\sigma_T$. This was expected due to the mold geometry and the flow field which allowed for mostly random fiber orientation localized to the LW plane and little out-of-plane alignment. For these materials, with the removal of the skin layer, $\sigma_T$ increased by a factor of 5 while $\sigma_L$ remained fairly unchanged. The increase in $\sigma_T$ was associated with the removal of fiber depleted skin [Spahr et al 1990] and highly oriented shear layer where fibers would had the lowest out-of-plane orientation [Bay and Tucker, 1992].

Foaming a fiber-filled composite resulted in a slight decrease in the conductivity for the L direction and up to two orders of magnitude decrease in the T direction (Figure 5.8a). After skin removal, significant drop in $\sigma_L$ by foaming was also observed (Figure 5.8b) revealing that solid skin had been contributing to the $\sigma_L$ before the skin removal, in a parallel resistor array with the foam core. The values of $\sigma_T$ for the foam composites were similar before and after the skin removal. From Figure 5.8 it is generally seen that a higher void content is accompanied with a larger drop in electrical conductivity.

Figure 5.9 shows the electrical conductivities for nonfoam and foam injection molded COC/mCF(15vol%) and COC/cCF(10vol%) composites prepared in mold C. Similar to the results for mold A, foaming has significantly reduced the electrical conductivity of the composites particularly in the through plane direction. Therefore either for mold A or C foaming decreases electrical conductivity of the CF composites. However, in a previous work which used mold
Figure 5.8. Electrical conductivity of nonfoam and foam injection molded COC/mCF(15 vol%) and COC/cCF(10 vol%) composites produced by mold A at 5 cc/s. a: before machining LW skin and b: after machining LW skin (0.6 mm).
C [Motlagh et al., 2008], foaming at similar injection molding conditions improved the through plane conductivity of the composite containing 10 vol% CF and 2 vol% CB.

Table 5.5 depicts average cell size of the composites. The average cell size for mCF(15) foam composites with 21 vol% and 26 vol% void content is 48 and 64 microns, respectively. And that is 28 and 67 microns for cCF(10) composites with 15 vol% and 24 vol% void content, respectively. Decrease in both $\sigma_L$ and $\sigma_T$ with foaming was less significant for cCF composite than mCF composite (Figure 5.8 and 5.9). Since mCF and cCF composites at higher foaming degree have relatively the same cell size, thus the larger fiber length in the latter has been most likely responsible for the less drop in conductivity. The volume excluded bubbles are less distractive to the connectivity of the longer fibers.

In both Figures 5.8 and 5.9, the through plane conductivity of the COC/cCF composite with a higher degree of foaming is slightly higher than that of the composite with lower degree of foaming. This is likely because of lower cell density at higher void content (compare A5 with A6 and C5 with C6 in Table 5.5) leading to reduced number of cells and consequently fewer interruptions to the fiber-fiber contacts.
Figure 5.9. Electrical conductivity of nonfoam and foam injection molded COC/mCF(15 vol%) and COC/cCF(10 vol%) composites produced by mold C at 10 cc/s.
5.3.3.3. Hybrid Composites

The electrical conductivity of COC/cCF-CB composites is shown in Figure 5.10. As seen before skin removal, foaming has strongly improved the through-plane conductivity of the hybrid composites particularly for the one with 0.75 vol% CB. Indeed more than one order of magnitude drop in through-plane electrical conductivity of carbon fiber composites due to foaming has turned into more than one order of magnitude improvement in that only by adding 0.75 vol% CB. However the inclusion of foam has not considerably influenced $\sigma_L$. Fibers are not significantly oriented in the through-plane direction; Carbon black aggregates have promoted transfer of electrons in the through-plane direction by enhancing fiber-fiber contacts (Motlagh et al. 2007) and foaming has further promoted this mechanism most likely by squeezing the fillers between the cells. Skin removal enhanced $\sigma_T$ of the nonfoam composites by around one order of magnitude but did not remarkably affect $\sigma_T$ of the foam composites. Consequently when the LW skin was removed, through-plane conductivities of the foam composites were similar to their counterpart nonfoam composites. As seen in this chapter and Chapter 3, skin removal enhances the through-plane conductivity of the solid composites; however, for the foam composites containing carbon fiber this was not observed. At this point we can not fully explain the reason(s); however, it may be associated with the exposure of the cells after skin removal.
Figure 5.10. Electrical conductivity of COC/cCF(10)-CB(0.75) and COC/cCF(10)-CB(2.5) composites prior and after LW skin removal (0.6 mm).
5.3.4. Batch Foaming

To compare the effect of foaming in the presence of flow (as in injection molding) with that in the static condition, a series of samples were foamed in a batch process as listed in Table 5.7. Nonfoam injection molded bars from Mold A were placed in a high pressure vessel under an atmosphere of N₂ at 15 MPa, 90 °C for 18 hrs to dissolve N₂ in the polymer. The pressure was released and samples were quickly weighed to determine the amount of absorbed gas which was found to be in the range of 0.2-0.3 wt%. Then they were immediately transferred to a heated air oven at 170°C or 195°C under atmospheric pressure. A temperature of 170 °C was chosen so that the shape of the sample could be more or less retained while expansion was occurring – an important issue in order to measure electrical conductivity. Gas adsorption decreases the glass transition temperature (T_g) [Krause et al., 2001, Hwang and Cha, 2002]. By using data given in these references it was estimated that the T_g of pure COC (130 °C) can decrease to around 110 °C due to N₂ absorption. However it was not possible to properly foam the composites at temperatures below 150 °C due to the inclusion of fillers that increase T_g [Droste and Dibenedetto, 1969] and viscosity. After four to ten minutes, the samples were taken out of the oven and allowed to cool down under ambient conditions.

As shown in Figure 5.11 the cell size and content were not uniform through the sample thickness. The areas close to the surface had larger cells and higher void content due to temperature gradient across the thickness of the part imposed by oven heating. The cells in the core were much finer. Table 5.7 shows the foaming condition and the resulting properties.

The void content was variable among the samples in the range of about 20-60 vol%. This range was comparable to the foam injection molded samples,
### Table 5.7. Properties of the injection molded composites foamed by batch process

<table>
<thead>
<tr>
<th>Run</th>
<th>Filler</th>
<th>Oven Temp (°C)</th>
<th>Time in oven (min)</th>
<th>Void in oven content (Vol%)</th>
<th>Fiber Length (μm)</th>
<th>$\sigma_L$ (S/cm)</th>
<th>$\sigma_w$ (S/cm)</th>
<th>$f_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d0</td>
<td>mCF15</td>
<td>170</td>
<td>10</td>
<td>0</td>
<td></td>
<td>0.1781</td>
<td>0.0401</td>
<td></td>
</tr>
<tr>
<td>d1</td>
<td>mCF15</td>
<td>170</td>
<td>7</td>
<td>59</td>
<td></td>
<td>$5.2 \times 10^{-6}$</td>
<td>$4.4 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>c0</td>
<td>CCF10</td>
<td>170</td>
<td>10</td>
<td>0</td>
<td>206</td>
<td>0.0338</td>
<td>0.0030</td>
<td>0.11</td>
</tr>
<tr>
<td>c1</td>
<td>CCF10</td>
<td>170</td>
<td>4</td>
<td>36</td>
<td>217</td>
<td>$5.4 \times 10^{-6}$</td>
<td>$4.2 \times 10^{-5}$</td>
<td>0.09</td>
</tr>
<tr>
<td>c2</td>
<td>CCF10</td>
<td>170</td>
<td>7</td>
<td>68</td>
<td></td>
<td>$&lt;10^{-8}$</td>
<td>$&lt;10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>e0</td>
<td>CB3</td>
<td>170</td>
<td>10</td>
<td>0</td>
<td></td>
<td>0.0058</td>
<td>0.0061</td>
<td></td>
</tr>
<tr>
<td>e1</td>
<td>CB3</td>
<td>170</td>
<td>5</td>
<td>18</td>
<td></td>
<td>0.0032</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td>e2</td>
<td>CB3</td>
<td>170</td>
<td>8</td>
<td>59</td>
<td></td>
<td>$1.7 \times 10^{-5}$</td>
<td>$2.1 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>f0</td>
<td>CB6</td>
<td>170</td>
<td>10</td>
<td>0</td>
<td></td>
<td>0.0088</td>
<td>0.0084</td>
<td></td>
</tr>
<tr>
<td>f1</td>
<td>CB6</td>
<td>170</td>
<td>6</td>
<td>33</td>
<td></td>
<td>0.0013</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>f2</td>
<td>CB6</td>
<td>170</td>
<td>9</td>
<td>56</td>
<td></td>
<td>$6.0 \times 10^{-5}$</td>
<td>$5.0 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>b0</td>
<td>mCF15CB2.5</td>
<td>170</td>
<td>10</td>
<td>0</td>
<td>128</td>
<td>0.0596</td>
<td>0.0153</td>
<td>0.13</td>
</tr>
<tr>
<td>b1</td>
<td>mCF15CB2.5</td>
<td>170</td>
<td>4</td>
<td>48</td>
<td>132</td>
<td>$2.8 \times 10^{-5}$</td>
<td>$2.3 \times 10^{-6}$</td>
<td>0.16</td>
</tr>
<tr>
<td>b2</td>
<td>mCF15CB2.5</td>
<td>170</td>
<td>10</td>
<td>56</td>
<td></td>
<td>$3.0 \times 10^{-5}$</td>
<td>$2.7 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>a0</td>
<td>CCF10CB2.5</td>
<td>170</td>
<td>10</td>
<td>0</td>
<td>175</td>
<td>0.0622</td>
<td>0.0218</td>
<td>0.11</td>
</tr>
<tr>
<td>a1</td>
<td>CCF10CB2.5</td>
<td>170</td>
<td>4</td>
<td>29</td>
<td>185</td>
<td>0.0001</td>
<td>$1.3 \times 10^{-5}$</td>
<td>0.12</td>
</tr>
<tr>
<td>a2</td>
<td>CCF10CB2.5</td>
<td>170</td>
<td>5</td>
<td>61</td>
<td>184</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.16</td>
</tr>
<tr>
<td>g1</td>
<td>CCF10CB2.5</td>
<td>195</td>
<td>4</td>
<td>53</td>
<td></td>
<td>$5.7 \times 10^{-5}$</td>
<td>$9.4 \times 10^{-6}$</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Conductivity of the non-foamed ones were measured after heat treatment at 170°C for 10 minutes.
having void content of about 25-40 vol% at the core. Due to the high viscosity, there was concern whether growing bubbles could have broken the fibers during expansion. Fiber length results shown in Appendix A Table A.1 indicate that this was not the case. As seen in Figure 5.12 for samples with lower void content (a1, c1) the cell size was around 10 to 15 microns compared to ~30 microns for foam injection molded samples. Samples with higher void content (a2 and f2) show an average cell size of ~40 microns compared to ~70 microns for foam injection molded samples. Finer cell size in batch processes is very common and has been observed in numerous studies [Krause et al., 2001; Arora et al., 1998; Goel and Beckman, 1994]. It was of interest to see how foaming at these conditions influence fiber orientation and electrical conductivity. As seen in Table 5.7, no significant change took place for fT even at void volume contents as high as 60%.

The electrical conductivity of all the composites drastically dropped. The through plane conductivities of the foams were below $1 \times 10^{-9}$ S/cm, lower than the limit of the measurement apparatus and, therefore no value has been reported. This very low conductivity was due to the high degree of the foaming close to the surface. Only for COC/CB6 (f1) a through-plane conductivity of $3 \times 10^{-8}$ S/cm was obtained. For measurements in the L and W directions, this high foam skin was machined off during sample preparation. Table 5.7 indicates that the electrical conductivity change due to foaming was the greatest for carbon fiber composites by up to a decrease of 6 orders of magnitude, followed by hybrid composites with a decrease of up to 3 orders of magnitude. Foaming had the least effect on the electrical conductivity of carbon black composites. This observation is attributed to the relative length scale of the fillers and cells as discussed before. The decrease in electrical conductivity by foaming is much more pronounced in the batch process samples than in injection molded samples. This could arise from the smaller cell size and lack of filler reorientation and localization in the batch process all because of extremely high viscosity at lower temperature (170 °C.
compared to 300 °C) and under no shear condition. Figure 5.13 demonstrates that the growing bubbles have expanded around the fibers without pushing them away.

Figure 5.11. Fractured surface of batch foam composite a1 (COC/cCF10CB2.5, void content 29 vol%) obtained by SEM (flow direction is from left to right and vertical is the thickness direction).
Figure 5.12. Micrographs showing fractured surface of batch foam composites obtained by SEM (flow direction is horizontal and vertical is the thickness direction).
Figure 5.12. (contd) Micrographs showing fractured surface of batch foam composites obtained by SEM (flow direction is horizontal and vertical is the thickness direction).
Figure 5.13. SEM images from fractured surface of batch foam composites showing interaction of bubbles and fibers.
5.4. DISCUSSION

5.4.1. Fiber Orientation

This section discusses that rotation of a fiber by a growing cell in a flowing melt is very complicated. Melt viscosity, flow rate, gas pressure inside the cell, cell size, fiber length, fiber-fiber interactions and fiber length distribution will be suggested as important factors.

5.4.1.1. Rotation of a single fiber

Ideally if a cell nucleates in the proximity of a fiber end as shown in Figure 5.14 and grows to push the fiber to rotate, the degree of fiber rotation can be calculated by:

\[
\tan \alpha = \frac{d_{\text{cell}}}{2 \ell_{\text{fiber}}} = \frac{d_{\text{cell}}}{\ell_{\text{fiber}}} \rightarrow \alpha = \tan^{-1}\left(\frac{d_{\text{cell}}}{\ell_{\text{fiber}}}\right)
\]

(5.1)

which implies that fiber rotation will be significant only if the cell diameter is comparable in magnitude to the fiber length. If based on the results obtained in this study a typical diameter of 30 microns for the cell and fiber length of 150 microns for the fiber is assumed, the ideal angle of rotation obtained from equation would be just 11°. Such small change would not effectively enhance the friction.

Rotation of a fiber by a growing cell in vicinity of the fiber is extremely difficult due to the high viscosity of the melt and consequently large hydrodynamic forces acting on the fiber. The very simplified calculations in Appendix B show that only for a single fiber transported in the polymer melt, a
Figure 5.14. Schematic showing rotation of a single fiber by a growing cell

huge gas pressure inside the growing cell is required to overcome the hydrodynamic force acting on the fiber and reorient the fiber. Albeit without considering fiber-fiber interactions which hinder free rotation of the fiber.

5.4.1.2. Fiber-fiber interactions

As Figure 5.15 schematically illustrates, in the concentrated regime where the distance between the fibers is in the order of a fiber diameter, the fiber-fiber interactions can interfere with the rotation of a fiber by the cell growth. When the neighboring fibers retard or prevent the fiber from rotation, cell growth may either continue toward the areas where it can grow more freely i.e. polymer rich areas or only displace the fiber without rotation. It was notable during optical analysis that there are matrix rich areas in the fiber composites. These areas can be seen in
Figure 5.15. Schematic showing fiber-fiber interactions that interfere with the rotation of a fiber by a growing cell.

Figure 5.16. Optical micrographs showing matrix rich areas among fiber rich areas for composite A4 (COC/cCF10). Left: LW plane and Right: LT plane.
Figure 5.16 before foaming. As seen in Figure 5.16 cells usually appeared in these areas inferring that their expansion did not effectively interact with the fibers at the far distance to reorient them. This has been probably one major reason not to observe significant change in $f_T$ for most foam carbon fiber composites. It only does if the cell size is larger than the size of the matrix rich area and in that case a large group of fibers are likely to be influenced by the expansion of the large cell (Figure 5.6 middle).

Based on above discussion fiber reorientation can be significant if the cell size is large enough compared to the fiber length and size of the matrix rich areas. Also to prevent bubble-bubble interference it is suggested that a distance at least in the order of cell size exists between the cells. This distance along with preferred cell size determines the window for the void content that results in significant fiber rotation. For uniformly distributed cells as illustrated in Figure 5.17 the relationship between cell size, distance between cells and void content can be drawn as follows:

$$x_{cell} = \frac{A_{cells}}{A_{total}} = \frac{4 \times (\pi D_{cell}^2 / 4)}{S^2} \rightarrow S = \sqrt{\frac{\pi}{x_{cell}}} D_{cell}$$

and $S = 2G + 2D_{cell} \rightarrow$

$$G = \sqrt{\frac{\pi}{4x_{cell}}} - 1 D_{cell}$$

(5.2)

where $x_{cell}$ is void content and $G$ is the distance between the cells. This equation gives that at void content of 78 vol% the gap between cells reaches zero. At void contents less than 40 vol% the gap will be larger than cell diameter. For 30 vol% void content and a cell diameter of 200 microns, equation (5.2) gives a gap of 254 microns.
5.4.2. Electrical Conductivity

Schulz [1981] has proposed a model for the thermal conductivity of porous quasi-homogenous composite. It is a composite that its stereometric parameters (particle concentration, shape and orientation) are constant within a representative volume. For a closed cell quasi-homogenous composite:

\[ \sigma_p = \sigma_\infty (1-P)^X \]  
\[ X = \frac{1 - \cos^2 \alpha}{1-F} + \frac{\cos^2 \alpha}{2F} \]
where $\sigma_p$ and $\sigma_0$ are thermal conductivities of porous and nonporous composite, respectively. $P$, $F$ and $\cos^2\alpha$ are the volume fraction, shape factor and orientation factor of the cells, respectively. $F$ is zero for lamella shape and maximum 0.5 for cylindrical cells. $\cos^2\alpha$ varies from zero (unidirectional oriented cells along the heat flow direction) to one (cells are perpendicularly oriented in regards to heat flow direction). Equation 5.3 predicts the highest drop in conductivity for a composite containing lamella shape cells which are perpendicularly oriented to the heat flow. However, the equation does not consider the effect of cell size. As Equation 5.3 indicates, with increasing $X$ any porosity will cause a larger drop in thermal conductivity. For spherical cell which is the closest case for our samples, $F$ and $\cos^2\alpha$ are 1/3. Therefore equation 5.3 simplifies to:

\[ \sigma_p = \sigma_0 (1 - P)^{1.5} \]  

(5.5)

It is assumed that the analogy presented for thermal conductivity of foam composites can be used for the electrical conductivity. The model above does not consider cell size and the morphological change occurred by foaming, such as change in fiber-fiber contacts, but is useful to determine the lower and upper bounds.

5.4.2.1. Carbon Fiber Composites

Consider the carbon fiber composites produced by mold A with the given conductivities in Figure 5.8. At the core of the foam composites with shot size of 85% the cell volume content is around 25vol% for which equation 5.5 predicts a reduction of 35% in electrical conductivity. However Figure 5.8b demonstrates much more reduction (~one order of magnitude for $\sigma_{3D}$) than 35% predicted by the model. This is because of the fact that the conductivity of the conductive phase (polymer-fiber composite) in the foam composite is less than that in the
solid composite due to decrease in the fiber-fiber contacts. But equation 5.3 assumes constant conductivity \( \sigma_0 \) prior and after introducing the bubbles. If cells can be considered as a whole volume (one large cubic bubble), then the foam composite can be assumed as two parallel resistors (one is the whole volume of the cells and the other is the composite). Then cells will not interfere with the connectivity of the fibers and the conductivity of the foam composite will be equal to \( \sigma_0 (1-P) \) which is the upper bound. However if the cells act as volume exclusions then they have the role of diluting fiber concentration so that new fiber concentration in the foam will be equal to original fiber concentration multiplied by \( (1-P) \) i.e. 7.5 vol% and 11.25 vol% for cCF(10) and mCF(15) composites, respectively. Then the conductivity of the foam composite is equivalent to the conductivity of a solid composite with the new lowered fiber concentration which can be calculated by the standard percolation model:

\[
\sigma_C = \sigma_F (\varphi - \varphi_{\text{Crit}})^t
\]  

where \( \sigma_C \) is conductivity of composite, \( \sigma_F \) is conductivity of conductive filler, \( \varphi \) is volume fraction of conductive filler (where \( \varphi > \varphi_{\text{Crit}} \)), \( \varphi_{\text{Crit}} \) is the volume fraction of filler at the percolation threshold, and \( t \) is the critical exponent. To use this equation a percolation threshold of \( \sim 5.5 \) vol% and \( t = 3 \) for the COC/cCF(10) with AR=25 can be estimated by using literature data [Motlagh 2007a, Bigg 1979, Clignerman 2001b]. Inserting these values in equation 5.6, leads to:

\[
\sigma_{7.5\%} / \sigma_{10\%} = 0.09 \text{ which, is close to the reduction seen in Figure 9b. Therefore for the foam carbon fiber composites possessing the specified fiber length and cell size, foaming reduces the number of fibers contributing to the electron transfer. The possible increase in the fiber concentration between the struts by cell growth to compensate the volume exclusion effect of the cells does not seem to be significantly occurring.}
The observed decrease in the through-plane conductivity for COC/CF composites with foaming is a function of cell size. A change in back pressure and hold pressure will cause a change in the cell size which can be used to evaluate the effect of cell size on electrical conductivity. By increasing back pressure from 10 MPa to 20 MPa in foam injection molding of COC/cCF(10), the cell size decreased from 67 microns to 31 microns. The obtained through-plane conductivity of the foam composite with smaller cell size was two orders of magnitude lower than that of the composite with larger cells. Also increasing hold pressure from 0 MPa to 100 MPa, decreased the void content from 23% to 9% and cell size from 67 to 32 microns (cell density from $0.8 \times 10^5$ to $3.2 \times 10^5$ cells/cm$^3$) without a noticeable change in the through-plane conductivity. The foam composite with smaller void content must have shown significantly higher conductivity but it appears that larger number of smaller cells has compensated the effect of smaller void content. Therefore it can be seen that the through-plane conductivity of the COC/CF composites decreases with decrease in cell size at a constant void content. Further details for the effects of back pressure and hold pressure are given in Appendix C.

5.4.2.2. Carbon Black Composites

The increase in conductivity via foaming could be due to a number of reasons:

(i) *length scale effect*: since the size of carbon black aggregates (30-100 nm) is much smaller than the size of the bubbles (Table 5.5), the connectivity of carbon black aggregates is not significantly influenced by the presence of the bubbles. The SEM micrographs shown in Figure 5.18 illustrate the large difference between the size of the CB aggregates and a typical cell. It also shows that CB aggregates are present at the surface of the bubble. However this can only
lead the foam composite to approach the upper bound conductivity which can be obtained by the parallel resistors analogy i.e $\sigma_0(1-P)$.

(ii) **orientation effect:** It has been mentioned that more random orientation of conductive filler decreases the percolation threshold and consequently increases the electrical conductivity at a certain concentration [Kortschot 1988]. Foaming may have changed the orientation of the carbon black clusters toward more through-plane orientation due to the biaxial extensional flow at the bubble surface. This effect is not considerable because only a small fraction of aggregates are located in the vicinity of bubbles that can be influenced by the bubbles. Sample calculations in Appendix D estimate that only less than 1% (4%) of carbon black aggregates can be located within 0.5 (5) $\mu$m distance from the bubbles.

(iii) **phase effect:** distribution of filler in a polymer matrix is not completely homogeneous. The degree of heterogeneity depends on mixing conditions, filler size, filler-matrix interaction, polymer morphology (semicrystalline or amorphous) and molding conditions. A more heterogeneous composite with randomly oriented particles gives a lower percolation threshold, more pronounced effect for nano size fillers such as carbon black [Bridge et al., 1988&1990; Wessling, 1991]. This is why statistical models, which assume random dispersion of fillers, predict a larger percolation threshold than experimental data [Kortschot, 1988]. The higher the degree of spatial inhomogeneity of the filler, the lower is the percolation threshold and the higher the electrical conductivity [Kozlowski, 1995]. Gubbles et al. [1995] convincingly proved that increasing compression molding time of PE/PS blends containing carbon black promotes segregation of carbon black aggregates and localizes them at the interface resulting in much lower percolation threshold. For the composites in this study, Figures 5.18b and 5.18c show that the distribution of CB in the
Figure 5.18. SEM image of the fractured surface of foam injection molded COC/CB3.4: (a) a large cell and the surrounding solid areas. Area b and c as shown on the image are presented at higher magnifications in Figure 5.18 (b) and (c).
Figure 5.18. SEM image of the fractured surface of foam injection molded COC/CB3.4: (b) near the cell
Figure 5.18. SEM image of the fractured surface of foam injection molded COC/CB3.4: (c) inside the cell
matrix and on the cell surface is heterogeneous. It is likely that aggregate segregation has been promoted or CB clusters have been enlarged by facilitation of CB transfer in the less viscous gas laden melt. SEM micrographs in Figure 5.19 show that the number of CB clusters encapsulated in COC matrix is less in the foam composite than in the non-foam one. In other words the CB cluster size has increased via foaming. This was observed both at the core and the skin regions. CB clusters most likely start to form after the relatively large hydrodynamic forces disappear at the end of filling when inter-particle forces become important.

(iv) particle-particle gap: It is well known that in CB composites there is no intimate contact between the particles and that electron conduction takes place via electron tunneling i.e. electrons hop between CB particles. The tunneling current exponentially increases with decreasing gap [Sheng et al. 1978]. Indeed the gap size controls the conductivity and it must be around 10 nm or less for the tunneling to occur. For the COC polymer in this study with a molecular weight of \( \text{MW}_n = 54 \text{ kg/mol} \) a nominal radius of gyration of 165 nm can be estimated for the chain size. Therefore the distance that CB aggregates must travel to reach the minute gap (<10 nm) is within the chain size [Wessling, 1991]. Thermal vibration and van der Waals forces promote CB aggregates to come close and make coagulates [Kato and Miyashita, 1990]. The dissolved nitrogen in the polymer melt decreases the glass transition temperature leading to increase in chain mobility. Two CB aggregates approach each other easier through a more flexible chain resulting in smaller gap and higher tunneling current and consequently higher electrical conductivity.

Briefly, the length scale effect can be responsible to minimize the drop in electrical conductivity but not any increase over that of the non-foam composite. Orientation effect does not influence majority of the aggregates. Phase effect and gap size reduction seem to be the primary reasons in enhancing electrical conductivity.
conductivity of the foam CB composites. This can be supported by our observation that electrical conductivity of the foam injection molded CB composite was very close to that of the non-foam composite prepared in compression molding. Table 5.8 shows that non-foam injection molded composites had much lower conductivity than compression molded ones. Others have also reported that compression molded composites have higher electrical conductivity than injection molded composites due to more heterogeneous filler distribution [Kato and Miyashita, 1990]. On the other hand foam injection molded composites have reached conductivities comparable to the compression molded composites (Table 5.8). This suggests that the distribution of carbon black aggregates in the foam injection molded composites has approached that of the compression molded composites. It has been shown that in compression molding CB aggregates have enough time to coagulate and reach the equilibrium state by the actions of thermal vibrations and van der Waals forces, but in injection molding the aggregates do not attain the equilibrium state as the melt cools down fast and the structure freezes [Kato and Miyashita, 1990, Pinto et al., 1999]. Therefore carbon black coagulation and phase segregation has been promoted in the gas-laden melt by lower viscosity which facilitates long range interactions of CB aggregates and higher chain mobility that accelerates aggregates coagulation. Furthermore when injecting the foam composites, due to the presence of non-conductive gas bubbles, the melt spends more time to solidify giving more chance to CB aggregates to coagulate. It was observed that foam injection molded parts needed 10-15 seconds longer cooling time as compared to the non-foam parts to have an acceptable dimensional stability when demolded.

Increase in mold thickness was accompanied by increase in electrical conductivity for the solid COC/CB composites in all directions. These observations can be attributed to the effect of mold thickness on the orientation of CB aggregates during mold filling and the morphology development during
cooling stage. Increase in mold thickness creates composites with more randomly
oriented particles which can improve the conductivity. A thicker part needs
longer cooling time which can give more time for CB aggregates to segregate
after the end of filling leading to improvement in electrical conductivity. On the
other hand the magnitude of improvement in the through plane conductivity by
foaming was larger for the thinner COC/CB parts compared to the thicker parts
revealing that for thinner part, foaming comparatively induces more segregation
of CB aggregates. Further information are given in Appendix C.

The mechanism for the increase in electrical conductivity of carbon black
composites by foaming needs to be studied in further detail and more evidence is
required to explain the phenomena. However it was not feasible in the course of
this research to do that due to the time constraints.

Table 5.8. Electrical conductivity of compression molded [Motlagh et al 2007]
and injection molded COC/CB composites. Numbers in the brackets relate to
conductivities of the samples after LW skin removal (i.e. core)

<table>
<thead>
<tr>
<th>CB vol%</th>
<th>Compression molded</th>
<th>Injection molded</th>
<th>Foam injection molded</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \sigma_L )</td>
<td>( \sigma_T )</td>
<td>( \sigma_L )</td>
</tr>
<tr>
<td>3.4</td>
<td>0.07</td>
<td>0.014</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>(0.012)</td>
<td>(0.0015)</td>
<td>(0.057)</td>
</tr>
<tr>
<td>4.2</td>
<td>0.16</td>
<td>0.041</td>
<td>0.023</td>
</tr>
</tbody>
</table>
Figure 5.19. SEM micrographs from fractured surface of COC/CB (3.4 vol%) composite: (a) nonfoam composite
Figure 5.19. SEM micrographs from fractured surface of COC/CB(3.4 vol%) composite (b) foam composite
5.4.3. Overview

Table 5.9 summarizes the changes in electrical conductivity occurring by foaming for the three different cases:
- Carbon black composites
- Carbon fiber composites
- Carbon fiber-carbon black hybrid composites

and two foaming procedures:
- Foam injection molding
- Batch foaming

Also the involving forces which can influence particle movement have been shown. The table also includes the magnitude for relative size of the cell to filler.

Decrease in conductivity is seen for the batch foamed composites revealing that in the absence of flow, bubble growth can not significantly influence the particles. Volume exclusion effect of the cells causes decrease in electrical conductivity. In foam injection molding, conductivity of the carbon black and hybrid composites improves with foaming but not the carbon fiber composites. Therefore it is suggested that the force applied by the growing bubble along with flow dynamic forces have relocated carbon black aggregates toward a more agglomerated structure. Other factors such as longer cooling time and presence of nitrogen molecules may have promoted the agglomeration process. For carbon fiber foam composites where the cell size and carbon fiber diameter have the same order of magnitude, the size exclusion effect is the primary factor causing decrease in electrical conductivity.
Table 5.9. Summary for the effects of foaming on electrical conductivity

<table>
<thead>
<tr>
<th>forces</th>
<th>foam injection molding</th>
<th>batch foaming</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- growing bubble</td>
<td>- growing bubble</td>
</tr>
<tr>
<td></td>
<td>- dynamic forces by flow</td>
<td></td>
</tr>
<tr>
<td>cell size/particle size</td>
<td>change in through-plane electrical conductivity by foaming</td>
<td></td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>( \approx 1 )</td>
<td>( \downarrow )</td>
</tr>
<tr>
<td>Carbon black</td>
<td>( \approx 1000 )</td>
<td>( \uparrow )</td>
</tr>
<tr>
<td>Carbon fiber-carbon black</td>
<td>( \approx 1 ) and ( \approx 1000 )</td>
<td>( \uparrow )</td>
</tr>
</tbody>
</table>

5.5. CONCLUSIONS

In injection molding, foaming influenced the electrical conductivity of carbon black (CB), carbon fiber (CF) and hybrid CF-CB composites. Foaming increased electrical conductivity of CB composites in the in-plane direction, and increased electrical conductivity as much as an order of magnitude in the through-plane direction. The increase in conductivity by foaming was more significant at lower CB content. Improved carbon black coagulation leading to either an increase in cluster size or a decrease in particle-particle gap was proposed as the reason for the observed improvement.
Foaming reduced the electrical conductivity of CF composites, particularly in the through-plane direction. The reduction in in-plane electrical conductivities was larger for composite samples with shorter fibers and higher void content.

Through-plane conductivity of hybrid CF-CB composites increased with foaming, without a considerable change in the in-plane conductivity. Contrary to decrease in the through-plane conductivity for COC/cCF(10 vol%) with foaming, one order of magnitude improvement in the through-plane conductivity was observed for COC/cCF(10 vol%)-CB(0.75 vol%) with foaming.

Higher back pressure resulted in finer cell size and larger drop in the through-plane electrical conductivity via foaming for the CF composites. By increasing hold pressure, the void content and cell size significantly decreased without a considerable change in electrical conductivity.

By increasing mold thickness for non-foam CB and hybrid composites, conductivity increased in the in-plane and through-plane directions due to the more random particle orientation. Foaming enhanced in-plane and through plane conductivities for the CB composites produced by the thicker mold; however the enhancement was less significant compared to that observed for the thinner parts. Also, foaming increased through-plane conductivity of the hybrid composite molded with the thicker mold.

The relative size of particles and cells was an important factor for the effect of foaming on electrical conductivity. If the cell size is on the order or lower than particle size e.g. fiber diameter then cells will significantly reduce the number of fiber-fiber contacts contributing in the conductive path. When the
particles, i.e. CB, are much smaller than average cell size, then the connectivity of the particles is not significantly reduced with foaming. In addition increase in effective CB concentration contributing to the electron transfer or decrease in particle-particle gap causes improvement in electrical conductivity with foaming.

In general fiber orientation by bubble growth was not illustrated by the average fiber orientation factors for most of the samples most likely due to high melt viscosity and hindering fiber-fiber interactions; however, it was shown that fibers can be reoriented toward through-plane direction in the vicinity of large cells. The extent of drop in electrical conductivity for CF composites with foaming is associated with orientation of fibers i.e. less drop in the direction that fibers are preferably aligned.

In batch foaming, all foamed samples exhibited a large reduction in conductivity which can be corresponded to the lack of particle re-localization and rotation due to the absence of dynamic forces of flow and very high viscosity of the melt.
REFERENCES


- Pinto, G; Cipriano, L G; Ana, J M (1999) Polym Comp, 20, 804-808.


Chapter 6

Summary

6.1. Conclusions

Electrical conductivity and dynamic rheological properties of cyclic olefin copolymer composites containing combinations of carbon fiber (CF) and carbon black (CB) with varying concentrations were investigated as compared to the composites containing only one of the fillers. It was found that combinations of these fillers, except at high carbon fiber content, synergistically create electron pathways within the matrix and improve the composite electrical conductivity. The synergism is more significant where the concentration(s) of the filler(s) is around percolation threshold. Synergism appeared when one of the fillers was at a concentration below percolation. A simple semi-empirical model was proposed to estimate the electrical conductivity for the hybrid composites. For the hybrid composites the best trade off between viscosity (to be kept low) and conductivity (to maximize) was found where concentrations of the carbon fiber were several fold higher than carbon black. Consequently, these composites remained processable in traditional processing equipment such as injection molding machinery.

With an established strategy for maximizing the electrical conductivity the subsequent work focused on the goal of improving the isotropic nature of this property for an injection molding-grade composite material. This research investigated whether foaming could sufficiently disrupt the preferential flow induced alignment of fibers during mold filling and thereby increase the
frequency of their orientation in a more favourable direction to improve through-plane conductivity. A fractional factorial of experiments was used to screen the effects of injection rate, melt temperature and mold temperature on fiber orientation and electrical conductivity for the foam and nonfoam COC composites containing 10 vol% carbon fiber and 2 vol% carbon black. It was found that foaming at low injection speed and high melt temperature could enhance the through-plane fiber orientation factor by more than two folds, and consequently through-plane electrical conductivity by more than one order of magnitude. The concurrence of the melt flow and bubble growth was considered to be the key mechanism for fiber reorientation while the cell size and shape play an important role so as to not disrupt the conductive paths spanning the bulk of the composite.

More detailed experiments followed in an effort to reveal the important features of foaming based on the positive findings from the preliminary trials. For the molded parts foaming increased electrical conductivity of CB composites in the in-plane direction up to five folds, and as much as an order of magnitude in the through-plane direction. Improved carbon black coagulation leading to either an increase in cluster size or decrease in particle-particle gap was postulated as the reason for the observed improvement. Foaming reduced electrical conductivity of CF composites particularly in the through-plane direction. Volume exclusion effect of the cells was the primary reason for decrease in electrical conductivity of the CF composites. Through-plane conductivity of hybrid CF-CB composites increased with foaming by up to one order of magnitude without considerable changes in-plane conductivity, due to improved agglomeration of carbon black aggregates and the interplay of carbon black to act as bridges between carbon fibers.

The relative size of particles and cells was an important factor of the foams in regards to electrical conductivity. If the size of the foam cell was in the
same or lower order compared to the filler particles (i.e. the carbon fibers) then the cells significantly reduced the number of fiber-fiber contacts contributing in the conductive path. When the particles, i.e. CB, were considerably smaller than the average cell size then the connectivity of the particles was not significantly reduced with foaming.

Observed decrease in electrical conductivity for CB, CF and CF-CB composites in batch foaming revealed that particle relocalization and reorientation can not occur in batch foaming due to the absence of flow dynamic forces as well as the large viscosity of the melt.

In general fiber orientation by bubble growth is very difficult to accomplish due to the high melt viscosity and hindrances from fiber-fiber interactions; however, it was shown that fibers could be reoriented toward through-plane direction in the vicinity of large cells by foaming. The change in the average fiber orientation will be significant if the cells are much larger than the fiber length, and that foaming progresses in the presence of a shear field.

6.2. Contributions to Knowledge

The important contributions of this research are as following:

• Study of the existence of electrical conductivity synergism for the thermoplastic composites containing combinations of carbon fiber and carbon black with varying concentrations including levels where one filler was below its percolation threshold.

• Use of rheometry to estimate electrical percolation threshold for polymer carbon fiber composites.

• Investigating feasibility of foaming to disrupt preferential fiber orientation in injection molding.
• Evaluating the importance of relative size of cells and particles on electrical conductivity and particle orientation in carbon filled foam polymer composites.

• Comparing the effects of batch foaming- as a process without flow- and foam injection molding- as a flow involved process- on the electrical conductivity of the resultant foam parts.

6.3. Recommendations for Future Work

Although the combination of carbon fiber and carbon black was experimentally studied in this work, modelling electrical conductivity of hybrid fiber-particle composites needs particular attention and will certainly achieve significant merit. Conventional carbon fillers were utilized in the current research, however examining the electrical conductivity synergism for combinations of carbon fiber with large aspect ratio nanofillers such as carbon nanotubes and highly conductive nanofillers such as metal nano powders or metal coated nano particles is highly recommended. Precise structural analysis of carbon black composites is still required to understand the differences between the morphology of carbon black aggregates in the foam and non foam composites. To better include the size effects of fillers and cells on electrical conductivity and particle orientation, a broader range of particle length scale and cell size should be considered. In particular using carbon nanofibers and nanotubes are highly recommended. Modelling electrical conductivity for foam polymer composites and modelling of fiber rotation in foam injection molding was of great interest to the author however it was not achievable due to the time limitation.
Appendix A: Fiber Length\textsuperscript{1}

Generally short fiber composites have a broad range fiber length distribution as shown for instance in Figure A.1. Usually a single mean value is used to represent the average value of the broad distribution. In this study the weighted average fiber length was obtained according to the following equation:

\[ L_w = \frac{\sum_{i=1}^{n} \ell_i^2}{\sum_{i=1}^{n} \ell_i} \]  

(A.1)

where \( \ell_i \) is the length of fiber \( i \), \( n \) is the number of fibers and \( L_w \) is the weighted average fiber length.

Table A.1 presents the weighted average fiber lengths found in the carbon fiber precursors and selected foam and non-foam composites prepared in the injection molding machine. Adding chemical blowing agent reduced the degree of fiber breakage due to lower stress acting on the fibers as a result of the reduced viscosity in the gas laden melt. Consequently the average fiber length is higher (on average \( \sim 12\% \)) for the foam composites as compared to the non foam counterparts [Zhang and Thompson, 2005]. Fibers in the moldings containing cCF are about 50\% longer than those in the moldings containing mCF. The intention was to evaluate the effects of fiber length on the fiber reorientation caused by foaming as well as electrical conductivity of the foamed composites.

\textsuperscript{1}References are listed at the end of chapter 5.
Figure A.1. Fiber length distribution of nonfoam injection molded COC/mCF (15 vol%) composite
**Table A.1.** Fiber length of carbon fiber precursors and selected composites from Table 5.4 (IM= injection molding/molded).

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition</th>
<th>Description</th>
<th>Weighted Average Length (L_w, (\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COC/mCF15</td>
<td>before IM</td>
<td>150</td>
</tr>
<tr>
<td>A1</td>
<td>COC/mCF15</td>
<td>nonfoam IM part</td>
<td>126</td>
</tr>
<tr>
<td>A3</td>
<td>COC/mCF15</td>
<td>foam IM part</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>COC/cCF40 precursor</td>
<td>before IM</td>
<td>570</td>
</tr>
<tr>
<td>A4</td>
<td>COC/cCF10</td>
<td>nonfoam melt exiting injection nozzle</td>
<td>261</td>
</tr>
<tr>
<td>A6</td>
<td>COC/cCF10</td>
<td>foam melt exiting injection nozzle</td>
<td>290</td>
</tr>
<tr>
<td>A4</td>
<td>COC/cCF10</td>
<td>nonfoam IM part</td>
<td>172</td>
</tr>
<tr>
<td>A6</td>
<td>COC/cCF10</td>
<td>foam IM part</td>
<td>181</td>
</tr>
<tr>
<td>A22</td>
<td>cCF10-CB2.5</td>
<td>nonfoam IM part</td>
<td>188</td>
</tr>
<tr>
<td>A23</td>
<td>cCF10-CB2.5</td>
<td>foam IM part</td>
<td>207</td>
</tr>
</tbody>
</table>

The average standard deviation for fiber length values reported was 8% based on three sets of 500 fibers for each value.
According to Table A.1 it was found that before injection molding the fibers in the cCF precursor (COC/cCF40) were about 400% longer than those in COC/mCF(15 vol%). But at the nozzle exit, fibers in COC/cCF(10 vol%), which was prepared by letting down the cCF precursor, were twice as long than those in COC/mCF(15 vol%). In the final moldings, fibers in COC/cCF10 were approximately one and half times longer than those in the mCF compound. This showed that longer fibers experienced much higher degree of attrition in the plasticating extruder and injection path. The severe fiber breakage for the cCF precursor precluded our intentions to have a larger difference between the length of carbon fibers in the final molded parts of the mCF and cCF composites. Such a difference in length would have more definitively allowed evaluation of the relationship between fiber length and cell size on fiber orientation and electrical conductivity.

Lower carbon fiber concentration was used for the cCF composite samples (10 vol%) as compared to mCF samples (15 vol%) to take into account the effect of fiber length on electrical conductivity and degree of fiber-fiber interactions. Increased fiber length means a lower percolation threshold and increased electrical conductivity [Bigg, 1979; Clingerman, 2001a]. Lower CF concentrations were needed for composites with longer fibers, so that both cCF and mCF composites ideally show similar conductivities. The approximate percolation thresholds for the corresponding average fiber lengths of mCF and cCF in the composites were estimated by referring to Bigg [1979]. Then by using a standard percolation model and inserting the other estimated parameters from [Motlagh, 2007; Clingerman, 2001b] it was predicted that to achieve a similar conductivity for the cCF composite to that of mCF at 15 vol%, a concentration of around 10 vol% cCF is needed. In addition the number of fiber-fiber interactions is an important factor in developing the final fiber orientation state [Folgar and Tucker, 1984; Arp and Mason, 1977; Jackson et al., 1986; Anczurowski and
Mason, 1967]. With increased fiber length or concentration, the degree of fiber-fiber interactions increases and this was the second reason for using lower CF concentration in the cCF composites so that approximately the same number of the interactions exist in both systems. As fiber-fiber interactions increase, the motion and reorientation of the fibers by flow becomes more hindered leading to a less preferential orientation along the main flow direction [Spahr et al., 1990, McClelland and Gibson, 1990]. The degree of fiber-fiber interactions depends on the concentration regime which can be determined by fiber aspect ratio (AR) and volume fraction ($\phi$) using the following definitions [Papathanausiou, 1997]:

\[
\begin{align*}
\phi &< \frac{1}{(AR)^2} & \text{Dilute} & & (A.2) \\
\frac{1}{(AR)^2} &< \phi < \frac{1}{(AR)} & \text{Semi-concentrated} & & (A.3) \\
\phi \times (AR) &> 1 & \text{Concentrated} & & (A.4)
\end{align*}
\]

From Table A1 an average AR of 19 and 25 was calculated for the mCF and cCF composites, respectively. According to Equation (A.4) both mCF15 and cCF10 composites fall in the concentrated regime where the former is slightly more concentrated than the latter due to the larger $AR \times \phi$ (2.9 compared to 2.5) leading to approximately same number of fiber-fiber interactions for the both systems.
Appendix B. Simplified rotation of a fiber by bubble growth

This appendix considers a very simplified case in which a single fiber as shown in Figure 5.14 is ideally pushed by a growing bubble at its end and starts to rotate. Of course for a precise analysis orientation tensors must be used and many further factors and possibilities have to be considered.

The growing cell will be able to rotate the fiber if it can overcome the resisting hydrodynamic force (drag force) acting on the fiber. Cox [1970] calculated the drag force, $F_D$, applied by a viscous fluid at velocity $U$ (whose motion is governed by Stokes flow) on a rigid cylinder (length $l$ and radius $r$) placed in the flow direction:

$$F_D = \frac{4\pi \mu U}{\ln(2l/r) - 0.8}$$  \hspace{1cm} (B.1)

Viscosity ($\mu$) can be replaced by power law equation:

$$\mu = m\dot{\gamma}^{n-1}$$  \hspace{1cm} (B.2)

where $m$ is consistency factor, $n$ (<1 for polymer melts) is power law index and $\dot{\gamma}$ is shear rate which for a slit geometry with gap $b$ can be expressed as:

$$\dot{\gamma} = \frac{n + 1}{n} \frac{U}{b} \left( \frac{\dot{\gamma}}{\dot{\gamma}} \right)^{1/n} \sim \frac{n + 1}{n} \frac{U}{b}$$  \hspace{1cm} (B.3)

Inserting equations (B.2) and (B.3) in (B.1) gives:

\[ \]
\[ F_D \sim \frac{4\pi l}{\ln(2l/r)} m \left( \frac{n}{n+1} \right)^{1-n} b^{1-n} U^n \]  

(B.4)

According to equation (B.4) drag force on a fiber increases with fiber aspect ratio, fluid velocity, consistency factor and decreases as the fluid becomes more shear thinning. The force applied by a growing cell \( F_g \) on a fiber can be estimated by:

\[ F_g = (P_g - P_m) \times A_C \]  

(B.5)

where \( P_g \) is gas pressure inside the cell, \( P_m \) is melt pressure and \( A_C \) is contact area between the cell and the fiber. The cell will be able to push the fiber to rotate if the magnitude of \( F_g \) is larger than \( F_d \). A sample calculation can show the magnitude of the drag force acted on the fiber. For COC/mCF(15) injecting at 5cc/s into mold A:

\[
\dot{\gamma} \sim \frac{n+1}{n} \frac{U}{b} \sim \frac{0.41+1}{0.41 \times 0.00155} = 288 \text{ s}^{-1}
\]

from equation (5.13): \( \dot{\gamma} \)

\[
\mu = \frac{4\pi \times 291 \times 147 \times 10^{-6} \times 0.13}{\ln(2 \times 20) - 0.8} = 0.024 \text{ N}
\]

from equation (5.11): \( F_D \)

Since the typical size of the bubble is much larger than the fiber diameter, the maximum contact area between a bubble and a fiber can be approximated as:

\[ A_C \sim \text{fiber diameter} \times \text{average bubble diameter} \sim 7 \times 10^{-6} \times 40 \times 10^{-6} = 2.8 \times 10^{-10} \text{ m}^2 \]

Then from equation (B.5) and by having \( F_g = F_D \):

\[ 0.024 = (P_g - P_m) \times 2.8 \times 10^{-10} \Rightarrow P_g - P_m = 86 \text{ MPa} \]

A cell should have such a huge internal pressure above the melt pressure to enforce a fiber to rotate, however still in the dilute regime, where fiber-fiber interactions do not play any role.
Appendix C: Process Related Influences

C.1. Back Pressure

Back pressure is a major processing factor controlling the cell size. An increase in back pressure increases gas dissolution in the polymer and also provides higher pressure drop during injection. Both of these effects lead to an increase in the number of nucleated cells and consequently a decrease in cell size [Kharbas et al., 2003]. Based on this fact we produced foam composite with finer cells and evaluated the change in conductivity (Table C.1). Sample A7 corresponds to the COC/cCF(10) foam composite produced at the exact same condition as sample A6 however with the back pressure of 20 MPa instead of 10 MPa. This change has significantly reduced $\sigma_T$. The average cell size of 31 $\mu$m and 67 $\mu$m was obtained for these composites produced at 20 MPa and 10 MPa back pressure, respectively. The $f_T$ values are quite close at 0.14 and 0.15 for both foam composites, thus finer cell size has likely induced more reduction in the through-plane conductivity. Since fibers are hardly oriented in the T direction, aligned fiber contacts play a major role in transporting electrons in this direction. As seen in Figure C.1, for a given void content, finer cells mean a higher number of cells which will likely cause more break up of these contacts.

\[\text{References are given at the end of chapter 5}\]
Table C.1. Effect of back pressure on the properties of foam injection molded COC/cCF(10).

<table>
<thead>
<tr>
<th>Code</th>
<th>Back Pressure</th>
<th>Density (g/cc)</th>
<th>Foam vol%</th>
<th>f_T</th>
<th>f_L</th>
<th>f_W</th>
<th>D_n (μm)</th>
<th>σ_L (S/cm)</th>
<th>σ_W (S/cm)</th>
<th>Log(σ_T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A6</td>
<td>10</td>
<td>0.828</td>
<td>24</td>
<td>0.09</td>
<td>0.62</td>
<td>67</td>
<td>0.029</td>
<td>0.005</td>
<td>-6.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>67</td>
<td>0.025</td>
<td>0.005</td>
<td>-6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.001**</td>
<td></td>
<td></td>
<td>-6.2</td>
</tr>
<tr>
<td>A7</td>
<td>20</td>
<td>0.839</td>
<td>23</td>
<td>0.12</td>
<td>0.60</td>
<td>31</td>
<td>0.29</td>
<td>0.004</td>
<td>0.003</td>
<td>-8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.024</td>
<td>0.005</td>
<td>0.003</td>
<td>-8</td>
</tr>
</tbody>
</table>

* f values obtained from LT plane. f_W in the parentheses were obtained from WT plane.

** Italic numbers are the conductivity values after LW skin removal by 0.6 mm.
Figure C.1. The hypothetical diagram comparing decrease in the number of fiber-fiber contacts by the presence of small and large cells.
C.2. Hold Pressure

Hold pressure during injection molding cycle plays an important role in the properties of prepared composites. For all previous foam composites in this paper no holding stage was applied during injection molding. However it was of great interest to see if exerting hold pressure can induce any change in the properties of the foam composites. Figure C.2 depicts that packing pressure did not significantly affect the measured electrical conductivity of the foam COC/cCF(10) composite. Changing hold pressure from 0 MPa to 100 MPa reduced the cell content from 23 vol% to 9 vol% and cell size from 67 μm to 32 μm (increase in cell density from $0.8 \times 10^5$ to $3.2 \times 10^5$ cells/cm$^3$, Table 5.5) but did not notably change the fiber orientation (Table 5.6). With a large decrease in void content (from 23 to 9 vol%) the fibers must preserve better connectivity leading to improved conductivity for the composite produced at 100 MPa hold pressure. But the much higher cell density probably has caused fewer fiber-fiber contacts and negated the effect of lower void content resulting in no significant change in the conductivity.
Figure C.2. Effect of hold pressure on the electrical conductivity of foam injection molded COC/cCF(10)-CB(2.5) composites at 15% reduced density. “core” corresponds to the samples with machined LW skin (0.6 mm).
C.3. Mold Thickness

According to Table 5.3, two molds with different thicknesses of 3.1 mm (thin mold, A) and 6.2 mm (thick mold, B) were used to evaluate the effect of mold thickness on electrical conductivity of foam and nonfoam composites. A thicker mold should exhibit more through-plane particle orientation and improved conductivity. Figure C.3a shows the measured electrical conductivity of the nonfoam and foam COC/CB(3.4) composites produced by the two molds. Considering only the nonfoam composites, it is seen that conductivity of the thicker part is higher in all directions compared to the thinner geometry.

Foaming led to one and two orders of magnitude improvement in $\sigma_T$ for the composites produced by the thick mold (mold B) and the thin mold (mold A), respectively. Likewise Figure C.3b illustrating electrical conductivity of the same samples after removing LW skin shows the same trends observed in Figure C.3a i.e. improvement in $\sigma_T$ via foaming, more pronounced for the composite produced by the thin mold. Comparing Figure C.3a and b indicates that skin removal has caused more improvement in $\sigma_T$ of the thinner samples.
Figure C.3. Electrical conductivity of injection molded COC/CB(3.4) composites produced by mold B (thickness 6.2 mm) and mold A (thickness 3.1 mm). a: before removing LW skin and b: after removing LW skin (0.6 mm)
Appendix D. Fraction of carbon black aggregates in vicinity of cells

For foam COC/CB (3.4 vol%) IMD4:
- Cell density ($n_c$) $\sim 10^6$ cells/cm$^3$
- Typical cell size: 60 $\mu$m

From our TEM analysis for CB aggregates:
- Nominal particle size: 30nm
- Typical aggregate size: 200nm $\sim$ 180nm
- Number of particles in each aggregate: 6

Carbon black (Ketjenblack EC600JD) has a nominal porosity of 75 vol% [Naoi, 2005].

To calculate aggregate density:

Basis: 1 cc of IMD4 composite, 30 vol% void content
Actual CB volume fraction ($\varphi_{CB}$) = $0.034 \times (1-0.3)/(1-0.75)$ = 0.1

Volume of one carbon black primary particle:
$v_{CB} = \pi (D)^3/6 = \pi (30)^3/6 = 14130$ nm$^3$

Volume of aggregate:
$v_{agg} = 6 \times 14130 = 84780$ nm$^3$
Aggregate density ($n_{agg}$) = $V_{CB}/v_{agg} = 0.1/(84780 \times 10^{-21}) = 1.2 \times 10^{15}$ aggregate/cc
To calculate number of aggregates within 500 nm distance from cell surface (shell):

\[ V_{\text{shell}} = \frac{\pi}{6} \times (D_o^3 - D_i^3) = \frac{\pi}{6} \times (60.5^3 - 60^3) = 2850 \text{ microns}^3 \]

Number of aggregates in the shell volume: \( n_{\text{sh}} = \frac{V_{\text{shell}} \times \varphi_{\text{CB}}}{V_{\text{agg}}} = (2850 \times 10^9) \times 0.1 / 84780 = 3.4 \times 10^6 \text{ aggregates/cell} \)

In one cc there is 10^6 cells. Therefore total number of aggregates within 500 nm of the cells in 1 cc: \( 10^6 \times 3.4 \times 10^6 \sim 3.4 \times 10^{12} \text{ aggregates around cells which, is less that 1\% of the total aggregates in 1 cc (1.2 \times 10^{15}).} \)