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Karl R. Haapala

The research explored in this thesis helps provide a better understanding of efforts that have been undertaken to more precisely calculate environmental impacts and human health risks, such as energy consumption, carbon footprint, and toxicity, to support environmental sustainability assessment of products. The work is comprised of two research objectives, the first research objective explores the integration of the environmental aspect of sustainability performance into the design of common products, manufacturing processes, and relevant supply chain networks to assist decision makers. The second research objective explores the challenges of safety concerns, human health risks, and toxicological responses in developing novel products. The framework developed for the first objective relies on manufacturing and supply chain unit process modeling, and is demonstrated for the evaluation of backpack design variants. It is shown that simultaneous consideration of manufacturing and supply chain processes can impact decision-making and improve product sustainability from an environmental perspective at the design stage. For the second objective, nanomaterials are a focus due to their potential to enable advanced technologies; however, little is known about their effects on the environment and human health. This research builds on a prior investigation of the stability and toxicity characteristics of zinc oxide nanoparticles (ZnO NPs) used in metalworking nanofluids (MWnF™). For stability analysis and toxicological assessment, the dynamic light scattering (DLS) method and the zebrafish assay method are applied, respectively, to evaluate the development of TiO_2 and ZnO MWnF™ formulations. In general, the results reveal addition of these NPs causes a higher mortality rate in comparison to NP-free formulations. From this thesis research, it is concluded that integrating evaluation of sustainable manufacturing and use performance into early product development provides the opportunity for improved engineering decision making. As a contribution, a point of departure is established for the research community to move current efforts forward for concurrent consideration of multiple stages of the product life cycle in pursuit of environmental, economic, and social sustainability. By pursuing this path, future research will ease some of the most challenging recent issues faced by decision makers globally, including use of non-renewable resources, GHG emissions and climate change, human health risks, toxicity, and potential health hazards.

Sustainability Assessment during Early Product Development: The Manufacturing Case and the Use Case

by
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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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TABLE OF CONTENTS

Page

Chapter 1 - Introduction 1

1.1 Overview 1

1.2 Motivation 1

1.3 Background 3

1.4 Research Objectives 7

1.5 Research Tasks 7

1.6 Thesis Outline 10

Chapter 2 - Literature Review 12

2.1 Chapter Overview 12

2.2 Manufacturing Case 13

2.2.1 Background 13

2.2.2 Sustainability Metrics 14

2.2.3 Current Methods and Tools for Environmental Sustainability 15

2.2.4 Sustainable Manufacturing Process Considerations 21

2.2.5 Sustainable Supply Chain Considerations 26

2.3 Use Case 28

TABLE OF CONTENTS (Continued)

page

2.3.1 Background 28

2.3.2 Machining Processes Improvement and Uncertainties about Nanoparticles 30

2.3.3 Nanofluid Stability... 33

2.3.4 Toxicology Evaluation... 34

2.3.5 Zebrafish Exposure Test 35

2.4 Prior Research Limitations, Summary, and Conclusions 36

2.4.1 Manufacturing Case 36

2.4.2 Use Case... 37

Chapter 3 - Sustainability Assessment during Early Product Development: The Manufacturing Case 39

Abstract 40

3.1 Introduction... 41

3.2 Background 43

3.3 Related Research... 49

3.3.1 Manufacturing Process Considerations... 50

TABLE OF CONTENTS (Continued)

page

3.3.2 Supply Chain Considerations 55

3.4 Research Methodology 57

3.5 Energy Consumption and Carbon Footprint Analysis 65

3.5.1 Supply Chain Network 65

3.5.2 Raw Material Processing 70

3.5.3 Fiber manufacturing process 73

3.5.4 Injection Molding Process 74

3.5.5 Fabric Manufacturing 76

3.5.6 Textile Product Assembly 77

3.6 Summary and Conclusions 83

Chapter 4 - Sustainability Assessment during Early Product Development: The Use Case 86

Abstract 87

4.1 Introduction 88

4.2 Background 90

4.3 Related Research 93

TABLE OF CONTENTS (Continued)

page

4.4 Fluid Stability 95

4.4.1 Stability Evaluation 97

4.4.2 Stability Evaluation Procedure 98

4.5 Toxicity Evaluation 99

4.5.1 Toxicity Evaluation Procedure 101

4.6 Results and Discussion 103

4.6.1 Fluid Stability Evaluation 103

4.6.2 Toxicity Evaluation 106

4.7 Conclusions 113

Chapter 5 - Summary and Conclusions 117

5.1 Chapter Overview 117

5.2 Research Summary 117

5.3 Conclusions 121

5.3.1 Conclusions: Manufacturing Case 122

5.3.2 Conclusions: Use Case 123

5.4 Contributions 125

TABLE OF CONTENTS (Continued)

page

5.4.1 Contributions: Manufacturing Case 125

5.4.2 Contributions: Use Case 126

5.5 Opportunities for Future Research 127

5.5.1 Opportunities for Future Research: Manufacturing Case 128

5.5.2 Opportunities for Future Research: Use Case 129

Bibliography 131

Appendices 144

LIST OF FIGURES

Figure Page

1.1. Integrating energy and carbon footprint quantification into manufacturing process flow and supply chain network design (adapted from [8]) 4

1.2. Thesis overview... 9

2.1. Life cycle assessment processes [38] 20

3.1. Influence of design on product life cycle stages from cradle to grave (Bohm et al., 2010)... 45

3.2. U.S. greenhouse gas emissions for 2010 (based on CO_2e) (U.S. EPA, 2012).. 48

3.3. Disassembled view of Backpack 2 58

3.4. Schematic of supply chain network alternatives for textile product manufacturing... 61

3.5. Backpack manufacturing process flow with textile production flow...... 64

3.6. Comparison of the energy consumption for backpack manufacturing and supply chain networks 81

3.7. Comparison of the carbon footprint for backpack manufacturing and supply chain networks 82

4.1. Effect of time on average ZnO NP size.. 104

4.2. Effect of time on average TiO_2A NP size 104

4.3. Effect of time on average TiO_2B NP size.. 105

LIST OF FIGURES (Continued)

Figure | Page

4.4. Mortality rate among samples exposed to suspensions with and without ZnO NPs 107

4.5. Mortality rate among samples exposed to suspensions with and without TiO_2A NPs.. 108

4.6. Mortality rate among samples exposed to suspensions with and without TiO_2B NPs.. 108

4.7. Average number of malformations among surviving samples exposed to suspensions with and without ZnO and TiO_2A NPs 109

4.8. Mortality rate among samples exposed to suspensions with 5 g/L NPs 110

4.9. Mortality rate among samples exposed to suspensions with 7.5 g/L NPs 111

4.10. Mortality rate among samples exposed to suspensions with 10 g/L NPs 111

LIST OF TABLES

Table Page

3.1. Supply chain network alternatives 63

3.2. Average emissions and energy conversion factors for various transportation modes a[120], b[121] 66

3.3. Two supply chain network alternatives for backpack production........... 67

3.4. Backpack transportation impact analysis results for supply chain Alternative A 68

3.5. Backpack transportation impact analysis results for supply chain Alternative B 69

3.6. Carbon footprint conversion factors for selected countries [126]........... 72

3.7. Backpack raw material processing impacts for the two supply chain design alternatives 73

3.8. Backpack fiber and component production impacts for the two supply chain design alternatives 75

3.9. Backpack fabric manufacturing impacts for the two supply chain design alternatives.. 77

3.10. Energy consumption and carbon footprint of final backpack manufacturing and assembly 78

3.11. Overall energy consumption and carbon footprint for production of two backpack design variants for supply chain Alternative A....................... 79

3.12. Overall energy consumption and carbon footprint for production of two backpack design variants for supply chain Alternative B 80

LIST OF TABLES (Continued)

Table Page

4.1. Properties of the selected ZnO and two types of TiO_2 NPs (NanoAmor, 2014).. 96

4.2. Effect of Time on average NP size.. 106

5.1. Comparison of the two research tasks... 121

LIST OF APPENDICES

Appendix Page

A The Textile Manufacturing Process Chain 144

B Energy Consumption and Carbon Footprint Database 145

C Energy Consumption Database Coding 148

D Carbon Footprint Database Coding 150

E Toxicology Observation Details 152

F Statistical Analysis of Toxicity Evaluation Results (Tukey Test) 160

G Statistical Analysis of Toxicity Evaluation Results 162

H Logistic Regression and Tukey Test RStudio Coding 164

LIST OF APPENDIX TABLES

Table		Page
E.1	Incidence rate of endpoints in zebrafish exposed to MWF dilutions (lower concentrations plate)	153
E.2	Incidence rate of endpoints in zebrafish exposed to MWF dilutions (higher concentrations plate)	154
E.3	Incidence rate of endpoints in zebrafish exposed to 5 g/L ZnO MWnF™ dilutions (lower concentrations plate)	155
E.4	Incidence rate of endpoints in zebrafish exposed to 5 g/L ZnO MWnF™ dilutions (higher concentrations plate)	156
E.5	Incidence rate of endpoints in zebrafish exposed to 5 g/L TiO2A MWnF™ dilutions (lower concentrations plate)	157
E.6	Incidence rate of endpoints in zebrafish exposed to 5 g/L TiO2A MWnF™ dilutions (higher concentrations plate)	158
E.7	Incidence rate of endpoints in zebrafish exposed to 10 g/L TiO2A MWnF™ dilutions (lower concentrations plate)	159
F.1	Tukey test results	160

CHAPTER 1 - INTRODUCTION

1.1 Overview

The current chapter presents the motivation of the research conducted as a part of this thesis followed by the background to address the research objectives. It describes the problem statement, research tasks, and outline of the thesis.

1.2 Motivation

Integration of sustainability principles including environmental, economic, and societal aspects into product design and manufacturing processes is crucial for decision makers. Product design is an activity that has substantial effects on global sustainability, e.g., in terms of the economic aspect, investing 5-7% of the entire product cost in its early design can decrease total cost by 70-80% [1]. In terms of the environmental aspect of sustainability, 1667×10^6 metric tons of carbon dioxide will be emitted annually by the industrial sector alone in United States by 2030 which makes it imperative to design products that are environmentally sustainable [2].

Due to the important role of designers in early product development and the existing uncertainties regarding product embodiments at the early design stage, different tools and methods are needed for designers to consider all aspects of sustainability [3]. From this perspective, a new challenge faced by designers is the need to shift the centering of product design from only the economic aspect to encompass the environmental and social aspects as well.

Products require various processes and processing steps to convert raw materials into the final product. While some manufacturers are pursuing integrating sustainability principles into the product design, the environmental aspect remains often not well accounted for in the early product development stage. A quantitative assessment of environmental impact of products and services requires the collection of a wide array of data, which is time and cost intensive, especially for a complex design [4]. Thus, a need exists for further investigation in this arena.

Some of the most challenging recent issues faced by decision makers globally include use of non-renewable resources, GHG emissions and climate change, human health risks, toxicity, and potential health hazards [5], [6]. Choices made by designers can have a significant impact on environmental impacts. As such, materials, manufacturing processes, transportation, and product end-of-life should be considered in the early design stage [1]. Product environmental impacts from raw material extraction, materials processing, and manufacturing operations to transportation and the use phase can be evaluated at the early design stage using a variety of techniques. Approaches such as design for environment (DfE) or eco-design, life cycle engineering (LCE), life cycle assessment (LCA), and quality function deployment (QFD) can assist in assessing the environmental sustainability of products, which will be described in Chapter 2. Limitations of these approaches, however, such as time intensity in data collection and inaccuracy in defining the scope, remain a focus of this research and will also be discussed in Chapter 2.

1.3 Background

Throughout manufacturing industry, interest and activity toward integrating a life cycle perspective into the product design process has continued to increase. Due to recent concerns over the rate of non-renewable energy consumption and associated emissions and health concerns, industry has sought methods and technologies to support energy efficiency practices and reduction of human health risks during product manufacturing, use, and end-of-life.

The primary approach for improving decisions related to environmental performance is life cycle assessment (LCA). LCA is a decision support method that can assist the evaluation of product and environment interactions through all stages of the product life cycle, including raw material extraction and processing, manufacturing and assembly operations, product use, product end-of-life, and related transportation processes [1], [7]. These stages encompass what is often referred to as the *cradle-to-grave* product life cycle. Another boundary commonly considered is the *cradle-to-gate* product life cycle, which encompasses material extraction through the product manufacturing "gate." Process-based LCA requires data and information to be collected for each process within the system boundary. With this knowledge, the total energy and carbon footprint can be calculated for various supply chain configurations to determine the preferred route to product manufacture. These approaches are illustrated in Figure 1.1.

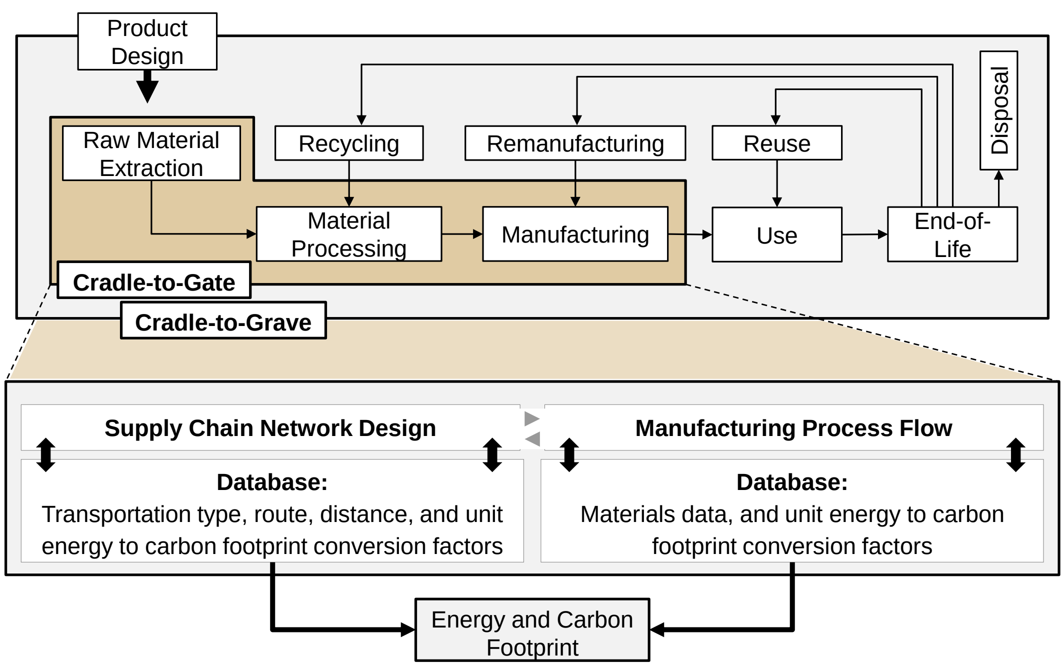

Figure 1.1 Integrating energy and carbon footprint quantification into manufacturing process flow and supply chain network design (adapted from [8])

One of the challenges faced by decision makers at early design stage is consideration of environmental impacts. By using LCA, efforts have been undertaken to more precisely calculate environmental impacts, such as energy consumption, carbon footprint, radiation, and toxicity, to support sustainability assessment of products [9]–[12]. Hertwich and Peters, for example showed that 72% of greenhouse gas (GHG) emissions result from household consumption and related transportation [13]. In terms of energy consumption and carbon footprint, O'Driscoll showed that it is expected that worldwide energy demand and price will continue to increase [14]; thus, determining the total energy consumption of a product during its life helps stakeholders and designers explore new ways to improve energy efficiency.

Consideration of human health risks and safety risen up to another challenge. Similarly, the product use phase must be addressed in LCA studies in order to carry out industry needs in development of new products. For example, the health of manufacturing company and plant workers is highly important to avoid cancers and fluid contaminants, [15]–[17]. In terms of nanotechnology, nanoparticle (NP) is a growing topic, yet researchers around the globe have been investigating on its potential health hazards such as pulmonary and cardiovascular diseases and air pollutants [18].

Final challenge is supporting data and decision making methods. Importantly, product design changes affect the environmental impacts and human health risks associated with the manufacturing processes and supply chain activities that are often poorly understood by design teams due to the amount of information gathering necessary to support analysis. Using collected data and suggested improvements gathered by researchers can accelerate the future studies. For instance, Hasanbeigi and Price provided a review of energy use and efficiency improvement opportunities for major processing activities across the textile supply chain [19]. Several studies demonstrated potential improvements through process planning using input-output process modeling and optimization based approaches [20]–[22].

In developing new products, challenges such as safety concerns, human health risks, and toxicological responses of the products arise. Thus, assessment methods and applications need to be explored to assist engineers in reducing product environmental impacts and human health risks from the early stages of product development. These challenges will be addressed in this research by investigating the product manufacturing and product use phases.

1.4 Research Objectives

One purpose of this research is the integration of the environmental sustainability aspect into the design of products, manufacturing processes, and relevant supply chain networks to assist decision makers. Energy consumption and the related carbon footprint of product manufacturing from raw material extraction to assembly of the final product need to be evaluated. Thus, a comprehensive process-based approach to estimate the cradle-to-gate energy consumption and related carbon footprint for product design variants needs to be pursued.

The other purpose of this study is to assist early stage design decisions by understanding the environmental and human health impacts of products during their use phase. To ensure the safety of new products, technology, and services, precautionary concerns regarding the products use phase must be considered during their development to avoid human health risks and environmental impacts.

1.5 Research Tasks

The research presented herein is comprised of the tasks presented below to address the above research objectives.

Task 1. Sustainability Assessment during Early Product Development: The Manufacturing Case. The main objective of this task is to consider the environmental sustainability of the manufacturing processes and relevant supply chain networks during early product development through process-based modeling for common products. New methods must assist design decision makers to more precisely calculate environmental metrics, such as energy consumption and carbon footprint. The research conducted under this task develops a method to predict the cradle-to-gate energy consumption and carbon footprint during the design stage for global production of textile-based products. In a demonstration of the approach, two backpacks with variant designs are selected as comparative products to investigate the influence of design changes on environmental impacts of product manufacturing processes and supply chain networks. The system boundary includes raw material extraction, materials processing, manufacturing operations, and transportation for each backpack component.

Task 2. Sustainability Assessment during Early Product Development: The Use Case. The objective of this task is to investigate precautionary environmental and human health concerns of product use during early product development through experimental analysis for novel products. For instance, for nanotechnologies it is especially critical to better understand and mitigate harm during early product development. The environmental and human health impacts of nanoparticles (NPs) are often uncertain or unknown. Since the addition of NPs to metalworking fluids (MWFs) is a new technology, the change in the stability and biological responses of the MWF needs to be explored. Thus, to ensure the safety of using NPs in MWFs, toxicological assessment of metalworking nanofluids (MWnF™) must be undertaken. To ensure a viable fluid, however, evaluation of the stability of NPs in the base fluid must be conducted prior to toxicological assessment.

Figure 1.2 presents the overall scope of this thesis including the research objectives and research tasks.

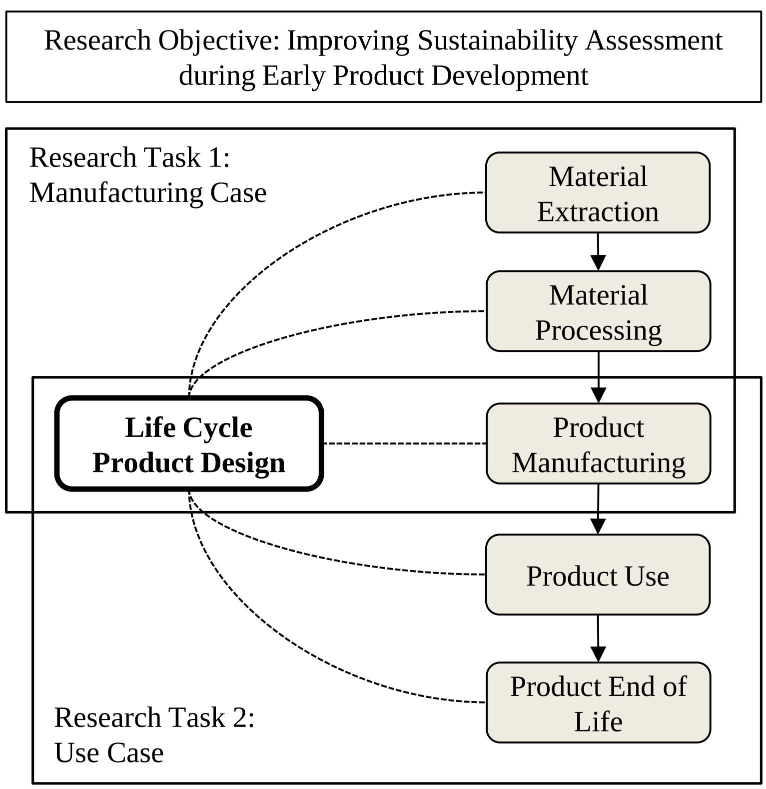

Figure 1.2 Thesis overview

1.6 Thesis Outline

This thesis has five chapters. Chapter 1 provides the motivation of the research, a brief background, research objectives, research tasks, and research outline.

Chapter 2 provides a literature review of the recent studies related to the integration of supporting sustainability principles into the design of products, manufacturing processes, relevant supply chain networks, and the use phase to assist decision makers. This review summarizes the past and current findings and identifies the research gaps leading to support the methods applied in this current research. First, the importance of and need for the integration of supporting sustainability principles into product design at the early design stage is described. Second, the current methods and tools for assessing product environmental sustainability are discussed. Third, environmental sustainability metrics, sustainable manufacturing processes from raw material extraction to finished product, and supply chain processes are reviewed. Finally, environmental precautionary design principles for development of new products and technologies are explored.

Chapter 3 describes a comprehensive process-based approach which is developed to estimate the cradle-to-gate energy consumption and related carbon footprint for product design variants. The approach accounts for energy use and related carbon footprint to support the simultaneous design of the manufacturing process flows and related supply chain network within a cradle-to-gate scope. The system boundary includes raw material extraction, materials processing, manufacturing operations, and transportation for each component of two backpack design variants.

Chapter 4 presents the investigations of the stability and toxicity of several metal working nanofluids MWnF™ formulations. In this part of the research, investigating the product use phase in order to address the industry needs in developing new products with a precautionary approach is described. Testing methods, related methodologies, research outcomes, findings, and learnings are provided.

Chapter 5 summarizes and concludes the research discussed in the previous chapters. A discussion about the findings and obstacles is presented. The results, conclusions, contributions, and opportunities for future work are discussed as they relate each research task (i.e., the manufacturing case and the use case).

CHAPTER 2 - LITERATURE REVIEW

2.1 Chapter Overview

In the first part of this chapter, the importance of the integration of supporting sustainability principles into the product design at early design stage is given. A review of current methods and tools used in assessing the environmental sustainability of products, processes, and system is included. Then, a review of the recent literature on environmental sustainability metrics, sustainable manufacturing process, and supply chain processes is presented.

In the second part of this chapter, the investigation of the environmental concerns during the product use phase is given. First, a brief background of the MWFs and the abilities to improve the machining processes is provided. Then, a review of recent literature on how adding NPs to MWF can improve MWF characteristics is described. Since, the literature has been shown that adding NPs such as CuO and Al_2O_3 to MWF can be a toxic [23], [24], therefore the toxicology tests need to be reviewed. However, before doing the toxicity test, the stability of MWnF™'s stability needs to be discussed.

2.2 Manufacturing Case

2.2.1 Background

Integration of sustainability principles into product design and manufacturing processes is crucial for decision makers as it helps them consider environmental, economic, and societal aspects of sustainability during the product design. Product design is an activity that has substantial effects on global sustainability. As such, materials, manufacturing processes, transportation, and end-of-life should be considered in the early design stage [1]. Pursuing the application of design for environment (DfE) during the early product design stage, for example, mitigates environmental impacts and boosts product competiveness [25]. In economic terms, investing 5-7% of the product cost in its early design can decrease its total cost by 70-80% [1]. In the social context, sustainability aims to encourage companies to conduct business in a responsible manner by providing information about the potential social impacts derived from activities in the life cycle of a product [26]. Due to the important role of designers in product design and existing uncertainties of the design stage, different tools and methods are needed for designers to consider all aspects of sustainability [3], including environmental, economic and societal.

2.2.2 Sustainability Metrics

Two key measures of product environmental impacts are energy consumption and carbon footprint. It is expected that worldwide energy demand and price will continue to increase, thus determining the total energy consumption of a product during its life helps stakeholders and designers explore new ways to improve energy efficiency [14]. Hertwich and Peters showed that 72% of greenhouse gas (GHG) emissions result from household consumption and related transportation. GHGs include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and halogenated compounds and can be compared on the basis of carbon dioxide equivalents (CO_2e) [13]. Thus, carbon footprint can be determined with respect to direct and indirect greenhouse gas (GHG) emissions across the product life cycle.

The importance of using energy consumption and carbon footprint as (1) environmental impact measures of manufacturing activities, (2) as indicators of global climate change, high energy consumption, and health concerns, and (3) their use in assisting governmental decision makers have been reported widely in the literature [9]–[12]. By evaluating energy consumption of product manufacturing and the associated CO_2 and other GHG releases during product design, the environmental performance of the product can be improved. Such improvements can provide competitiveness in the marketplace by appealing to environmentally conscious consumers, as well as by reducing operational costs of energy consuming products.

2.2.3 Current Methods and Tools for Environmental Sustainability

To have environmentally friendly product to address the industrial needs and environment policies, several tools have been explored are presented below.

2.2.3.1 Design for Environment

Design for environment, or eco-design, is a design method which considers environmental impacts, human health, and safety during development of a product, from material extraction to end-of-life [27]. Occupational and consumer safety, resource protection, pollution prevention, waste reduction, and recyclability are applications of DfE as per Fiksel's framing of the concept. Reducing carbon footprint and supply chain cost simultaneously during design stage is a recommended use of the DfE [28]. These authors demonstrated that decision maker choices can have a significant impact on total transportation cost and environmental impacts during product manufacturing. Johansson introduced six areas of concern to improve integration of eco-design in product design development: management, customer relationships, supplier relationships, development process, competence, and motivation [29]. Several methods and tools related to the eco-design, along with a discussion of their advantages and disadvantages are available for designers and decision makers to solve different problems during product design [30].

2.2.3.2 Life Cycle Engineering

Life cycle engineering (LCE) is the application of scientific principles in the product design and manufacturing stages to protect the environment and natural resources with special attention to the economic aspect of product cost [31]. Hence, LCE provides a basis for understanding the environmental attributes at each stage of the product life cycle and, consequently, supplies a foundation to decision making before manufacturing takes place [31]. Thoughtful attention should be paid to the redesign of the product for environmental performance as well as economic and social in order to improve the design [1].

2.2.3.3 Eco-design Checklist

Methods have been developed to assist design decision making. Eco-design checklists, for example, offer a qualitative tool as a checklist that uses a list of questions and items to assess the product environmental impacts at the early design stage [32]. This tool helps designers decide whether a product or material is harmful to the environment or not. Different questions can be used in this method that are convenient to answer, such as “what are the significant environmental aspects of the product during its life cycle?” or “which eco-design guideline should be used for the specific product?” [33]. This tool is subjective when it is compared to LCA-based tools, is mostly used in the early design stage, and requires knowledge and experience [1].

2.2.3.4 Quality Function Deployment

Quality function deployment (QFD) based tools are familiar to designers in meeting specific requirements. QFD tools can be semi-quantitative or semi-qualitative, which makes them amenable to being applied to consider potential environmental impacts during the early design stage, while satisfying customer needs [32]. Masui et al. presented a method based on QFD that considers environmental aspects and product quality requirements simultaneously in the early design stage to improve product quality [34]. The focus of QFD-based tools is on product specification development, which is different from the perspective of LCA-based tools [1]. Additionally, methods such as artificial neural networks and fuzzy logic can be applied to QFD-based tools because they are simpler, and they generate more customer-based, higher quality products [35].

2.2.3.5 Life Cycle Assessment

Life cycle assessment (LCA) is a decision support tool that can assist eco-design through the evaluation of product and environment interactions with respect to the energy and material flows through all stages of the product life from cradle-to-grave, including raw material extraction, manufacturing processes, transportation, use, remanufacturing, reuse and recycling, and, ultimately, disposal, [1], [7]. LCA is the most popular and widely used method in comprehensively assessing various environmental impacts, such as energy use and global warming potential (GWP). While LCA is appropriate for a quantitative assessment of environmental impact of products and services, it requires the collection of a wide spread of data, which is time and cost intensive, especially for a complex design [4].

LCA has been used as a support tool in an eco-design approach considering the uncertainties of the design stage, and integrating multi-objective optimization [36], it demonstrates a solution's utility in assisting designers. A challenge faced by designers is the need to shift the framing of product design from being relevant only to the economic aspect to all sustainability aspects [37]. An effort in this direction is a new eco-design methodology that takes advantage of LCA and visual tools to correlate environmental impacts with product function in the early design stage [37]. Such developments can assist designers in more quickly navigating the design space. Various impact assessment methods do exist to support designers in evaluating the potential environmental impacts of their decisions. For example, ReCiPe 2008 is an impact assessment method that is relatively new to practice [38]. It is based on the integration of prior methods, and considers eighteen midpoint impacts (e.g., ecotoxicity, acidification, and fossil depletion) and three endpoints (i.e., human health, ecosystem quality, and resource availability).

LCA performed to undertake the studies with the aim of energy consumption optimization which is a restraint in industries [39]. LCA guidelines have been widely provided by the International Organization for Standardization (ISO) 14040 family of standards [40]. LCA consists of four stages shown in Figure 2.1 [38], [39]–[44].

1. Goal and scope definition: In this stage, product system description, system boundaries, functional unit, assumptions and limitations are defined. The processes considered in LCA analysis will be determined by system boundaries. Functional unit quantifies what is being studied precisely, e.g. a simple backpack in this study.

2. Life cycle inventory (LCI): In this stage, all basis and relevant data are gathered and organized to build up the environmental impacts and identify potential impacts improvements. LCA process in this stage needs an accurate and detailed

collected data. This data can be collected from companies, organizations, experiments, literature, and available data bases.

3. Life cycle impact assessment (LCIA): This stage helps to provide the indicators to analyze the potential contributions of the emission and resources explored in LCI stage. LCIA evaluate and assess the environmental impacts and human health risks of the resources and release identified in LCI stage.

4. Life cycle interpretation: In this stage the information from the conclusion identified in last stages will be qualified, checked, and evaluated to present them in manner of requirements described in goal and scope of the study. Based on ISO definition, this stage must introduce the conclusions, explain the limitations, and propose the recommendations [39].

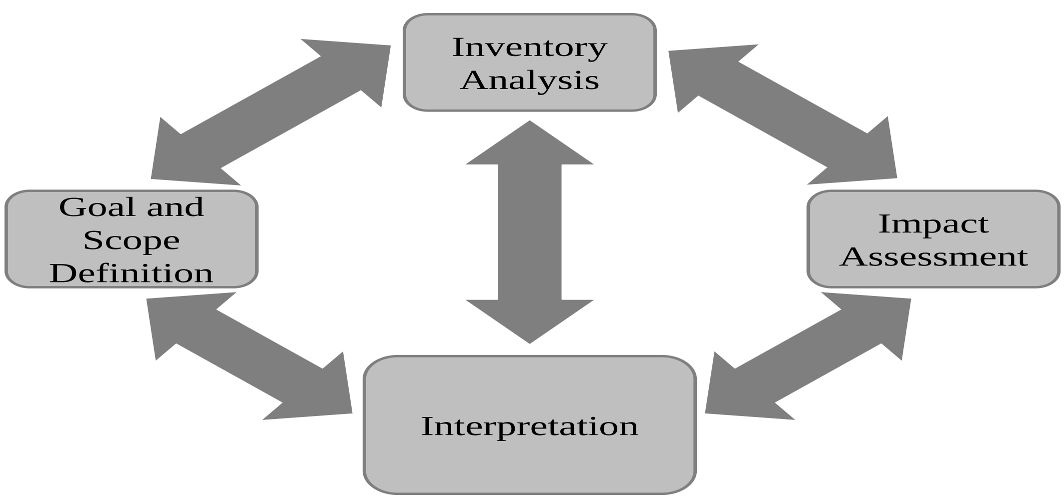

Figure 2.1 Life cycle assessment processes [39]

LCA is the most popular and widely used method in comprehensively assessing various environmental impacts, such as energy use and global warming potential (GWP). While LCA is appropriate for a quantitative assessment of environmental impact of products and services, it requires the collection of a wide spread of data, which is time and cost intensive, especially for a complex design [4]. In overall, LCA is a complex method provided the collected data to evaluate the inputs and outputs of the product system by assessing the environmental impacts [46]. LCA can identify the potential ways to improve the product environmental impacts during its life cycle.

2.2.4 Sustainable Manufacturing Process Considerations

Sustainable product development requires the analysis of manufacturing processes and supply chain network activities, simultaneously. Thus, the energy consumption and carbon footprint for each process must be considered from cradle to gate. Products require various processes and processing steps to convert raw materials into the final product. The synthetic textile manufacturing process chain, for example, starts with the chemical processes to produce polymers, followed by fiber manufacturing, yarn processing, fabric production, and final product manufacturing processes (Appendix A). Due to the variety of the processes in textile manufacturing, different facilities are needed to produce the finished product, which leads to a large amount of energy use. Hasanbeigi and Price provided a review of energy use and efficiency improvement opportunities for major processing activities across the textile supply chain [19]

Product design and manufacturing processes need to be studied at the early design stage to understand the economic and environmental aspects simultaneously [47]. Giachetti presented an analytical tool that helps designers decide what materials and processes should be used by employing a ranking system to reduce the environmental impact [48]. This decision support system was created especially for aiding material selection based on a designer's preference. On the other hand, manufacturing process-related environmental impacts can be minimized and improved by looking at three categories: process improvement, new process development, and process planning [1]. New process development can lead to replacing conventional manufacturing processes with new processes exhibiting lower environmental impact. New manufacturing processes, e.g. additive manufacturing, may help designers address environmental impacts, in addition to product costs, in certain applications. Similarly, a metalworking fluid delivery system can be improved by using a water-based fluid or by switching to a gas-based lubrication system [49]. Another study found that replacing shot peening and dry turning with laser shock peening and laser assisted turning, respectively, could significantly reduce environmental impacts [50]. Several studies have demonstrated potential improvements through process planning using input-output process modeling and optimization based approaches [20]–[22]. To improve environmental performance of the textile industry, including energy consumption and carbon footprint, efforts during the design phase can focus on decisions that impact manufacturing processes. For instance, energy efficiency in yarn spinning processes, weaving processes, wet processing, and fiber production can be improved by different solutions [19].

One goal of this research is to determine cradle-to-grave energy consumption and related carbon footprint of a product, which has been widely studied. For example, reducing the energy consumption and related carbon footprint of conventional metal manufacturing processes, such as turning, has been one of the widespread subjects in this area [51], [52]. Haapala et al. studied a set of manufacturing processes, e.g., sand casting, bending, welding, and laser cutting, for the production of large steel products [53]. The objective was to estimate materials and energy use and associated wastes using a spreadsheet tool. A recent study by Dietmair and Verl described an approach to determine the energy consumption of production equipment and demonstrated the method for the milling process [54]. Similarly, Diaz et al. investigated the energy consumption of the milling process by measuring the material removal rates and studying the power demand to find and characterize the energy consumption [55]. According to a review of engineering research in sustainable manufacturing, fundamental aspects include metric definition and decision making, which are key tasks at the early design stage [56].

Researchers have established a method to analyze manufacturing processes and quantify related energy consumption based on LCA, known as Unit Process Life Cycle Inventory (UPLCI) in the United States and as the Cooperative Effort on Process Emissions in Manufacturing (CO_2PE!) in Europe [57]–[59]. According to these methods, energy consumption and carbon footprint in product manufacturing processes can be evaluated by using the literature, tools, software, or experiments. First, the energy consumption of each manufacturing process would be explored. Second, the related carbon footprint can be measured either directly from the manufacturing processes or by using a conversion factor. For instance, Alsaffar et al. looked at how changes in the design of a three-ring binder affected manufacturing and supply chain impacts [60]. The study was conducted using LCA software (SimaPro) and compared eight three-ring binder design alternatives. It was found that transportation impacts were low compared to material and manufacturing impacts. The same characteristic was found when applying a process-based approach for bicycle pedal manufacturing [61].

The manufacturing research community continues to invest in product design and process modeling projects to enhance the environmental performance of manufacturing processes and systems. This is often approached by focusing on reducing the energy consumption, and hence the carbon footprint, of manufacturing activities. A microeconomics-based model which represents reduction in energy consumption, carbon footprint, and total cost has been investigated [62]. Fang et al. applied linear programming to consider the power and optimize energy consumption for scheduling a set of manufacturing processes [22].

Duflou et al. divided the manufacturing activities into the five level including unit process, machine system, facility, multi-factory system, and supply chain [63]. In each level, a variety of options were discussed to improve the energy efficiency, optimize the manufacturing system, and reduce the environmental impacts. Umeda et al. proposed the framework to integrate the product life cycle and product design to reduce the environmental impacts and resources. They reviewed methods and tools related to LCE as well as some practical cases to apply life cycle planning [64]. In addition to manufacturing-process related research, efforts have focused on reduction of energy consumption and carbon footprint from a supply chain perspective.

2.2.5 Sustainable Supply Chain Considerations

Due to globalization, products are often assembled in one location, while components may originate from geographically dispersed locations. Thus, supply chain considerations are as important as manufacturing processes in product life cycle impacts. Total cost and environmental impacts reduction for transportation of raw material to the manufacturing companies and transportation of the final products to the customers are main concerns of academic and industry researchers. Reverse logistics (RL), for example, is a topic which involves the collection and handling of used products, which can be managed to reduce product cost and environmental impacts from a systems perspective [65]. Recently, Ilgin and Gupta reviewed 540 peer-reviewed papers to examine the current research progress in environmentally conscious manufacturing and product recovery (ECMPRO) [65]. They focused on four phases of the product life cycle: design, supply chain networks, remanufacturing, and disassembly. Another review of the sustainable supply chain management literature was completed by Seuring and Müller, which referenced 191 published papers from 1994-2004 [66]. They identified two different strategies, i.e., for supply chain management risk and performance and for sustainable products.

Carbon emissions which result from a product supply chain have been identified as a threat to the global warming [67]. Carbon footprint can be measured and compared for different supply chain modes and networks. For instance, rail transport has been shown to have a 3-9% lower carbon footprint than other transportation modes [68]. Chiu et al. investigated a product design framework based on a graph theory optimization methodology with the combination of LCA which accounts for cost and carbon footprint at the product development phase [28]. Their approach was applied to minimize the cost and carbon footprint of a global supply chain for bicycle manufacturing. The results showed that product environmental impacts can be reduced during the early design stage. Bevilacqua et al. performed a study on the effect of different supply chain networks on the carbon footprint of textile product manufacturing (a wool sweater) [69]. With the help of Monte Carlo simulation, variations of transportation type, combinations of transportation type and route, and selection of suppliers were explored to assess the supply chain carbon footprint.

Predicting supply chain carbon footprint is a topic that designers need to consider at the early design stage. This understanding can only be fully developed if all information about distributors, supplier companies, and customer stores exist. Due to the different suppliers of raw materials, different transportation methods, and diverse systems of distribution to the customers, many different supply chain networks can be designed.

Paying attention to the environmental consequences of the transportation motivates decision makers to integrate supply chain considerations into the product design decisions. In this research, efforts focus on addressing how different supply chain transportation modes and routes affect energy consumption and related carbon footprint.

2.3 Use Case

2.3.1 Background

Metalworking fluids (MWFs) are used in machining processes to decrease the heat created by the machining operations, reduce the effect of friction, provide lubricity, and enhance thermal conductivity [70]. Due to the large use of MWFs globally, which is more than 500 million gallons annually, industrial stakeholders are concerned about the sustainability of using MWFs [71]. Manufacturing sustainability performance (e.g., environmental, economic, health and safety aspects) can be enhanced by improving the efficiency of MWFs. For instance, improving the heat transfer properties of MWFs can reduce the rate of cutting tool replacement, which is highly expensive [72]. To enhance the environmental aspect, using biocide-free MWFs compared to the conventional mineral oil based have been investigated by Winter et al., which led to better results with regard to the measured machining forces and workpiece surface roughness [73]. To reduce the environmental and worker health impacts, minimum quantity lubrication (MQL) sprays of MWFs can be applied, which also has shown better performance and enhanced penetration into the cutting zone compared to conventional water-based fluid [74]–[77]. Microfiltration can reduce health risks and environmental impacts of using MWFs [78]. Zhao et al. developed a framework to evaluate the economics of microfiltration implementation along with its environmental performance [79]. Choosing an appropriate MWF from among all existing products can affect the lifetime and operation of milling machines [80]. To avoid the risks and recognize the potential hazard of using MWnF™, the sustainability of nanofluids needs to be discussed [81].

Adding nanoparticles (NPs) can improve MWF performance. Previous studies have shown that nanoparticle (NP) additives to MWFs will decrease the friction resistance, improve the lubricity and thermal conductivity, reduce the cutting force, and improve the machining performance more than NP-free MWFs [82]–[84]. The advantages of using metalworking nanofluids (MWnF™) can be expressed as follows: saving energy and fluid consumption, reduction of related economic and environmental impacts, and enhancement of cutting tool life.

2.3.2 Machining Processes Improvement and Uncertainties about Nanoparticles

In this section, first prior studies shown that NPs additives to MWFs improved the MWF performance will be presented. Secondly, a literature related to the uncertainties about NPs life cycle environmental performance specifically during the use phase will be explored.

Tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2) NPs were investigated as additives and found to play a key role of solid lubrication where fluids were unable to support the loads under severe conditions [82]. Mosleh et al. showed that using certain concentrations of WS_2 and MoS_2 as additives in the modified oil for metal forming reduced the wear volume in testing of 440C ball-titanium sheet pairs and 440C ball-steel sheet pairs by 25-30% and 55-65%, respectively [84]. While the coefficient of friction (COF) of the 440C ball-titanium sheet pair was reduced by 10%, no improvement was noticed in the COF of the 440C ball-steel sheet pair.

LotfizadeDehkordi et al. employed a UV–Vis spectrophotometer and indicated that thermal conductivity enhancement was observed by using a high concentration of TiO_2 in water-based nanofluids [85]. The thermal conductivity of water nanofluids increased with increasing concentrations of Al_2O_3 and TiO_2 NPs

[86]. Using a 3% by volume alumina and a 1% by volume multi-walled carbon nanotube (MWCNT) nanofluids (NFs) in place of soluble oil was shown to significantly reduce the force, energy, and temperature of cutting [87]. Hu and Dong used 20 nm titanium oxide NPs as an additive to 500 SN base oil to evaluate the tribological properties of the fluid [88]. The results indicated that adding NPs decreased the COF by 12%, and the wear resistance and load capacity of the fluid were improved. Turgut et al. conducted a study to investigate the thermal conductivity and viscosity measurements of water-based TiO_2 nanofluid [89]. The results showed that with a 3% volume fraction of TiO_2, the thermal conductivity improved by 7.4% compared to the base fluid. The viscosity increased with the increase in volume fraction of NPs. McCook et al. added different NPs to an epoxy matrix to test the COF and wear resistance by using a linear reciprocating pin-on-disk tribometer [90]. Optimum wear resistance was observed with a 1% by volume ZnO and 14.5% by volume polytetrafluoroethylene (PTFE) NPs. Similarly, optimal COF reduction was found with 3.5% by volume ZnO and 14.5% by volume PTFE NPs.

Kotnarowski added CuO NPs to SN 100 and Hydrorafinat II basic oils to evaluate the COF reduction [91]. They concluded that adding 0.25% by volume CuO NPs is most effectively, and results in 10-25% reduction in COF. Shen et al. found that adding 5-20% by volume of 100 nm MoS_2 NPs to three different fluids (paraffin, soybean oil, and CANMIST) decreased the COF in grinding of cast iron by 30-50% [92]. Khandekar et al. studied metal cutting performance using a nano-cutting fluid made by adding 1% by volume of Al_2O_3 to a conventional cutting fluid [93]. The results showed that nano-cutting fluid decreased cutting force, tool wear, and surface roughness compared to the conventional cutting fluid.

Although MWnF™ improves the tribological properties of the base fluid, there are uncertainties about their life cycle environmental performance, specifically during the use phase. The toxicity of MWnF™ is one of the uncertainties that must be considered in their development [94]. Hoet et al. provided a comprehensive review of data analysis on health risks of using nanomaterials [6]. Even though the advantages of NPs are widely discussed in literature, the potential health risks of NPs are little known since the development of nanomaterials is in its early stages. Different nanomaterial attributes such as size, shape, and morphology need to be considered to evaluate the toxicity and develop biologically and environmentally safer MWnF™ formulations [18], [95].

Bai et al. studied the toxicity of 30 nm ZnO NPs in a water suspension using a zebrafish embryo test [96]. The results indicated that 0.05 and 0.1 % fraction of ZnO NPs cause mortality of the zebrafish embryos. In lower concentrations (1–25 mg/L), malformations such as body and tail deformation were observed.

2.3.3 Nanofluid Stability

Unsuspended aggregated particles cause the machining efficiency reduction and result in inaccurate toxicity test because of settling out of suspension [96], [97]. Thus, the first step is preparing the stable suspension prior to toxicology evaluation.

To improve the stability of NPs in the NF, ultrasonication can be applied. Ultrasonic frequency waves help to fully disperse the NPs in the mixture and fragment the agglomerate particles [98]. Xia et al. studied the preparation of stable nitrendipine nanosuspensions by using ultrasonication and improved the dissolution rate of the oral bioavailability drug [99]. Nanofluid stability improvement was reported by Sahakian in preparation of ZnO NPs for an MWnF™ by using the ultrasonication [100].

Abdullah et al. showed that both TiO_2 and ZnO can be dispersed stably in oil-based fluid and can be used as lubricant additives [101]. Adding TiO_2 will decrease the COF and increase wear resistance and load carrying capacity of MWFs [88]. Adding ZnO to a lubricant can enhance the lubricity and reduce a friction [102]. In addition, the low dissolution rate of ZnO and TiO_2 NPs in water makes them suitable candidates for suspensions with a variety of concentrations.

2.3.4 Toxicology Evaluation

Before realizing the commercial benefits of nanomaterials in industry, potential health hazards and exposure of nanoscale materials, such as inhalation and dermal routes of exposure, must be investigated [18]. To be assured that the materials are safe to use, the characteristics of the NPs such as size, shape, dissolution rate, and agglomeration state must be known [103]. Hussain et al. presented a review of physical and chemical characteristics of NPs to determine the exposure protocols and how nanomaterials affect living organisms [104]. A study by Lademann et al. revealed that TiO_2 used in sunscreens can penetrate to the hair follicle and stratum corneum [105]. Similarly, Baroli et al. studied the penetration of metallic NPs in human skin and the results revealed that NPs can penetrate to the hair follicle and stratum corneum, but they were unable to enter to the skin [106].

Hussain et al. studied the toxic effect of NPs including TiO_2 for use in industry with the in vitro rat liver derived cell line method [107]. The results revealed that a lower dose (10-50 mg/mL) of 40 nm TiO_2 NPs had no effect on mitochondrial function, while at the higher dose (100-250 mg/mL), significant effects existed. Chen et al. investigated the in vivo acute toxicity of TiO_2 NPs on adult mice by injecting various doses [108]. Passive behavior, loss of appetite, tremors, and lethargy were the signs that were exhibited in the treated mice when the deposited NPs were found in liver, kidney, and lung. Wu et al. studied the penetration of P25 (21 nm) TiO_2 NPs in mice skin and after 60 days, the results revealed that NPs can penetrate to the skin and reach several organs [109].

Beckett et al. tested a 500 μg/m^3 concentration of ZnO NPs for 2 hours on healthy human subjects, and no significant effects on respiratory, hematologic, or cardiovascular issues were observed [110]. A study by Wang et al., however found that oral exposure to varying doses of 20 nm and 120 nm ZnO NPs given to mice can cause damage to the liver, spleen, and pancreas [111]. Bai et al. studied the exposure of zebrafish to 30 nm ZnO NPs added to water in order to find the mortality and malformations of fish caused by varying concentrations of NPs [96]. They revealed that the mortality range for ZnO NPs is between 50 to 100 mg/L and the malformation range is between 1 to 25 mg/L.

2.3.5 Zebrafish Exposure Test

To assess human health risks and toxicological assessment, mammals have been used, which is cost and time consuming. The zebrafish model is a good alternative since it is a rapid toxicity evaluation model and the organisms are morphologically and psychologically similar to mammals [112]. Zebrafish organs are genetically similar to human organs and, thus the model allows researchers to have access to the evolvement stages to investigate a variety of human diseases [113]. Each female zebrafish can spawn hundreds of eggs per day and the fish organs will be developed within 48 hours [114]. To have statistically powerful assays, toxicological tests using zebrafish embryos can be repeated multiple times. It is noted that the zebrafish model is not a comprehensive solution to investigate all variety of human diseases, however, and other standard human toxicity testing should be completed before commercializing nano-based products.

2.4 Prior Research Limitations

While prior research discussed in this chapter has been widely applied to assess product environmental sustainability performance during manufacturing and use, several limitations exist [44], [97], [115], as summarized below.

2.4.1 Manufacturing Case

Studies dependent on LCA tools need to provide an assessment of the environmental performance of products and processes. Application of process-based approaches by industry practitioners to simultaneously analyze the manufacturing and supply chain energy consumption and carbon footprint during early product design has the following limitations:

- Time and cost intensity and errors involved in data collection, which result in incorrect data.
- Broad scope and boundaries which result in inaccurate results.
- Complexity and variability of product manufacturing processes, which is time and resource consuming.
- Data gathering requires review of many disparate sources and lack of pre-defined processes and data availability
- Selection metrics, weighting, data sources, which result in inaccuracy in defining the scope and boundaries of the system

2.4.2 Use Case

This research explored the challenges of safety concerns, human health risks, and toxicological responses in developing new products. In terms of the potential of NPs to improve MWF performance, several limitations and obstacles faced by researchers should be taken into consideration. Limitations associated with prior research reported in the literature include:

- While NP aggregation degrades fluid stability and tribological performance [97], stability of NPs in MWnF™ is rarely addressed in the literature. In particular, stabilizing TiO_2 NPs in a water- or oil-based fluid has not been addressed in the literature.

- Stability and biological responses of MWF with different NPs and diverse concentrations has not been addressed simultaneously in prior research.
- While shown to improve machining performance, there is not any published work on zebrafish toxicity assessment of TiO_2 MWnF™ with a commercial MWF as the base fluid.

CHAPTER 3 - SUSTAINABILITY ASSESSMENT DURING EARLY PRODUCT DEVELOPMENT: THE MANUFACTURING CASE

AUTHORS AND INSTITUTIONS

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Abstract

Throughout manufacturing industry, interest and activity toward integrating a life cycle perspective into the product design process has continued to increase. Due to recent concerns over the rate of non-renewable energy consumption and associated emissions, industry has sought methods and technologies to support energy efficiency practices and use of alternative energy sources during product manufacturing, use, and end-of-life. Efforts have been undertaken to more precisely calculate environmental metrics, such as energy consumption and carbon footprint, to support broader sustainable design decision making. Of specific focus in this paper, product design changes affect the environmental impacts associated with the manufacturing processes and supply chain – effects that are often poorly understood by design teams due to the amount of information gathering necessary to support analysis. The work reported endeavors to integrate sustainability principles into the design of products, manufacturing processes, and relevant supply chain networks to assist decision makers. In a demonstration of the approach, two backpacks with variant designs are selected as comparative products to investigate the influence of design change on environmental impacts of product manufacturing and supply chain networks. Energy consumption and the carbon footprint of backpack manufacturing from raw material extraction to assembly of the final product are evaluated. The system

boundary includes raw material extraction, materials processing, manufacturing operations, and transportation for each backpack component. The results show that manufacturing processes dominate the transportation-related environmental impacts. To the best of our knowledge, the reported work is the first to apply a comprehensive process-based approach to estimate the cradle-to-gate energy consumption and carbon footprint for textile-based product design variants.

Keywords

product design; textile manufacturing; cradle-to-gate life cycle assessment, supply chain management; environmental impacts; energy consumption; carbon footprint; sustainable product design

3.1 Introduction

Integration of sustainability principles into product design and manufacturing processes is crucial for decision makers as it helps them consider environmental, economic, and societal aspects of sustainability during the product design. Product design is an activity that has substantial effects on global sustainability. As such, materials, manufacturing processes, transportation, and end-of-life should be considered in the early design stage [1]. Pursuing the application of design for environment (DfE) during the early product design stage, for example, mitigates environmental impacts and boosts product competiveness [116]. In economic terms, investing 5-7% of the product cost in its early design can decrease its total cost by 70-80% [1]. In the social context, sustainability aims to encourage companies to conduct business in a responsible manner by providing information about the potential social impacts derived from activities in the life cycle of a product [26]. Due to the important role of designers in product design and existing uncertainties of the design stage, different tools and methods are needed for designers to consider all aspects of sustainability [3], including environmental, economic and societal.

The research reported herein describes a method to predict the cradle-to-gate energy consumption and carbon footprint during the design stage for global production of consumer goods. The method is then applied to demonstrate the evaluation of a textile-based product (a backpack). Prior to describing and demonstrating the approach, the background motivation and related research is presented. The paper concludes with a discussion of the developed method and a study of the results.

3.2 Background

Design for environment, or eco-design, is a design method which considers environmental impacts, human health, and safety during development of a product, from material extraction to end-of-life [27]. Occupational and consumer safety, resource protection, pollution prevention, waste reduction, and recyclability are applications of DfE as per [27] framing of the concept. Reducing carbon footprint and supply chain cost simultaneously during design stage is a recommended use of the DfE [28]. These authors demonstrated that decision makers' choices can have a significant impact on total transportation cost and environmental impacts during product manufacturing. Johansson introduced six areas of concern to improve integration of eco-design in product design development: management, customer relationships, supplier relationships, development process, competence, and motivation [29]. Several methods and tools related to the eco-design, along with a discussion of their advantages and disadvantages are available for designers and decision makers to solve different problems during product design [30].

Life cycle engineering (LCE) is the application of scientific principles in the product design and manufacturing stages to protect the environment and natural resources with special attention to the economic aspect of product cost [31]. Hence, LCE provides a basis for understanding the environmental attributes at each stage of the product life cycle and, consequently, supplies a foundation to decision making before manufacturing takes place [31]. Thoughtful attention should be paid to the redesign of the product for environmental performance as well as economic and social in order to improve the design [1].

Life cycle assessment (LCA) is a decision support tool that can assist eco-design through the evaluation of product and environment interactions with respect to the energy and material flows through all stages of the product life from cradle-to-grave, including raw material extraction, manufacturing processes, transportation, use, remanufacturing, reuse and recycling, and, ultimately, disposal, [1], [7] as shown in Figure 3.1. LCA is the most popular and widely used method in comprehensively assessing various environmental impacts, such as energy use and global warming potential (GWP). While LCA is appropriate for a quantitative assessment of environmental impact of products and services, it requires the collection of a wide spread of data, which is time and cost intensive, especially for a complex design [4].

LCA has been used as a support tool in an eco-design approach considering the uncertainties of the design stage, and integrating multi-objective optimization [36], it demonstrates a solution's utility in assisting designers. A challenge faced by designers is the need to shift the framing of product design from being relevant only to the economic aspect to all sustainability aspects [37]. An effort in this direction is a new eco-design methodology that takes advantage of LCA and visual tools to correlate environmental impacts with product function in the early design stage [37]. Such developments can assist designers in more quickly navigating the design space. Various impact assessment methods do exist to support designers in evaluating the potential environmental impacts of their decisions. For example, ReCiPe 2008 is an impact assessment method that is relatively new to practice [38]. It is based on the integration of prior methods, and considers eighteen midpoint impacts (e.g., ecotoxicity, acidification, and fossil depletion) and three endpoints (i.e., human health, ecosystem quality, and resource availability).

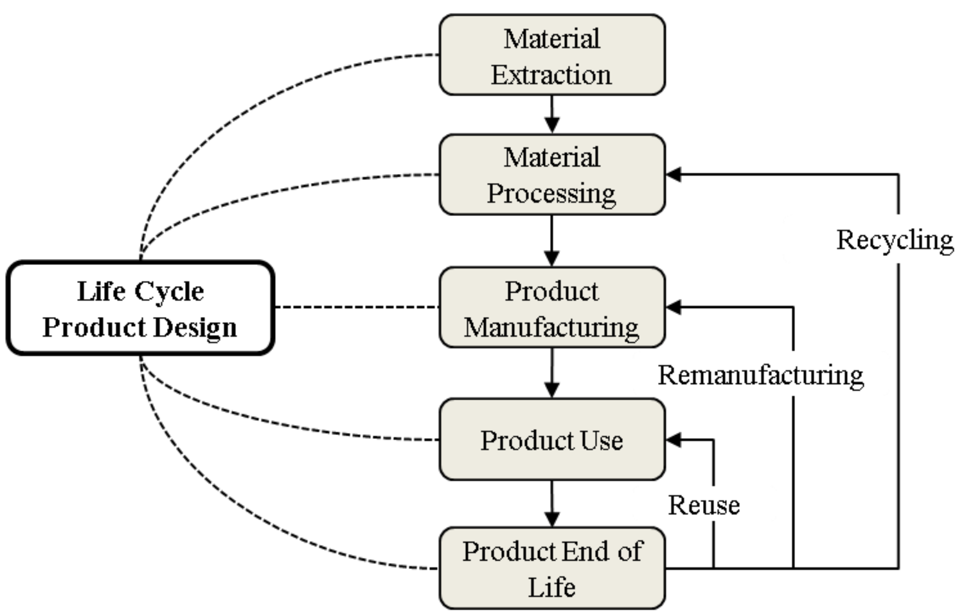

Figure 3.1 Influence of design on product life cycle stages from cradle to grave (Bohm et al., 2010)

Other methods have been developed to assist design decision making. Eco-design checklists, for example, offer a qualitative tool as a checklist that uses a list of questions and items to assess the product environmental impacts at the early design stage [32]. This tool helps designers decide whether a product or material is harmful to the environment or not. Different questions can be used in this method that are convenient to answer, such as “what are the significant environmental aspects of the product during its life cycle?” or “which eco-design guideline should be used for the specific product?” [33]. This tool is subjective when it is compared to LCA-based tools, is mostly used in the early design stage, and requires knowledge and experience [1].

Quality function deployment (QFD) based tools are familiar to designers in meeting specific requirements. QFD tools can be semi-quantitative or semi-qualitative, which makes them amenable to being applied to consider potential environmental impacts during the early design stage, while satisfying customer needs [32]. Masui et al. presented a method based on QFD that considers environmental aspects and product quality requirements simultaneously in the early design stage to improve product quality [34]. The focus of QFD-based tools is on product specification development, which is different from the perspective of LCA-based tools [1]. Additionally, methods such as artificial neural networks and fuzzy logic can be applied to QFD-based tools because they are simpler, and they generate more customer-based, higher quality products [35]. Thus, environmental metrics are a key aspect of sustainable design decision making, and are discussed below.

Two key measures of product environmental impacts are energy consumption and carbon footprint. It is expected that worldwide energy demand and price will continue to increase, thus determining the total energy consumption of a product during its life helps stakeholders and designers explore new ways to improve energy efficiency [14]. Hertwich and Peters showed that 72% of greenhouse gas (GHG) emissions result from household consumption and related transportation. GHGs include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and halogenated compounds and can be compared on the basis of carbon dioxide equivalents (CO_2e) [13]. Thus, carbon footprint can be determined with respect to direct and indirect greenhouse gas (GHG) emissions across the product life cycle. Figure 3.2 shows the contributions of various GHG emissions in the U.S. for 2010. It can be seen that CO_2 accounts for more than three-fourths of total GHG emissions.

The importance of using energy consumption and carbon footprint as (1) environmental impact measures of manufacturing activities, (2) as indicators of global climate change, high energy consumption, and health concerns, and (3) their use in assisting governmental decision makers have been reported widely in the literature [9]–[12].

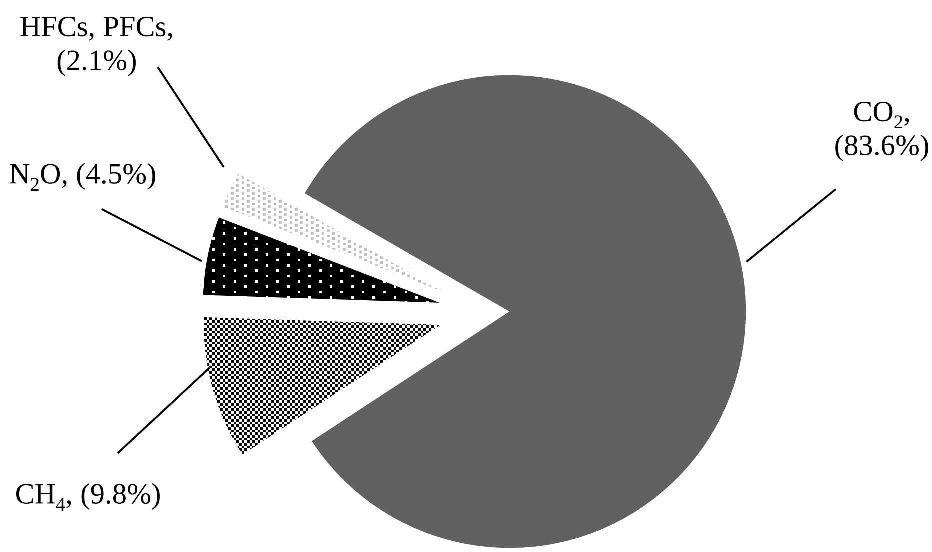

Figure 3.2 U.S. greenhouse gas emissions for 2010 (based on CO_2e) (U.S. EPA, 2012)

By evaluating energy consumption of product manufacturing and the associated CO_2 and other GHG releases during product design, the environmental performance of the product can be improved. Such improvements can provide competitiveness in the marketplace by appealing to environmentally conscious consumers, as well as by reducing operational costs of energy consuming products.

3.3 Related Research

The research presented herein is an extension of the work reported by Alsaffar and coworkers [61]. They presented a framework to reduce the energy consumption and carbon footprint from the cradle-to-gate perspective, considering conventional product manufacturing and supply chain networks simultaneously. Unit process modeling (UPM) was used as the primary analysis method and, to demonstrate the framework, bicycle pedal manufacturing was investigated. The pedal assembly was comprised of ten components using several materials, including steel, aluminum, and plastic. Manufacturing processes employed included casting, turning, milling, cutting, and drilling, which were modeled to evaluate the energy consumption for the production of each component. Efforts were made to consider more than one process flow alternative for each component to make the analysis more robust, which also included supply chain impact. Several raw materials supply chain network scenarios were assumed to elucidate transportation-related effects. The alternatives with the lowest environmental impact, measured using carbon footprint, were selected for each component to achieve the lowest overall cradle-to-gate carbon footprint. It was shown that simultaneous consideration of manufacturing and supply chain processes can impact decision making and improve product life cycle environmental performance in the design stage.

The current research undertakes a similar approach with a focus on textile product manufacturing. Work included extending the generalized models for underlying materials and components representative of textile-based products. In an application of the extended method, two backpacks are examined to demonstrate that the unit process modeling framework can be extended to assist designers in reducing the environmental impacts of various products, materials, and manufacturing processes. The methodology is described in greater detail in Section 3.4, below, with the balance of this section discussing the related supporting literature.

3.3.1 Manufacturing Process Considerations

Sustainable product development requires the analysis of manufacturing processes and supply chain network activities, simultaneously. Thus, the energy consumption and carbon footprint for each process must be considered from cradle to gate. Products require various processes and processing steps to convert raw materials into the final product. The synthetic textile manufacturing process chain, for example, starts with the chemical processes to produce polymers, followed by fiber manufacturing, yarn processing, fabric production, and final product manufacturing processes. Due to the variety of the processes in textile manufacturing, different facilities are needed to produce the finished product, which leads to a large amount of energy use. Hasanbeigi and Price provided a review of energy use and efficiency improvement opportunities for major processing activities across the textile supply chain [19]. Other researchers have widely explored these opportunities in the textile industry [19], [119], [120], and they are not reviewed herein.

Product design and manufacturing processes need to be studied at the early design stage to understand the economic and environmental aspects simultaneously [47]. Giachetti presented an analytical tool that helps designers decide what materials and processes should be used by employing a ranking system to reduce the environmental impact [48]. This decision support system was created especially for aiding material selection based on a designer's preference. On the other hand, manufacturing process-related environmental impacts can be minimized and improved by looking at three categories: process improvement, new process development, and process planning [1]. New process development can lead to replacing conventional manufacturing processes with new processes exhibiting lower environmental impact. New manufacturing processes, e.g. additive manufacturing, may help designers address environmental impacts, in addition to product costs, in certain applications. Similarly, a metalworking fluid delivery system can be improved by using a water-based fluid or by switching to a gas-based lubrication system [49]. Another study found that replacing shot peening and dry turning with laser shock peening and laser assisted turning, respectively, could significantly reduce environmental impacts [50]. Several studies have demonstrated potential improvements through process planning using input-output process modeling and optimization based approaches [20]–[22]. To improve environmental performance of the textile industry, including energy consumption and carbon footprint, efforts during the design phase can focus on decisions that impact manufacturing processes. For instance, energy efficiency in yarn spinning processes, weaving processes, wet processing, and fiber production can be improved by different solutions [19].

One goal of this research is to determine cradle-to-grave energy consumption and related carbon footprint of a product, which has been widely studied. For example, reducing the energy consumption and related carbon footprint of conventional metal manufacturing processes, such as turning, has been one of the widespread subjects in this area [51], [52]. Haapala et al. studied a set of manufacturing processes, e.g., sand casting, bending, welding, and laser cutting, for the production of large steel products [53]. The objective was to estimate materials and energy use and associated wastes using a spreadsheet tool. A recent study by Dietmair and Verl described an approach to determine the energy consumption of production equipment and demonstrated the method for the milling process [54]. Similarly, Diaz et al. investigated the energy consumption of the milling process by measuring the material removal rates and studying the power demand to find and characterize the energy consumption [55]. According to a review of engineering research in sustainable manufacturing, fundamental aspects include metric definition and decision making, which are key tasks at the early design stage [56].

Researchers have established a method to analyze manufacturing processes and quantify related energy consumption based on LCA, known as Unit Process Life Cycle Inventory (UPLCI) in the United States and as the Cooperative Effort on Process Emissions in Manufacturing (CO_2PE!) in Europe [57]–[59]. According to these methods, energy consumption and carbon footprint in product manufacturing processes can be evaluated by using the literature, tools, software, or experiments. First, the energy consumption of each manufacturing process would be explored. Second, the related carbon footprint can be measured either directly from the manufacturing processes or by using a conversion factor. For instance, Alsaffar et al. looked at how changes in the design of a three-ring binder affected manufacturing and supply chain impacts [60]. The study was conducted using LCA software (SimaPro) and compared eight three-ring binder design alternatives. It was found that transportation impacts were low compared to material and manufacturing impacts. The same characteristic was found when applying a process-based approach for bicycle pedal manufacturing [61].

The manufacturing research community continues to invest in product design and process modeling projects to enhance the environmental performance of manufacturing processes and systems. This is often approached by focusing on reducing the energy consumption, and hence the carbon footprint, of manufacturing activities. A microeconomics-based model which represents reduction in energy consumption, carbon footprint, and total cost has been investigated [62]. Fang et al. applied linear programming to consider the power and optimize energy consumption for scheduling a set of manufacturing processes.

Duflou et al. divided the manufacturing activities into the five level including unit process, machine system, facility, multi-factory system, and supply chain [63]. In each level, a variety of options were discussed to improve the energy efficiency, optimize the manufacturing system, and reduce the environmental impacts. Umeda et al. proposed the framework to integrate the product life cycle and product design to reduce the environmental impacts and resources [64]. They reviewed methods and tools related to LCE as well as some practical cases to apply life cycle planning. In addition to manufacturing-process related research, efforts have focused on reduction of energy consumption and carbon footprint from a supply chain perspective.

3.3.2 Supply Chain Considerations

Due to globalization, products are often assembled in one location, while components may originate from geographically dispersed locations. Thus, supply chain considerations are as important as manufacturing processes in product life cycle impacts. Total cost and environmental impacts reduction for transportation of raw material to the manufacturing companies and transportation of the final products to the customers are main concerns of academic and industry researchers. Reverse logistics (RL), for example, is a topic which involves the collection and handling of used products, which can be managed to reduce product cost and environmental impacts from a systems perspective [65]. Recently, Ilgin and Gupta reviewed 540 peer-reviewed papers to examine the current research progress in environmentally conscious manufacturing and product recovery (ECMPRO) [65]. They focused on four phases of the product life cycle: design, supply chain networks, remanufacturing, and disassembly. Another review of the sustainable supply chain management literature was completed by Seuring and Muller, which referenced 191 published papers from 1994-2004 [66]. They identified two different strategies, i.e., for supply chain management risk and performance and for sustainable products.

Carbon emissions which result from a product supply chain have been identified as a threat to the global warming [67]. Carbon footprint can be measured and compared for different supply chain modes and networks. For instance, rail transport has been shown to have a 3-9% lower carbon footprint than other transportation modes [68].Chiu et al. investigated a product design framework based on a graph theory optimization methodology with the combination of LCA which accounts for cost and carbon footprint at the product development phase [28]. Their approach was applied to minimize the cost and carbon footprint of a global supply chain for bicycle manufacturing. The results showed that product environmental impacts can be reduced during the early design stage. Bevilacqua et al. performed a study on the effect of different supply chain networks on the carbon footprint of textile product manufacturing (a wool sweater) [69]. With the help of Monte Carlo simulation, variations of transportation type, combinations of transportation type and route, and selection of suppliers were explored to assess the supply chain carbon footprint.

Predicting supply chain carbon footprint is a topic that designers need to consider at the early design stage. This understanding can only be fully developed if all information about distributors, supplier companies, and customer stores exist. Due to the different suppliers of raw materials, different transportation methods, and diverse systems of distribution to the customers, many different supply chain networks can be designed.

Paying attention to the environmental consequences of the transportation motivates decision makers to integrate supply chain considerations into the product design decisions. In this research, efforts focus on addressing how different supply chain transportation modes and routes affect energy consumption and related carbon footprint. Since textile product manufacturing requires multiple production processes at different locations, many supply chain alternatives can be defined by a single product design. In the following section, this complexity will be addressed, as well as the product manufacturing processes, in the development of the research methodology. It will then be demonstrated with the application of a case study for backpack design.

3.4 Research Methodology

Simultaneous consideration of manufacturing processes and supply chain design alternatives is pursued to reduce the cradle-to-gate energy consumption and related carbon footprint for textile-based products. While prior studies have applied standard LCA tools to analyze textile product manufacturing processes or supply chain networks independently, the present work is the first known study to develop and apply a comprehensive process-based modeling approach to assess them simultaneously. The environmental impact of manufacturing processes and supply chain networks with different transportation modes is explored in this study. Two actual backpacks are considered in an application of the method.

The main focus of this research is to explore the energy consumption and related carbon footprint and the existing tradeoffs between different product designs and supply chain networks. Eastlick and Haapala proposed the general steps to choose the most sustainable design alternative as follows: 1) generate the design alternatives, 2) choose the sustainability metrics, 3) determine relative importance of metrics and evaluate them, 4) generate alternative rankings and 5), compare and contrast the alternatives [121].

Figure 3.3: Disassembled view of Backpack 2

In the approach developed and applied herein, the steps to analyze the environmental impacts of textile-based product manufacturing processes and supply chain alternatives are as follows: 1) Disassemble the backpacks, 2) Determine the component compositions, masses, and dimensions, 3) Create the supply chain network including modes and distances, 4) Collect supply chain and manufacturing process data from technical literature, 5) Conduct environmental impact assessment, and 6) Interpret and compare results.

Two backpacks were selected for product dissection, or disassembly, to determine their component and material composition (Figure 3.3). The selected backpacks are made from similar materials, but vary in design. While the first backpack (Backpack 1) had wheels, two handles (carry and pull), and four compartments, the second backpack (Backpack 2) had no wheels, one handle (carry), and three compartments. After dissection, the mass and dimensions were measured for each component in the finished product, as well as recording the material type. Then, for each fabric piece, the maximum overall length and width dimensions were measured. These dimensions were used to estimate the size of the fabric blank from which each piece was cut. The masses of the fabric blanks and plastic components were calculated and aggregated for each material type.

Figure 3.4 shows the major nodes of a textile product supply chain network for product a composed of i materials; the suppliers (Sj) of materials, fiber, fabric, and components; supplier warehouses (Wj); small distribution centers (DSk); large distribution centers (DLk); and the final product manufacturer (M). Nodes of the supply chain are connected by links which represent different transportation modes and distances. It can be assumed that bolts of fabric and plastic components are produced by independent suppliers. These will be shipped to the manufacturing company for cutting, sewing, and finishing.

In addition to the geometry, designers can specify different materials from which to construct a backpack, which define the part masses, supply chain networks, and resulting energy consumption and carbon footprint. New manufacturing processes having less environmental impact and end-of-life management strategies for the finished product, such as recycling, can also be considered in the design stage. It is noted that four primary materials are typically used to produce backpacks, including polyester, polypropylene, nylon, and polyethylene. Raw material suppliers are located in various locations globally, but primarily in Asia. Major suppliers were identified in Japan, Thailand, Vietnam, South Korea, and Taiwan. Materials must be transported to the various manufacturers and distribution centers. The distribution centers are assumed to be located in Japan, Vietnam, and China. The manufacturing company is assumed to be located in Guangdong, China. Locations and distances were determined with the assistance of a major outdoor gear manufacturer and using online tools [122]. Table 3.1 shows possible supply chain alternatives, raw material suppliers, distributions, distances, and transportation modes.

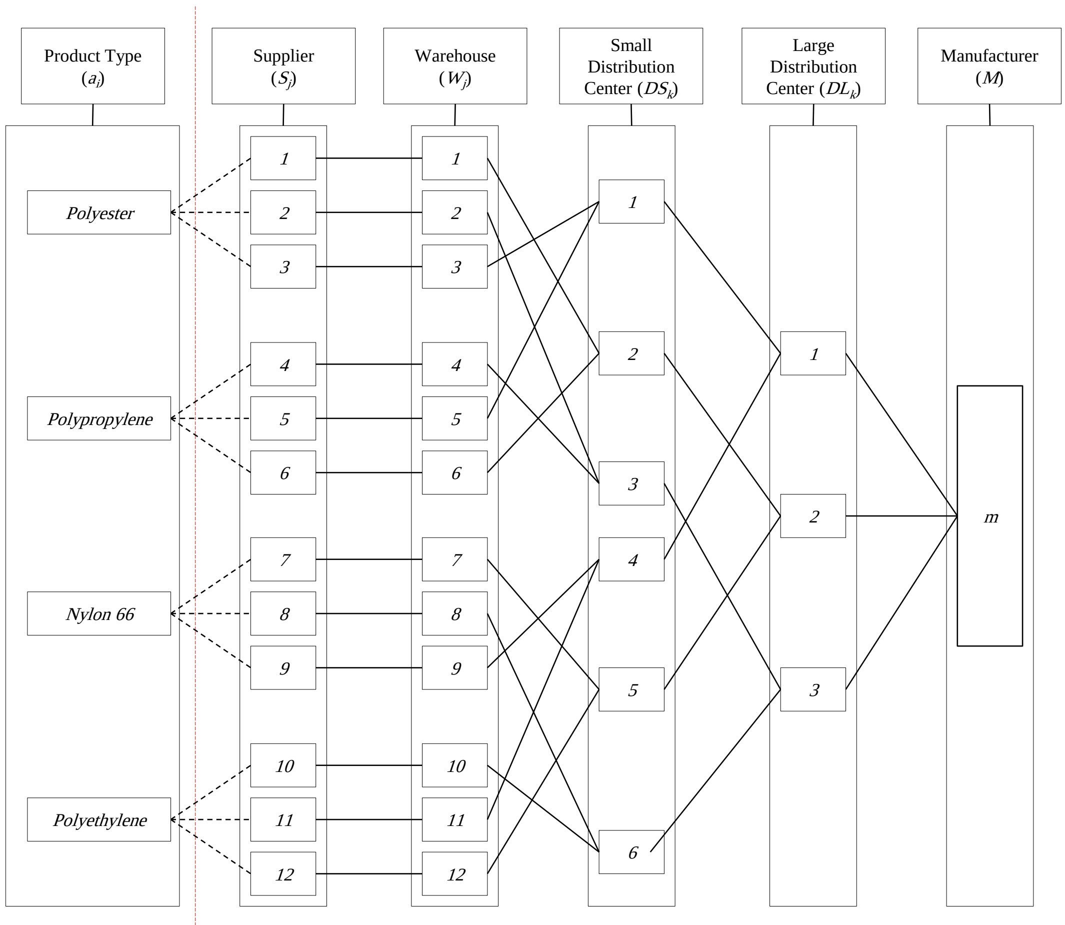

Figure 3.4 Schematic of supply chain network alternatives for textile product manufacturing

The table outlines several modes and routes for materials and parts to follow from the initial supplier to the final product manufacturer. For instance, to transport polyester fiber from Tokyo, Japan to Yamaguchi, Japan, three different modes are available (i.e., road, rail, or a combination of both), but to transport polyester fiber from Kagoshima, Japan to Shanghai, China, only one option is available (deep-sea container). Since alternative modes exist, different supply chain scenarios can be explored in terms of their sustainability performance, as demonstrated below for energy consumption and carbon footprint. It is noted that the final destination of all piece-parts is Guangdong, China where the manufacturing company is located.

This study applied the life cycle inventory (LCI) method to explore the environmental impacts of textile manufacturing using the example of backpack design. The goal of this study is to evaluate the energy consumption and carbon footprint of backpack manufacturing from a cradle-to-gate perspective. Raw material processing, fiber manufacturing, fabric manufacturing, and transport of the materials and parts are considered. Figure 3.5 shows the backpack manufacturing process flow, with additional detail presented for textile production.

To produce a backpack, four different materials are usually needed, as mentioned above. Each material production route starts with raw material manufacturing. Then different process flows, such as fiber production, are applied.

Table 3.1 Supply chain network alternatives

Alternative	From	To	Distance (km)	Air	Road	Intermodal Road/Rail	Rail	Deep-Sea Container
1	Tokyo, Japan	Yamaguchi, Japan	824.3		x	x	x	
	Yamaguchi, Japan	Kagoshima, Japan	258.1		x	x	x	
	Kagoshima, Japan	Shanghai, China	807.4					x
	Shanghai, China	Guangdong, China	1212.2		x	x	x	
2	Tokyo, Japan	Guangdong, China	2891	x				
3	Seoul, South Korea	Guangdong, China	2352.9					x
4	Bangkok, Thailand	Da Nang, Vietnam	862.2		x	x	x	
	Da Nang, Vietnam	Guangdong, China	928.5					x
5	Bangkok, Thailand	Guangdong, China	1811.3		x	x	x	
6	Ho Chi Minh City, Vietnam	Guangdong, China	1522.2	x				
7	Ho Chi Minh City, Vietnam	Da Nang, Vietnam	607.3		x	x	x	
	Da Nang, Vietnam	Guangdong, China	928.5					X
8	Ho Chi Minh City, Vietnam	Guangdong, China	2146		x	x	x	
9	Taipei, Taiwan	Guangdong, China	797	x				X

Fabric production (e.g., knitting) is the final step to produce the raw materials to produce a backpack (aside from the plastic and metal components). To create and assemble shaped fabric panels, different types of cutting and sewing operations are needed.

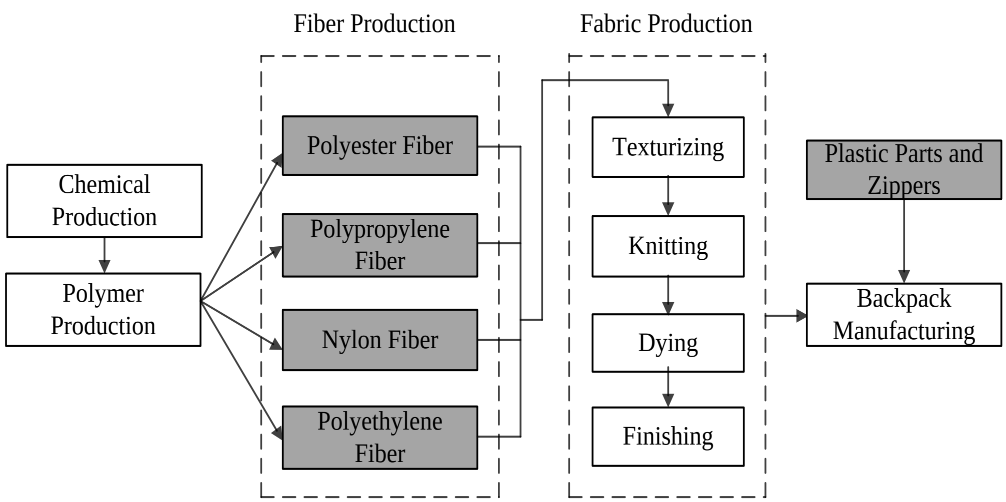

Figure 3.5 Backpack manufacturing process flow with textile production flow

To find energy consumption and carbon footprint of backpack manufacturing, several studies from literature have been reviewed. The quality of this study will be dependent upon the data quality and availability. A simple backpack is selected as a functional unit. The study system boundary includes material extraction, material processing, manufacturing operations, and transportation. Use and end-of-life phases are excluded. Since using backpacks are not harmful for the environment and are non-energy use objects, the use phase is not applicable.

3.5 Energy Consumption and Carbon Footprint Analysis

Finding the environmental impacts of each material and component can be time consuming for a designer, and the results are dependent upon the data quality and availability. The aim of this study is to explore the impacts of early product design on energy consumption and carbon footprint, and provide a method that can be more generally applied to the evaluation of textile-based products.

The supporting data is gathered from the literature and the analysis is based on data collected for two backpack designs.

3.5.1 Supply Chain Network

There are a myriad of feasible supply chain network alternatives available for material and component production and transport. The carbon footprint (*CF*) of the supply chain network for material or component *i* can be calculated using Eq. 1:

$$CF_i = m_i * \sum_n d_n * \alpha_n \tag{3.1}$$

Where m_i is the mass of material or component *i* to be transported, d_n is the distance using transportation mode *n*, and α_n is the average emission factor for transportation mode *n*. Similarly, the energy consumption (*EC*) of the supply chain network for material or component *i* can be calculated using Eq. 2:

$$EC_i = m_i * \sum_n d_n * \beta_n \quad (3.2)$$

where β_n is the average energy conversion factor. Common values for α_n and β_n can be found in Table 3.2. This data assumes that transport energy is from direct fuel combustion, and does not utilize electrical energy.

Table 3.2 Average emissions and energy conversion factors for various transportation modes [a][123], [b][124]

Transport Mode	Emission Factor ($g\ CO_2e$/t-km)[a]	Energy Factor (MJ/t-km)[b]
Road	62	2.426
Rail	22	0.209
Intermodal road/rail	26	1.317
Deep-sea container	8	0.160
Air freight	602	6.900

For this study, two different supply chain networks were chosen arbitrarily from among all the possible alternatives.

Table 3.3 Two supply chain network alternatives for backpack production

Alternative	Leg	From	To	Distance (km)	Transport Mode	Component Production by Material Type
A	1	Tokyo, Japan	Yamaguchi, Japan	824	Road	All Materials
	2	Yamaguchi, Japan	Kagoshima, Japan	258	Rail	
	3	Kagoshima, Japan	Shanghai, China	807	Deep-sea container	
	4	Shanghai, China	Guangdong, China	1212	Intermodal road/rail	
B	1	Tokyo, Japan	Yamaguchi, Japan	824	Rail	Polyester
	2	Yamaguchi, Japan	Kagoshima, Japan	258	Intermodal road/rail	
	3	Kagoshima, Japan	Shanghai, China	807	Deep-sea container	
	4	Shanghai, China	Guangdong, China	1212	Road	
	5	Bangkok, Thailand	Da Nang, Vietnam	862	Rail	Polyethylene
	6	Da Nang, Vietnam	Guangdong, China	928	Deep-sea container	
	7	Taipei, Taiwan	Guangdong, China	797	Deep-sea container	Nylon 6
	8	Tokyo, Japan	Guangdong, China	2891	Air	Polypropylene

Selected supply chain alternatives, origin locations, distribution centers, distances, transportation modes, and fabric and components transported are described in

Table 3.3. For supply chain Alternative A, all fabrics and components originate from Tokyo, Japan, while for Alternative B, they come from different countries. The final destination is Guangdong, China, where the backpack manufacturing company is located.

Tables 3.4 and 3.5 present the energy consumption and carbon footprint results for each backpack design variant for supply chain Alternatives A and B, respectively.

Table 3.4 Backpack transportation impact analysis results for supply chain Alternative A

Backpack	Leg	Component Mass (g)	Energy Consumption (MJ)	Carbon Footprint ($g\ CO_2e$)	Total Energy Consumption (MJ)	Total Carbon Footprint ($kg\ CO_2e$)
1	1	1837	3.67	90	6.94	0.2
	2	1837	0.10	10		
	3	1837	0.23	20		
	4	1837	2.93	60		
2	1	496	0.99	30	1.87	0.05
	2	496	0.02	3		
	3	496	0.06	3		
	4	496	0.79	156		

Table 3.5 Backpack transportation impact analysis results for supply chain Alternative B

Backpack	Leg	Component Mass (g)	Energy Consumption (MJ)	Carbon Footprint ($g\ CO_2e$)	Total Energy Consumption (MJ)	Total Carbon Footprint ($kg\ CO_2e$)
1	1	518	0.08	10	8.15	0.6
	2	518	0.17	3		
	3	518	0.06	3		
	4	518	1.52	39		
	5	916	0.16	17		
	6	916	0.14	7		
	7	119	0.01	1		
	8	284	5.66	494		
2	1	359	0.06	7	1.74	0.06
	2	359	0.12	2		
	3	359	0.05	2		
	4	359	1.05	27		
	5	43	0.01	1		
	6	43	0.01	1		
	7	85	0.01	1		
	8	9	0.18	16		

Regardless of the backpack design, it can be seen that total energy consumption and carbon footprint of supply chain Alternative B is greater than Alternative A.

The effect of using air freight in Alternative B causes the domination of the other transportation modes due to the higher energy and emissions conversion factors.

3.5.2 Raw Material Processing

Four raw materials were identified as the key materials in constructing backpacks: polyester, polypropylene, nylon, and high density polyethylene. Polyester is the most popular man-made fiber in textile and industrial manufacturing that is manufactured from mineral oil [125], [126]. To produce polyester, ethylene is first obtained from the naphtha fraction of the crude oil. Then, ethylene is oxidized to produce a glycol monomer. Finally, polymerization of the glycol monomer takes place in liquid form with the aid of catalysts to produce polyethylene terephthalate (PET) polyester [126]. Cherrett et al. conducted an ecological footprint analysis of three different fibers including cotton, hemp, and polyester [127]. Results showed that polyester fiber manufacturing is the most energy intensive among the three. The total energy consumption of manufacturing polyester fiber is 104,479 MJ/t [127].

Polypropylene resin production steps include extraction and refining of oil and natural gas, production of propylene from natural gas and refined oil, and, finally, production of polypropylene from propylene [128]. Keoleian et al. performed LCA studies for various materials and processes to update values for GHGs, regulated emissions, and energy use in the GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) model, which has been developed by Argonne National Laboratory [128]. Among other materials, steel, aluminum, polypropylene, and nylon 6 were investigated. The total energy consumption of polypropylene resin production is 66,129 MJ/t [128].

Two types of nylon (nylon 6 and nylon 66) are available and selected based on tenacity, which is a measure of a fabric's ability to resist tearing. It is assumed that nylon 6 is used in backpack production. The production of nylon starts from extraction of crude oil and natural gas, production of pyrolysis gas and naphtha from processed natural gas and crude oil, and the production of benzene from pyrolysis gas and naphtha. Next, cyclohexanone is produced using the benzene and phenol, and then caprolactam is produced from the cyclohexanone. Finally, nylon 6 is produced from caprolactam [128]. The total energy consumption of nylon 6 resin production is 97,362 MJ/t [128].

The other components of the backpacks are assumed to be made from high-density polyethylene, which has a large strength to density ratio. polyethylene resin manufacturing steps include the extraction and refining of oil and gas, production of ethylene, and finally the production of polyethylene from ethylene [128]. The total energy consumption of polyethylene resin manufacturing processes is 67,248 MJ/t [128].

To calculate carbon footprint, the amount of electricity required must be determined and the relevant country must be identified. The emissions conversion factor for electricity generation is dependent on the sources of energy for the electrical grid, which vary by geographic location (Table 3.6).

Table 3.6 Carbon footprint conversion factors for selected countries [129]

Country	CF Factor (g CO_2e/kWh)
China	867.81
Japan	488.93
Taiwan	738.56
Thailand	598.65

Table 3.7 summarizes the raw material processing energy consumption and carbon footprint for the two backpacks and two supply chain alternatives. It should be noted that energy consumption includes electricity generation from a variety of sources as defined by the electrical grid, which in turn impact carbon footprint.

As the same processes are used, the energy consumption for Alternatives A and B are assumed to be equal, though they may vary from supplier to supplier in reality. Because of the different sources of energy for the electrical grid in each location, however, the effect on carbon footprint results are demonstrated. The carbon footprint of Alternative B is larger than Alternative A for each backpack, similar to what was found for the transportation results.

Table 3.7 Backpack raw material processing impacts for the two supply chain design alternatives

Backpack	Materials	Component Mass (g)	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)	
				Alternative A	Alternative B
1	Polyester	518	54.14	7.3	7.3
	Polypropylene	284	18.40	2.8	2.8
	Nylon 6	119	12.81	1.7	2.6
	Polyethylene	916	67.85	9.2	11.3
	Total	1837	155.45	21.0	24.0
2	Polyester	359	37.50	5.1	5.1
	Polypropylene	9	0.60	0.1	0.1
	Nylon 6	85	9.17	1.2	1.9
	Polyethylene	43	3.19	0.4	0.5
	Total	496	50.49	6.8	7.6

3.5.3 Fiber manufacturing process

After producing the raw material, the next step of the backpack manufacturing is polyester and nylon fiber production. Yarn spinning is the most energy consuming process of fiber manufacturing, using 72% of the process energy in the form of electricity [130]. Thus, only the yarn spinning process is considered in estimating the energy consumption and carbon footprint of fiber manufacturing. Koc and Kaplan calculated the total energy consumption of the yarn spinning process for different yarn counts (linear density) [130]. Assuming that the yarn count is 20 tex (grams per 1000 meters) for combed weaving yarn used for backpack fabric, the total spinning energy consumption is 3.64 kWh/kg of yarn [130]. The carbon footprint will vary based on the associated energy generation profile for each supplier location.

3.5.4 Injection Molding Process

In this study, it is assumed that the accessory parts used are made of polypropylene and polyethylene. The main manufacturing process is injection molding, which uses polypropylene and polyethylene resins as raw input materials to produce the final parts. The injection molding process steps include heating the PP or polyethylene resin, injection of molten resin to the mold, cooling the mold with water, and ejecting the final product [128]. It should be noted that the total calculated energy consumption and carbon footprint excludes the resin manufacturing and transportation, which is calculated in raw materials processing section. The total energy consumption for injection molding of polyethylene is 16.7 MJ/kg, and the total energy consumption and carbon footprint of injection molding of PP is 6.7 MJ/kg [128]. Table 3.8 summarizes the results for fiber and component manufacturing processes for the two backpacks and two supply chain alternatives.

Table 3.8 Backpack fiber and component production impacts for the two supply chain design alternatives

Backpack	Materials	Component Mass (g)	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)	
				Alternative A	Alternative B
1	Polyester	518	6.79	0.9	0.9
	Polypropylene	284	1.9	0.3	0.3
	Nylon 6	119	1.56	0.2	0.3
	Polyethylene	916	16.90	2.3	2.8
	Total	1837	27.35	3.7	4.3
2	Polyester	359	4.70	0.6	0.6
	Polypropylene	9	0.06	0.1	0.1
	Nylon 6	85	1.12	0.1	0.2
	Polyethylene	43	0.79	0.1	0.1
	Total	496	6.68	0.9	1

3.5.5 Fabric Manufacturing

The steps in fabric production are weaving and wet processing, which includes preparation, dyeing, printing, and finishing. The amount of electricity needed for weaving preparation, such as automatic winding, classical wending, and warping, is 2.3 MJ/kg, which is negligible compared to wet processing [131]. The average electrical energy and fossil fuel required for weaving are 21 MJ/kg and 13 MJ/kg, respectively [132]. The average amount of electricity and fuel for wet processing, including dyeing and finishing, provided by Visvanathan et al. are 45.4 MJ/kg and 70 MJ/kg, respectively [132]. Consequently, it is concluded that the total energy consumption needed for fabric manufacturing is 151.5 MJ/kg.

Table 3.9 summarizes the results of fabric manufacturing processes for the two backpacks and two supply chain alternatives. The total energy consumption and carbon footprint of the fabric manufacturing processes dedicated to both polyester and nylon 6 for each backpack are shown.

The primary driver for variation in fabric manufacturing carbon footprint is due to the nylon fabric, which is sourced from Japan for Alternative A and from Taiwan for Alternative B. Since Taiwanese electricity has a larger carbon footprint, a larger carbon footprint is reflected in backpacks produced using supply chain Alternative B.

Table 3.9 Backpack fabric manufacturing impacts for the two supply chain design alternatives

Backpack	Materials	Component Mass (g)	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)	
				Alternative A	Alternative B
1	Polyester	518	78.46	10.6	10.6
	Nylon 6	119	18.08	2.4	3.7
	Total	637	96.53	13	14.3
2	Polyester	359	54.34	7.4	7.4
	Nylon 6	85	12.90	1.7	2.6
	Total	444	67.24	9.1	10

3.5.6 Textile Product Assembly

Textile product manufacturing and assembly includes cutting, sewing, finishing including ironing and pressing, and packaging. Due to a lack of published information, apparel manufacturing is used to represent backpack manufacturing [133]. The energy requirement for final product manufacturing, assembly, and packaging of polyester product is 24 MJ/kg. [133].

Table 10 shows the results for final manufacturing, assembly, and packaging of the two backpack design variants. It can be noted that only sewn fabric parts are included in this calculation; the parts attached to the final product by gluing are excluded. Process energy information was available for polyester product manufacturing, and it is assumed that final product manufacturing using nylon 6 requires the same amount of energy. Supply chain alternatives are not considered for final backpack manufacturing as both backpacks will be produced at the same location (Guangdong, China).

Table 3.10 Energy consumption and carbon footprint of final backpack manufacturing and assembly

Backpack	Materials	Component Mass (g)	Total Energy (MJ)	Carbon Footprint (kg CO_2e)
1	Polyester	518	12.45	3
	Nylon 6	119	2.87	0.7
	Total	637	15.32	3.7
2	Polyester	359	8.62	2.1
	Nylon 6	85	2.05	0.5
	Total	444	10.67	2.6

Tables 11 and 12 summarize the energy consumption and carbon footprint of manufacturing Backpacks 1 and 2 from a cradle-to-gate perspective for supply chain Alternatives A and B. To calculate the environmental impacts of each backpack design variant, raw material production, injection molding, fiber and fabric manufacturing, and assembly processes are considered, in addition to two different supply chain alternatives.

Table 3.11 Overall energy consumption and carbon footprint for production of two backpack design variants for supply chain Alternative A

Manufacturing and Transportation Activities	Backpack 1A		Backpack 2A	
	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)
Raw Material Processing	155.45	21	50.49	6.8
Component Manufacturing Processes (Fiber, Plastic Parts)	27.35	3.7	6.68	0.9
Fabric Manufacturing	96.53	13	67.24	9.1
Backpack Assembly	15.32	3.7	10.67	2.6
Transportation	6.94	0.2	1.87	0.05
Total Energy Consumption	301.59	-	136.95	-
Total Carbon Footprint	-	41.6	-	19.45

As expected, the differences in mass and materials used between the two backpack design variants caused a disparity in the predicted manufacturing and supply chain energy consumption and carbon footprint. Since the total weight of the Backpack 1 design is approximately four times that of the Backpack 2, it exhibited higher environmental impacts, in terms of energy consumption and carbon footprint, due to materials processing and transportation. Though the weight of Backpack 1 is four times the weight of Backpack 2, total energy consumption of the Backpack 1 is only twice the level of Backpack 2. By normalizing the results on a per unit mass basis, the energy consumption to produce Backpack 1 and 2 is 160.4 MJ/kg and 272.1 MJ/kg, respectively. Similarly, the normalized carbon footprints of Backpack 1 and 2 are 10.4 kg CO_2e/kg and 21.2 kg CO_2e/kg, respectively. Figure 3.6 presents a comparison of the energy consumption for the major manufacturing processes for each backpack design.

Table 3.12 Overall energy consumption and carbon footprint for production of two backpack design variants for supply chain Alternative B

Manufacturing and Transportation Activities	Backpack 1B		Backpack 2B	
	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)	Energy Consumption (MJ)	Carbon Footprint (kg CO_2e)
Raw Material Processing	155.45	24	50.49	7.6
Component Manufacturing Processes (Fiber, Plastic Parts)	27.35	4.3	6.68	1
Fabric Manufacturing	96.53	14.3	67.24	10
Backpack Assembly	15.32	3.7	10.67	2.6
Transportation	8.15	0.6	1.74	0.06
Total Energy Consumption	302.8	-	136.82	-
Total Carbon Footprint	-	46.9	-	21.26

An evident difference between Backpacks 1A and 1B is transportation energy consumption, which is 6.9 and 8.2 MJ, respectively. For Backpack 2, the transportation energy consumption for Alternatives A and B is estimated to be

1.87 and 1.74 MJ, respectively, a reduction over Backpack 1 which is largely due to omission of air transport. It can also be seen that supply chain Alternative B results in an increase in transportation energy consumption for Backpack 1, while it is reduced for Backpack 2, a disparity due to the variation in materials and components used. It can be noted that manufacturing energy will be the same for each supply chain alternative, due to the use of the same manufacturing process set for a single backpack design.

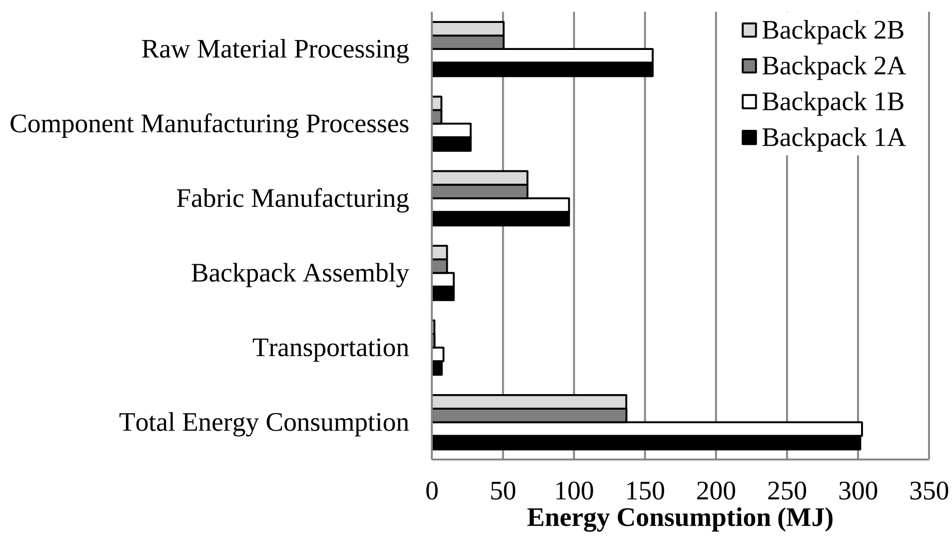

Figure 3.6 Comparison of the energy consumption for backpack manufacturing and supply chain networks

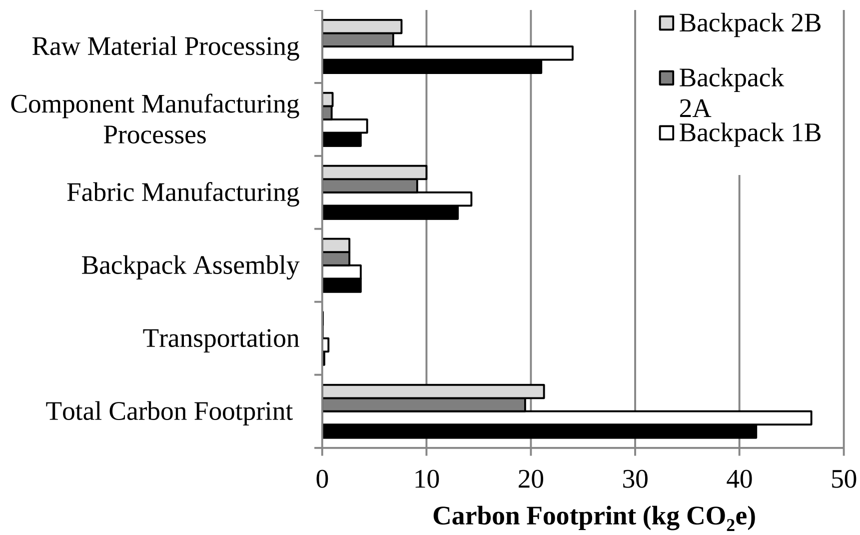

Figure 3.7 Comparison of the carbon footprint for backpack manufacturing and supply chain networks

Figure 3.7 presents the carbon footprint for backpack manufacturing processes and transportation activities for each backpack scenario. Backpack 1B has the largest carbon footprint. For Backpack 1A and 1B, the raw material processes dominate the other processes in terms of carbon footprint. For Backpack 2A and 2B, however, fabric manufacturing processes have a larger carbon footprint than other processes. For each backpack scenario, the carbon footprint of manufacturing dominates that of transportation. In general, supply chain Alternative B has a larger carbon footprint than Alternative A.

3.6 Summary and Conclusions

This study reported the integration of sustainability principles into the design of products, manufacturing processes, and relevant supply chain networks to assist decision makers, specifically for textile-based products. Two backpacks with variant designs were selected to investigate the effect of design decisions on the environmental impacts of product manufacturing and supply chain activities. The energy consumption and carbon footprint of these activities are evaluated from raw material extraction to assembly of the final product. Raw material extraction, materials processing, manufacturing operations, and transportation for each backpack material and component were considered. Information gathered from previous studies is utilized to assist with the environmental impact assessment undertaken in this research. Two different supply chain alternatives with various points of origin, distribution centers, distances, and transportation modes are considered for each backpack's materials and components.

In the study, the carbon footprint due to transportation was found to be low (0.2-1.2%) compared to manufacturing, which demonstrates the importance of understanding the direct influence of product design on manufacturing processes and equipment. In other cases, however, the supply chain may have a greater effect on carbon footprint, and should be considered. As expected, it was found that air transport carbon footprint dominated that of other transportation modes due to a large emissions factor. For Backpack 1, the total manufacturing and transportation carbon footprint is three times greater for Alternative B than Alternative A. It was found that 30% of the carbon footprint is due to fabric manufacturing for Backpack 1, while it contributed to half of the carbon footprint for Backpack 2. Fabric manufacturing carbon footprint is primarily driven by wet processing, which uses fossil fuel-based thermal energy for steam and heat.

This is the first known study to apply a process-based approach to simultaneously analyze the manufacturing and supply chain energy consumption and carbon footprint for textile-based products, which can assist industry practitioners during early product design. Different product design and manufacturing alternatives can be explored in the context of supply chain configuration and associated energy consumption and carbon footprint. Moreover, the general approach can be extended to analyze different material types used in the textile industry. The method presented is a generally applicable approach, and that the backpack case study is a general example for this approach. However, that the life cycle inventories constructed and the modeling results will facilitate future studies of the textile industry. This data and information was previously not compiled or available from a single source. Data gathering required review of many disparate sources, an activity to which practitioners can devote little time. Due to the dearth of available actual data, the demonstration of the general approach reported herein was conducted by using data collected from the literature. These gathered data and sources can be of benefit to future studies.

The general approach described can be applied to evaluate any product. The supply chain and process models reported, however, are applicable to a more limited number of textile-based products – specifically those that use polyester and nylon fabrics and/or plastic components. These may include jackets, hand bags, gear bags, and other outdoor products, in addition to backpacks. The transportation, polymer processing, and yarn production processes can be applied to any polyester or nylon textile product, while fabric production processes would vary depending on the type of material used and final product.

Future research should consider the effect of a low mass to volume ratio for some textile products on transportation environmental impacts. Calculated impacts may underestimate the actual impact for low density products, which are volume-limited, rather than mass-limited for transport. Future studies can apply the methodology presented herein along with known supplier and manufacturer data to generate more accurate results for specific studies. Finally, the cradle-to-gate analysis approach can be extended to consider the entire textile product life cycle by modeling distribution, use, and end-of-life treatment processes and activities, which are also influenced by the product design.

CHAPTER 4 - SUSTAINABILITY ASSESSMENT DURING EARLY PRODUCT DEVELOPMENT: THE USE CASE

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Abstract

Adding nanoparticles (NPs) to metalworking fluids (MWFs) has been shown to improve performance in metal cutting. Zinc oxide nanoparticles (ZnO NPs) and titanium dioxide nanoparticles (TiO_2 NPs), for example, have exhibited the ability to improve the lubricant performance, decrease the heat created by machining operations, reduce friction and wear, and enhance thermal conductivity. ZnO and TiO_2 NPs also exhibit a lower cost than many other NPs. Precautionary concerns of human health risks and environmental impacts however, are especially important when adding NPs to MWFs. The goal of this research is to investigate precautionary environmental and human health concerns of product use during early design and development. This research builds on a prior investigation of the stability and toxicity characteristics of NPs used in metalworking nanofluids (MWnF™). In the prior research, one type of NP at one level of concentration was studied. In this research, three different types of NPs with different morphology (size and shape) and a range of concentrations in the base fluid are explored. In the presented work, mixtures of a microemulsion (TRIM® MicroSol® 585XT), which is commercially available, two different types of TiO_2 NPs (referred to as TiO_2A and TiO_2B) and one type of ZnO NP are used to evaluate MWnF™ stability and toxicity. For stability analysis and toxicological assessment, the dynamic light scattering (DLS) method and the zebrafish assay method are

applied, respectively. The results reveal that, in general, addition of these NPs causes a higher mortality rate in comparison to the NP-free formulation. The lowest rate of zebrafish malformation occurred at 5 g/L TiO_2A NP, which was even lower than for the base fluid. This result is particularly promising for future MWnF™ development, given that the mortality rate for 5 g/L TiO_2A is similar for the base fluid.

Keywords

Nanotoxicology, Nanofluid Stability, Zinc Oxide Nanoparticles, Titanium Dioxide Nanoparticles

4.1 Introduction

Metalworking fluids (MWFs) are used in machining processes to decrease the heat created by the machining operations, reduce the effect of friction, provide lubricity, and enhance thermal conductivity [70]. Due to the large use of MWFs globally, which is more than 500 million gallons annually, industrial stakeholders are concerned about the sustainability of using MWFs [71]. Manufacturing sustainability performance (e.g., environmental, economic, health and safety aspects) can be enhanced by improving the efficiency of MWFs. For instance, improving the heat transfer properties of MWFs can reduce the rate of cutting tool replacement, which is highly expensive [72]. To enhance the environmental aspect, using biocide-free MWFs compared to the conventional mineral oil based have been investigated by Winter et al., which led to better results with regard to the measured machining forces and workpiece surface roughness [73]. To reduce the environmental and worker health impacts, minimum quantity lubrication (MQL) sprays of MWFs can be applied, which also has shown better performance and enhanced penetration into the cutting zone compared to conventional water-based fluid [74]–[77]. Microfiltration has also been shown to reduce health risks and environmental impacts of using MWFs [78]. Zhao et al. developed a framework to evaluate the economics of microfiltration implementation along with its environmental performance [79]. Choosing an appropriate MWF from among all existing products can affect the lifetime and operation of milling machines [80].

Adding nanoparticles (NPs) can improve MWF performance. Previous studies have shown that nanoparticle (NP) additives to MWFs will decrease the friction resistance, improve the lubricity and thermal conductivity, reduce the cutting force, and improve the machining performance more than NP-free MWFs [82], [84], [91]. The advantages of using metalworking nanofluids (MWnF™) can be expressed as follows: saving energy and fluid consumption, reduction of related economic and environmental impacts, and enhancement of cutting tool life. To avoid the risks and recognize the potential hazard of using metalworking nanofluid (MWnF™), the sustainability of nanofluids needs to be evaluated [81].

The goal of this research is to investigate precautionary environmental and human health concerns of product use during early design and development. For nanotechnologies it is especially critical to better understand and mitigate harm during early development. This research builds on a prior investigation of two main characteristics of NPs used in metalworking nanofluids (i.e., stability and toxicity). In an application of the presented method, two different types of TiO_2 NPs and a ZnO NP are used to demonstrate the stability and biological responses (mortality and malformations) of several metalworking nanofluid formulations.

4.2 Background

In this section, prior studies that found NPs additives to improve MWF performance will be presented. Next, literature related to the uncertainties about NPs life cycle environmental performance will be explored specifically during the use phase.

Tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2) NPs were investigated as additives and found to play a key role of solid lubrication where fluids were unable to support the loads under severe conditions [82]. Mosleh et al.

showed that using certain concentrations of WS_2 and MoS_2 as additives in the modified oil for metal forming reduced the wear volume in testing of 440C ball-titanium sheet pairs and 440C ball-steel sheet pairs by 25-30% and 55-65%, respectively [84]. While the coefficient of friction (COF) of the 440C ball-titanium sheet pair was reduced by 10%, no improvement was noticed in the COF of the 440C ball-steel sheet pair.

LotfizadeDehkordi et al. employed a UV–Vis spectrophotometer and indicated that thermal conductivity enhancement was observed by using a high concentration of TiO_2 in water-based nanofluids [85]. The thermal conductivity of water- based nanofluids increased with increasing concentrations of Al_2O_3 and TiO_2 NPs [86]. Using a 3% by volume alumina and a 1% by volume multi-walled carbon nanotube (MWCNT) nanofluids (NFs) in place of soluble oil was shown to significantly reduce the force, energy, and temperature of cutting [87]. Hu and Dong used 20 nm titanium oxide NPs as an additive to 500 SN base oil to evaluate the tribological properties of the fluid [88]. The results indicated that adding NPs decreased the COF by 12%, and the wear resistance and load capacity of the fluid were improved. Turgut et al. conducted a study to investigate the thermal conductivity and viscosity measurements of water-based TiO_2 nanofluid [89]. The results showed that with a 3% volume fraction of TiO_2, the thermal conductivity improved by 7.4% compared to the base fluid. The viscosity increased with the increase in volume fraction of NPs. McCook et al. added different NPs to an epoxy matrix to test the COF and wear resistance by using a linear reciprocating pin-on-disk tribometer [90]. Optimum wear resistance was observed with a 1% by volume ZnO and 14.5% by volume polytetrafluoroethylene (PTFE) NPs. Similarly, optimal COF reduction was found with 3.5% by volume ZnO and 14.5% by volume PTFE NPs.

Kotnarowski added CuO NPs to SN 100 and Hydrorafinat II basic oils to evaluate the COF reduction [91]. They concluded that adding 0.25% by volume CuO NPs is most effectively, and results in 10-25% reduction in COF. Shen et al. found that adding 5-20% by volume of 100 nm MoS_2 NPs to three different fluids (paraffin, soybean oil, and CANMIST) decreased the COF in grinding of cast iron by 30-50% [92]. Khandekar et al. studied metal cutting performance using a nano-cutting fluid made by adding 1% by volume of Al_2O_3 to a conventional cutting fluid [93]. The results showed that nano-cutting fluid decreased cutting force, tool wear, and surface roughness compared to the conventional cutting fluid.

Although MWnF™ improves the tribological properties of the base fluid, there are uncertainties about their life cycle environmental performance, specifically during the use phase. The toxicity of MWnF™ is one of the uncertainties that must be considered in their development [94]. Hoet et al. provided a comprehensive review of data analysis on health risks of using nanomaterials [6].

Even though the advantages of NPs are widely discussed in literature, the potential health risks of NPs are little known since the development of nanomaterials is in its early stages. Different nanomaterial attributes such as size, shape, and morphology need to be considered to evaluate the toxicity and develop biologically and environmentally safer MWnF™ formulations [18], [95].

4.3 Related Research

In previous research by the authors, different concentrations of 20 nm ZnO NPs were added to a commercially available semi-synthetic microemulsion (TRIM® MicroSol® 585XT) to investigate the cutting force and temperature in turning of a titanium alloy (Ti-6Al-4V) [100]. Machining tests revealed that the lowest temperature and cutting force occurred at 0.5% by weight of ZnO NPs in the MWF. Two main characteristics of NPs used in metalworking nanofluids (i.e., stability and toxicity) were also investigated. The authors investigated the stability of mixtures 20 nm ZnO NPs and different dispersants in a microemulsion (TRIM® MicroSol® 585XT) [94]. They concluded that none of the dispersants improved the stability of ZnO NPs compared to the base mixture. Thus, the surfactants contained in the base fluid were deemed to be sufficient for dispersion of NPs.

The results of toxicological assessment via a zebrafish assay showed that the ZnO MWnF™ had a significantly higher toxicity than the prepared microemulsion for a range of concentrations. Further investigation for precautionary development of metalworking nanofluids was suggested. Similarly, Bai et al. studied the toxicity of 30 nm ZnO NPs in a water suspension using a zebrafish embryo test [96]. The results indicated that 0.05 and 0.1 % by volume fraction of ZnO NPs cause mortality of the zebrafish embryos. In lower concentrations (1–25 mg/L), malformations such as body and tail deformation were observed.

The current research undertakes a similar approach with a focus on stability and toxicity of different NPs with variety of concentrations. The objective of this research is to apply the zebrafish model for different NPs of different morphology (size and shape) to determine the potential of NP additives to MWFs to improve the machining performance, while maintaining the same level or improved toxicity. Two types of TiO_2 NPs and one type of ZnO NP are used to evaluate the stability and biological responses of titanium dioxide and zinc oxide metalworking nanofluids. The evaluation is described in greater detail in the sections below.

4.4 Fluid Stability

Agglomeration of NPs is a key issue to consider in nanofluid (NF) preparation. Clusters form from particles aggregation, and settle out of suspension based on Stokes' Law. This law shows that settling velocity (υ_s) is proportional to the square of particle size (R) (Eq. 1):

$$\upsilon_s = \frac{2(\rho_p - \rho_f)}{9\mu} g \cdot R^2 \qquad [1]$$

where v_s is the particle's velocity, g is the gravitational acceleration, μ is the dynamic viscosity, R is the radius of the spherical object, and ρ_p and ρ_f are the mass density of the particles and fluid, respectively. Unsuspended aggregated particles cause the machining efficiency reduction and result in inaccurate toxicity test because of settling out of suspension [96], [97].

To improve the stability of NPs in the NF, ultrasonication can be applied. Ultrasonic frequency waves help to fully disperse the NPs in the mixture and fragment the agglomerate particles [98]. Xia et al. studied the preparation of stable nitrendipine nanosuspensions by using ultrasonication and improved the dissolution rate of the oral bioavailability drug [99]. Nanofluid stability improvement was reported by Sahakian in preparation of ZnO NPs for an MWnF™ by using the ultrasonication [100]. In the current study, the Sonics®

VCX 750 horn ultrasonicator is used to accomplish deagglomeration and suspension of NPs.

For this research, two different types of TiO_2 NPs and a ZnO NP were chosen as potential additives. The low cost of these two NPs compared to the other NPs is one advantage [134]. Abdullah et al. showed that both TiO_2 and ZnO can be dispersed stably in oil-based fluid and can be used as lubricant additives [101]. Adding TiO_2 will decrease the COF and increase wear resistance and load carrying capacity of MWFs [88]. Adding ZnO to a lubricant can enhance the lubricity and reduce a friction [102]. In addition, the low dissolution rate of ZnO and TiO_2 NPs in water makes them suitable candidates for suspensions with a variety of concentrations. The properties of the selected ZnO and TiO_2 NPs are shown in Table 4.1.

Table 4.1 Properties of the selected ZnO and two types of TiO_2 NPs [134]

Property	ZnO	TiO_2A	TiO_2B
Purity	99.5%	99%	99%
Average Particle Size	20 nm	20 nm	15 nm
Specific Surface Area	50 m2/g	210 m2/g	240 m2/g
Color	Milky White	White	White
Morphology	Nearly Spherical	Spherical	Irregular-angular
True Density	5.606 g/cm3	3.9 g/cm3	3.9 g/cm3
Solubility in Water	Insoluble	Insoluble	Insoluble

4.4.1 Stability Evaluation

In this study, a dynamic light scattering (DLS) method, which measures the hydrodynamic diameter of colloids in a fluid medium, was applied. The particles hydrodynamic diameter, which is the diameter of a hypothetical sphere, can be calculated by measuring the intensity variation of scattered laser light through a fluid [135]. ZetaSizer Nano ZS DLS device (Malvern Instruments, Westborough, MA) was used to measure the size of NPs dispersed in the MWnF™ colloids.

In DLS, the hydrodynamic diameter of particles is measured based on the speed of the variations of the laser travel time. It is noteworthy that DLS calculates the size using Stokes-Einstein equation (Eq. 2):

$$D= \frac{k_B T}{6\pi\eta r} \qquad [2]$$

where D is the diffusion constant, k_B is Boltzmann’s constant, T is the absolute temperature, η is a viscosity, and r is the radius of the spherical particle. To calculate the hydrodynamic diameter, fluid viscosity for each suspension must be provided as an input for the DLS instrument while temperature and radius are measured by the device.

4.4.2 Stability Evaluation Procedure

Three different concentrations (i.e., 5, 7.5, and 10 g/L) of each NP were prepared as 40 mL suspensions in a medium of semi-synthetic microemulsion and nanopure water (1:13 ratio). Then, the suspensions were sonicated by using a VCX 750 ultrasonicator (Sonics and Materials Inc., Newtown, CT) for 15 minutes. Finally, the solutions rested for two hours to cool prior to testing with the DLS instrument.

Measuring the average hydrodynamic diameter (Z_{ave}) of colloids in the medium is a means to evaluate the stability of the suspensions. A lower Z_{ave} indicates lower agglomeration and smaller colloids. From each suspension, samples (1.6 mL) were pipetted into cuvettes and inserted into the DLS instrument. Z_{ave} measurements are replicated eight times and each of the replicates was repeated three times. To evaluate the stability of the suspensions, these tests were repeated after a month. The stable suspensions exhibit a similar Z_{ave} after a month compared to the initial Z_{ave}. After evaluation, the safety performance of stable suspensions was assessed using toxicity tests as described below.

4.5 Toxicity Evaluation

In developing MWnF™ formulations, issues that must be considered include use phase environmental impacts and human health. Investigating the fluids use phase is important since machinists have interactions with the fluids [15]–[17]. Since the environmental and human health impacts of NP-based products are often uncertain or unknown, it is especially critical to better understand and mitigate harm during product development of MWnF™ formulations. Part of the product design processing is the use phase which led decision makers to make safe products to use. Fluid hazards such as being flammable, poisonous and toxic need to be considered in early product design. In this research to ensure the safety of using NPs in MWFs, toxicological assessment of metalworking nanofluids (MWnF™) must be undertaken. A few examples and related studies to the toxicological assessment are described below.

Before realizing the commercial benefits of nanomaterials in industry, potential health hazards and exposure of nanoscale materials, such as inhalation and dermal routes of exposure, must be investigated [18]. To be assured that the materials are safe to use, the characteristics of the NPs such as size, shape, dissolution rate, and agglomeration state must be known [103]. Hussain et al. presented a review of physical and chemical characteristics of NPs to determine the exposure protocols and how nanomaterials affect living organisms [104]. A study by Lademann et al.

revealed that TiO_2 used in sunscreens can penetrate to the hair follicle and stratum corneum [105].

Hussain et al. studied the toxic effect of NPs including TiO_2 for use in industry with the in vitro rat liver derived cell line method [107]. The results revealed that a lower dose (10-50 mg/mL) of 40 nm TiO_2 NPs had no effect on mitochondrial function, while at the higher dose (100-250 mg/mL), significant effects existed. Chen et al. investigated the in vivo acute toxicity of TiO_2 NPs on adult mice by injecting various doses [108]. Passive behavior, loss of appetite, tremors, and lethargy were the signs that were exhibited in the treated mice when the deposited NPs were found in liver, kidney, and lung. Wu et al. studied the penetration of P25 (21 nm) TiO_2 NPs in mice skin and after 60 days, the results revealed that NPs can penetrate to the skin and reach several organs [109].

Beckett et al. tested a 500 $\mu g/m^3$ concentration of ZnO NPs for 2 hours on healthy human subjects, and no significant effects on respiratory, hematologic, or cardiovascular issues were observed [110]. A study by Wang et al., however found that oral exposure to varying doses of 20 nm and 120 nm ZnO NPs given to mice can cause damage to the liver, spleen, and pancreas [111]. Bai et al. studied the exposure of zebrafish to 30 nm ZnO NPs added to water in order to find the mortality and malformations of fish caused by varying concentrations of NPs

[96]. They revealed that the mortality range for ZnO NPs is between 50 to 100 mg/L and the malformation range is between 1 to 25 mg/L.

As seen above, mammals have been used to assess human health risks and toxicological effects which is cost and time consuming. The zebrafish model is a good alternative since it is a rapid toxicity evaluation model and the organisms are morphologically and psychologically similar to mammals [112]. Zebrafish organs are genetically similar to human organs and, thus the model allows researchers to have access to the evolvement stages to investigate a variety of human diseases [113]. Each female zebrafish can spawn hundreds of eggs per day and the fish organs will be developed within 48 hours [114]. To have statistically powerful assays, toxicological tests using zebrafish embryos can be repeated multiple times. It is noted that the zebrafish model is not a comprehensive solution to investigate all variety of human diseases, however, and other standard human toxicity testing should be completed before commercializing nano-based products.

4.5.1 Toxicity Evaluation Procedure

Volume-based serial dilution zebrafish assay experiments were conducted for MWF and MWnF™ formulations to identify the relative toxic potential of the selected NPs. Various concentrations of NPs with a 7.5% volume concentration of semi-synthetic fluid were used in the preparation of suspensions. Suspensions required dilution to obtain meaningful zebrafish assay results. To dilute the MWnF™ suspensions, fishwater, a 0.26 g/L mixture of sea salt (Instant Ocean®, Blacksburg, VA) and deionized water, is used. The suitable range of pH for zebrafish embryos is 6.5 to 7.5. Thus, pH was adjusted to that range using hydrochloric acid.

The toxicity evaluation procedure used in this study was previously reported [136]. First, the chorion was enzymatically removed after seven hours post fertilization (7 hpf) to yield more accurate results. The chorion is natural layer around the zebrafish embryos, which protects the embryo. Next, the prepared solutions were pipetted into two similar 96-well plates, which allowed 24 replicates for each concentration, thus, improving the statistical analysis. The dechorionated embryos were then placed to the plate suspensions to be tested. A control group was placed in fishwater without any suspensions. Plates were kept at standard laboratory conditions of 28°C on a 14h light:10h dark photoperiod. To perform the toxicology assessment, 24 developmental endpoints were considered, and were examined at 24 hpf and 120 hpf. Developmental endpoints include morphological malformations, behavioral abnormalities, and embryo mortality [136]. The dose-response characteristics of the fluid were recorded and compared using different concentrations of the NPs.

4.6 Results and Discussion

This section presents an analysis of the results of the stability and toxicity evaluations which were described above.

4.6.1 Fluid Stability Evaluation

First, the suspensions were prepared with 5 g/L of NPs (TiO_2A, TiO_2B, and ZnO) in the semi-synthetic microemulsion and nanopure water (1:13 by volume ratio). After 15 minutes of sonication, the suspensions were cooled for two hours, which allowed large particles to settle out of suspension to prevent fluctuations in size measurements. The above procedures were repeated for the 7.5 and 10 g/L concentrations of NPs in the semi-synthetic microemulsion and nanopure water (1:13 ratio). In all suspensions, the concentration of the initial microemulsion is 7.5% by volume.

The effect of shelf time, defined as the time after preparation of the suspension, on the stability of suspensions was investigated to assess stability. The stability of the suspensions over a long period of time is necessary for a viable, commercializable product. The Z_{ave} values for each MWnF™ suspension was measured using DLS at 7 hours, 120 hours, and 1 month after preparation

(Figures 4.1-4.3). Because of the aggregation and precipitation of NP clusters over time, the Z_{ave} of all suspensions has a decreasing trend.

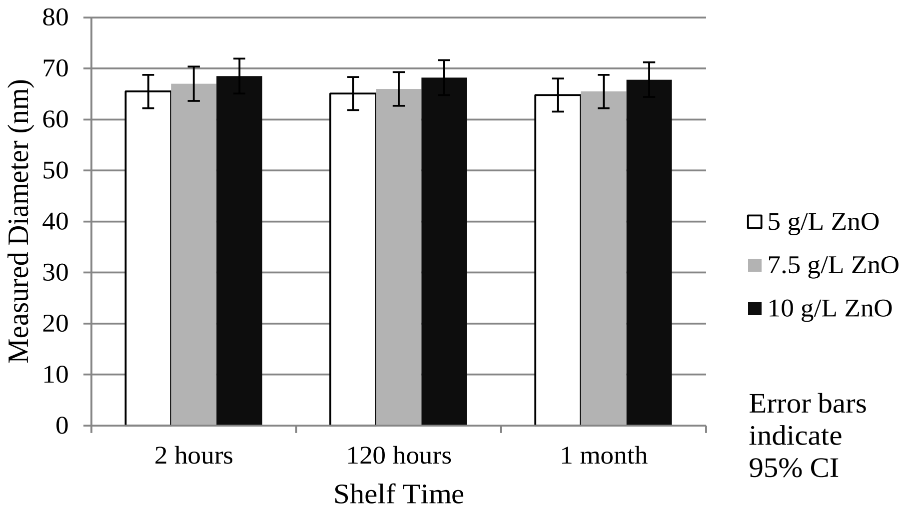

Figure 4.1 Effect of time on average ZnO NP size

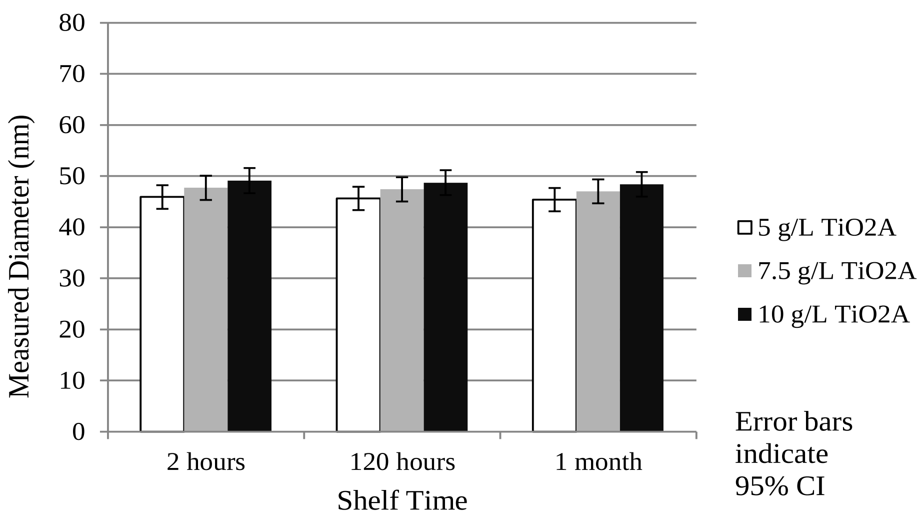

Figure 4.2 Effect of time on average TiO_2A NP size

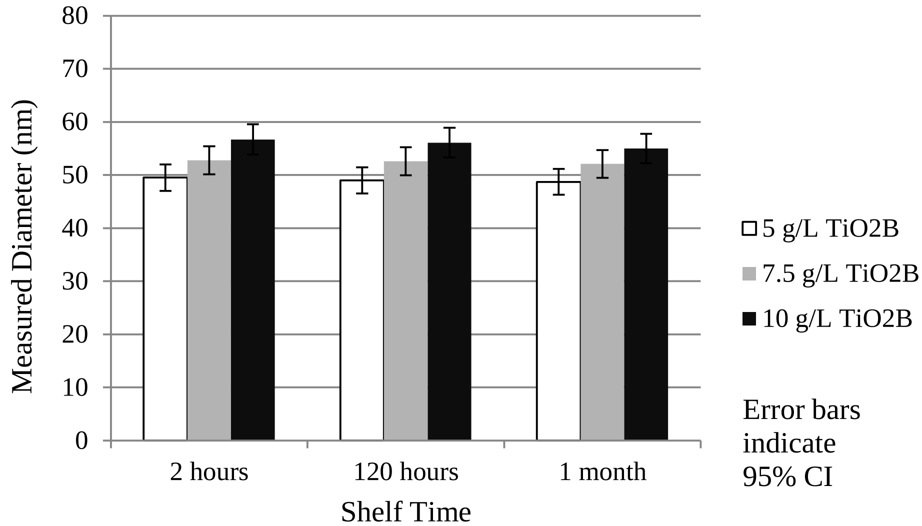

Figure 4.3 Effect of time on average TiO_2B NP size

From the results, average measured size decreases with decreasing NP concentration. It is speculated that the opportunities for aggregation increase as numbers of particles increase. Table 4.2 presents the change in measured size for each NP type after 120 hours and one month compared to two hours after preparation.

It can be seen that the percent reductions are low (0.37-2.99%) and the variation is small. As a result, the mixture of NPs in the base fluid was exhibited to be constant over a one month period which is necessary for this type of product.

Table 4.2 Effect of time on average NP size

Type of Suspension	% Reduction compared to 2 hours after preparation	
	120 hours	1 month
5 g/L ZnO	0.61	1.06
7.5 g/L ZnO	1.49	2.23
10 g/L ZnO	0.43	1.02
5 g/L TiO2A	0.65	1.08
7.5 g/L TiO2A	0.62	1.46
10 g/L TiO2A	0.81	1.42
5 g/L TiO2B	1.01	1.61
7.5 g/L TiO2B	0.37	1.32
10 g/L TiO2B	1.05	2.99

4.6.2 Toxicity Evaluation

Toxicity evaluation proceeded with stable formulations identified in the stability evaluation phase. The zebrafish model introduced above was used to examine the toxicity effect of all three NPs at different concentrations in the base fluid. First, the critical toxic concentration region of the base fluid was determined by employing a dose range-finding experiment. The critical range is defined as the range of concentrations that bounds the lethal point. The mixture was diluted in a serial manner based on semi-synthetic fluid concentration until the critical region was found. The lethal point for the base fluid was found to be 120 parts per million (ppm). The fluid did not affect zebrafish embryos at micro emulsion concentrations below 15 ppm.

With the critical region identified, NPs were added to the base fluid in varying concentrations (i.e., 0 g/L, 5 g/L, 7.5 g/L, and 10 g/L) to assess the effect of NP additions on the biological responses of zebrafish embryos. Figures 4.4, 4.5, and 4.6 show the mortality results for each of the concentrations evaluated. Mortality rate is the ratio of deceased zebrafish to the total sample size tested. From the results, it can be seen that suspensions containing NPs resulted in a considerably higher mortality rate than formulations without the NPs added for each of the three NP types and concentrations examined, except in the case of 5 g/L TiO_2A.

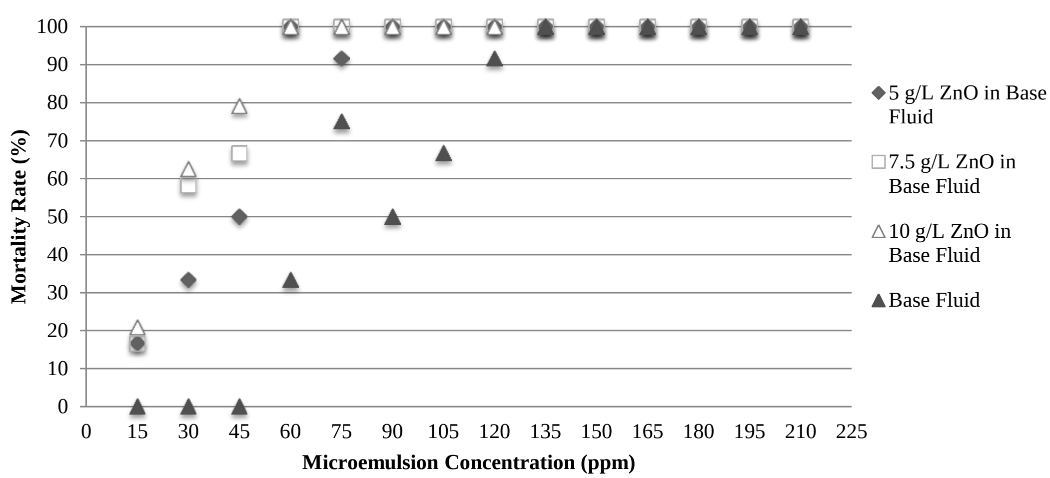

Figure 4.4 Mortality rate among samples exposed to suspensions with and without ZnO NPs

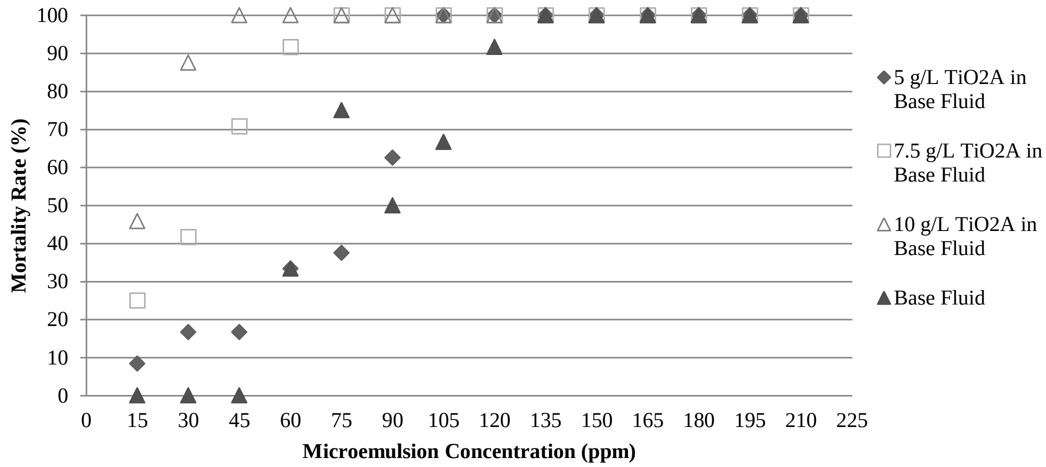

Figure 4.5 Mortality rate among samples exposed to suspensions with and without TiO_2A NPs

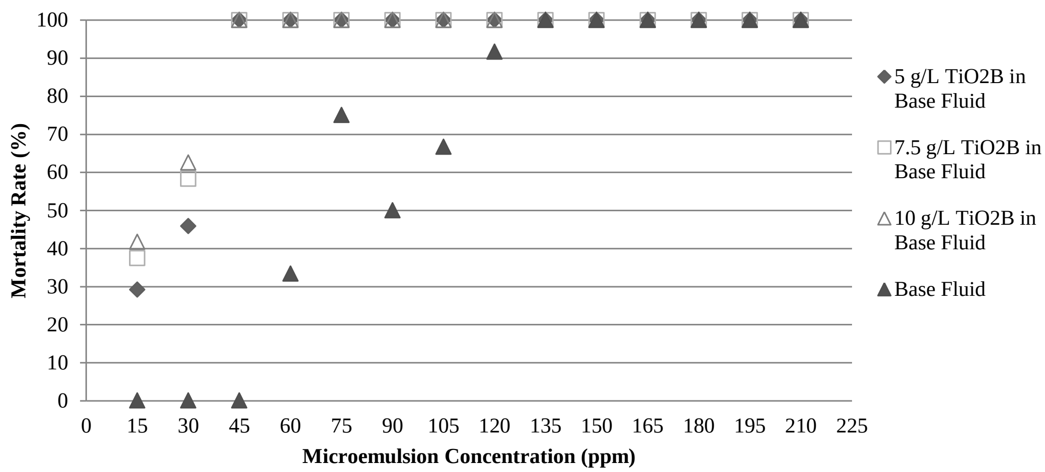

Figure 4.6 Mortality rate among samples exposed to suspensions with and without TiO_2B NPs

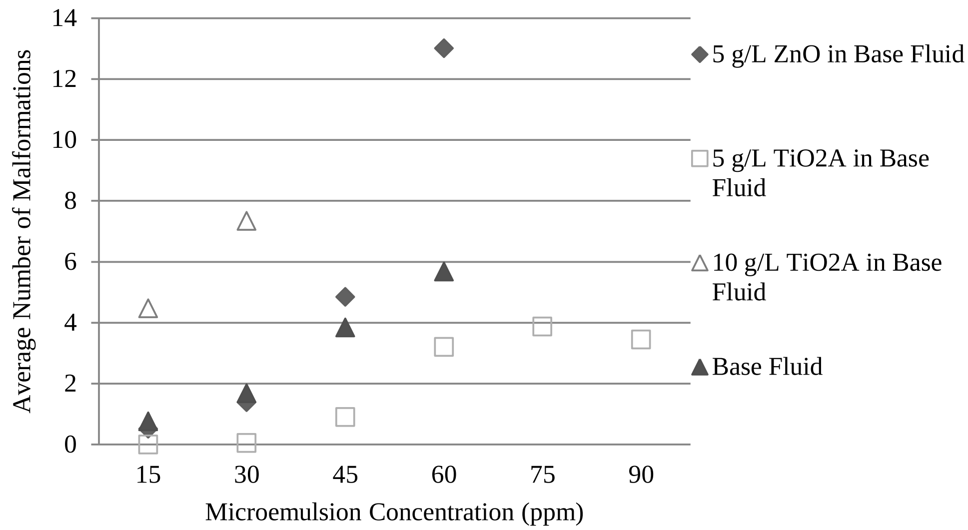

Figure 4.7 Average number of malformations among surviving samples exposed to suspensions with and without ZnO and TiO_2A NPs

For the base fluid, 5 and 10 g/L TiO_2A, and 5g/L ZnO NPs, the rate of zebrafish embryos malformations was recorded for dilutions levels that did not cause mortality. Due to the resource limitations, malformation comparison between suspensions was only possible for these experimental conditions. Figure 4.7 presents the average number of malformations between the surviving zebrafish after 5 days of exposure for TiO_2A and ZnO suspensions. The results revealed zebrafish embryos exposed to the suspensions with NPs have higher rates of malformation than the base fluid. The lowest rate of zebrafish malformation occurred at 5 g/L TiO_2A NP, which was remarkably, consistently lower than for the base fluid. This result is particularly promising, given that the mortality rate for 5 g/L TiO_2A is similar for the base fluid.

Figures 4.8-4.10 provide a comparison of mortality results for samples exposed to MWnF™ suspensions with 5, 7.5, and 10 g/L NP concentrations.

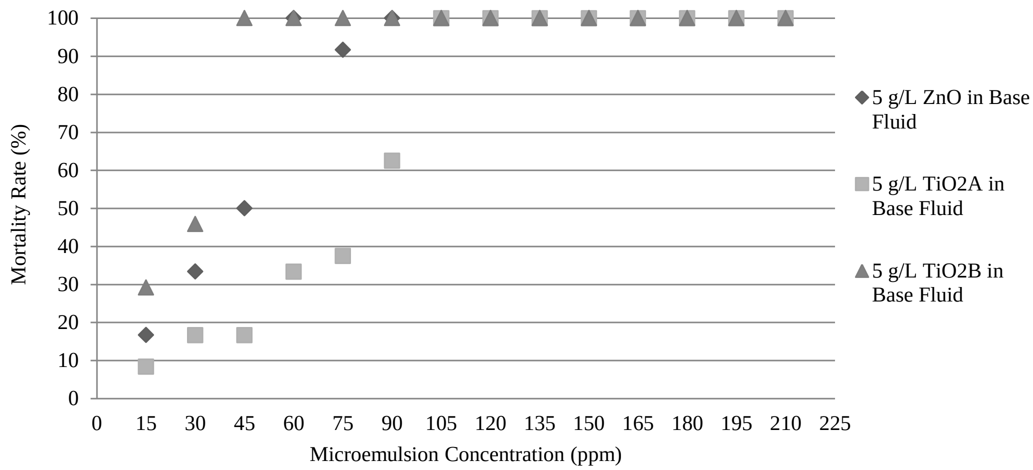

Figure 4.8 Mortality rate among samples exposed to suspensions with 5 g/L NPs

It can be seen that, for each concentration of 5 g/L MWnF™ formulations, TiO_2A NP has the lowest mortality rate followed by ZnO NP and TiO_2B NP, respectively. For example, at 90 ppm microemulsion concentration while mortality rate for ZnO and TiO_2B NPs is 100%, this amount is only 60% for TiO_2A NP.

For 7.5 g/L MWnF™ formulations, the mortality rates for each NP is vary and it cannot be concluded which one is safer than the others. For instance, while at 15 ppm microemulsion concentration, mortality rate for ZnO NP is lower than other

NPs, at 30 ppm microemulsion concentration TiO_2A NP has the lowest mortality rate.

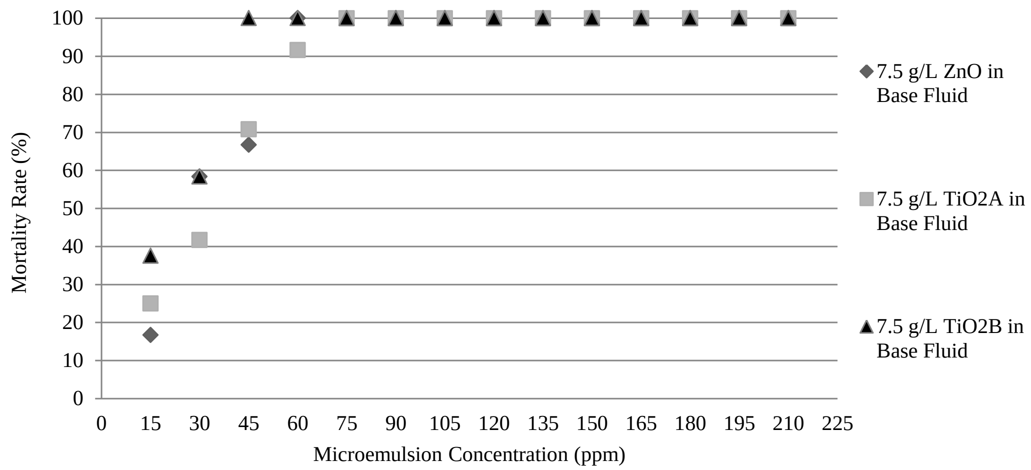

Figure 4.9 Mortality Rate among Samples Exposed to Suspensions with 7.5 g/L NPs

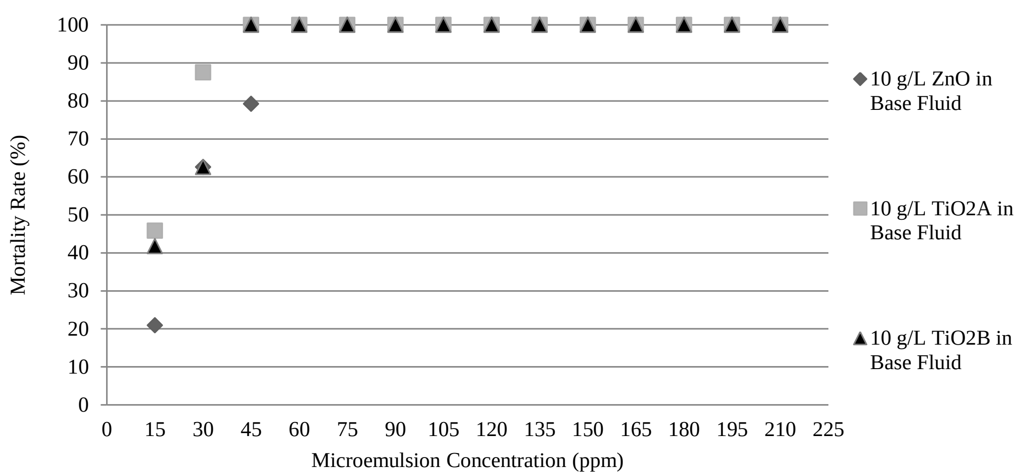

Figure 4.10 Mortality rate among samples exposed to suspensions with 10 g/L NPs

Similar to the 7.5 g/L NPs MWnF™ formulations, mortality rate for suspensions with 10 g/L NPs is vary. Regardless of NP types, the mortality rate in each concentration is significantly higher than the base fluid for suspensions with 10 g/L NPs.

4.6.3 Statistical Analysis of Toxicity Evaluation Results

Initially, a dose finding experiment was undertaken for the base fluid without NPs to indicate the concentration after which significant impacts on zebrafish occur, known as the critical toxic concentration. The base fluid was diluted iteratively by order of magnitude, based on semi-synthetic fluid concentration, until discovering the range of critical toxic concentration. Meticulous inspections were then carried out to indicate the critical toxic concentration with more accuracy. It was found that the fluid significantly affects zebrafish at concentrations above 15 ppm, and concentrations over 120 ppm were found to be lethal for zebrafish. Dilutions of 5, 7.5, and 10 g/L NPs suspension were prepared at concentrations of 15-210 ppm to evaluate the effect of NP additions on biological responses of zebrafish.

To verify the significance of the biological responses for each formulation, statistical analysis was conducted using mortality results (Appendices F and G). The recorded mortality rates were compared using the Tukey test method (Appendix F). From the above figures, it appears increasing the NP concentration does increase mortality rate, however, due to the scarcity of data, results were only found to be significantly different when comparing 10 g/L TiO_2A, 7.5 g/L TiO_2B, and 10 g/L TiO_2B to the base fluid. Prior work has shown that mortality rate varies significantly, however, when comparing the results for individual NP concentration levels [137]. Thus, future work would need to examine more levels within the critical concentration range to establish more points for comparison of overall formulation toxicity.

4.7 Conclusions

This research investigated the precautionary environmental and human health concerns of product use during early development of MWnF™ formulations. The main objective is to assist early stage design decisions by understanding the environmental and human health impacts of novel products, such as MWnF™, during use. In this study, the stability, using dynamic light scattering, and biological responses, using zebrafish assays, for two types of TiO_2 NPs and one type of ZnO NP MWnF™ formulations are explored for several concentrations. Due to the uncertainties in environmental and human health impacts, it is especially critical to better understand these implications and mitigate harm during the early development of nanotechnologies. As such, this research emphasizes the precautionary concerns of human health risks and environmental impacts through an experimental approach when adding NPs to MWFs to improve machining performance.

This study explored the effects of adding different NPs with varying concentrations to MWFs to assess MWnF™ (metalworking nanofluid) stability and toxicological performance. These attributes are indicators of shelf life and safety for viable commercialization use over time. The mixture of NPs in the base fluid was found to be stable over a one month period. The measured size reduction of NPs in the mixtures after 120 hours and after one month was less than a 2% and 3%, respectively for all formulations compared to the measured size at 2 hours post-preparation. As a result, while all suspensions had a decreasing trend in measured size, it was concluded that all suspensions were sufficiently stable to proceed toxicity evaluation.

During toxicity evaluation using the zebrafish mode, addition of NPs was found to cause a higher mortality rate in comparison to the NP free formulation. A higher average number of malformations was also observed with addition of NPs. Higher mortality rates were observed with higher concentrations of all three NPs. For instance, at a 45 ppm microemulsion concentration for the ZnO NP mixture, the mortality rate was 0%, 50%, 68%, and 79% for the base fluid, 5 g/L ZnO NP, 7.5 g/L ZnO NP, and 10 g/L ZnO NP, respectively. Higher concentrations of each NP caused mortality of all zebrafish at lower concentration. For example, for the

TiO_2A NP mixture, 5 g/L TiO_2A NP was found to be lethal at 105 ppm, while the lethal point for 10 g/L TiO_2A NP was 45 ppm. Among all 5 g/L NPs concentrations, TiO_2A NP had the lowest mortality rate. The lowest rate of zebrafish malformation also occurred at 5 g/L TiO_2A NP, which was even lower than for the base fluid. This result is particularly promising for future MWnF™ development, given that the mortality rate for 5 g/L TiO_2A is similar for the base fluid.

In prior research, only one type of NP and one concentration in the base fluid was studied. In this study, three different types of NPs with different morphology (size and shape) and a range of concentrations were explored. This is the first study to explore the stability and toxicity of different MWnF™ formulations using a prepared MWF microemulsion (TRIM® MicroSol 585XT in water) as the base fluid. Regardless of the NP morphology (size and shape), higher concentration of NPs were found to increase the toxicity significantly. One purpose of this research was to identify a potential NP additive to improve MWF machining performance, while maintaining or improving the toxicity. As mentioned above, the 5 g/L TiO_2A MWnF™ formulations is a promising choice based on the conducted experiments for stability and toxicity.

Although all three NPs are potential MWF additives, that can enhance tribological characteristics, the safety of MWnF™ formulations from a toxicological point of view remains a concern. For future research, different NPs with different morphology (size and shape) and variety of concentrations can be explored. The effect of different base fluids on stability, toxicity, and machining performance must be evaluated. Finally, life cycle assessment approaches must be applied to understand comprehensive costs and environmental impacts of the production, use, and end of life of MWnF™ products.

In developing new products, challenges such as safety concerns, human health risks, and toxicological responses of the products arise. The approach applied in this study can be used to assist decision makers in reducing use phase product environmental impacts and human health risks from the early stages of product development. In closing, it must be iterated that use phase safety of MWnF™ also can be enhanced by a training programs and appropriate personal protective equipment within industry.

CHAPTER 5 - SUMMARY AND CONCLUSIONS

5.1 Chapter Overview

This chapter summarizes the work presented herein and concludes the findings and results of the two research studies, individually. A discussion about the findings, limitations, and recommendations for future work is presented.

5.2 Research Summary

Some of the most challenging recent issues faced by decision makers globally include use of non-renewable resources, GHG emissions and climate change, human health risks, toxicity, and potential health hazards. Increases of global population, quality of life, and affluence have led to the significant increase in energy consumption, materials, waste, and safety and cost concerns. While energy can be generated in a number of ways, including use of renewable resources, the primary resources for generating the majority of needed energy comes from non-renewable resources, e.g., fossil fuels, which are accompanied by a number of environmental impacts that are endangering the current generation and threating the well-being of future generations. Thus, precautionary evaluation of environmental impacts and human health concerns of product manufacturing and use must be considered during early product development through model-based methods experimental analysis.

The research explored in this thesis helps provide a better understanding of the efforts that have been undertaken to more precisely calculate environmental impacts and human health risks, such as energy consumption, carbon footprint, and toxicity, to support environmental sustainability of products. The research is comprised of two research objectives. The first research objective explored the integration of the environmental aspect of sustainability performance into the design of products, manufacturing processes, and relevant supply chain networks to assist decision makers. The second research objective explored the challenges of safety concerns, human health risks, and toxicological responses in developing new products.

In Chapter 2, a review composed largely of recent research literature identified current research needs and supported the novelty of this work. It pointed out the need to perform human health and environmental impacts through all stages of the product life cycle from cradle-to-grave, including raw material extraction, manufacturing processes, transportation, use, and end-of-life. Life cycle assessment (LCA) was introduced as an appropriate method for quantitative assessment of environmental impacts across the entire life cycle of products and services. Finally, a review of environmental precautionary design principles for development of new products and technologies was explored.

In Chapter 3 (manuscript 1), the first case (manufacturing) reported the integration of environmental sustainability principles into the early design and development of products, manufacturing processes, and relevant supply chain networks to assist decision makers, specifically for textile-based products. Two backpacks with variant designs were selected to investigate the effect of design decisions on the environmental impacts of product manufacturing and supply chain activities. The energy consumption and carbon footprint of these activities process from raw material extraction to assembly of the final product were evaluated using a process-based approach. Two different supply chain alternatives with various points of origin, distribution centers, distances, and transportation modes were considered for each backpack's materials and components. The work applied comprehensive process models to estimate cradle-to-gate energy consumption and carbon footprint for the product design variants.

In Chapter 4 (manuscript 2), the second case (use) investigated the precautionary environmental and human health concerns of product use during early design and development was investigated. Adding nanoparticles (NPs) to metalworking fluids (MWFs) has been shown to improve MWFs performance in metal cutting, but related precautionary concerns of human health risks and environmental impacts have not been addressed by prior research. To demonstrate an approach for such evaluation, three different types of NPs with different morphology (size and shape) and a range of concentrations in the base fluid were explored to determine the stability and biological responses of the metalworking nanofluids. For stability analysis and toxicological assessment, the dynamic light scattering (DLS) method and zebrafish assay method were applied, respectively. The results revealed that addition of NPs causes a higher mortality rate and more malformations in surviving specimens in comparison to the NP free formulation. One formulation (5 f/L TiO_2A NP) was identified as potentially promising, however.

Overall, due to the important role of designers in product design and the existing uncertainties in the early design stage, this research iterates the need to shift the centering of product design from only the economic aspect to encompass the environmental and social aspects as well. This is accomplished through two research tasks, encompassing divergent life cycle phases and product types, as introduced in chapter 1 and summarized in Table 5.1.

Table 5.1 Comparison of the two research tasks

	Task 1	Task 2
Phase	Manufacturing Case	Use case
Approach	Process-Based Modeling	Experimental Analysis
Product	Common	Novel
Supply Chain	Existing	Developing
Metrics	Energy, CO_2	Stability, Toxicity

5.3 Conclusions

This research examined the environmental impacts and human health concerns of common and novel products at the early design stage. As a result of the research summarized above, several key findings have emerged. The overall, substantial, and common conclusion which has been drawn from both studies is:

- Integration of the life cycle environmental and human health aspects into the design of products at the earliest stages provides the opportunity of improving the sustainability performance even without actual information from product manufacturing and use.

5.3.1 Conclusions: Manufacturing Case

This case study reported the integration of sustainability principles into the design of products, manufacturing processes, and relevant supply chain networks to assist decision makers, specifically for textile-based products. The conclusions are drawn as below:

1. Simultaneous consideration of manufacturing processes and supply chain network designs provide the opportunity to achieve better environmental performance for a given product, and can yield a better understanding of the environmental impacts generated by the manufacturing processes and supply chain activities at the design stage.
2. The manufacturing upstream processes are often the most impactful in the cradle-to-gate life cycle of the product. For instance in this case, the energy consumption and related carbon footprint due to transportation were found to be low (0.2-1.2%) compared to manufacturing, which demonstrates the importance of understanding the direct influence of product design on manufacturing phase impacts.
3. In pursuit of enhancing the overall environmental performance of the product, process planning can be changed and improved. For example, it was found that 30% of the carbon footprint is due to fabric manufacturing for Backpack 1, while fabric manufacturing contributed to 50% of the

carbon footprint for Backpack 2. Fabric manufacturing carbon footprint is primarily driven by wet processing, which uses fossil fuel-based thermal energy for steam and heat. This fossil fuel-based energy can be changed to renewable sources of energy to enhance the overall environmental performance.

4. Global supply chains can utilize sea transport for the greatest possible reduction of carbon dioxide equivalent emission as compared to airfreight transportation. Air transport carbon footprint dominated that of other transportation modes due to a large emission factor.

5.3.2 Conclusions: Use Case

This study investigated precautionary environmental and human health concerns of product use during early design and development by examining the case of metalworking nanofluids (MWnF^{TM}). Adding nanoparticles (NPs) to metalworking fluids (MWFs) has been shown to improve performance in metal cutting. The conclusions are drawn as below:

1. The effect of time on the stability of NPs suspensions were investigated in this study. The measured size of NPs in the base fluid was exhibited to be constant over a one month period, which is necessary for stability. The size reduction percentage of NP mixtures after 120 hours and after one

month was less than a 2% and 3%, respectively when compared the size at two ours post production. As a result, while all suspensions had a decreasing trend in NP size, it was concluded that all suspensions were stable.

2. Addition of NPs causes a higher mortality rate in comparison to the NP free formulation. For instance, at 15 ppm microemulsion concentration, while mortality rate for the base fluid is 0%, the mortality rate for 5 g/L TiO_2A NP, 5 g/L ZnO NP, and 5 g/L TiO_2B NP is 8.3%, 16.7%, and 29.2%, respectively.
3. A higher mortality rate was observed with higher concentrations of all three NPs. For instance, at 45 ppm microemulsion concentration of the ZnO NP mixture, the mortality rate was 0%, 50%, 68%, and 79% for the base fluid, 5 g/L ZnO NP, 7.5 g/L ZnO NP, and 10 g/L ZnO NP, respectively. Higher concentrations of each NP caused mortality of all zebrafish at a lower concentration. For example, for the TiO_2A NP mixture, 5 g/L TiO_2A NP was found to be lethal at 105 ppm, while the lethal point for 10 g/L TiO_2A NP was 45 ppm.
4. A comparison of all 5 g/L NP concentrations, found TiO_2A NP had the lowest mortality rate. The lowest rate of zebrafish malformation also occurred at 5 g/L TiO_2A NP, which was even lower than for the base fluid.

This result is particularly promising, given that the mortality rate for 5 g/L TiO_2A is similar for the base fluid.

5.4 Contributions

The work undertaken within this thesis focused on integration of supporting sustainability principles into the design of products, manufacturing processes, relevant supply chain networks, and use phase to assist design and manufacturing decision makers. Contributions of this research are described below.

5.4.1 Contributions: Manufacturing Case

The work reported endeavors to integrate sustainability principles into the design of products, manufacturing processes, and relevant supply chain networks to assist decision makers.

1. The research conducted under this task develops a method to predict the cradle-to-gate energy consumption and carbon footprint during the design stage for global production of textile-based products. This study motivates engineers to use the demonstrated approach to evaluate environmental impact trade-offs between the variant product designs for environmentally sustainable manufacturing processes and supply chains.

2. The general approach can be extended to analyze different material types used in the textile industry. The method presented is a generally applicable approach, and the backpack case study provides a demonstration of the approach. The life cycle inventories constructed and the modeling results will facilitate future studies within the textile industry (Appendices C, D, and E). This data and information was previously not compiled or available from a single source.

5.4.2 Contributions: Use Case

This study explored the effects of adding different NPs with varying concentrations to MWFs to assess MWnF™ (metalworking nanofluid) stability and toxicological performance.

1. The research involved the extension of the prior toxicity studies of metalworking nanofluid (MWnF™). Previous research investigated the stability and toxicity of ZnO (20 nm) MWnF™ formulations with 5 g/L NPs base fluid concentration. In this study three different types of NPs (two different types of TiO_2 and one type of ZnO) with different morphology (size and shape) and a variety of concentrations (i.e., 5, 7.5, 10 g/L) in the base fluid were explored.

2. It was found that mortality rate relationship between NP concentrations in the base fluid is not linear (Appendix G). For instance, the mortality rate at 15 ppm microemulsion concentration for the 5 and 10 g/L ZnO NP mixture is 16% and 21%, respectively; this amount became 33% and 62% at 30 ppm microemulsion concentration.
3. There is not any published work on zebrafish toxicity assessment of TiO_2 NPs MWnF™ with a commercial MWF as the base fluid. Further, this is the first study that investigates stability and toxicity of TiO_2 NP in an oil-based suspension simultaneously. Prior work only focused on machining performance and toxicity in water. The study revealed that a 5 g/L TiO_2 NP formulation may be a potential additive to the MWF to improve the machining performance, while maintaining MWF toxicity performance.

5.5 Opportunities for Future Research

During the course of this research assumptions were made and limitations of current methods and techniques were identified. The following opportunities for each case are outlined below

5.5.1 Opportunities for Future Research: Manufacturing Case

The demonstrated approach presented motivates researchers to continue and meet the challenges when assessing competing objectives with uncertain data as in the case of early design stage for environmentally sustainable manufacturing process and supply chains. The opportunities for future research are:

1. New metrics, in addition to energy consumption and associated carbon footprint such as solid wastes, water consumption and material use can strengthen the results. Moreover, all three sustainability principles including environmental, economic, and societal aspects can be integrated into product design and manufacturing processes. For instance, product cost and workers health risks can add new dimensions in the decision making processes. One limitation can be a data availability which can be solved by working directly with manufacturing companies and industries.
2. Current work investigated only two phases of the product life cycle (i.e., manufacturing and use). Additional life cycle phases, e.g. end-of-life scenarios e.g. disposal, landfill, remanufacturing, and recycling can be considered and deducted to completely assess the sustainability performance. Environmental impacts in terms of global warming potential (GWP) can be measured and compared for different scenarios.

5.5.2 Opportunities for Future Research: Use Case

This presented study developed new settings for evaluating MWnF™s. The main objective was to assist early stage design decisions by understanding the environmental and human health impacts of products, such as MWnF™, during the manufacturing and use phases. Below are the highlighted potential future research opportunities:

1. In terms of nanofliud stability, there are some instruments and methods that can rank the relative stability of nano suspensions such as UV–Vis spectrophotometer and Zeta potential (ζ) which can be analytically determined from measurement of electrokinetic phenomena [138]. The limitation of this method is finding dielectric constant of the fluid and required instruments for measuring this constant which was not available at the time of this research at Oregon State University. Considering Zeta potential instead of hydrodynamic diameter of colloids in a fluid medium helps to determine the stability of the fluids more accurately. Future studies can use this method which is widely used and the results are more reliable than the measured size.
2. In terms of nanofliud toxicity, although it has been discovered that tribological characteristics of the understudy cutting fluid can be enhanced through addition of ZnO and TiO_2 NPs, further investigation is needed on

safety aspects of MWnF™. Zebrafish model is not a comprehensive solution to investigate all variety of human diseases however, and other standard human toxicity testing should be completed before commercializing nano-based products. Properties of NP rather than size and morphology, could contribute to the toxicity results. These properties such as: mass, composition, surface area, surface chemistry, reactivity, thermal response, and energetic behavior can be considered in future research to have more accurate toxicity results.

3. Considering improvement of machining performance and toxicity of MWnF™ formulations simultaneously will be a problem for the future research to be explored. The research plan must be to determine the potential NP additives to MWFs to improve the machining performance, while maintaining the same level or improved toxicity.

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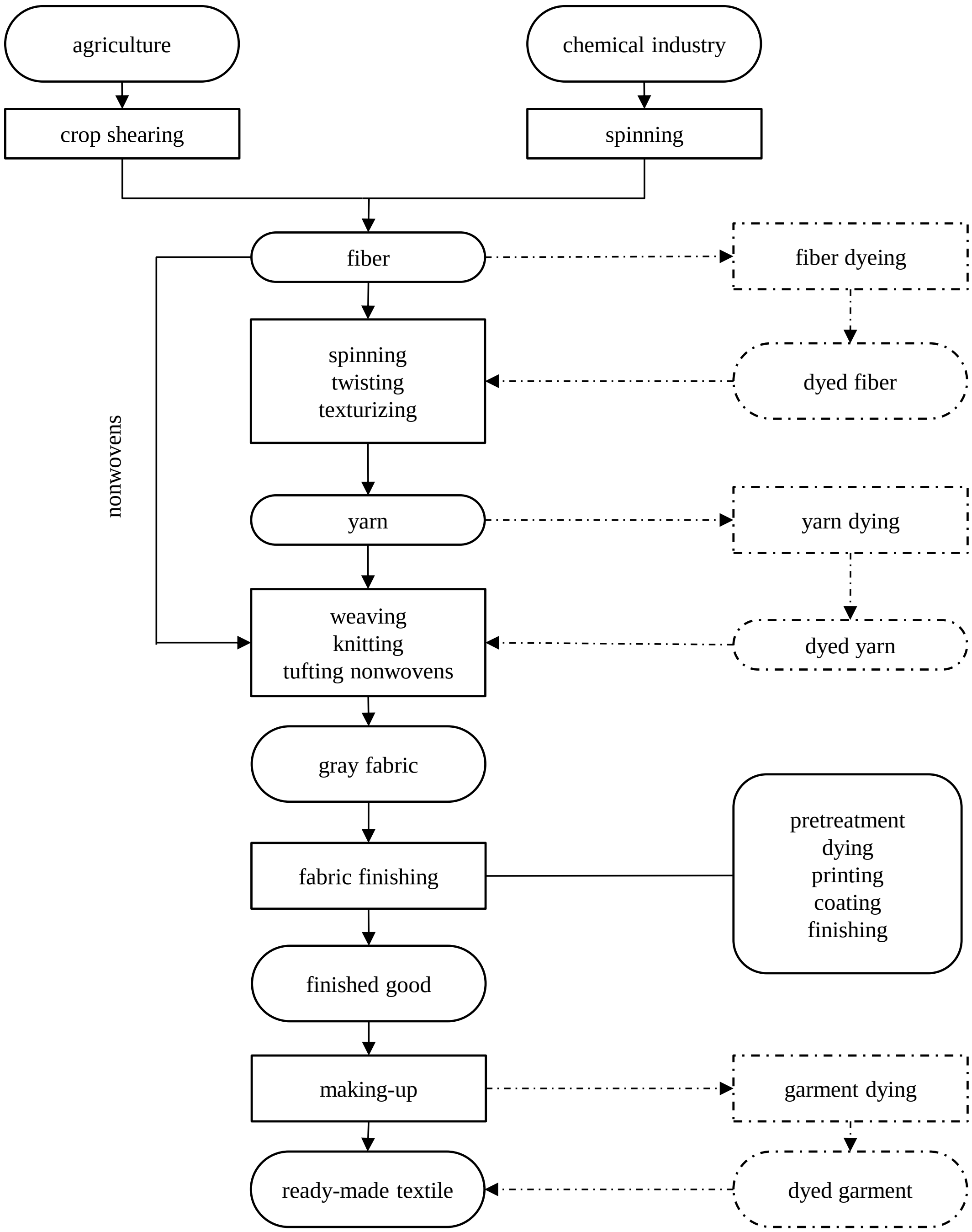
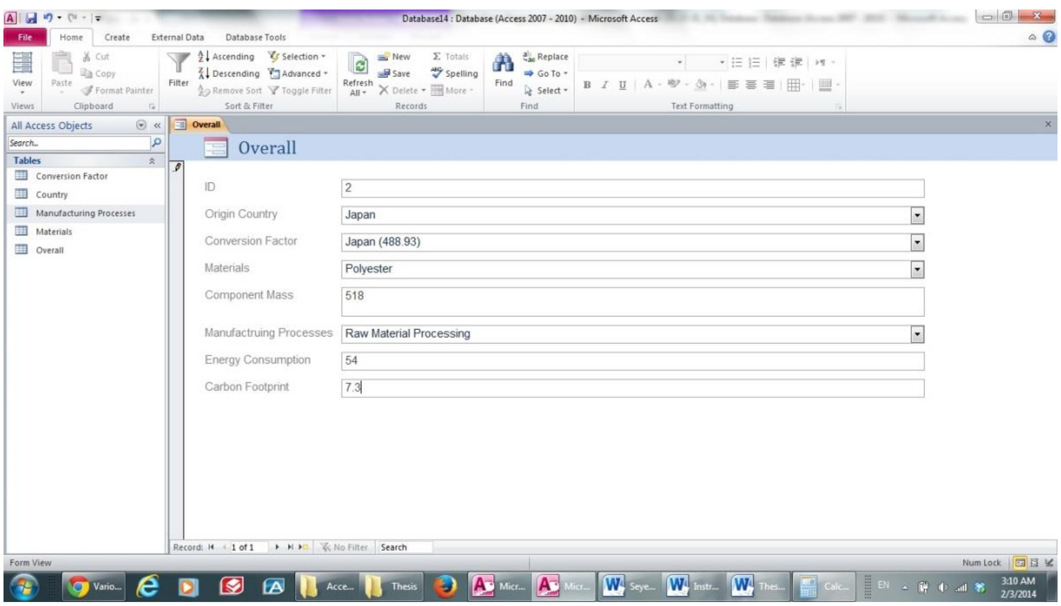
APPENDICES

Appendix A: The Textile Manufacturing Process Chain



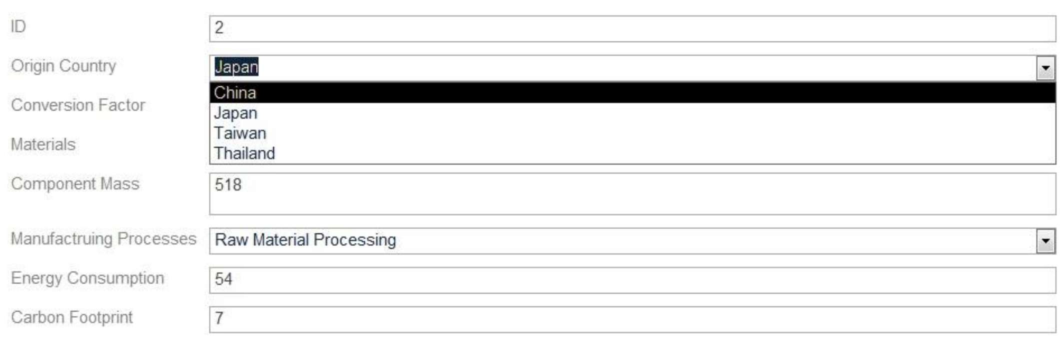
Appendix B: Energy Consumption and Carbon Footprint Database

The data base created contains four tables as input data and also an overall table which will be an output to calculate the energy consumption and related carbon footprint amount. The input tables including conversion factor, country of origin, manufacturing processes, and materials can be modified for the goal of the research. The overall energy consumption and related carbon footprint will be calculated automatically based on the input data.

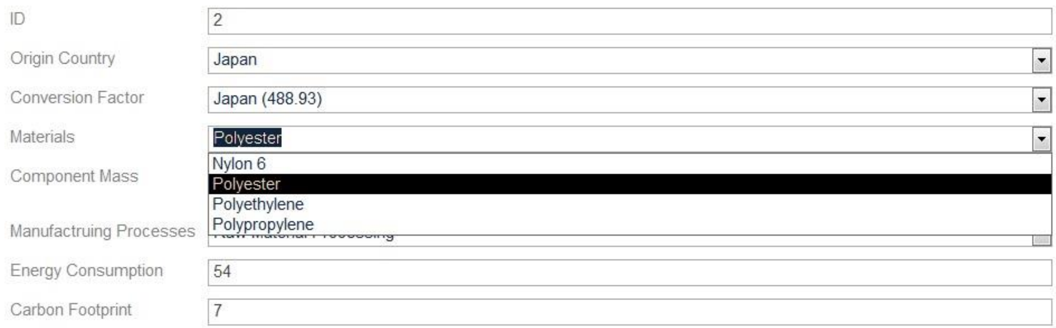


Next figure illustrated how initial data such as origing country, conversion factor, materials, component mass, and manufacturing process can be selected to find the results.

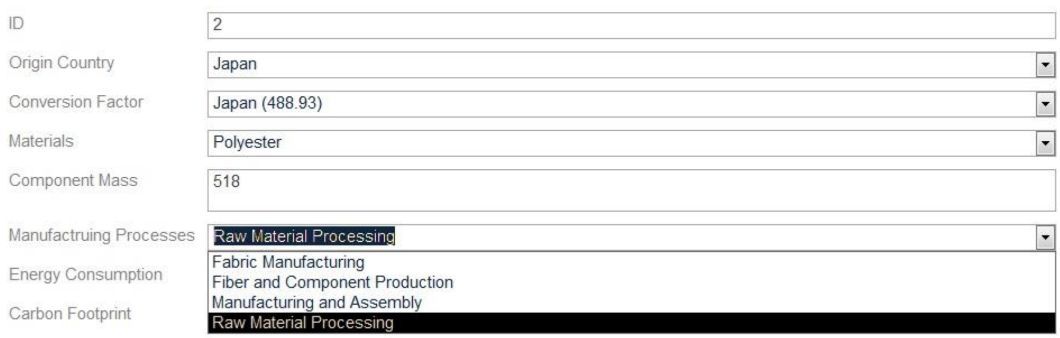
First, the manufacturing company must be selected among available countries. This can be modified for adding the new location. For instance, in this case, Japan is selected where the manufacturing company is located. Then the conversion factor based on the selected country must be chosen.



In the next step material must be selected among available materials. This can be modified for adding new materials. For instance, in this case, Polyester is selected.



In the last step manufacturing process must be selected among available processes. This can be modified for adding new processes. For instance, in this case, raw material processing is chosen.



Appendix C: Energy Consumption Database Coding

This is VBA coding part from the database created to calculate energy consumption. It checks the origin manufacturing country to select the related conversion factor. Then, based on the type of material and manufacturing process, it calculates the amount of energy consumption.

```
Option Compare Database
Option Explicit
Private Sub Energy_Consumption_Click()
Dim ec, mp As Double
If Materials = "Polyester" and Manufacturing Processes = "Raw Material
Processing" Then
mp = 0.104
ec = mp* Material Mass
End If
If Materials = "Polypropylene" and Manufacturing Processes = "Raw Material
Processing" Then
mp = 0.064
ec = mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Raw Material
Processing" Then
mp = 0.107
ec = mp* Material Mass
End If
If Materials = "Polyethylene" and Manufacturing Processes = "Raw Material
Processing" Then
mp = 0.074
ec = mp* Material Mass
End If
If Materials = "Polyester" and Manufacturing Processes = "Fiber and Component
Production" Then
mp = 0.013
ec = mp* Material Mass
End If
```

```
If Materials = "Polypropylene" and Manufacturing Processes = "Fiber and Component Production" Then
mp = 0.006
ec = mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Fiber and Component Production" Then
mp = 0.013
ec = mp* Material Mass
End If
If Materials = "Polyethylene" and Manufacturing Processes = "Fiber and Component Production" Then
mp = 0.036
ec = mp* Material Mass
End If
If Materials = "Polyester" and Manufacturing Processes = "Fabric Manufacturing" Then
mp = 0.151
ec = mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Fabric Manufacturing" Then
mp = 0.151
ec = mp* Material Mass
End If
If Materials = "Polyester" and Manufacturing Processes = "Manufacturing and Assembly" Then
mp = 0.024
ec = mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Manufacturing and Assembly" Then
mp = 0.024
ec = mp* Material Mass
End Sub
```

Appendix D: Carbon Footprint Database Coding

This is VBA coding part from the database created to calculate carbon footprint. It checks the origin manufacturing country to select the related conversion factor. Then, based on the type of material and manufacturing process, it calculates the amount of carbon footprint.

```
Option Compare Database
Option Explicit
Private Sub Carbon_Footprint_Click()
Dim cf, mp As Double
If Materials = "Polyester" and Manufacturing Processes = "Raw Material Processing" and Origin Country = "China" Then
mp = 0.014
cf = 867.81*mp* Material Mass
End If
If Materials = "Polypropylene" and Manufacturing Processes = "Raw Material Processing" and Origin Country = "China" Then
mp = 0.009
cf = 867.81*mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Raw Material Processing" and Origin Country = "China" Then
mp = 0.014
cf = 867.81*mp* Material Mass
End If
If Materials = "Polyethylene" and Manufacturing Processes = "Raw Material Processing" and Origin Country = "China" Then
mp = 0.01
cf = 867.81*mp* Material Mass
End If
If Materials = "Polyester" and Manufacturing Processes = "Fiber and Component Production" and Origin Country = "Japan" Then
mp = 0.0017
cf = 488.93*mp* Material Mass
End If
```

```
If Materials = "Polypropylene" and Manufacturing Processes = "Fiber and Component Production" and Origin Country = "Japan" Then
mp = 0.001
cf = 488.93*mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Fiber and Component Production" and Origin Country = "Japan" Then
mp = 0.0016
cf = 488.93*mp* Material Mass
End If
If Materials = "Polyethylene" and Manufacturing Processes = "Fiber and Component Production" and Origin Country = "Japan" Then
mp = 0.0025
cf = 488.93*mp* Material Mass
End If
If Materials = "Polyester" and Manufacturing Processes = "Fabric Manufacturing" and Origin Country = "Thailand" Then
mp = 0.02
cf = 598.65*mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Fabric Manufacturing" and Origin Country = "Thailand
" Then
mp = 0.0201
cf = 598.65*mp* Material Mass
End If
If Materials = "Polyester" and Manufacturing Processes = "Manufacturing and Assembly" and Origin Country = "Taiwan" Then
mp = 0.0057
cf = 738.56*mp* Material Mass
End If
If Materials = "Nylon 6" and Manufacturing Processes = "Manufacturing and Assembly" and Origin Country = "Taiwan" Then
mp = 0.0058
cf = 738.56*mp* Material Mass
End If
End Sub
```

Appendix E: Toxicology Observation Details

This appendix contains the incidence rates of the observed 23 endpoints for zebrafish embryos exposed to suspensions at different concentrations of MWF. At 24 hpf, four endpoints were evaluated, including mortality (mort), developmental progression (dp), spontaneous movement (sm), and notochord (nc). The remaining 19 were evaluated at 120 hpf and included body axis (axis), brain, circulation (circ), eye, caudal fin (fin-c), pectoral fin (fin-p), jaw, otic vessicle (otic), pigment, pericardial edema (PE), yolk sac edema (YSE), snout, swim bladder (SB), trunk, somite, and touch response (tr) [136]. The following tables contain all of the malformation data collected in the course of this thesis research. Malformations for each set of experimental conditions were not collected due to time and resource limitations.

Table E.1 Incidence rate of endpoints in zebrafish exposed to MWF dilutions (lower concentrations plate)

	Endpoint	Control	15ppm	30ppm	45ppm	60ppm	75ppm	90ppm	105ppm
24 hpf	mort	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	dp	8.3%	0.0%	0.0%	0.0%	0.0%	0.0%	8.3%	8.3%
	nc	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	sm	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	8.3%
120 hpf	mort	0.0%	0.0%	0.0%	0.0%	33.3%	75.0%	50.0%	66.7%
	axis	0.0%	0.0%	0.0%	8.3%	16.7%	8.3%	25.0%	8.3%
	brain	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	circ	8.3%	0.0%	0.0%	0.0%	41.7%	16.7%	25.0%	16.7%
	eye	8.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-C	8.3%	0.0%	0.0%	41.7%	33.3%	16.7%	41.7%	16.7%
	fin-P	8.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	jaw	0.0%	33.3%	50.0%	75.0%	50.0%	8.3%	33.3%	8.3%
	otic	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	pigment	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	PE	16.7%	25.0%	41.7%	91.7%	66.7%	25.0%	50.0%	33.3%
	YSE	8.3%	16.7%	41.7%	41.7%	66.7%	25.0%	50.0%	33.3%
	snout	0.0%	0.0%	33.3%	100.0%	66.7%	25.0%	50.0%	33.3%
	SB	0.0%	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	somite	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	tr	8.3%	0.0%	0.0%	8.3%	41.7%	16.7%	50.0%	16.7%

Table E.2 Incidence rate of endpoints in zebrafish exposed to MWF dilutions (higher concentrations plate)

	Endpoint	Control	120ppm	135ppm	150ppm	165ppm	180ppm	195ppm	210ppm
24 hpf	mort	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	8.3%	8.3%
	dp	0.0%	16.7%	8.3%	0.0%	8.3%	8.3%	0.0%	16.7%
	nc	8.3%	0.0%	0.0%	0.0%	0.0%	8.3%	8.3%	0.0%
	sm	0.0%	0.0%	0.0%	0.0%	25.0%	75.0%	91.7%	91.7%
120 hpf	mort	0.0%	91.7%	100.0%	91.7%	100.0%	100.0%	91.7%	91.7%
	axis	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	brain	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	circ	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	eye	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-C	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	fin-P	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	jaw	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	otic	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	pigment	16.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	PE	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	YSE	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	snout	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	SB	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	somite	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	tr	0.0%	8.3%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%

Table E.3 Incidence rate of endpoints in zebrafish exposed to 5 g/L ZnO MWnF™ dilutions (lower concentrations plate)

	Endpoint	Control	15ppm	30ppm	45ppm	60ppm	75ppm	90ppm	105ppm
24 hpf	mort	8.3%	16.7%	33.3%	33.3%	83.3%	41.7%	91.7%	83.3%
	dp	0.0%	0.0%	0.0%	8.3%	8.3%	25.0%	8.3%	0.0%
	nc	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	sm	0.0%	0.0%	0.0%	25.0%	8.3%	41.7%	8.3%	16.7%
120 hpf	mort	0.0%	0.0%	0.0%	16.7%	16.7%	50.0%	8.3%	16.7%
	axis	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	brain	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	circ	0.0%	0.0%	0.0%	25.0%	0.0%	8.3%	0.0%	0.0%
	eye	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-C	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	fin-P	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	jaw	0.0%	0.0%	8.3%	8.3%	0.0%	0.0%	0.0%	0.0%
	otic	0.0%	0.0%	0.0%	8.3%	0.0%	0.0%	0.0%	0.0%
	pigment	0.0%	8.3%	16.7%	8.3%	0.0%	0.0%	0.0%	0.0%
	PE	0.0%	0.0%	58.3%	33.3%	0.0%	8.3%	0.0%	0.0%
	YSE	0.0%	33.3%	8.3%	41.7%	0.0%	8.3%	0.0%	0.0%
	snout	0.0%	0.0%	0.0%	41.7%	0.0%	8.3%	0.0%	0.0%
	SB	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	somite	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	tr	0.0%	0.0%	0.0%	25.0%	0.0%	8.3%	0.0%	0.0%

Table E.4 Incidence rate of endpoints in zebrafish exposed to 5 g/L ZnO MWnF™ dilutions (higher concentrations plate)

	Endpoint	Control	120ppm	135ppm	150ppm	165ppm	180ppm	195ppm	210ppm
24 hpf	mort	0.0%	75.0%	75.0%	50.0%	91.7%	91.7%	91.7%	83.3%
	dp	0.0%	16.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	nc	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	sm	0.0%	16.7%	16.7%	33.3%	8.3%	0.0%	0.0%	0.0%
120 hpf	mort	8.3%	25.0%	25.0%	50.0%	8.3%	8.3%	8.3%	16.7%
	axis	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	brain	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	circ	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	eye	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-C	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-P	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	jaw	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	otic	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	pigment	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	PE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	YSE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	snout	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	SB	8.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	somite	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	tr	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Table E.5 Incidence rate of endpoints in zebrafish exposed to 5 g/L TiO_2A MWnF™ dilutions (lower concentrations plate)

	Endpoint	Control	15ppm	30ppm	45ppm	60ppm	75ppm	90ppm	105ppm
24 hpf	mort	4.2%	0.0%	12.5%	8.3%	12.5%	37.5%	54.2%	83.3%
	dp	0.0%	0.0%	0.0%	4.5%	4.8%	0.0%	0.0%	0.0%
	nc	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	sm	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
120 hpf	mort	0.0%	4.2%	4.2%	10.0%	4.8%	0.0%	18.2%	16.7%
	axis	0.0%	0.0%	0.0%	5.0%	20.0%	46.6%	66.6%	0.0%
	brain	0.0%	0.0%	0.0%	0.0%	10.0%	0.0%	0.0%	0.0%
	circ	0.0%	0.0%	0.0%	35.0%	35.0%	40.0%	55.5%	0.0%
	eye	0.0%	0.0%	0.0%	5.0%	15.0%	20.0%	22.2%	0.0%
	fin-C	0.0%	0.0%	5.0%	0.0%	30.0%	6.6%	22.2%	0.0%
	fin-P	0.0%	0.0%	0.0%	5.0%	20.0%	20.0%	11.1%	0.0%
	jaw	0.0%	0.0%	0.0%	0.0%	20.0%	33.3%	22.2%	0.0%
	otic	0.0%	0.0%	0.0%	0.0%	10.0%	0.0%	0.0%	0.0%
	pigment	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	PE	0.0%	0.0%	0.0%	25.0%	55.0%	93.3%	77.7%	0.0%
	YSE	0.0%	0.0%	0.0%	10.0%	35.0%	6.6%	22.2%	0.0%
	snout	0.0%	0.0%	0.0%	0.0%	10.0%	26.6%	0.0%	0.0%
	SB	0.0%	0.0%	0.0%	0.0%	5.0%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	10.0%	0.0%	11.1%	0.0%
	somite	0.0%	0.0%	0.0%	0.0%	5.0%	0.0%	0.0%	0.0%
	tr	0.0%	0.0%	0.0%	10.0%	25.0%	53.3%	11.1%	0.0%

Table E.6 Incidence rate of endpoints in zebrafish exposed to 5 g/L TiO_2A MWnF™ dilutions (higher concentrations plate)

	Endpoint	Control	120ppm	135ppm	150ppm	165ppm	180ppm	195ppm	210ppm
24 hpf	mort	0.0%	58.3%	70.8%	70.8%	87.5%	87.5%	95.8%	91.6%
	dp	0.0%	18.2%	14.3%	14.3%	66.7%	66.7%	100.0%	100.0%
	nc	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	sm	0.0%	90.2%	0.0%	100.0%	100.0%	100.0%	100.0%	100.0%
120 hpf	mort	8.3%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
	axis	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	brain	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	circ	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	eye	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-C	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-P	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	jaw	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	otic	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	pigment	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	PE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	YSE	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	snout	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	SB	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	somite	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	tr	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Table E.7 Incidence rate of endpoints in zebrafish exposed to 10 g/L TiO_2A MWnF™ dilutions (lower concentrations plate)

	endpoint	Control	15ppm	30ppm	45ppm	60ppm	75ppm	90ppm	105ppm
24 hpf	mort	0.0%	25.0%	41.6%	41.6%	70.8%	100.0%	100.0%	100.0%
	dp	4.2%	5.5%	35.7%	35.7%	57.1%	0.0%	0.0%	0.0%
	nc	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	sm	0.0%	5.5%	35.7%	28.5%	57.1%	0.0%	0.0%	0.0%
120 hpf	mort	8.3%	27.7%	64.3%	100.0%	100.0%	0.0%	0.0%	0.0%
	axis	4.5%	30.7%	60.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	brain	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	circ	0.0%	30.7%	40.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	eye	0.0%	7.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-C	0.0%	38.5%	40.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	fin-P	0.0%	46.1%	40.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	jaw	0.0%	84.6%	60.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	otic	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	pigment	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	PE	4.5%	92.3%	60.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	YSE	0.0%	61.5%	60.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	snout	0.0%	7.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	SB	0.0%	30.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	trunk	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	somite	0.0%	0.0%	20.0%	0.0%	0.0%	0.0%	0.0%	0.0%
	tr	0.0%	15.4%	60.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Appendix F: Statistical Analysis of Toxicity Evaluation Results (Tukey Test)

Recorded mortality rates are compared to draw conclusions regarding the effect of different NPs on toxicity of suspensions using the Tukey test method (in RStudio software).

Test Procedure: The Tukey test compares all possible pairs of means based on a studentized range distribution with a 95% confidence interval. Table G.1 presents all pairs comparisons by showing the difference in mean, lower confidence and higher confidence intervals, and the p-value. Each comparison having p-value less than 0.05 indicates a significant difference between a pair. No assumption can be made for the results with a p-value more than 0.1.

Table F.1 Tukey test results

Pair Comparison	Mean difference	Lower Confidence Interval	Higher Confidence Interval	P-Value
10TiO2B-10TiO2A	-4.166667	-56.661	48.327667	0.9999999
10ZnO-10TiO2A	-10.119095	-62.613429	42.375238	0.9997429
10ZnO-10TiO2B	-5.952429	-58.446762	46.541905	0.9999972
5TiO2A-10TiO2A	-51.190476	-103.68481	1.303857	0.0617569
5TiO2A-10TiO2B	-47.02381	-99.518143	5.470524	0.1163642
5TiO2A-10ZnO	-41.071381	-93.565714	11.422952	0.2542961
5TiO2B-10TiO2A	-8.333333	-60.827667	44.161	0.999949
5TiO2B-10TiO2B	-4.166667	-56.661	48.327667	0.9999999
5TiO2B-10ZnO	1.785762	-50.708572	54.280095	1
5TiO2B-5TiO2A	42.857143	-9.637191	95.351476	0.2044843
5ZnO-10TiO2A	-20.238095	-72.732429	32.256238	0.957209

Pair Comparison	Mean difference	Lower Confidence Interval	Higher Confidence Interval	P-Value
5ZnO-10TiO2B	-16.071429	-68.565762	36.422905	0.9908105
5ZnO-10ZnO	-10.119	-62.613333	42.375333	0.9997429
5ZnO-5TiO2A	30.952381	-21.541952	83.446714	0.6444409
5ZnO-5TiO2B	-11.904762	-64.399095	40.589572	0.9990461
7.5TiO2A-10TiO2A	-14.880963	-67.375297	37.61337	0.9947356
7.5TiO2A-10TiO2B	-10.714297	-63.20863	41.780037	0.9995901
7.5TiO2A-10ZnO	-4.761868	-57.256202	47.732465	0.9999996
7.5TiO2A-5TiO2A	36.309513	-16.184821	88.803846	0.4214228
7.5TiO2A-5TiO2B	-6.54763	-59.041963	45.946703	0.9999935
7.5TiO2A-5ZnO	5.357132	-47.137202	57.851465	0.9999989
7.5TiO2B-10TiO2A	-5.357143	-57.851476	47.137191	0.9999989
7.5TiO2B-10TiO2B	-1.190476	-53.68481	51.303857	1
7.5TiO2B-10ZnO	4.761952	-47.732381	57.256286	0.9999996
7.5TiO2B-5TiO2A	45.833333	-6.661	98.327667	0.1377324
7.5TiO2B-5TiO2B	2.97619	-49.518143	55.470524	1
7.5TiO2B-5ZnO	14.880952	-37.613381	67.375286	0.9947357
7.5TiO2B-7.5TiO2A	9.52382	-42.970513	62.018154	0.9998441
7.5ZnO-10TiO2A	-13.095238	-65.589572	39.399095	0.9979914
7.5ZnO-10TiO2B	-8.928571	-61.422905	43.565762	0.9999089
7.5ZnO-10ZnO	-2.976143	-55.470476	49.518191	1
7.5ZnO-5TiO2A	38.095238	-14.399095	90.589572	0.3534328
7.5ZnO-5TiO2B	-4.761905	-57.256238	47.732429	0.9999996
7.5ZnO-5ZnO	7.142857	-45.351476	59.637191	0.9999863
7.5ZnO-7.5TiO2A	1.785725	-50.708608	54.280059	1
7.5ZnO-7.5TiO2B	-7.738095	-60.232429	44.756238	0.9999728
BF-10TiO2A	-58.333333	-110.827667	-5.839	**0.0181633**
BF-10TiO2B	-54.166667	-106.661	-1.672333	**0.0378189**
BF-10ZnO	-48.214238	-100.708572	4.280095	0.0977539
BF-5TiO2A	-7.142857	-59.637191	45.351476	0.9999863
BF-5TiO2B	-50	-102.494333	2.494333	0.0745009
BF-5ZnO	-38.095238	-90.589572	14.399095	0.3534328
BF-7.5TiO2A	-43.45237	-95.946703	9.041963	0.1895342
BF-7.5TiO2B	-52.97619	-105.470524	-0.481857	**0.0461785**
BF-7.5ZnO	-45.238095	-97.732429	7.256238	0.1495165

Appendix G: Statistical Analysis of Toxicity Evaluation Results (Logistic Regression)

First, a quadratic logistic regression model was developed for each set of recorded mortalities (Eq. G.1).

$$T_{MR} = aX + bX2 + cX3 + dX4 + e \qquad [G.1]$$

where T_{MR} shows the mortality rate and X represents the concentrations level (ppm). To indicate how well the experimental data points fit the models, the coefficients of determination (R^2) were calculated. The toxicity model parameters and R^2 values are shown in Table G.1 for each fluid formulation evaluated. It can be seen that the models fit the experimental data well (R^2 = 0.920-0.991).

Table G.1 Model parameters and coefficients of determination

Fluid Formulation	Coefficient of X (a)	Coefficient of X^2 (b)	Coefficient of X^3 (c)	Coefficient of X^4 (d)	Intercept (e)	R^2
Base fluid	$-8.43*10^{-1}$	$3.36*10^{-2}$	$-2.26*10^{-4}$	$4.57*10^{-7}$	2.37	0.939
5 g/L ZnO in Base Fluid	2.83	$-2.00*10^{-2}$	$4.63*10^{-5}$	$-6.34*10^{-9}$	-27.38	0.935
7.5 g/L ZnO in Base Fluid	4.20	$-4.61*10^{-2}$	$2.15*10^{-4}$	$-3.64*10^{-7}$	-36.22	0.972
10 g/L ZnO in Base Fluid	4.54	$-5.39*10^{-2}$	$2.69*10^{-4}$	$-4.81*10^{-7}$	-35.07	0.991
5 g/L TiO_2A in Base Fluid	-2.35	$5.75*10^{-2}$	$-3.71*10^{-4}$	$7.52*10^{-7}$	36.50	0.968
7.5 g/L TiO_2A in Base Fluid	3.13	$-2.82*10^{-2}$	$1.05*10^{-4}$	$-1.36*10^{-7}$	-20.71	0.979
10 g/L TiO_2A in Base Fluid	4.00	$-5.42*10^{-2}$	$2.98*10^{-4}$	$-5.74*10^{-7}$	1.55	0.943
5 g/L TiO_2B in Base Fluid	4.65	$-5.59*10^{-2}$	$2.81*10^{-4}$	$-5.04*10^{-7}$	-33.93	0.920
7.5 g/L TiO_2B in Base Fluid	4.19	$-5.18*10^{-2}$	$2.65*10^{-4}$	$-4.84*10^{-7}$	-17.33	0.944
10 g/L TiO_2B in Base Fluid	3.93	$-4.89*10^{-2}$	$2.52*10^{-4}$	$-4.61*10^{-7}$	-9.31	0.949

Appendix H: Logistic Regression and Tukey Test RStudio Coding

This is RStudio coding to read the file containing the concentrations and mortality rate. Then, a quadratic logistic regression model was developed for each set of recorded mortalities. Lastly, the Tukey test for all possible pairs of means based on a studentized range distribution with a 95% confidence interval was developed.

```
sample<-read.csv("c:/rdata.csv",header=T)

sample[,1]

install.packages("aod")

install.packages("ggplot2")

library(aod)

library(ggplot2)

attach(sample)

ppm[15:28]

ppm2<-ppm^2

ppm3<-ppm^3

ppm4<-ppm^4

head(sample)

mylogit <- glm(X10tib ~ ppm+ppm2+ppm3+ppm4)

R2 <- cor(X10tib,predict(mylogit))^2
```

```
summary(mylogit)

sample2<-read.csv("c:/rdata2.csv",header=T)

myaov <- aov(sample2$mort ~ sample2$type)

TukeyHSD(myaov, 'sample2$type', conf.level=0.95)
```