EXPERIMENTAL EVALUATION OF THE MECHANICAL PROPERTIES OF RECYCLED HIGH-DENSITY POLYETHYLENE (rHDPE) BLENDED WITH TALC FILLER, FOR ENGINEERING APPLICATIONS

by

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DEDICATION

I wholeheartedly dedicate this work to my beloved parents, Mr. and Mrs. Isilyumu Aaron Malyuta, for their endless love, support, and encouragement. They have always supported my endeavors and have been a constant source of inspiration, giving me strength even when I thought of giving up. They have continually provided me with their moral, spiritual, and financial support.

I also dedicate this work to my beloved wife and children, whose love, devotion, and prayers have inspired me to strive for intellectual achievements. I know how much this dedication will mean to them. Furthermore, I extend my gratitude to my brothers, sisters, relatives, mentors, and friends who have shared their words of love and encouragement with me, motivating me to persist until I finished this work.

Lastly, I dedicate this work to my God and my Ancestors, who have guided and empowered me with their strength, protection, and skills, and have given me a healthy life. I offer all of these accomplishments to you in gratitude.

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VITA

Daniel Aaron Isilyumu Malyuta, "Malyuta", was born in Buyogo, Tanzania in 1985. He is the son of Isilyumu Aaron Malyuta and Flora Bujiku and is the fourth child in a family of nine children, comprising six brothers and three sisters. Between 1993 and 2008, Malyuta received his primary and secondary education, including ordinary level and advanced level/high school, in Mwanza, Kagera, and Shinyanga regions of Tanzania. In 2008, after completing high school, he enrolled in undergraduate studies at the University of Dar es Salaam in Tanzania, where he graduated with a Bachelor of Science degree (Hons) in Civil and Structural Engineering in November 2012.

In August 2013, Malyuta moved to the United States of America after receiving a Graduate Research Assistantship and admission to the graduate program at the University of Tennessee at Chattanooga (UTC). In August 2015, he completed his Master of Science degree in Civil Engineering, as well as a Post Baccalaureate Certificate in Engineering Management (Construction Management), from UTC.

After completing his master's degree, Malyuta worked as a lecturer with the University of Dar es Salaam and as a structural engineer with several construction and consultation companies in Tanzania, where he gained experience in structural analysis and design for over three years. In January 2019, he was registered as a Professional Engineer (PEng: Civil Engineering) by the Engineers' Registration Board (ERB) of the United Republic of Tanzania.

In January 2019, Malyuta joined the Ph.D. program at Montana State University in Bozeman, after receiving a Graduate Research Assistantship and admission to the graduate program. He completed his Doctor of Philosophy (Ph.D.) in Civil Engineering with a concentration in Structural Engineering in July 2023. Throughout his studies and work at various institutions and companies, Malyuta performed various tasks, responsibilities, and training in his area of expertise, civil and structural engineering.

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ABSTRACT

The extensive use of thermoplastic products, particularly high-density polyethylene (HDPE), has led to significant plastic waste, posing environmental threats. To manage thermoplastic waste, recycling is the preferred method; however, this has not been wholly effective due to technological and economic challenges and limitations. Large-scale applications of recycled HDPE (rHDPE) can incentivize recycling and create new revenue streams. HDPE is a well-established thermoplastic for engineering applications, and components made of HDPE have desirable properties such as high strength-to-weight ratio, ease of processing, availability, low cost, and excellent chemical and corrosion resistance. With concerns about the fate of plastics at end-of-life, there is a growing interest in strategies to utilize rHDPE in place of virgin HDPE (vHDPE). This study focused on investigating the mechanical and thermal properties of rHDPE-talc blends across various talc filler contents and temperatures, and across four recycling generations, as understanding these properties is crucial for application. Following ASTM standards, tests for tensile strength, elastic modulus, storage modulus, nominal yield stiffness, nominal yield strain, impact strength, and melt flow index were performed. Dynamic mechanical analysis and differential scanning calorimetry were also carried out. Results show that talc content and temperature affect tensile strength, elastic modulus, nominal stiffness, yield strain, impact strength, and storage modulus. Melting temperature decreased while crystallinity increased with talc filler content increase. Compared to neat HDPE and in most cases vHDPE-talc blends, rHDPE-talc blends perform better. Response Surface Methodology was applied using the Central Composite Design statistical experimental design approach to further study the stiffness and strength of rHDPE as functions of temperature and talc filler content. It revealed significant correlations for practical applications. Increasing the number of thermal reprocessing cycles decreased tensile strength, elastic modulus, impact strength, and storage modulus, while nominal yield strain and melt flow index increased. Crystallinity and melting temperature minimally decreased with increased thermal reprocessing cycles. Despite these changes, most of the properties of both the neat rHDPE and its talc blends remain comparable to the virgin counterparts, even after the fourth recycling generation. This implies that the recycled materials can be suitable for use in existing applications of vHDPE.

CHAPTER ONE

INTRODUCTION

1.1 Motivation and Problem Scale

Thermoplastics are recyclable carbon-based plastics produced in a factory. For decades, they have gained more attention and recognition for being ideal for several applications due to their excellent chemical and corrosion resistance, low density, ease of processing, availability, cost, and adequate strength to weight ratio [1-3]. However, in their everyday use, thermoplastics have become one of the biggest threats and agents of destruction to global environmental conservation and marine life through pollution, which significantly impacts human and animal health and ecosystems [4-8].

According to the 2021 United Nations Environment Programme (UNEP) report, the world has achieved significant economic growth over the past few decades, accompanied by large amounts of pollution with significant impacts on human health and ecosystems [6]. The report further highlights that plastic waste is the largest, most harmful and most persistent fraction of marine litter, accounting for at least 85 percent of total marine waste and environmental pollution [5, 6]. In fact, plastic pollution is one of the fastest-growing environmental challenges, and the management of plastic wastes is a challenging task with many limitations [4-6]. Several efforts and methods have been used to manage and solve thermoplastic waste problems, including landfill, incineration, pyrolysis, bioremediation, and recycling, most of which are destructive, harmful and produce noxious gases that contribute to global warming [4, 8]. Thermoplastic recycling is acknowledged as the best method in thermoplastic waste management, as it is the most

environmentally friendly, cheap, with few to no limitations, and can be a non-damaging process that leaves the polymeric material without significant degradation or with only minor modifications in properties [4, 9]. However, the current recycling rate is very low. According to the 2021 UNEP report, plastic recycling rates are less than 10 percent, and plastics-related greenhouse gas emissions are significant [5, 6]. Geyer et al. estimated that approximately 6,300 million metric tons of plastic waste had been generated (of which 4.4% was HDPE), of which only 9% was recycled, 12% was incinerated, and 79% was accumulated in landfills or the natural environment. On a global scale, it was estimated that a cumulative total of 8.3 billion metric tons of waste virgin plastics have been produced as of 2017. Roughly, 12,000 million metric tons of plastic waste will be in landfills or the natural environment by the year 2050 if the current production and waste management trends continue [10]. According to the United States Environmental Protection Agency (US EPA), 32.37 million metric tons of plastic waste had been generated by the year 2018 (cumulative 1960-2018) in the US, of which only 2.8 million metric tons (8.66%) were recycled, and 5.1 million metric tons (15.75%) were combusted with energy recovery, while about 24.47 million metric tons (75.59%) were accumulated in landfills [11].

1.2 High Density Polyethylene (HDPE)

High-density polyethylene (HDPE) is a commonly used thermoplastic polymer due to its versatility, which allows it to be adapted for several functions. It is frequently used to manufacture food and chemical packaging, such as containers for drinks, motor oil, detergent, and more [1]. Polyethylene (PE) has the highest production volume of all polymers, with HDPE being one of the cheapest [1]. Specifically due to its strength-to-weight ratio, excellent chemical and corrosion resistances, and availability. Due to that, HDPE and its composites have emerged to be suitable

and appropriate for a wide range of applications. This includes various engineering applications, such as structural elements like beams, columns, trusses, slabs, load bearing walls, shear walls, guard rail components (to road edges, bridge edges, buildings, etc.), fluid storage tanks, critical connections (screws, bolts, nuts, etc.), and more. Due to the recyclability of HDPE and efforts to increase thermoplastic recycling rates, using recycled HDPE (rHDPE) instead of or partially replacing virgin HDPE (vHDPE) for large volume applications, will help make HDPE recycling more economical and reduce vHDPE waste. Extensively using rHDPE in several applications will come with environmental benefits; however, it is crucial to understand the mechanical properties of rHDPE and its associated composites or blends before replacing vHDPE and other plastics with rHDPE. Previous studies have explored the physical, mechanical, chemical, thermal, morphological, and other properties of HDPE and its composites/blends and provided valuable findings. For instance, studies have shown that rHDPE can exhibit comparable properties, with little to no differences, to vHDPE for up to three thermal recycling generations [12-18]. The current research focused on the experimental study of the mechanical properties of rHDPE and rHDPE blended with talc filler across a range of application temperatures and thermal recycling generations. If rHDPE-talc blends exhibit comparable performances to vHDPE-talc blends, then using rHDPE in place of or in addition to vHDPE can increase recycling rates and help reduce thermoplastic waste.

1.3 Talc

Talc is a naturally occurring inorganic mineral that is mined from the earth. It is composed of magnesium, silicon, oxygen, and hydrogen ($Mg_3Si_4O_{10}(OH)_2$) and can be used as a filler material [19-21]. Talc has several applications due to its high chemical stability, affordability, and

availability [21, 22]. Like other filler materials, talc filler can optimize or affect several properties of thermoplastics, including static mechanical properties (such as stiffness and strength), appearance, chemical structure, microstructure, physical properties, and dynamic mechanical properties. Additionally, talc filler is added to polymeric materials to reduce overall cost of the blend and to improve thermal stability [2, 13, 14, 16, 17, 23-25]. According to the literature, talc filler has been explored in blends with HDPE and other polymers and the blends have shown good performance based on tensile strength, modulus, stiffness, and density [24, 26]. The theory behind this is that composite or blend materials have two phases: the reinforcing phase and the matrix phase, which holds the reinforcement and forms the desired shape. The mechanical performance of the composites is a function of the reinforcing phase; however, the matrix phase also makes its own significant contribution to composite properties such that the synergistic effect of both the matrix and reinforcing phase plays a significant role. Therefore, talc acts as reinforcement to the polymer to improve the overall properties of the matrix system [27, 28]. The way in which the filler material optimizes matrix properties depends on filler type and properties, such as surface functional groups, surface activity, surface area, particle size, orientation, concentration/content, dispersion, particulate shape, and the interfacial adhesion of the filler particles [25, 29-34]. For example, at low talc filler contents of approximately 3 wt% or less, talc filler acts as a nucleating agent by reducing spherulite size and shortening processing time [35]. At higher contents of approximately 10-40 wt%, talc acts as a reinforcing filler, increasing elastic modulus and stiffness, and reducing strain-to-break and impact strength [36]. However, there has been little research on the material and mechanical properties of rHDPE blended with talc filler, which is a knowledge gap and motivates the research performed here.

1.4 Temperature

The mechanical properties, performance, and strength of HDPE, like other polymers, are highly sensitive to the temperatures they are exposed to during service, which can limit their usage [37]. To achieve optimal polymer performance, the temperature should remain within the range of the glass transition temperature, T_g (or ductile-brittle transition temperature-DBTT) and the crystalline melting temperature, T_m. The T_g is where there is a disordered amorphous solid, while T_m is the temperature at which the solid becomes a disordered melt [38]. Thus, it is essential to avoid service temperatures below the minimum operating temperature, close to T_g, or above the maximum operating temperature, close to T_m, to ensure practical use. Researchers have found that a specific range of increasing temperatures can cause drastic decreases in polymer strength and stiffness, as well as increases in yield and break strains [37, 39-44]. Similarly, the response of structural members made of rHDPE-talc blends will differ at varying temperatures. This implies that, if rHDPE qualifies to be used in engineering applications, then, designing rHDPE for structural applications will depend on the intended use, such as outdoor decks or docks/pier, and may require data on the material's responses across different temperature ranges, such as freezing vs. hot sunny days. Therefore, this study considers testing temperature as a variable, and the literature suggests that it has not been extensively explored for rHDPE-talc blends within the specified temperature ranges.

Merah et al. conducted a study on the effect of temperature on the tensile properties of HDPE, PE-100 pipe material, with temperatures ranging from -10^{o}C to 70^{o}C, which revealed that yield strength and elastic modulus decreased linearly with increasing temperature, while the yield strain showed a slight increase [37]. Merah et al. also investigated the effect of temperatures

ranging from -10°C to 70°C on the mechanical properties of chlorinated polyvinyl chloride (CPVC) and found that the yield strength and elastic modulus decreased linearly with increasing temperature [42]. Hitt and Gilbert examined the tensile properties of PVC at temperatures ranging from 23°C to 180°C and found that stress at break decreased steadily with increasing temperature, while elongation at break showed a maximum between 80°C and 90°C and a minimum between 130°C and 170°C [39]. Bronnikov et al. studied the thermal and mechanical properties of drawn polymers over a wide temperature range of 100 K to 800 K (-173.15°C to 526.85°C) using polyethylene (PE), polyethylene terephthalate (PET), nylon 6, nylon 610, and poly (viny1 alcohol) (PVA), and reported that Young's modulus and yield stress decrease with increasing temperature [43]. Bond's study indicated that the tensile strength of HDPE pressure pipe material decreased from 21 MPa at 23°C to 10 MPa at 60°C [44].

1.5 Thermal Recycling

Thermoplastic properties are subject to change after thermal recycling, as the molecular weight and hence the crystallinity ratio of the material are affected, which in return affects the brittleness of the material and other mechanical properties [45-48]. For example, the change in elastic modulus may be explained by the change in density, which may cause a change in material crystallinity when repeating the recycling process [12, 46, 49]. The current study further examined the impact of thermal recycling cycles/repetitions on the properties of rHDPE-talc filler blends.

1.6 Objectives

The motivations and technology gaps support the need for this study. The study specifically investigated tensile properties, impact strength, dynamic mechanical properties (flexural stiffness)

using dynamical mechanical analysis (DMA), and thermal properties (crystalline structure) using differential scanning calorimetry (DSC). These properties play a significant role in engineering applications. Melt flow index (MFI) testing was performed to investigate rHDPE quality and scanning electron microscope (SEM) imaging was used to examine the uniformity and dispersion of talc filler particles in the polymer matrix. The tests were conducted to investigate rHDPE properties in relation to talc filler content, temperature, and number of thermal recycling generations. To achieve the goals of the study, the following objectives were addressed:

1. Experimentally investigate the tensile properties of rHDPE as functions of talc filler content (0-48 wt%), at room temperature, and across a broad range of testing temperatures from -56.6^{o}C to 56.6^{o}C. This experimental study focused on investigating the tensile strength at yield (σ_{TY}), elastic modulus (E), elastic nominal stiffness (k), and nominal yield strain (ε_{NY}).

   It was hypothesized that blends made of rHDPE and talc filler exhibit higher yield tensile strength, elastic modulus, and elastic nominal stiffness, but lower nominal yield strain, compared to neat rHDPE.

2. Evaluate the flexural properties (flexural stiffness) of rHDPE as functions of talc filler content and temperature through dynamic mechanical analysis (DMA). DMA is a technique in which the elastic and viscous response of a sample under oscillating load are monitored against temperature, time, or frequency where the frequency of oscillation is proportional to the modulus (stiffness) of the material [50, 51]. In this study, the storage modulus (E'), loss modulus (E''), and the tangent of delta (tan δ) of each rHDPE-talc filler blend were measured as functions of temperature.

3. Carry out an experimental statistical analysis and develop polynomial response models using Response Surface Methodology (RSM) by utilizing the experimental data from Objectives 1 and 2, for some selected properties, as functions of talc filler content and testing temperature. The hypothesis was that there is a significant statistical impact of talc filler content and testing temperature on the rHDPE tensile properties and flexural stiffness, and that the developed response models would yield significant predictive performances.
4. Investigate the effects of the number of thermal reprocessing cycles (recycling generations) up to the fourth generation. Properties considered were tensile properties (strength, modulus, strain), storage modulus by DMA, impact resistance, MFI, and crystalline structure by DSC. Tests were performed for neat rHDPE, 24 wt% and 48 wt% talc filler contents.

1.7 Methods

The objectives were achieved using experimental methods following ASTM standards. For tensile tests, specimens were tested in direct tension, using an MTS Criterion C43 testing machine, following ASTM D638–14: Standard Test Method for Tensile Properties of Plastics. Specimen pre-test conditioning for the different temperatures was achieved using a temperature-controlled chamber, following conditioning procedures of ASTM D618: Practice for Conditioning Plastics for Testing. MFI test was measured using a Melt Flow Apparatus (Model: Ray-Ran MFR100, UK), according to ASTM D 1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. Flexural stiffness tests of rHDPE-talc filler blend samples were performed using dynamic mechanical analysis (DMA) in a three-point bending fixture of a TA Instruments Q800 dynamic mechanical analyzer (DMA) following ASTM D5023: Standard Test Method for Plastics: Dynamic Mechanical Properties: In Flexure (Three-Point Bending). To

investigate the impact strength, Charpy impact tests were conducted using a P.A. Hilton (Hampshire, U.K.) HSM4 pendulum impact tester in accordance with ASTM D6110-18: Standard test method for determining the Charpy impact resistance of notched specimens of plastics. Effects in the crystalline structure and thermal properties of rHDPE-talc blends in relation to thermal reprocessing were investigated using DSC, on a TA Instruments Discovery DSC 250, following ASTM E793: Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry.

A statistical analysis approach was used to develop response models for certain properties through a statistical design procedure called Response Surface Methodology (RSM). RSM is a collection of statistical and mathematical techniques used for developing, improving, and optimizing processes. It offers several advantages over linear prediction methods, especially for examining the impact of interactions between multiple input variables/factors that potentially influence the performance measure, effect, response, or quality characteristic of the product or process [52]. Linear prediction methods are not capable of accounting for interactions between different variables/predictors, compared to non-linear methods [53-57]. RSM is a powerful and effective research tool for developing adequate responses/models, as demonstrated by studies conducted by Berry et al. and Simon, among others [58-63]. To apply RSM, statistical experimental design procedure (design of experiment-DOE) was used to investigate the effects of the key independent variables, talc filler content and testing temperature, on the intended properties/responses. RSM uses DOE to fit a model by least squares technique [64], and the central composite design (CCD) DOE was used. CCD is the most commonly used fractional factorial design in response surface modeling for optimization and finding best possible products, and it

provides maximum information in a minimum experimental trial [65]. The CCD model is an integral part of response surface mythology [66], is more accurate than other ways of optimization model construction, and does not require a three-level factorial experiment for building a second-order quadratic model [67]. CCD contains three types, including circumscribed design (CCC), inscribed design (CCI), and face centered design (CCF). For this study, CCC was adopted because it provides high quality predictions over the entire design space compared to CCI and CCF [65]. The validity, performance, and adequacy of each created model were assessed using well-defined statistical procedures (the diagnostic checking tests) provided by analysis of variance (ANOVA). ANOVA is a statistical technique that includes F-test, t-test, degrees of freedom, coefficient of determination, and standard error for analyzing measurements depending on several kinds of effects operating simultaneously [68].

1.8 Expected Significance of the Study

The establishment and development of new applications for thermoplastics could serve as an effective means of mitigating thermoplastic waste problems and environmental disturbances. This could widen the availability of green materials in regions that have an abundance of thermoplastic waste, contributing to overall sustainable development. Furthermore, as more applications for larger volumes of rHDPE arise, recycling can become more economically viable and reduce the amount of accumulated vHDPE waste. This would not only bring down the cost but also add value to rHDPE in society, increase HDPE recycling rates, and address environmental issues simultaneously. If rHDPE properties prove to be viable, composite structural members, among other components, that are currently made with vHDPE could be made cheaper and greener with rHDPE. This could help make these novel materials more competitive with existing options

for stakeholders seeking non-traditional, more sustainable material options. Therefore, as previously mentioned, this study aims to explore the mechanical properties of rHDPE in relation to talc filler content, temperature, and number of thermal reprocessing cycles. This is a crucial research step in eventually evaluating the potential use of this recycled material in various applications. It is essential to determine whether rHDPE has acceptable mechanical properties comparable to vHDPE (and other thermoplastic polymers) for use in a broad range of applications, including engineering applications. The developed models would serve as useful tools to predict the studied properties of rHDPE as functions of talc filler content and application temperature. In conjunction with other experimental findings, the idea of using rHDPE in engineering applications, either in lieu of or in part to replace vHDPE, will gain scientific theory and practical knowledge.

1.9 Preface

This dissertation examines the mechanical properties of rHDPE in relation to talc filler content, temperature, and number of thermal reprocessing cycles. The dissertation is organized into five chapters. Chapter 1 introduces the research background, problem scale, objectives, methods, and expected significance of the study. Chapter 2 presents a study on the tensile properties of rHDPE blended with talc filler. The study investigates the tensile strength, elastic nominal stiffness, and nominal yield strain of the material with varying talc filler weight contents (0, 20, 28, and 38 wt%). The study finds that an increase in talc filler content leads to an increase in tensile strength and elastic nominal stiffness, and a decrease in nominal yield strain. This chapter is a republication of work that has been accepted and published in a peer-reviewed journal. Chapter 3 presents a study on the application of Response Surface Methodology (RSM) to model the tensile properties and flexural stiffness of rHDPE as functions of talc filler content and temperature. The

study uses experimental statistical analysis to determine the impact of talc filler content and temperature on the mechanical properties of rHDPE. Results show that there is a significant statistical impact of talc filler content and testing temperature on the rHDPE tensile properties and flexural stiffness. The developed response models show significant predictive performances. This chapter is a republication of work that has been submitted and is currently under review in a peer-reviewed journal. Chapter 4 presents the investigation of the impact of thermal recycling and talc filler content on the material properties of rHDPE. The study evaluates the MFI, tensile properties, impact resistance, storage modulus, and thermal properties of rHDPE-talc filler blends. This chapter is a final draft of work that will be submitted to a peer-reviewed journal. Finally, Chapter 5 provides overall conclusions for the research and discusses recommendations for future work. Each chapter has its own abstract and introduction sections, results and conclusion sections. A cumulative reference section is provided after Chapter 5.

CHAPTER TWO

AN INVESTIGATION INTO THE TENSILE PROPERTIES OF RECYCLED HIGH-DENSITY POLYETHYLENE (rHDPE) BLENDED WITH TALC FILLER

Contribution of Authors and Co-Authors

Manuscript in Chapter 2.

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Contributions: Designed experiments and methodology, performed experiments and investigation, Formal data analysis, Writing - original manuscript draft, Visualization

Co-Author: Kirsten Matteson

Contributions: Supervision, Conceptualization, Resources, Writing – review and manuscript editing, Funding acquisition

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AN INVESTIGATION INTO THE TENSILE PROPERTIES OF RECYCLED HIGH-DENSITY POLYETHYLENE (rHDPE) BLENDED WITH TALC FILLER

Abstract

High-density polyethylene (HDPE) is a well-established thermoplastic; however, with concerns about the fate of plastics at end-of-life, there is a growing interest in strategies to utilize recycled HDPE (rHDPE) in place of virgin HDPE (vHDPE). This study investigated the tensile properties of rHDPE/talc blends (0, 20, 28, and 38 wt% talc) and adequate talc dispersion was found in the blends using SEM imaging. Increases in tensile strength (up to 20.4%), elastic nominal stiffness (up to 93.5%), and a decrease in nominal yield strain (up to 50%) were observed for rHDPE with increasing talc content. The trends observed indicate that rHDPE could be a viable alternative/supplement to vHDPE for use in large volume structural applications. If talc filler particle dispersion can be well monitored, the rHDPE/talc blends have significant potential to be used and hence reduce the amount of virgin material needed; however, additional properties should be further explored.

2.1 Introduction

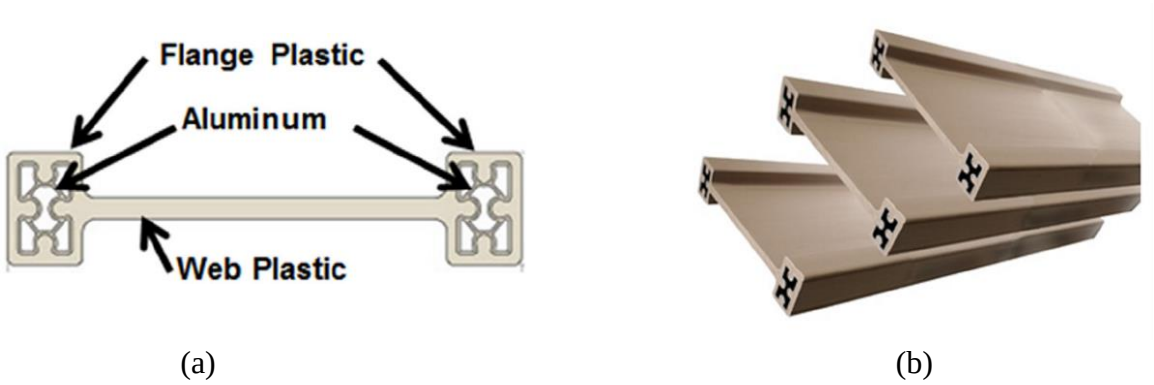
According to United States Environmental Protection Agency (US EPA) 32.37 million metric tons of plastic waste had been generated by the year 2018 (cumulative 1960-2018), of which only 2.8 million metric tons (8.66%) were recycled and 5.1 million metric tons (15.75%) were combusted with energy recovery, while about 24.47 million metric tons (75.59%) were accumulated in landfills [11]. Polymer wastes cause environmental destruction, increase pressure

on landfills, cause destruction of marine life [7], and can result in other ecological problems [8]. Using recycled polymers in more applications will help mitigate these issues.

Recycled and virgin thermoplastic polymers are increasingly being used in many applications in light of their adequate strengths, low densities, and ease of manufacturing [2]. The total production volume of all polyethylene (PE) types is the highest of all polymers, and high-density polyethylene (HDPE) is among the cheapest of all polymers [1]. HDPE is one of the most versatile thermoplastic polymers that is currently used in its virgin and recycled states (vHDPE and rHDPE, respectively) to make food and chemical packaging such as bottles for drinks, motor oil, detergent, and the like [1]. HDPE is readily available at economical prices, is easy to process, is lightweight, and exhibits excellent chemical and corrosion resistance [1], making it suitable across a range of engineering applications. Because of the recyclability of HDPE, using rHDPE in lieu of vHDPE has its environmental benefits, and as more applications for larger volumes of rHDPE arise, recycling can become more economical and the amount of vHDPE waste can be reduced.

A study by Peterson (Matteson) et al. [24] explored vHDPE co-extruded with aluminum to produce plastic-aluminum composite I-beams for use in structural applications, such as decking understructures and docks/piers. Figure 2.1 shows the polymer-aluminum I-beam cross section (a) and length profile (b) as presented in the study [24]. A range of 0-38 wt% talc filler weight contents was explored for the vHDPE used for the I-beams. Talc is a naturally occurring mineral (inorganic), mined from the earth, composed of magnesium, silicon, oxygen, and hydrogen [19-21]. Talc has vast applications as a filler material in several industries, due to its high chemical stability, cheap availability, and its demand continues to grow [21, 22]. Fillers, such as talc, are

often added to polymeric materials to not only reduce overall cost, but also to improve several properties such as stiffness, strength, and thermal stability [2, 13, 14, 16, 17, 23-25]. For example, at low talc filler contents of approximately 3 wt% or less, talc filler acts as a nucleating agent, by reducing spherulite size and shortening processing time [35]. At higher contents of approximately 10-40 wt%, talc acts as a reinforcing filler, increasing elastic modulus and stiffness, but reducing strain-to-break and impact strength [36].



(a) (b)

Figure 2.1: Plastic–aluminum composite I-beams: (a) cross-section; (b) length profile [24].

Introducing mineral fillers, into thermoplastic polymers affects several properties including appearance assessed by color analysis (not performed in this research), chemical structure assessed by fourier-transform infrared (FTIR) spectroscopy (not performed in here), microstructure assessed by optical microscopy (SEM), static mechanical properties assessed by tensile tests in this study, dynamic mechanical properties assessed by dynamical mechanical analysis (DMA-not performed in here), thermal properties and crystalline structure examined using differential scanning calorimetry (DSC-not performed in here). In a two-phase blend made up of a continuous polymeric matrix and particle fillers, the filler properties (type, surface functional groups, surface activity, surface area, particle size, orientation, concentration, shape, and the interfacial adhesion

of the filler particles) and manufacturing methods are important factors influencing the mechanical and physical properties of the blend [25, 29-34]. Therefore, the results from this study are specific to the materials properties and method used.The current study focused on investigating the properties of rHDPE across the same range of talc filler contents as those in the study by Peterson et al. The goal was to investigate the effects of increasing talc filler contents on rHDPE tensile properties, make comparisons to vHDPE from a study that used similar ASTM standards (to determine if the rHDPE/talc filler blends have acceptable tensile properties, comparable to the currently used virgin thermoplastics), and evaluate the feasibility of using rHDPE in the same structural applications as those of vHDPE. If rHDPE exhibits acceptable and comparable properties, then incorporating rHDPE into the plastic-aluminum composite I-beams (and of course potentially other large volume structural applications) would reduce the cost of the specimens and help make these novel composites more competitive with other existing choices for contractors looking for non-traditional, more sustainable material options.

Previous studies have shown that rHDPE (with no talc filler) can exhibit close, and in some cases higher, tensile properties (tensile strength and elastic modulus) compared to vHDPE [12-17], and in polymers, these properties (especially elastic modulus), can be maintained up to three or more generations of recycling [12, 69]. In the case of polyethylene, thermal recycling can lead to changes in the molecular weight and in the crystallinity ratio (increased crystallinity) of the material as recycling continues, which can increase the brittleness of the material [45, 46]. This behavior may be attributed to the possible degradation caused by main chain scissions accompanied by an increase in the molecular weight. The chains of material with high molecular weight can be tangled easily, and therefore the flow resistance is high, producing a more brittle

material. The change in elastic modulus may be explained by the decrease in density, which may cause a decrease in material crystallinity when repeating the recycling process [12, 46, 49]. The tradeoff between gaining some higher tensile properties while increasing the brittleness of a material can be acceptable, and sometimes even desirable, in certain engineering applications.

As part of the current research, dog-bone specimens blended from rHDPE and talc were tested in direct tension according to ASTM D638 standards. Talc filler contents ranged from 0-38% and a mimum of five specimens were tested for each talc content. During testing, load and displacement were recorded, from which tensile strength, elastic nominal stiffness, and nominal yield strain were calculated. Results from these tests are then analyzed to determine the effects of using recycled material and the effect of varying talc filler content.

2.2 Methods and Materials

2.2.1 Materials

The recycled HDPE used in this study has a density of 0.942 g/cm^3 and a melt flow index of 0.8 g/10 min, measured at 190°C, using a load of 2.16 kg, in a Melt Flow Apparatus (Model: Ray-Ran MFR100, UK). The talc for this study was purchased from Luzenac America, Inc., Centennial, CO, USA, and has a loose bulk density of 0.432 g/cm^3, a particle size distribution with a median diameter of 9.6 microns, and a specific gravity of 2.8 (density equal to 2.8 g/cm^3) [70]. The rHDPE and talc used for this study are shown in Figure 2.2. The findings of this study are specific to the properties of the materials used and specimen preparation parameters.

(a) (b)

Figure 2.2: Materials used: (a) rHDPE; (b) talc filler.

2.2.2 Specimen Preparation

The test specimens were prepared/blended (by thermal recycling) with the twin-screw extrusion method, using a Haake MiniLab Rheomex CTW5 machine, and then injection molded by HAAKE MiniJet Pro, using a mold for ASTM type V dog-bone specimens for tensile tests, and no coupling agent was used. The specimen preparation procedures, measuring techniques, test procedures, and calculations were performed according to ASTM D638-14 standards. The dog-bone test specimens were prepared with the following four contents by weight of talc filler: 0 wt% (neat), 20 wt%, 28 wt%, and 38 wt%. The processing parameters included a maximum working temperature of 190^{o}C, extruder screw speed of 100 rpm, mold temperature of 70^{o}C, and injection pressure of 450 bars. It took 3-5 minutes after being introduced into the extruder for the materials to attain stable viscosity, and the residence time was approximately 5 minutes.

Following the ASTM standard, at least five specimens, at each talc weight percent, were prepared and tested. All specimens were kept at room temperature and ambient humidity before

and during testing; no additional specimen conditioning was performed. Figure 2.3 shows example of specimen before testing (top), and specimen dimensions, in mm (bottom).

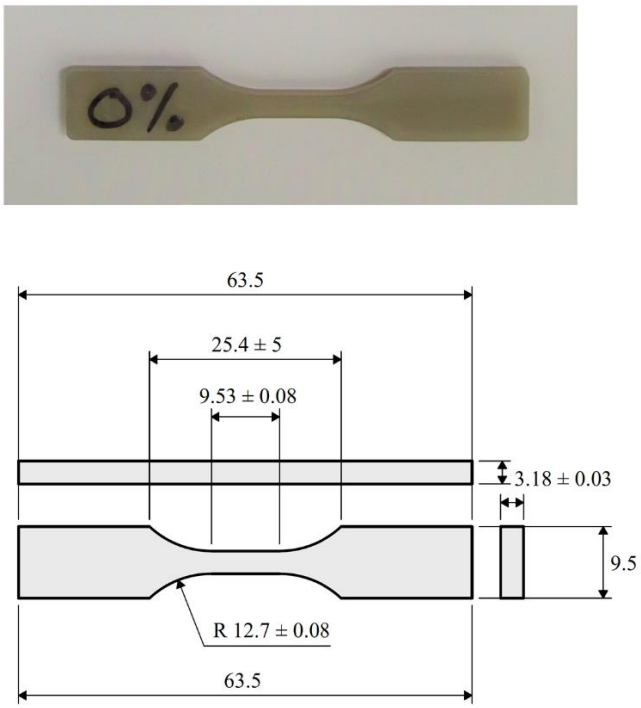


Figure 2.3: Example specimen before testing (top), and specimen dimensions, in mm (bottom).

Talc filler dispersion, uniformity, and the relative chemical composition of key elements in the rHDPE/talc specimens were examined through microstructure imaging on a Zeiss SUPRA 55VP scanning electron microscope (SEM) on 20 wt%, 28 wt% and 38 wt% talc samples. Before imaging, the samples were cleaned with ethanol, attached to aluminum mounts using carbon sticky dots, and then sputter-coated with carbon to a thickness of 20 nm, using Cressington Carbon Coater 108carbon/A. SEM images were captured at 250 µm magnification and a working distance of 8.5 mm with an SE2 detector. Examination of the relative chemical composition of key inorganic

elements was achieved on an Oxford Xplore energy dispersive X-ray (EDS) detector, collecting data over the entire displayed area.

2.2.3 Mechanical Testing

The testing was performed at Montana State University (MSU), per ASTM D638-14, on an MTS Criterion C43 testing machine, with a 1kN load cell. Force-displacement data were recorded throughout all tests. An extensometer was not used, and the displacement data is the change in grip separation, which does not capture the local extensions, and therefore the stress-strain curves obtained from cross head data indicated the global tensile response over the entire specimen volume between the grips [71]. Care was taken during assembling the samples in grips for tests, and this is because a slight misalignment of the axial load in a tensile test is sufficient enough to cause premature failure at the grips [72] that may result in inaccurate findings. Properties of interest for this study were calculated from the force-displacement data, including the tensile strength, nominal yield strain, and elastic nominal stiffness. Because an extensometer was not used, the nominal stiffness and nominal yield strain values are of qualitative utility only (ASTM D638-14 11.3); however, the same methods were used for the previously published data on vHDPE with which comparisons are made. The extension rate during testing was 1 mm/min per Table 1 of ASTM D638-14, reasonable for simulating static loading. Other details pertaining to the ASTM calculations are provided below.

- Nominal strain (nominal engineering strain) was calculated by dividing the change in grip separation by the original grip separation.
- Stress (engineering stress) was calculated by dividing the force by the average original cross-sectional area in the gage length segment (middle narrow portion) of each dog-bone specimen.

- Tensile strength was determined as the maximum stress reached by the specimen.
- Nominal yield strain was identified as the nominal strain value at the maximum stress (at tensile strength).
- The change in grip separation should not be used for calculating elastic modulus (ASTM D638-14 Note 11), and therefore, elastic nominal stiffness, k, was considered and defined here as the slope of the initial linear portion, in the elastic range, of the stress vs. nominal strain curve. Elastic nominal stiffness is synonymous with elastic modulus and was used for qualitative comparisons herein.

2.2.4 Halpin-Tsai Elastic Nominal Stiffness Prediction

Halpin and Tsai created a model to predict the elastic modulus (the Halpin-Tsai model) for polymer composite materials consisting of randomly distributed short fibers, that can also be applied for anisotropic mineral fillers such as talc [73]. This model was applied to the test data obtained here in order to examine the reinforcing effect of the talc filler on the elastic nominal stiffness, k, of the rHDPE/talc blends. The model predictions were compared with the test data for the same talc contents to determine the performance of the model in comparison to the elastic nominal stiffness results obtained here. The Halpin-Tsai model for the research performed here is provided in Equation 2.1 and Equation 2.2. First, η is calculated using Equation 2.1.

$$\eta = \frac{(E_f/E_m)-1}{(E_f/E_m)+\zeta} \tag{2.1}$$

where E_f is the modulus of elasticity of the filler, E_m is the modulus of elasticity of the matrix, and ζ is an empirical parameter obtained by the equation ζ = 2(a/b), with (a/b) equal to the aspect ratio of the filler/fiber. For the research performed here, E_f was taken as the elastic modulus of the

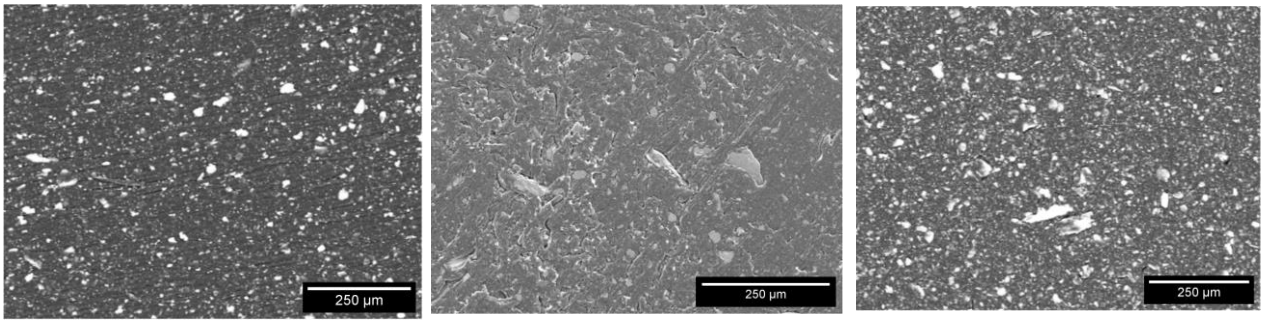
talc (70 GPa [73]). E_m was taken as the elastic modulus of neat HDPE, which has been reported as a range of values in the literature. A range of 500-1550 MPa [1, 74, 75] were explored for the present research. The shape of a filler is an important factor as it affects the processing as well as properties of the polymer. Talc has a platelet shape, and its aspect ratio (a/b) was taken as 2 such that ζ equals 4. Using these values, η can be calculated and then used in Equation 2.2.

$$k_c = k_m \left[\frac{1+\zeta\eta\varphi_f}{1-\eta\varphi_f}\right] \tag{2.2}$$

where k_c is the elastic nominal stiffness of the composite/blend, k_m is the elastic nominal stiffness of the matrix, ζ and η have been previously discussed, and φ_f is the volume fraction of the fiber/filler. φ_f was calculated from the talc weight fractions (0 wt%, 20 wt%, 28 wt%, and 38 wt%) using the rHDPE density (0.942 g/cm^3) and the talc filler density (2.8 g/cm^3).

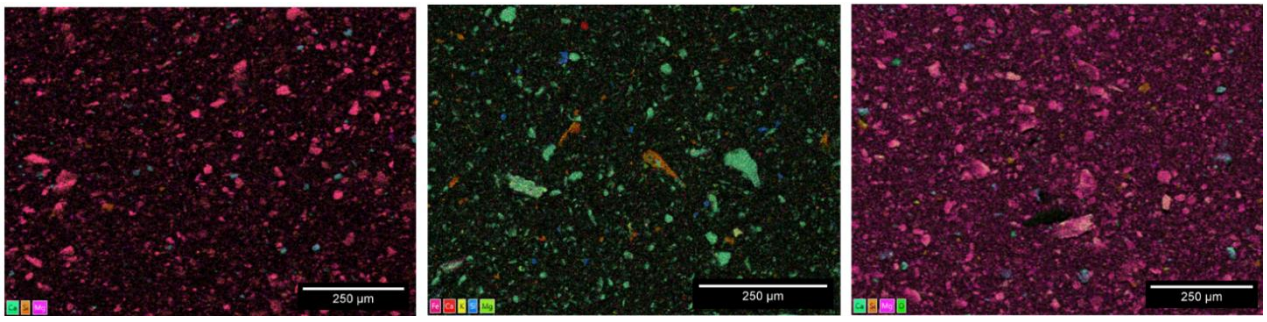
2.3 Results and Discussion

Evaluated blends of rHDPE/talc indicated a flat surface under SEM, with minimal gaps between talc and the polymer as indicated in micrographs (Figure 2.4 and Figure 2.5). These micrographs generally show a good dispersion of talc filler particles in the rHDPE polymer, as shown by the textured surfaces (Figure 2.4) and the relative chemical composition of key inorganic elements (Figure 2.5).



(a) (b) (c)

Figure 2.4: SEM micrographs (textured surface) of (a) rHDPE-20 wt% talc, (b) rHDPE-28 wt% talc, and (c) rHDPE-38 wt% talc. (Magnification is indicated on every figure).



(a) (b) (c)

Figure 2.5: The relative chemical composition of key inorganic elements: (a) rHDPE-20 wt% talc, (b) rHDPE-28 wt% talc, and (c) rHDPE-38 wt% talc.

The results for tensile strength, nominal yield strain, and elastic nominal stiffness for the rHDPE/talc blends were averaged across all specimens for each talc content. Example specimens of each talc content after testing are shown in Figure 2.6 and typical stress vs. nominal strain curves are shown in Figure 2.7 for each talc filler content. Brittleness and ductility as functions of talc filler content can be observed in Figure 2.6 from the broken areas of the failed samples, and Figure 2.7 at which the curves indicate the higher the brittleness the lower the yielding strain; this implies that the higher the talc filler content, the lower the ductility, and the vice versa.

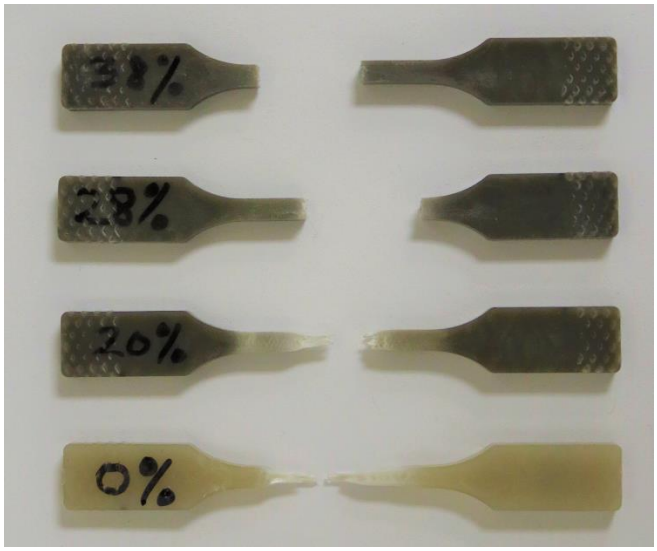


Figure 2.6: Example specimens after testing. From bottom to top: 0%, 20%, 28%, and 38% talc contents, by weight.

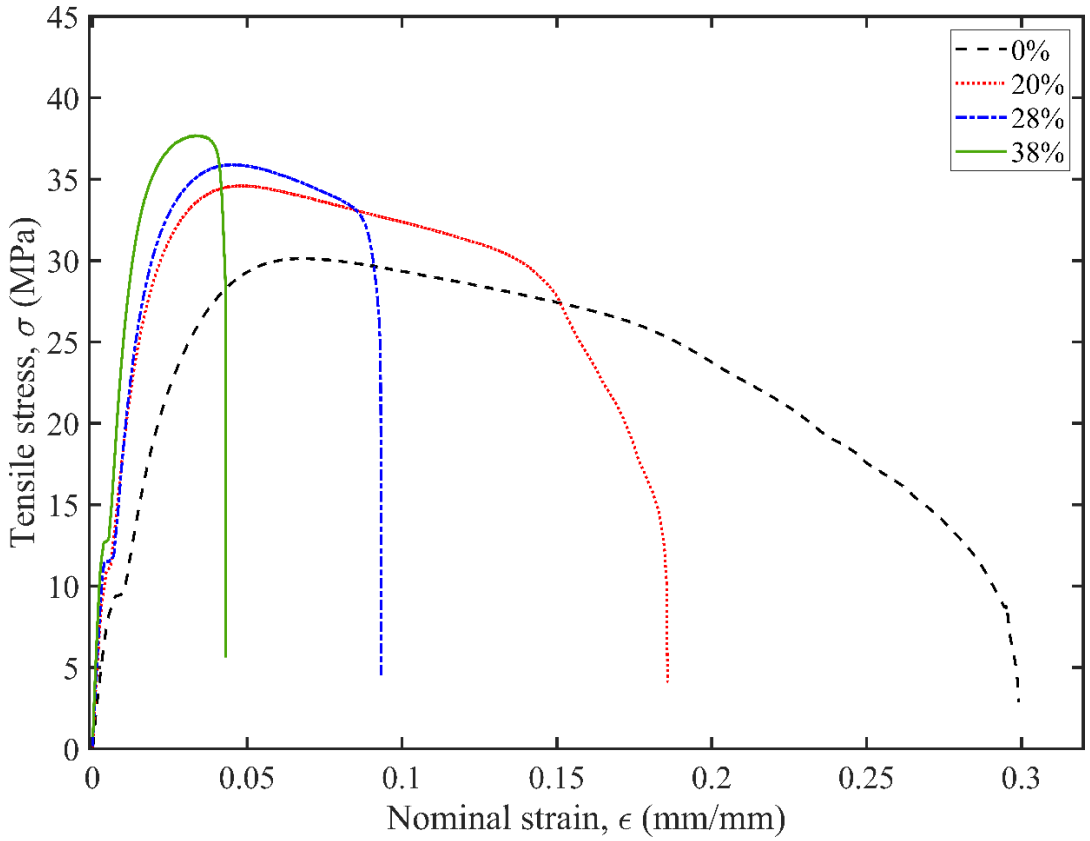


Figure 2.7: Typical stress vs. nominal strain curves for tested specimens.

The tensile strength, elastic nominal stiffness, and nominal yield strain results, and their corresponding standard deviations and coefficients of variation, are summarized in Table 2.1. The results show that there are increases in tensile strength and elastic nominal stiffness of rHDPE as the talc content increases from 0 wt% to 38 wt%. The tensile strength increased 20.3% from 30.6 MPa for neat to 36.8 MPa for 38 wt% talc blends. The elastic nominal stiffness increased from 1720 MPa for neat to 3330 MPa for 38 wt% talc blends, almost doubling with a 93.5% increase. As the talc content increases, there is a decrease in nominal yield strain, ranging from 0.066 for neat to 0.033 for 38 wt% talc blends, a 50% decrease, showing an increase in brittleness with increase in talc filler. The observed increase in strength and stiffness with increasing talc content is consistent with what has been observed in conventional plastics with added fillers. As a fine particulate filler is added to plastic, to a certain amount, it will enhance the toughness of the matrix as it affects the morphological and physical properties, such as internal adhesion, molecular weight, and density [76, 77].

Coefficient of variation (CoV) is calculated as the ratio of the standard deviation to the mean multiplied by 100%, and CoV values are used here to analyze the dispersion of the results independent of the variable's measurement unit [78, 79]. The higher the CoV, the greater the dispersion in the variable and vice versa. A CoV exceeding 30 percent is often indicative of problems in the data or that the experiment is out of control and therefore testing would need to be repeated to possibly obtain meaningful data [79]. As shown in Table 2.1, the CoVs of all data sets are 10% or lower, indicating repeatability from specimen to specimen and an overall low scatter in the test results.

Table 2.1: rHDPE/talc blends tensile testing results. Standard deviations (std) and coefficients of variation (CoV) are shown in parentheses next to each value.

Talc content (wt%)	Tensile strength MPa (std/CoV)	Elastic nominal stiffness, k MPa (std/CoV)	Nominal yield strain m/m x 10^{-2} (std/CoV)
0	30.6 (2.2/7.0%)	1720 (97.3/5.7%)	6.59 (0.43/6.4%)
20	34.4 (1.4/4.2%)	2260 (122/5.4%)	4.73 (0.21/4.5%)
28	35.2 (1.4/3.9%)	2650 (137/5.2%)	4.60 (0.23/5.1%)
38	36.8 (2.1/5.8%)	3330 (145/4.4%)	3.29 (0.34/10.0%)

The measured tensile strength, elastic nominal stiffness, and the nominal yield strain are plotted versus talc content in Figure 2.8. Also included in Figure 2.8 are the elastic nominal stiffnesses predicted using the Halpin-Tsai model. As previously discussed, a range of E_m values were used to evaluate the elastic nominal stiffness using the model. A value of E_m equal to 1000 MPa (the average value suggested in the literature for neat HDPE [1, 74, 75]) was used and yielded the best comparison. Even though, it was further observed that there is no noticeable or significant difference to the Halpin-Tsai results when using any E_m value in a range of 500-1550 MPa. The resulting Halpin-Tsai model elastic nominal stiffnesses are plotted on Figure 2.8. This E_m value, along with the other variables discussed for Equation 1, resulted in a constant value for η equal to 0.9013. The elastic nominal stiffness results from the tested rHDPE specimens exhibit close values with those from the Halpin-Tsai model, and both results show the increase in elastic nominal stiffness with talc content. This indicates that orthorhombic structure did not change with either filler type or concentration from 0 to 38 wt%, and that the only variations that may be found in the structure are the changes of crystallinity and crystallized size that depend both on type of filler and concentration [80].

The increases in tensile strength and elastic nominal stiffness and decrease in nominal yield strain with increase in talc filler content have been discussed; however, the shapes of the plots shown in Figure 2.8 warrant further discussion. Linear trendlines have been added to the plots, with the equations indicated. These results show linear relationships between increase in talc content and increases in both tensile strength and elastic nominal stiffness (trendlines with R^2 = 0.99 and 0.94, respectively). Similarly, there is a linear relationship between increase in talc content and decrease in nominal yield strain (trendline with R^2 = 0.97). The slopes ($\Delta y/\Delta x$) of these trendlines can be associated with the change in material property (y-axes) with respect to a 1% increase in talc filler content; for example, a 1% increase in talc filler content results in an approximate 0.16 MPa (trendline slope) increase in tensile strength for the range explored. Additionally, although not shown on Figure 2.8 for sake of clarity, a linear trendline for the Halpin-Tsai model results in an equation of $k = 40\phi + 1657$, with R^2 = 0.98. Comparing this to the trendline for the data gathered herein (shown on Figure 2.8 as $k = 41\phi + 1613$) further highlights how well the model fits the elastic nominal stiffnesses studied here, with only a 2.4% difference in slope and 2.7% difference in y-intercept.

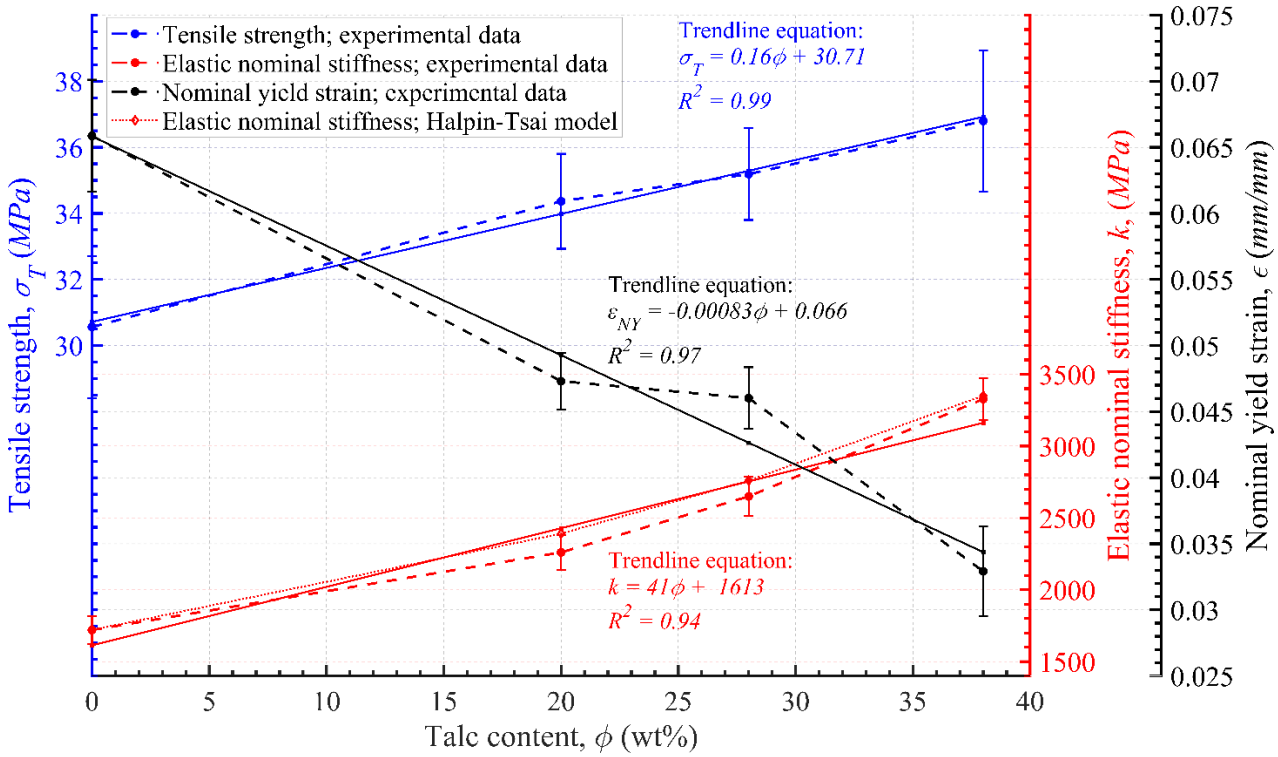


Figure 2.8: rHDPE tensile strength, elastic nominal stiffness, and nominal yield strain as functions of talc filler content.

Comparing to another study on neat rHDPE, the tensile strength obtained in this study, 30.6 MPa (Table 2.1) is similar but slightly lower than the average value obtained by Pattanakul et al. of 34.4 MPa [15]. Additionally, comparing the tensile strength trends of neat rHDPE from this study with neat vHDPE of other studies, the rHDPE exhibits close, and in some cases higher, tensile strength compared to vHDPE [12-17, 24]. The affects that recycling has on the molecular weight, density, and crystallinity have been studied extensively by other researchers. In plastic thermal recycling, which escalates the temperature beyond the melting point, polymer chains break apart, thereby affecting the brittleness as a result of changes in the crystallinity (more brittle: higher elastic modulus, lower strain) [46, 49]. The differences in results in different studies can also be explained based on Melt Flow Index (MFI), which is the measure of the molten viscosity of a

polymer (polymer quality), determined by measuring the amount of material which flows through an aperture of a fixed size during a fixed time period at a set temperature when placed under a fixed load. Typically, trends have been observed correlating a higher molecular weight (lower MFI) to improved mechanical properties of extruded parts and vice versa [81].

The research performed herein also compared the results of tensile properties of rHDPE/talc blends (Table 2.1) with the results of vHDPE/talc blends obtained using data from the study by Peterson et al. [24], and the results are plotted in Figure 2.9, across the same range of talc contents. As previously discussed, Figure 2.9 further confirms increases in tensile strength and elastic nominal stiffness with increase in talc content for both virgin and recycled HDPEs. Additionally, it was observed that the tensile properties of rHDPE obtained in this study are higher than those of the vHDPE for both the neat and talc blended specimens. This comparison is not definitive because of additives present in the vHDPE/talc blends; however, the results are promising and warrant further investigation on the potential of including rHDPE (at least in part) in the formulation of the plastic for the plastic-metal composites and other structural applications discussed herein.

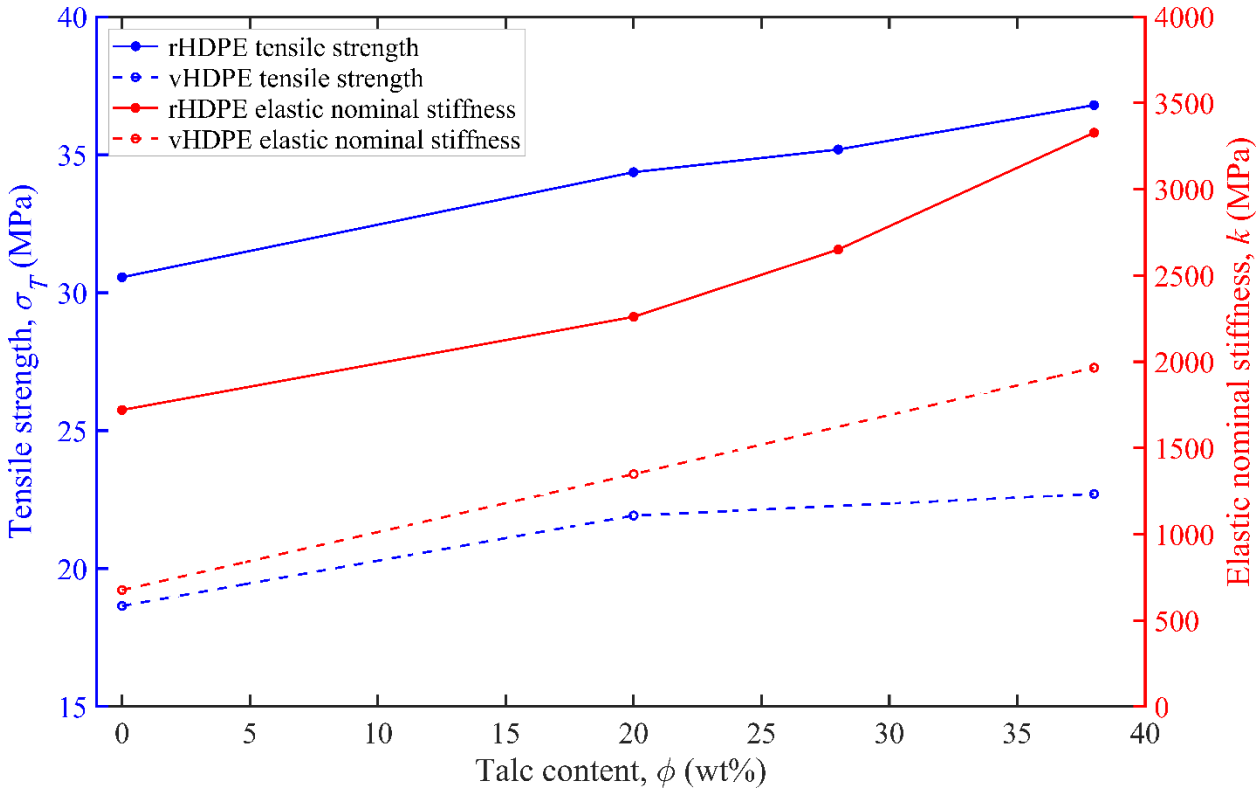


Figure 2.9: Comparison of tensile strength and elastic nominal stiffness of rHDPE (current study) and vHDPE (calculated using data from the study by Peterson et al. [24]).

The percent changes in tensile strength, elastic nominal stiffness, and nominal yield strain, relative to their respective neat values are tabulated in Table 2.2, and plotted as functions of talc content in Figure 2.10. For vHDPE, a talc content of 20 wt% resulted in a 20.5% increase in tensile strength and a 49.0% increase in elastic nominal stiffness, compared to neat vHDPE. Similarly, the rHDPE exhibited a 12.5% increase in tensile strength and a 31.5% increase in elastic nominal stiffness for the 20 wt% talc increase. Likewise, a talc content increase of 38 wt% resulted in a 16.0% increase in tensile strength and a 74.2% increase in elastic nominal stiffness for vHDPE, while rHDPE exhibited a 20.4% increase in tensile strength and a 93.5% increase in elastic nominal

stiffness. Overall, very similar trends are observed between rHDPE and vHDPE, best shown by the data plotted on Figure 2.10.

Table 2.2: Percent changes in tensile strength, elastic nominal stiffness, and nominal yield strain, as functions of percent talc content increase compared to neat vHDPE [24] and rHDPE.

Talc content increase from neat, (wt%)	Virgin or Recycled	Tensile strength increase (%)	Elastic nominal stiffness increase (%)	Nominal yield strain decrease (%)
20	vHDPE	20.5	49.0	17.0
	rHDPE	12.5	31.5	28.2
28	rHDPE	15.1	54.2	30.1
38	vHDPE	16.0	74.2	58.6
	rHDPE	20.4	93.5	50.0

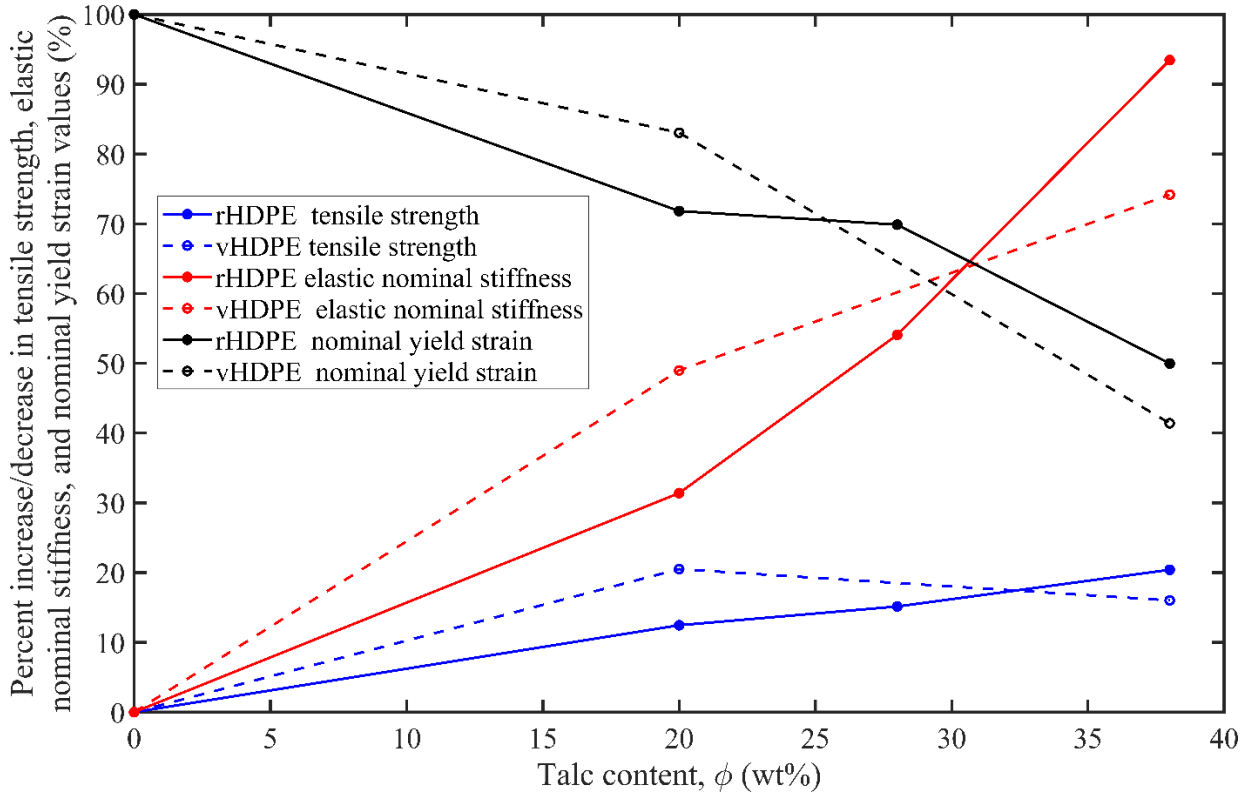


Figure 2.10: Percent changes in tensile strength, elastic nominal stiffness, and nominal yield strain, as functions of % talc content increase, compared to neat HDPE for both virgin and recycled.

2.4 Conclusions

This study investigated the tensile properties of rHDPE/talc filler blends and focused specifically on the tensile strength, elastic nominal stiffness, and nominal yield strain across the counterpart talc filler contents previously explored by Peterson et al. for vHDPE/talc filler blends used in structural applications, primarily plastic-aluminum composite I-beams [24]. This was done to make clear comparisons between vHDPE and rHDPE blended with talc filler. The following conclusions are drawn from this study.

- The tensile strength results found for neat rHDPE in this study are similar to those for neat rHDPE found in previous studies.
- Adding talc filler to rHDPE increases the brittleness (observed through decreased nominal yield strain) and thereby has a negative effect on overall ductility, following the same trends previously shown for vHDPE.
- For rHDPE, there are linear relationships between increase in talc filler content (across the range of 0-38 wt%) and increases in tensile strength and elastic nominal stiffness and decrease in nominal yield strain. More specifically, for the rHDPE/talc blends studied here, per 1 wt% increase in talc content:
    - Tensile strength increases by about 0.16 MPa.
    - Elastic nominal stiffness increases by about 41 MPa.
    - Nominal yield strain decreases by about 0.00083 mm/mm.

These trends are consistent with previous research on vHDPE across the same range of talc filler content.

- The Halpin-Tsai model performs well for the elastic nominal stiffness, k, explored here for rHDPE/talc blends. Comparing the trendlines for the data gathered herein and the Halpin-Tsai model, there is only a 2.4% difference in slope and 2.7% difference in y-intercept.

Despite the thermal processing/recycling of HDPE, the trends of the results obtained here are consistent to findings from previously published studies on vHDPE. Also, the melt flow index measured indicates the good quality of the rHDPE, and the talc filler dispersion evaluation by SEM imaging shows a good dispersion of talc filler particles in the rHDPE/talc blends, further supporting the results found. The findings are promising, considering the potential for rHDPE to be a viable alternative material to its virgin counterpart used in structural applications. Replacing or supplementing vHDPE with rHDPE has the potential to significantly reduce the amount of virgin material needed, especially in large volume applications such as the plastic-aluminum composites discussed herein used primarily for decking understructures.

Although the findings here are promising, there is a need to investigate other properties of rHDPE/talc blends, such as the effects of temperature to the tensile and flexural properties. The response of structural members made of rHDPE/talc blends will differ at different temperatures and the structural design will depend on the intended application (e.g., outdoor deck or dock/pier) and may require data on the material responses over different temperature ranges (freezing vs. hot sunny days). Additionally, the susceptibility to weathering of the rHDPE/talc blends should be investigated. Finally, considering the effect on ductility/crystallinity and strain-to-break that both recycling and inclusion of talc filler have on the rHDPE, impact strength should also be investigated.

Acknowledgements

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CHAPTER THREE

EXPERIMENTAL STATISTICAL MODELING OF TENSILE PROPERTIES AND FLEXURAL STIFFNESS OF RECYCLED HIGH-DENSITY POLYETHYLENE (rHDPE) THERMOPLASTIC USING RESPONSE SURFACE METHODOLOGY (RSM)

Contribution of Authors and Co-Authors

Manuscript in Chapter 3.

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Co-Author: Kirsten Matteson

Contributions: Supervision, Conceptualization, Resources, Writing – review and manuscript editing, Funding acquisition

Co-Author: Michael Berry

Contributions: Conceptualization, Resources, Writing – review

Co-Author: Dilpreet Bajwa

Contributions: Conceptualization, Resources, Writing – review

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Manuscript Information

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EXPERIMENTAL STATISTICAL MODELING OF TENSILE PROPERTIES AND FLEXURAL STIFFNESS OF RECYCLED HIGH-DENSITY POLYETHYLENE (rHDPE) THERMOPLASTIC USING RESPONSE SURFACE METHODOLOGY (RSM)

Abstract

The widespread use of thermoplastic products, particularly high-density polyethylene (HDPE), in daily activities has led to the generation and accumulation of large amounts of plastic waste. This waste poses a significant threat to the environment due to the challenges and limitations in effectively managing plastic waste. The establishment of new large volume applications of recycled HDPE (rHDPE) would incentivize recycling by creating new revenue streams. Before rHDPE (specifically rHDPE-talc blends) can be used more heavily in lieu of or in addition to virgin HDPE (vHDPE), its material properties in relation to application temperatures must be better understood. This study focused on characterizing tensile and flexural properties of rHDPE-talc blends across broad ranges of talc filler content and temperature. Experimentally, tensile strength, elastic modulus, storage modulus, and nominal yield strain data were collected. Tensile strength and elastic modulus were observed to increase with an increase in talc content and decrease with increase in temperature. Conversely, yield strain was observed to decrease with an increase in talc content and increase with increase in temperature. Response Surface Methodology (RSM) was then applied using the Central Composite Design (CCD) statistical experimental design approach to further study the stiffness and strength of rHDPE and the effects that temperature and talc filler content have on these properties. The surfaces generated in this analysis fit the data well, with coefficients of determination greater than 0.95 for all but one property which was 0.80. The evaluation of model performance revealed that the surfaces yielded good correlation and statistical

significance such that they provide useful relationships and can be considered for use in practical applications when evaluating the use of rHDPE-talc blends for engineering applications.

3.1 Introduction

Thermoplastic waste is a significant contributor to global environmental problems, including land pollution and destruction, increase on landfill pressure, decrease of water and air quality through contamination, endangerment and destruction of marine life and animal species, and other ecological problems. Managing this waste can be a challenging task [4, 7, 8]. Efforts to manage plastic waste have been underway for years, and include methods such as landfilling, incineration, pyrolysis, bioremediation, and recycling. However, despite these efforts, low recycling rates due to economic and technological factors result in large amounts of thermoplastic polymer waste remaining unaddressed, exacerbating environmental problems [4]. On a global scale, it was estimated that as of 2015, approximately 6,300 million metric tons of plastic waste had been cumulatively generated, and that a cumulative total of approximately 8,300 million metric tons of waste virgin plastics have been produced as of 2017 [10]. According to the United States Environmental Protection Agency (US EPA), 32.37 million metric tons of plastic waste had been generated in the US by the year 2018 (cumulative 1960-2018), of which only 2.8 million metric tons (8.66%) were recycled, and 5.1 million metric tons (15.75%) were combusted with energy recovery, while about 24.47 million metric tons (75.59%) were accumulated in landfills. Globally, it was roughly estimated that 12,000 million metric tons of plastic waste will be in landfills or in the natural environment by the year 2050 if the current production and waste management trends continue [10, 11].

Recycled and virgin thermoplastic polymers and their composites are increasingly gaining attention and recognition for being ideal for several applications. This is due to their high strength to weight ratio, ease of processing, availability, low cost, and excellent chemical and corrosion resistance [1-3]. These properties make thermoplastics suitable across a range of engineering applications, including engineered structural members. A common thermoplastic, high-density polyethylene (HDPE), is one of the most versatile thermoplastic polymers that can be adapted into several different functions [1]. The total production volume of all polyethylene (PE) types is the highest of all polymers, and HDPE is among the cheapest of all polymers [1]. Previous studies have shown that neat recycled HDPE (rHDPE) exhibits comparable mechanical properties to neat virgin HDPE (vHDPE) [12-17]. Mechanical properties of course play a large role in engineering applications of any material; however, in thermoplastics, these properties are subject to change after thermal recycling, as the molecular weight and hence the crystallinity ratio of the material are affected, which in return affects the brittleness of the material and other mechanical properties [45-48]. For example, the change in elastic modulus may be explained by the change in density, which may cause a change in material crystallinity when repeating the recycling process [12, 46, 49]. Also, it has been revealed by other studies that factors like sample preparation and processing parameters (such as extruding time, temperature, and if there is a coupling agent present) affect the recycled thermoplastic engineering properties. A better understanding of the mechanical properties of rHDPE and associated composites or blends is needed before vHDPE and other plastics can be more prevalently replaced with rHDPE. If comparable or similar performances are obtained with rHDPE, then there will be motivation for recycling rates to increase, as there will be more revenue streams for high volumes of rHDPE. Recycled HDPE, either on its own or as a

composite combined with other materials, may be suitable for several engineering applications including structural elements such as beams, columns, trusses, slabs, load bearing walls, guard rail components (to road edges, bridge edges, buildings, etc.), fluid storage tanks, critical connections (screws, bolts, nuts, etc.), and the like. As more applications for larger volumes of recycled polymers arise, using rHDPE in lieu of or in addition to vHDPE will help recycling become more economical, thereby reducing the amount of vHDPE waste.

In this study, talc filler was used to improve the properties of rHDPE. Mineral fillers, such as talc, serve as reinforcing agents when added to polymer matrices, resulting in new composite materials with optimized properties that differ and may be superior to those of the individual components [27]. Talc is a naturally occurring inorganic mineral composed of magnesium, silicon, oxygen, and hydrogen [19-21]. As a filler material, it is widely used due to its high chemical stability, affordability, and availability [21, 22]. The addition of talc to thermoplastics affects various properties, including static mechanical properties, appearance, chemical structure, microstructure, physical properties, and dynamic mechanical properties. It also generally reduces the cost of the blend and improves thermal stability [2, 13, 14, 16, 17, 23-25]. The results from this study are specific to the filler and other material properties, specimen preparation parameters, and methods used. This is because the way in which the filler material optimizes matrix properties depends on manufacturing methods, filler type and properties, such as surface functional groups, surface activity, surface area, particle size, orientation, concentration/content, dispersion, particulate shape, and the interfacial adhesion of the filler particles [25, 29-34]. For instance, at low filler contents of around 3 wt% or less, talc acts as a nucleating agent, reducing spherulite size and processing time. At higher filler contents of around 10-40 wt%, talc acts as a reinforcing agent

to the polymer matrix, increasing elastic modulus and stiffness, and reducing strain-to-break and impact strength [27, 35, 36]. Previous research has shown that talc filler has a positive impact on the mechanical properties of rHDPE and vHDPE, including tensile strength, modulus, strain, and stiffness [18, 24]. However, there has been limited research on the material and mechanical properties of rHDPE-talc blends, which motivated the research performed in this study and specifically, this research investigated a talc filler range of 0 to 48 wt%.

The mechanical properties, performance, and strength of HDPE, like other polymers, are highly sensitive to the temperatures they are exposed to during service, which can limit their usage [37]. To achieve optimal polymer performance, the temperature should remain within the range of the glass transition temperature, T_g (or ductile-brittle transition temperature-DBTT) and the crystalline melting temperature, T_m. The T_g is where there is a disordered amorphous solid, while T_m is the temperature at which the solid becomes a disordered melt [38]. That means, it is essential to avoid service temperatures below the minimum operating temperature, close to T_g, or above the maximum operating temperature, close to T_m, to ensure practical use. Researchers have found that a specific range of increasing temperatures can cause drastic decreases in polymer strength and stiffness, as well as increases in yield and break strains [37, 39-44]. Similarly, the response of structural members made of rHDPE-talc blends will differ at varying temperatures. This implies that, if rHDPE qualifies to be used in structural applications, then, designing rHDPE for structural applications will depend on the intended use, such as outdoor decks or docks/piers, and may require data on the material response across different temperature ranges, such as freezing vs. hot sunny days. Therefore, this study considers temperature as an affecting variable across a range that has not been extensively explored for rHDPE-talc blends. Previous studies have investigated

separately the effects of filler materials and temperature on the mechanical and physical properties of thermoplastic polymers, including density, strength, modulus, and strain/elongation [18, 26, 33, 37, 82-86]. The research discussed herein investigated the combined effects of talc filler content and temperature. Specifically, this research investigated the effects of temperature on mechanical properties of rHDPE, across temperature ranges of -56.6^{o}C to 56.6^{o}C for tensile properties, and -125^{o}C to 80^{o}C for flexural stiffness. Criteria considered in deciding these temperature ranges include the experiences of previous studies, deflection temperature (a measure of a polymer's ability to bear a given load at elevated temperatures), the HDPE thermal properties (T_g and T_m), and the extreme temperatures of the MTS machine testing chamber (so that the testing can be achieved) [87-89].

The objective of this study was to investigate and quantify the combined effects that filler content and temperature have on the mechanical properties of rHDPE-talc blends. The explored mechanical properties include tensile strength, elastic modulus, nominal yield strain, and flexural stiffness. Experimental methods following ASTM standards were used to achieve the objective. Response surface methodology (RSM) was statistically used to further evaluate the properties, following central composite design (CCD) as a statistical experimental design procedure (DOE). Response surfaces for tensile strength, elastic modulus, nominal yield strain, and storage modulus were generated. Overall, a better understanding of the material properties of rHDPE-talc blends is a crucial research step in eventually evaluating the potential use of this recycled material. It is essential to determine whether rHDPE has mechanical properties comparable to vHDPE (and other thermoplastic polymers) for use in a broad range of engineering applications.

3.2 Materials and Methods

3.2.1 Materials

The recycled HDPE used in this study has a density of 0.942 g/cm^3 and a melt flow index (MFI) of 0.8 g/10 min. The talc for this study was purchased from Luzenac America, Inc., Centennial, CO, USA [70], and has a loose bulk density of 0.432 g/cm^3, a particle size distribution with a median diameter of 9.6 microns, and a density equal to 2.8 g/cm^3 [70]. The rHDPE and talc used for this study are shown in Figure 3.1.

(a) (b)

Figure 3.1: Materials used: (a) rHDPE; (b) talc filler.

3.2.2 Blended Specimen Fabrication

Blends of rHDPE and talc were prepared for talc filler contents of 0 wt%, 7 wt%, 24 wt%, 41 wt% and 48 wt%. Materials were mixed in a Thermo Fisher Scientific HAAKE Minilab II dual screw extruder (Haake MiniLab Rheomex CTW5 machine) at 100 rpm and 190^{o}C for at least 5 minutes to attain stable viscosity, and no coupling agent was used. Compounded blend melt was

injected into a Minijet Pro injection molder, with a 190°C barrel temperature and a 60°C mold temperature. An ASTM type V dog-bone specimen mold was used for the tensile test samples and a DMA sample mold (Part #557-2295, 60 mm × 10 mm × 1 mm beams) was used for the flexural stiffness test samples. Injection molding temperatures were determined based on HDPE melting temperature, and high mold temperatures were required due to the thin mold used for the DMA flexural samples. An injection pressure of 750 bar was applied for 10 seconds, followed by a post pressure of 450 bar for 60 seconds. Per ASTM standards, at least 5 specimens for each talc content and test type were prepared. Figure 3.2 shows example tensile and flexural test specimens and specimen dimensions.

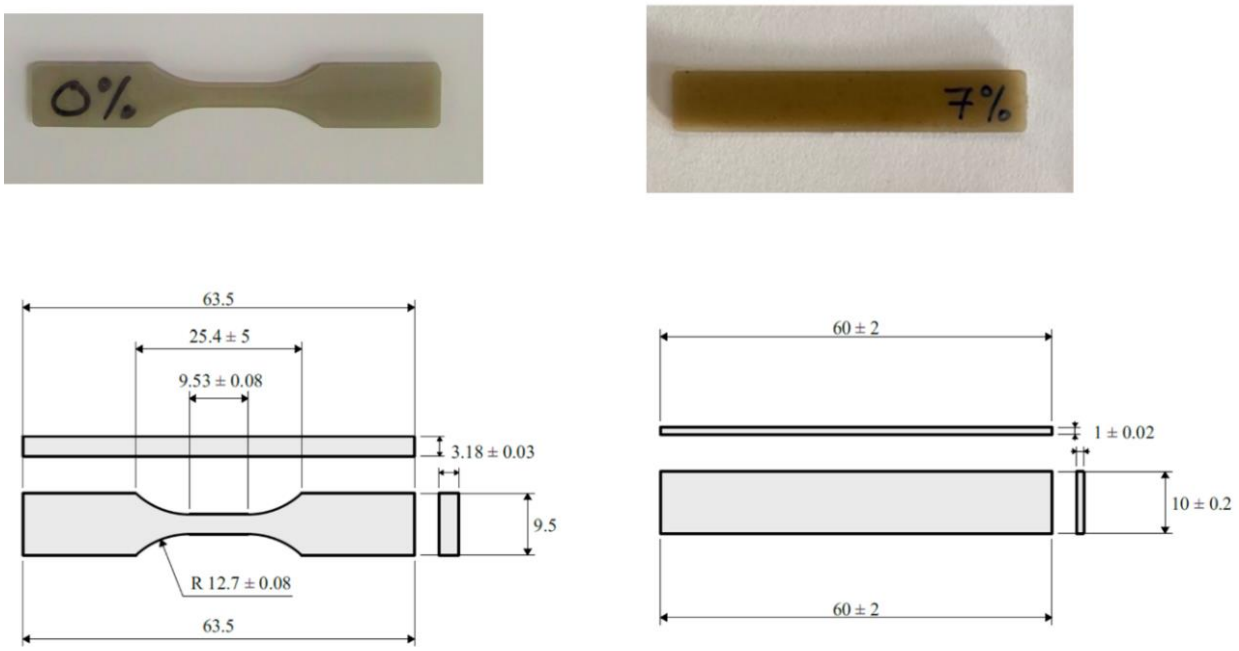

Figure 3.2: Example of the tensile (left) and flexural (right) specimens before testing (top), and specimen dimensions, in mm (bottom).

3.2.3 MFI and SEM Material Characterization

The Melt Flow Index (MFI) test was measured at 190°C, using a load of 2.16 kg, in a Melt Flow Apparatus (Model: Ray-Ran MFR100, UK) to examine the quality of HDPE through viscosity, directly related to MFI. This test was carried out according to ASTM D 1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. The MFI measured, 0.8 g/10 min, indicates the rHDPE used in this study is good quality, as past studies have found that typically a polymer material with lower MFI (below 1.0 g/10 min) has improved mechanical properties for extruded parts [81].

To characterize the microstructure and nano-structural features of rHDPE-talc blends, the talc filler dispersion, uniformity, and the relative chemical composition of the rHDPE-talc blend specimens were examined through microstructure imaging on a Zeiss SUPRA 55VP scanning electron microscope (SEM), for the following DOE talc levels: 7 wt%, 24 wt%, 41 wt% and 48 wt%. Before imaging, the samples were cleaned with ethanol, attached to aluminum mounts using carbon sticky dots, and then sputter-coated with carbon to a thickness of 20 nm, using Cressington Carbon Coater 108 carbon/A. SEM images were captured at 250 μm magnification and a working distance of 8.5 mm with an SE2 detector, and were performed at an accelerating voltage of 3 kV. Evaluated blends of rHDPE-talc indicated a flat surface under SEM, with minimal gaps between talc and the polymer as indicated in the micrographs (Figure 3.3). These micrographs generally show a good dispersion of talc filler particles in the rHDPE polymer, as shown by the textured surfaces (Figure 3.3).

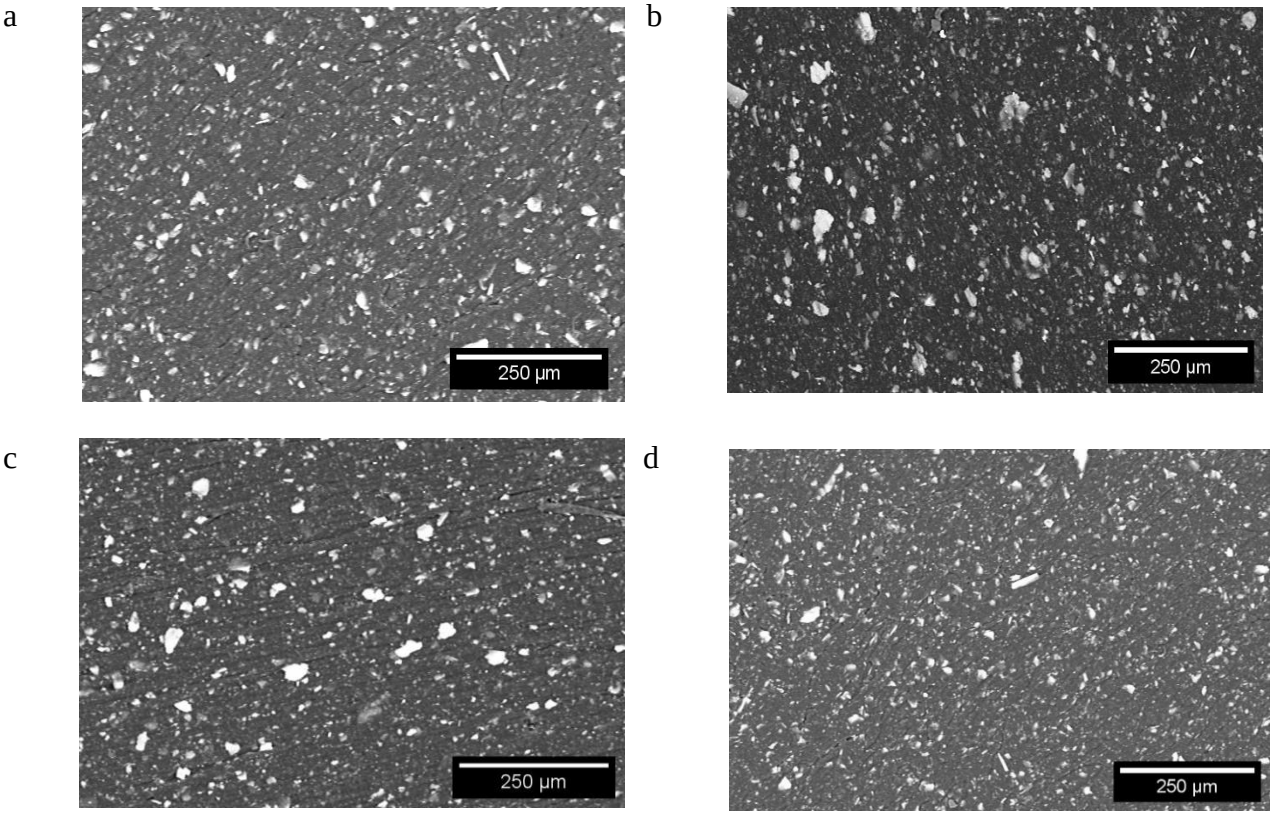

Figure 3.3: SEM micrographs of (a) rHDPE-7 wt% talc, (b) rHDPE-24 wt% talc, (c) rHDPE-41 wt% talc, and (d) rHDPE-48 wt% talc.

3.2.4 Methods

To achieve the objective of this research, experimental procedures following ASTM standards were used. Response Surface Methodology (RSM) following a statistical experimental design approach was applied. This section discusses the details of these methods.

3.2.4.1 Experimental Methods. For tensile tests, specimens were tested in direct tension, using an MTS Criterion C43 testing machine, with a 1 kN capacity load cell and temperature chamber, following ASTM D638–14: Standard Test Method for Tensile Properties of Plastics. Tensile properties of rHDPE were tested as functions of talc filler content (range of 0 wt% to 48 wt%), and testing temperature (temperature range of -56.6^{o}C to 56.6^{o}C). The temperature chamber

had overall limits of -129°C (minimum) and 315°C (maximum), and targeted testing temperatures within that range were well achieved. Specimen pre-test conditioning for the different temperatures was achieved using a temperature-controlled chamber and following conditioning procedures of ASTM D618: Practice for Conditioning Plastics for Testing. At least 5 specimens per talc content, and at every designated temperature, were tested. Load vs. displacement data were recorded. Additionally, an extension indicator (extensometer), with a maximum strain error of 0.0002 mm/mm was used up to 0.5% strain, and automatically and continuously recorded elongation values used to calculate the elastic modulus. Overall, tensile strength at yield (σ_{TY}), elastic modulus (E), and nominal yield strain (ε_{NY}) were calculated from the primary data. This test method is designed to produce tensile property data for the control and specification of plastic materials, data that is also useful for qualitative characterization and for research and development, and moreover, test data obtained by this test method have been found to be useful in engineering design [90]. The following bullets explain how the tensile properties of interest were obtained, following ASTM D618:

- Tensile stress (σ_T) was calculated by dividing the force by the average original cross-sectional area in the gage length segment (middle narrow portion) of each specimen, and the tensile strength (σ_{TY}) was taken as the maximum tensile stress; i.e. it was calculated by dividing the maximum load (at yield) sustained by the specimen by the average original cross-sectional area in the gage length segment of the specimen.

- Percent elongation (Strain, ε) is the change in gage length relative to the original specimen gage length, expressed as a percent. Percent elongation at yield (Yield strain, ε_Y) was

calculated by reading the change in gage length at the yield point, dividing that by the original gage length (grip separation), and multiplying by 100.

- Nominal strain (ε_N) is the change in grip separation relative to the original grip separation expressed as a percent. The nominal strain at yield (ε_{NY}) was calculated by reading the extension (change in grip separation) at the yield point, dividing that extension by the original grip separation, and multiplying by 100.

- Modulus of elasticity (E) was calculated by extending the initial linear portion of the stress-strain curve (strain calculated with extensometer readings) and dividing the difference in stress ($\Delta\sigma_T$) corresponding to any segment of section on this straight line by the corresponding difference in strain ($\Delta\varepsilon$).

Flexural stiffness tests of rHDPE-talc filler blend samples were performed using dynamic mechanical analysis (DMA) in a three-point bending fixture of a TA Instruments Q800 dynamic mechanical analyzer (DMA). All samples were tested at a frequency of 1 Hz, initial amplitude of 1 μm, and a force track of 125%. The temperature was equilibrated at -125°C for 2.5 minutes, then ramped to 80°C at a constant rate of 5°C/min. The considered temperature range captures the behaviors of HDPE within its T_g (-135°C) and T_m (136°C). The storage modulus (E'), loss modulus (E''), and the tangent of delta ($tan\ \delta$) of each blend were measured as functions of temperature and talc filler content. These are the parameters used to describe the viscoelastic behavior of a material that are often determined/calculated through DMA according to ASTM standards. The following bullets explain a general overview of how these parameters were calculated:

- Storage modulus (E') represents the energy stored and recovered by a material when subjected to an oscillating stress or strain. It is calculated as the ratio of the stress or strain amplitude to the corresponding strain or stress amplitude. Mathematically, E' = Stress (or Strain) amplitude/Strain (or Stress) amplitude.
- Loss modulus (E'') represents the energy dissipated or lost by a material during the oscillatory deformation. It is calculated in a similar way to the storage modulus, but using a 90-degree phase shift between stress and strain. Mathematically, E'' = Stress (or Strain) amplitude/Strain (or Stress) amplitude (at a 90-degree phase shift).
- Tangent of delta (tan δ) is a dimensionless parameter that represents the ratio of the loss modulus to the storage modulus. It quantifies the damping or energy dissipation characteristics of a material, expressed mathematically as $tan\ \delta = E'' / E'$

3.2.4.2 Response Surface Methodology. RSM was used to develop polynomial response models by utilizing statistical modeling strategies. RSM offers advantages over linear prediction methods for examining the interaction impacts of multiple factors, as linear prediction methods are not capable of accounting for interactions between different variables/predictors [53-57]. RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. The most extensive applications of RSM are in situations where several input variables potentially influence the performance measure or quality characteristic of the product or process [52]. RSM has been found to be a powerful and effective research tool for developing adequate models, especially when there is an interaction between several independent variables that influence an effect or a response. For example, in a study conducted by Berry et al. on optimization of concrete mixtures containing reclaimed asphalt pavement, RSM was used to

investigate the effects of key mix parameters on concrete responses (slump, air content, and compressive strength), and it adequately characterized the behavior of the concrete mixtures [58]. Similarly, Simon conducted a study for the United States Federal Highway Administration (FHWA) and revealed RSM to be a valuable and effective tool to use in concrete mix design after performing a study on concrete mix optimization using statistical methods [59]. Many other researchers, from polymers, material science, composites, concrete, etc., have used RSM in their studies and revealed that RSM is a good statistical tool for researching several interacting variables [60-63]. Mathematically, RSM uses an experimental design to fit a model by least squares technique [64].

The adequacy, validity, and predictive performance of the models were then revealed using the diagnostic tests provided by analysis of variance (ANOVA). Additional experimental testing was employed for assessing model predictive performance. ANOVA is a statistical technique that includes F-test, t-test, degrees of freedom, coefficient of determination, and standard error for analyzing measurements depending on several factors operating simultaneously, to decide which kinds of effects are important to estimate optimum responses/results [68].

The polynomial response models that were considered in this study for each response were of the second-degree general form, as indicated in Equation 3.1:

$$z_j = f(x_j, y_j) + \epsilon_j = \beta_o + \beta_1 x_j + \beta_2 x_j^2 + \beta_3 y_j + \beta_4 y_j^2 + \beta_5 x_j y_j + \epsilon_j \quad (3.1)$$

Where:

$x_j, y_j \quad (1 \leq j \leq n)$ represents *n* independent variables: talc filler content and testing temperature for the current study.

z_j $(1 \leq j \leq n)$ represents the *n* dependent variable: the particular response of interest (strength, modulus, or strain) for the current study.

$\beta_0, \beta_1, \ldots\ldots\ldots \beta_5$ are the model coefficients/parameters that were obtained by a regression analysis statistical approach, for each response.

ϵ_j, $(1 \leq j \leq n)$ represents a sequence of *n* residual errors. That is, ϵ_j represents the difference between the value of the dependent variable predicted by the model, $f(x_j, y_j)$, and the experimentally observed value, z_j: $\epsilon_j = z_j - f(x_j, y_j)$.

The subscript *j* refers to the j^{th} individual or unit in the population.

Creating RSM models involved three steps: 1) estimating the parameters/coefficients of the model, 2) assessing the significancy/validity of the model parameters, and 3) evaluating the predictive performance of the model. Details are included in the following bullets:

- Estimating the parameters/coefficients of the models was achieved using R studio statistical software (RStudio, PBC., v.2022.12.0+353/R 4.2.1), which uses the theory of least squares method (LSM) at which the values of β_i, in Equation 3.1, were computed such that the squared vertical distance (residual error, ϵ) between each point (x_j, y_j, z_j) and the non-linear response model $z_j = f(x_j, y_j)$, is minimized.
- Post analysis and plotting of the response models and experimental results were accomplished using MATLAB (MathWorks, Inc., R2022b, v. 9.13.0.2126072).
- The R^2 and *p*-values were used to assess the validity of each model.
    - R^2 is the overall goodness-of-fit measure (relative predictive power). It is a statistical measure of how well the regression model approximates the actual data. The value of R^2

varies between 0 and 1 and the closer the value is to 1, the more accurate the model [91]. R^2 of every model was calculated using Equation 3.2.

$$R^2 = 1 - \left(\frac{SSR}{SST}\right) = 1 - \frac{\sum(z_j - \hat{z}_j)^2}{\sum(z_j - \bar{z}_j)^2} \qquad 1 \leq j \leq n \tag{3.2}$$

Where:

SSR stands for the *sum squared regression*; the sum of the residuals/errors squared (also referred to as sum of squares for errors, SSE), and SST stands for the *total sum of squares*; the sum of the squared distances the data is away from the mean.

$\hat{z}_j$ is the model predicted value of the experimentally observed values, z_j.

$\bar{z}_j$ is the mean value of the observed/experimental data.

- The *p*-values were used to assess statistical significance of the regression terms for each response; that is, at a significance level of about 5% ($\alpha = 0.05$), representing a confidence interval of 95%, terms with p-values equal to or less than 0.05 will be designated to be significant. This procedure is used to reduce/eliminate the insignificant terms in the model.

- The response surface models were further evaluated via predicted-versus-observed by residual and normal Q-Q (quantile-quantile) plots.
- Randomly selected values of talc filler content and test temperature were used to obtain a set of new test data and predicted data to assess the predictive performance of the created response surface models.

3.3 Results and Discussion

3.3.1 Experimental Results

A statistical experimental design procedure (DOE) was used to determine the tests to run over a given range of parameters. The focus was to investigate the effects of the talc filler content and temperature on the tensile and flexural properties (tensile strength, elastic modulus, nominal yield strain, and storage modulus). The central composite design (CCD) DOE was used. CCD is the most commonly used fractional factorial design in response surface modeling, for both optimization and finding the best possible product and model from ongoing batches, and gives maximum information in a minimum experimental trial [65, 66]. CCD contains three types: 1) circumscribed design (CCC), the original form of CCD, 2) inscribed design (CCI), a scaled down version of CCC, and 3) face centered design (CCF), a design with star points at the center of each face of the factorial space, where star points, in CCD, represent new extreme values (low and high) for each factor in the design [65]. CCC was adopted, because it provides high quality results over the entire design space compared to CCI and CCF [65]. A CCD model is more accurate than other ways of optimization model construction, and does not require a three-level factorial experiment for building a second-order quadratic model [67].

Figure 3.4 shows the layout of the CCC design that includes the coded values, and the corresponding designated absolute values of talc and temperature for the DOE used in this study. Also included in Figure 3.4 is the layout of temperature and talc data used during validation. This depicts how the measured data are positioned in the surface area in relation to talc filler contents and temperature. Table 3.1 indicates the measured responses (test results) after running the

designated tests for tensile properties and storage modulus. CCC coded values and the corresponding designated absolute values are included in Table 3.1.

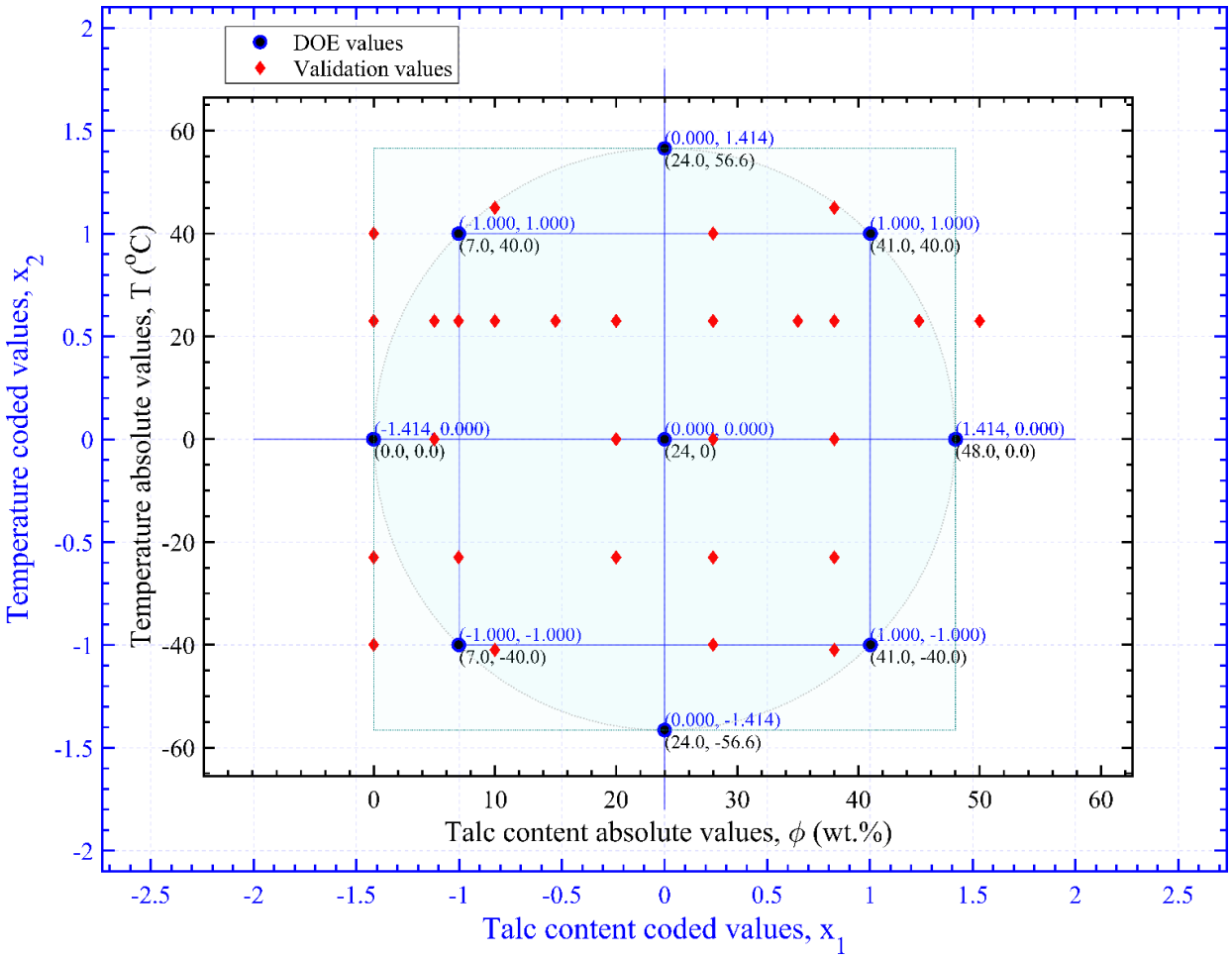

Figure 3.4: Layout of CCC coded values, the corresponding designated absolute values of talc and temperature for the DOE, and the layout of temperature and talc data used in validation (red diamonds).

Table 3.1: Measured responses (test results) for tensile properties and storage modulus. CCC coded values and the corresponding designated absolute values are also included.

	Designated Variables: Design of Experiment (DOE): Central Composite Design (CCD): Circumscribed design (CCC)				Measured Responses (Test Results)			
	Coded variables		Natural/Absolute variables		Tensile Test			Flexural Test
	Talc, ϕ (x_1)	Temp., T (x_2)	Talc, ϕ (wt%)	Temp., T (^oC)	Tensile strength, σ_{TY} (MPa)	Nominal yield strain, ε_{NY} (m/m)	Elastic modulus, E (MPa)	Storage modulus, E' (MPa)
Factorial runs 2^2	-1	-1	7.0	-40	42.1	0.0324	3510	19400
	-1	1	7.0	40	25.3	0.0775	1460	26200
	1	-1	41.0	-40	58.5	0.0210	7310	27500
	1	1	41.0	40	28.9	0.0442	3120	21200
Axial runs 2x2	1.4142	0	48.0	0	45.5	0.0228	6960	27300
	-1.4142	0	0.0	0	35.1	0.0485	2470	9690
	0	1.4142	24.0	56.6	22.7	0.0625	1260	38200
	0	-1.4142	24.0	-56.6	52.4	0.0293	4680	23000
Center point	0	0	24.0	0	41.8	0.0330	3600	18500
	0	0	24.0	0	44.0	0.0331	3210	18500
	0	0	24.0	0	42.6	0.0340	3430	18500
	0	0	24.0	0	41.0	0.0338	2190	18500
	0	0	24.0	0	46.0	0.0310	3590	18500
	0	0	24.0	0	43.0	0.0383	3030	18400
	0	0	24.0	0	45.4	0.0325	2810	18500
	0	0	24.0	0	46.8	0.0368	2470	18400

Tensile test results show different changes in behavior with the changes in application temperature and talc filler content in rHDPE (Figure 3.6). With the addition of talc filler, the tensile strength and elastic modulus of rHDPE are observed to increase, while a decrease in nominal yield strain is observed, confirmed in a previous study [18]. These tensile properties are comparable to the previously revealed properties of vHDPE with talc filler. In contrast, the increase in application temperature is observed to decrease the tensile strength and elastic modulus of rHDPE, and

increase the nominal yield strain, and vice versa. These are the temperature effect trends that were hypothesized, as mechanical properties of polymers are very sensitive to service temperatures [37].

Experimental DMA results are shown in Figure 3.5; (blue) storage modulus, (red) loss modulus, and (black) $tan\ \delta$ of rHDPE, as functions of temperature and talc filler content for the designated values of the DOE. As indicated, DMA results show different shifts in behavior with the change in talc filler content in rHDPE. This implies that talc filler has a significant impact on rHDPE dynamic mechanical properties. Both blends indicate a drastic increase in storage and loss moduli after approximately 20ºC. These same trends have been observed in previous works; however, past studies have not heavily focused on examining the mechanism responsible for this drastic change and shifts in storage and loss moduli of HDPE as temperature increases [92]. Within the temperature range of approximately -80ºC to 35ºC, it has been observed that all blends of rHDPE exhibit a significant increase in the storage modulus while experiencing minimal increase in the loss modulus upon the addition of talc filler. This observation suggests that the incorporation of talc filler into rHDPE enhances the ability of the blends to store and recover energy when subjected to oscillating stress or strain. Additionally, it indicates that there is reduced dissipation or loss of energy during this oscillatory deformation. The results for the tangent of delta ($tan\ \delta$) show a slight change with the addition of talc filler, indicating an increase in the damping behavior of rHDPE. These results signify a desirable effect of talc filler to rHDPE, as it enhances the capacity of the material to absorb and dissipate energy. Consequently, talc filler proves to be a viable option for optimizing the material properties of rHDPE.

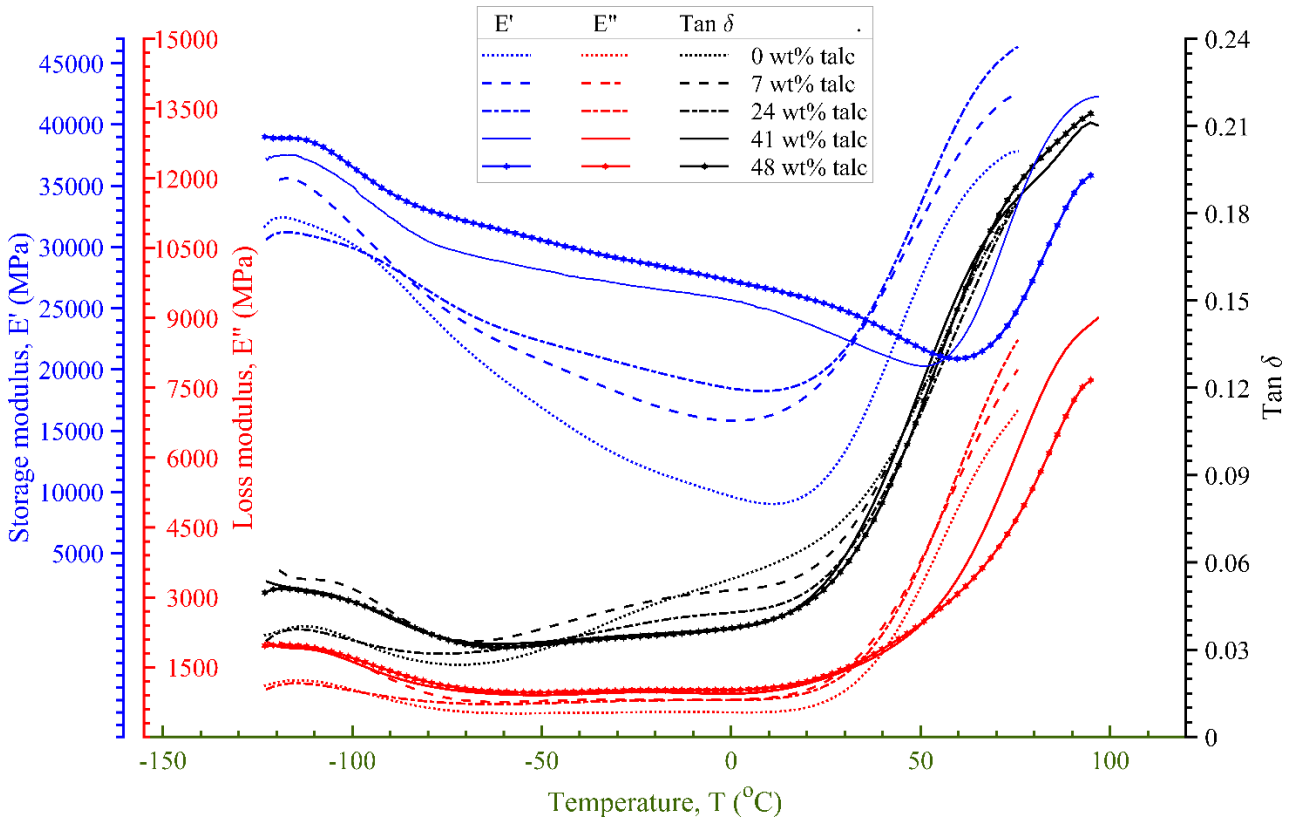

Figure 3.5: DMA results for (blue) storage modulus, (red) loss modulus, and (black) $tan\ \delta$, for DOE talc contents in rHDPE.

3.3.2 Response Surface Methodology Results

3.3.2.1 Model Development. After conducting the DOE and running the tests described in Section 3.3.1, model development commenced. This involved fitting the surfaces to the results as explained in Section 3.2.4.2. Table 3.2 presents a summary of the model coefficients/parameters results. The table includes the R^2 and p-values which were used to assess the overall goodness-of-fit, significance, and validity of the models and parameters. Based on the ANOVA performed, the response surfaces were extracted from Table 3.2, and are presented in Equations 3.3, 3.4, 3.5 and 3.6. The response surfaces were then plotted in Figure 3.6. Also included in Figure 3.6 are the

designated experimental absolute values of talc filler content and temperature for the DOE used in this study.

Table 3.2: Regression coefficients and ANOVA results.

				Intercept	x_1 (Talc, ϕ)	x_1^2 (ϕ^2)	x_2 (Temp., T)	x_2^2 (T^2)	$x_1 * x_2$ ($\phi * T$)
Tensile Properties	Tensile Strength, σ_{TY}	$R^2 = 0.97$ Adj. $R^2 = 0.96$	β	43.832 (34.093)	4.341 (0.556)	-1.812 (-0.0063)	-11.045 (-0.163)	-3.192 (-0.002)	-3.198 (-0.0047)
			p-value	$1.9x10^{-14}$	$7.7x10^{-5}$	0.023	$1.55x10^{-8}$	$8.21x10^{-4}$	$7.48x10^{-3}$
	Nominal Yield Strain, ε_{NY}	$R^2 = 0.96$ Adj. $R^2 = 0.94$	β	0.0341 (0.0514)	-0.0101 ($-8.5x10^{-4}$)	0.0015 ($5.3x10^{-6}$)	0.0144 (0.00055)	0.0067 ($4.18x10^{-6}$)	-0.0054 ($-8x10^{-6}$)
			p-value	$9.7x10^{-11}$	$1x10^{-5}$	0.25	$4.1x10^{-7}$	$3.08x10^{-4}$	0.0113
	Elastic Modulus, E	$R^2 = 0.95$ Adj. $R^2 = 0.92$	β	3040 (2630)	1480 (-52.3)	838 (2.9)	-1380 (-15.8)	-32.5 (-0.0203)	-533 (-0.784)
			p-value	$5.52x10^{-9}$	$4.98 x10^{-6}$	$5.37x10^{-4}$	$8.91 x10^{-6}$	0.85	0.048
DMA Flexural Stiffness	Storage Modulus, E'	$R^2 = 0.80$ Adj. $R^2 = 0.70$	β	18473.16 (13068)	3500.54 (244.48)	-232.21 (-0.8035)	2749.51 (184.33)	5820.29 (3.6377)	-3275.00 (-4.8162)
			p-value	$2.87x10^{-8}$	0.0157880	0.851217	0.0458531	0.0006974	0.08386

Note: Gray-shaded *p*-values indicate statistical insignificance of a parameter at a confidence interval of 95%. β in parentheses indicate natural values of the parameters which were obtained based on the relationship between the coded and absolute values; x_1 = (Talc-24)/17 and x_2 = Temp/40.

Tensile strength at yield: $\sigma_{TY} = 34.093 + 0.556\phi - 0.0063\,\phi^2 - 0.163T - 0.002T^2 - 0.0047\,\phi\,T$ (3.3)

Nominal yield strain: $\varepsilon_{NY} = 0.0514 - 8.5x10^{-4}\phi + 5.3x10^{-6}\,\phi^2 + 0.00055T + 4.18x10^{-6}T^2 + 8.01x10^{-6}\,\phi\,T$ (3.4)

Elastic modulus: $E = 2630 - 52.3\,\phi + 2.9\,\phi^2 - 15.8T - 0.0203T^2 - 0.784\,\phi\,T$ (3.5)

Storage modulus: $E' = 13100 + 244\,\phi - 0.803\,\phi^2 + 184T + 3.64T^2 - 4.82\phi\,T$ (3.6)

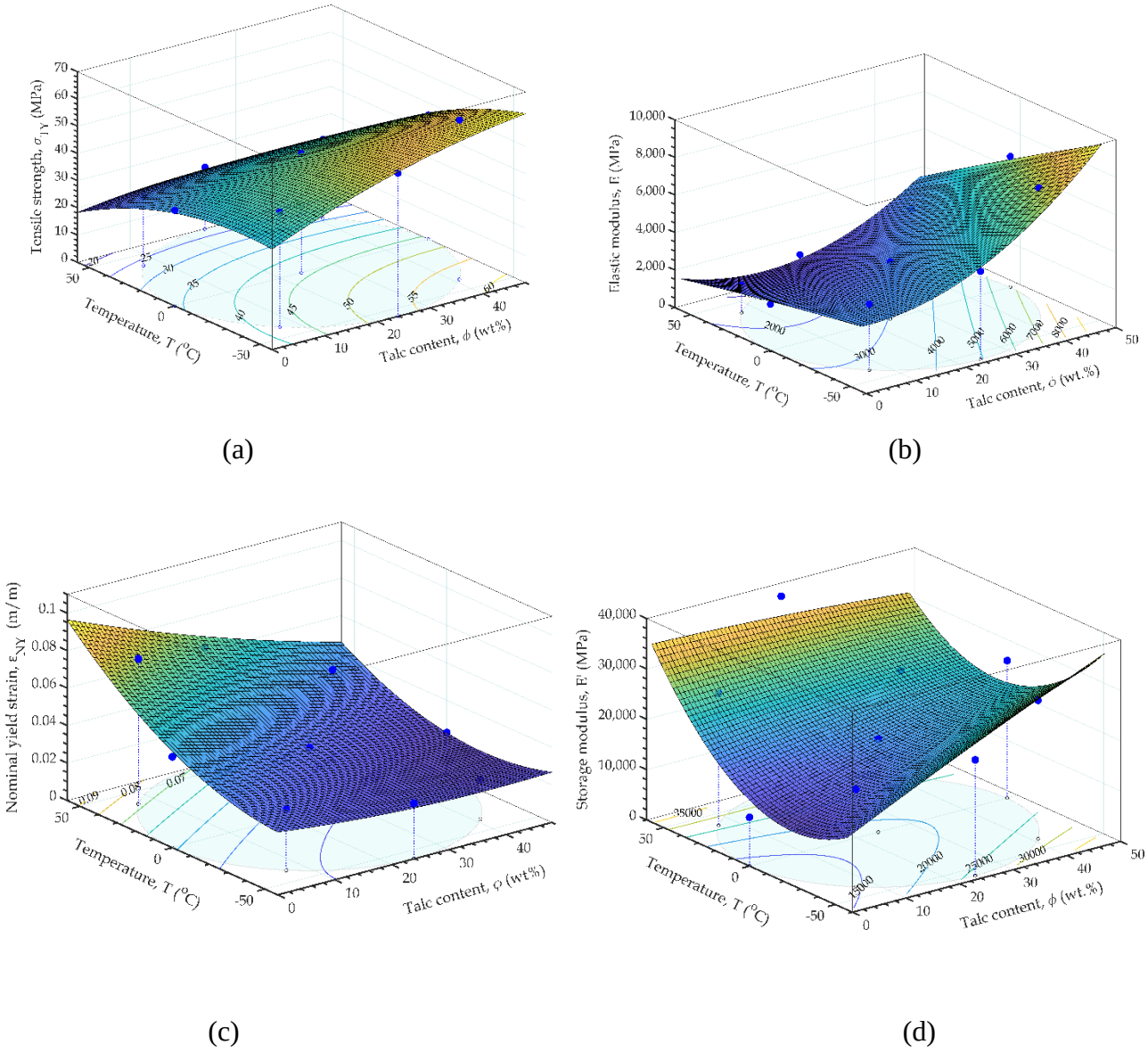

Figure 3.6: Response surface models for tensile strength, elastic modulus, nominal yield strain, and storage modulus. The blue dots represent the measured values of talc filler content and temperature for the DOE.

Coefficients of determination (R^2) for all created models (Table 3.2) are above 0.80 which indicates good fit, strong impact, and good correlation of temperature and talc filler content to the measured mechanical properties of rHDPE (all but one are above 0.94). The p-values indicate the

statistical significance of the regression terms for each response at a confidence interval of 95%, which implies the significant simultaneous interaction of the terms. However, based on p-values, some coefficients are found to be insignificant in the models. Specifically, the term ϕ^2 was found to be insignificant for ε_{NY} and E', the term T^2 was insignificant for E, and the interaction term ϕT was insignificant for E'. This implies that these insignificant terms can be ignored in practical application of properties prediction, with insignificant effects. When these insignificant terms were not considered and the surfaces were adjusted and re-evaluated, the adjusted coefficient of determinations (adj. R^2) still indicated good fit and correlation. Specifically, adj. R^2 of σ_{TY}, E, ε_{NY}, and E', were 0.96. 0.92, 0.94, and 0.70, respectively. Residual and normal Q-Q results of these properties yielded another positive indicator of model predictive power. For better statistical models, residuals should be normally distributed, and the Q-Q Plot will reveal this. If residuals follow close to a straight line on this plot, it is a good indication that they are normally distributed.

3.3.2.2 Model Predictive Performance. The performance of prediction models can be assessed using a variety of methods and metrics. R2 was used in this study to evaluate the predictive performance of the created models using ANOVA. It was used by previous works and is the most common performance measure for continuous outcomes [93]. Randomly selected talc filler content and temperature values (as shown in Figure 3.4) were used to collect the mechanical properties data that was used to assess the model performance as explained in Section 3.2.4.2. Table 3.3 summarizes the selected values, test results and model estimated results.

Table 3.3: Selected values of talc filler content and temperature, test results, model estimated results, and R^2, for validating the response models.

Natural/Absolute variables		Tensile Test						Flexural Test	
		Tensile strength, σ_{TY} (MPa)		Nominal yield strain, ε_{NY} (m/m)		Elastic modulus, E (MPa)		Storage modulus, E' (MPa)	
		$R^2 = 0.90$		$R^2 = 0.87$		$R^2 = 0.77$		$R^2 = 0.65$	
Talc, ϕ (wt%)	Temp., T (°C)	Test results	Predicted results	Test results	Predicted results	Test results	Predicted results	Test results	Predicted results
0	23	30.6	29.3	0.0659	0.0663	1790	2250	10300	19200
15	23	34.2	34.6	0.0500	0.0520	2180	1850		
20	23	34.4	35.7	0.0473	0.0477	2460	2010		
28	23	35.2	36.9	0.0460	0.0415	2700	2560		
35	23	37.2	37.3	0.0387	0.0366	3480	3340		
38	23	36.8	37.3	0.0329	0.0347	3530	3770		
45	23	36.7	36.8	0.0299	0.0305	4300	4960		
50	23	35.4	36.0	0.0276	0.0278	5010	5990		
0	40	23.0	24.4	0.0996	0.0802	1550	1960	19900	26300
5	23	32.2	31.4	0.0587	0.0613	1700	1970		
7	23	32.4	32.1	0.0560	0.0593	1790	1900	18700	20100
10	23	33.2	33.1	0.0542	0.0565	2100	1840		
10	45	25.3	25.5	0.0733	0.0731	1210	1290		
28	40	29.6	29.8	0.0553	0.0516	1730	1890		
38	45	26.9	26.7	0.0492	0.0464	2370	2740		
38	0	48.8	46.2	0.0362	0.0268	5250	4830		
5	0	42.3	36.7	0.0549	0.0473	3160	2440		
28	0	46.3	44.8	0.0282	0.0318	4000	3440		
20	0	37.3	42.7	0.0460	0.0365	2190	2740		
20	-23	46.2	47.6	0.0311	0.0297	4300	3450		
28	-40	56.4	53.4	0.0292	0.0253	5000	4910		
28	-23	46.5	50.5	0.0343	0.0264	4400	4290		
7	-23	38.1	41.1	0.0321	0.0365	3010	2880	17300	13200
10	-41	36.9	44.3	0.0274	0.0311	3790	3330		
38	-41	55.8	56.8	0.0325	0.0236	5490	6660		
38	-23	48.1	53.0	0.0311	0.0233	4000	5860		
0	-40	38.2	37.4	0.0314	0.0360	2900	3220	14900	11500
0	-23							12000	10800
0	-10							10500	11600
7	10							16200	16600
7	-10							16200	13600
24	20							19000	21300
24	-20							19800	18600
24	40							26700	27000
24	-40							21500	21500
41	20							23800	22900
41	-20							26600	23500
48	30							24600	24800
48	-30							29100	27600

Except the R^2 for storage modulus, all other R^2 values in Table 3.3 are above 0.76. This implies there are significant interactions and impacts between the two variables, talc filler and temperature, on the rHDPE tensile and flexural properties. In real life applications, this means that the response surface models generated from this analysis, for tensile strength, elastic modulus, and nominal yield strain significantly characterize the behaviors of rHDPE as functions of talc filler content and temperature. This implies that these models could be considered for use in practical applications.

3.4 Conclusions

This study was performed to evaluate the effects of talc filler content and temperature on tensile and flexural properties of rHDPE, using experimental procedures via ASTM test standards and statistical methods. It was observed that there are significant interactions and impacts between talc filler content and temperature on the tensile and flexural properties of rHDPE. Specifically, the study revealed the following.

- It was observed that rHDPE blended with talc filler is a promising polymer-filler combination, for more applications outside of its current uses, based on its measured mechanical properties in relation to neat HDPE and vHDPE-talc blends. It was observed that increasing talc filler content within the range of 0 wt% to 48 wt% generally increased tensile strength (σ_{TY}) and elastic modulus (E). Nominal yield strain (ε_{NY}) was observed to decrease with talc content increase. With the increase in temperature within the range of -56.6^{o}C to 56.6^{o}C, there was a general decrease in σ_{TY} and E, while an increase in ε_{NY} was observed. Storage modulus (*E'*) was observed to increase with both talc filler content and temperature (these can be depicted in Figure 3.6). For example,

- At 40°C and 24 wt% talc content, σ_{TY} was observed to be 22.7 MPa, and it was increased to 58.5 MPa at -40°C and 41 wt% talc, which explains the increase with talc filler increase and the decrease with temperature increase, and vice versa.
- At 56.6°C and 24 wt% talc content, E was 1260 MPa and at -40°C and 41 wt% talc content, it was 7310 MPa. This explains the increase with talc content increase and the decrease with temperature increase.
- At 40°C and 7 wt% talc content, ε_{NY} was 0.0775 m/m, and decreased to 0.0210 m/m at -40°C and 41 wt% talc content. This explains the decrease with talc filler content, but the increase with temperature increase.
- At 0°C and 0 wt% talc content, *E'* was 9690 MPa, and at 56.6°C and 24 wt% talc content, it was 38200 MPa, which explains the increase with both talc filler content and temperature.

- For the flexural stiffness testing (Figure 3.5), across a temperature range of -125°C to 80°C, there were drastic increases in storage and loss moduli after approximately 20°C, as has been revealed in previous works by other researchers [92].
- It was observed that RSM is a useful, reliable, and efficient method for examining impacts generated from the interaction of multiple factors. CCD analysis provided valuable insight into the tensile properties and flexural stiffness of rHDPE as functions of talc filler content and temperature.
- The response surfaces generated in this investigation for tensile strength, elastic modulus, nominal yield strain, and storage modulus fit well with the measured data used to create them. They yielded good correlation, with R^2 values of 0.97, 0.95, 0.96, and 0.80, respectively.

- The evaluation of the model performance, using a different data set, as explained in Section 3.2.4.2, indicated good fits between the validation data and the generated surfaces for tensile strength, elastic modulus, and nominal yield strain, with R^2 values of 0.90, 0.77, and 0.87, respectively. The measured data used to validate the storage modulus response surface did not yield as good of a fit ($R^2 = 0.65$) compared to those of tensile properties; however, a R^2 of 0.65 can still statistically be considered a good fit.

Overall, tensile strength, elastic modulus, nominal yield strain, and storage modulus were quantified for rHDPE across 0 wt% to 48 wt% talc filler content and -56.5ºC to 56.6ºC temperature range. If these values meet desired design strengths/limitations for a particular application, replacing vHDPE (or other thermoplastics), at least in part with rHDPE is a viable option. This would increase recycling rates and using rHDPE could become more economical, thereby reducing the amount of vHDPE waste. The findings of this study are promising, and they can be considered in practical applications of rHDPE blended with talc filler in decision making, design, and use of these materials in engineering applications. There are of course additional factors that would be useful to consider for optimizing the use of rHDPE in large volume engineering applications and additional research is warranted. For example, it would be useful to investigate the effects of thermal recycling repetitions (including inherent property deterioration) and different types of fillers on the overall material properties of rHDPE blends across all application temperatures. This would be useful information and particularly valuable as the recycling of HDPE becomes increasingly incentivized and, consequently, more economical.

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CHAPTER FOUR

IMPACTS OF THERMAL RECYCLING AND TALC FILLER CONTENT ON MATERIAL PROPERTIES OF RECYCLED HIGH-DENSITY POLYETHYLENE

Contribution of Authors and Co-Authors

Manuscript in Chapter 4.

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Contributions: Supervision, Conceptualization, Resources, Writing – review and manuscript editing, Funding acquisition

Co-Author: Michael Berry

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Manuscript Information

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IMPACTS OF THERMAL RECYCLING AND TALC FILLER CONTENT ON THE MATERIAL PROPERTIES OF RECYCLED HIGH-DENSITY POLYETHYLENE (rHDPE)

Abstract

Thermoplastic components can be ideal for several different engineering applications due to their high strength-to-weight ratio, ease of processing, availability, low cost, weathering and excellent chemical and corrosion resistance. However, the application of thermoplastic materials has emerged as a threat to the environment and marine ecosystems. Recycling is recognized as being the most environmentally friendly, nondestructive, and cost-effective method for managing thermoplastic waste, with minimal limitations. The aim of this research is to investigate the effect of thermal recycling on the material properties of recycled high-density polyethylene (rHDPE) talc blends. Talc filler was used to optimize rHDPE properties, at 0 wt%, 24 wt% and 48 wt% talc filler weight contents. The test sample blends were thermally reprocessed four times by extrusion and injection molded to examine the thermal recycling effects on material properties. Tests for tensile properties, melt flow index and impact resistance were performed. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were also carried out. Generally, tensile strength, elastic modulus, impact strength, and storage modulus decreased with increased thermal reprocessing cycles while nominal yield strain and melt flow index increased. The crystallinity and melting temperature of rHDPE decreased with increased thermal reprocessing repetitions. Despite the impacts of thermal reprocessing on the mechanical and thermal properties of rHDPE-talc blends, the degradations were slight even after thermal generation 4, and the properties are still superior compared to neat virgin HDPE. Overall, the results imply that recycled HDPE and its talc blends have viable properties and may be used in current applications of virgin HDPE.

4.1 Introduction

Thermoplastics (recyclable plastics) are polymeric materials widely used in the plastic processing industry. Their extensive use in commonplace objects has emerged as a significant hazard, critical threat, and disruptor to the preserving the environment and marine ecosystems [4, 7, 8]. Various techniques, approaches, and strategies have been employed to tackle and address the issues pertaining to thermoplastic waste management. These methods include landfilling, incineration, pyrolysis, bioremediation, and recycling. However, some of these methods and approaches are accompanied by limitations and challenges, while others may be destructive, hazardous, and harmful, leading to the production of noxious gases that contribute to the issue of global warming [4, 8]. Thermoplastic recycling is widely acknowledged as the most effective method for managing thermoplastic waste, primarily due to its low environmental impact, cost-effectiveness, minimal limitations compared to alternative methods, and non-destructive nature with the potential to leave the properties of the polymeric material largely unaltered [4, 9]. However, despite these benefits, the current recycling rates remain low due to a range of constraints and limitations, both economic and technological [4]. For example, in 2017, the global plastic waste generation reached approximately 6,300 million metric tons, with only 9% of all plastic recycled, 12% incinerated, and 79% accumulating in landfills or the natural environment. By 2017, an estimated 8.3 billion metric tons of virgin plastic waste had been produced globally, and without a change in production and waste management trends, an estimated 12,000 million metric tons of plastic waste will be in landfills or the environment by 2050 [10]. In 2018, the United States Environmental Protection Agency (US EPA) reported a cumulative total of 32.37 million metric tons of plastic waste generated between 1960 and 2018 in the United States, with

only 8.7% recycled, 15.7% combusted for energy recovery, and 75.6% accumulating in landfills [11]. Recent practical applications suggest that thermoplastic-based components are increasingly gaining attention and recognition as ideal materials for a range of engineering applications due to their high strength-to-weight ratio, ease of processing, availability, low cost, and excellent chemical and corrosion resistance [1-3]. In the automotive, aerospace, and construction industries, for example, components such as bumpers, wheel rims, wall panels, door panels, window panels, plumbing components, roofing components, stair balusters, guardrails, fence panels, and beams are now commonly fabricated using thermoplastic composites.

High-density polyethylene (HDPE) is a highly versatile thermoplastic primarily used for packaging applications. Reusing HDPE through recycling for these applications and expanding to other applications, can help mitigate the thermoplastic waste problem. This will also increase the availability of more sustainable materials in areas with high thermoplastic waste, reduce environmental disturbances, promote the use of "greener" construction practices, and facilitate overall sustainable development. Polyethylene generally has the highest total production volume of all polymers, and HDPE is one of the least expensive [1]. Previous studies have examined the physical, mechanical, chemical, thermal, morphological, and other properties of virgin HDPE (vHDPE) and recycled HDPE (rHDPE), including their composites/blends, and have revealed that rHDPE can exhibit comparable or even superior properties to vHDPE, with no significant material differences between vHDPE and rHDPE for up to the third thermal generation [12-18]. The effects of talc filler on tensile properties of rHDPE have been investigated in previous studies at Montana State University [18].

Talc is a naturally occurring inorganic mineral composed of magnesium, silicon, oxygen, and hydrogen that has several applications as a filler material due to its high chemical stability, affordability, and availability [19-22], and was the filler material used in the current study. Thermoplastics can be combined with mineral fillers (including talc) to form a composite or blend with optimized properties, such as improved stiffness, strength, density, and modulus [2, 24, 26, 27]. Generally, introducing talc as a filler material into thermoplastics affects the static mechanical properties, appearance, chemical structure, microstructure, physical properties, and dynamic mechanical properties. Talc also reduces the overall cost of the blend and improves thermal stability [2, 13, 14, 16, 17, 23-25]. In a two-phase composite or blend made up of a continuous polymeric (thermoplastic) matrix and particle filler, filler properties are significant factors in determining the mechanical and physical properties of the composite/blend. For example, filler type, concentration/content, dispersion, size, orientation, shape of the filler particulates, and interfacial adhesion are the factors responsible for the composite properties [31-34]. Therefore, the results from this study are specific to the filler and constituent material properties, specimen preparation parameters, and preparation methods.

Thermoplastic properties are subject to change after thermal recycling as the molecular weight and hence the crystallinity ratio of the material are affected, which in turn affects the material brittleness and other mechanical properties [45-48]. For example, the change in elastic modulus may be attributed to the change in density, which may cause a change in material crystallinity when repeating the recycling process [12, 46, 49]. The current study also examines the impact of thermal recycling on rHDPE properties (along with the impact of talc filler).

A better understanding of the mechanical properties of rHDPE and associated composites or blends is required before vHDPE can be replaced (at least in part) with rHDPE across a wide range of possible applications. In this investigation, testing was performed for melt flow index (MFI), tensile properties (tensile strength, elastic modulus, and yield strain), impact resistance, and flexural stiffness (storage modulus, loss modulus, and tan delta). Dynamic mechanical analysis (DMA) was used to analyze flexural stiffness (storage modulus), and differential scanning calorimetry (DSC) was used to examine thermal properties (crystallinity and melting temperature). ASTM standards were followed. Three different talc filler contents (0 wt%, 24 wt%, and 48 wt%) were used to prepare rHDPE-talc blends. Four consecutive thermal recycling generations were performed. The study's primary objective was to determine how thermal recycling affects rHDPE-talc blend properties, thereby shedding light on whether the recycled blends are viable for engineering applications, even after multiple generations of thermal recycling. The hypothesis is that with the increasing number of thermal recyclings, some degradation will occur; however, it is expected that the degradation will remain minimal and reasonable. The results of the investigation could expedite thermoplastic recycling and reduce polymer waste.

4.2 Materials and Methods

4.2.1 Materials

This research used rHDPE with a density of 0.942 g/cm^3 and MFI of 0.79 g/10 min. The talc was procured from Luzenac America, Inc., Centennial, CO, USA [70]. The talc had a loose bulk density of 0.432 g/cm^3, a particle size distribution with a median diameter of 9.6 microns, and a density of 2.8 g/cm^3 [70]. A visual representation of the rHDPE and talc used in the study is depicted in Figure 4.1.

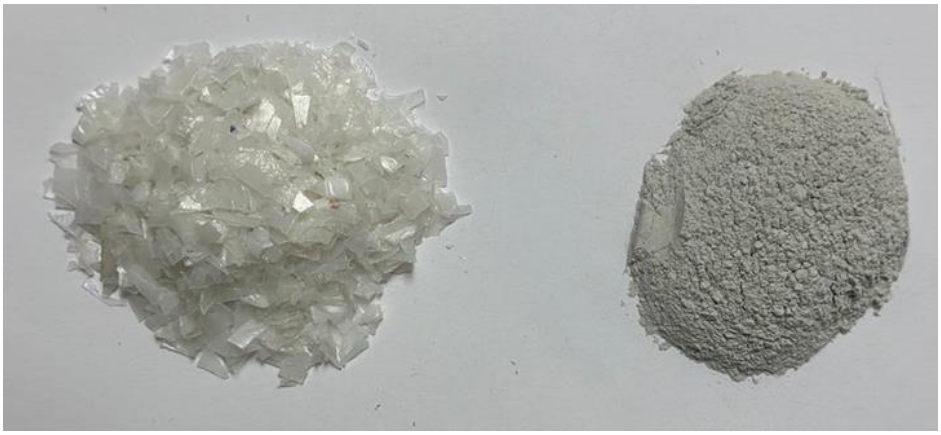


Figure 4.1: Materials used: rHDPE (left) and talc filler (right).

4.2.2 Blended Specimen Preparation

Blends of rHDPE and talc filler were prepared with three different talc filler contents: 0 wt%, 24 wt%, and 48 wt%. The blends were mixed in a Thermo Fisher Scientific HAAKE Minilab II dual screw extruder (Haake MiniLab Rheomex CTW5 machine). The extruder speed was set at 100 rpm and temperature at 190^{o}C. The residence/dwell time was approximately 5 minutes. The resulting compounded blend was then injected into a Minijet Pro injection molder with a barrel temperature of 190^{o}C and a mold temperature of 60^{o}C. An ASTM type V dog-bone specimen mold was used for the tensile test samples (Figure 4.2 a), while a DMA sample mold (Part #557-2295, 60 mm × 10 mm × 1 mm beams) was used for the flexural stiffness and impact strength test samples (Figure 4.2 b). Injection molding temperatures were determined based on the melting temperature of the HDPE, and high mold temperatures were necessary due to the thin mold used for the DMA and impact strength samples. An injection pressure of 750 bar was applied for 10 seconds, followed by a post pressure of 450 bar for 60 seconds. To comply with ASTM standards, a minimum of 5 specimens per formulation were prepared for each talc content and test type. After the first round of thermal recycling, these blends were referred to as “generation 1” and were subjected to testing.

Subsequently, the remaining materials from generation 1 and the tested samples were once again extruded under the same processing conditions to obtain “generation 2” samples, which were then tested. The tested samples and remaining materials from generation 2 were consecutively extruded, mold injected, and tested. This process was repeated a total of four times to produce “generation 4” (fourth time recycled) specimens.

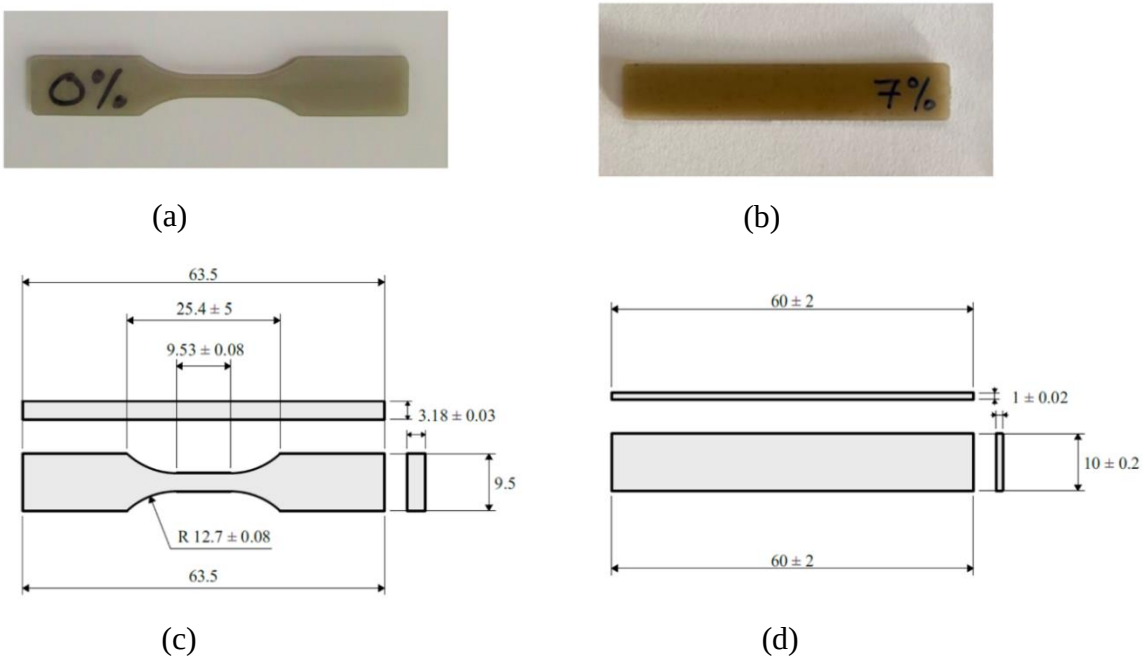
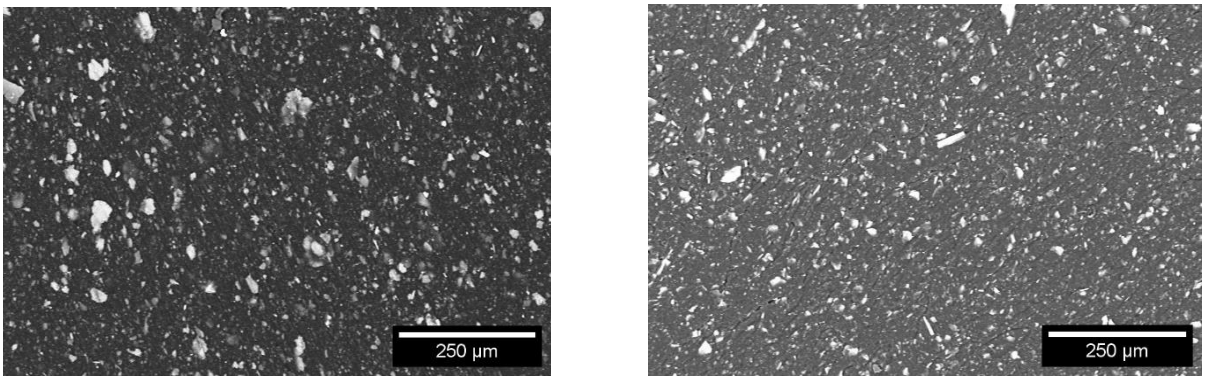


Figure 4.2: Example of a (a) tensile and (b) flexural specimen before testing, and specimen dimensions, in mm; (c) tensile, and (d) flexural.

To characterize the micro and nano-structural features of rHDPE blends with talc filler 24 wt% and 48 wt%, the dispersion and uniformity of talc filler were examined through microstructure imaging on a Zeiss SUPRA 55VP scanning electron microscope (SEM). Before imaging, the samples were cleaned with ethanol, attached to aluminum mounts using carbon sticky dots, and then sputter-coated with carbon to a thickness of 20 nm, using Cressington Carbon Coater

108 carbon/A. SEM images were captured at 250 µm magnification and a working distance of 8.5 mm with an SE2 detector, performed at an accelerating voltage of 3 kV. The SEM micrographs of rHDPE-talc blends indicated talc filler to be well dispersed with minimal gaps between talc and the polymer as indicated in Figure 4.3. These micrographs generally show a uniform dispersion of talc filler particles in the rHDPE polymer.



(a) (b)

Figure 4.3: SEM micrographs (textured surface) of (a) rHDPE-24 wt% talc, and (b) rHDPE-48 wt% talc from first recycling generation.

4.2.3 Testing

A series of mechanical tests were performed following ASTM standards to characterize the shift in mechanical properties of talc blended rHDPE samples after each thermal recycling cycle. Three different blends (0, 24, and 48 wt%) were tested over four thermal recycling generations. The tests were carried out at room temperature (23^{o}C). For each sample, primary data was collected followed by the determination of tensile strength, elastic modulus, elastic yield strain, and impact strength. Furthermore, melt flow index, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC) tests were executed. Five replicates were used for

every test, and the results presented are the averages of the tested specimens. The following sections (4.2.3.1-4.2.3.5) provide more detail on the methods used in these tests.

4.2.3.1 Melt Flow Index (MFI) Test. A Melt Flow Index (MFI) test was carried out exclusively on neat rHDPE (0% talc) for every thermal reprocessing generation. This test aimed to investigate the impact of thermal reprocessing cycles on the viscosity of HDPE, which is closely linked to MFI, and hence, determines the quality of rHDPE. Prior research has shown that polymers with lower MFI (less than 1.0 g/10 min) have higher/superior mechanical properties for extruded components [81, 94]. The test was performed using an Extrusion Plastometer (Tinius Olsen, Model MP 600, Norwood, PA) in accordance with ASTM D 1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. The temperature was maintained at 190^{o}C, with a load of 2.16 kg. At least five replications were tested for each recycling generation.

4.2.3.2 Tensile Properties Test. Tensile testing was performed using an MTS Criterion C43 tensile testing machine, with a 1 kN load cell, and the crosshead speed was set at 1 mm/min, following ASTM D638-14: Standard Test Method for Tensile Properties of Plastics [90]. Forces and displacements were the primary data obtained, and then the tensile properties of interest were determined, including tensile strength at yield (σ_{TY}), elastic modulus (E), and nominal yield strain (ε_{NY}). An extension indicator (extensometer), with a maximum strain error of 0.0002 mm/mm was used up to 0.5% strain (ε), and automatically and continuously recorded elongation values used to calculate the elastic modulus. The following bullets explain how tensile properties of interest were obtained.

- The calculation of tensile stress (σ_T) involved dividing the force applied to each specimen by the average original cross-sectional area in the gage length segment, which refers to the middle narrow portion of the specimen. Therefore, the maximum tensile stress (σ_{TY}) was the maximum stress sustained by the specimen.
- Nominal strain (ε_N) was calculated by measuring the change in grip separation (change in gage length) relative to the original grip separation and expressing it as a percentage. The nominal strain at yield (ε_{NY}) was determined by dividing the change in gage length at the yield point by the original grip separation and multiplying it by 100.
- Modulus of elasticity (E) was calculated as the slope of the initial linear portion of the stress-strain curve ($E = \Delta\sigma_T/\Delta\varepsilon$).

4.2.3.3 Impact Strength Test. To investigate the effects of thermal reprocessing on impact resistance, Charpy impact tests were conducted on four different thermal recycling generations, considering different filler contents of neat, 24 wt%, and 48 wt% talc. The testing was performed using a P.A. Hilton (Hampshire, U.K.) HSM4 pendulum impact tester in accordance with ASTM D6110-18: Standard test method for determining the Charpy impact strength of notched specimens of plastics [95]. The samples used were v-notched on the midpoint of the 10 × 60 mm surface, with a 2 mm depth notch inclined at 45°. A 0.39 kg impact weight and 79.21° initial angle were used during testing.

4.2.3.4 Flexural Stiffness Test. To investigate the effects of thermal reprocessing on rHDPE flexural stiffness (storage modulus), dynamic mechanical analysis (DMA) tests were performed for 0 wt%, 24 wt% and 48 wt% talc filler contents, over a temperature range of -125°C to 80°C. Blends from first and fourth thermal recycling generations were tested. This temperature

range was selected to capture the behaviors of HDPE within its glass transition temperature (T_g) of -135ºC and its melting point temperature (T_m) of 136ºC. The DMA tests were performed using a three-point bending fixture on a TA Instruments Q800 dynamic mechanical analyzer, measuring the storage modulus (E') for each blend (talc filler content) as a function of temperature. Storage modulus (elastic response or elastic storage modulus) is the ratio of the elastic stress to strain, which indicates the ability of a material to store energy elastically, that is, the storage modulus is a measure of the energy stored in the material. All samples were tested at a frequency of 1 Hz, an initial amplitude of 1 μm, and a force track of 125%. The temperature was equilibrated at -125°C for 2.5 minutes and then ramped to 80°C at a constant rate of 5°C/min.

4.2.3.5 Differential Scanning Calorimetry (DSC). Effects in the crystalline structure of rHDPE-talc blends in relation to thermal reprocessing were investigated using DSC, on four different thermal recycling generations. The study examined neat, 24 wt%, and 48 wt% talc filler content samples, and the properties of interest were crystallinity (χ_c) and melt temperature/melting point (T_m). To perform the analysis, a TA Instruments Discovery DSC 250 with a RSC90 cooling unit (with a minimum temperature of -180°C) was utilized. The analysis was carried out by adding samples to approximately 10 mg of polymer in Tzero hermetic aluminum pans, then heated from a temperature of -150°C, ramped at a rate of 10°C/min, up to 160°C. With the initial temperature provided, it was anticipated that the glass transition temperature (T_g) would be detected by the DSC analysis; however, Figure 4.6 demonstrates that the DSC instrument did not successfully identify/capture the T_g. The percentage crystallinity of rHDPE in a blend was calculated using the heat of fusion of 293 J/g for fully crystalline HDPE (100% crystalline enthalpy), following the

methodology established by previous researchers, such as Aggarwal et al, and Kessler, and calculated using Equation 4.1 [9, 92, 96-100].

$$\text{Crystallinity level } (\chi_c) = \frac{\Delta H_{exp}}{\Delta H} \times \frac{1}{W_f} \times 100\% \quad (4.1)$$

where ΔH_{exp} is the experimental heat of fusion/crystallization determined from DSC, ΔH is the assumed heat of fusion/crystallization of fully crystalline HDPE, and W_f is the weight fraction of the matrix, rHDPE, in the blends.

4.3 Results and Discussions

4.3.1 Effect of Thermal Reprocessing on Tensile Properties, Impact Strength, and MFI

The tensile properties, impact strength, and MFI of blends of rHDPE with talc filler content (0, 24, and 48 wt%) were measured at different thermal reprocessing generations (1 through 4). Table 4.1 shows the summary of the results. From thermal generation 1 to 4, the tensile strength (σ_{TY}) decreased minimally with a maximum decrease of 6.2% for the neat specimens. For 0, 24, and 48 wt% talc contents, the elastic modulus (E) decreased by 8.8%, 9.9%, and 10.5%, respectively, from thermal generation 1 to 4. Similarly, the impact strength also decreased from generation 1 to 4, specifically by 20.1%, 21.2%, and 17.7%, for 0, 24, and 48 wt% talc contents respectively. Nominal yield strain and MFI increased with the increase in the number of thermal reprocessing cycles. For 0, 24, and 48 wt% talc contents, the nominal yield strain increased by 15.9%, 21.4%, and 35.3%, respectively, from thermal generation 1 to 4. The MFI of the neat rHDPE increased by 37.9% from thermal generation 1 to 4, although stayed below 1.0 up to thermal generation 3 (Table 4.1). As previously discussed, polymers with lower MFI (less than 1.0

g/10 min) have good quality and can generally maintain performance after recycling. Generation 4 had an MFI of 1.1 g/10min, which can still be considered good quality.

Table 4.1: Mechanical properties and MFI of rHDPE-talc filler blends for the conducted thermal reprocessing/recycling generations.

Talc filler content	Thermal recycling generation	Tensile strength, σ_{TY} (MPa)		Elastic Modulus (MPa)		Nominal yield strain, ε_{NY} (m/m)		Average Chapy impact strength (kJ/m^2)		Melt flow index, MFI (g/10 min)	
			%ge decrease/ increase		%ge decrease/ increase		%ge decrease/ increase		%ge decrease/ increase		%ge decrease/ increase
0%	1	30.6		1790		0.0659		36.39		0.79	
	2	30.0	-1.73	1750	-2.23	0.0681	+3.44	33.82	-7.07	0.83	4.94
	3	29.0	-5.02	1740	-2.96	0.0711	+7.93	31.05	-14.69	0.96	21.15
	4	28.7	-6.19	1630	-8.83	0.0764	+15.94	29.07	-20.13	1.10	37.94
24%	1	36.4		2600		0.0405		46.57			
	2	36.2	-0.72	2460	-5.30	0.0422	+4.29	42.81	-8.09		
	3	35.9	-1.47	2350	-9.62	0.0450	+11.20	39.08	-16.08		
	4	35.5	-2.54	2340	-9.85	0.0491	+21.42	36.71	-21.17		
48%	1	35.6		5100		0.0295		19.59			
	2	35.0	-1.74	4830	-5.30	0.0341	+15.45	18.56	-5.28		
	3	34.6	-2.86	4570	-10.33	0.0384	+30.18	17.35	-11.46		
	4	34.2	-3.99	4570	-10.45	0.0399	+35.27	16.13	-17.66		

Note: The listed percent increases (+) and decrease (-) are found by comparing to the first generation values.

The degradation in these properties could be attributed to the high temperature (190°C) and mechanical stress during extrusion, which produced heat and shear stress simultaneously, leading to the degradation of the polymer. Previous works on HDPE thermoplastics have also revealed these trends, and some discussed that as the number of thermal reprocessing cycles of HDPE increases, the molecular weight and density are decreased. This is caused by the successive cutting of the long polymer chains, inducing a more branched structure approaching that of low-density polyethylene. Additionally, the chains of material with low molecular weight cannot be tangled easily, and therefore the flow resistance goes down producing a less brittle material, and hence

lowered mechanical properties, including tensile strength, elastic modulus, and impact strength [9, 12, 46, 49, 101].

It was observed that, generally the materials even after generation 4 were still found to exhibit superior properties compared to neat virgin HDPE. Since the published data is limited for recycled HDPE-talc blends, a comparison is made here with unfilled HDPE. For example, the average tensile strength of unfilled HDPE (with MFI in the range of 0.15-7 g/10 min and density in the range of 0.949-0.957 g/cm^3) ranges between 20.89 MPa and 22.2 MPa [94], and that of 0 wt% at fourth generation found in this study as 28.7 MPa. The average Charpy impact strength (notched) of unfilled HDPE (with MFI in the range of 0.025 - 1610 g/10 min) is 19.2 kJ/m^2, and that of 0 wt% at fourth generation is 29.1 kJ/m^2. Likewise, the average elastic modulus of unfilled HDPE is 976 MPa [74], and elastic modulus of 0 wt% at fourth generation is 1630 MPa.

4.3.2 Effect of Talc Filler on Tensile Properties and Impact Strength

Table 4.1 also presented a summary of the tensile test and Charpy impact strength (I_s) results as a function of talc filler content for all four thermal recycling generations. Trends show that with the talc filler content increase from 0 to 48 wt% for thermal generations 1 to 4, elastic modulus increased while nominal yield strain decreased. These results support the trends observed in our previous study of rHDPE-talc blends, for thermal generation 1 tested at room temperature [18]. The results showed that both tensile strength and Charpy impact strength, for all thermal generations, increased as the talc filler content increased from 0 to 24 wt% but then decreased for talc filler content going from 24 to 48 wt%. The decreased yield strain, increased stiffness, and other improved properties observed in the rHDPE polymer matrix can be attributed to the reinforcement effect of talc when dispersed in the matrix. Talc particles have a lamellar (plate-

like) structure with a high aspect ratio, which allows them to align during extrusion and effectively reinforce the HDPE matrix, enhancing the stiffness, toughness, and strength of the material by affecting the morphological and physical properties, such as internal adhesion, molecular weight, and density. Also, the presence of talc filler restricts the movement of the polymer chains (chain mobility) within the HDPE matrix, which impedes the sliding and rotation of polymer chains, and reduces the material's ability to deform, resulting in decreased strain [76, 77, 102].

Due to the finding of decreased tensile strength at 48 wt% talc content, additional tensile strength (σ_{TY}) data for generation 1 at room temperature was gathered from our previous research and are plotted on Figure 4.4, with a polynomial trendline (R^2 equal to 0.93). Overall, the trendline reveals a decrease of σ_{TY} after reaching a maximum tensile strength of 36.5 MPa at a talc filler content of 37.3 wt%. Also included in Figure 4.4 are the elastic modulus and nominal yield strain trends for generation 1 data from our previous research. Generally, there is an optimal range for talc filler content to enhance matrix properties, and exceeding this range (excessive filler content) may lead to agglomeration or poor dispersion, compromising the integrity of the matrix [35, 36, 102]. It is important to note that there is no single "optimum" talc content observed in the current research because it depends on the specific property of interest. For instance, tensile strength appears to reach its maximum at a 37.3% content, while the elastic modulus (which correlates with stiffness) continues to increase even after this content, although a drop is observed at 50 wt%. The compatibility between the talc filler and the polymer matrix is crucial for achieving enhanced mechanical properties. Polymer-filler compatibility refers to the ability of a polymer matrix to effectively incorporate and disperse fillers within its structure. Therefore, at lower filler content, the compatibility might be favorable, leading to improved properties; however, at higher filler

contents, the compatibility may deteriorate, resulting in reduced properties [27, 35, 36, 103, 104]. The results show that 48 wt% talc content is most likely in the range where compatibility is deteriorating, and the tensile strengths of the specimens were decreasing.

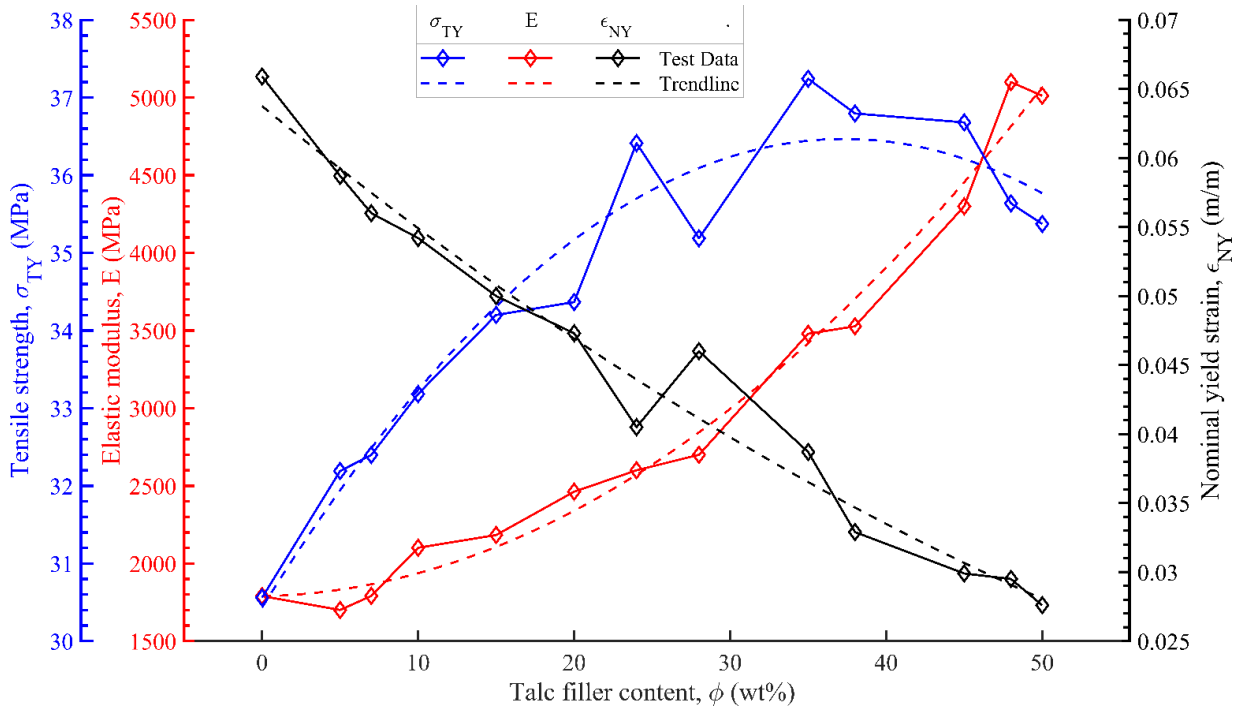


Figure 4.4: Effect of talc filler on tensile strength (σ_{TY}) of rHDPE, for the first generation thermal recycling.

4.3.3 Effect of Thermal Reprocessing and Talc Filler on Flexural Stiffness via DMA

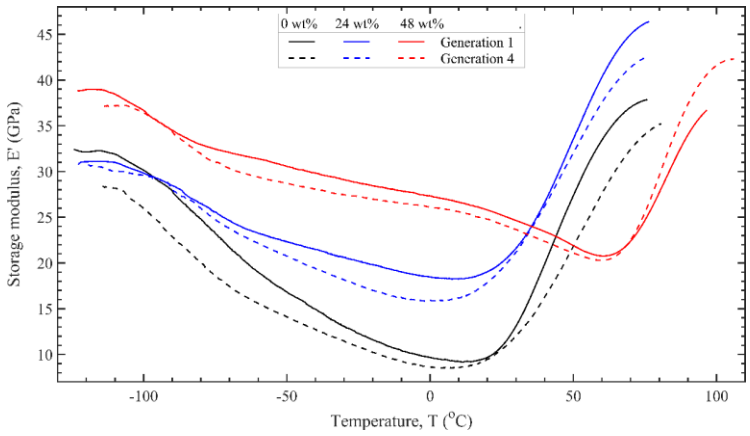
Figure 4.5 (a) indicates the results of storage modulus (E') of rHDPE blended with talc filler at thermal reprocessing generations 1 and 4. Generally, the storage modulus increased with the increase in talc filler, up until the point of minimum (E'). This suggests that the incorporation of talc filler into rHDPE enhances the ability of the blends to store and recover energy when subjected to oscillating stress or strain. The results for loss modulus (E'') and tangent of delta ($tan\ \delta$) show a slight change with the addition of talc filler (up to 48 wt%), as indicated in Figure 4.5

(b) and (c), respectively, which indicates that the dissipation or loss of energy during the oscillatory deformation is insignificant. These results signify a desirable effect of talc filler to rHDPE, as it enhances the capacity of the material to absorb and dissipate energy.

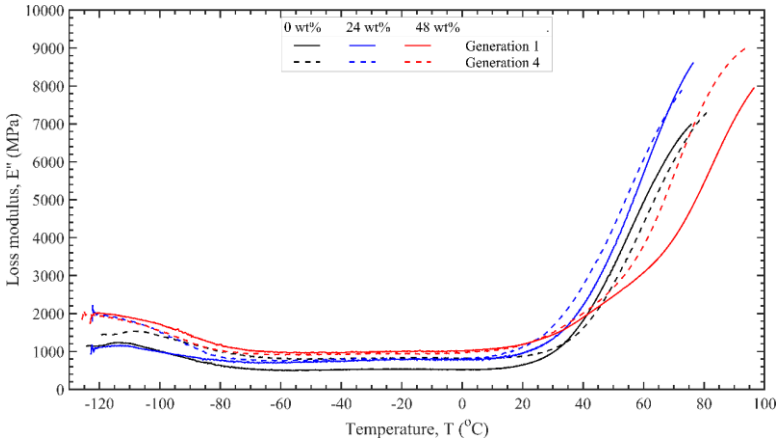
Filler materials can act as reinforcing agents in the polymer matrix, as explained prior, and this enhances the mechanical properties of the polymer including stiffness, strength, and storage modulus. Additionally, the presence of filler materials in a polymer matrix can hinder the mobility of polymer chains, and therefore, as the filler content increases, the spaces between polymer chains become smaller, limiting their ability to move and deform under an applied force. This reduced chain mobility leads to increased stiffness and higher storage modulus (higher ability to store energy).

As the number of thermal reprocessing cycles increased, the storage modulus (E') decreased. However, the cumulative decrease for all blends is considered small, as shown on Figure 4.5 (a). The overall decreases were expected due to the shorter polymer chains resulting from the repetitive thermal recycling, accompanied by an anticipated decrease in overall molecular weight and density. A related study of thermal recycling effects on rHDPE properties revealed similar trends [9]. The results for loss modulus (E'') and the tangent of delta ($tan\ \delta$) show a minimal change with the number of thermal reprocessing cycles from generation 1 to 4, as indicated in Figure 4.5 (b) and (c), respectively. This minimal change indicates the insignificant change in energy loss or dissipation, indicative of the good damping behavior of rHDPE during oscillatory deformation even when the material undergoes thermal reprocessing up to the fourth generation. Certain behaviors shown in Figure 4.5 (a), including the shifts in the minima of E' values and minima locations between generations 1 and 4, warrant further discussion. Unexpectantly, the

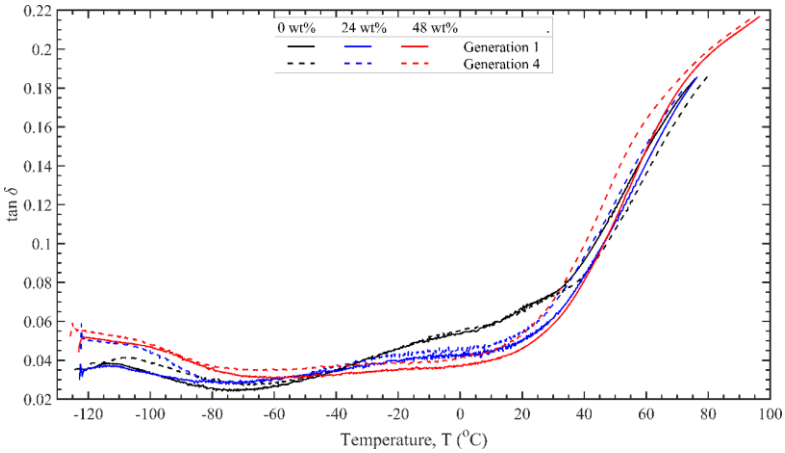
minimum value of E' for the 24 wt% talc specimens falls before the 0 wt%. Also, the graph for 0 wt% talc intersected with the graph for 24 wt% talc at -96°C. Finally, on the 48 wt% talc graphs, the thermal generation 4 data intersects the generation 1 data immediately after reaching the minimum value of E'. Additional results and discussion will be included in the final manuscript. Also, these shifts indicate that the interaction between the filler and polymer, coupled with the increases in talc content and thermal reprocessing cycles, influences other thermal properties (beyond T_m) and other material behaviors that were not investigated in this study, such as glass transition temperature (T_g), coefficient of thermal expansion (CTE), heat deflection temperature (HDT), heat capacity (C_p), thermal conductivity, specific heat, decomposition temperature (T_d), and thermal stability. E', E'', and $tan\ \delta$ of rHDPE-talc blends show approximately corresponding increases and shifts immediately after their minimum values, which may be attributed to an α-transition [92, 105]. However, this study did not investigate E', E'', and $tan\ \delta$ with an α-transition, and shift in storage modulus with an α-transition has not been the focus of past work examining the α-transition of HDPE [92]. Consequently, these behaviors warrant further avenues of research to explore the mechanisms underlying such occurrences and shifts, as were observed here.



(a)



(b)



(c)

Figure 4.5: DMA (Storage modulus, loss modulus, and tan delta) curves of rHDPE-talc filler blends for thermal generations 1 and 4.

4.3.4 Effect of Thermal Reprocessing and Talc Filler on Thermal Properties

Table 4.2 and Figure 4.6 show the results of the DSC analyses of rHDPE blended with different contents of talc filler. Generally, the melting temperature (T_m) decreased minimally with the increase in talc filler content, and the degree/level of crystallinity (χ_c) increased minimally with talc filler content. From 0 to 48 wt% talc content, crystallinity increased by an average of 3.4% for all generations. Likewise, melting temperature decreased by an average of 1.5%. The decrease in T_m and increase in χ_c may be attributed to the decreasing amount of polymer in the blends as talc content increases; however, the changes were slight.

Generally, crystallinity and melting temperature decreased with an increased number of thermal reprocessing cycles. For instance, cumulatively, for 0, 24, and 48 wt% talc content, crystallinity decreased by 4.3%, 5.2%, and 4.6%, respectively, when generation 4 is compared to generation 1. Figure 4.7 show the effect of thermal recycling generations on the melting temperature and crystallinity. Likewise, melting temperature for 0, 24, and 48 wt% talc content decreased by 1.2%, 0.5%, and 0.9%, respectively, from thermal generation 1 to 4. The effects were small, but may be explained by the decrease in molecular weight and density which may, in certain cases, cause a decrease in material crystallinity with repetition of the thermal recycling process. This finding is similar to previous studies performed on reinforced polyethylene [9, 12, 49, 101]. Thermal reprocessing subjects a polymer to an elevated temperature (190^{o}C), causing its molecular structure to change and undergo some degradation due to chains cross-linking or scission, as previously discussed, which typically affects the melting behavior of the polymer [106]. Each repeated thermal reprocessing cycle introduced additional heating and cooling, which is anticipated to cause additional chain rearrangements and further disruptions of the existing ordered crystalline structure of the polymer. As a result, the polymer chains may become more disordered,

leading to a decrease in crystallinity, as observed here for neat, 24 wt%, and 48 wt% talc content. This trend is similar to a previous study performed on neat HDPE and HDPE/wood flour composites [9].

Table 4.2: DSC analysis of blends of rHDPE and talc, at thermal generations 1 through 4.

Property	Talc filler content (wt%)	Thermal recycling/reprocessing generations			
		1	2	3	4
Melting temperature, T_m (°C)	0	136.28	135.48 (-0.6)	135.15 (-0.8)	134.58 (-1.2)
	24	134.96	134.73 (-0.2)	134.23 (-0.5)	134.26 (-0.5)
	48	133.73	133.46 (-0.2)	133.39 (-0.3)	132.52 (-0.9)
Crystallinity level, χ_c (%)	0	61.51	60.75 (-1.2)	59.58 (-3.1)	58.89 (-4.3)
	24	63.42	61.11 (-3.6)	60.23 (-5.0)	60.14 (-5.2)
	48	63.80	62.46 (-2.1)	61.84 (-3.1)	60.90 (-4.6)

Note: The numbers in parentheses indicate the percentage decrease found by comparing to the first generation values.

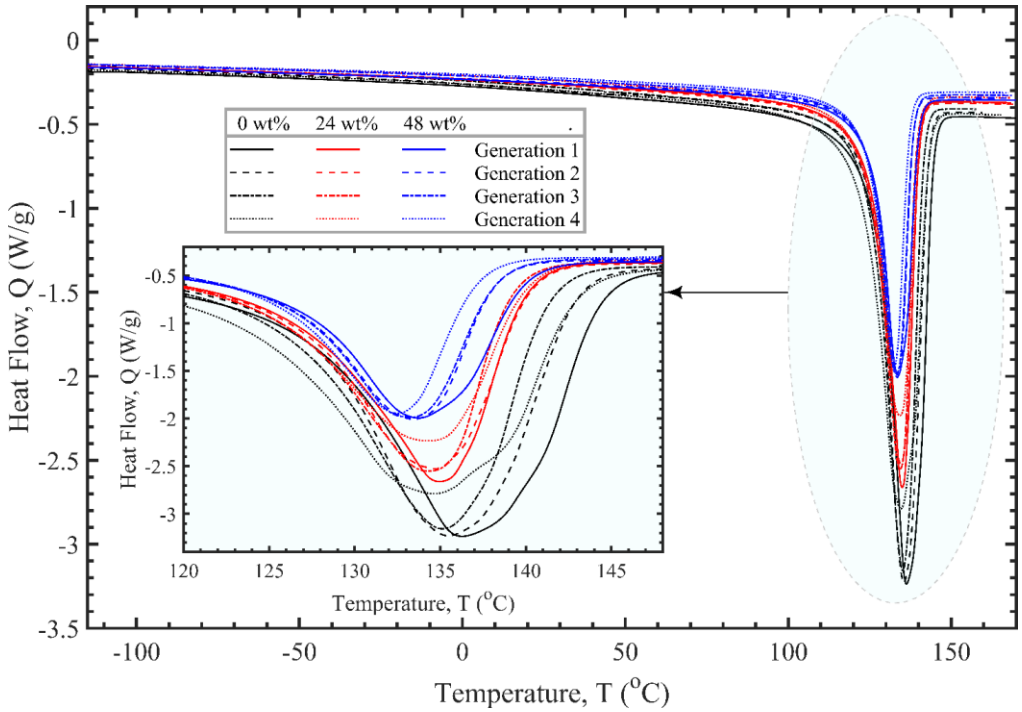
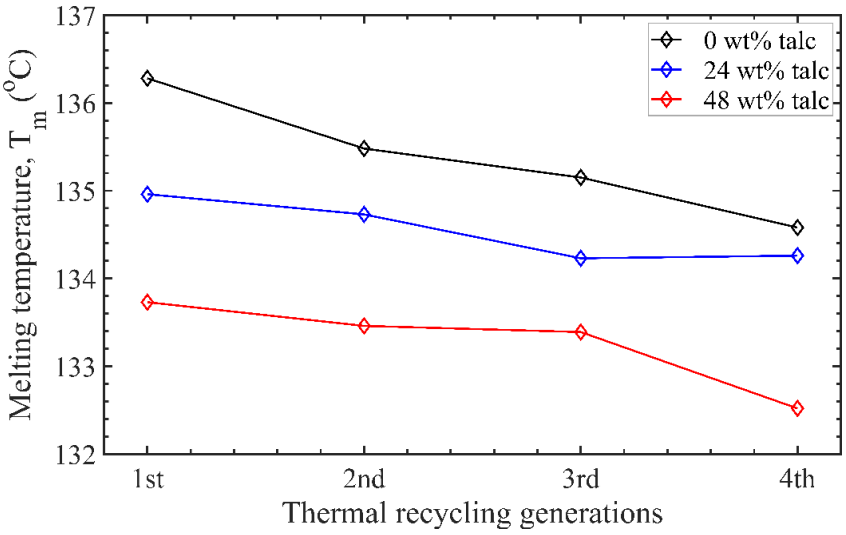
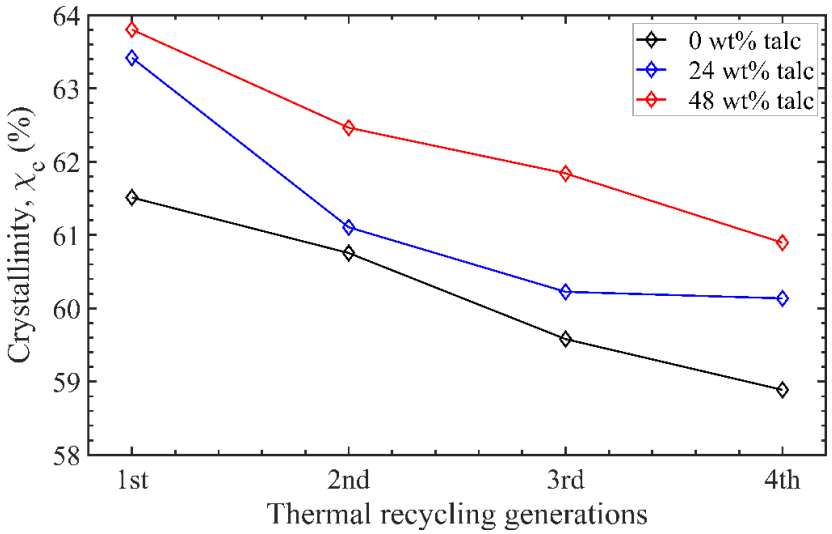


Figure 4.6: DSC curves of rHDPE blended with different talc filler contents, at thermal generations 1 through 4.



(a)



(b)

Figure 4.7: Effect of thermal recycling generations on the (a) melting temperature and (b) crystallinity of rHDPE at different talc filler contents.

4.4 Conclusions

Recycled HDPE specimens, filled with 0 wt%, 24 wt% and 48 wt% talc filler contents, were prepared by extrusion followed by injection molding, and thermal reprocessed up to four

times. The primary objective of the study was to investigate the effect of thermal reprocessing on selected properties of rHDPE in relation to talc filler content. Tensile strength, elastic modulus, impact strength and storage modulus slightly decreased with an increase in the number of thermal reprocessing cycles, while nominal yield strain and melt flow index increased. The investigated properties were found to be optimized with talc filler; however, tensile and impact strengths were negatively impacted at 48 wt% talc, due to the possible explanations presented in Section 4.3.2. Overall, the study revealed the following main conclusions.

- There is a small effect of number of thermal reprocessing cycles on tensile strength. For 0, 24, and 48 wt% talc contents, the tensile strength decreased by 6.2%, 2.5%, and 4%, respectively, from thermal generation 1 to 4.
- The quality of the rHDPE up to generation 3 remained superior considering the MFI was less than 1.0 g/10 min. For generation 4, the quality can still be considered good with an MFI of 1.1 g/10min.
- With the initial addition of 24 wt% talc, tensile strength increased by an average of 21.7% for all generations, then decreased at 48 wt% talc content. At 48 wt% talc content, tensile strength increased an average of 18% when compared to neat rHDPE. Likewise, with the initial addition of 24 wt% talc, impact strength increased by an average of 26.7% for all generations, and then decreased drastically at 48 wt% talc content, an average of 45% decrease when compared to 0 wt% talc.
- The melting temperature decrease was minimal (maximum 1.2%) for all blends, from recycling generation 1 to 4.
- Generally, the crystallinity level of rHDPE slightly decreased with increased number of

thermal reprocessing repetitions. From thermal recycling generations 1 to 4, crystallinity decreased a maximum of 5.2% for all blends.

- Possible reasons for the changes in melting temperature and crystallinity with thermal reprocessing include 1) the main chain scissions of the polymer, accompanied by an anticipated decrease in the molecular weight and density, caused by the repetitive thermal recycling process and 2) the high temperature (190°C) and mechanical stress during extrusion, which produced heat and shear stress simultaneously, leading to the degradation of the polymer [9, 101].
- Generally, melting temperature decreased minimally with the increase in talc filler content, and degree of crystallinity minimally increased with talc filler. From 0 to 48 wt% talc content, crystallinity increased by an average of only 3.4% for all generations, and melting temperature decreased by an average of only 1.5%.

Generally, the effects of talc on rHDPE can be considered significant for the investigated properties when compared to virgin HDPE. Despite the thermal reprocessing, the changes in the mechanical and thermal properties of rHDPE, from the 1st to the 4th generations, were found to be minimal. This implies that rHDPE and rHDPE-talc blends have viable, suitable, and qualifying properties for various applications compared to the current applications of neat vHDPE and its talc blends. The findings of this research will facilitate future studies on the suitability and adequacy of using rHDPE thermoplastic polymers blended with talc filler in lieu of (or at least in part) vHDPE in structural engineering applications.

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CHAPTER FIVE

CONCLUSIONS

The work comprising this dissertation focused on an extensive investigation of the mechanical and thermal properties of rHDPE thermoplastic. In recent times, there has been a growing interest in thermoplastics and their composites across various fields, including numerous engineering applications. The primary objective of this study was to explore the potential of rHDPE and rHDPE-talc blends to serve as a viable alternative to vHDPE in engineering applications by evaluating its mechanical and thermal properties. These properties are essential and critical factors that play a crucial role in determining the suitability of any material for engineering applications. In addition to the overall investigation of rHDPE properties, the study specifically considered the following three influential factors that affect the mechanical properties of thermoplastics: 1) talc filler content, 2) temperature, and 3) the number of thermal reprocessing cycles. Talc filler, an inorganic material, is often used in polymers to optimize material properties and decrease cost. The experimental techniques employed in this study followed the standards set by the American Society for Testing and Materials (ASTM). These techniques encompassed a range of testing including tensile, impact, melt flow index (MFI), Differential Scanning Calorimetry (DSC), and flexural stiffness testing using Dynamic Mechanical Analysis (DMA). To further explore the relationship between the stiffness and strength of rHDPE with talc filler content and temperature, Response Surface Methodology (RSM) was employed following the Central Composite Design (CCD) as a statistical/experimental design of experiments (DOE). Overall, the research methodology facilitated a comprehensive analysis of how the properties are affected by talc filler, temperature, and recycling generations. The investigation was carried out in three

phases, as detailed in chapters 2, 3, and 4, to fully address the intended objectives. The remaining subsections of this chapter detail the specific conclusions drawn from the three phases of the study.

5.1 Conclusions from Phase One: Tensile Properties of rHDPE-talc Blends at Room Temperature

In this phase, the study examined the tensile properties of rHDPE-talc filler blends at room temperature. Specifically, the study focused on tensile strength, elastic nominal stiffness, and nominal yield strain across various talc filler contents (0, 20, 28, and 38 wt%) previously investigated by Peterson et al. in their research on vHDPE-talc filler blends used in structural applications [24]. Additionally, the Halpin-Tsai model was employed to analyze the test data obtained in this study, aiming to assess the reinforcing effect of talc filler on the elastic nominal stiffness (k) of the rHDPE-talc blends. The findings from this phase revealed that increasing the talc content resulted in improvements in tensile strength (up to 20.4%) and elastic nominal stiffness (up to 93.5%), while the nominal yield strain decreased (up to 50%). The following specific conclusions can be drawn from the findings:

- The tensile strength results obtained for neat rHDPE in this study align with those reported in previous studies.
- The addition of talc filler to rHDPE leads to increased brittleness, as evidenced by a decrease in nominal yield strain, thereby adversely affecting overall ductility. This trend is consistent with observations made for vHDPE in previous studies.
- For rHDPE, there exists a linear relationship between an increase in talc filler content (ranging from 0 to 38 wt%) and the following changes:
    - Tensile strength increases by approximately 0.16 MPa per 1 wt% increase in talc content.

- Elastic nominal stiffness increases by approximately 41 MPa per 1 wt% increase in talc content.
- Nominal yield strain decreases by approximately 0.00083 mm/mm per 1 wt% increase in talc content.

These trends align with previous research conducted on vHDPE with similar variations in talc filler content.

- The Halpin-Tsai model demonstrates good performance when applied to analyze the elastic nominal stiffness (*k*) of rHDPE-talc blends investigated in this study. A comparison between the trendlines derived from the gathered data and the Halpin-Tsai model reveals only a 2.4% difference in slope and a 2.7% difference in y-intercept.

5.2 Conclusions from Phase Two: Tensile and Flexural Properties of rHDPE-talc Blends, and Response Surface Methodology (RSM)

Moving on to the second phase, the study aimed to characterize and comprehensively evaluate the tensile and flexural properties of rHDPE-talc blends across a wide range of talc filler content (0 to 48 wt%) and temperature (-56.6^{o}C to 56.6^{o}C). Response Surface Methodology (RSM) was utilized, along with the central composite design (CCD), as a statistical experimental design procedure (DOE). The analysis revealed that increasing the talc content led to higher tensile strength and elastic modulus, whereas an increase in temperature resulted in lower values for these properties. Conversely, the yield strain decreased with an increase in talc content but increased with rising temperature. The talc filler content primarily influenced the storage modulus, loss modulus, and tan delta, which generally exhibited an upward trend. Furthermore, the generated surfaces yielded satisfactory fits to the data, with coefficients of determination greater than 0.94

for most of the investigated properties, except for the storage modulus, which yielded a coefficient of determination of 0.80. The evaluation of model performance demonstrated strong correlation and statistical significance, providing valuable relationships for practical applications involving the use of rHDPE-talc blends in various applications. Generally, the findings from this phase revealed significant interactions between talc filler content and temperature, particularly in relation to the tensile and flexural properties of rHDPE. The following key observations were made:

- Increasing the talc filler content within the range of 0 wt% to 48 wt% generally led to higher tensile strength (σ_{TY}) and elastic modulus (E), while the nominal yield strain (ε_{NY}) tended to decrease with increasing talc content.
- When considering the temperature range of -56.6^{o}C to 56.6^{o}C, it was observed that both tensile strength and elastic modulus showed a general decrease with the increase in temperature, while the nominal yield strain exhibited an increase. The storage modulus (*E'*) demonstrated an overall increase with talc filler content.
    - At 40^{o}C and 24 wt% talc content, the tensile strength was measured at 22.7 MPa, while at -40^{o}C and 41 wt% talc content, it increased to 58.5 MPa. This exemplifies the influence of talc filler content and temperature on the observed changes in tensile strength.
    - Similarly, the elastic modulus (E) increased from 1260 MPa at 56.6^{o}C and 24 wt% talc content to 7310 MPa at -40^{o}C and 41 wt% talc content, highlighting the impact of both talc content and temperature on E.
    - Nominal yield strain decreased from 0.0775 m/m at 40^{o}C and 7 wt% talc content to 0.0210 m/m at -40^{o}C and 41 wt% talc content, illustrating the decrease with talc content increase, and increase with temperature, of this property.

- The storage modulus exhibited a substantial increase from 9690 MPa at 0°C and 0 wt% talc content to 38200 MPa at 56.6°C and 24 wt% talc content, indicating the influence of both talc content and temperature, on this property.

- In terms of flexural stiffness testing, a significant increase in storage and loss moduli was observed after approximately 20°C, consistent with findings from previous studies by other researchers [92].
- The study demonstrated that Response Surface Methodology (RSM) is a practical, reliable, and efficient approach for analyzing the impacts resulting from the interaction of multiple factors. The Central Composite Design (CCD) analysis provided valuable insights into the tensile properties and flexural stiffness of rHDPE in relation to talc filler content and temperature.
- The response surfaces generated in this investigation for tensile strength, elastic modulus, nominal yield strain, and storage modulus showed a strong fit with the measured data, as evidenced by high coefficients of determination (R^2) of 0.97, 0.95, 0.96, and 0.80, respectively.
- The model performance evaluation, utilizing a separate data set, indicated good agreement between the validation data and the generated surfaces for tensile strength, elastic modulus, and nominal yield strain, with R^2 values of 0.90, 0.77, and 0.87, respectively. Although the fit for the storage modulus response surface was slightly lower ($R^2 = 0.65$) compared to those of the tensile properties, it still exhibited a statistically significant correlation.

5.3 Conclusions from Phase Three: Effect of Thermal Recycling and Talc Filler on the Material Properties of rHDPE

In this third phase, the research aimed to investigate the effect of thermal recycling on the material properties of rHDPE-talc blends. Two different talc filler weight contents, 24 wt% and 48 wt%, were considered, along with neat rHDPE serving as a control. The test samples were subjected to thermal reprocessing up to four times to assess the impact of recycling on the material properties. Overall, tensile strength, elastic modulus, impact strength, and storage modulus decreased with an increasing number of thermal reprocessing cycles. Conversely, nominal yield strain and melt flow index showed an increase. The crystallinity level of rHDPE slightly decreased with an increased number of thermal reprocessing repetitions. Similarly, the melting temperature of rHDPE slightly decreased with an increase in the number of thermal recycling cycles. Compared to neat rHDPE, the properties of rHDPE were found to be optimized with talc filler, and exhibited enhancements, indicating better performance, and as a result, the use of talc filler emerges as a practical choice for enhancing the material properties of rHDPE; however, tensile and impact strengths decreased at 48 wt% talc content. The study revealed the following specific conclusions:

- There is a small effect of number of thermal reprocessing cycles on tensile strength. For 0, 24, and 48 wt% talc contents, the tensile strength decreased by 6.2%, 2.5%, and 4%, respectively, from thermal generation 1 to 4.
- The quality of the rHDPE up to generation 3 remained superior considering the MFI was less than 1.0 g/10 min. For generation 4, the quality can still be considered good with an MFI of 1.1 g/10min.
- With the initial addition of 24 wt% talc, tensile strength increases by an average of 21.7% for all generations, then decreases at 48 wt% talc content. Tensile strength increases an average of

18% at 48 wt% talc content compared to 0 wt% talc. Likewise, with the initial addition of 24 wt% talc, impact strength increases by an average of 26.7% for all generations, and then decreases drastically at 48 wt% talc content, an average of 45% decrease when compared to 0 wt% talc.

- Generally, the crystallinity level of rHDPE slightly decreased with increased number of thermal reprocessing repetitions. From recycling generations 1 to 4, crystallinity only decreased by up to 5.2% for all blends.
- Likewise, the melting temperature of rHDPE slightly decreased with the increase in number of thermal recycling generations. The melting temperature decreased by a maximum of 1.2% for all blends, from recycling generation 1 to 4.
- Possible reasons for the changes in melting temperature and crystallinity include 1) the main chain scissions of the polymer, accompanied by a decrease in the molecular weight and density, caused by the repetitive thermal recycling process and 2) the high temperature (190°C) and mechanical stress during extrusion, which produced heat and shear stress simultaneously, leading to the degradation of the polymer [9, 101].
- Generally, melting temperature decreased minimally with the increase in talc filler content, and degree of crystallinity increased minimally with talc filler. From 0 to 48 wt% talc content, crystallinity increased by an average of only 3.4% for all generations, and melting temperature decreased by an average of only 1.5%.
- Generally, the effects of talc on rHDPE can be considered significant for the investigated properties when compared to virgin HDPE. Despite the thermal reprocessing observed to influence the mechanical and thermal properties of rHDPE, from the 1^{st} to the 4^{th} generations,

the changes or degradations were found reasonable and slight. This implies that rHDPE and rHDPE-talc blends have viable, suitable, and qualifying properties for various applications compared to the current applications of neat vHDPE and its talc blends. The findings by this research will facilitate future studies on the suitability and adequacy of using recycled HDPE thermoplastic polymers blended with talc filler in lieu of (or at least in part) virgin HDPE in structural engineering applications.

5.4 Concluding Remarks

In summary, the three phases of this study focused on investigating the effects of talc filler content, temperature, and the number of thermal reprocessing cycles on the material properties of rHDPE. The findings shed light on the relationships between these factors and the mechanical and thermal properties of rHDPE, providing valuable insights for engineering applications. Generally, the effects of talc can be considered significant based on the investigated properties and in relation to neat rHDPE and vHDPE. With that, it can be observed that rHDPE blended with talc filler is a promising polymer-filler combination, for broader and larger volume applications outside of its current uses.

Despite thermal reprocessing (up to four generations) observed to impact the mechanical and thermal properties of rHDPE, the changes or degradations were found reasonable in these properties, and the quality can still be considered high, especially when compared to neat virgin HDPE.

The findings of this study are promising, and they suggest that rHDPE (especially rHDPE-talc blends) possesses viable and suitable properties, qualifying it for utilization in current applications where neat virgin HDPE and its talc blends are employed. If the values quantified

here align with the desired design strengths and limitations for a specific application, then this replacement of vHDPE (or other thermoplastics) at least partially with rHDPE is a viable option. This would increase recycling rates and using rHDPE could become more economical, thereby reducing the amount of vHDPE waste. However, there are of course additional factors that would be useful to consider for optimizing the use of rHDPE in large-volume engineering applications, such as weathering degradation and the addition of other fillers on the overall material properties of rHDPE blends across all application temperatures. This would be useful information and particularly valuable as the recycling of HDPE becomes increasingly incentivized and, consequently, more economical. Therefore, the findings of this research will facilitate future studies on the suitability and adequacy of using rHDPE thermoplastic polymers blended with talc filler in structural engineering applications.

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